Chemostratigraphical characterisation of lower Silurian black shales from the Formigoso Formation (southern Cantabrian Mountains, Spain)

Timothy Ferriday

PhD Thesis
(October 2014)

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1. International/Inter-laboratory standards utilised

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<th>STANDARD</th>
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<th>Origin</th>
<th>Year</th>
<th>Institution</th>
<th>Reference</th>
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<td>GRANITE</td>
<td>Ailsa Craig island in the firth of Clyde, SW Scotland</td>
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<td>(Govindaraju 1984)</td>
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<td>(Govindaraju 1980)</td>
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<td>1967</td>
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<td>(La Roche)</td>
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Table 1 The table displays International/Inter-laboratory standards utilised for calibration of the Niton XL3i. (IL) refers to Inter-laboratory standard. Data taken from 'GeoReM Database' accessed online - 28/02/2012 - http://georem.mpch-mainz.gwdg.de/
2. Calibration curves

2.1 Mining Cu/Zn mode

Major Element Calibrations; Mining Mode (240s) - Helium

- Calibration of Al (Helium)
  - Formula: \( \text{IF}((\text{COUNT}(\text{RAW DATA})=1, (\text{RAW DATA} - 11.291)/0.841,**)) \)

- Calibration of Ca (Helium)
  - Formula: \( \text{IF}((\text{COUNT}(\text{RAW DATA})=1, (\text{RAW DATA} - 11.41)/1.07,**)) \)

- Calibration of Fe (Helium)
  - Formula: \( \text{IF}((\text{COUNT}(\text{RAW DATA})=1, (\text{RAW DATA} - 1541)/1.063,**)) \)

- Calibration of K (Helium)
  - Formula: \( \text{IF}((\text{COUNT}(\text{RAW DATA})=1, (\text{RAW DATA} - 1311)/0.657,**)) \)

- Calibration of Mg (Helium)
  - Formula: \( \text{IF}((\text{COUNT}(\text{RAW DATA})=1, (\text{RAW DATA} - 3433)/0.887,**)) \)

- Calibration of Mn (Helium)
  - Formula: \( \text{IF}((\text{COUNT}(\text{RAW DATA})=1, (\text{RAW DATA} - 43.33)/1.08 **)) \)

**Figure 2.1.1** Calibration curves for the Niton X3t XRF using the Cu/Zn Mining mode for 240s and the addition of helium purging for increased accuracy of the lighter elements. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.

Calibration Formula: \( \text{IF}((\text{COUNT}(\text{RAW DATA})=1, (\text{RAW DATA} - \text{intercept})/\text{slope},**)) \)
Figure 2.1.2 Calibration curves for the Niton XL3t XRF using the Cu/Zn Mining mode for 240s and the addition of helium purging for increased accuracy of the lighter elements. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.
Figure 2.1.3 Calibration curves for the Niton XL3t XRF using the Cu/Zn Mining mode for 240s and the addition of helium purging for increased accuracy of the lighter elements. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.
Figure 2.1.4 Calibration curves for the Niton XL3t XRF using the Cu/Zn Mining mode for 240s and the addition of helium purging for increased accuracy of the lighter elements. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.
2.2 **Soil mode**

**Major Element Calibrations; Soil Mode (120s)**

- **Calibration of Ca**
- **Calibration of Fe**
- **Calibration of K**
- **Calibration of Mn**
- **Calibration of Ti**

**Figure 2.2.1** Calibration curves for the Niton XL3t XRF using the Soil mode for 120s. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.

Calibration Formula: $\text{IF(COUNT(RAW DATA)=1,(RAW DATA-intercept)/slope,**)}$
Trace Element Calibrations: Soil Mode (120s)

Calibration of Ba

![Graph showing calibration curve for Ba]

Formula: \( y = 10.52x + 0.030 \)

Calibration of Cr

![Graph showing calibration curve for Cr]

Formula: \( y = 16.97x + 0.859 \)

Calibration of Cu

![Graph showing calibration curve for Cu]

Formula: \( y = 1.63x + 0.163 \)

Calibration of Ni

![Graph showing calibration curve for Ni]

Formula: \( y = 1.74x + 0.851 \)

Calibration of Pb

![Graph showing calibration curve for Pb]

Formula: \( y = 0.59x + 0.788 \)

Calibration of Rb

![Graph showing calibration curve for Rb]

Formula: \( y = 12.33x + 0.9 \)

**Figure 2.2.2** Calibration curves for the Niton XL3t XRF using the Soil mode for 120s. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.
Figure 2.2.3 Calibration curves for the Niton XSi XRF using the Soil mode for 120s. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.
Figure 2.2.4 Calibration curves for the Niton Xl3t XRF using the Soil mode for 120s. The formulas above (calculated from the relevant curves) were used to calibrate RAW uncalibrated data, the relevant elemental formulas were simply applied to the uncalibrated data.
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1.1 Selected elements and calibration files used

There are several differing analysis modes available with the Niton XL3t XRF analyser as described in the previous methodology chapter. The differing analysis modes in most cases analyse the same suites of elements, there are only a select few elements that differ from mode to mode. The Mining Cu/Zn mode focuses upon the major elements (and the lightest of elements; via helium purging of the detector crystal) and the soil mode better suited for analysing the trace elements. This meant that particular elements had to be selected from one of the varying analysis modes (the mode that was best for that particular element was selected). The following table (Table 8.1.1) displays all major and trace elements and from which mode they were selected;

<table>
<thead>
<tr>
<th>Element</th>
<th>Type</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>%</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>Si</td>
<td>ppm</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>TiO₂</td>
<td>%</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>Ti</td>
<td>ppm</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>Ag</td>
<td>ppm</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>As</td>
<td>ppm</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>Au</td>
<td>ppm</td>
<td>Soil</td>
</tr>
<tr>
<td>Ba</td>
<td>ppm</td>
<td>Soil (Cal)</td>
</tr>
<tr>
<td>Bi</td>
<td>ppm</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>Cd</td>
<td>ppm</td>
<td>Soil</td>
</tr>
<tr>
<td>Cl</td>
<td>ppm</td>
<td>Mining Cu/Zn</td>
</tr>
<tr>
<td>Co</td>
<td>ppm</td>
<td>Soil</td>
</tr>
</tbody>
</table>

Table 8.1.1 Elements selected form which modes, also displaying which calibration files were used (Cal). The red colouring signifies the major elements and the blue, the trace elements.

The calibration process of the elements is described in the methodology chapter, the table above (Table 8.1.1) shows which calibration files were applied. The majority of the major element values were calibrated other than the Mn values. Whereas the trace elements only a select few were calibrated. This was because most of the trace element concentrations for the log localities were very low (near to detection limits) and the elemental values of the calibration standards were significantly higher, meaning that when the calibration curves were applied it had too much of an effect on the results; i.e., pushing them into negative ppm values.
1.2 Elemental errors

The previous section describes which elements were selected from the differing analytical modes; the following table (Tables 8.2.1 below) displays the average 2 sigma errors and ranges for these selected elements. The elemental errors and ranges are based on the entire geochemical dataset (approximately 3594 readings).

<table>
<thead>
<tr>
<th>Element</th>
<th>Mode</th>
<th>Average Form. Value</th>
<th>Ave. Lab Error %</th>
<th>Ave. Lab Error value</th>
<th>Ave. Field Error %</th>
<th>Ave. Field Error value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major</td>
<td></td>
<td>Wt%</td>
<td>(+/-) %</td>
<td>(+/-) ppm</td>
<td>(+/-) %</td>
<td>(+/-) ppm</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Mining</td>
<td>29.94</td>
<td>1.10</td>
<td>0.33</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CaO</td>
<td>Mining</td>
<td>0.24</td>
<td>30.83</td>
<td>0.07</td>
<td>35.48</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Soil</td>
<td>6.71</td>
<td>0.60</td>
<td>0.04</td>
<td>0.79</td>
<td>0.05</td>
</tr>
<tr>
<td>K₂O</td>
<td>Mining</td>
<td>3.81</td>
<td>1.51</td>
<td>0.06</td>
<td>1.77</td>
<td>0.07</td>
</tr>
<tr>
<td>MgO</td>
<td>Mining</td>
<td>1.11</td>
<td>31.42</td>
<td>0.35</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>MnO</td>
<td>Soil</td>
<td>0.06</td>
<td>35.02</td>
<td>0.02</td>
<td>46.81</td>
<td>0.03</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Mining</td>
<td>51.54</td>
<td>0.80</td>
<td>0.31</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Mining</td>
<td>1.14</td>
<td>1.31</td>
<td>0.01</td>
<td>2.11</td>
<td>0.02</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Trace</th>
<th>Mode</th>
<th>ppm</th>
<th>(+/-) %</th>
<th>(+/-) ppm</th>
<th>(+/-) %</th>
<th>(+/-) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Mining</td>
<td>59.03</td>
<td>33.18</td>
<td>19.58</td>
<td>12.83</td>
<td>7.57</td>
</tr>
<tr>
<td>As</td>
<td>Mining</td>
<td>25.59</td>
<td>14.56</td>
<td>3.73</td>
<td>9.46</td>
<td>2.42</td>
</tr>
<tr>
<td>Au</td>
<td>Soil</td>
<td>8.88</td>
<td>62.71</td>
<td>5.57</td>
<td>58.03</td>
<td>5.15</td>
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<tr>
<td>Ba</td>
<td>Soil</td>
<td>461.37</td>
<td>8.56</td>
<td>39.47</td>
<td>6.38</td>
<td>29.44</td>
</tr>
<tr>
<td>Bi</td>
<td>Mining</td>
<td>61.81</td>
<td>24.26</td>
<td>14.99</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cd</td>
<td>Soil</td>
<td>13.31</td>
<td>57.62</td>
<td>7.67</td>
<td>41.18</td>
<td>5.48</td>
</tr>
<tr>
<td>Cl</td>
<td>Mining</td>
<td>615.85</td>
<td>4.35</td>
<td>26.80</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>Co</td>
<td>Soil</td>
<td>125.74</td>
<td>55.94</td>
<td>70.34</td>
<td>26.05</td>
<td>32.75</td>
</tr>
<tr>
<td>Cr</td>
<td>Soil</td>
<td>121.02</td>
<td>11.76</td>
<td>14.24</td>
<td>20.64</td>
<td>24.96</td>
</tr>
<tr>
<td>Cu</td>
<td>Soil</td>
<td>29.26</td>
<td>29.41</td>
<td>8.60</td>
<td>11.57</td>
<td>3.39</td>
</tr>
<tr>
<td>Cs</td>
<td>Soil</td>
<td>36.45</td>
<td>29.23</td>
<td>10.65</td>
<td>3.4</td>
<td>12.39</td>
</tr>
<tr>
<td>Hg</td>
<td>Soil</td>
<td>6.64</td>
<td>54.47</td>
<td>3.61</td>
<td>56.76</td>
<td>3.77</td>
</tr>
<tr>
<td>Mo</td>
<td>Mining</td>
<td>4.77</td>
<td>39.30</td>
<td>1.88</td>
<td>40.99</td>
<td>1.96</td>
</tr>
<tr>
<td>Nb</td>
<td>Mining</td>
<td>19.50</td>
<td>8.35</td>
<td>1.81</td>
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<td>N/A</td>
</tr>
<tr>
<td>Ni</td>
<td>Soil</td>
<td>84.17</td>
<td>28.26</td>
<td>25.78</td>
<td>35.81</td>
<td>30.14</td>
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<tr>
<td>P</td>
<td>Mining</td>
<td>320.82</td>
<td>14.78</td>
<td>47.43</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Pb</td>
<td>Mining</td>
<td>42.05</td>
<td>26.96</td>
<td>11.50</td>
<td>28.37</td>
<td>12.10</td>
</tr>
<tr>
<td>Rb</td>
<td>Soil</td>
<td>15.11</td>
<td>51.38</td>
<td>9.28</td>
<td>54.4</td>
<td>8.22</td>
</tr>
<tr>
<td>S</td>
<td>Mining</td>
<td>155.18</td>
<td>3.09</td>
<td>4.79</td>
<td>4.82</td>
<td>7.48</td>
</tr>
<tr>
<td>Sc</td>
<td>Soil</td>
<td>927.73</td>
<td>12.78</td>
<td>118.54</td>
<td>47.6</td>
<td>441.60</td>
</tr>
<tr>
<td>Se</td>
<td>Soil</td>
<td>27.74</td>
<td>48.59</td>
<td>13.48</td>
<td>24.09</td>
<td>6.68</td>
</tr>
<tr>
<td>Sm</td>
<td>Soil</td>
<td>22.36</td>
<td>56.22</td>
<td>12.12</td>
<td>49.77</td>
<td>11.13</td>
</tr>
<tr>
<td>Sn</td>
<td>Soil</td>
<td>2.74</td>
<td>57.10</td>
<td>1.57</td>
<td>53.94</td>
<td>1.48</td>
</tr>
<tr>
<td>Sr</td>
<td>Soil</td>
<td>26.85</td>
<td>45.70</td>
<td>12.27</td>
<td>27.53</td>
<td>7.39</td>
</tr>
<tr>
<td>Te</td>
<td>Soil</td>
<td>190.26</td>
<td>2.83</td>
<td>5.00</td>
<td>2.43</td>
<td>4.62</td>
</tr>
<tr>
<td>Th</td>
<td>Soil</td>
<td>51.59</td>
<td>44.96</td>
<td>23.30</td>
<td>21.78</td>
<td>11.24</td>
</tr>
<tr>
<td>U</td>
<td>Soil</td>
<td>13.91</td>
<td>24.12</td>
<td>3.36</td>
<td>28.18</td>
<td>3.92</td>
</tr>
<tr>
<td>V</td>
<td>Soil</td>
<td>10.91</td>
<td>44.95</td>
<td>4.91</td>
<td>55.42</td>
<td>6.05</td>
</tr>
<tr>
<td>W</td>
<td>Soil</td>
<td>24.85</td>
<td>57.79</td>
<td>16.65</td>
<td>60.13</td>
<td>17.47</td>
</tr>
<tr>
<td>Zn</td>
<td>Mining</td>
<td>62.44</td>
<td>25.40</td>
<td>15.86</td>
<td>48.69</td>
<td>30.40</td>
</tr>
<tr>
<td>Zr</td>
<td>Mining</td>
<td>134.45</td>
<td>2.50</td>
<td>3.36</td>
<td>3.25</td>
<td>4.37</td>
</tr>
</tbody>
</table>

Table 8.2.1 The average errors were calculated from the entire geochemical database (approximately 3594 readings per element). The errors that seem relatively high are associated to the lower absolute elemental values (predominantly the trace elements). I.e. an average value of 9.35ppm U has a +/- 2 sigma error of 44.95% (or +/- 4.2 ppm). The concentrations are so low that the 2 sigma errors are higher. Some of the elemental concentrations are close to the detection limits. The table gives a direct comparison between the lab errors and the field errors. The Average Formigoso Fm values (Average Form. Value) were calculated from the 496 shale samples from all locations, excluding zero values (values below detection limit). The colours represent the differing analysis modes; Pink equal to the Mining Cu/Zn mode and green signifying the Soil mode. The field readings only contain soil mode readings, as liquid helium was not taken into the field.
1.3 Aralla Section

The following section documents all geochemical results for the Aralla section. The Aralla section consists of 241 samples. The sampling interval within the Formigoso Fm. (Bernesga Mb. and Villasimpliz Mb.) was set at 25cm; this was also the case for all of the other localities, other than the Aralla HR Log (every cm). The samples numbers for the Aralla section are displayed in the table below (Table 8.3.1); please also refer to the Aralla sedimentary log section (showing the sample location in regards to the log section) in the Results Chapter. and the results tables in Appendix B part 2.

<table>
<thead>
<tr>
<th>Aralla</th>
<th>Barrios Fm. (upper) - at contact with Getino Bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aralla 1</td>
<td>Barrios Fm. (upper) - at contact with Getino Bed</td>
</tr>
<tr>
<td>Aralla 2 + 3</td>
<td>Getino Bed (beds 1 + 2)</td>
</tr>
<tr>
<td>Aralla 4-184</td>
<td>Lower Formigoso Fm. (Bernesga Mb.) 37m+</td>
</tr>
<tr>
<td></td>
<td>after Aralla.184 - 27.3m gap in section</td>
</tr>
<tr>
<td>Aralla 185-241</td>
<td>Upper Formigoso Fm. (Villasimpliz Mb.)</td>
</tr>
</tbody>
</table>

Table 8.3.1 – The corresponding sample numbers for the Aralla section; also refer to the sedimentary log for the Aralla section in the Results Chapter.
Figure 8.3.1.1: All major element variation curves for the Aralla section. Each sample number represents a 25cm interval. The coloured regions indicate the differing lithologies (starting with the Barrios Fm + Getino bed (yellow) followed by the Bernesga Mb. of the Formigoso Fm (Grey) overlain by the sand/siltstone intercalations (red) of the Villasimpliz Mb. upper Formigoso Fm. The dashed line represents a break in the stratigraphy (27.3m).
1.3.2 Trace Elements

Figure 8.3.2.1: Trace element variation curves for the Aralla section. Each sample number represents a 25cm interval. The coloured regions indicate the differing lithologies (starting with the Barrios Fm + Getino bed (yellow) followed by the Bernesga Mb. of the Formigoso Fm (Grey) overlain by the sand/siltstone intercalations (red) of the Villasimpliz Mb. upper Formigoso Fm. The dashed line represents a break in the stratigraphy (27.3m).
Figure 8.3.2.2: Trace element variation curves for the Aralla section. Each sample number represents a 25cm interval. The coloured regions indicate the differing lithologies (starting with the Barrios Fm + Getino bed (yellow) followed by the Bernesga Mb. of the Formigoso Fm (Grey) overlain by the sand/siltstone intercalations (red) of the Villasimpliz Mb. upper Formigoso Fm. The dashed line represents a break in the stratigraphy (27.3m).
Figure 8.3.2.3: Trace element variation curves for the Aralla section. Each sample number represents a 25cm interval. The coloured regions indicate the differing lithologies (starting with the Barrios Fm + Getino bed (yellow) followed by the Bernesga Mb. of the Formigoso Fm (Grey) overlain by the sand/siltstone intercalations (red) of the Villasimpliz Mb. upper Formigoso Fm. The dashed line represents a break in the stratigraphy (27.3m).
Figure 8.3.2.4: Trace element variation curves for the Aralla section. Each sample number represents a 25cm interval. The coloured regions indicate the differing lithologies (starting with the Barrios Fm + Getino bed (yellow) followed by the Bernesga Mb. of the Formigoso Fm (Grey) overlain by the sand/siltstone intercalations (red) of the Villasimpliz Mb. upper Formigoso Fm. The dashed line represents a break in the stratigraphy (27.3m).

1.3.3 Elemental Enrichment Factors (EF) for all localities

The following section combines the geochemical data for all of the localities. The geochemical data for the basal Formigoso Fm (Bernesga Mb.) was averaged in order to give an average Formigoso Fm. shale for each of the locations, all elemental values below detection limits (zero values) were excluded from the averaging process. These locality shale averages were also combined to produce an average Formigoso Fm shale representative of the entire dataset. The individual locality averages can be compared to determine elemental differences within the formation laterally.

The following table (Table 8.3.3.1) displays the values for the shale averages compared to the world composites selected (below);

1. Average Shale; Turekian and Wedepohl (1961)
3. Average black shale; Vine & Tourtelot (1970)
5. Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985)
<table>
<thead>
<tr>
<th>Element</th>
<th>Type</th>
<th>Mode</th>
<th>Aralia Shale</th>
<th>Caldas Shale</th>
<th>La Majua Shale</th>
<th>Sena Shale</th>
<th>Villanueva Shale</th>
<th>Ave. Form Shale</th>
<th>Shale Av. (1)</th>
<th>Shale Av. (2)</th>
<th>Ave. Black Shale (1)</th>
<th>SCo-T (1)</th>
<th>PAAS (2)</th>
<th>PA-UCC (6)</th>
<th>Upper Crust (7)</th>
<th>NASC (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>ppm</td>
<td>M</td>
<td>117.1</td>
<td>98.0</td>
<td>76.9</td>
<td>59.9</td>
<td>71.0</td>
<td>49.0</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>ppm</td>
<td>M</td>
<td>29.46</td>
<td>29.93</td>
<td>31.01</td>
<td>29.24</td>
<td>30.10</td>
<td>29.95</td>
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</tr>
<tr>
<td>V</td>
<td>ppm</td>
<td>M</td>
<td>0.23</td>
<td>0.25</td>
<td>0.28</td>
<td>0.21</td>
<td>0.21</td>
<td>0.24</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>P</td>
<td>ppm</td>
<td>S</td>
<td>5.74</td>
<td>10.43</td>
<td>6.21</td>
<td>6.09</td>
<td>6.12</td>
<td>6.72</td>
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</tr>
<tr>
<td>Nb</td>
<td>ppm</td>
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<td>5.47</td>
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<td>5.26</td>
<td>5.59</td>
<td>5.61</td>
<td>5.72</td>
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</tr>
<tr>
<td>Hg</td>
<td>ppm</td>
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<td>4.3406</td>
<td>4.3609</td>
<td>4.2603</td>
<td>4.6988</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Co</td>
<td>ppm</td>
<td>S</td>
<td>3.92</td>
<td>3.74</td>
<td>3.32</td>
<td>4.10</td>
<td>4.00</td>
<td>3.98</td>
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<td></td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Cd</td>
<td>ppm</td>
<td>S</td>
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<td>393.99</td>
<td>375.92</td>
<td>326.54</td>
<td>330.05</td>
<td>316.82</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Mn</td>
<td>ppm</td>
<td>S</td>
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Table 8.3.3.1: Displaying the average Formigoso Fm. (Bernerfa Member) Shale averages for each of the localities compared to various world composites. Values below detection limit (zero values) were excluded from the dataset when averaging.
Figure 8.3.3.1 Enrichment factor diagrams for all localities (just the shale values Bernesga Mb. averaged), Aralla (upright dash), Cadas de Luna (triangle), La Majua (upright cross), Sena de Luna (diagonal cross), Villanueva (diamond). Normalised to the world composites: Average black shale (a), Average shale (b + c), SCO-1 (d), NASC (e) and PAAS (f). The high enrichments of Ag, Te and Hg (Cinnabar HgS) could be related to the predominantly granitic hinterland coupled with fluid flow activity.
Figure 8.3.3.2 Enrichment factor diagrams for all localities (just the shale values Bernesga Mb. averaged), Aralla (upright dash), Caldas de Luna (triangle), La Majua (upright cross), Sena de Luna (diagonal cross), Villanueva (diamond). Normalised to the world composites; Upper crust (a), PA-UCC (b), Bulk continental crust (c) and Chondrites (d + e).
Figure 8.3.3 Enrichment factor diagrams for the average Formigoso Fm. Shale. Normalised to the world composites; Average black shale (a), Average shale (b + c), SCO-1 (d), NASC (e) and PAAS (f). The high enrichments of Ag, Te and Hg (Cinnabar HgS) could be related to the predominantly granitic hinterland coupled with fluid flow activity.
Figure 8.3.3. Enrichment factor diagrams for the average Formigoso Fm. Shale. Normalised to the world composites: Upper crust (a), PA-UCC (b), Bulk continental crust (c) and Chondrites (d + e) as composites.
1.3.4 Elemental cross-plots

Figure 8.3.4.1: Showing the cross-plots of Al₂O₃ to; K₂O, TiO₂, MgO, Rb, Cr and Zr for the Aralla section (241 samples). All show positive correlations except for Zr, a slight positive correlation in the upper silt/sand intercalations and a negative correlation in the basal organically enriched shales (the lower the enrichment of Zr (detrital influx) the higher the Al₂O₃ concentrations). The basal shales and the upper silt/sand intercalations form separate clusters as highlighted.
Figure 8.3.4.2: Cross-plots of Al_{2}O_{3} versus (vs.) SiO_{2}/Al_{2}O_{3}, Fe_{2}O_{3}/Al_{2}O_{3} and K_{2}O/Al_{2}O_{3} for the Aralla section (241 samples) all showing negative correlations indicating the presence of clay minerals. The SiO_{2}/Al_{2}O_{3} cross-plot indicates the maturity of the sandstone intercalations and shales, the differing lithologies cluster (labelled).

Figure 8.3.4.3: Showing the geochemical ratios of Cr/V and Ni for the Aralla section (241 samples). The ratios can be compared between localities to determine environment differences/changes laterally (redox states, redox sensitive elements). Plots a + b display the ratios plotted against stratigraphy, the differing lithologies are clearly evident (the contrast between the basal shales and the upper silt/sand intercalations is apparent). The dashed line represents a gap of 27.3m in the stratigraphy. Cr, Ni and V are redox sensitive elements. Hence the enrichment shown in the V vs. Cr cross plot towards the organically enriched anoxic shales. The V vs. Cr cross plot shows a strong positive correlation (the higher the V values the higher the Cr values).
Figure 8.3.4.4: Showing grain size (SiO$_2$/Al$_2$O$_3$ and Rb/K$_2$O) and redox state (Cu/Zn) for the Aralla section (241 samples), indicating the maturity of the Formigoso Fm., the lower the silica content, smaller the grain size. The contrast in grain size and silica content is seen at the contact to the underlying Barrios Fm, and the upper sand/siltstone intercalations (Villasimpliz Mb.). The dashed line represents a gap in the stratigraphy of 27.3m.

Figure 8.3.4.5: MgO Cross plots of Fe$_2$O$_3$, MnO, (Cr+Ni) and V for the Aralla section (241 samples) all show positive correlations.
Figure 8.3.4.6: Harker type major element variation diagrams for the Aralla section (241 samples), clearly discriminating between the upper sand/silt intercalations and the organically enriched basal shales. CaO readings were just above the detection limit of the Niton XL3t.
Figure 8.3.4.7: Cross plots of Al₂O₃, U, Th, Cs and Ba vs. K₂O for the Aralla section (241 samples) all showing positive correlations. The U cross plot showing the organically enriched basal shales, the higher the U content, the higher the total organic carbon (TOC), using U as a proxy for organic content and redox indicator. Note the sandstones are depleted in U (detrital influxes, bringing O₂ enriched sediment into the anoxic environment; perturbation of the anoxic bottom waters).
Figure 8.3.4.8: Showing Cr/Rb, V/Rb, Th/U, Ba/Rb and Zr/Rb ratios for the Aralla section (241 samples). The values are normalised to Rb as it is inert with respect to biogenic processes unlike Al₂O₃ and SiO₂. The Th/U ratio can be used as a redox proxy. The differing lithologies are labelled with the dashed line representing a gap of 27.3m in the stratigraphy. The previous elemental cross plot ratios.
Figure 8.3.4.9: TOC cross-plots for the Aralia section (all 241 samples); trace elements of ‘strong euxinic affinity’ a) U, b) V, c) Zn and d) Pb all of the trace elements are Al normalized \((x10^{-4})\). Trace elements of ‘weak euxinic affinity’ e) Cu, f) Ni and g) Cr again all Al normalized \((x10^{-4})\) following the scheme of Algeo & Maynard (2004).
Figure 8.3.4.10: Selected major element vs. Al$_2$O$_3$ variation diagrams for the Formigoso Fm at Aralla (a + b), displaying all 241 samples. The solid line in (a) represents a probable detrital trend (DT). The ranges of K$_2$O/Al$_2$O$_3$ ratios in K-feldspars and clays (plot (b)) after Cox et al. (1995). Selected trace element vs. Al$_2$O$_3$ variation diagrams (c-e).

f) Th vs. Th/U plot (McLennan et al., 1993) for Aralla samples (241 samples). Dashed lines: Th/U ratio and Th content of UCC; circle: PAAS (Taylor and McLennan, 1985); fields for depleted mantle sources and Australian shales (AS) from McLennan et al. (1993). Arrows indicate direction of trends for weathering (U loss) and enrichment (U gain).

g+h) Zr/Sc vs. Th/Sc plots (McLennan et al., 1993) for (a) Formigoso Fm at Aralla (all 241 samples); (b) modern muds from trailing edge (TE, passive margin), continental arc (CA), and forearc (FA) settings (data from McLennan et al., 1990). Solid line connecting stars B (basalt) and F (felsic volcanic rock), illustrates the trend expected in first-cycle sediments due to magmatic evolution from mafic to felsic end members; star G is average granite (Condie, 1993). UCC and PAAS from Taylor and McLennan (1985). Arrow illustrates the trend produced by zircon concentration during sedimentary sorting and recycling.
Figure 8.3.4.11: Geochemical plots for the Aralla section (all 241 samples utilised). a) Showing V/(V+Ni) vs. TOC; the higher the TOC values the lower the sedimentation rate (V/(V+Ni) values have to be above 0.5 in order for the organic carbon to be preserved (not oxidised, Rimmer, 2004), the sedimentation rate indicator taken from Arthur & Sagemann, 1994). b) Represents the TOC values vs. stratigraphy (every data point is equivalent to 25cm). b,c & d) the selected geochemical indices for the Aralla section (all 241 samples). Note that when the TOC and V/(V+Ni) values decrease (V/(V+Ni) throughout) and the Mn/Al increases (samples 185 onwards) it suggests oxygenation of the sediments. The sands/silt intercalations are bringing oxygen rich sediments into the otherwise anoxic (oxygen depleted environment) and in turn perturbate the overlying water column (reoxygenation).
Figure 8.3.4.12: Utilising all geochemical data from the Aralla section (all 241 samples). a) shows Zr/Ti ratios used as a provenance proxy; high Zr/Ti ratios point towards granitic rocks (G1 granite: Zr/Ti is 0.14) or clastic sediments (average phanerzoic quartz arenite: Zr/Ti is 0.13; Boryta and Condie, 1990). Lower Zr/Ti ratios around 0.067 represent the composition of the average upper crust (Taylor and McLennan, 1985). The ‘North American shale composite’ (NASC) has a Zr/Ti ratio of 0.043. Lower Zr/Ti ratios are indicative of basic igneous rocks; Andean volcanic rocks yield Zr/Ti ratios between 0.024 for basalts and 0.034 for andesites (Ewart, 1982). Lowest Zr/Ti ratios around 0.01 represent primitive magmas of OIB’s and MORB’s (from Bonn, 2004). b) Signifies palaeosalinity (using Rb/K ratios), the dashed line values were taken from Cambell & Williams, 1965. c-f) palaeo-redox indicators; the ratio lines are documented in the table. g) Th/U Ratios for Aralla, any value <2 implies anoxic (Fertl, 1979), organically rich black shale genesis.

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Jones and Manning (1994), Hatch and Leventha (1992), Kimura ve Watanabe (2001)
Figure 8.3.4.13: Geochemical data representative of the Aralla section (241 samples) a) V/Al vs. stratigraphy and b) correlation of V with TOC.

Figure 8.3.4.14: Geochemical data from the Aralla section (all 241 samples). a) Scatter plot showing heavy mineral indicating element vs. major component. b) TOC values vs. stratigraphy. c + d) Fe₂O₃ and Fe₂O₃/Al₂O₃ vs. stratigraphy, and finally e + f) V and Zn vs. TOC.
Figure 8.3.4.15: All data from the Aralla section (241 samples); a) SiO₂ vs. Al₂O₃ concentrations are plotted relative to the idealized composition of the observed minerals (after Cullers & Podkovyrov, 2000). The majority of the variation in composition may be related to variations in quartz and clay minerals-muscovite. b) Fe₂O₃ total vs. Al₂O₃ concentrations plotted relative to the composition of the observed minerals, again much of the variation in composition may be accounted for by variations in quartz and clay minerals-muscovite.

Figure 8.3.4.16: Representing all data from the Aralla section (241 samples). Redox sensitive elements (V and Cr) showing positive correlations with TOC values; a) Cr (ppm) vs. TOC, b) V (ppm) vs. TOC, c) Cr (wt %) vs. TOC and d) V (wt %) vs. TOC.
Figure 8.3.4.17: Representing all data from the Aralla section (241 samples). Al<sub>2</sub>O<sub>3</sub> bivariate diagrams of major element composition along with estimated elemental mineral compositions (from Descourvieres et al., 2011).
Figure 8.3.4.18: Cross-plots showing the various geochemical ratios: $(Zr+Rb)/Sr$, Th/U and Zr/Rb. The plots represent sample data from the Aralla section (all 241 samples). Th/U is used as a redox indicator; the dashed black line representing a Th/U ratio of 2, less than 2 indicates anoxic after Fertl, 1979. Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with $Al_2O_3$, $TiO_2$, and $K_2O$ in the clay fraction); high values reflect coarse grained units, lower values in clay stones and shales. $(Zr+Rb)/Sr$ ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values found in samples with little carbonate.
Figure 8.3.4.19: Cross-plot of Ni vs. Cr representing all data from the Aralla section (241 samples).

Figure 8.3.4.20: Representing all data from the Aralla section (241 samples). The ratios Ni/V and V/Cr (Jones and Manning, 1994) are redox indicators.
Figure 8.3.4.21: Geochemical data from the Aralla section (all 241 samples). Selected elements and ratios plotted vs. stratigraphy.

Figure 8.3.4.22: Representing the relationship between Al₂O₃ and Ba for all Aralla data (241 samples).
Figure 8.3.4.23: Representing all data from the Aralla section (241 samples). a) Plot of U/Pb ratios vs. U concentrations (ppm). Samples generally reflect elevated U concentrations relative to North American Shale Composite (Condie, 1993). b) TOC (wt.%) vs. U concentrations (ppm). The U content of NASC is plotted for reference (samples are enriched in U relative to the NASC composite). U and TOC exhibit a perfect correlation as TOC values were generated using the U (ppm) values as a proxy.

Figure 8.3.4.24: All diagrams represent the data from the Aralla section (241 samples). a) Th vs. Sc (in log scale) and b) Th vs. U diagrams (modified after McLennan et al., 1990, and Luchi et al., 2003). c) Fe₂O₃/K₂O vs. SiO₂/Al₂O₃ d) log SiO₂/Al₂O₃ vs. log (Fe₂O₃/K₂O) of Herron (1986). e) Th/Sc vs. Zr/Sc (log scale) diagram after McLennan et al., (1993), reflecting reworking through Zr/Sc and upper crust felsic input through Th/Sc. Numbers identify the mean values for 1,OIA, 2,CIA, 3, ACM and 4, PM following Bathia and Crook (1986). f) TiO₂ vs. Ni, fields for acidic and basic source materials after Floyd et al., (1989).
Figure 8.3.4.25: Displaying all data from the Aralla section (241 samples). Th/Sc vs. Zr/Sc plot (Mongelli et al., 2006), the samples depart from the compositional trend indicating zircon addition suggestive of a recycling effect.

Figure 8.3.4.26: Representing all data from the Aralla section (241 samples). Zr vs. SiO$_2$, a positive relationship is apparent, indication that the Zr is indeed associated with the Quartz (heavy fraction).
Figure 8.3.4.27: TiO$_2$ vs. Ni bivariate plot for shale samples from the Aralla section (all 241 samples), fields after Floyd et al., 1989.

Figure 8.3.4.28: Representing all data from the Aralla section (241 samples). The trace elements are normalised to Al and then multiplied by $10^{-4}$. As, Cr, Cu, Ni, V, Zn vs. stratigraphy.
Figure 8.3.4.29: Geochemical classification based on the criteria listed in Table b (above) for the Aralla dataset (all 241 samples). The geochemical classification values (y-axis of plot a) reflect the following: Score of 4 = floodplain mudstone, Score of 7 = brackish water or lacustrine, Score of 10 = marginal marine mudstone, Score of 13 or 16 = marine mudstone (= marine band). If a sample has a very high Zr/U value (above 65), it is presumed to contain abundant heavy minerals and is awarded a final score of 2. If a sample comes from a coal, it is awarded a default score of 0, (classification of Pearce et al., 2010).

Mo and P₂O₅ values for the Aralla section are near/below detection limits.

Based on the criteria above the depositional environment of the Formigoso Fm. at the Aralla section is classified as borderline; brackish water or Lacustrine - marginal marine mudstone (which fits with the Rb/K ratios for palaeosalinity). With the introduction of the upper sand/silt intercalations the geochemical classification values decrease; the lowest values being 6 between floodplain mudstone and brackish water, indicating an increased terrestrial input (prograding delta?).
Figure 8.3.4.30: Representing all data from the Aralla section (241 samples). A) SiO$_2$/Al$_2$O$_3$ vs. TOC and B) Zr/Rb vs. TOC. The SiO$_2$/Al$_2$O$_3$ and Zr/Rb ratios are renowned grain size proxies, plotted against TOC (Total Organic Carbon) values. The zones for hydrocarbon potential (TOC cut off values) based on Bordenave et al., (1993). The plots discriminate between the basal shales (lower member) of the Formigoso Fm and the sands/silts (upper member). The higher the grain size proxy the lower the TOC (within the coarser grained units there is a relationship between grain size and TOC). The TOC values for the basal shales act independently of the grain size values, the grain size remains consistent yet the TOC levels vary; this is most likely due to changes in the redox state.
Figure 8.3.4.31(a): Plots representing data from the Aralla section (all 241 samples), showing the relationship between $\text{Al}_2\text{O}_3$, selected trace elements and $\text{Fe}_2\text{O}_3$. The plots show the relationship between the Cantabrian formations (predominantly the Formigoso Fm) trace element: $\text{Al}_2\text{O}_3$ ratios and the World Shale Average (WSA, plotted as star, taken from Gromet et al., 1984), the Zr vs. $\text{Al}_2\text{O}_3$ also includes the Upper Crust (UC) and North American Shale Composite (NASC).
Figure 8.3.4.31(b): Plots representing data from the Aralla section (all 241 samples). The plots show the relationship between various trace elements within the Cantabrian formations (predominantly the Formigoso Fm).
Figure 8.3.4.32: Representing data from the Aralla section (all 241 samples). a) Chemical classification, after Herron, 1986. b) Plot of discriminant functions 1 and 2 for shales (after Roser and Korsch (1988)). Discriminant function 1 = \((-1.773 \times \text{TiO}_2\%\) + (0.607 \times \text{Al}_2\text{O}_3\%\) + (0.76 \times \text{Fe}_2\text{O}_3\text{T}\%\) + (\(-1.5 \times \text{MgO}\%\) + (0.616 \times \text{CaO}\%\) + (0.509 \times \text{Na}_2\text{O}\%\) + (\(-1.5 \times \text{K}_2\text{O}\%\) + (\(-9.09). Discriminant function 2 = (0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (\(-0.25 \times \text{Fe}_2\text{O}_3\text{T}\%) + (\(-1.142 \times \text{MgO}\%\) + (0.432 \times \text{Na}_2\text{O}\%) + (1.426 \times \text{K}_2\text{O}\%) + (\(-6.861). Provenance fields are after Roser and Korsch (1988). P1 = mafic and lesser intermediate igneous provenance; P2 = intermediate igneous provenance; P3 = felsic igneous provenance and P4 = recycled-mature polycyclic quartzose detritus. c) Distribution of K and Rb relative to a K/Rb ratio of 230 (=main trend of Shaw, 1968).

Figure 8.3.4.33: Representing all Zr vs. Cr data from the Aralla section (241 samples). Variations in the Zr and Cr values are likely to reflect changes in the sediment provenance.
Figure 8.3.4.34: Cross plot of Mo (ppm) and TOC (wt%) values from the Aralla section (all 241 samples). Evidently the Mo concentrations are near/below the detection limit.

Figure 8.3.4.35: Representing data from the Aralla section (all 241 samples). a) V/Cr used as a palaeoredox proxy. b) V/Cr ratio vs. TOC. c) Mo/Al ratio vs. TOC (Mo values are near/below the detection limit).
Figure 8.3.4.36: Representing all data from the Aralla section (241 samples). a + b) plots of the detrital parameter Th vs. Zr and Th vs. Ti. c + d) Cross plots of Th as detrital monitor vs. authigenic uranium (U-aut) and V (ppm).

Figure 8.3.4.37: Representing all data from the Aralla section (241 samples). a) Scatter plot of V/(V + Ni) vs. degree of pyritization (DOP), displaying average shale (Turekian & Wedepohl, 1961) and average continental crust. b) DOP vs. stratigraphy; the lines representing DOP values are from Wignall, 1994. c) Represents an idealized plot of a uniform DOP with increasing TOC, (a+c).
Figure 8.3.4.38: Displaying all data from the Aralla section (241 samples), provenance and source signature diagrams. a) Th vs. Sc. Th is an incompatible element that is enriched in silicic rocks, and Sc is a compatible element that is enriched in mafic rocks. Th/Sc ratios near unity represent the upper continental crust (UC) the Th/Sc ratios near 0.6 suggest a more mafic component (Totten et al., 2000). b) Th/Sc vs. Cr/Th the samples lie upon a curve consistent with mixing of a continental source enriched in incompatible elements (Th) and a more mafic source enriched in compatible elements (Cr, Sc). The values for UC, Granites and mid-oceanic-ridge-basalts (MORB) are given for comparison (Totten et al., 2000). c) Th vs. Sc relation and d) Th/Sc vs. Cr/Th.
Figure 8.3.4.39: Representing all data from the Aralla section (241 samples). MgO/Al2O3 vs. K2O/Al2O3 cross plot including the fields of kaolinite, illite/K-feldspar and chlorite (Turgeon + Brumsack, 2006).
Figure 8.3.4.40: Representing all data from the Aralla section (241 samples). Diagrams used for discriminating the differing lithologies (basal shales; lower member and the sand/silt intercalations; upper member).
Figure 8.3.4.41: Showing data from the Aralla section (all 241 samples). a) cross-plot of SiO$_2$ vs. Al$_2$O$_3$ shows an enrichment of SiO$_2$ over Al$_2$O$_3$ in comparison to the World Average Shale (WSA) of Turekian & Wedephol, 1961. b + c) TOC vs. Al$_2$O$_3$ and SiO$_2$, showing that the TOC values vary as the Al$_2$O$_3$/SiO$_2$ content remain consistent.

Figure 8.3.4.42: Representing all data from the Aralla section (241 samples). Plot of total organic carbon (TOC wt.%) against authigenic uranium content ($U_{auth}$). The correlation between TOC and total U would be 1:1 as the TOC values have been generated by using U as a proxy. Yet the $U_{auth}$ values use Th values in order to correct for detrital uranium.
Figure 8.3.4.43: Representing all data from the Aralla section (241 samples). Elemental Sr/Al, Mn/Al, Si/Al, Ba/Al, Zr/Al ratios plotted against TOC and stratigraphy.
1.3.5  \( \text{Na}_2\text{O} \) plots

![Figure 8.3.5.1: Displaying data from the Aralla section (all 241 samples). a) Bivariate SiO\(_2\) wt.% vs. (Al\(_2\)O\(_3\)+K\(_2\)O+Na\(_2\)O) wt.% palaeoclimate discrimination diagram, fields after Suttner and Dutta (1986), b) Provenance discrimination diagram for shales (after Roser and Korsch, 1988). Discriminant Discriminant function 1 = (-1.773 × TiO\(_2\)) + (0.607 × Al\(_2\)O\(_3\)) + (0.76 × Fe\(_2\)O\(_3\)) + (−1.5 × MgO%) + (0.616 × CaO%) + (0.509 × Na\(_2\)O%) + (−1.22 × K\(_2\)O%) + (−9.09). Discriminant function 2 = (0.445 × TiO\(_2\)) + (0.07 × Al\(_2\)O\(_3\)) + (−0.25 × Fe\(_2\)O\(_3\)) + (−1.142 × MgO%) + (0.432 × Na\(_2\)O%) + (1.426 × K\(_2\)O%) + (−6.861) c) SiO\(_2\)/Al\(_2\)O\(_3\) vs. K\(_2\)O/Na\(_2\)O after Kampunzu et al., 2005. d) Discriminant function diagram after Roser and Korsch (1988); Discriminant function I = (−1.773 × TiO\(_2\)) + (0.607 × Al\(_2\)O\(_3\)) + (0.76 × Fe\(_2\)O\(_3\)(total)) + (−1.5 × MgO) + (0.616 × CaO) + (0.509 × Na\(_2\)O) + (−1.224 × K\(_2\)O) + (−9.09); Discriminant function II = (0.445 × TiO\(_2\)) + (0.07 × Al\(_2\)O\(_3\)) + (−0.25 × Fe\(_2\)O\(_3\)(total)) + (−1.142 × MgO) + (0.438 × CaO) + (1.475 × Na\(_2\)O) + (1.426 × K\(_2\)O) + (−6.861). e) Al/Ti ratio (Akul’shina (1976) + Kiipli et al., 2012) and climate: Al\(_2\)O\(_3\)/TiO\(_2\)<20 for humid, 20–30 for semi-humid and semi-arid, and >30 for arid climate.}
Figure 8.3.5.2: Displaying data from the Aralla section (all 241 samples). a) Tectonic setting discrimination diagram (Bhatia, 1983). **Discriminant function 1** = −0.0447×SiO₂% + (−0.972×TiO₂%) + (0.008×Al₂O₃%) + (−0.267×Fe₂O₃%) + (0.208×FeO%) + (−3.082×MnO%) + (0.140×MgO%) + (0.195×CaO%) + (0.719×Na₂O%) + (−0.032×K₂O%) + (7.510×P₂O₅%). **Discriminant function 2** = (−0.421×SiO₂%) + (1.988×TiO₂%) + (−0.526×Al₂O₃%) + (−0.907×CaO%) + (−0.117×Na₂O%) + (−1.840×K₂O%) + (7.244×P₂O₅%). b) Th/U versus Th plot after McLennan et al., (1993). c) Log (Na₂O/K₂O) vs Log (SiO₂/Al₂O₃) scheme of Pettijohn et al., (1972) and d) other tectonic discrimination (Descourvieres et al., 2011).
1.3.6 Histograms (major elements & redox ratios)

Figure 8.3.6.1: Histograms and cumulative frequency representing the major oxides a) SiO$_2$ values b) Al$_2$O$_3$ values c) K$_2$O values and d) TiO$_2$ values, using all sample data (241 samples) from the Aralla section. Wt% vs. frequency for the histograms and cumulative frequency for the curve.

Figure 8.3.6.2: Histograms and cumulative frequency curves representing all sample data for the Aralla section. a) Showing the calculated degree of pyritization (DOP); A = Anaerobic (0-0.4); R = Restricted (0.45-0.75); I = In hospitable (0.55-1) ranges from Raiswell et al., 1988. b + c) Palaeo-redox proxies V/(V + Ni) and V/Cr. Ranges for inferred bottom-water conditions for V/Cr, <2 oxic, 2-4.25 dysoxic, >4.25 suboxic-anoxic from Jones and Mann (1994); ranges for V/(V + Ni), <0.46 oxic, 0.46-0.6 dysoxic, 0.54-0.82 suboxic-anoxic, >0.84 euxinic are from Hatch and Leventhal (1992).
1.3.7 K, Th and U bubble plots

Figure 8.3.7.1: Bubbles plots of K₂O, Th and U for the Aralla section. a) Representing all the sample data from the Aralla section (241 samples), b) Showing just the basal shales (lower member, 181 samples) of the Formigoso Fm.). The K₂O, Th and U contents were analysed by X-Ray Fluorescence (XRF) whole rock analysis, the bubble size is proportional to U content.
1.3.8 Ternary diagrams

The symbols for the differing lithologies within the ternary plots remain consistent throughout all ternary diagrams; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). For the expanded plots the key is given alongside each figure.

Figure 8.3.8.1: Ternary diagram of Ross & Bustin, (2009) showing relative proportions of major shale/mud rock components; SiO$_2$ (quartz), Al$_2$O$_3$ (clays) and CaO (carbonates), displaying data from the Aralla section (all 241 samples). The Key for the expanded plot is shown to the left of the figure, the key for the inset ternary (top right); square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.), the ‘Average shale’ also shown as star (after Wedepohl, 1971).
Figure 8.3.8.2: Aralla section (all 241 samples) ternary 10Al$_2$O$_3$ - 200TiO$_2$ - Zr (Mongelli et al., 2006) plot showing possible sorting effects, the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).

Figure 8.3.8.3: Aralla section (all 241 samples) ternary 15Al$_2$O$_3$ - 300TiO$_2$ - Zr plot (Mongelli et al., 2006) showing possible sorting effects, the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).
Figure 8.3.8.4: TOC–S–Fe relationships (Ross & Bustin (2009) for the Aralla section (all 241 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.).

Figure 8.3.8.5: TOC–TS10–Fe ternary diagram for the Aralla samples (all 241). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). The construction and principles of the diagram based on Dean and Arthur (1989) and Arthur and Sageman (1994).
Figure 8.3.8.6: Degree of pyritization of sediments from the Aralla section (all 241 samples) in the Fe(x) - total organic carbon (TOC) - S₂ (following stoichiometry of pyrite-FeS₂) system (relative weight ratios). Reactive Fe (Fe(x)) is calculated with Fe(x) = Fe – 0.25 × Al (Mosher et al., 2006). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.).
Figure 8.3.8.7: Al–Mg–Ca diagram (Garnier et al., 2008) showing the distribution of the shales and sands from the Formigoso Fm. at Aralla (all 241 samples were used). Inset ternary (top left); the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.), the domains of evaporites and meta-evaporites, and of platformal marls and shales are from Moine et al., (1981). The key for the expanded plot is towards the right of the figure.
Figure 8.3.8.8: The ternary diagrams top right (inset): (A) Ternary plot of (Cu+Co+Ni)10 – Fe – Mn showing various generic fields (Mohapatra 2009), displaying all data (241 samples) from Aralla section (B) Chemical composition of the formations at the Aralla section (all 241 samples) in terms of components Fe – Mn – Al+Si. The arrow indicates the decreasing clastic input. The key for the expanded plots is found towards the upper left of the figure.
Figure 8.3.8.9: Th – (Cr + Ti)/1000 – Zr/10 ternary plot (Hessler & Donald, 2006). Showing all 241 samples from the Aralla section, a clear differentiation between the basal shales (Bernesga Mb.) and the upper sands/silts (Villasimpliz Mb.). The key for the upper left ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.).

Figure 8.3.8.10: Al₂O₃, MgO and Fe₂O₃ ternary plot representing data from the Aralla section (all 241 samples). There are two differing trends between the basal shales (Bernesga Mb.) and the upper sands/silts (Villasimpliz Mb.), possibly a result of differing provenance sources or maybe just a grain size effect. The key for the upper left ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.).
Figure 8.3.8.11: Al₂O₃, MgO * 10 and Fe₂O₃ - (expanded plot of previous (Figure 8.3.8.10)) representing data from the Aralla section (all 241 samples). Two differing trends seen, possibly resulting from differing provenance sources or maybe just a grain size effect. The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.).

Figure 8.3.8.12: Fe₂O₃, Al₂O₃ and MnO ternary plot; represents data from the Aralla section (all 241 samples). The key for the upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). The key for the expanded plot is seen towards the left of the figure.
Figure 8.3.8.13: Distribution of Fe$_2$O$_3$, Al$_2$O$_3$ and SiO$_2$ within the Aralla section (241 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.), compared with several ideal clay minerals, including chamosite (Chm), berthierine (Ber) thin/long rectangle to represent variable compositions, kaolin and muscovite (Ka/Mu), nontronite (Non), illite thick/long rectangle and glauconite (Gla) (Konhauser et al., 1998, Konhauser & Urrutia, 1999 and Eickmann et al., 2009). The key for the expanded plot is seen towards the left of the figure.

Figure 8.3.8.14: Distribution of K$_2$O, Al$_2$O$_3$ and SiO$_2$ from the Aralla section (all 241 samples analysed). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.) compared to several ideal clay minerals, including, kaolin (Ka), muscovite (Mu) , illite (ill) long rectangle (representing varying compositions) and glauconite (Gla) (Konhauser et al., 1998 & 1999) are labelled. The key for the expanded plot is seen towards the left of the figure.
Figure 8.3.8.15: Th, As/10 and U ternary plot, representing data from the Aralla section (all 241 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). There is a clear deference between the basal shales of the Bernesga Mb. and the sands/silts of the Villasimpliz Mb., the sands/silts are depleted in U. There appears to be up to four differing families within the shales (most probably representing the cyclicity of the redox sensitive elements).

Figure 8.3.8.16: Major geochemical components Al₂O₃ x 5 - SiO₂ - CaO x 2 (relative weight ratios) for the Aralla section (All 241 samples shown). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal
crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). Data points for average shale (Wedepohl, 1971, 1991), kaolinite and K-feldspar are shown for comparison.

Figure 8.3.8.17: Ternary plot for Fe₂O₃, K₂O and Al₂O₃, showing all samples from the Aralla section (241 samples). The upper right ternary; square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.), the key towards the left of the figure is for the exploded diagram. The shales cluster away from the sand/silt intercalations. A clear maturity trend towards the Barrios Fm. is also evident.
Figure 8.3.8.18: Ternary plot for SiO$_2$/Al$_2$O$_3$, TiO$_2$ and MgO, expressing all samples from the Aralla section (241 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). The shales cluster away from the sand/silt intercalations, there appears to be two distinct families of shale and possibly up to four families of the silts/sand.

Figure 8.3.8.19: Ternary plot for U*20, Zr and Sr, expressing all samples from the Aralla section (241 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.) The shales (enriched in Sr and U) cluster away from the sand/silt intercalations that plot towards the heavy element Zr.
Figure 8.3.8.20: Ternary plot for K₂O, Th and U, showing all samples from the Aralla section (241 samples). The ternary plot (upper right); square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). The key is valid for the exploded diagram. The shales (depleted in K₂O (feldspar fragments) in relation to the sandstones) cluster away from the sand/silt intercalations. Note that either side of the diagram the shales appear highly enriched in U and the sands opposite show U depletion.

Figure 8.3.8.21: Ternary plot representing all data for the Aralla section (241 samples) showing the relationship between K₂O*5, Th and U as previously (Figure 8.3.8.20) yet a higher factor for K values. The Majority of the sands/silts cluster towards the K₂O enrichment, K₂O resides mostly within the detrital faction.
Figure 8.3.8.22: Ternary plot (Ratcliffe, 2007) representing all data for the Aralla section (241 samples) showing the relationship between the heavy elements; Zr, Cr and Ni. The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bermesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). The sands cluster towards Zr.

Figure 8.3.8.23: Ternary plot representing samples from the Aralla section (all 241). Cross-plot constructed to characterise between the Shales (differing subunits?) and the sands/silts, clearly geochemically separated.
Figure 8.3.8.24: Ternary diagram Fe$_2$O$_3$ – MgO – SiO$_2$/Al$_2$O$_3$ representing data from the Aralla section (all 241 samples). The upper right ternary; square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). The expanded plot clearly discriminates between the shales and the silt/sand intercalations.

Figure 8.3.8.25: Ternary diagram Zr – Cr – Ni, representing data from the Aralla section (all 241 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.). The plot clearly discriminates between the shales and the silt/sand intercalations.
Figure 8.3.8.26: CIA ternary diagram, $\text{Al}_2\text{O}_3$ – $\text{CaO} + \text{Na}_2\text{O} – \text{K}_2\text{O}$ (after Nesbitt and Young, 1982), displaying data from the Aralla section (all 241 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.).

Figure 8.3.8.27: $\text{Al}_2\text{O}_3$ – (CaO + Na$_2$O + K$_2$O) – (Fe$_2$O$_3$ + MgO) ternary diagram (Hayashi et al., 1997), representing data from the Aralla section (all 241 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) and the upright crosses – upper Formigoso Fm. (Villasimpliz Mb.)
1.3.9 Clay typing for all localities

Figure 8.3.9.1: Cross plots between K2O (Wt%) and Th (ppm) (Schlumberger Well Services 2009) for all study locations, discriminating the radioactive minerals present according to their thorium and potassium concentrations. The plots show only the basal Bernesga Mb. shale data from each of the five localities. a) Aralla section, b) Caldas de Luna section, c) La Majua section, d) Sena de Luna section and e) Villanueva section.
1.3.10 Index of Compositional Variation (ICV)

Figure 8.3.10.1: Values of K$_2$O/Al$_2$O$_3$ ratio for K-feldspars and clay minerals (left hand figure), the stars represent values for specific minerals indicated; data from Deer et al., 1966, diagrams from Cox, 1995. Values for the Index of Compositional Variation (ICV – right hand figure); (Fe$_2$O$_3$ + K$_2$O + Na$_2$O + CaO + MgO + MnO + TiO$_2$)/Al$_2$O$_3$, stars represent values for specific minerals indicated, The arrows show the range of values for the particular mineral group, data from Deer et al., 1966, diagrams from Cox, 1995.
Figure 8.3.10.2: a) $K_2O/Al_2O_3$ ratio for the Aralla section (in order to discriminate K-feldspars and clay minerals). The stars represent values for specific minerals indicated, data from Deer et al., 1966, overlay from Cox, 1995. b) expanded plot of the original (a). c) Index of Compositional Variation (ICV): $(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3$ for the Aralla section, the stars represent values for specific minerals indicated, the arrows show the range of values for the particular mineral group, data from Deer et al., 1966, overlay Cox, 1995. d) Expanded plot of the original (c); possible cyclicity apparent within the ICV values.

$K_2O/Al_2O_3$ - range of Bernesga Mb. (shales) at Aralla: 0.0804-0.1620

$K_2O/Al_2O_3$ - range of Villasimpliz Mb. (sandstone intercalations) at Aralla: 0.0933-0.2259

$K_2O/Al_2O_3$ - average of Bernesga Mb. (shales) at Aralla: 0.1333

$K_2O/Al_2O_3$ - average of Villasimpliz Mb. (sandstone intercalations) at Aralla: 0.1791

ICV - range of Bernesga Mb. (shales) at Aralla: 0.3423-0.7831 (1.5004 including Fe spike)

ICV - range of Villasimpliz Mb. (sandstone intercalations) at Aralla: 0.4635-1.3832 (lower range may be siltstone horizon)

ICV - average of Bernesga Mb. (shales) at Aralla: 0.4519

ICV - average of Villasimpliz Mb. (sandstone intercalations) at Aralla: 0.6989
1.3.11 Chemical Index of Alteration (CIA), PIA & CIW

Figure 8.3.11.1: Representing data from the Aralla section (all 241 samples). The ‘Chemical Index of Alteration’ (CIA) (Nesbitt and Young, 1982, Taylor and McLennan, 1985) is a well-established parameter for determining the degree of weathering and is the most accepted of the available weathering indices. During the degradation of feldspars, Ca, Na, and K are removed and clay minerals with a higher fraction of Al are formed. The CIA is estimated from the proportion of Al₂O₃ vs. the weathering-prone oxides. This index measures the degree of feldspar decomposition to secondary clay products, where CIA values of about 50 indicate fresh bedrock (no chemical weathering), and values of 75-100 indicate complete conversion of feldspars to aluminous clay minerals (intense chemical weathering; see Fedo et al., 1995):

\[
\text{CIA} = \left[ \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \right] \times 100
\]

A) Kaolinite has a CIA value of 100 and represents the highest degree of weathering. Illite is between 75 and c. 90, muscovite at 75, the feldspars at 50. Fresh basalts have values between 30 and 45, fresh granites and granodiorites of 45 to 55 (Nesbitt and Young, 1982; Fedo et al., 1995). B) Expanded plot, focusing within the Illite Zone (muscovite line also shown).
The average CIA value for the Bernesga Mb. (black shales) at Aralla: **84.73** (high degree of weathering refer to Mosher et al., 2006 p.6).

Figure 8.3.11.2: Representing all data from the Aralla section (241 samples), the 'Plagioclase Index of Alteration' (PIA; Fedo et al., 1995)

\[
\text{PIA} = \left( \frac{\text{Al}_2\text{O}_3 - \text{K}_2\text{O}}{\text{(Al}_2\text{O}_3 - \text{K}_2\text{O} + \text{CaO} + \text{Na}_2\text{O})} \right) \times 100
\]

PIA values of around 50 represent unaltered crystalline bedrock and values approaching 100 indicate significant production of secondary aluminous clay minerals.

A) Displays the PIA values for the Aralla section, and B) Expanded plot of the PIA values.

The average PIA value for the Bernesga Mb. (black shales) at Aralla: **94.83**
Figure 8.3.11.3: Representing all data from the Aralla section (241 samples), the ‘Chemical Index of Weathering’ (CIW; Harnois, 1988).

\[
CIW = \frac{[\text{Al}_2\text{O}_3]}{[\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O}]} \times 100
\]

The CIW index increases with the degree of depletion of the soil or sediment in Na and Ca, relative to Al. The value of this index increases as the degree of weathering increases, and the difference between CIW index values of the silicate parent rock and soil or sediment reflects the amount of weathering experienced by the weathered material (Harnois, 1988).

A) Showing the CIW values for the Aralla section. B) Expanded plot of the CIW values.

The average CIW value for the Bernesga Mb. (black shales) at Aralla: **95.5**
1.3.12 Gamma-ray log and Total Organic Carbon (TOC)

The following section documents the calculated gamma ray (API)/ TOC values for the Aralla section (all 241 samples). The API values were calculated following the protocol in the methodology chapter, the same goes for the TOC values calculated after Fertl & Chillingar, 1988, also documented in the methods chapter.
Figure 8.3.12.1: Showing whole rock K$_2$O, Th and U values for the Aralla section (every data point represents 25cm of stratigraphy) from the Barrios Fm. (Aralla 1), Getino Beds (Aralla 2+3 in green) and throughout the Formigoso Fm. Aralla 3-184 contain the basal shales (or lower Bernesga Mb., light grey) there is then a break in the section of 27.3m (represented by the grey shaded line) which is followed by sand and silt intercalations (or upper Villasimpliz Mb., dark grey). Note the cyclic behaviour of the U values (prominent 3 cycles within the first 60 samples). The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite data, suggesting a ~4Myr time span (from the lowest of the Alargada Biozone to the upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each, the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons. There is a significant shift in the data after the 3rd cycle (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The figure above also displays, Gamma-ray (GR), Computed Gamma-ray (CGR) and Total Organic Carbon (TOC) values for the Aralla section. Note the cyclic behaviour of the GR and TOC values (prominent 3 cycles within the first 60 samples). The basal Bernesga Mb. shales (lower member of Formigoso Fm.) has been given rough age constrains at the base and top using graptolite data, suggesting a ~4Myr time span.

The GR values were calculated by converting K$_2$O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using $6.69U + 2.54Th + 10.64K_2O = API$ after (http://server4.oersted.dtu.dk/research/RI/SNG/SNG-logs.html). CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: $3.9637\times\ln(\text{Uranium Values}) - 5.6873$. This formula was calculated after Fertl & Chillingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean’ shales of Luning (2000).
Figure 8.3.12.2: Showing whole rock K₂O, Th and U values for the Aralla section (every data point represents 25cm of stratigraphy) from the Barrios Fm. (Aralla 1), Getino Beds (Aralla 2+3 in green) and throughout the Formigoso Fm. Aralla 3-184 contain the basal shales (or lower Bernesga Mb., light grey) there is then a break in the section of 27.3m (represented by the grey shaded line) which is followed by sand and silt intercalations (or upper Villasimpliz Mb., dark grey). Note the cyclic behaviour of the U values (prominent 3 cycles within the first 60 samples). The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~ 8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons. There is a significant shift in the data after the 3rd cycle (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The figure above also displays, Gamma-ray (GR), Computed Gamma-ray (CGR) and Total Organic Carbon (TOC) values for the Aralla section. Note the cyclic behaviour of the GR and TOC values (prominent 3 cycles within the first 60 samples). The basal Bernesga Mb. shales (lower member of Formigoso Fm.) has been given rough age constrains at the base and top using graptolite data, suggesting a ~4Myr time span.

The GR values were calculated by converting K₂O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using \( 8U + 4Th + 16K2O = API \) after Elis, 1987 and Doveton, 2004. CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function:

\[ =3.9637 \times \ln(\text{Uranium Values}) - 5.6873 \]

This formula was calculated after Fertl & Chillingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
1.3.13 Hydrothermal Overprint

Figure 8.3.13: Bostrom (1973) diagram; the analysed sediments (all 241 samples from the Aralla section) are compared to argillite (T) and hydrothermal (H) end members whose mixing is modelled by the H-T curve. PAAS and NASC (Gromet et al., 1984) are reported for comparison.
1.3.14 Bioproductivity Reconstruction (Barium proxy) & SEM/DOP

Figure 8.3.14.1: a) Al/Ti ratio, data from the Aralla section, shaded region indicates approximate range in shales, pelagic clay, andesite and hydrothermal sediment, and the dashed lines representing oceanic crust & granite Al/Ti ratios after Murray & Leinen, 1996. It shows that the shales of the Formigoso Fm. are enriched in Al (as seen in the EF diagrams) giving the higher Al/Ti ratios, pushing towards the granitic composition, this fits with the bulk composition of basal granitic hinterland.

To test whether the Al enrichment is due to the granitic composition of the hinterland the Fe/Al ratio is used (b). The ranges after Gordon et al., 1996 in Murray & Leinen, 1996 (labelled a-e); if the sediment source were composed of pure granite (Al/Ti ~ 40; Taylor and McLennan, 1985), it could be the cause of the elevated Al/Ti. Upper crust (Fe/Al ~ 0.42, a), PAAS (~0.57, b), pelagic clay (~0.77, c), and, bulk continental crust (~0.84, d) (Taylor and McLennan, 1985). In granite, Fe/Al ~ 0.28, e (Taylor and McLennan, 1985). From this it can be inferred that the Formigoso Fm. basal shale composition is closest to that of a granitic source.

c) Table displaying Al/Ti ratios of modern day terrestrial source material, aeolian dust and marine sediments modified after Zabel et al., (1999), comparison of the Formigoso Fm. Al/Ti ratios to that of modern day environments (Aralla ranging from ~12-36 sat within the deep-sea sediments ranges, yet higher range 36 comparable to that of surface sediments (equatorial pacific) .

d) TiO₂ vs. Al₂O₃ cross plot including all data from the Aralla section (241 samples). The plot shows a near prefect correlation between TiO₂ and Al₂O₃ (R² = 0.874) indicating that the elements are associated with the clay mineralisation and that neither are enriched in relation to each other (no biogenic input). This meant that both elements could be used when calculating the primary production (or palaeoproductivity).

Hydrothermal tests were also carried out (refer to previous figure) to determine if the Formigoso Fm. had undergone any extensive alteration due to pululating hydrothermal fluids, thus, overprinting the true geochemistry (hydrothermal elements anyhow). The tests carried out suggested that the basal Bernesga Mb. of the Formigoso Fm. had not been effected by any hydrothermal overprinting however the upper Villasimpliz Mb. (sands and silts) had been effected yet not significantly (slightly more porous). Therefore, the Ba values of the Formigoso Fm. have not been significantly altered by hydrothermal activity, at least in the lower Bernesga Mb.
Figure 8.3.14: Representing the calibrated elemental values for the Aralla section, all the elements and ratios are plotted against stratigraphy (Aralla 1 being the oldest, Aralla 241 the youngest), sampled at 25cm intervals. The sample No. X-axis of these plots are inverted in relation to all previous plots, as they are to be used in well log form. A set or averaged Ba/Al and Ba/Ti ratio is used for the calculation of the Ba_{bio}, for each location, yet graphs e & f show the variation of Ba/Al and Ba/Ti ratios for the Aralla section.
<table>
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<tr>
<th>Area/material</th>
<th>Detrital Ba/Al ratio</th>
<th>Reference</th>
</tr>
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<td>Ba/Al ratios abundance of aluminosilicate detritus</td>
<td>0.005 – 0.01</td>
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<td>Krauskopf, 1967</td>
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<td>Taylor and Mckenman, 1985; Wedepohl, 1995</td>
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<td></td>
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<td>0.0027[a]</td>
<td>(1) Gingele and Dahnke, 1994; (a) Pfeiffer et al., 2004</td>
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<td>(Congo Fan)</td>
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</tr>
<tr>
<td>Eastern Mediterranean Sea</td>
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<td></td>
<td>Rütten, 2001</td>
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</tr>
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<td>Arabian Sea</td>
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<td>0.0039(b)</td>
<td>(3) Emeis, 1993; (b) Schmoual et al., 2001</td>
</tr>
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**Figure 8.3.14.3:** Tables displaying the global Ba/Al average values for area/materials and regions, modified after Pfeiffer et al., 2004. The Ba/Al values (highlighted) for the Atlantic Ocean off West Africa (0.0045) and organic rich sediment (0.0032) are closest to the global crustal average value (0.0037) after Pfeiffer et al., 2004 used in this project. The 0.0045 ratio of the African sediments is closest to that of the basal Gondwanan hinterland values.
Figure 8.3.14.4: Biogenic barium or $Ba_{\text{bio}}$ (also called $Ba_{\text{excess}}$) & $Ba_{\text{bio(min)}}$ values calculated for the Aralla section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) $Ba_{\text{bio}} = Ba_{\text{tot}} - (Al \times Ba/Al_{\text{aluminosilicate}})$ from Pfeifer et al., 2001

2) $Ba_{\text{bio}} = Ba_{\text{tot}} - (Al \times Ba/Ti_{\text{aluminosilicate}})$ from Bonn et al., 1998

The total $Ba$, $Ba_{\text{bio}}$ and $Ba_{\text{bio(min)}}$ values are plotted against stratigraphy Aralla 1 being the oldest and Aralla 241 the youngest, the sampling interval was set at 25cm. A number of ratios were selected for the aluminosilicate fraction and these were as follows:

1) $Ba/Al_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.002913

2) $Ba/Al_{\text{(min)}}$ ratio (minimum Bernesga Mb. $Ba/Al$ ratio at the Aralla section) = 0.001204

3) $Ba/Al_{\text{aluminosilicate}}$ ratio (global ave.) = 0.0037

The global crustal average $Ba/Al_{\text{aluminosilicate}} = 0.0037$, from Pfeifer et al., 2004 & Pirrung et al., 2008 (0.007 is the most widely used global average crustal value from Pirrung et al., 2008 p. 7, original ref; Dymond et al., 1992; Nürnberg et al., 1997). I used 0.0037 as Gingele and Dahmke (1994) used 0.004 in; Pfeifer et al., 2001 (p. 5) they stated that sediments north of 30°S are prone to higher weathering conditions due to higher humidity (fits with my humidity proxies and Silurian global reconstructions), the 0.0037 ratio is lower than that of the global ave. 0.007 which means it pushes the data away from the negative values; it gives the most convincing results, Pfeifer et al., 2004. When comparing the 0.0037 ratio to the values shown in the previous tables (Pfeifer et al., 2004) it can be seen that it is closest to that of the African sediment; 0.0045 of Rutsch et al., 1995 and the organic rich sediment; 0.0032 of Rutten, 2001. The average $Al/Ba$ ratios for the Formigoso Fm. (0.002813) are also closest to that of the organic rich sediment of Rutten, 2001.

4) $Ba/Ti_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.068156

5) $Ba/Ti_{\text{(min)}}$ ratio (minimum Bernesga Mb. $Ba/Ti$ ratio at the Aralla section) = 0.014883

6) $Ba/Ti_{\text{aluminosilicate}}$ ratio (global ave.) = 0.126
The global crustal average Ba/Ti aluminosilicate ratio (global ave.) = 0.126, used for this study from Turekian and Wedepohl, 1961 in; Bonn et al., 1998 (0.14 average upper continental crust Wedepohl, 1995 in; Pirrung et al., 2008 p.6).

The Ba/Al_{min} and Ba/Ti_{min} values for the Aralla section were used after Babu et al., 2002 as the Ba_{bio} values calculated cannot be negative. The ave. Formigoso Fm. Ba/Al and Ba/Ti ratios are too high, meaning that the calculated Ba_{bio} values were negative, when using the lowest ratios in the area (Aralla) for Ba/Al and Ba/Ti it pushes the Ba_{bio} values into positive values as shown on graphs a and b. Graph c uses the global averages for Ba/Al (0.0037) and Ba/Ti (0.126) as a direct comparison.

The Ba/Al_{min} and AR Ba_{bio} values for the Aralla section were used after Babu et al., 2002 as the Ba_{bio} values calculated cannot be negative. The ave. Formigoso Fm. Ba/Al and Ba/Ti ratios are too high, meaning that the calculated Ba_{bio} values were negative, when using the lowest ratios in the area (Aralla) for Ba/Al and Ba/Ti it pushes the Ba_{bio} values into positive values as shown on graphs a and b. Graph c uses the global averages for Ba/Al (0.0037) and Ba/Ti (0.126) as a direct comparison.

Figure 8.3.14: Accumulation rates of the biogenic barium (AR Ba_{bio} and AR Ba_{bio(min)}) expressed in g cm^{-2} kyr^{-1}, calculated for the Aralla section using the following formulas from Pfeifer et al., 2001;

1) \( AR \, Ba_{bio} = Ba_{bio} \times MAR/100 \) (where MAR = Mass accumulation rate in g cm^{-2} kyr^{-1})

2) \( MAR = SR \times DBD \) (where SR = sedimentation rate in cm kyr^{-1} and DBD = dry bulk density in g cm^{-3})

The sedimentation rate (SR) was calculated by using graptolite age constraints of the basal shales of the Formigoso Fm. and the number of samples taken. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a timespan of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; then the 181 shale samples from the lower Bernesga Mb. (sampled at intervals of 25cm) can be assigned an age of ~22099yrs per sample. The first 4 meters of the Aralla section were then analysed at a higher resolution of 1cm (age representation of ~883.97yrs per reading). From this an approximate average SR of 1.11603cm kyr^{-1} was calculated, however, this average SR does not take into consideration condensed horizons within the basal Bernesga Mb.; represented by the mass accumulation horizons of monograptid graptolites within the basal section (mass graptolite zones representing starved basin conditions).

The dry bulk density (DBD) was estimated by taking the average shale density ranges 1.8 – 2.8 g cm^{-3} (Glover, 2000). Both the lower range value and upper range DBD values were used in the calculations.

The two MAR values used;
1) $2.008854 \text{ g cm}^{-2} \text{ kyr}^{-1}$ (lowest range using 1.8 g cm$^{-3}$ DBD)

2) $3.124884 \text{ g cm}^{-2} \text{ kyr}^{-1}$ (highest range using 2.8 g cm$^{-3}$ DBD)

a) Represents the AR Ba$\text{bio}$ & AR Ba$\text{bio(min)}$ calculated using the upper and lower MAR values listed above and the Ba$\text{bio}$ & Ba$\text{bio(min)}$ values from the previous figure (the ave. Formigoso Fm. Ba/Al ratio and lowest Ba/Al ratio from Aralla). b) The AR Ba$\text{bio}$ & AR Ba$\text{bio(min)}$ calculated using the upper and lower MAR values listed above and the Ba$\text{bio}$ & Ba$\text{bio(min)}$ values from the previous figure (ave. Formigoso Fm. Ba/Ti ratio and lowest Ba/Ti ratio from Aralla). c) The AR Ba$\text{bio}$ calculated using the upper and lower MAR values listed above and the Ba$\text{bio}$ values from the previous figure (global ave. Ba/Al ratio). d) The AR Ba$\text{bio}$ calculated using the upper and lower MAR values listed above and the Ba$\text{bio}$ values from the previous figure (global ave. Ba/Ti ratio).

Figure 8.3.14.6: The flux of Ba to the sea floor (or $F_{\text{Ba}}$) was calculated using the following formulas from Pfeifer et al., 2001 and Bonn et al., 1998 for the Aralla section:

1) $F_{\text{Ba}} = \text{AR Ba}_{\text{bio}} / 0.209 \log(\text{MAR}) - 0.213$ expressed in mg cm$^{-2}$ kyr$^{-1}$

2) %Ba$\text{pres} = 20.9 \log(\text{MAR}) - 21.3$

The amount of Ba dissolved at the sediment water interface (or $F_{\text{Ba}}$) is calculated by dividing the AR Ba$\text{bio}$ by the %Ba$\text{pres}$ (or % of preserved Ba). a) Shows $F_{\text{Ba}}$ and $F_{\text{Ba(min)}}$ using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Al ave. ratio and the Aralla Ba/Al min value (calculated AR Ba$\text{bio}$ and AR Ba$\text{bio(min)}$ for Ba/Al ratios). b) Shows $F_{\text{Ba}}$ and $F_{\text{Ba(min)}}$ using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Ti ave. ratio and the Aralla Ba/Ti min value (calculated AR Ba$\text{bio}$ and AR Ba$\text{bio(min)}$ for Ba/Ti ratios). c) shows $F_{\text{Ba}}$ using the previously calculated upper and lower MAR values and the global Ba/Al ave. ratio (global AR Ba$\text{bio}$ for Ba/Al) and d) shows $F_{\text{Ba}}$ using the upper and lower MAR values and the global Ba/Ti ave. ratio (global AR Ba$\text{bio}$ for Ba/Ti).
Figure 8.3.14.7: The calculation of new production or ($P_{\text{new}}$ and $P_{\text{new(min)}}$) for the Aralla section following the formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) $P_{\text{new}} = 1.95 \times 1.41$ expressed in gC m$^{-2}$ yr$^{-1}$

a) Showing the $P_{\text{new}}$ and $P_{\text{new(min)}}$ values for the Aralla section using the previously calculated upper and lower MAR values and $F_{\text{Ba}}$ flux values using the Ba/Al ratios. b) Showing the $P_{\text{new}}$ and $P_{\text{new(min)}}$ values for the Aralla section using the previously calculated upper and lower MAR values and $F_{\text{Ba}}$ flux values using the Ba/Ti ratios. c) Showing the $P_{\text{new}}$ values for the Aralla section using the previously calculated upper and lower MAR values and $F_{\text{Ba}}$ flux values using the global ave. Ba/Al ratio. d) Showing the $P_{\text{new}}$ values for the Aralla section using the previously calculated upper and lower MAR values and $F_{\text{Ba}}$ flux values using the global ave. Ba/Ti ratio.
Figure 8.3.14: The calculation of primary production or palaeoproductivity (PP and PP_{min}) for the Aralla section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998;

1) \( PP = 20 \left( P_{\text{new}} \right)^{0.5} \) expressed in gC m\(^{-2}\) yr\(^{-1}\)

a) Showing the PP and PP_{min} values for the Aralla section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the Ba/Al ratios. b) Showing the PP and PP_{min} values for the Aralla section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the Ba/Ti ratios. c) Showing the PP values for the Aralla section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the global Ba/Al ratio. d) Showing the PP values for the Aralla section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the global Ba/Ti ratio.
1.3.15 3D Environmental Reconstruction Models

Figure 8.3.15.1: General 3D plots (same data shown from differing perspectives) showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. X-Ray Fluorescence (XRF) was used for the whole-rock geochemical analysis. The plots represent all sample data from the Aralla section (241 samples). Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic conditions after Fertl, 1979. There is no U within the sandstones (oxic); this explains why they fall in the anoxic zone (0 values for ratio). Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales. The (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values are generally found in samples with little carbonate.
Figure 8.3.15.2: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Si/Al, showing data from the Aralla section (all 241 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents freshwater to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 ‘oxic’, 0.46-0.60 ‘dysoxic’, 0.54-0.82 ‘suboxic-anoxic’ and >0.82 ‘euxinic’ (Hatch and Leventhal, 1992). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al$_2$O$_3$, TiO$_2$, and K2O in the clay fraction) high values reflect course grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.

Note the how the diagrams discriminate between the clustered black shales and the trending sands/silts or detrital influx (particularly apparent in graph C).
Figure 8.3.15.3: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Zr/Rb (contrasting grain size proxy to the previous figure Si/Al), displaying data from the Aralla section (all 241 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 'oxic', 0.46 - 0.60 'dysoxic', 0.54 - 0.82 'suboxic-anoxic' and >0.82 'euxinic' (Hatch and Leventhal, 1992). The Zr/Rb ratio is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect course grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input 'detrital influx' therefore rising sea-level or basin subsidence.

Note the how the diagrams discriminate between the clustered black shales and the trending sands/silts or detrital influx (particularly apparent in graph C).
Figure 8.3.15.4: Geochemical environmental reconstruction, using the ratios Rb/K, Th/U and Si/Al, displaying data from the Aralla section (all 241 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic (Fertl, 1979). There is no U within the sandstones (oxic); explaining they fall into the anoxic zone (0 values for ratio). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect course grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.

Note the how the diagrams discriminate between the clustered black shales and the trending sands/silts or detrital influx (particularly apparent in graph C).
1.3.16 Cyclicity

Figure 8.3.16.1: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Aralla section, 181 samples (Aralla 4 – Aralla 184). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the U ppm values from the base (sample No. 1) to the top (sample No. 181) of the lower member, cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0069444</td>
<td>= 1/(0.0069444/22099 yrs)</td>
<td>3.18 Myr</td>
</tr>
<tr>
<td>0.01875</td>
<td>= 1/(0.01875/22099 yrs)</td>
<td>1.17 Myr</td>
</tr>
<tr>
<td>0.025964</td>
<td>= 1/(0.025964/22099 yrs)</td>
<td>851.14 Kyr</td>
</tr>
<tr>
<td>0.038194 (highest intensity)</td>
<td>= 1/(0.038194/22099 yrs)</td>
<td>576.59 Kyr</td>
</tr>
<tr>
<td>0.045833</td>
<td>= 1/(0.045833/22099 yrs)</td>
<td>482.16 Kyr</td>
</tr>
<tr>
<td>0.070833</td>
<td>= 1/(0.070833/22099 yrs)</td>
<td>311.98 Kyr</td>
</tr>
<tr>
<td>0.11458</td>
<td>= 1/(0.11458/22099 yrs)</td>
<td>192.66 Kyr</td>
</tr>
<tr>
<td>0.20903</td>
<td>= 1/(0.20903/22099 yrs)</td>
<td>105.72 Kyr</td>
</tr>
<tr>
<td>0.26317</td>
<td>= 1/(0.26317/22099 yrs)</td>
<td>83.97 Kyr</td>
</tr>
<tr>
<td>0.30347</td>
<td>= 1/(0.30347/22099 yrs)</td>
<td>72.82 Kyr</td>
</tr>
<tr>
<td>0.47917</td>
<td>= 1/(0.47917/22099 yrs)</td>
<td>46.11 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the Aralla section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.3.16.2: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Aralla section, 181 samples (Aralla 4 – Aralla 184). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) to the top (sample No. 181) of the lower member, cyclicity is apparent in the V values. b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00625</td>
<td>1/(0.00625/22099 yrs)</td>
<td>3.39 Myr</td>
</tr>
<tr>
<td>0.020139</td>
<td>1/(0.020139/22099 yrs)</td>
<td>1.08 Myr</td>
</tr>
<tr>
<td>0.025694</td>
<td>1/(0.025694/22099 yrs)</td>
<td>860.08 Kyr</td>
</tr>
<tr>
<td>0.038889</td>
<td>1/(0.038889/22099 yrs)</td>
<td>568.25 Kyr</td>
</tr>
<tr>
<td><strong>0.045833</strong> (highest intensity)</td>
<td>1/(0.045833/22099 yrs)</td>
<td><strong>482.16 Kyr</strong></td>
</tr>
<tr>
<td>0.10278</td>
<td>1/(0.10278/22099 yrs)</td>
<td>215.01 Kyr</td>
</tr>
<tr>
<td>0.23264</td>
<td>1/(0.23264/22099 yrs)</td>
<td>94.99 Kyr</td>
</tr>
<tr>
<td>0.32222</td>
<td>1/(0.32222/22099 yrs)</td>
<td>68.58 Kyr</td>
</tr>
<tr>
<td>0.35764</td>
<td>1/(0.35764/22099 yrs)</td>
<td>61.79 Kyr</td>
</tr>
<tr>
<td>0.37986</td>
<td>1/(0.37986/22099 yrs)</td>
<td>58.17 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the Aralla section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.3.16.3: Showing the first 3 cycles (lower Bernesga Mb. of the Formigoso Fm.) for the Aralla section, all 65 samples (Aralla 4 – Aralla 68). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member). a) shows the U ppm values from the base (sample No. 1) towards the middle (sample No. 65) of the Bernesga Mb. cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

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<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.019631</td>
<td>1/(0.019631/22099 yrs)</td>
<td>1.13 Myr</td>
</tr>
<tr>
<td>0.042669 (highest intensity)</td>
<td>1/(0.042669/22099 yrs)</td>
<td>514.3 Kyr</td>
</tr>
<tr>
<td>0.21289</td>
<td>1/(0.21289/22099 yrs)</td>
<td>103.8 Kyr</td>
</tr>
<tr>
<td>0.25781</td>
<td>1/(0.25781/22099 yrs)</td>
<td>85.71 Kyr</td>
</tr>
<tr>
<td>0.30273</td>
<td>1/(0.30273/22099 yrs)</td>
<td>72.99 Kyr</td>
</tr>
<tr>
<td>0.47852</td>
<td>1/(0.47852/22099 yrs)</td>
<td>46.18 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the Aralla section Bernesga Mb. (the first three cycles of the previous figures). The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.3.16.4: Showing the first 3 cycles (lower Bernesga Mb. of the Formigoso Fm.) for the Aralla section, all 65 samples (Aralla 4 – Aralla 68). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) towards the middle (sample No. 65) of the Bernesga Mb. cyclicity is apparent in the V values. b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.019531</td>
<td>$1/(0.019531/22099\text{ yrs})$</td>
<td>1.13 Myr</td>
</tr>
<tr>
<td>0.042969 (highest intensity)</td>
<td>$1/(0.042969/22099\text{ yrs})$</td>
<td>514.3 Kyr</td>
</tr>
<tr>
<td>0.11133</td>
<td>$1/(0.11133/22099\text{ yrs})$</td>
<td>198.4 Kyr</td>
</tr>
<tr>
<td>0.23828</td>
<td>$1/(0.23828/22099\text{ yrs})$</td>
<td>92.7 Kyr</td>
</tr>
<tr>
<td>0.35938</td>
<td>$1/(0.35938/22099\text{ yrs})$</td>
<td>61.4 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the Aralla section Bernesga Mb. (the first three cycles of the previous figures). The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
1.3.17 High resolution sea-level oscillations (using redox sensitive elements)

Figure 8.3.17.1: Ordovician and Silurian sea-level curves modified after Munnecke et al., (2010). Highlighting the area of interest within the Silurian curves (approximate ages of the Formigoso Fm. (lower Bernesga Mb.) as given by graptolite horizons spanning ~4myr from base to top, refer to Geological Setting Chapter).
Figure 8.3.17.2: Please refer to the following figure for caption
Figure 8.3.17.3: Using high resolution whole rock geochemistry (specifically the redox sensitive elements U + V) to reconstruct a part of the lower Silurian sea-level curve. (a) represents the sea-level curve of Loydell, 1998 (cropped from previous Ordovician and Silurian sea-level figure) spanning from the Aeronian/Telychian boundary (436 Ma) to the middle Telychian Monoclimacis Graptolite Zone (~432 Ma), the approximate age constraints for the Bernesga Mb. of the Formigoso Fm. (b) showing all shale data from the Aralla section (181 samples every 25 cm), V values are indicated by the red curve, U values in blue. (c) Displaying the first 3 cycles expanded from (b) and finally (d) showing the high resolution (1 cm scale) data. Cyclicity is evident in (b-d) as confirmed by Fourier analysis. (b) Shows cyclicity which is comparable to Loydell’s 1998 global sea-level curve (highlighted in (a)). (d) The highest resolution data can be superimposed on this curve to produce a new High resolution sea level curve for the lower Silurian (or the lowermost to middle Telychian).
1.4 Aralla – High Resolution (HR) Section

The following section documents the geochemical results for the Aralla High Resolution Log section (or Aralla HR Log). The Aralla HR section consists of 339 field readings. The analysis interval within the Getino Beds and the lower most Formigoso Fm. (Bernesga Mb.) was set at 1cm.

The analysis numbers for the Aralla HR section are displayed in the table below (Table 8.4.1); please also refer to the base of the Aralla log section (showing the region analysed) in the Results Chapter and the results tables in Appendix A, B or C etc....

<table>
<thead>
<tr>
<th>Aralla HR</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>HR 1-31</td>
<td>Getino Bed at a 1cm resolution</td>
</tr>
<tr>
<td>HR 32-252</td>
<td>Formigoso Fm. (Bernesga Member) at a 1cm resolution</td>
</tr>
<tr>
<td></td>
<td>after HR 252 – 39cm gap in section</td>
</tr>
<tr>
<td>HR 253-339</td>
<td>Formigoso Fm. (Bernesga Member) at a 1cm resolution</td>
</tr>
</tbody>
</table>

Table 8.4.1 – The corresponding analysis numbers for the Aralla HR section; also refer to the sedimentary log for the Aralla section in the Results Chapter; the Aralla HR log section is highlighted at the base of the Aralla log.
1.5.4 **Major Elements**

Figure 8.4.1.1: Major element variation curves for the Aralla high resolution (HR) log section. Each analysis number represents a 1cm interval. The coloured regions indicate the differing lithologies, Getino beds (green) followed by the Formigoso Fm. (grey), the dashed line represents a break (ill exposure) of 39cm in the stratigraphy.
1.5.5 Trace Elements

Figure 8.4.2.1: Trace element variation curves for the Aralla high resolution (HR) log section. Each analysis number represents a 1cm interval. The coloured regions indicate the differing lithologies. Getino Beds (green) followed by the Formigoso Fm. (grey), the dashed line represents a break (ill exposure) of 39cm in the stratigraphy.
Figure 8.4.2. Trace element variation curves for the Aralla high resolution (HR) log section. Each analysis number represents a 1cm interval. The coloured regions indicate the differing lithologies: Getino Beds (green) followed by the Formigoso Fm. (grey), the dashed line represents a break (ill exposure) of 39cm in the stratigraphy.
Figure 8.4.2.3: Trace element variation curves for the Aralla high resolution (HR) log section. Each analysis number represents a 1 cm interval. The colored regions indicate the differing lithologies, Getino Beds (green) followed by the Formigoso Fm. (grey), the dashed line represents a break (ill exposure) of 39 cm in the stratigraphy.
1.5.6 **Cyclicity – High resolution U & V**

Figure 8.3.16.5: Displaying high resolution data of the first cycle (lower Bernesga Mb. of the Formigoso Fm.) for the Aralla section, 309 samples (HR 32 – HR 339). The field analysis was carried out at 1cm intervals (each sample represents ~883.97y calculated from graptolite assemblages at base and top of lower member) a) shows the U ppm values from the base (sample No. 1) to the top (sample No. 309), cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0044788</td>
<td>$1/(0.0044788/883.97\text{ yrs})$</td>
<td>197.36 Kyr</td>
</tr>
<tr>
<td>0.03298</td>
<td>$1/(0.03298/883.97\text{ yrs})$</td>
<td>26.8 Kyr</td>
</tr>
<tr>
<td>0.07899</td>
<td>$1/(0.07899/883.97\text{ yrs})$</td>
<td>11.0 Kyr</td>
</tr>
<tr>
<td>0.14129</td>
<td>$1/(0.14129/883.97\text{ yrs})$</td>
<td>6.2 Kyr</td>
</tr>
<tr>
<td><strong>0.1816</strong> (highest intensity)</td>
<td>$1/(0.1816/883.97\text{ yrs})$</td>
<td><strong>4.8 Kyr</strong></td>
</tr>
<tr>
<td>0.26792</td>
<td>$1/(0.26792/883.97\text{ yrs})$</td>
<td>3.2 Kyr</td>
</tr>
<tr>
<td>0.41205</td>
<td>$1/(0.41205/883.97\text{ yrs})$</td>
<td>2.1 Kyr</td>
</tr>
<tr>
<td>0.48168</td>
<td>$1/(0.48168/883.97\text{ yrs})$</td>
<td>1.8 Kyr</td>
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Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the Aralla HR section, lower Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.3.16.6: Displaying high resolution data of the first cycle (lower Bernesga Mb. of the Formigoso Fm.) for the Aralla section, 309 samples (HR 32 – HR 339). The field analysis was carried out at 1 cm intervals (each sample represents ~883.97 yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) to the top (sample No. 309), cyclicity is apparent in the V values. b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
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<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0040717 (highest intensity)</td>
<td>= 1/(0.0040717/883.97 yrs)</td>
<td>217.1 Kyr</td>
</tr>
<tr>
<td>0.023208</td>
<td>= 1/(0.023208/883.97 yrs)</td>
<td>38 Kyr</td>
</tr>
<tr>
<td>0.029316</td>
<td>= 1/(0.029316/883.97 yrs)</td>
<td>30.1 Kyr</td>
</tr>
<tr>
<td>0.054153</td>
<td>= 1/(0.054153/883.97 yrs)</td>
<td>16.3 Kyr</td>
</tr>
<tr>
<td>0.25163</td>
<td>= 1/(0.25163/883.97 yrs)</td>
<td>3.5 Kyr</td>
</tr>
<tr>
<td>0.26547</td>
<td>= 1/(0.26547/883.97 yrs)</td>
<td>3.3 Kyr</td>
</tr>
<tr>
<td>0.30619</td>
<td>= 1/(0.30619/883.97 yrs)</td>
<td>2.8 Kyr</td>
</tr>
<tr>
<td>0.44707</td>
<td>= 1/(0.44707/883.97 yrs)</td>
<td>1.9 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the Aralla HR section, lower Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling intervals.
1.5 Caldas de Luna Section

The following section documents all geochemical results for the Caldas de Luna section. The Caldas section consists of 98 samples; all 98 are representative of the Basal Formigoso Fm. (Bernesga Mb.). The sampling interval within the Bernesga Mb. was set at 25 cm, as is the case for all other sampling locations (other than the Aralla HR field analysis). Please also refer to the Caldas de Luna log section (showing the sample location in regards to the log section) in the Results Chapter, and the results tables in Appendix B part 2.
1.5.1 Major Elements

Figure 8.5.1.1: All major element variation curves for the Caldas de Luna log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
1.5.2 Trace Elements

Figure 8.5.2.1: All trace element variation curves for the Caldas de Luna log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
Figure 8.5.2: All trace element variation curves for the Caldas de Luna log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
Figure 8.5.2.3: All trace element variation curves for the Caldas de Luna log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
Figure 8.5.2.4: All trace element variation curves for the Caldas de Luna log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
1.5.3 Elemental cross-plots

Figure 8.5.3.1: Showing the cross-plots of $\text{Al}_2\text{O}_3$ to $\text{K}_2\text{O}$, $\text{TiO}_2$, $\text{MgO}$, $\text{Rb}$, $\text{Cr}$ and $\text{Zr}$ for the Caldas de Luna section (98 samples). All show positive correlations except for $\text{Zr}$, a negative correlation in the basal organically enriched shales (the lower the enrichment of $\text{Zr}$ (detrital influx) the higher the $\text{Al}_2\text{O}_3$ concentrations).
Figure 8.5.3.2: Cross-plots of $\text{Al}_2\text{O}_3$ vs. $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ for the Caldas de Luna section (98 samples), all showing negative correlations indicating the presence of clay minerals. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ cross plot indicates the maturity of the shales.

Figure 8.5.3.3: Showing the geochemical ratios of Cr/V and Ni for the Caldas de Luna section (98 samples). The ratios can be compared between localities to determine environment differences/changes laterally (redox states, redox sensitive elements). Plots a + b display the ratios plotted against stratigraphy. Cr, Ni and V are redox sensitive elements. Hence the enrichment shown in the V vs. Cr cross plot towards the organically enriched anoxic shales. The V vs. Cr cross plot shows a strong positive correlation (the higher the V values the higher the Cr values).
Figure 8.5.3.4: Showing grain size (SiO$_2$/Al$_2$O$_3$ and Rb/K$_2$O) and redox state (Cu/Zn) for the Caldas de Luna section (98 samples), indicating the maturity of the Formigoso Fm., the lower the silica content, smaller the grain size.
Figure 8.5.3.5: Harker type major element variation diagrams for the Caldas de Luna section (98 samples). The CaO readings were just above the detection limit.
Figure 8.5.3.6: Cross plots of Al$_2$O$_3$, U, Th, Cs and Ba vs. K$_2$O for the Caldas de Luna section (98 samples), all showing positive correlations. The U cross plot showing the organically enriched basal shales, the higher the U content, the higher the total organic carbon (TOC), using U as a proxy for organic content and redox indicator.

Figure 8.5.3.7: MgO cross plots of Fe$_2$O$_3$, MnO, (Cr+Ni) and V for the Caldas de Luna section (98 samples), all showing positive correlations.
Figure 8.5.3.8: Showing Cr/Rb, V/Rb, Th/U, Ba/Rb and Zr/Rb ratios for the Caldas de Luna section (98 samples). The values are normalised to Rb as it is inert with respect to biogenic processes unlike \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \). The Th/U ratio can be used as a redox proxy.
Figure 8.5.3.9: TOC cross-plots for the Caldas de Luna section (all 98 samples); trace elements of ‘strong euxinic affinity’ (Algeo & Maynard, 2004) a) U, b) V, c) Zn and d) Pb all of the trace elements are Al normalized (x10⁻⁴). Trace elements of ‘weak euxinic affinity’ e) Cu, f) Ni and g) Cr again all Al normalized (x10⁻⁴).
Figure 8.5.3.10: Selected major element vs. $\text{Al}_2\text{O}_3$ variation diagrams for the Formigoso Fm. (Bernesga Mb.) at Caldas de Luna (a + b), displaying all 98 samples. The ranges of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios in K-feldspars and clays (plot (b)) (Cox et al., 1995.) Selected trace element vs. $\text{Al}_2\text{O}_3$ variation diagrams (c-e).

f) $\text{Th}$ vs. $\text{Th}/\text{U}$ plot (McLennan et al., 1993) for the Caldas de Luna samples (all 98 samples). Dashed lines: $\text{Th}/\text{U}$ ratio and $\text{Th}$ content of UCC; circle: PAAS (Taylor and McLennan, 1985); fields for depleted mantle sources and Australian shales (AS) from McLennan et al., 1993. Arrows indicate direction of trends for weathering ($\text{U}$ loss) and enrichment ($\text{U}$ gain).

g+h) $\text{Zr}/\text{Sc}$ vs. $\text{Th}/\text{Sc}$ plots (McLennan et al., 1993) for (a) Formigoso Fm. at the Caldas de Luna section (all 98 samples); (b) modern muds from trailing edge (TE, passive margin), continental arc (CA), and forearc (FA) settings (data from McLennan et al., 1990). Solid line connecting stars B (basalt) and F (felsic volcanic rock), illustrates the trend expected in first-cycle sediments due to magmatic evolution from mafic to felsic end members; star G is the average granite (Condie, 1993). UCC and PAAS from Taylor and McLennan (1985), the arrow illustrates the trend produced by zircon concentration during sedimentary sorting and recycling.
Figure 8.5.3.11: Geochemical plots for the Caldas de Luna section (all 98 samples utilised). a) Showing V/(V+Ni) vs. TOC; the higher the TOC values the lower the sedimentation rate (V/(V+Ni) values have to be above 0.5 in order for the organic carbon to be preserved (not oxidised, Rimmer, 2004), the sedimentation rate indicator taken from Arthur & Sagemann, 1994). b) Represents the TOC values vs. stratigraphy (every data point is equivalent to 25cm). c) & d) the selected geochemical indices for the Caldas de Luna section (all 98 samples).
Figure 8.5.3.12: Utilising all geochemical data from the Caldas de Luna section (all 98 samples). a) shows Zr/Ti ratios used as a provenance proxy; high Zr/Ti ratios point towards granitic rocks (G1 granite: Zr/Ti is 0.14) or clastic sediments (average phanerozoic quartz arenite: Zr/Ti is 0.13; Boryta and Condie, 1990). Lower Zr/Ti ratios around 0.067 represent the composition of the average upper crust (Taylor and McLennan, 1985). The ‘North American shale composite’ (NASC) has a Zr/Ti ratio of 0.043. Lower Zr/Ti ratios are indicative of basic igneous rocks; Andean volcanic rocks yield Zr/Ti ratios between 0.024 for basalts and 0.034 for andesites (Ewart, 1982). Lowest Zr/Ti ratios around 0.01 represent primitive magmas of OIB’s and MORB’s (Bonn, 2004). b) Signifies palaeosalinity (using Rb/K ratios), the dashed line values were taken from Campbell & Williams, 1965. c-f) palaeo-redox indicators; the ratio lines are documented in the table. g) Th/U Ratios for Caldas de Luna, any value <2 implies anoxic (Fertl, 1979), organically rich black shale genesis.
Figure 8.5.3.13: Geochemical data representative of the Caldas de Luna section (all 98 samples) a) V/Al vs. stratigraphy and b) correlation of V with TOC.

Figure 8.5.3.14: Geochemical data from the Caldas de Luna section (all 98 samples). a) Scatter plot showing heavy mineral indicating element vs. major component. b) TOC values vs. stratigraphy. c + d) Fe₂O₃ vs. stratigraphy and Fe₂O₃/Al₂O₃ (normalised with Al) vs. stratigraphy. e + f) V and Zn vs. TOC.
Figure 8.5.3.15: All data from the Caldas de Luna section (98 samples); a) SiO$_2$ vs. Al$_2$O$_3$ concentrations are plotted relative to the idealized composition of the observed minerals (Cullers & Podkovyrov, 2000). The majority of the variation in composition may be related to variations in quartz and clay minerals-muscovite. b) Fe$_2$O$_3$ total vs. Al$_2$O$_3$ concentrations plotted relative to the composition of the observed minerals, again much of the variation in composition may be accounted for by variations in quartz and clay minerals-muscovite.

Figure 8.5.3.16: Representing all data from the Caldas de Luna section (98 samples). Redox sensitive elements (V and Cr) showing positive correlations with TOC values; a) Cr (ppm) vs. TOC, b) V (ppm) vs. TOC, c) Cr (wt %) vs. TOC and d) V (wt %) vs. TOC,
Figure 8.5.3.17: Representing all data from the Caldas de Luna section (98 samples). Al₂O₃ bivariate diagrams of major element composition along with estimated elemental mineral compositions (Descourvieres et al., 2011).
Figure 8.5.3.18: Cross-plots showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. The plots represent sample data from the Caldas de Luna section (all 98 samples). Th/U is used as a redox indicator; the dashed black line representing a Th/U ratio of 2, less than 2 indicates anoxic (Fertl, 1979). Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al$_2$O$_3$, TiO$_2$, and K$_2$O in the clay fraction); high values reflect course grained units, lower values in clay stones and shales. (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values found in samples with little carbonate.
Figure 8.5.3.19: Cross-plot of Ni (ppm) vs. Cr (ppm) representing all data from the Caldas de Luna section (98 samples).

Figure 8.5.3.20: Representing all data from the Caldas de Luna section (98 samples). The ratios Ni/V and V/Cr (Jones and Manning, 1994) are redox indicators.
Figure 8.5.3.21: Geochemical data from the Caldas de Luna section (all 98 samples). Selected elements and ratios plotted vs. Stratigraphy.

Figure 8.5.3.22: Representing the relationship between Al₂O₃ and Ba for all Caldas de Luna data (98 samples).
Figure 8.5.3.23: Representing all data from the Caldas de Luna section (98 samples). a) Plot of U/Pb ratios vs. U concentrations (ppm). Samples generally reflect elevated U concentrations relative to North American Shale Composite (Condie, 1993). b) TOC (wt.% vs. U concentrations (ppm). The U content of NASC is plotted for reference (samples are enriched in U relative to the NASC composite). U and TOC exhibit a perfect correlation as TOC values were generated using the U (ppm) values as a proxy (Fertl & Chillingar (1988)).

Figure 8.5.3.24: All diagrams represent the data from the Caldas de Luna section (98 samples). a) Th vs. Sc (in log scale) and b) Th vs. U diagrams (McLennan et al., 1990, and Luchi et al., 2003). c) FeO/FeO (K2O vs. SiO2/O3) d) log SiO2/O3 vs. log (FeO/FeO (K2O) (Herron (1986)) e) Th/Sc vs. Zr/Sc (log scale) (McLennan et al., (1993)), reflecting reworking through Zr/Sc and upper crust felsic input through Th/Sc. Numbers identify the mean values for 1)OIA, 2)CIA, 3) ACM and 4, PM following Bathia and Crook (1986). f) TiO2 vs. Ni, fields for acidic and basic source materials (Floyd et al., (1989)).
Figure 8.5.3.25: Displaying all data from the Caldas de Luna section (98 samples). Th/Sc vs. Zr/Sc plot (Mongelli et al., 2006), the samples depart from the compositional trend, indicating zircon addition suggestive of a recycling effect, modified after.

Figure 8.5.3.26: Representing all data from the Caldas de Luna section (98 samples). Zr vs. SiO₂, a positive relationship is apparent, indication that the Zr is indeed associated with the Quartz (heavy fraction).
Figure 8.5.3.27: TiO$_2$ vs. Ni bivariate plot (fields after Floyd et al., 1989) for shale samples from the Caldas de Luna section (all 98 samples).

Figure 8.5.3.28: Representing all data from the Caldas de Luna section (98 samples). The trace elements are normalised to Al and then multiplied by $10^{-4}$. As, Cr, Cu, Ni, V, Zn vs. Stratigraphy.
Figure 8.5.3.2: Geochemical classification (Pearce et al. 2010) based on the criteria listed in Table b (above) for the Caldas de Luna dataset (all 98 samples). The geochemical classification values (y-axis of plot a) reflect the following: Score of 4 = floodplain mudstone, Score of 7 = brackish water or lacustrine, Score of 10 = marginal marine mudstone, Score of 13 or 16 = marine mudstone (= marine band). If a sample has a very high Zr/U value (above 65), it is presumed to contain abundant heavy minerals and is awarded a final score of 2. If a sample comes from a coal, it is awarded a default score of 0 (Pearce et al., 2010).

Mo and P$_2$O$_5$ values for the Caldas de Luna section are near/below detection limits.

Based on the criteria above the depositional environment of the Formigoso Fm. at the Caldas de Luna section is classified as borderline; brackish water or Lacustrine - marginal marine mudstone (which fits with the Rb/K ratios for palaeosalinity).
Figure 8.5.3.30: Representing all data from the Caldas de Luna section (98 samples). A) SiO$_2$/Al$_2$O$_3$ vs. TOC and B) Zr/Rb vs. TOC. The SiO$_2$/Al$_2$O$_3$ and Zr/Rb ratios are renowned grain size proxies, plotted against TOC (Total Organic Carbon) values. The zones for hydrocarbon potential (TOC cut off values) after Bordenave et al., (1993). The TOC values for the basal shales act independently of the grain size values, the grain size remains consistent yet the TOC levels vary; this is most likely due to changes in the redox state.
Figure 8.5.3.31(a): Plots representing data from the Caldas de Luna section (all 98 samples), showing the relationship between Al$_2$O$_3$, selected trace elements and Fe$_2$O$_3$. The plots show the relationship between the Cantabrian formations (predominantly the Formigoso Fm) trace element:Al$_2$O$_3$ ratios and the World Shale Average (WSA, plotted as star, taken from Gromet et al., 1984), the Zr vs. Al$_2$O$_3$ also includes the Upper Crust (UC) and North American Shale Composite (NASC).
Figure 8.5.3.31(b): Plots representing data from the Cañad de Luna section (all 98 samples). The plots show the relationship between various trace elements within the Cantabrian formations (predominantly the Formigoso Fm.).
Figure 8.5.3.32: Representing data from the Caldas de Luna section (all 98 samples). a) Chemical classification, after Herron, 1986. b) Plot of discriminant functions 1 and 2 for shales (after Roser and Korsch (1988). Discriminant function 1 = \((-1.773 \times \text{TiO}_2\%) + (0.607 \times \text{Al}_2\text{O}_3\%) + (0.76 \times \text{Fe}_2\text{O}_3\text{T}%) + (-1.5 \times \text{MgO}\%) + (0.616 \times \text{CaO}\%) + (0.509 \times \text{Na}_2\text{O}\%) + (-1.22 \times \text{K}_2\text{O}\%) + (-9.09). Discriminant function 2 = (0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\text{T}%) + (-1.142 \times \text{MgO}\%) + (0.432 \times \text{Na}_2\text{O}\%) + (1.426 \times \text{K}_2\text{O}\%) + (-6.861). Provenance fields are after Roser and Korsch (1988). P1 = mafic and lesser intermediate igneous provenance; P2 = intermediate igneous provenance; P3 = felsic igneous provenance and P4 = recycled-mature polycyclic quartzose detritus. c) Distribution of K and Rb relative to a K/Rb ratio of 230 (= main trend of Shaw, 1968).

Figure 8.5.3.33: Representing all Zr vs. Cr data from the Caldas de Luna section (98 samples). Variations in the Zr and Cr values are likely to reflect changes in the sediment provenance.
Figure 8.5.3.34: Cross plot of Mo (ppm) and TOC (wt%) values from the Caldas de Luna section (all 98 samples). Evidently the Mo (ppm) concentrations are near/below the detection limit.

Figure 8.5.3.35: Representing data from the Caldas de Luna section (all 98 samples). a) V/Cr used as a palaeoredox proxy. b) V/Cr ratio vs. TOC. c) Mo/Al ratio versus TOC (Mo values are near/below the detection limit).
Figure 8.5.3.36: Representing all data from the Caldas de Luna section (98 samples). a + b) plots of the detrital parameter Th vs. Zr and Th vs. Ti. c + d) Cross plots of Th as detrital monitor vs. authigenic uranium (U-aut) and V (ppm).

Figure 8.5.3.37: Representing all data from the Caldas de Luna section (98 samples). a) Scatter plot of V/(V + Ni) vs. degree of pyritization (DOP), displaying average shale (Turekian & Wedephol, 1961) and average continental crust. b) DOP vs. stratigraphy; the lines representing DOP values are from Wignall, 1994. c) Represents an idealized plot of a uniform DOP with increasing TOC, (a+c).
Figure 8.5.3.38: Displaying all data from the Caldas de Luna section (98 samples), provenance and source signature diagrams. 

a) Th vs. Sc. Th is an incompatible element that is enriched in silicic rocks, and Sc is a compatible element that is enriched in mafic rocks. Th/Sc ratios near unity represent the upper continental crust (UC) the Th/Sc ratios near 0.6 suggest a more mafic component (Totten et al., 2000).

b) Th/Sc vs. Cr/Th (Totten et al., 2000).

c) Th vs. Sc relation and d) Th/Sc vs. Cr/Th (Descourvieres et al., 2011).
Figure 8.5.3.39: Representing all data from the Caldas de Luna section (98 samples). MgO/Al\textsubscript{2}O\textsubscript{3} vs. K\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} cross plot including the fields of kaolinite, illite/K-feldspar and chlorite (clay typing) (Turgeon + Brumsack, 2006).
Figure 8.5.3.40: Representing all data from the Caldas de Luna section (98 samples). Diagrams used for discriminating the differing lithologies.

Figure 8.5.3.41: Showing all data from the Caldas de Luna section (all 98 samples). a) cross-plot of SiO₂ vs. Al₂O₃ shows an enrichment of SiO₂ over Al₂O₃ in comparison to the World Average Shale (WSA) of Turekian & Wedephol, 1961. b + c) TOC vs. Al₂O₃ and SiO₂, showing that the TOC values vary as the Al₂O₃/SiO₂ content remain consistent.
Figure 8.5.3.42: Representing all data from the Caldas de Luna section (98 samples). Plot of total organic carbon (TOC wt.%) against authigenic uranium content (U$_{auth}$). The correlation between TOC and total U would be 1:1 as the TOC values have been generated by using U as a proxy. Yet the U$_{auth}$ values use Th values in order to correct for detrital uranium.

Figure 8.5.3.43: Representing all data from the Caldas de Luna section (98 samples). Elemental Sr/Al, Mn/Al, Si/Al, Ba/Al, Zr/Al ratios plotted against TOC and stratigraphy.
1.5.4 $\text{Na}_2\text{O}$ plots

Figure 8.5.4.1: Displaying data from the Caldas de Luna section (all 98 samples). a) Provenance discrimination diagram for shales (after Roser and Korsch, 1988). Discriminant function 1 = \((-1.773 \times \text{TiO}_2\%) + (0.607 \times \text{Al}_2\text{O}_3\%) + (0.76 \times \text{Fe}_2\text{O}_3\%) + (0.616 \times \text{CaO}\%) + (0.509 \times \text{Na}_2\text{O}\%) + (1.426 \times \text{K}_2\text{O}\%) + (-9.09)\). Discriminant function 2 = \((0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\%) + (-1.142 \times \text{MgO}\%) + (0.432 \times \text{Na}_2\text{O}\%) + (1.426 \times \text{K}_2\text{O}\%) + (-6.861)\). b) Bivariate $\text{SiO}_2$ wt.% vs. $(\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O})$ wt.% palaeoclimate discrimination diagram, fields after Suttner and Dutta (1986). c) $\text{SiO}_2/\text{Al}_2\text{O}_3$ vs. $\text{K}_2\text{O}/\text{Na}_2\text{O}$ after Kampunzu et al., 2005. d) Discriminant function diagram after Roser and Korsch (1988); Discriminant function I = \((-1.773 \times \text{TiO}_2\%) + (0.607 \times \text{Al}_2\text{O}_3\%) + (0.76 \times \text{Fe}_2\text{O}_3\%) + (0.616 \times \text{CaO}\%) + (0.509 \times \text{Na}_2\text{O}\%) + (-1.224 \times \text{K}_2\text{O}\%) + (-9.09)); Discriminant function II = \((0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\%) + (-1.142 \times \text{MgO}\%) + (0.438 \times \text{CaO}\%) + (1.475 \times \text{Na}_2\text{O}\%) + (1.426 \times \text{K}_2\text{O}\%) + (-6.861)\). e) Akul'shina (1976) + Kipli et al., (2012): $\text{Al}/\text{Ti}$ ratio and climate: $\text{Al}_2\text{O}_3/\text{TiO}_2 < 20$ for humid, 20–30 for semi-humid and semi-arid, and >30 for arid climate.
1.5.5 **Histograms (major elements & redox ratios)**

**Figure 8.5.5.1:** Histograms and cumulative frequency representing the major oxides a) SiO$_2$ values b) Al$_2$O$_3$ values c) K$_2$O values and d) TiO$_2$ values, using all sample data (98 samples) from the Caldas de Luna section. Wt% vs. frequency for the histograms and cumulative frequency for the curve.

**Figure 8.5.5.2:** Histograms and cumulative frequency curves representing all sample data for the Caldas de Luna section. a) Showing the calculated degree of pyritization (DOP); A = Anaerobic (0-0.4); R = Restricted (0.45-0.75); I = Inhospitable (0.55-1) ranges from Raiswell *et al.*, 1988. b + c) palaeo-redox proxies V/(V + Ni) and V/Cr. Ranges for inferred bottom-water conditions for V/Cr, <2 oxic, 2-4.25 dysoxic, >4.25 suboxic-anoxic (Jones and Manning (1994)); ranges for V/(V + Ni), <0.46 oxic, 0.46-0.6 dysoxic, 0.54-0.82, suboxic-anoxic, >0.84 euxinic (Hatch and Leventhal (1992)).
1.5.6 *K, Th and U bubble plots*

**Figure 8.5.6.1:** Bubble plot displaying $K_2O$, Th and U concentrations for the Caldas de Luna section, representing all sample data (98 samples). $K_2O$ and Th and U contents were analysed by X-Ray Fluorescence (XRF) whole rock analysis, the bubble size is proportional to U content.
1.5.7 Ternary diagrams

Figure 8.5.7.1: Ternary diagram showing relative proportions of major shale/mud rock components; \( \text{SiO}_2 \) (quartz), \( \text{Al}_2\text{O}_3 \) (clays) and \( \text{CaO} \) (carbonates) (Ross & Bustin, 2009), displaying data from the Caldas de Luna section (all 98 samples). The Key for the expanded plot is shown to the left of the figure, the key for the inset ternary (top right); diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the ‘Average shale’ also shown as star (after Wedepohl, 1971).

Figure 8.5.7.2: Caldas de Luna section (all 98 samples) ternary \( 10\text{Al}_2\text{O}_3 - 200\text{TiO}_2 - \text{Zr} \) (Mongelli et al., 2006), diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).
Figure 8.5.7.3: Caldas de Luna section (all 98 samples) ternary 15Al2O3 - 300TiO2 - Zr (Mongelli et al., 2006), diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).

Figure 8.5.7.4: TOC–S–Fe relationships for the Caldas de Luna section (all 98 samples). The diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.5.7.5: TOC–TS10–Fe ternary diagram for the Caldas de Luna samples (all 98). The diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The construction and principles of the diagram based on Dean and Arthur (1989) and Arthur and Sageman (1994).

Figure 8.5.7.6: Degree of pyritization of sediments from the Caldas de Luna section (all 98 samples) in the Fe(x) - total organic carbon (TOC) - S2 (following stoichiometry of pyrite-FeS2) system (relative weight ratios). Reactive Fe (Fe(x)) is calculated with Fe(x) = Fe – 0.25 x Al (Mosher et al., 2006). The diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.5.7.7: Al–Mg–Ca (Garnier et al., 2008) diagram showing the distribution of the shales from the Formigoso Fm at Caldas de Luna (all 98 samples were used). Inset ternary (top left): diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the domains of evaporites and meta-evaporites, and of platformal marls and shales are from Moine et al., (1981). The key for the expanded plot is towards the right of the figure.
Figure 8.5.7.8: The ternary diagrams top right (inset); (A) Ternary plot of \((\text{Cu+Co+Ni}) \times 10 - \text{Fe} - \text{Mn}\) showing various generic fields (Bonatti et al., 1976; Mohapatra 2009), displaying all data (98 samples) from the Caldas de Luna section (B) Chemical composition of the formation at the Caldas de Luna section (all 98 samples) in terms of components \(\text{Fe} - \text{Mn} - \text{Al+Si}\) (Mohapatra 2009). The arrow indicates the decreasing clastic input, modified after. The key for the expanded plots is found towards the upper left of the figure.
Figure 8.5.7.9: Th − (Cr + Ti)/1000 − Zr/10 (Hessler & Donald, 2006) ternary plot showing all 98 samples from the Caldas de Luna section. The key for the upper left ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.5.7.10: Al₂O₃, MgO and Fe₂O₃ ternary plot representing data from the Caldas de Luna section (all 98 samples). The key for the upper left ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.5.7.11: Al$_2$O$_3$, MgO * 10 and Fe$_2$O$_3$ - (expanded plot of previous (Figure 8.5.7.10)) representing data from the Caldas de Luna section (all 98 samples). The diagonal crosses representing the basal Formigoso Fm. (Bernesga Mb.).

Figure 8.5.7.12: Fe$_2$O$_3$, Al$_2$O$_3$ and MnO ternary plot; represents data from the Caldas de Luna section (all 98 samples). The key for the upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key for the expanded plot is seen towards the upper left of the figure.
Figure 8.5.7.13: Distribution of Fe₂O₃, Al₂O₃ and SiO₂ within the Caldas de Luna section (98 samples). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), compared with several ideal clay minerals, including chamosite (Chm), berthierine (Ber) thin/long rectangle to represent variable compositions, kaolin and muscovite (Ka/Mu), nontronite (Non), illite thick/long rectangle and glauconite (Gla) (Konhauser et al., 1998, Konhauser & Urrutia, 1999 and Eickmann et al., 2009). The key for the expanded plot is seen towards the left of the figure.

Figure 8.5.7.14: Distribution of K₂O, Al₂O₃ and SiO₂ from the Caldas de Luna section (all 98 samples analysed). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) compared to several ideal clay minerals, including, kaolin (Ka), muscovite (Mu), illite (ill) long rectangle (representing varying compositions) and glauconite (Gla) are labelled (Konhauser et al., 1998 & 1999). The key for the expanded plot is seen towards the left of the figure.
Figure 8.5.7.15: Th, As/10 and U ternary plot, representing data from the Caldas de Luna section (all 98 samples). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.5.7.16: Major geochemical components $\text{Al}_2\text{O}_3 \times 5 - \text{SiO}_2 - \text{CaO} \times 2$ (relative weight ratios) (Hetzel et al., 2011) for the Caldas de Luna section (All 98 samples shown). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the data points for average shale (Wedepohl, 1971, 1991), kaolinite and K-feldspar are shown for comparison.
Figure 8.5.7.17: Ternary plot for Fe$_2$O$_3$, K$_2$O and Al$_2$O$_3$/10, showing all samples from the Caldas de Luna section (98 samples). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the key towards the left of the figure is for the exploded diagram.

Figure 8.5.7.18: Ternary plot for SiO$_2$/Al$_2$O$_3$, TiO$_2$ and MgO, expressing all samples from the Caldas de Luna section (98 samples). Diagonal crosses representing the basal Formigoso Fm. (Bernesga Mb.). The figure shows a possible maturity trend within the basal organically rich shales.
Figure 8.5.7.19: Ternary plot for U*20, Zr and Sr, expressing all samples from the Caldas de Luna section (98 samples). The diagonal crosses represent the basal Formigoso Fm. (Bernesga Mb.), the 'hot' shales trend towards uranium enrichment.

Figure 8.5.7.20: Ternary plot for K2O, Th and U, showing all samples from the Caldas de Luna section (98 samples). The ternary plot (upper right); diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key towards the left of the figure is valid for the exploded diagram. Note that a select few of the basal shales appear highly enriched in U and the coarser silt horizons show U depletion.
Figure 8.5.7.21: Ternary plot representing all data for the Caldas de Luna section (98 samples) showing the relationship between K$_2$O$^*$5, Th and U as previously (Figure 8.5.7.20) yet a higher factor for K$_2$O values. The Majority of the shale/silts cluster towards the K$_2$O enrichment, K$_2$O resides mostly within the detrital fraction.

Figure 8.5.7.22: Ternary plot representing all data for the Caldas de Luna section (98 samples) showing the relationship between the heavy elements; Zr, Cr and Ni (Ratcliffe, 2007). The diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.). The figure shows a clear maturity trend for the basal shales.
Figure 8.5.7.23: Ternary plot (Ratcliffe et al., 2007) representing samples from the Caldas de Luna section (all 98). Cross-plot constructed to characterise between the Shales (differing subunits) and the sands/silts.

Figure 8.5.7.24: Ternary diagram Fe₂O₃ – MgO – SiO₂/Al₂O₃ (Ratcliffe et al., 2007) representing data from the Caldas de Luna section (all 98 samples). The upper right ternary; diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.). The expanded plot shows a clear maturity trend.
Figure 8.5.7.25: CIA ternary diagram, Al₂O₃ – CaO + Na₂O – K₂O (after Nesbitt and Young, 1982), displaying data from the Caldas de Luna section (all 98 samples). The diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.5.7.26: Al₂O₃ – (CaO + Na₂O + K₂O) – (Fe₂O₃ + MgO) ternary diagram (Hayashi et al., 1997), representing data from the Caldas de Luna section (all 98 samples). The diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.).
1.5.8  Index of Compositional Variation (ICV)

Figure 8.5.8.1: a) $K_2O/Al_2O_3$ ratio for the Caldas de Luna section (in order to discriminate K-feldspars and clay minerals). The stars represent values for specific minerals indicated, data from Deer et al., 1966, overlay from Cox, 1995. b) expanded plot of the original (a). c) Index of Compositional Variation (ICV); $(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3$, for the Caldas de Luna section, the stars represent values for specific minerals indicated, the arrows show the range of values for the particular mineral group, Deer et al., 1966, overlay from Cox, 1995. d) Expanded plot of the original ‘c’), cyclicity apparent within the ICV values.

$K_2O/Al_2O_3$ - range of Bernesga Mb. (shales) at Caldas de Luna: 0.0734-0.1875

$K_2O/Al_2O_3$ - average of Bernesga Mb. (shales) at Caldas de Luna: 0.1255

ICV - range of Bernesga Mb. (shales) at Caldas de Luna: 0.3313-0.6686 (2.4046 including Fe spike)

ICV - average of Bernesga Mb. (shales) at Caldas de Luna: 0.5935
1.5.9 **Chemical Index of Alteration (CIA), PIA & CIW**

**Figure 8.5.9.1:** Representing data from the Caldas de Luna section (all 98 samples). The ‘Chemical Index of Alteration’ (CIA) (Nesbit and Young, 1982, Taylor and McLennan, 1985) is a well-established parameter for determining the degree of weathering and is the most accepted of the available weathering indices (Bahlburg & Dobrzinski, 2009). During the degradation of feldspars, Ca, Na, and K are removed and clay minerals with a higher fraction of Al are formed. The CIA is estimated from the proportion of $\text{Al}_2\text{O}_3$ vs. the weathering-prone oxides (Mosher et al., 2006). This index measures the degree of feldspar decomposition to secondary clay products, where CIA values of about 50 indicate fresh bedrock (no chemical weathering), and values of 75-100 indicate complete conversion of feldspars to aluminous clay minerals (intense chemical weathering; see Fedo et al., 1995):

$$\text{CIA} = \left[ \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \right] \times 100$$

A) Kaolinite has a CIA value of 100 and represents the highest degree of weathering. Illite is between 75 and c. 90, muscovite at 75, the feldspars at 50. Fresh basalts have values between 30 and 45, fresh granites and granodiorites of 45 to 55 (Nesbitt and Young, 1982; Fedo et al., 1995). B) Expanded plot, focusing within the Illite Zone (muscovite line also shown).

The average CIA value for the Bernesga Mb. (black shales) at Caldas de Luna: **85.28**
Figure 8.5.9.2: Representing all data from the Caldas de Luna section (98 samples), the ‘Plagioclase Index of Alteration’ (PIA; Fedo et al., 1995).

PIA = \left[ \frac{(\text{Al}_2\text{O}_3 - \text{K}_2\text{O})}{((\text{Al}_2\text{O}_3 - \text{K}_2\text{O}) + \text{CaO} + \text{Na}_2\text{O})} \right] \times 100

PIA values of around 50 represent unaltered crystalline bedrock and values approaching 100 indicate significant production of secondary aluminous clay minerals.

High CIA and PIA values (i.e., 75–100) indicate intensive weathering in the source area whereas low values (i.e., 60 or less) indicate low weathering in source area. The high variations in CIA and PIA values may, however, be due to the low concentrations (sometimes below or near detection limits) of the alkalis and alkaline earth elements rather than variable degrees of source area weathering (Osae et al., 2006).

A) Displays the PIA values for the Caldas de Luna section, after Fedo et al., 1995 & Moosavirad et al., 2011 and B) Expanded plot of the PIA values, PIA calculation from Moosavirad et al., 2011.

The average PIA value for the Bernesga Mb. (black shales) at Caldas de Luna: 94.83
Figure 8.5.9.3: Representing all data from the Caldas de Luna section (98 samples), the ‘Chemical Index of Weathering’ (CIW; Harnois, 1988).

\[
\text{CIW} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O})} \times 100
\]

The CIW index increases with the degree of depletion of the soil or sediment in Na and Ca, relative to Al. The value of this index increases as the degree of weathering increases, and the difference between CIW index values of the silicate parent rock and soil or sediment reflects the amount of weathering experienced by the weathered material, from Harnois, 1988.

A) Showing the CIW values for the Caldas de Luna section, modified after Harnois, 1988 & Moosavirad et al., 2011 and B) Expanded plot of the CIW values. Calculations from Moosavirad et al., 2011 (p.6-7 use to describe differences in CIA, PIA and CIW).

The average CIW value for the Bernesga Mb. (black shales) at Caldas de Luna: **95.46**
1.5.10 Gamma-ray log and Total Organic Carbon (TOC)

The following section documents the calculated gamma ray (API)/ TOC values for the Caldas de Luna section (all 98 samples). The API values were calculated following the protocol detailed within the methodology chapter, the same for the TOC values calculated after Fertl & Chillingar, 1988, also documented in the methods chapter.
Figure 8.5.10.1: Showing whole rock K$_2$O, Th and U values for the Caldas de Luna section (every data point represents 25cm of stratigraphy). Samples 1-98 contain the basal shales (or Bernesga Mb. of the Formigoso Fm.). There is a gap in the stratigraphy (~1m) at the base of the Formigoso Fm. (The contact is not exposed - missing the very basal shales and Getino Beds). Note the cyclic behaviour of the U values. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~ 8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~2209yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons. There is a significant shift in the data after the 2nd cycle (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The figure above also displays, Gamma-ray (GR), Computed Gamma-ray (CGR) and Total Organic Carbon (TOC) values for the Caldas de Luna section. Note the cyclic behaviour of the GR and TOC values (prominent 2 cycles within the first 48 samples). The basal Bernesga Mb. shales (lower member of Formigoso Fm.) has been given rough age constrains at the base and top using graptolite data, suggesting a ~ 4Myr time span.

The GR values were calculated by converting K$_2$O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using 6.69U + 2.54Th + 10.64K$_2$O = API after (http://server4.oersted.dtu.dk/research/RI/SNG/SNG-logs.html). CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: =3.9637*LN(Uranium Values)-5.6873. This formula was calculated after Fertl & Chillingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the 'hot shale' threshold, the dashed line (120API) is the average value for the 'lean shales' of Luning (2000).
Figure 8.5.10.2: Showing whole rock $K_2O$, Th and U values for the Caldas de Luna section (every data point represents 25cm of stratigraphy). Samples 1-98 contain the basal shales (or Bernesga Mb. of the Formigoso Fm.). There is a gap in the stratigraphy (~1m) at the base of the Formigoso Fm. (The contact is not exposed - missing the very basal shales and Getino Beds). Note the cyclic behaviour of the U values. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons. There is a significant shift in the data after the 2nd cycle (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The figure above also displays, Gamma-ray (GR), Computed Gamma-ray (CGR) and Total Organic Carbon (TOC) values for the Caldas de Luna section. Note the cyclic behaviour of the GR and TOC values (prominent 2 cycles within the first 48 samples). The basal Bernesga Mb. shales (lower member of Formigoso Fm.) has been given rough age constrains at the base and top using graptolite data, suggesting a ~4Myr time span.

The GR values were calculated by converting $K_2O$, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using $8U + 4Th + 16K_2O = API$ after Ellis, 1987 and Doveton, 2004. CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using $U ppm$ values and the following function: $=3.9637*LN(Uranium Values)-5.6873$. This formula was calculated after Fertl & Chilingar (1988) $U$ versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt\% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
1.5.11 *Hydrothermal Overprint*

Figure 8.5.11.1: Bostrom (1973) diagram; the analysed sediments (all 98 samples from the Caldas de Luna section) are compared to argillite (T) and hydrothermal (H) end members whose mixing is modelled by the H-T curve. PAAS and NASC (Gromet et al., 1984) are reported for comparison.
1.5.12 Bioproductivity Reconstruction (Barium proxy) & SEM/DOP

Figure 8.5.12: a) Al/Ti ratio, data from the Caldas de Luna section, shaded region indicates approximate range in shales, pelagic clay, andesite and hydrothermal sediment, and the dashed lines representing oceanic crust & granite Al/Ti ratios after Murray & Leinen, 1996. It shows that the shales of the Formigoso Fm. are enriched in Al (as seen in the EF diagrams) giving the higher Al/Ti ratios, pushing towards the granitic composition, this fits with the bulk composition of basal granitic hinterland.

To test whether the Al enrichment is due to the granitic composition of the hinterland the Fe/Al ratio is used (b). The ranges after Gordon et al., 1996 in Murray & Leinen, 1996 (labelled a-e); if the sediment source were composed of pure granite (Al/Ti ~ 40; Taylor and McLennan, 1985), it could be the cause of the elevated Al/Ti. Upper crust (Fe/Al ~ 0.42, a), PAAS (~0.51, b), pelagic clay (~0.77, c), and, bulk continental crust (~0.84, d) (Taylor and McLennan, 1985). In granite, Fe/Al ~ 0.28, e (Taylor and McLennan, 1985). From this it can be inferred that the Formigoso Fm. basal shale composition is closest to that of a granitic source.

c) Table displaying Al/Ti ratios of modern day terrestrial source material, aeolian dust and marine sediments modified after Zabel et al., 1999, comparison of the Formigoso Fm Al/Ti ratios to that of modern day environments (Caldas de Luna ranging from ~21-39 sat within the deep-sea sediments ranges, yet higher range 39 comparable to that of surface sediments (equatorial pacific)).

d) TiO₂ vs. Al₂O₃ cross plot including all data from the Caldas de Luna section (98 samples). The plot showing a weak correlation between TiO₂ and Al₂O₃ (R² = 0.034). Both elements were used when calculating the primary production (or palaeoproductivity).

Hydrothermal tests were also carried out (refer to previous figure) to determine if the Formigoso Fm. had undergone any extensive alteration due to pululating hydrothermal fluids, thus, overprinting the true geochemistry (hydrothermal elements anyhow). The tests carried out suggested that the basal Bernesga Mb. of the Formigoso Fm. had not been effected by any hydrothermal overprinting however the upper Villasimpliz Mb. (sands and silts) had been effected yet not significantly (slightly more porous). Therefore, the Ba values of the Formigoso Fm. have not been significantly altered by hydrothermal activity, at least for the lower Bernesga Mb.
Figure 8.5.12.2: Representing the calibrated elemental values for the Caldas de Luna section, all the elements and ratios are plotted against stratigraphy (Caldas 1 being the oldest, Caldas 98 the youngest), sampled at 25cm intervals. The sample No. X-axis of these plots are inverted in relation to all previous plots, as they are to be used in well log form. A set or averaged Ba/Al and Ba/Ti ratio is used for the calculation of the $\text{Ba}_{\text{bio}}$, for each location, yet graphs e & f show the variation of Ba/Al and Ba/Ti ratios for the Caldas de Luna section.
Figure 8.5.12.3: Tables displaying the global Ba/Al average values for area/materials and regions. (Pfeifer et al., 2004). The Ba/Al values (highlighted) for the Atlantic Ocean off West Africa (0.0045) and organic rich sediment (0.0032) are closest to the global crustal average value (0.0037). The 0.0045 ratio of the African sediments is closest to that of the basal Gondwanan hinterland values.
Figure 8.5.12.4: Biogenic barium or $Ba_{bio}$ (also called $Ba_{excess}$) & $Ba_{bio(min)}$ values calculated for the Caldas de Luna section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) $Ba_{bio} = Ba_{tot} - (Al \times Ba/Al_{aluminosilicate})$ from Pfeifer et al., 2001

2) $Ba_{bio} = Ba_{tot} - (Al \times Ba/Ti_{aluminosilicate})$ from Bonn et al., 1998

The total $Ba$, $Ba_{tot}$ and $Ba_{bio(min)}$ values are plotted against stratigraphy Caldas 1 being the oldest and Caldas 98 the youngest, the sampling interval was set at 25cm. A number of ratios were selected for the aluminosilicate fraction and these were as follows:

1) $Ba/Al_{aluminosilicate}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.002913

2) $Ba/Al_{min}$ ratio (minimum Bernesga Mb. Ba/Al ratio at the Caldas de Luna section) = 0.001481

3) $Ba/Al_{aluminosilicate}$ ratio (global ave.) = 0.0037

The global crustal average $Ba/Al_{aluminosilicate} = 0.0037$, from Pfeifer et al., 2004 & Pirrung et al., 2008 (0.007 is the most widely used global average crustal value from Pirrung et al., 2008 p. 7, original ref; Dymond et al., 1992; Nürnberg et al., 1997). I used 0.0037 as Gingele and Dahmke (1994) used 0.004 in; Pfeifer et al., 2001 (p. 5) they stated that sediments north of 30°S are prone to higher weathering conditions due to higher humidity (fits with my humidity proxies and Silurian global reconstructions), the 0.0037 ratio is lower than that of the global ave. 0.007 which means it pushes the data away from the negative values; it gives the most convincing results, Pfeifer et al., 2004. When comparing the 0.0037 ratio to the values shown in the previous tables (Pfeifer et al., 2004) it can be seen that it is closest to that of the African sediment; 0.0045 of Rutsch et al., 1995 and the organic rich sediment; 0.0032 of Rutten, 2001. The average Al/Ba ratios for the Formigoso Fm. (0.002913) are also closest to that of the organic rich sediment of Rutten, 2001.

4) $Ba/Ti_{aluminosilicate}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.068156

5) $Ba/Ti_{min}$ ratio (minimum Bernesga Mb. Ba/Ti ratio at the Caldas de Luna section) = 0.022215

6) $Ba/Ti_{aluminosilicate}$ ratio (global ave.) = 0.126.

The global crustal average $Ba/Ti_{aluminosilicate}$ ratio (global ave.) = 0.126, used for this study from Turekian and Wedepohl, 1961 in; Bonn et al., 1998 (0.14 average upper continental crust Wedepohl, 1995 in; Pirrung et al., 2008 p.6). The $Ba/Al_{min}$ and $Ba/Ti_{min}$ values for the Caldas de Luna section were used after Babu et al., 2002 as the $Ba_{bio}$ values calculated cannot be negative. The ave. Formigoso Fm $Ba/Al$ and $Ba/Ti$ ratios are too high, meaning that the calculated $Ba_{bio}$ values were
negative, when using the lowest ratios in the area (Caldas de Luna) for Ba/Al and Ba/Ti it pushes the $\text{Ba}_{\text{bio}}$ values into positive values as shown on graphs a and b. Graph c uses the global averages for Ba/Al (0.0037) and Ba/Ti (0.126) as a direct comparison.

**Figure 8.5.12.5:** Accumulation rates of the biogenic barium ($\text{AR Ba}_{\text{bio}}$ and $\text{AR Ba}_{\text{bio(min)}}$) expressed in $\text{g cm}^{-2}\text{kyr}^{-1}$, calculated for the Caldas de Luna section using the following formulas from Pfeifer et al., 2001:

1) $\text{AR Ba}_{\text{bio}} = \text{Ba}_{\text{bio}} \times \text{MAR/100}$ (where MAR = Mass accumulation rate in $\text{g cm}^{-2}\text{kyr}^{-1}$)

2) $\text{MAR} = \text{SR} \times \text{DBD}$ (where SR = sedimentation rate in cm kyr$^{-1}$ and DBD = dry bulk density in $\text{g cm}^{-3}$)

The sedimentation rate (SR) was calculated by using graptolite age constraints of the basal shales of the Formigoso Fm. and the number of samples taken. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alarga Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a timespan of ~ 8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; then the 181 shale samples from the Aralla section, lower Bernesga Mb. (sampled at intervals of 25cm) can be assigned an age of ~22099yrs per sample. The first 4 meters of the Aralla section were then analysed at a higher resolution of 1cm (age representation of ~883.97yrs per reading). From this an approximate average SR of 1.11603 cm kyr$^{-1}$ was calculated, however, this average SR does not take into consideration condensed horizons within the basal Bernesga Mb.; represented by the mass accumulation horizons of monograptid graptolites within the basal section (mass graptolite zones representing starved basin conditions).

The dry bulk density (DBD) was estimated by taking the average shale density ranges 1.8 – 2.8 $\text{g cm}^{-3}$ (Glover, 2000). Both the lower range value and upper range DBD values were used in the calculations.

The two MAR values used;

1) $2.008854 \text{ g cm}^{-2}\text{kyr}^{-1}$ (lowest range using 1.8 $\text{g cm}^{-3}$ DBD)

2) $3.124884 \text{ g cm}^{-2}\text{kyr}^{-1}$ (highest range using 2.8 $\text{g cm}^{-3}$ DBD)

a) Represents the $\text{AR Ba}_{\text{bio}}$ & $\text{AR Ba}_{\text{bio(min)}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ & $\text{Ba}_{\text{bio(min)}}$ values from the previous figure (the ave. Formigoso Ba/Al ratio and lowest Ba/Al ratio from Caldas de Luna). b) The $\text{AR Ba}_{\text{bio}}$ & $\text{AR Ba}_{\text{bio(min)}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ & $\text{Ba}_{\text{bio(min)}}$ values from the previous figure (ave. Formigoso Ba/Ti ratio and lowest Ba/Ti ratio from Caldas de Luna). c) The $\text{AR Ba}_{\text{bio}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ values from the previous figure (global ave. Ba/Al ratio).
The AR \( \text{Ba}_{\text{bio}} \) calculated using the upper and lower MAR values listed above and the \( \text{Ba}_{\text{bio}} \) values from the previous figure (global ave. Ba/Ti ratio).

**Figure 8.5.12.6**: The flux of Ba to the sea floor (or \( F_{\text{Ba}} \)) was calculated using the following formulas from Pfeifer et al., 2001 and Bonn et al., 1998 for the Caldas de Luna section;

1) \( F_{\text{Ba}} = \frac{\text{AR} \text{ Ba}_{\text{bio}}}{0.209 \log(\text{MAR}) - 0.213} \) expressed in mg cm\(^{-2}\) kyr\(^{-1}\)

2) \( \%\text{Ba}_{\text{pres}} = 20.9 \log(\text{MAR}) - 21.3 \)

The amount of Ba dissolved at the sediment water interface (or \( F_{\text{Ba}} \)) is calculated by dividing the AR \( \text{Ba}_{\text{bio}} \) by the \( \%\text{Ba}_{\text{pres}} \) (or % of preserved Ba). a) Shows \( F_{\text{Ba}} \) and \( F_{\text{Ba(min)}} \) using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Al ave. ratio and the Caldas de Luna Ba/Al min value (calculated AR \( \text{Ba}_{\text{bio}} \) and AR \( \text{Ba}_{\text{bio(min)}} \) for Ba/Al ratios). b) Shows \( F_{\text{Ba}} \) and \( F_{\text{Ba(min)}} \) using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Ti ave. ratio and the Caldas de Luna Ba/Ti min value (calculated AR \( \text{Ba}_{\text{bio}} \) and AR \( \text{Ba}_{\text{bio(min)}} \) for Ba/Ti ratios). c) shows \( F_{\text{Ba}} \) using the previously calculated upper and lower MAR values and the global Ba/Al ave. ratio (global AR \( \text{Ba}_{\text{bio}} \) for Ba/Al) and d) shows \( F_{\text{Ba}} \) using the upper and lower MAR values and the global Ba/Ti ave. ratio (global AR \( \text{Ba}_{\text{bio}} \) for Ba/Ti).
Figure 8.5.12.7: The calculation of new production or ($P_{new}$ and $P_{new(min)}$) for the Caldas de Luna section following the formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) $P_{new} = 1.95 \times (F_{Ba})^{1.41}$ expressed in gC m$^{-2}$ yr$^{-1}$

a) Showing the $P_{new}$ and $P_{new(min)}$ values for the Caldas de Luna section using the previously calculated upper and lower MAR values and $F_{Ba}$ flux values using the Ba/Al ratios. b) Showing the $P_{new}$ and $P_{new(min)}$ values for the Caldas de Luna section using the previously calculated upper and lower MAR values and $F_{Ba}$ flux values using the Ba/Ti ratios. c) Showing the $P_{new}$ values for the Caldas de Luna section using the previously calculated upper and lower MAR values and $F_{Ba}$ flux values using the global ave. Ba/Al ratio. d) Showing the $P_{new}$ values for the Caldas de Luna section using the previously calculated upper and lower MAR values and $F_{Ba}$ flux values using the global ave. Ba/Ti ratio
Figure 8.5.12.8: The calculation of primary production or palaeoproductivity (PP and PP_{min}) for the Caldas de Luna section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998;

1) \( PP = 20 \left( \frac{P_{\text{new}}}{10} \right)^{0.5} \) expressed in gC m\(^{-2}\) yr\(^{-1}\)

a) Showing the PP and PP_{min} values for the Caldas de Luna section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the Ba/Al ratios. b) Showing the PP and PP_{min} values for the Caldas de Luna section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the Ba/Ti ratios. c) Showing the PP values for the Caldas de Luna section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the global Ba/Al ratio. d) Showing the PP values for the Caldas de Luna section using the previously calculated upper and lower MAR values and the \( P_{\text{new}} \) values using the global Ba/Ti ratio.
1.5.13 3D Environmental Reconstruction Models

Figure 8.5.13.1: General 3D plots (same data shown from differing perspectives) showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. X-Ray Fluorescence (XRF) was used for the whole-rock geochemical analysis. The plots represent all sample data from the Caldas de Luna section (98 samples). Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic conditions after Fertl, 1979. There is no U within a select few of the coarser grained silt stone horizons (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales. The (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values are generally found in samples with little carbonate.
Figure 8.5.13.2: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Si/Al, showing data from the Caldas de Luna section (all 98 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 ‘oxic’, 0.46-0.60 ‘dysoxic’, 0.54-0.82 ‘suboxic-anoxic’ and >0.82 ‘euxinic’ (Hatch and Leventhal, 1992). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.
Figure 8.5.13.3: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Zr/Rb (contrasting grain size proxy to the previous figure Si/Al), displaying data from the Caldas de Luna section (all 98 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 ‘oxic’, 0.46-0.60 ‘dysoxic’, 0.54-0.82 ‘suboxic-anoxic’ and >0.82 ‘euxinic’ (Hatch and Leventhal, 1992). The Zr/Rb ratio is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.
Figure 8.5.13.4: Geochemical environmental reconstruction, using the ratios Rb/K, Th/U and Si/Al, displaying data from the Caldas de Luna section (all 98 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic (Fertl, 1979). There is no U within a select few of the coarser grained silt stone horizons (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input 'detrital influx' therefore rising sea-level or basin subsidence.
1.5.14 Cyclicity

Figure 8.5.14.1: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Caldas de Luna section, 98 samples (Caldas 1 – Caldas 98). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the U ppm values from the base (sample No. 1) to the top (sample No. 98) of the lower member, cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually the sample numbers are shown on the X-axis.

Frequencies (plots c and d, above) | Calculations of periodicity | Cyclicity values
--- | --- | ---
0.014175 (highest intensity) | = 1/(0.014175/22099 yrs) | 1.55 Myr
0.05799 | = 1/(0.05799/22099 yrs) | 381.08 Kyr
0.087629 | = 1/(0.087629/22099 yrs) | 251.18 Kyr
0.15593 | = 1/(0.15593/22099 yrs) | 141.73 Kyr
0.30541 | = 1/(0.30541/22099 yrs) | 72.35 Kyr
0.36856 | = 1/(0.36856/22099 yrs) | 59.96 Kyr

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the Caldas de Luna section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.5.14.2: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Caldas de Luna section, 98 samples (Caldas 1 – Caldas 98). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) to the top (sample No. 98) of the lower member, cyclicity is apparent in the V values. b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.012887</td>
<td>1/(0.012887/22099 yrs)</td>
<td>1.71 Myr</td>
</tr>
<tr>
<td>0.056701 (highest intensity)</td>
<td>1/(0.056701/22099 yrs)</td>
<td>389.74 Kyr</td>
</tr>
<tr>
<td>0.10438</td>
<td>1/(0.10438/22099 yrs)</td>
<td>211.71 Kyr</td>
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<tr>
<td>0.24098</td>
<td>1/(0.24098/22099 yrs)</td>
<td>91.704 Kyr</td>
</tr>
<tr>
<td>0.29639</td>
<td>1/(0.29639/22099 yrs)</td>
<td>74.56 Kyr</td>
</tr>
<tr>
<td>0.36469</td>
<td>1/(0.36469/22099 yrs)</td>
<td>60.59 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the Caldas de Luna section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.5.14.3: Showing the first 2 cycles (Lower Bernesga Mb. of the Formigoso Fm.) for the Caldas de Luna section, all 32 samples. Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the U ppm values from the base (sample No. 1) towards the middle (sample No. 32) of the Bernesga Mb. cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.060484 (highest intensity)</td>
<td>1/(0.060484/22099 yrs)</td>
<td>365.36 Kyr</td>
</tr>
<tr>
<td>0.22581</td>
<td>1/(0.22581/22099 yrs)</td>
<td>97.86 Kyr</td>
</tr>
<tr>
<td>0.27823</td>
<td>1/(0.27823/22099 yrs)</td>
<td>79.42 Kyr</td>
</tr>
<tr>
<td>0.32661</td>
<td>1/(0.32661/22099 yrs)</td>
<td>67.66 Kyr</td>
</tr>
<tr>
<td>0.39516</td>
<td>1/(0.39516/22099 yrs)</td>
<td>55.92 Kyr</td>
</tr>
<tr>
<td>0.46371</td>
<td>1/(0.46371/22099 yrs)</td>
<td>47.65 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the Caldas de Luna section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.5.14.4: Showing the first 2 cycles (Lower Bernesga Mb. of the Formigoso Fm.) for the Caldas de Luna section, all 32 samples. Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) towards the middle (sample No. 32) of the Bernesga Mb. cyclicity is apparent in the V values. b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually the sample numbers are shown on the X-axis.

**Frequencies (plots c and d, above)**

<table>
<thead>
<tr>
<th>Frequencies</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.060484 (highest intensity)</td>
<td>1/(0.060484/22099 yrs)</td>
<td>365.36 Kyr</td>
</tr>
<tr>
<td>0.10484</td>
<td>1/(0.10484/22099 yrs)</td>
<td>210.78 Kyr</td>
</tr>
<tr>
<td>0.29839</td>
<td>1/(0.29839/22099 yrs)</td>
<td>74.06 Kyr</td>
</tr>
<tr>
<td>0.5</td>
<td>1/(0.5/22099 yrs)</td>
<td>44.19 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the Caldas de Luna section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
1.6 La Majua Section

The following section documents all geochemical results for the La Majua section. The La Majua section consists of 70 samples. The sampling interval within the Getino Beds was set to every bed; the Formigoso Fm. (Bernesga Mb.) was set at 25cm, this was also the case for all of the other localities, other than the Aralla HR Log (every cm). The samples for the La Majua section are displayed in the table below (Table 8.6.1); please also refer to the La Majua sedimentary log section (showing the sample location in regards to the log section) in the Results Chapter. and the results tables in Appendix B part 2.

<table>
<thead>
<tr>
<th>La Majua</th>
<th>Upper Barrios Fm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La Majua 1</td>
<td>The Getino Beds (bed by bed sampled)</td>
</tr>
<tr>
<td>La Majua 2-31</td>
<td>Formigoso Fm. (Bernesga Mb.) after 46 – slight gap</td>
</tr>
<tr>
<td>La Majua 32-46</td>
<td>Formigoso Fm. (Bernesga Mb.) – from quarried section</td>
</tr>
</tbody>
</table>

Table 8.6.1 – The corresponding sample numbers for the La Majua section; also refer to the sedimentary log for the La Majua section in the Results Chapter.
1.7.4 Major Elements

Figure 8.6.1.1: All major element variation curves for the La Majua section. Each sample number represents a 25cm interval (within the Formigoso Fm. (Bernesga Mb.)), the Getino Beds were sampled bed by bed. The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey)).
1.7.5 Trace Elements

Figure 8.6.2.1: Trace element variation curves for the La Majua section. Each sample number represents a 25cm interval (within the Formigoso Fm. (Bernesga Mb.)) the Getino Beds were sampled bed by bed. The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
Figure 8.6.2.2: Trace element variation curves for the La Majua section. Each sample number represents a 25cm interval (within the Formigoso Fm. (Bernesga Mb.)) the Getino Beds were sampled bed by bed. The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
Figure 8.6.2.3: Trace element variation curves for the La Majua section. Each sample number represents a 25cm interval (within the Formigoso Fm. (Bernesga Mb.)) the Getino Beds were sampled bed by bed. The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
Figure 8.6.2.4: Trace element variation curves for the La Majua section. Each sample number represents a 25cm interval (within the Formigoso Fm. (Bernesga Mb.)) the Getino Beds were sampled bed by bed. The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
1.7.6 Elemental cross-plots

Figure 8.6.3.1: Showing the cross-plots of \( \text{Al}_2\text{O}_3 \) to: \( \text{K}_2\text{O}, \text{TiO}_2, \text{MgO}, \text{Rb}, \text{Cr} \) and \( \text{Zr} \) for the La Majua section (70 samples). All show positive correlations except for \( \text{Zr} \), a slight positive correlation in the Getino Beds and a negative correlation in the basal organically enriched shales (the lower the enrichment of \( \text{Zr} \) (detrital influx) the higher the \( \text{Al}_2\text{O}_3 \) concentrations). The basal shales and the Getino Beds form separate clusters.

Figure 8.6.3.2: Cross-plots of \( \text{Al}_2\text{O}_3 \) vs. \( \text{SiO}_2/\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3 \) and \( \text{K}_2\text{O}/\text{Al}_2\text{O}_3 \) for the La Majua section (70 samples) all showing negative correlations indicating the presence of clay minerals. The \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) cross-plot indicates the maturity of the sandstone intercalations and shales.
Figure 8.6.3.3: Showing the geochemical ratios of Cr/V and Ni for the La Majua section (70 samples). The ratios can be compared between localities to determine environment differences/changes laterally (redox states, redox sensitive elements). Plots a + b display the ratios plotted against stratigraphy, the differing lithologies are clearly evident (the contrast between the Getino Beds and basal shales of the Formigoso Fm.). Cr, Ni and V are redox sensitive elements. Hence the enrichment shown in the V vs. Cr cross plot towards the organically enriched anoxic shales. The V vs. Cr cross plot shows a strong positive correlation (the higher the V values the higher the Cr values).

Figure 8.6.3.4: Showing grain size (SiO2/Al2O3 and Rb/K2O) and redox state (Cu/Zn) for the La Majua section (70 samples), indicating the maturity of the Formigoso Fm., the lower the silica content, smaller the grain size. The contrast in grain size and silica content is seen at the contact to the underlying Barrios Fm. and Getino Beds.
Figure 8.6.3.5: Harker type major element variation diagrams for the La Majua section (70 samples), clearly discriminating between the Getino Beds and the organically enriched basal shales. CaO readings were just above the detection limit of the Niton XL3t.
Figure 8.6.3.6: Cross plots of $\text{Al}_2\text{O}_3$, $\text{U}$, $\text{Th}$, $\text{Cs}$ and $\text{Ba}$ vs. $\text{K}_2\text{O}$ for the La Majua section (70 samples) all showing positive correlations. The U cross plot showing the organically enriched basal shales, the higher the U content, the higher the total organic carbon (TOC), using U as a proxy for organic content and redox indicator. Note the sandstones (Getino Beds) are depleted in U (detrital influxes, bringing $\text{O}_2$ enriched sediment into the anoxic environment; perturbation of the anoxic bottom waters).

Figure 8.6.3.7: MgO crossplots of $\text{Fe}_2\text{O}_3$, $\text{MnO}$, (Cr+Ni) and V for the La Majua section (70 samples), all showing positive correlations.
Figure 8.6.3.8: Showing Cr/Rb, V/Rb, Th/U, Ba/Rb and Zr/Rb ratios for the La Majua section (70 samples). The values are normalised to Rb as it is inert with respect to biogenic processes unlike Al₂O₃ and SiO₂. The Th/U ratio can be used as a redox proxy. The differing lithologies are labelled.
Figure 8.6.3.9: TOC cross-plots for the La Majua section (all 70 samples); trace elements of ‘strong euxinic affinity’ (Algeo & Maynard, 2004) a) U, b) V, c) Zn and d) Pb all of the trace elements are Al normalized (x10⁴). Trace elements of ‘weak euxinic affinity’ e) Cu, f) Ni and g) Cr again all Al normalized (x10⁴).
Figure 8.6.3.10: Selected major element vs. Al$_2$O$_3$ variation diagrams for the Formigoso Fm. at La Majua (a + b), displaying all 70 samples. The solid line in (a) represents a probable detrital trend (DT). The ranges of K$_2$O/Al$_2$O$_3$ ratios in K-feldspars and clays (plot (b)) (Cox et al. (1995)). Selected trace element vs. Al$_2$O$_3$ variation diagrams (c-e).

f) Th vs. Th/U plot (McLennan et al., 1993) for La Majua samples (70 samples). Dashed lines: Th/U ratio and Th content of UCC; circle: PAAS (Taylor and McLennan, 1985); fields for depleted mantle sources and Australian shales (AS) from McLennan et al. (1993). Arrows indicate direction of trends for weathering (U loss) and enrichment (U gain).

g+h) Zr/Sc vs. Th/Sc plots (McLennan et al., 1993) for (a) Formigoso Fm. at La Majua (all 70 samples); (b) modern muds from trailing edge (TE, passive margin), continental arc (CA), and forearc (FA) settings (McLennan et al., 1990). Solid line connecting stars B (basalt) and F (felsic volcanic rock), illustrates the trend expected in first-cycle sediments due to magmatic evolution from mafic to felsic end members; star G is average granite (Condie, 1993). UCC and PAAS from Taylor and McLennan (1985). Arrow illustrates the trend produced by zircon concentration during sedimentary sorting and recycling.
**Figure 8.6.3.11:** Geochemical plots for the La Majua section (all 70 samples utilised). a) Showing V/(V+Ni) vs. TOC; the higher the TOC values the lower the sedimentation rate (V/(V+Ni) values have to be above 0.5 in order for the organic carbon to be preserved (not oxidised, Rimmer, 2004), the sedimentation rate indicator after Arthur & Sagemann, 1994). b) Represents the TOC values vs. stratigraphy (every data point is equivalent to 25cm, other than the Getino Beds – bed by bed scale). b,c & d) the selected geochemical indices for the La Majua section (all 70 samples). Note that when the TOC and V/(V+Ni) values decrease (V/(V+Ni) throughout) and the Mn/Al increase it suggests oxygenation of the sediments.
Figure 8.6.3.12: Utilising all geochemical data from the La Majua section (all 70 samples). a) shows Zr/Ti ratios used as a provenance proxy; high Zr/Ti ratios point towards granitic rocks (G1 granite: Zr/Ti is 0.14) or clastic sediments (average phanerozoic quartz arenite: Zr/Ti is 0.13; Boryta and Condie, 1990). Lower Zr/Ti ratios around 0.067 represent the composition of the average upper crust (Taylor and McLennan, 1985). The ‘North American shale composite’ (NASC) has a Zr/Ti ratio of 0.043. Lower Zr/Ti ratios are indicative of basic igneous rocks; Andean volcanic rocks yield Zr/Ti ratios between 0.024 for basalts and 0.034 for andesites (Ewart, 1982). Lowest Zr/Ti ratios around 0.017 represent primitive magmas of OIB’s and MORB’s (Bonn, 2004). b) Signifies palaeosalinity (using Rb/K ratios), the dashed line values were taken from Campbell & Williams, 1965. c-f) palaeo-redox indicators; the ratio lines are documented in the table. g) Th/U Ratios for La Majua, any value <2 implies anoxic (Fertl, 1979), organically rich black shale genesis.

<table>
<thead>
<tr>
<th>Oxic</th>
<th>Dysoxic</th>
<th>Suboxic-Anoxic</th>
<th>Euxinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Co</td>
<td>&lt; 5</td>
<td>5 - 7</td>
<td>&gt; 7</td>
</tr>
<tr>
<td>V/Cr</td>
<td>&lt; 2</td>
<td>2 - 4.25</td>
<td>&gt; 4.25</td>
</tr>
<tr>
<td>V/(V+Ni)</td>
<td>&lt; 0.46</td>
<td>0.46 - 0.60</td>
<td>0.54 - 0.82</td>
</tr>
<tr>
<td>U/Th</td>
<td>&lt; 0.75</td>
<td>0.75 - 1.25</td>
<td>&gt; 1.25</td>
</tr>
<tr>
<td>V/Sc</td>
<td>&lt; 9.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8.6.3.13: Geochemical data representative of the La Majua section (70 samples) a) V/Al vs. stratigraphy and b) correlation of V with TOC.

Figure 8.6.3.14: Geochemical data from the La Majua section (all 70 samples). a) Scatter plot showing heavy mineral indicating element vs. major component. b) TOC values vs. stratigraphy. c + d) Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ vs. stratigraphy and finally e + f) V and Zn vs. TOC.
Figure 8.6.3.15: All data from the La Majua section (70 samples); a) SiO$_2$ vs. Al$_2$O$_3$ concentrations are plotted relative to the idealized composition of the observed minerals (Cullers & Podkovyrov, 2000). The majority of the variation in composition may be related to variations in quartz and clay minerals-muscovite. b) Fe$_2$O$_3$ total vs. Al$_2$O$_3$ concentrations plotted relative to the composition of the observed minerals (Cullers & Podkovyrov, 2000), again much of the variation in composition may be accounted for by variations in quartz and clay minerals-muscovite.

Figure 8.6.3.16: Representing all data from the La Majua section (70 samples). Redox sensitive elements (V and Cr) showing positive correlations with TOC values; a) Cr (ppm) vs. TOC, b) V (ppm) vs. TOC, c) Cr (wt %) vs. TOC and d) V (wt %) vs. TOC.
Figure 8.6.3.17: Representing all data from the La Majua section (70 samples). \( \text{Al}_2\text{O}_3 \) bivariate diagrams of major element composition along with estimated elemental mineral compositions (after Descourvieres et al., 2011).
Figure 8.6.3.18: Cross-plots showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. The plots represent sample data from the La Majua section (all 70 samples). Th/U is used as a redox indicator; the dashed black line representing a Th/U ratio of 2, less than 2 indicates anoxic (Fertl, 1979). Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction); high values reflect coarse grained units, lower values in clay stones and shales. (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values found in samples with little carbonate.

Figure 8.6.3.19: Cross-plot of Ni vs. Cr representing all data from the La Majua section (70 samples).
Figure 8.6.3.20: Representing all data from the La Majua section (70 samples). The ratios Ni/V and V/Cr (Jones and Manning, 1994) are redox indicators.

Figure 8.6.3.21: Geochemical data from the La Majua section (all 70 samples). Selected elements and ratios plotted vs. stratigraphy.

Figure 8.6.3.22: Representing the relationship between Al$_2$O$_3$ and Ba for the La Majua section (70 samples).
Figure 8.6.3.23: Representing all data from the La Majua section (70 samples). a) Plot of U/Pb ratios vs. U concentrations (ppm). Samples generally reflect elevated U concentrations relative to North American Shale Composite (Condie, 1993). b) TOC (wt.% vs. U concentrations (ppm). The U content of NASC is plotted for reference (samples are enriched in U relative to the NASC composite). U and TOC exhibit a perfect correlation as TOC values were generated using the U (ppm) values as a proxy (Fertl & Chillingar (1988)).

Figure 8.6.3.24: All diagrams represent the data from the La Majua section (70 samples). a) Th vs. Sc (in log scale) and b) Th vs. U diagrams (McLennan et al., 1990, and Luchi et al., 2003). c) Fe₂O₃/K₂O vs. SiO₂/Al₂O₃ d) log SiO₂/Al₂O₃ vs. log (Fe₂O₃/K₂O) of Herron (1986). e) Th/Sc vs. Zr/Sc (log scale) diagram (McLennan et al., 1993), reflecting reworking through Zr/Sc and upper crust felsic input through Th/Sc. Numbers identify the mean values for 1,OIA, 2,CIA, 3, ACM and 4, PM following Bathia and Crook (1986). f) TiO₂ vs. Ni, fields for acidic and basic source materials after Floyd et al., (1989).
Figure 8.6.3.25: Displaying all data from the La Majua section (70 samples). Th/Sc vs. Zr/Sc plot (Mongelli et al., 2006), the samples depart from the compositional trend indicating zircon addition suggestive of a recycling effect.

Figure 8.6.3.26: Representing all data from the La Majua section (70 samples). Zr versus SiO₂, a positive relationship is apparent, indication that the Zr is indeed associated with the Quartz (heavy fraction).
Figure 8.6.3.27: TiO$_2$ vs. Ni bivariate plot for shale samples from the La Majua section (all 70 samples), fields after Floyd et al., 1989.

Figure 8.6.3.28: Representing all data from the La Majua section (70 samples). The trace elements are normalised to Al and then multiplied by 10$^{-4}$. As, Cr, Cu, Ni, V, Zn vs. stratigraphy.
Figure 8.6.3.29: Geochemical classification (Pearce, 2010) based on the criteria listed in Table b (above) for the La Majua dataset (all 70 samples). The geochemical classification values (y-axis of plot a) reflect the following: Score of 4 = floodplain mudstone, Score of 7 = brackish water or lacustrine, Score of 10 = marginal marine mudstone, Score of 13 or 16 = marine mudstone (= marine band). If a sample has a very high Zr/U value (above 65), it is presumed to contain abundant heavy minerals and is awarded a final score of 2. If a sample comes from a coal, it is awarded a default score of 0 (Pearce, 2010).

Mo and P2O5 values for the La Majua section are near/below detection limits.

Based on the criteria above the depositional environment of the Formigoso Fm. at the La Majua section is classified as borderline; brackish water or Lacustrine - marginal marine mudstone (which fits with the Rb/K ratios for palaeosalinity).
Figure 8.6.3.30: Representing all data from the La Majua section (70 samples). A) SiO$_2$/Al$_2$O$_3$ vs. TOC and B) Zr/Rb vs. TOC. The SiO$_2$/Al$_2$O$_3$ and Zr/Rb ratios are renowned grain size proxies, plotted against TOC (Total Organic Carbon) values. The zones for hydrocarbon potential (TOC cut off values) based on Bordenave et al., (1993). The plots discriminate between the basal shales (lower member) of the Formigoso Fm. and the sands/silts (Getino Beds). The higher the grain size proxy the lower the TOC (within the coarser grained units there is a relationship between grain size and TOC). The TOC values for the basal shales act independently of the grain size values, the grain size remains consistent yet the TOC levels vary; this is most likely due to changes in the redox state.
Figure 8.6.3.31a: Plots representing data from the La Majua section (all 70 samples), showing the relationship between Al$_2$O$_3$, selected trace elements and Fe$_2$O$_3$. The plots show the relationship between the Cantabrian formations (predominantly the Getino Beds and Formigoso Fm.) trace element:Al$_2$O$_3$ ratios and the World Shale Average (WSA, plotted as star, taken from Gromet et al., 1984), the Zr vs. Al$_2$O$_3$ also includes the Upper Crust (UC) and North American Shale Composite (NASC).
Figure 8.6.3.31b: Plots representing data from the La Majua section (all 70 samples). The plots show the relationship between various trace elements within the Cantabrian formations (predominantly the Getino Beds and Formigoso Fm.).

Figure 8.6.3.32: Representing data from the La Majua section (all 70 samples). a) Chemical classification, after Herron, 1986. b) Plot of discriminant functions 1 and 2 for shales (after Roser and Korsch 1988). Discriminant function 1 = (−1.773 × TiO$_2$%) + (0.607 × Al$_2$O$_3$%) + (0.76 × Fe$_2$O$_3$T%) + (−1.5 × MgO%) + (0.509 × Na$_2$O%) + (−1.22 × K$_2$O%) + (−9.09). Discriminant function 2 = (0.445 × TiO$_2$%) + (0.07 × Al$_2$O$_3$%) + (−0.25 × Fe$_2$O$_3$T%) + (−1.142 × MgO%) + (0.432 × Na$_2$O%) + (1.426 × K$_2$O%) + (−6.861). Provenance fields are after Roser and Korsch (1988). P1 = mafic and lesser intermediate igneous provenance; P2 = intermediate igneous provenance; P3 = felsic igneous provenance and P4 = recycled-mature polycyclic quartzose detritus. c) Distribution of K and Rb relative to a K/Rb ratio of 230 (=main trend of Shaw, 1968).
Figure 8.6.3.33: Representing all Zr vs. Cr data from the La Majua section (70 samples). Variations in the Zr and Cr values are likely to reflect changes in the sediment provenance.

Figure 8.6.3.34: Cross plot of Mo (ppm) and TOC (wt%) values from the La Majua section (all 70 samples). Evidently the Mo concentrations are near/below the detection limit.
Figure 8.6.3.35: Representing data from the La Majua section (all 70 samples). a) V/Cr used as a palaeoredox proxy. b) V/Cr ratio vs. TOC.

Figure 8.6.3.36: Representing all data from the La Majua section (70 samples). a + b) plots of the detrital parameter Th vs. Zr and Th vs. Ti. c + d) Cross plots of Th as detrital monitor vs. authigenic uranium (U-aut) and V (ppm).
Figure 8.6.3.37: Representing all data from the La Majua section (70 samples). a) Scatter plot of V/(V + Ni) vs. degree of pyritization (DOP), displaying average shale (Turekian & Wedephol, 1961) and average continental crust. b) DOP vs. stratigraphy; the lines representing DOP values are from Wignall, 1994. c) Represents an idealized plot of a uniform DOP with increasing TOC, (a+c).

Figure 8.6.3.38: Displaying all data from the La Majua section (70 samples), provenance and source signature diagrams. a) Th vs. Sc. Th is an incompatible element that is enriched in silicic rocks, and Sc is a compatible element that is enriched in mafic rocks. Th/Sc ratios near unity represent the upper continental crust (UC) the Th/Sc ratios near 0.6 suggest a more mafic component (Totten et al., 2000). b) Th/Sc vs. Cr/Th the samples lie upon a curve consistent with mixing of a continental source enriched in incompatible elements (Th) and a more mafic source enriched in compatible elements (Cr, Sc). The values for UC, Granites and mid-oceanic-ridge-basalts (MORB) are given for comparison (Totten et al., 2000). c) Th vs. Sc relation and d) Th/Sc vs. Cr/Th.
Figure 8.6.3.39: Representing all data from the La Majua section (70 samples). MgO/Al₂O₃ vs. K₂O/Al₂O₃ cross plot including the fields of kaolinite, illite/K-feldspar and chlorite (clay typing) (of Turgeon + Brumsack, 2006).
Figure 8.6.3.40: Representing all data from the La Majua section (70 samples). Diagrams used for discriminating the differing lithologies (Getino Beds and basal shales; Bernesga Mb.).

Figure 8.6.3.41: Showing data from the La Majua section (all 70 samples). a) cross-plot of SiO₂ vs. Al₂O₃ shows an enrichment of SiO₂ over Al₂O₃ in comparison to the World Average Shale (WSA) of Turekian & Wedephol, 1961. b + c) TOC vs. Al₂O₃ and SiO₂, showing that the TOC values vary as the Al₂O₃/SiO₂ content remain consistent
Figure 8.6.3.42: Representing all data from the La Majua section (70 samples). Plot of total organic carbon (TOC wt.%) against authigenic uranium content ($U_{\text{auth}}$). The correlation between TOC and total U would be 1:1 as the TOC values have been generated by using U as a proxy. Yet the $U_{\text{auth}}$ values use Th values in order to correct for detrital uranium.

Figure 8.6.3.43: Representing all data from the La Majua section (70 samples). Elemental Sr/Al, Mn/Al, Si/Al, Ba/Al, Zr/Al ratios plotted against TOC and stratigraphy.
1.7.7 $\text{Na}_2\text{O}$ plots

Figure 8.6.4.1: Displaying data from the La Majua section (all 70 samples). a) Provenance discrimination diagram for shales (after Roser and Korsch, 1988); Discriminant Discriminant function 1 = $(-1.773 \times \text{TiO}_2\%) + (0.607 \times \text{Al}_2\text{O}_3\%) + (0.76 \times \text{Fe}_2\text{O}_3\% ) + (-1.5 \times \text{MgO}\%) + (0.616 \times \text{CaO}\%) + (0.509 \times \text{Na}_2\text{O}\%) + (-1.22 \times \text{K}_2\text{O}\%) + (-9.09)$. Discriminant function 2 = $(0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\% ) + (-1.142 \times \text{MgO}\%) + (0.432 \times \text{Na}_2\text{O}\%) + (1.426 \times \text{K}_2\text{O}\%) + (-6.861)$. b) Bivariate $\text{SiO}_2$ wt.% vs. $(\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O})$ wt.% palaeoclimate discrimination diagram, fields after Suttner and Dutta (1986). c) $\text{SiO}_2/\text{Al}_2\text{O}_3$ vs. $\text{K}_2\text{O}/\text{Na}_2\text{O}$ after Kampunzu et al., 2005. d) Discriminant function diagram after Roser and Korsch (1988); Discriminant function I = $(-1.773 \times \text{TiO}_2\%) + (0.607 \times \text{Al}_2\text{O}_3\%) + (0.76 \times \text{Fe}_2\text{O}_3\% ) + (-1.224 \times \text{K}_2\text{O}\%) + (-9.09)$; Discriminant function II = $(0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\% ) + (-1.142 \times \text{MgO}\%) + (0.438 \times \text{CaO}\%) + (1.475 \times \text{Na}_2\text{O}\%) + (1.426 \times \text{K}_2\text{O}\%) + (-6.861)$. e) Akul'shina (1976) + Kiipli et al., (2012): $\text{Al}/\text{Ti}$ ratio and climate: $\text{Al}_2\text{O}_3/\text{TiO}_2$ <20 for humid, 20–30 for semi-humid and semi-arid, and >30 for arid climate.
1.7.8 **Histograms (major elements & redox ratios)**

**Figure 8.6.5.1:** Histograms and cumulative frequency representing the major oxides a) SiO$_2$ values b) Al$_2$O$_3$ values c) K$_2$O values and d) TiO$_2$ values, using all sample data (70 samples) from the La Majua section. Wt% vs. frequency for the histograms and cumulative frequency for the curve.

**Figure 8.6.5.2:** Histograms and cumulative frequency curves representing all sample data for the La Majua section. a) Showing the calculated degree of pyritization (DOP); A = Anaerobic (0-0.4); R = Restricted (0.45-0.75); I = Ininhospitable (0.55-1) ranges from Raiswell *et al*., 1988. b + c) palaeo-redox proxies V/(V + Ni) and V/Cr. Ranges for inferred bottom-water conditions for V/Cr, <2 oxic, 2-4.25 dysoxic, >4.25 suboxic-anoxic from Jones and Manning (1994); ranges for V/(V + Ni), <0.46 oxic, 0.46-0.6 dysoxic, 0.54-0.82 suboxic-anoxic, >0.84 euxinic (Hatch and Leventhal (1992)).
1.7.9  K, Th and U bubble plots

Figure 8.6.6.1: Bubbles plots of K$_2$O, Th and U for the La Majua section. a) Representing all the sample data from the La Majua section (70 samples), b) Showing just the basal shales (Bernesga Mb. of the Formigoso Fm.). The K$_2$O, Th and U contents were analysed by X-Ray Fluorescence (XRF) whole rock analysis, the bubble size is proportional to U content,
1.7.10 *Ternary diagrams*

The symbols for the differing lithologies within the ternary plots remain consistent throughout all ternary diagrams; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). For the expanded plots the key is given alongside each figure.

![Ternary diagram](image)

**Figure 8.6.7.1**: Ternary diagram showing relative proportions of major shale/mud rock components; SiO$_2$ (quartz), Al$_2$O$_3$ (clays) and CaO (carbonates), displaying data from the La Majua section (all 70 samples). The Key for the expanded plot is shown to the left of the figure, the key for the inset ternary (top right); square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the ‘Average shale’ also shown as star (after Wedepohl, 1971).
Figure 8.6.7.2: La Majua section (all 70 samples) ternary $10\text{Al}_2\text{O}_3$ - $200\text{TiO}_2$ - Zr plot (Mongelli et al., 2006) showing possible sorting effects, the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).

Figure 8.6.7.3: La Majua section (all 70 samples) ternary $15\text{Al}_2\text{O}_3$ - $300\text{TiO}_2$ - Zr plot showing possible sorting effects, the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).
Figure 8.6.7.4: TOC–S–Fe relationships for the La Majua section (all 70 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.6.7.5: TOC–TS10–Fe ternary diagram for the La Majua samples (all 70). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The construction and principles of the diagram based on Dean and Arthur (1989) and Arthur and Sageman (1994).
Figure 8.6.7.6: Degree of pyritization of sediments from the La Majua section (all 70 samples) in the Fe(x) - total organic carbon (TOC) - S2 (following stoichiometry of pyrite-FeS2) system (relative weight ratios). Reactive Fe (Fe(x)) is calculated with Fe(x) = Fe – 0.25 × Al (Mosher et al., 2006). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.6.7.7: Al–Mg–Ca diagram showing the distribution of the Getino beds and basal shales of the Formigoso Fm at La Majua (all 70 samples). Inset ternary (top left); the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the domains of evaporites and meta-evaporites, and of platformal marls and shales are from Moine et al., (1981). The key for the expanded plot is towards the right of the figure.
Figure 8.6.7.8: The ternary diagrams top right (inset); (A) Ternary plot of (Cu+Co+Ni)10 – Fe – Mn (Bonatti et al., 1976 and Mohapatra 2009) showing various genetic fields, displaying all data (70 samples) from the La Majua section, (B) Chemical composition of the formations at the La Majua section (all 70 samples) in terms of components Fe – Mn – Al+Si. The arrow indicates the decreasing clastic input. The key for the expanded plots is found towards the upper left of the figure.
Figure 8.6.7.9: Th − (Cr + Ti)/1000 − Zr/10 (Hessler & Donald, 2006) ternary plot showing all 70 samples from the La Majua section, a clear differentiation between the Getino beds and the basal shales (Bernesga Mb.). The key for the upper left ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), chemical components after.

Figure 8.6.7.10: Al₂O₃, MgO and Fe₂O₃ ternary plot representing data from the La Majua section (all 70 samples). There are two differing trends between the Getino Beds and the basal shales (Bernesga Mb.), possibly a result of differing provenance sources or maybe just a grain size effect. The key for the upper left ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.6.7.11: $\text{Al}_2\text{O}_3$, $\text{MgO} \times 10$ and $\text{Fe}_2\text{O}_3$ - (expanded plot of previous (Figure 8.6.7.10)) representing data from the La Majua section (all 70 samples). Two differing trends seen, possibly resulting from differing provenance sources or maybe just a grain size effect. The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.6.7.12: $\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3$ and $\text{MnO}$ ternary plot; represents data from the La Majua section (all 70 samples). The key for the upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key for the expanded plot is seen towards the left of the figure.
Figure 8.6.7.13: Distribution of Fe$_2$O$_3$, Al$_2$O$_3$ and SiO$_2$ within the La Majua section (70 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), compared with several ideal clay minerals, including chamosite (Chm), berthierine (Ber) thin/long rectangle to represent variable compositions, kaolin and muscovite (Ka/Mu), nontronite (Non), illite thick/long rectangle and glauconite (Gla) (Konhauser et al., 1998, Konhauser & Urrutia, 1999 and Eickmann et al., 2009). The key for the expanded plot is seen towards the left of the figure.

Figure 8.6.7.14: Distribution of K$_2$O, Al$_2$O$_3$ and SiO$_2$ (Konhauser et al., 1998 & 1999) from the La Majua section (all 70 samples analysed). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), compared to several ideal clay minerals, including, kaolin (Ka), muscovite (Mu), illite (ill) long rectangle (representing varying compositions) and glauconite (Gla) are labelled. The key for the expanded plot is seen towards the left of the figure.
Figure 8.6.7.15: Th, As/10 and U ternary plot, representing data from the La Majua section (all 70 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). There is a clear deference between the Getino Beds and the basal shales of the Bernesga Mb., the sands/silts are depleted in U.

Figure 8.6.7.16: Major geochemical components Al$_2$O$_3 \times 5$ - SiO$_2$ - CaO x 2 (relative weight ratios) for the La Majua section (All 70 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), data points for average shale (Wedepohl, 1971, 1991), kaolinite and K-feldspar are shown for comparison (Hetzel et al., 2011).
Figure 8.6.7.17: Ternary plot for Fe$_2$O$_3$, K$_2$O and Al$_2$O$_3$, showing all samples from the La Majua section (70 samples). The upper right ternary; square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the key towards the left of the figure is for the exploded diagram. The shales cluster away from the Getino Beds, a clear maturity trend towards the Barrios Fm. is also evident.

Figure 8.6.7.18: Ternary plot for SiO$_2$/Al$_2$O$_3$, TiO$_2$ and MgO, expressing all samples from the La Majua section (70 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the shales cluster away from Getino Beds.
Figure 8.6.7.19: Ternary plot for U*20, Zr and Sr, expressing all samples from the La Majua section (70 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The shales (enriched in Sr and U) cluster away from the Getino Beds that plot towards the heavy element Zr.

Figure 8.6.7.20: Ternary plot for K₂O, Th and U, showing all samples from the La Majua section (70 samples). The ternary plot (upper right); square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key is valid for the exploded diagram. The shales (depleted in K₂O (feldspar fragments)) in relation to the Getino Beds, cluster away. Note that either side of the diagram the shales appear highly enriched in U and the sands opposite show U depletion.
Figure 8.6.7.21: Ternary plot representing all data for the La Majua section (70 samples) showing the relationship between K₂O*5, Th and U as previously (Figure 8.6.7.20) yet a higher factor for K values. The Majority of the Getino Beds cluster towards the K₂O enrichment, K₂O resides mostly within the detrital faction.

Figure 8.6.7.22: Ternary plot representing all data for the La Majua section (70 samples) showing the relationship between the heavy elements; Zr, Cr and Ni (Ratcliffe, 2007). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The sands of the Getino Beds cluster towards Zr.
Figure 8.6.7.23: Ternary plot representing samples from the La Majua section (all 70). Cross-plot constructed to characterise between the Shales (differing subunits?) and the Getino Beds, clearly geochemically separated.

Figure 8.6.7.24: Ternary diagram Fe₂O₃ – MgO – SiO₂/Al₂O₃ representing data from the La Majua section (all 70 samples). The upper right ternary; square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The expanded plot clearly discriminates between the Getino beds and the shales of the Bernesga Mb.
Figure 8.6.7.25: CIA ternary diagram, $\text{Al}_2\text{O}_3 - \text{CaO} + \text{Na}_2\text{O} - \text{K}_2\text{O}$ (after Nesbitt and Young, 1982), displaying data from the La Majua section (all 70 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.6.7.26: $\text{Al}_2\text{O}_3 - (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) - (\text{Fe}_2\text{O}_3 + \text{MgO})$ ternary diagram after Hayashi et al., 1997, representing data from the La Majua section (all 70 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
1.7.11 Index of Compositional Variation (ICV)

Figure 8.6.8.1: a) $K_2O/Al_2O_3$ ratio for the La Majua section (in order to discriminate K-feldspars and clay minerals). The stars represent values for specific minerals indicated, data from Deer et al., 1966, overlay from Cox, 1995. b) expanded plot of the original (a). c) Index of Compositional Variation (ICV); $(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3$, for the La Majua section, the stars represent values for specific minerals indicated, the arrows show the range of values for the particular mineral group, data from Deer et al., 1966, overlay from Cox, 1995. d) Expanded plot of the original ‘c’), possible cyclicity apparent within the ICV values.

$K_2O/Al_2O_3$ - range of Bernesga Mb. (shales) at La Majua: 0.0919-0.1294

$K_2O/Al_2O_3$ - range of Getino Beds at La Majua: (-0.0548) 0.0009 -0.1398

$K_2O/Al_2O_3$ - average of Bernesga Mb. (shales) at La Majua: 0.1073

$K_2O/Al_2O_3$ - average of Getino Beds at La Majua: 0.0832

ICV - range of Bernesga Mb. (shales) at La Majua: 0.3288-0.5519

ICV - range of Getino Beds at La Majua: 0.3935-7.1688 (12.7452 with Fe spike)

ICV - average of Bernesga Mb. (shales) at La Majua: 0.4023

ICV - average of Getino Beds at La Majua: 1.6549
1.7.12 Chemical Index of Alteration (CIA), PIA & CIW

The Chemical Index of Alteration (CIA) (Nesbitt and Young, 1982; Taylor and McLennan, 1985) is a well-established parameter for determining the degree of weathering and is the most accepted of the available weathering indices (Bahlburg & Dobrzinski, 2009). During the degradation of feldspars, Ca, Na, and K are removed and clay minerals with a higher fraction of Al are formed. The CIA is estimated from the proportion of Al$_2$O$_3$ vs. the weathering-prone oxides (after Mosher et al., 2006). This index measures the degree of feldspar decomposition to secondary clay products, where CIA values of about 50 indicate fresh bedrock (no chemical weathering), and values of 75-100 indicate complete conversion of feldspars to aluminous clay minerals (intense chemical weathering; see Fedo et al., 1995):

\[
\text{CIA} = \left[ \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \right] \times 100
\]

A) Kaolinite has a CIA value of 100 and represents the highest degree of weathering. Illite is between 75 and c. 90, muscovite at 75, the feldspars at 50. Fresh basalts have values between 30 and 45, fresh granites and granodiorites of 45 to 55 (Nesbitt and Young, 1982; Fedo et al., 1995). B) Expanded plot, focusing within the Illite Zone (muscovite line also shown).

The average CIA value for the Bernesga Mb. (black shales) at La Majua: 87.2

Figure 8.6.9.1: Representing data from the La Majua section (all 70 samples). The 'Chemical Index of Alteration' (CIA) (Nesbitt and Young, 1982, Taylor and McLennan, 1985) is a well-established parameter for determining the degree of weathering and is the most accepted of the available weathering indices (Bahlburg & Dobrzinski, 2009). During the degradation of feldspars, Ca, Na, and K are removed and clay minerals with a higher fraction of Al are formed. The CIA is estimated from the proportion of Al$_2$O$_3$ vs. the weathering-prone oxides (after Mosher et al., 2006). This index measures the degree of feldspar decomposition to secondary clay products, where CIA values of about 50 indicate fresh bedrock (no chemical weathering), and values of 75-100 indicate complete conversion of feldspars to aluminous clay minerals (intense chemical weathering; see Fedo et al., 1995):

\[
\text{CIA} = \left[ \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \right] \times 100
\]

A) Kaolinite has a CIA value of 100 and represents the highest degree of weathering. Illite is between 75 and c. 90, muscovite at 75, the feldspars at 50. Fresh basalts have values between 30 and 45, fresh granites and granodiorites of 45 to 55 (Nesbitt and Young, 1982; Fedo et al., 1995). B) Expanded plot, focusing within the Illite Zone (muscovite line also shown).
Figure 8.6.9.2: Representing all data from the La Majua section (70 samples), the ‘Plagioclase Index of Alteration’ (PIA; Fedo et al., 1995).

\[
\text{PIA} = \left(\frac{\text{Al}_2\text{O}_3 - \text{K}_2\text{O}}{\left(\text{Al}_2\text{O}_3 - \text{K}_2\text{O}\right) + \text{CaO} + \text{Na}_2\text{O}}\right) \times 100
\]

High CIA and PIA values (i.e., 75–100) indicate intensive weathering in the source area whereas low values (i.e., 60 or less) indicate low weathering in source area. The high variations in CIA and PIA values may, however, be due to the low concentrations (sometimes below or near detection limits) of the alkalis and alkaline earth elements rather than variable degrees of source area weathering, from Osae et al., 2006.

A) Displays the PIA values for the La Majua, and B) Expanded plot of the PIA values, PIA calculation from Moosavirad et al., 2011.

The average PIA value for the Bernesga Mb. (black shales) at La Majua: 95.76
Figure 8.6.9.3: Representing all data from the La Majua section (70 samples), the ‘Chemical Index of Weathering’ (CIW; Harnois, 1988).

\[ \text{CIW} = \left( \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O}} \right) \times 100 \]

The CIW index increases with the degree of depletion of the soil or sediment in Na and Ca, relative to Al. The value of this index increases as the degree of weathering increases, and the difference between CIW index values of the silicate parent rock and soil or sediment reflects the amount of weathering experienced by the weathered material, from Harnois, 1988.

A) Showing the CIW values for the La Majua section, modified after Harnois, 1988 & Moosavirad et al., 2011 and B) Expanded plot of the CIW values. Calculations from Moosavirad et al., 2011 (p.6-7 use to describe differences in CIA, PIA and CIW).

The average CIW value for the Bernesga Mb. (black shales) at La Majua: **96.2**
1.7.13 Gamma-ray log and Total Organic Carbon (TOC)

The following section documents the calculated gamma ray (API)/ TOC values for the La Majua section (all 70 samples). The API values were calculated after Ellis, 1987, found in the methodology chapter, the same goes for the TOC values calculated after Fertl & Chillingar, 1988, also documented in the methods chapter.
Figure 8.6.10.1: Showing whole rock K₂O, Th and U values for the La Majua section (every data point for the Formigoso Fm. represents 25cm of stratigraphy, for the Getino Beds every bed was sampled - not every 25cm) from the Barrios Fm. (La Majua 1), Getino Beds (La Majua 2 - 32 in green) and the lower Bernesga Mb. of the Formigoso Fm. La Majua 32 - 70 (light grey). Note the cyclic behaviour of the U values. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~ 8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons.

There is a clear differentiation between the Formigoso Fm. and the underlying Getino Beds. The basal ‘hot’ shales of the Formigoso Fm. appear to be missing when compared to the other localities.

The GR values were calculated by converting K₂O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using 6.69U + 2.54Th + 10.64K₂O = API after (http://server4.oersted.dtu.dk/research/RI/SNG/SNG-logs.html). CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: =3.9637*LN(Uranium Values)-5.6873. This formula was calculated after Fertl & Chillingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
Figure 8.6.10.2: Showing whole rock K\textsubscript{2}O, Th and U values for the La Majua section (every data point for the Formigoso Fm. represents 25cm of stratigraphy, for the Getino Beds every bed was sampled - not every 25cm) from the Barrios Fm. (La Majua 1), Getino Beds (La Majua 2 - 32 in green) and the lower Bernesga Mb. of the Formigoso Fm. La Majua 32 - 70 (light grey). Note the cyclic behaviour of the U values. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinocozan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons.

There is a clear differentiation between the Formigoso Fm. and the underlying Getino Beds. The basal ‘hot’ shales of the Formigoso Fm. appear to be missing when compared to the other localities.

The GR values were calculated by converting K\textsubscript{2}O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using 8U + 4Th + 16K\textsubscript{2}O = API after Elis, 1987 and Doveton, 2004. CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: 
\[=3.9637*\ln(\text{Uranium Values})-5.6873\]. This formula was calculated after Fertl & Chillingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
1.7.14 Hydrothermal Overprint

**Figure 8.6.11.1:** Bostrom (1973) diagram; the analysed sediments (all 70 samples from the La Majua section) are compared to argillite (T) and hydrothermal (H) end members whose mixing is modelled by the H-T curve. PAAS and NASC (Gromet et al., 1984) are reported for comparison.
1.7.15 Bioproductivity Reconstruction (Barium proxy) & SEM/DOP

Figure 8.6.12.1: a) Al/Ti ratio, data from the La Majua section, shaded region indicates approximate range in shales, pelagic clay, andesite and hydrothermal sediment, and the dashed lines representing oceanic crust & granite Al/Ti ratios after Murray & Leinen, 1996. It shows that the shales of the Formigoso Fm. are enriched in Al (as seen in the EF diagrams) giving the higher Al/Ti ratios, pushing towards the granitic composition, this fits with the bulk composition of basal granitic hinterland.

To test whether the Al enrichment is due to the granitic composition of the hinterland the Fe/Al ratio is used (b). The ranges after Gordon et al., 1996 in Murray & Leinen, 1996 (labelled a-e); if the sediment source were composed of pure granite (Al/Ti ~ 40; Taylor and McLennan, 1985), it could be the cause of the elevated Al/Ti. Upper crust (Fe/Al ~ 0.42, a), PAAS (~0.51, b), pelagic clay (~0.77, c), and, bulk continental crust (~0.84, d) (Taylor and McLennan, 1985). In granite, Fe/Al ~ 0.28, e (Taylor and McLennan, 1985). From this it can be inferred that the Formigoso Fm. basal shale composition is closest to that of a granitic source.

c) Table displaying Al/Ti ratios of modern day terrestrial source material, aeolian dust and marine sediments modified after Zabel et al., 1999, comparison of the Formigoso Fm. Al/Ti ratios to that of modern day environments (La Majua ranging from ~22-32 sat within the deep-sea sediments ranges, yet higher range 32 comparable to that of surface sediments (equatorial pacific)).

d) TiO₂ vs. Al₂O₃ cross plot including all data from the La Majua section (70 samples). The plot shows the correlation between TiO₂ and Al₂O₃ ($R^2 = 0.119$) indicating that the elements are associated with the clay mineralisation and that neither are enriched in relation to each other (no biogenic input). This meant that both elements could be used when calculating the primary production (or palaeoproductivity).

Hydrothermal tests were also carried out (refer to previous figure) to determine if the Formigoso Fm. had undergone any extensive alteration due to peckling hydrothermal fluids, thus, overprinting the true geochemistry (hydrothermal elements anyhow). The tests carried out suggested that the basal Bernesga Mb. of the Formigoso Fm. had not been affected by any hydrothermal overprinting however the upper Villasimpliz Mb. (sands and silts) had been affected yet not significantly (slightly more porous). Therefore, the Ba values of the Formigoso Fm. have not been significantly altered by hydrothermal activity, at least in the lower Bernesga Mb.
Figure 8.6.12.2: Representing the calibrated elemental values for the La Majua section, all the elements and ratios are plotted against stratigraphy (La Majua 1 being the oldest, La Majua 70 the youngest), sampled at 25cm intervals (other than the Getino Beds, bed by bed). The sample No. (X-axis) of these plots are inverted in relation to all previous plots, as they are to be used in well log form. A set or averaged Ba/Al and Ba/Ti ratio is used for the calculation of the $\text{Ba}_{\text{bio}}$, for each location, yet graphs e & f show the variation of Ba/Al and Ba/Ti ratios for the La Majua section.
Figure 8.6.12.3: Tables displaying the global Ba/Al average values for area/materials and regions, modified after Pfeifer et al., 2004. The Ba/Al values (highlighted) for the Atlantic Ocean off West Africa (0.0045) and organic rich sediment (0.0032) are closest to the global crustal average value (0.0037) after Pfeifer et al., 2004 used in this project. The 0.0045 ratio of the African sediments is closest to that of the basal Gondwanan hinterland values.

<table>
<thead>
<tr>
<th>Area/material</th>
<th>Detrital Ba/Al ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba/Al ratios abundance of aluminosilicate detritus</td>
<td>0.005 – 0.01</td>
<td>Taylor and McLennan, 1985; Taylor, 1964; Rosler and Lange, 1972</td>
</tr>
<tr>
<td>shale</td>
<td>0.0073</td>
<td>Turekian and Wedepohl, 1961</td>
</tr>
<tr>
<td>shale</td>
<td>0.006</td>
<td>Krauskopf, 1967</td>
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<tr>
<td>average post Archean shale crust</td>
<td>0.0065</td>
<td>Taylor and McLennan, 1985</td>
</tr>
<tr>
<td>crust</td>
<td>0.0052</td>
<td>Taylor, 1964</td>
</tr>
<tr>
<td>upper continental crust</td>
<td>0.0068</td>
<td>Taylor and McLennan, 1985; Wedepohl, 1995</td>
</tr>
<tr>
<td>upper continental crust</td>
<td>0.0063</td>
<td>Wedepohl, 1995</td>
</tr>
<tr>
<td>continental crust</td>
<td>0.0073</td>
<td>Dymond et al., 1992</td>
</tr>
<tr>
<td>global</td>
<td>0.0075</td>
<td>Wedepohl, 1991</td>
</tr>
<tr>
<td></td>
<td>0.0065</td>
<td>Bowen, 1979</td>
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<td></td>
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<table>
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<tr>
<th>Region</th>
<th>Detrital Ba/Al ratio (estimated)</th>
<th>Detrital Ba/Al ratio (analysed)</th>
<th>Reference</th>
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<td>Atlantic</td>
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<td></td>
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<td>northern Argentine Basin</td>
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<td></td>
<td>Pfeifer et al., 2001</td>
</tr>
<tr>
<td>Southern Argentine Basin</td>
<td>0.006</td>
<td></td>
<td>Pfeifer et al., 2001</td>
</tr>
<tr>
<td>Atlantic ocean north of 30°S</td>
<td>0.004(1)</td>
<td>0.0027[a]</td>
<td>(1) Ginge and Dahnke, 1994; (a) Pfeifer et al., 2004</td>
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<tr>
<td>Southern Ocean</td>
<td>0.0067</td>
<td></td>
<td>Nüemberg et al. 1997</td>
</tr>
<tr>
<td>Atlantic sector</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atlantic Ocean off West Africa (Gongo Fan)</td>
<td>0.0045</td>
<td></td>
<td>Rutsch et al., 1995</td>
</tr>
<tr>
<td>Eastern Mediterranean Sea: oxic sediment</td>
<td>0.003</td>
<td></td>
<td>Rutten, 2001</td>
</tr>
<tr>
<td>organic rich sediment</td>
<td>0.0032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pacific</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Northern California shelf</td>
<td>0.007</td>
<td></td>
<td>Dean et al., 1997</td>
</tr>
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<td>Chilean continental slope:</td>
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<td>27.5°S</td>
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<td>0.0051[a]</td>
<td>(2) Klump et al., 2000; (a) Pfeifer et al., 2004</td>
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<td>0.0040[a]</td>
<td></td>
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<td>35°S</td>
<td>0.0088(2)</td>
<td>0.0034[a]</td>
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<td>Indian</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Arabian Sea</td>
<td>0.0035(3)</td>
<td>0.0039[b]</td>
<td>(3) Emeis, 1993; (b) Schenau et al., 2001</td>
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</table>
Biogenic barium or $\text{Ba}_{\text{bio}}$ (also called $\text{Ba}_{\text{bio(min)}}$) & $\text{Ba}_{\text{bio(min)}}$ values calculated for the La Majua section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) $\text{Ba}_{\text{bio}} = \text{Ba}_{\text{tot}} - (\text{Al} \times \text{Ba/Al}_{\text{aluminosilicate}})$ from Pfeifer et al., 2001

2) $\text{Ba}_{\text{bio}} = \text{Ba}_{\text{tot}} - (\text{Al} \times \text{Ba/Ti}_{\text{aluminosilicate}})$ from Bonn et al., 1998

The total Ba, $\text{Ba}_{\text{bio}}$ and $\text{Ba}_{\text{bio(min)}}$ values are plotted against stratigraphy La Majua 1 being the oldest and La Majua 70 the youngest, the sampling interval was set at 25cm (the Getino Beds were sampled bed by bed). A number of ratios were selected for the aluminosilicate fraction and these were as follows:

1) $\text{Ba/Al}_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.002913

2) $\text{Ba/Al}_{\text{(min)}}$ ratio (minimum Bernesga Mb. Ba/Al ratio at the La Majua section) = 0.002169

3) $\text{Ba/Al}_{\text{aluminosilicate}}$ ratio (global ave.) = 0.0037

The global crustal average $\text{Ba/Al}_{\text{aluminosilicate}} = 0.0037$, from Pfeifer et al., 2004 & Pirrung et al., 2008 (0.007 is the most widely used global average crustal value from Pirrung et al., 2008 p. 7, original ref; Dymond et al., 1992; Nürnberg et al., 1997). I used 0.0037 as Gingele and Dahmke (1994) used 0.004 in; Pfeifer et al., 2001 (p. 5) they stated that sediments north of 30°S are prone to higher weathering conditions due to higher humidity (fits with my humidity proxies and Silurian global reconstructions), the 0.0037 ratio is lower than that of the global ave. 0.007 which means it pushes the data away from the negative values; it gives the most convincing results, Pfeifer et al., 2004. When comparing the 0.0037 ratio to the values shown in the previous tables (Pfeifer et al., 2004) it can be seen that it is closest to that of the African sediment; 0.0045 of Rutsch et al., 1995 and the organic rich sediment; 0.0032 of Rutten, 2001. The average Al/Ba ratios for the Formigoso Fm. (0.002913) are also closest to that of the organic rich sediment of Rutten, 2001.

4) $\text{Ba/Ti}_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.068156

5) $\text{Ba/Ti}_{\text{(min)}}$ ratio (minimum Bernesga Mb. Ba/Ti ratio at the La Majua section) = 0.047084

6) $\text{Ba/Ti}_{\text{aluminosilicate}}$ ratio (global ave.) = 0.126.

The global crustal average $\text{Ba/Ti}_{\text{aluminosilicate}}$ ratio (global ave.) = 0.126, used for this study from Turekian and Wedepohl, 1961 in; Bonn et al., 1998 (0.14 average upper continental crust Wedepohl, 1995 in; Pirrung et al., 2008 p.6). The $\text{Ba/Al}_{\text{(min)}}$ and $\text{Ba/Ti}_{\text{(min)}}$ values for the La Majua section were used after Babu et al., 2002 as the $\text{Ba}_{\text{bio}}$ values calculated cannot be negative. The ave. Formigoso Fm. Ba/Al and Ba/Ti ratios are too high, meaning that the calculated $\text{Ba}_{\text{bio}}$ values were
negative, when using the lowest ratios in the area (La Majua) for Ba/Al and Ba/Ti it pushes the $\text{Ba}_{\text{bio}}$ values into positive values as shown on graphs a and b. Graph c uses the global averages for Ba/Al (0.0037) and Ba/Ti (0.126) as a direct comparison.

Figure 8.6.12.5: Accumulation rates of the biogenic barium (AR $\text{Ba}_{\text{bio}}$ and AR $\text{Ba}_{\text{bio(min)}}$) expressed in g cm$^{-2}$ kyr$^{-1}$, calculated for the La Majua section using the following formulas from Pfeifer et al., 2001;

1) $\text{AR Ba}_{\text{bio}} = \text{Ba}_{\text{bio}} \times \text{MAR/100}$ (where MAR = Mass accumulation rate in g cm$^{-2}$ kyr$^{-1}$)

2) $\text{MAR} = \text{SR} \times \text{DBD}$ (where SR = sedimentation rate in cm kyr$^{-1}$ and DBD = dry bulk density in g cm$^{-3}$)

The sedimentation rate (SR) was calculated by using graptolite age constraints of the basal shales of the Formigoso Fm. and the number of samples taken. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constraints at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a timespan of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; then the 181 shale samples from the Aralla section, lower Bernesga Mb. (sampled at intervals of 25cm) can be assigned an age of ~22099yrs per sample. The first 4 meters of the Aralla section were then analysed at a higher resolution of 1cm (age representation of ~883.97yrs per reading). From this an approximate average SR of 1.11603cm kyr$^{-1}$ was calculated, howev

The dry bulk density (DBD) was estimated by taking the average shale density ranges 1.8 – 2.8 g cm$^{-3}$ (Glover, 2000). Both the lower range value and upper range DBD values were used in the calculations.

The two MAR values used;

1) 2.008854 g cm$^{-2}$ kyr$^{-1}$ (lowest range using 1.8 g cm$^{-3}$ DBD)

2) 3.124884 g cm$^{-2}$ kyr$^{-1}$ (highest range using 2.8 g cm$^{-3}$ DBD)

a) Represents the AR $\text{Ba}_{\text{bio}}$ & AR $\text{Ba}_{\text{bio(min)}}$, calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ & $\text{Ba}_{\text{bio(min)}}$ values from the previous figure (the ave. Formigoso Fm. Ba/Al ratio and lowest Ba/Al ratio from La Majua). b) The AR $\text{Ba}_{\text{bio}}$ & AR $\text{Ba}_{\text{bio(min)}}$, calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ & $\text{Ba}_{\text{bio(min)}}$ values from the previous figure (ave. Formigoso Fm. Ba/Ti ratio and lowest Ba/Ti ratio from La Majua). c) The AR $\text{Ba}_{\text{bio}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ values from the previous figure (global ave. Ba/Al ratio). d) The
AR Ba\textsubscript{bio} calculated using the upper and lower MAR values listed above and the Ba\textsubscript{bio} values from the previous figure (global ave. Ba/Ti ratio).

\textbf{Figure 8.6.12.6:} The flux of Ba to the sea floor (or F\textsubscript{Ba}) was calculated using the following formulas from Pfeifer et al., 2001 and Bonn et al., 1998 for the La Majua section;

1) \( F_{\text{Ba}} = \frac{\text{AR } \text{Ba}_{\text{bio}}}{0.209 \log(\text{MAR}) - 0.213} \) expressed in mg cm\(^{-2}\) kyr\(^{-1}\)

2) \( \%\text{Ba}_{\text{pres}} = 20.9 \log(\text{MAR}) - 21.3 \)

The amount of Ba dissolved at the sediment water interface (or F\textsubscript{Ba}) is calculated by dividing the AR Ba\textsubscript{bio} by the \( \%\text{Ba}_{\text{pres}} \) (or % of preserved Ba). a) Shows \( F_{\text{Ba}} \) and \( F_{\text{Ba(min)}} \) using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Al ave. ratio and the La Majua Ba/Al min value (calculated AR Ba\textsubscript{bio} and AR Ba\textsubscript{bio(min)} for Ba/Al ratios). b) Shows \( F_{\text{Ba}} \) and \( F_{\text{Ba(min)}} \) using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Ti ave. ratio and the La Majua Ba/Ti min value (calculated AR Ba\textsubscript{bio} and AR Ba\textsubscript{bio(min)} for Ba/Ti ratios). c) shows \( F_{\text{Ba}} \) using the previously calculated upper and lower MAR values and the global Ba/Al ave. ratio (global AR Ba\textsubscript{bio} for Ba/Al) and d) shows \( F_{\text{Ba}} \) using the upper and lower MAR values and the global Ba/Ti ave. ratio (global AR Ba\textsubscript{bio} for Ba/Ti).
Figure 8.6.12.7: The calculation of new production or \( (P_{\text{new}} \text{ and } P_{\text{new(min)}}) \) for the La Majua section following the formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) \( P_{\text{new}} = 1.95 \ (F_{\text{Ba}}) \ 1.41 \) expressed in gC m\(^{-2}\) yr\(^{-1}\)

a) Showing the \( P_{\text{new}} \) and \( P_{\text{new(min)}} \) values for the La Majua section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the Ba/Al ratios. b) Showing the \( P_{\text{new}} \) and \( P_{\text{new(min)}} \) values for the La Majua section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the Ba/Ti ratios. c) Showing the \( P_{\text{new}} \) values for the La Majua section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the global ave. Ba/Al ratio. d) Showing the \( P_{\text{new}} \) values for the La Majua section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the global ave. Ba/Ti ratio.
Figure 8.6.12.8: The calculation of primary production or palaeoproductivity (PP and PP\(_{\text{min}}\)) for the La Majua section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) \[ PP = 20 \ (P_{\text{new}}) \ 0.5 \] expressed in gC m\(^{-2}\) yr\(^{-1}\)

a) Showing the PP and PP\(_{\text{min}}\) values for the La Majua section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the Ba/Al ratios. b) Showing the PP and PP\(_{\text{min}}\) values for the La Majua section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the Ba/Ti ratios. c) Showing the PP values for the La Majua section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the global Ba/Al ratio. d) Showing the PP values for the La Majua section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the global Ba/Ti ratio.
1.7.16 3D Environmental Reconstruction Models

Figure 8.6.13.1: General 3D plots (same data shown from differing perspectives) showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. X-Ray Fluorescence (XRF) was used for the whole-rock geochemical analysis. The plots represent all sample data from the La Majua section (70 samples). Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic conditions after Fertl, 1979. There is no U within a select few of the coarser grained silt stone horizons (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales. The (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values are generally found in samples with little carbonate.
Figure 8.6.13.2: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Si/Al, showing data from the La Majua section (all 70 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents freshwater to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 'oxic', 0.46-0.60 'dysoxic', 0.54-0.82 'suboxic-anoxic' and >0.82 ' euxinic' (Hatch and Leventhal, 1992). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the silicilastic input 'detrital influx' therefore rising sea-level or basin subsidence. There is little or no Ni within a select few of the coarser grained Getino Beds (less reducing); this explains why they fall in the extreme anoxic zone (when calculating the ratio (only works if Ni is present)).

Note the how the diagrams discriminate between the clustered black shales and the Getino Beds (particularly apparent in graph C).
Figure 8.6.13.3: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Zr/Rb (contrasting grain size proxy to the previous figure Si/Al), displaying data from the La Majua section (all 70 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 'oxic', 0.46-0.60 'dysoxic', 0.54-0.82 'suboxic-anoxic' and >0.82 ‘euxinic’ (Hatch and Leventhal, 1992). The Zr/Rb ratio is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence. There is little or no Ni within a select few of the coarser grained Getino Beds (less reducing); this explains why they fall in the extreme anoxic zone (when calculating the ratio (only works if Ni is present)).

Note the how the diagrams discriminate between the clustered black shales and the Getino Beds (particularly apparent in graph C).
Figure 8.6.13.4: Geochemical environmental reconstruction, using the ratios Rb/K, Th/U and Si/Al, displaying data from the La Majua section (all 70 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic (Fertl, 1979). There is no U within a select few of the coarser grained silt stone horizons (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.

Note the how the diagrams discriminate between the clustered black shales and the Getino Beds (particularly apparent in graph C).
1.7.17 Cyclicity

Figure 8.6.14.1: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the La Majua section, 39 samples (La Majua 32 – La Majua 70). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the U ppm values from the base (sample No. 1) to the middle (sample No. 39) of the lower member, cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

Frequencies (plots c and d, above) | Calculations of periodicity | Cyclicity values
--- | --- | ---
0.039474 (highest intensity) = 1/(0.039474/22099 yrs) | 559.83 Kyr
0.068816 = 1/(0.068816/22099 yrs) | 248.81 Kyr
0.125 = 1/(0.125/22099 yrs) | 176.79 Kyr
0.18092 = 1/(0.18092/22099 yrs) | 122.14 Kyr
0.21382 = 1/(0.21382/22099 yrs) | 103.35 Kyr
0.30592 = 1/(0.30592/22099 yrs) | 72.23 Kyr
0.36184 = 1/(0.36184/22099 yrs) | 61.07 Kyr
0.39474 = 1/(0.39474/22099 yrs) | 55.98 Kyr
0.45066 = 1/(0.45066/22099 yrs) | 49.03 Kyr

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the La Majua section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.6.14.2: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the La Majua section, 39 samples (La Majua 32 – La Majua 70). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) to the middle (sample No. 39) of the lower member, cyclicity is apparent in the V values. b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.026316 (highest intensity)</td>
<td>1/(0.026316/22099 yrs)</td>
<td>839.75 Kyr</td>
</tr>
<tr>
<td>0.13816</td>
<td>1/(0.13816/22099 yrs)</td>
<td>159.95 Kyr</td>
</tr>
<tr>
<td>0.19079</td>
<td>1/(0.19079/22099 yrs)</td>
<td>115.82 Kyr</td>
</tr>
<tr>
<td>0.22697</td>
<td>1/(0.22697/22099 yrs)</td>
<td>97.36 Kyr</td>
</tr>
<tr>
<td>0.33553</td>
<td>1/(0.33553/22099 yrs)</td>
<td>65.86 Kyr</td>
</tr>
<tr>
<td>0.41776</td>
<td>1/(0.41776/22099 yrs)</td>
<td>52.89 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the La Majua section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
1.7 Sena de Luna Section

The following section documents the geochemical results for the Sena de Luna section. The Sena de Luna section consists of 79 samples. The sampling interval within the Getino Beds was at a bed by bed scale, the lower most Formigoso Fm. (Bernesga Mb.) was sampled every 25cm. The analysis numbers for the Sena de Luna section are displayed in the table below (Table 8.3.1); please also refer to the Sena de Luna sedimentary log section (showing the sample location in regards to the log section) in the Results Chapter. and the results tables in Appendix B part 2

<table>
<thead>
<tr>
<th>Sena de Luna</th>
<th>Analysis Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sena 1</td>
<td>Barrios Fm. (upper) - at contact with Getino Bed</td>
</tr>
<tr>
<td>Sena 2-10</td>
<td>Getino Beds (bed by bed sampled)</td>
</tr>
<tr>
<td>Sena 11-47</td>
<td>Lower Formigoso Fm. (Bernesga Member)</td>
</tr>
<tr>
<td></td>
<td>after Sena 47 – 2m gap in the section</td>
</tr>
<tr>
<td>Sena 8-79</td>
<td>Lower Formigoso Fm. (Bernesga Member)</td>
</tr>
</tbody>
</table>

Table 8.3.1 – The corresponding sample numbers for the Sena de Luna section; also refer to the sedimentary log for the Sena de Luna section in the Results Chapter.
1.7.1 Major Elements

Figure 8.7.1.1: All major element variation curves for the Sena de Luna section. Each sample number represents a 25cm interval (other than the Getino Beds; bed by bed scale). The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
1.7.2 Trace Elements

Figure 8.7.2.1: Trace element variation curves for the Sena de Luna section. Each sample number represents a 25cm interval (other than the Getino Beds; bed by bed scale). The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
Figure 8.7.2: Trace element variation curves for the Sena de Luna section. Each sample number represents a 25cm interval (other than the Getino Beds; bed by bed scale). The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
Figure 8.7.2.3: Trace element variation curves for the Sena de Luna section. Each sample number represents a 25cm interval (other than the Getino Beds; bed by bed scale). The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
Figure 8.7.2.4: Trace element variation curves for the Sena de Luna section. Each sample number represents a 25cm interval (other than the Getino Beds; bed by bed scale). The coloured regions indicate the differing lithologies (starting with the Barrios Fm. + Getino Beds (yellow) followed by the Bernesga Mb. of the Formigoso Fm. (Grey).
1.7.3  **Elemental cross-plots**

![Cross-plots](image)

**Figure 8.7.3.1:** Showing the cross-plots of Al₂O₃ to; K₂O, TiO₂, MgO, Rb, Cr and Zr for the Sena de Luna section (79 samples). All show positive correlations except for Zr, a negative correlation in the basal organically enriched shales (the lower the enrichment of Zr (detrital influx) the higher the Al₂O₃ concentrations).

![Cross-plots](image)

**Figure 8.7.3.2:** Cross-plots of Al₂O₃ vs. SiO₂/Al₂O₃, Fe₂O₃/Al₂O₃ and K₂O/Al₂O₃ for the Sena de Luna section (79 samples), all showing negative correlations indicating the presence of clay minerals. The SiO₂/Al₂O₃ cross plot indicates the maturity of the shales.
Figure 8.7.3.3: Showing the geochemical ratios of Cr/V and Ni for the Sena de Luna section (79 samples). The ratios can be compared between localities to determine environment differences/changes laterally (redox states, redox sensitive elements). Plots a + b display the ratios plotted against stratigraphy. Cr, Ni and V are redox sensitive elements. Hence the enrichment shown in the V vs. Cr cross plot towards the organically enriched anoxic shales. The V vs. Cr cross plot shows a strong positive correlation (the higher the V values the higher the Cr values).

Figure 8.7.3.4: Showing grain size (SiO2/Al2O3 and Rb/K2O) and redox state (Cu/Zn) for the Sena de Luna section (79 samples), indicating the maturity of the Formigoso Fm., the lower the silica content, smaller the grain size.
Figure 8.7.3.5: Harker type major element variation diagrams for the Sena de Luna section (79 samples). The CaO readings were just above the detection limit.
Figure 8.7.3.6: Cross plots of $\text{Al}_2\text{O}_3$, $\text{U}$, $\text{Th}$, $\text{Cs}$ and $\text{Ba}$ vs. $\text{K}_2\text{O}$ for the Sena de Luna section (79 samples), all showing positive correlations. The $\text{U}$ cross plot showing the organically enriched basal shales, the higher the $\text{U}$ content, the higher the total organic carbon (TOC), using $\text{U}$ as a proxy for organic content and redox indicator.

Figure 8.7.3.7: $\text{MgO}$ cross plots of $\text{Fe}_2\text{O}_3$, $\text{MnO}$, ($\text{Cr}+\text{Ni}$) and $\text{V}$ for the Sena de Luna section (79 samples), all showing positive correlations.
Figure 8.7.3.8: Showing Cr/Rb, V/Rb, Th/U, Ba/Rb and Zr/Rb ratios for the Sena de Luna section (79 samples). The values are normalised to Rb as it is inert with respect to biogenic processes unlike Al$_2$O$_3$ and SiO$_2$. The Th/U ratio can be used as a redox proxy.
Figure 8.7.3.9: TOC cross-plots for the Sena de Luna section (all 79 samples); trace elements of ‘strong euxinic affinity’ (Algeo & Maynard, 2004) a) U, b) V, c) Zn and d) Pb all of the trace elements are Al normalized (x10^4). Trace elements of ‘weak euxinic affinity’ e) Cu, f) Ni and g) Cr again all Al normalized (x10^4).
Figure 8.7.3.10: Selected major element vs. Al$_2$O$_3$ variation diagrams for the Sena de Luna section (a + b), displaying all 79 samples. The ranges of K$_2$O/Al$_2$O$_3$ ratios in K-feldspars and clays (plot (b)) after Cox et al., 1995. Selected trace element vs. Al$_2$O$_3$ variation diagrams (c-e).

f) Th vs. Th/U plot (McLennan et al., 1993) for the Sena de Luna samples (all 79 samples). Dashed lines: Th/U ratio and Th content of UCC; circle: PAAS (Taylor and McLennan, 1985); fields for depleted mantle sources and Australian shales (AS) from McLennan et al., 1993. Arrows indicate direction of trends for weathering (U loss) and enrichment (U gain).

g+h) Zr/Sc vs. Th/Sc plots (McLennan et al., 1993) for (a) The Sena de Luna section (all 79 samples); (b) modern muds from trailing edge (TE, passive margin), continental arc (CA), and forearc (FA) settings (data from McLennan et al., 1990). Solid line connecting stars B (basalt) and F (felsic volcanic rock), illustrates the trend expected in first-cycle sediments due to magmatic evolution from mafic to felsic end members; star G is the average granite (Condie, 1993). UCC and PAAS from Taylor and McLennan (1985), the arrow illustrates the trend produced by zircon concentration during sedimentary sorting and recycling.
Figure 8.7.3.11: Geochemical plots for the Sena de Luna section (all 79 samples utilised). a) Showing $V/(V+Ni)$ vs. TOC; the higher the TOC values the lower the sedimentation rate ($V/(V+Ni)$ values have to be above 0.5 in order for the organic carbon to be preserved (not oxidised, Rimmer, 2004), the sedimentation rate indicator taken (Arthur & Sagemann, 1994). b) Represents the TOC values vs. stratigraphy (every data point is equivalent to 25cm (other than the Getino Beds; bed by bed). b,c & d) the selected geochemical indices for the Sena de Luna section (all 79 samples).
Figure 8.7.3.12: Utilising all geochemical data from the Sena de Luna section (all 79 samples). a) shows Zr/Ti ratios used as a provenance proxy; high Zr/Ti ratios point towards granitic rocks (G1 granite: Zr/Ti is 0.14) or clastic sediments (average phanerozoic quartz arenite: Zr/Ti is 0.13; Boryta and Condie, 1990). Lower Zr/Ti ratios around 0.067 represent the composition of the average upper crust (Taylor and McLennan, 1985). The ‘North American shale composite’ (NASC) has a Zr/Ti ratio of 0.043. Lower Zr/Ti ratios are indicative of basic igneous rocks; Andean volcanic rocks yield Zr/Ti ratios between 0.024 for basalts and 0.034 for andesites (Ewart, 1982). Lowest Zr/Ti ratios around 0.01 represent primitive magmas of OIB’s and MORB’s (Bonn, 2004). b) Signifies palaeosalinity (using Rb/K ratios), the dashed line values were taken from Campbell & Williams, 1965. c-f) palaeo-redox indicators; the ratio lines are documented in the table. g) Th/U Ratios for Sena de Luna, any value <2 implies anoxic (Fertl, 1979), organically rich black shale genesis.
Figure 8.7.3.13: Geochemical data representative of the Sena de Luna section (all 79 samples) a) V/Al vs. stratigraphy and b) correlation of V with TOC.

Figure 8.7.3.14: Geochemical data from the Sena de Luna section (all 79 samples). a) Scatter plot showing heavy mineral indicating element vs. major component. b) TOC values vs. stratigraphy. c + d) Fe$_2$O$_3$ vs. stratigraphy and Fe$_2$O$_3$/Al$_2$O$_3$ (normalised with Al) vs. stratigraphy. e + f) V and Zn vs. TOC.
Figure 8.7.3.15: All data from the Sena de Luna section (79 samples); a) SiO$_2$ vs. Al$_2$O$_3$ concentrations are plotted relative to the idealized composition of the observed minerals. The majority of the variation in composition may be related to variations in quartz and clay minerals-muscovite (Cullers & Podkovyrov, 2000). b) Fe$_2$O$_3$ total vs. Al$_2$O$_3$ concentrations plotted relative to the composition of the observed minerals, again much of the variation in composition may be accounted for by variations in quartz and clay minerals-muscovite.

Figure 8.7.3.16: Representing all data from the Sena de Luna section (79 samples). Redox sensitive elements (V and Cr) showing positive correlations with TOC values; a) Cr (ppm) vs. TOC, b) V (ppm) vs. TOC, c) Cr (wt %) vs. TOC and d) V (wt %) vs. TOC.
Figure 8.7.3.17: Representing all data from the Sena de Luna section (79 samples). Al₂O₃ bivariate diagrams of major element composition along with estimated elemental mineral compositions (Descourvieres et al., 2011).
Figure 8.7.3.18: Cross-plots showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. The plots represent sample data from the Sena de Luna section (all 79 samples). Th/U is used as a redox indicator; the dashed black line representing a Th/U ratio of 2, less than 2 indicates anoxic after Fertl, 1979. Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction); high values reflect course grained units, lower values in clay stones and shales. (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values found in samples with little carbonate.

Figure 8.7.3.19: Cross-plot of Ni vs. Cr representing all data from the Sena de Luna section (79 samples).
Figure 8.7.3.20: Representing all data from the Sena de Luna section (79 samples). The ratios Ni/V and V/Cr (Jones and Manning, 1994) are redox indicators.

Figure 8.7.3.21: Geochemical data from the Sena de Luna section (all 79 samples). Selected elements and ratios plotted vs. Stratigraphy.

Figure 8.7.3.22: Representing the relationship between Al₂O₃ and Ba for all Sena de Luna data (79 samples).
Figure 8.7.3.23: Representing all data from the Sena de Luna section (79 samples). a) Plot of U/Pb ratios vs. U concentrations (ppm). Samples generally reflect elevated U concentrations relative to North American Shale Composite (Condie, 1993). b) TOC (wt.%) vs. U concentrations (ppm). The U content of NASC is plotted for reference (samples are enriched in U relative to the NASC composite). U and TOC exhibit a perfect correlation as TOC values were generated using the U (ppm) values as a proxy, from Fertl & Chillingar (1988).

Figure 8.7.3.24: All diagrams represent the data from the Sena de Luna section (79 samples). a) Th vs. Sc (in log scale) and b) Th vs. U diagrams (McLennan et al., 1990, and Luchi et al., 2003). c) Fe₂O₃/K₂O vs. SiO₂/Al₂O₃ d) log SiO₂/Al₂O₃ vs. log (Fe₂O₃/K₂O) of Herron (1986). e) Th/Sc vs. Zr/Sc (log scale) diagram after McLennan et al., (1993), reflecting reworking through Zr/Sc and upper crust felsic input through Th/Sc. Numbers identify the mean values for 1, OIA, 2, CIA, 3, ACM and 4, PM following Bathia and Crook (1986). f) TiO₂ vs. Ni, fields for acidic and basic source materials after Floyd et al., (1989).
Figure 8.7.3.25: Displaying all data from the Sena de Luna section (79 samples). Th/Sc vs. Zr/Sc plot (Mongelli et al., 2006), the samples depart from the compositional trend, indicating zircon addition suggestive of a recycling effect.

Figure 8.7.3.26: Representing all data from the Sena de Luna section (79 samples). Zr vs. SiO₂, a positive relationship is apparent, indication that the Zr is indeed associated with the Quartz (heavy fraction).
Figure 8.7.3.27: TiO$_2$ vs. Ni bivariate plot for shale samples from the Sena de Luna section (all 79 samples), fields after Floyd et al., 1989.

Figure 8.7.3.28: Representing all data from the Sena de Luna section (79 samples). The trace elements are normalised to Al and then multiplied by $10^{-4}$. As, Cr, Cu, Ni, V, Zn vs. Stratigraphy.
Figure 8.7.3.29: Geochemical classification (Pearce et al. 2010) based on the criteria listed in Table b (above) for the Sena de Luna dataset (all 79 samples). The geochemical classification values (y-axis of plot a) reflect the following: Score of 4 = floodplain mudstone, Score of 7 = brackish water or lacustrine, Score of 10 = marginal marine mudstone, Score of 13 or 16 = marine mudstone (= marine band). If a sample has a very high Zr/U value (above 65), it is presumed to contain abundant heavy minerals and is awarded a final score of 2. If a sample comes from a coal, it is awarded a default score of 0 (Pearce et al., 2010).

Mo and P₂O₅ values for the Sena de Luna section are near/below detection limits.

Based on the criteria above the depositional environment of the Formigoso Fm. at the Sena de Luna section is classified as borderline; brackish water or Lacustrine - marginal marine mudstone (which fits with the Rb/K ratios for palaeosalinity).
Figure 8.7.3.30: Representing all data from the Sena de Luna section (79 samples). A) SiO$_2$/Al$_2$O$_3$ vs. TOC and B) Zr/Rb vs. TOC. The SiO$_2$/Al$_2$O$_3$ and Zr/Rb ratios are renowned grain size proxies, plotted against TOC (Total Organic Carbon) values. The zones for hydrocarbon potential (TOC cut off values) based on Bordenave et al., (1993). The TOC values for the basal shales act independently of the grain size values, the grain size remains consistent yet the TOC levels vary; this is most likely due to changes in the redox state.
Figure 8.7.3.31(a): Plots representing data from the Sena de Luna section (all 79 samples), showing the relationship between $\text{Al}_2\text{O}_3$, selected trace elements and $\text{Fe}_2\text{O}_3$. The plots show the relationship between the Cantabrian formations (predominantly the Formigoso Fm.) trace element:$\text{Al}_2\text{O}_3$ ratios and the World Shale Average (WSA, plotted as star, taken from Gromet et al., 1984), the $\text{Zr}$ vs. $\text{Al}_2\text{O}_3$ also includes the Upper Crust (UC) and North American Shale Composite (NASC) (Piper & Calvert, 2009).
Figure 8.7.3.31(b): Plots representing data from the Sena de Luna section (all 79 samples). The plots show the relationship between various trace elements within the Cantabrian formations (predominantly the Formigoso Fm.).

Figure 8.7.3.32: Representing data from the Sena de Luna section (all 79 samples). a) Chemical classification, after Herron, 1986. b) Plot of discriminant functions 1 and 2 for shales (after Roser and Korsch (1988). Discriminant function 1 = \((-1.773 \times TiO_2\%\) + \((0.607 \times Al_2O_3\%\) + \((0.76 \times Fe_2O_3\%\) + \((-1.5 \times MgO\%) + \((0.616 \times CaO\%) + \((0.509 \times Na_2O\%) + \((-1.22 \times K_2O\%\) + \((-9.09). Discriminant function 2 = \((0.445 \times TiO_2\%) + \((0.07 \times Al_2O_3\%\) + \((-0.25 \times Fe_2O_3\%) + \((-1.142 \times MgO\%) + \((0.432 \times Na_2O\%) + \((1.426 \times K_2O\%) + \((-6.861). Provenance fields are after Roser and Korsch (1988). P1 = mafic and lesser intermediate igneous provenance; P2 = intermediate igneous provenance; P3 = felsic igneous provenance and P4 = recycled-mature polycyclic quartzose detritus. c) Distribution of K and Rb relative to a K/Rb ratio of 230 (= main trend of Shaw, 1988).
Figure 8.7.3.33: Representing all Zr vs. Cr data from the Sena de Luna section (79 samples). Variations in the Zr and Cr values are likely to reflect changes in the sediment provenance.

Figure 8.7.3.34: Cross plot of Mo and TOC values from the Sena de Luna section (all 79 samples). Evidently the Mo (ppm) concentrations are near/below the detection limit.
Figure 8.7.3.35: Representing data from the Sena de Luna section (all 79 samples). a) V/Cr used as a palaeoredox proxy. b) V/Cr ratio vs. TOC. c) Mo/Al ratio vs. TOC (Mo values are near/below the detection limit).

Figure 8.3.7.36: Representing all data from the Sena de Luna section (79 samples). a + b) plots of the detrital parameter Th vs. Zr and Th vs. Ti. c + d) Cross plots of Th as detrital monitor vs. authigenic uranium (U-aut) and V (ppm).
Figure 8.3.7.37: Representing all data from the Sena de Luna section (79 samples). a) Scatter plot of V/(V + Ni) vs. degree of pyritization (DOP), displaying average shale (Turekian & Wedephol, 1961) and average continental crust. b) DOP vs. stratigraphy; the lines representing DOP values are from Wignall, 1994. c) Represents an idealized plot of a uniform DOP with increasing TOC, (a+c).

Figure 8.3.7.38: Displaying all data from the Sena de Luna section (79 samples), provenance and source signature diagrams. a) Th vs. Sc. Th is an incompatible element that is enriched in silicic rocks, and Sc is a compatible element that is enriched in mafic rocks. Th/Sc ratios near unity represent the upper continental crust (UC) the Th/Sc ratios near 0.6 suggest a more mafic component, (Totten et al., 2000). b) Th/Sc vs. Cr/Th the samples lie upon a curve consistent with mixing of a continental source enriched in incompatible elements (Th) and a more mafic source enriched in compatible elements (Cr, Sc). The values for UC, Granites and mid-oceanic-ridge-basalts (MORB) are given for comparison, (Totten et al., 2000). c) Th vs. Sc relation and d) Th/Sc vs. Cr/Th.
Figure 8.3.7.39: Representing all data from the Sena de Luna section (79 samples). MgO/Al₂O₃ vs. K₂O/Al₂O₃ cross plot including the fields of kaolinite, illite/K-feldspar and chlorite (clay typing) (Turgeon + Brumsack, 2006).
Figure 8.3.7.40: Representing all data from the Sena de Luna section (79 samples). Diagrams used for discriminating the differing lithologies (Getino Beds and basal shales; Bernesga Mb.).

Figure 8.3.7.41: Showing all data from the Sena de Luna section (all 79 samples). a) cross-plot of SiO₂ vs. Al₂O₃ shows an enrichment of SiO₂ over Al₂O₃ in comparison to the World Average Shale (WSA) of Turekian & Wedepohl, 1961. b + c) TOC vs. Al₂O₃ and SiO₂, showing that the TOC values vary as the Al₂O₃/SiO₂ content remain consistent.
Figure 8.3.7.42: Representing all data from the Sena de Luna section (79 samples). Plot of total organic carbon (TOC wt.%) against authigenic uranium content (U_{auth}). The correlation between TOC and total U would be 1:1 as the TOC values have been generated by using U as a proxy. Yet the U_{auth} values use Th values in order to correct for detrital uranium.

Figure 8.3.7.43: Representing all data from the Sena de Luna section (79 samples). Elemental Sr/Al, Mn/Al, Si/Al, Ba/Al, Zr/Al ratios plotted against TOC and stratigraphy.
1.7.4 Na$_2$O plots

**Figure 8.7.4.1:** Displaying data from the Sena de Luna section (all 79 samples). a) Provenance discrimination diagram for shales (after Roser and Korsch, 1988). Discriminant Discriminant function 1 = $(-1.773 \times \text{TiO}_2\% + (0.607 \times \text{Al}_2\text{O}_3\% + (0.76 \times \text{Fe}_2\text{O}_3\% + (-1.5 \times \text{MgO}\% + (0.616 \times \text{CaO}\% + (0.509 \times \text{Na}_2\text{O}\% + (-1.22 \times \text{K}_2\text{O}\% + (-9.09). Discriminant function 2 = (0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\% + (-1.142 \times \text{MgO}\% + (0.432 \times \text{Na}_2\text{O}\% + (1.426 \times \text{K}_2\text{O}\% + (-6.861). b) Bivariate SiO$_2$ wt.% vs. (Al$_2$O$_3$+K$_2$O+Na$_2$O) wt.% palaeoclimate discrimination diagram, fields after Suttner and Dutta (1986). c) SiO$_2$/Al$_2$O$_3$ vs. K$_2$O/Na$_2$O after Kampunzu et al., 2005. d) Discriminant function diagram after Roser and Korsch (1988); Discriminant function I = $(-1.773 \times \text{TiO}_2\% + (0.607 \times \text{Al}_2\text{O}_3\% + (0.76 \times \text{Fe}_2\text{O}_3\% + (-1.5 \times \text{MgO}\% + (0.616 \times \text{CaO}\% + (0.509 \times \text{Na}_2\text{O}\% + (-1.22 \times \text{K}_2\text{O}\% + (-9.09)$. Discriminant function II = (0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\% + (-1.142 \times \text{MgO}\% + (0.438 \times \text{CaO}\% + (1.475 \times \text{Na}_2\text{O}\% + (1.426 \times \text{K}_2\text{O}\% + (-6.861). e) Akul'shina (1976) + Kiipli et al., (2012): Al/Ti ratio and climate: Al$_2$O$_3$/TiO$_2$ <20 for humid, 20–30 for semi-humid and semi-arid, and >30 for arid climate.
1.7.5 **Histograms (major elements & redox ratios)**

**Figure 8.7.5.1:** Histograms and cumulative frequency representing the major oxides a) SiO$_2$ values b) Al$_2$O$_3$ values c) K$_2$O values and d) TiO$_2$ values, using all sample data (79 samples) from the Sena de Luna section. Wt% vs. frequency for the histograms and cumulative frequency for the curve.

**Figure 8.7.5.2:** Histograms and cumulative frequency curves representing all sample data for the Sena de Luna section. a) Showing the calculated degree of pyritization (DOP); A = Anaerobic (0-0.4); R = Restricted (0.45-0.75); I = Inhospitable (0.55-1) ranges from Raiswell et al., 1988. b + c) palaeo-redox proxies V/(V + Ni) and V/Cr. Ranges for inferred bottom-water conditions for V/Cr, <2 oxic, 2-4.25 dysoxic, >4.25 suboxic-anoxic from Jones and Manning (1994); ranges for V/(V + Ni), <0.46 oxic, 0.46-0.6 dysoxic, 0.54-0.82, suboxic-anoxic, >0.84 euxinic are from Hatch and Leventhal (1992).
1.7.6 K, Th and U bubble plots

Figure 8.7.6.1: Bubbles plots of K$_2$O, Th and U for the Sena de Luna section. a) Representing all the sample data from the Sena de Luna section (79 samples), b) Showing just the basal shales (Bernesga Mb., (68 samples) of the Formigoso Fm.). The K$_2$O, Th and U contents were analysed by X-Ray Fluorescence (XRF) whole rock analysis, the bubble size is proportional to U content.
1.7.7 Ternary diagrams

The symbols for the differing lithologies within the ternary plots remain consistent throughout all ternary diagrams; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). For the expanded plots the key is given alongside each figure.

Figure 8.7.7.1: Ternary diagram showing relative proportions of major shale/mud rock components; SiO$_2$ (quartz), Al$_2$O$_3$ (clays) and CaO (carbonates), displaying data from the Sena de Luna section (all 79 samples). The Key for the expanded plot is shown to the left of the figure, the key for the inset ternary (top right); square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the ‘Average shale’ also shown as star (after Wedepohl, 1971).
Figure 8.7.7.2: Sena de Luna section (all 79 samples) ternary 10Al$_2$O$_3$ - 200TiO$_2$ - Zr plot (Mongelli et al., 2006) showing possible sorting effects, the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).

Figure 8.7.7.3: Sena de Luna section (all 79 samples) ternary 15Al$_2$O$_3$ - 300TiO$_2$ - Zr (Mongelli et al., 2006) plot showing possible sorting effects, the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).
Figure 8.7.7.4: TOC–S–Fe relationships for the Sena de Luna section (all 79 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.7.7.5: TOC–TS10–Fe ternary diagram for the Sena de Luna samples (all 79). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The construction and principles of the diagram based on Dean and Arthur (1989) and Arthur and Sageman (1994).
Figure 8.7.7.6: Degree of pyritization of sediments from the Sena de Luna section (all 79 samples) in the Fe(x) - total organic carbon (TOC) - S2 (following stoichiometry of pyrite-FeS$_2$) system (relative weight ratios). Reactive Fe (Fe(x)) is calculated with Fe(x) = Fe – 0.25 × Al (Mosher et al., 2006). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.7.7.7: Al–Mg–Ca diagram showing the distribution of the Getino Beds and basal shales of the Formigoso Fm. at Sena de Luna (all 79 samples). Inset ternary (top left); the square represents the Barrios Fm., the triangles - Getino Beds,
diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the domains of evaporites and meta-evaporites, and of platformal marls and shales are from Moine et al., (1981). The key for the expanded plot is towards the right of the figure.

**Figure 8.7.7.8:** The ternary diagrams top right (inset); (A) Ternary plot of \((\text{Cu}+\text{Co}+\text{Ni})\times10 – \text{Fe} – \text{Mn}\) (Bonatti et al., 1976 and Mohapatra 2009) showing various generic fields, displaying all data (79 samples) from the Sena de Luna section, (B) Chemical composition of the formations at the Sena de Luna section (all 79 samples) in terms of components \(\text{Fe} – \text{Mn} – \text{Al+Si}\). The arrow indicates the decreasing clastic input. The key for the expanded plots is found towards the upper left of the figure.
Figure 8.7.7.9: Th - (Cr + Ti)/1000 - Zr/10 ternary (Hessler & Donald, 2006) plot showing all 79 samples from the Sena de Luna section, a clear differentiation between the Getino Beds and the basal shales (Bernesga Mb.). The key for the upper left ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.7.7.10: Al2O3, MgO and Fe2O3 ternary plot representing data from the Sena de Luna section (all 79 samples). There are two differing trends between the Getino Beds and the basal shales (Bernesga Mb.), possibly a result of differing provenance sources or maybe just a grain size effect. The key for the upper left ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.7.7.11: Al₂O₃, MgO * 10 and Fe₂O₃ - (expanded plot of previous (Figure 8.7.7.10)) representing data from the Sena de Luna section (all 79 samples). Two differing trends seen, possibly resulting from differing provenance sources or maybe just a grain size effect. The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.7.7.12: Fe₂O₃, Al₂O₃ and MnO ternary plot; represents data from the Sena de Luna section (all 79 samples). The key for the upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key for the expanded plot is seen towards the left of the figure.
**Figure 8.7.7.13:** Distribution of Fe$_2$O$_3$, Al$_2$O$_3$ and SiO$_2$ within the Sena de Luna section (79 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), compared with several ideal clay minerals, including chamosite (Chm), berthierine (Ber) thin/long rectangle to represent variable compositions, kaolin and muscovite (Ka/Mu), nontronite (Non), illite thick/long rectangle and glauconite (Gla) (Konhauser et al., 1998, Konhauser & Urrutia, 1999 and Eickmann et al., 2009). The key for the expanded plot is seen towards the left of the figure.

**Figure 8.7.7.14:** Distribution of K$_2$O, Al$_2$O$_3$ and SiO$_2$ (Konhauser et al., 1998 & 1999) from the Sena de Luna section (all 79 samples analysed). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), compared to several ideal clay minerals, including, kaolin (Ka), muscovite (Mu), illite (ill) long rectangle (representing varying compositions) and glauconite (Gla) are labelled. The key for the expanded plot is seen towards the left of the figure.
Figure 8.7.7.15: Th, As/10 and U ternary plot, representing data from the Sena de Luna section (all 79 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). There is a clear deference between the Getino Beds and the basal shales of the Bernesga Mb., the sands/silts are depleted in U.

Figure 8.7.7.16: Major geochemical components Al$_2$O$_3$ x 5 - SiO$_2$ - CaO x 2 (relative weight ratios) (Hetzel et al., 2011) for the Sena de Luna section (All 79 samples). The upper right ternary; the square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), data points for average shale (Wedepohl, 1971, 1991), kaolinite and K-feldspar are shown for comparison.
Figure 8.7.7.17: Ternary plot for Fe$_2$O$_3$, K$_2$O and Al$_2$O$_3$, showing all samples from the Sena de Luna section (79 samples). The upper right ternary; square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the key towards the left of the figure is for the exploded diagram. The shales cluster away from the Getino Beds, a clear maturity trend towards the Barrios Fm. is also evident.

Figure 8.7.7.18: Ternary plot for SiO$_2$/Al$_2$O$_3$, TiO$_2$ and MgO, expressing all samples from the Sena de Luna section (79 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the shales cluster away from Getino Beds.
Figure 8.7.7.19: Ternary plot for U*20, Zr and Sr, expressing all samples from the Sena de Luna section (79 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The shales (enriched in Sr and U) cluster away from the Getino Beds that plot towards the heavy element Zr.

Figure 8.7.7.20: Ternary plot for K₂O, Th and U, showing all samples from the Sena de Luna section (79 samples). The ternary plot (upper right); square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key is valid for the exploded diagram. The shales (depleted in K₂O (feldspar fragments)) in relation to the Getino Beds, cluster away. Note that either side of the diagram the shales appear highly enriched in U and the sands opposite show U depletion.
Figure 8.7.7.21: Ternary plot representing all data for the Sena de Luna section (79 samples) showing the relationship between K2O*5, Th and U as previously (Figure 8.6.7.20) yet a higher factor for K values. The Majority of the Getino Beds cluster towards the K2O enrichment, K2O resides mostly within the detrital faction.

Figure 8.7.7.22: Ternary plot representing all data for the Sena de Luna section (79 samples) showing the relationship between the heavy elements; Zr, Cr and Ni. The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The sands of the Getino Beds cluster towards Zr.
Figure 8.7.7.23: Ternary plot representing samples from the Sena de Luna section (all 79). Cross-plot constructed to characterise between the Shales (differing subunits?) and the Getino Beds, clearly geochemically separated.

Figure 8.7.7.24: Ternary diagram Fe₂O₃ – MgO – SiO₂/Al₂O₃ representing data from the Sena de Luna section (all 79 samples). The upper right ternary; square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The expanded plot clearly discriminates between the Getino Beds and the shales of the Bernesga Mb.
Figure 8.7.7.25: CIA ternary diagram, $\text{Al}_2\text{O}_3 \text{– CaO + Na}_2\text{O} \text{– K}_2\text{O}$ (after Nesbitt and Young, 1982), displaying data from the Sena de Luna section (all 79 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.7.7.26: $\text{Al}_2\text{O}_3 \text{– (CaO +Na}_2\text{O+K}_2\text{O) – (Fe}_2\text{O}_3 \text{+ MgO)}$ ternary diagram after Hayashi et al., 1997, representing data from the Sena de Luna section (all 79 samples). The square represents the Barrios Fm., the triangles - Getino Beds, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
1.7.8 **Index of Compositional Variation (ICV)**

**Figure 8.7.8.1:** a) $K_2O/Al_2O_3$ ratio for the Sena de Luna section (in order to discriminate K-feldspars and clay minerals). The stars represent values for specific minerals indicated, data from Deer *et al.*, 1966, overlay from Cox, 1995. b) expanded plot of the original (a). c) Index of Compositional Variation (ICV); $(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3$ for the Sena de Luna section, the stars represent values for specific minerals indicated, the arrows show the range of values for the particular mineral group, data from Deer *et al.*, 1966, overlay from Cox, 1995. d) Expanded plot of the original ‘c’), possible cyclicity apparent within the ICV values.

$K_2O/Al_2O_3$ - range of Bernesga Mb. (shales) at Sena de Luna: 0.1085-0.1915

$K_2O/Al_2O_3$ - range of Getino Beds at Sena de Luna: 0.2016-0.2651

$K_2O/Al_2O_3$ - average of Bernesga Mb. (shales) at Sena de Luna: 0.1410

$K_2O/Al_2O_3$ - average of Getino Beds at Sena de Luna: 0.2276

ICV - range of Bernesga Mb. (shales) at Sena de Luna: 0.3517-0.5616 (0.6552 with Fe spike)

ICV - range of Getino Beds at Sena de Luna: 0.7093-2.6287

ICV - average of Bernesga Mb. (shales) at Sena de Luna: 0.4299

ICV - average of Getino Beds at Sena de Luna: 1.4683
Chemical Index of Alteration (CIA), PIA & CIW

Figure 8.7.9.1: Representing data from the Sena de Luna section (all 79 samples). The ‘Chemical Index of Alteration’ (CIA) (Nesbitt and Young, 1982, Taylor and McLennan, 1985) is a well-established parameter for determining the degree of weathering and is the most accepted of the available weathering indices (Bahlburg & Dobrzinski, 2009). During the degradation of feldspars, Ca, Na, and K are removed and clay minerals with a higher fraction of Al are formed. The CIA is estimated from the proportion of Al₂O₃ vs. the weathering-prone oxides (after Mosher et al., 2006). This index measures the degree of feldspar decomposition to secondary clay products, where CIA values of about 50 indicate fresh bedrock (no chemical weathering), and values of 75-100 indicate complete conversion of feldspars to aluminous clay minerals (intense chemical weathering; see Fedo et al., 1995):

\[ \text{CIA} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \times 100 \]

A) Kaolinite has a CIA value of 100 and represents the highest degree of weathering. Illite is between 75 and c. 90, muscovite at 75, the feldspars at 50. Fresh basalts have values between 30 and 45, fresh granites and granodiorites of 45 to 55 (Nesbitt and Young, 1982; Fedo et al., 1995), after Bahlburg, 2009. B) Expanded plot, focusing within the Illite Zone (muscovite line also shown).

The average CIA value for the Bernesga Mb. (black shales) at Sena de Luna: 84.07
Figure 8.7.9.2: Representing all data from the Sena de Luna section (79 samples), the ‘Plagioclase Index of Alteration’ (PIA; Fedo et al., 1995).

\[
\text{PIA} = \left(\frac{\text{Al}_2\text{O}_3 - \text{K}_2\text{O}}{((\text{Al}_2\text{O}_3 - \text{K}_2\text{O}) + \text{CaO} + \text{Na}_2\text{O})}\right) \times 100
\]

High CIA and PIA values (i.e., 75–100) indicate intensive weathering in the source area whereas low values (i.e., 60 or less) indicate low weathering in source area. The high variations in CIA and PIA values may, however, be due to the low concentrations (sometimes below or near detection limits) of the alkalis and alkaline earth elements rather than variable degrees of source area weathering, from Osae et al., 2006.

A) Displays the PIA values for the Sena de Luna section; after Fedo et al., 1995 & Moosavirad et al., 2011 and B) Expanded plot of the PIA values, PIA calculation from Moosavirad et al., 2011.

The average PIA value for the Bernesga Mb. (black shales) at Sena de Luna: \textbf{94.62}
Figure 8.7.9.3: Representing all data from the Sena de Luna section (79 samples), the ‘Chemical Index of Weathering’ (CIW; Harnois, 1988).

\[
\text{CIW} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O})} \times 100
\]

The CIW index increases with the degree of depletion of the soil or sediment in Na and Ca, relative to Al. The value of this index increases as the degree of weathering increases, and the difference between CIW index values of the silicate parent rock and soil or sediment reflects the amount of weathering experienced by the weathered material, from Harnois, 1988.

A) Showing the CIW values for the Sena de Luna section, and B) Expanded plot of the CIW values. Calculations from Moosavirad et al., 2011.

The average CIW value for the Bernesga Mb. (black shales) at Sena de Luna: **95.35**
1.7.10 Gamma-ray log and Total Organic Carbon (TOC)

The following section documents the calculated gamma ray (API)/ TOC values for the Sena de Luna section (all 79 samples). The API values were calculated after Elis, 1987, found in the methodology chapter, the same goes for the TOC values calculated after Fertl & Chillingar, 1988, also documented in the methods chapter.
**Figure 8.7.10.1:** Showing whole rock $K_2O$, Th and U values for the Sena de Luna section (every data point for the Formigoso Fm. represents 25cm of stratigraphy, for the Getino Beds every bed was sampled - not every 25cm) from the Barrios Fm. (Sena 1), Getino Beds (Sena 2 - 10 in green) and the lower Bernesga Mb. of the Formigoso Fm. Sena 11 - 79 (light grey). Note the cyclic behaviour of the U values. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons.

There is a clear differentiation between the Formigoso Fm. and the underlying Getino Beds. The basal ‘hot’ shales of the Formigoso Fm. appear to be missing when compared to the other localities. There is a significant shift in the data towards the top of the Bernesga Mb. (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The GR values were calculated by converting $K_2O$, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using $6.69U + 2.54Th + 10.64K_2O = API$ after [http://server4.oersted.dtu.dk/research/RI/SNG/SNG-logs.html](http://server4.oersted.dtu.dk/research/RI/SNG/SNG-logs.html). CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: =3.9637*LN(Uranium Values) - 5.6873. This formula was calculated after Fertl & Chillingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
Figure 8.7.10.2: Showing whole rock K$_2$O, Th and U values for the Sena de Luna section (every data point for the Formigoso Fm. represents 25cm of stratigraphy, for the Getino Beds every bed was sampled - not every 25cm) from the Barrios Fm. (Sena 1), Getino Beds (Sena 2 - 10 in green) and the lower Bernesga Mb. of the Formigoso Fm. Sena 11 - 79 (light grey). Note the cyclic behaviour of the U values. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~ 8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons.

There is a clear differentiation between the Formigoso Fm. and the underlying Getino Beds. The basal ‘hot’ shales of the Formigoso Fm. appear to be missing when compared to the other localities. There is a significant shift in the data towards the top of the Bernesga Mb. (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The GR values were calculated by converting K$_2$O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using $8U + 4Th + 16K_2$O = API after Elis, 1987 and Doveton, 2004. CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: $=3.9637*LN$(Uranium Values) - 5.6873. This formula was calculated after Fertl & Chilingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
1.7.11 Hydrothermal Overprint

Figure 8.7.11.1: Bostrom (1973) diagram; the analysed sediments (all 79 samples from the Sena de Luna section) are compared to argillite (T) and hydrothermal (H) end members whose mixing is modelled by the H-T curve. PAAS and NASC (Gromet et al., 1984) are reported for comparison.
### 1.7.12 Bioproductivity Reconstruction (Barium proxy) & SEM/DOP

**Figure 8.7.12.1:**

- **a)** Al/Ti ratio, data from the Sena de Luna section, shaded region indicates approximate range in shales, pelagic clay, andesite and hydrothermal sediment, and the dashed lines representing oceanic crust & granite Al/Ti ratios after Murray & Leinen, 1996. It shows that the shales of the Formigoso Fm. are enriched in Al (as seen in the EF diagrams) giving the higher Al/Ti ratios, pushing towards the granitic composition, this fits with the bulk composition of basal granitic hinterland.

- To test whether the Al enrichment is due to the granitic composition of the hinterland the Fe/Al ratio is used (b). The ranges after Gordon *et al.*, 1996 in Murray & Leinen, 1996 (labelled a-e); if the sediment source were composed of pure granite (Al/Ti ~ 40; Taylor and McLennan, 1985), it could be the cause of the elevated Al/Ti. Upper crust (Fe/Al ~ 0.42, a), PAAS (~0.51, b), pelagic clay (~0.77, c), and, bulk continental crust (~0.84, d) (Taylor and McLennan, 1985). In granite, Fe/Al ~ 0.28, e (Taylor and McLennan, 1989). From this it can be inferred that the Formigoso Fm. basal shale composition is closest to that of a granitic source.

- **c)** Table displaying Al/Ti ratios of modern day terrestrial source material, aeolian dust and marine sediments modified after Zabel *et al.*, 1999, comparison of the Formigoso Fm Al/Ti ratios to that of modern day environments (Sena de Luna ranging from ~22-31 sat within the deep-sea sediments ranges, yet higher range 31 comparable to that of surface sediments (equatorial pacific)).

- **d)** TiO₂ vs. Al₂O₃ cross plot including all data from the Sena de Luna section (79 samples). The plot shows the correlation between TiO₂ and Al₂O₃ (R² = 0.908) indicating that the elements are associated with the clay mineralisation and that neither are enriched in relation to each other (no biogenic input). This meant that both elements could be used when calculating the primary production (or palaeoproductivity).

Hydrothermal tests were also carried out (refer to previous figure) to determine if the Formigoso Fm. had undergone any extensive alteration due to pululating hydrothermal fluids, thus, overprinting the true geochemistry (hydrothermal elements anyhow). The tests carried out suggested that the basal Bernesga Mb. of the Formigoso Fm. had not been effected by any hydrothermal overprinting however the upper Villasimpliz Mb. (sands and silts) had been effected yet not significantly (slightly more porous). Therefore, the Ba values of the Formigoso Fm. have not been significantly altered by hydrothermal activity, at least in the lower Bernesga Mb.
Figure 8.7.12.2: Representing the calibrated elemental values for the Sena de Luna section, all the elements and ratios are plotted against stratigraphy (Sena 1 being the oldest, Sena 79 the youngest), sampled at 25cm intervals (other than the Getino Beds, bed by bed). The sample No. (X-axis) of these plots are inverted in relation to all previous plots, as they are to be used in well log form. A set or averaged Ba/Al and Ba/Ti ratio is used for the calculation of the Ba\textsubscript{bio}, for each location, yet graphs e & f show the variation of Ba/Al and Ba/Ti ratios for the Sena de Luna section.
Figure 8.7.12.3: Tables displaying the global Ba/Al average values for area/materials and regions, modified after Pfeifer et al., 2004. The Ba/Al values (highlighted) for the Atlantic Ocean off West Africa (0.0045) and organic rich sediment (0.0032) are closest to the global crustal average value (0.0037) after Pfeifer et al., 2004 used in this project. The 0.0045 ratio of the African sediments is closest to that of the basal Gondwanan hinterland values.
Figure 8.7.12.4: Biogenic barium or $\text{Ba}_{\text{bio}}$ (also called $\text{Ba}_{\text{bio(min)}}$) & $\text{Ba}_{\text{bio(min)}}$ values calculated for the Sena de Luna section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998;

1) $\text{Ba}_{\text{bio}} = \text{Ba}_{\text{tot}} - (\text{Al} \times \text{Ba/Al}_{\text{aluminosilicate}}$) from Pfeifer et al., 2001

2) $\text{Ba}_{\text{bio}} = \text{Ba}_{\text{tot}} - (\text{Al} \times \text{Ba/Ti}_{\text{aluminosilicate}}$) from Bonn et al., 1998

The total Ba, $\text{Ba}_{\text{bio}}$ and $\text{Ba}_{\text{bio(min)}}$ values are plotted against stratigraphy Sena 1 being the oldest and Sena 79 the youngest, the sampling interval was set at 25cm (the Getino Beds were sampled bed by bed). A number of ratios were selected for the aluminosilicate fraction and these were as follows;

1) $\text{Ba/Al}_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.002913

2) $\text{Ba/Al}_{\text{min}}$ ratio (minimum Bernesga Mb. Ba/Al ratio at the Sena de Luna section) = 0.00

3) $\text{Ba/Al}_{\text{aluminosilicate}}$ ratio (global ave.) = 0.0037

The global crustal average Ba/Al$_{\text{aluminosilicate}}$ = 0.0037, from Pfeifer et al., 2004 & Pirrung et al., 2008 (0.007 is the most widely used global average crustal value from Pirrung et al., 2008 p. 7, original ref; Dymond et al., 1992; Nürnberg et al., 1997). I used 0.0037 as Gingeie and Dahmke (1994) used 0.004 in; Pfeifer et al., 2001 (p. 5) they stated that sediments north of 30°S are prone to higher weathering conditions due to higher humidity (fits with my humidity proxies and Silurian global reconstructions), the 0.0037 ratio is lower than that of the global ave. 0.007 which means it pushes the data away from the negative values; it gives the most convincing results, Pfeifer et al., 2004. When comparing the 0.0037 ratio to the values shown in the previous tables (Pfeifer et al., 2004) it can be seen that it is closest to that of the African sediment; 0.0045 of Rutsch et al., 1995 and the organic rich sediment; 0.0032 of Rutten, 2001. The average Al/Ba ratios for the Formigoso Fm. (0.002913) are also closest to that of the organic rich sediment of Rutten, 2001.

4) $\text{Ba/Ti}_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.068156

5) $\text{Ba/Ti}_{\text{min}}$ ratio (minimum Bernesga Mb. Ba/Ti ratio at the Sena de Luna section) = 0.002254

6) $\text{Ba/Ti}_{\text{aluminosilicate}}$ ratio (global ave.) = 0.126.

The global crustal average Ba/Ti$_{\text{aluminosilicate}}$ ratio (global ave.) = 0.126, used for this study from Turekian and Wedepohl, 1961 in; Bonn et al., 1998 (0.14 average upper continental crust Wedepohl, 1995 in; Pirrung et al., 2008 p.6). The Ba/Ti$_{\text{min}}$ and Ba/Ti$_{\text{min}}$ values for the Sena de Luna section were used after Babu et al., 2002 as the $\text{Ba}_{\text{bio}}$ values calculated cannot be negative. The ave. Formigoso Fm. Ba/Al and Ba/Ti ratios are too high, meaning that the calculated $\text{Ba}_{\text{bio}}$ values were
negative, when using the lowest ratios in the area (Sena de Luna) for Ba/Al and Ba/Ti it pushes the $\text{Ba}_{\text{bio}}$ values into positive values as shown on graphs a and b. Graph c uses the global averages for Ba/Al (0.0037) and Ba/Ti (0.126) as a direct comparison.

Figure 8.7.12.5: Accumulation rates of the biogenic barium (AR $\text{Ba}_{\text{bio}}$ and AR $\text{Ba}_{\text{bio(min)}}$) expressed in g cm$^{-2}$ kyr$^{-1}$, calculated for the Sena de Luna section using the following formulas from Pfeifer et al., 2001:

1) $\text{AR Ba}_{\text{bio}} = \text{Ba}_{\text{bio}} \times \text{MAR}/100$ (where MAR = Mass accumulation rate in g cm$^{-2}$ kyr$^{-1}$)

2) $\text{MAR} = \text{SR} \times \text{DBD}$ (where $\text{SR} = \text{sedimentation rate in cm kyr}^{-1}$ and $\text{DBD = dry bulk density in g cm}^{-3}$)

The sedimentation rate (SR) was calculated by using graptolite age constraints of the basal shales of the Formigoso Fm. and the number of samples taken. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; the base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a timespan of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; then the 181 shale samples from the Aralla section, lower Bernesga Mb. (sampled at intervals of 25cm) can be assigned an age of ~22099yrs per sample. The first 4 meters of the Aralla section were then analysed at a higher resolution of 1cm (age representation of ~883.97yrs per reading). From this an approximate average SR of 1.11603cm kyr$^{-1}$ was calculated, however, this average SR does not take into consideration condensed horizons within the basal Bernesga Mb.; represented by the mass accumulation horizons of monograptid graptolites within the basal section (mass graptolite zones representing starved basin conditions).

The dry bulk density (DBD) was estimated by taking the average shale density ranges 1.8 – 2.8 g cm$^{-3}$ (Glover, 2000). Both the lower range value and upper range DBD values were used in the calculations.

The two MAR values used;

1) 2.008854 g cm$^{-2}$ kyr$^{-1}$ (lowest range using 1.8 g cm$^{-3}$ DBD)

2) 3.124884 g cm$^{-2}$ kyr$^{-1}$ (highest range using 2.8 g cm$^{-3}$ DBD)

a) Represents the $\text{AR Ba}_{\text{bio}}$ & $\text{AR Ba}_{\text{bio(min)}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ & $\text{Ba}_{\text{bio(min)}}$ values from the previous figure (the ave. Formigoso Fm. Ba/Al ratio and lowest Ba/Al ratio from Sena de Luna). b) The $\text{AR Ba}_{\text{bio}}$ & $\text{AR Ba}_{\text{bio(min)}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ & $\text{Ba}_{\text{bio(min)}}$ values from the previous figure (ave. Formigoso Fm. Ba/Ti ratio and lowest Ba/Ti ratio from Sena de Luna). c) The $\text{AR Ba}_{\text{bio}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ values from the previous figure (global ave.
Ba/Al ratio). d) The AR $\text{Ba}_{\text{bio}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ values from the previous figure (global ave. Ba/Ti ratio).

Figure 8.7.12.6: The flux of Ba to the sea floor (or $F_{\text{Ba}}$) was calculated using the following formulas from Pfeifer et al., 2001 and Bonn et al., 1998 for the Sena de Luna section;

1) $F_{\text{Ba}} = \text{AR } \text{Ba}_{\text{bio}} / 0.209 \log(\text{MAR}) - 0.213$ expressed in mg cm$^{-2}$ kyr$^{-1}$

2) $\%\text{Ba}_{\text{pres}} = 20.9 \log(\text{MAR}) - 21.3$

The amount of Ba dissolved at the sediment water interface (or $F_{\text{Ba}}$) is calculated by dividing the AR $\text{Ba}_{\text{bio}}$ by the $\%\text{Ba}_{\text{pres}}$ (or % of preserved Ba). a) Shows $F_{\text{Ba}}$ and $F_{\text{Ba(min)}}$ using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Al ave. ratio and the Sena de Luna Ba/Al min value (calculated AR $\text{Ba}_{\text{bio}}$ and AR $\text{Ba}_{\text{bio(min)}}$ for Ba/Al ratios). b) Shows $F_{\text{Ba}}$ and $F_{\text{Ba(min)}}$ using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Ti ave. ratio and the Sena de Luna Ba/Ti min value (calculated AR $\text{Ba}_{\text{bio}}$ and AR $\text{Ba}_{\text{bio(min)}}$ for Ba/Ti ratios). c) Shows $F_{\text{Ba}}$ using the previously calculated upper and lower MAR values and the global Ba/Al ave. ratio (global AR $\text{Ba}_{\text{bio}}$ for Ba/Al) and d) shows $F_{\text{Ba}}$ using the upper and lower MAR values and the global Ba/Ti ave. ratio (global AR $\text{Ba}_{\text{bio}}$ for Ba/Ti).
Figure 8.7.12.7: The calculation of new production or \( (P_{\text{new}} \text{ and } P_{\text{new(min)}}) \) for the Sena de Luna section following the formula from Pfeifer et al., 2001 and Bonn et al., 1998;

1) \( P_{\text{new}} = 1.95 \left( F_{\text{Ba}} \right) 1.41 \) expressed in gC m\(^{-2}\) yr\(^{-1}\)

a) Showing the \( P_{\text{new}} \text{ and } P_{\text{new(min)}} \) values for the Sena de Luna section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the Ba/Al ratios.

b) Showing the \( P_{\text{new}} \text{ and } P_{\text{new(min)}} \) values for the Sena de Luna section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the Ba/Ti ratios.

c) Showing the \( P_{\text{new}} \) values for the Sena de Luna section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the global ave. Ba/Al ratio.

d) Showing the \( P_{\text{new}} \) values for the Sena de Luna section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the global ave. Ba/Ti ratio.
Figure 8.7.12.8: The calculation of primary production or palaeoproductivity (PP and \(PP_{\text{min}}\)) for the Sena de Luna section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) \(PP = 20 \times (P_{\text{new}}) 0.5\) expressed in gC m\(^{-2}\) yr\(^{-1}\)

a) Showing the PP and \(PP_{\text{min}}\) values for the Sena de Luna section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the Ba/Al ratios. b) Showing the PP and \(PP_{\text{min}}\) values for the Sena de Luna section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the Ba/Ti ratios. c) Showing the PP values for the Sena de Luna section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the global Ba/Al ratio. d) Showing the PP values for the Sena de Luna section using the previously calculated upper and lower MAR values and the \(P_{\text{new}}\) values using the global Ba/Ti ratio.
1.7.13 3D Environmental Reconstruction Models

Figure 8.7.13.1: General 3D plots (same data shown from differing perspectives) showing the various geochemical ratios: $(Zr+Rb)/Sr$, Th/U and Zr/Rb. X-Ray Fluorescence (XRF) was used for the whole-rock geochemical analysis. The plots represent all sample data from the Sena de Luna section (79 samples). Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic conditions after Fertl, 1979. There is no U within a select few of the coarser grained silt stone horizons/Getino Beds (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). Zr/Rb is used as a grain size indicator ($Zr$ associated with quartz grains, $Rb$ associated with $Al_2O_3$, $TiO_2$, and $K_2O$ in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales. The $(Zr+Rb)/Sr$ (Dypvik & Harris, 2001) ratio reflects the balance between clastic and carbonate components ($Sr$ is associated with CaO and MgO in carbonates), high values are generally found in samples with little carbonate.
Figure 8.7.13.2: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Si/Al, showing data from the Sena de Luna section (all 79 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 ‘oxic’, 0.46-0.60 ‘dysoxic’, 0.54-0.82 ‘suboxic-anoxic’ and >0.82 ‘euxinic’ (Hatch and Leventhal, 1992). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence. There is little or no Ni within a select few of the coarser grained Getino Beds (less reducing); this explains why they fall in the extreme anoxic zone (when calculating the ratio (only works if Ni is present)).

Note the how the diagrams discriminate between the clustered black shales and the Getino Beds (particularly apparent in graph C).
Figure 8.7.13.3: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Zr/Rb, showing data from the Sena de Luna section (all 79 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 'oxic', 0.46-0.60 'dysoxic', 0.54-0.82 'suboxic-anoxic' and >0.82 'euxinic' (Hatch and Leventhal, 1992). The Zr/Rb ratio is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input 'detrital influx' therefore rising sea-level or basin subsidence. There is little or no Ni within a select few of the coarser grained Getino Beds (less reducing); this explains why they fall in the extreme anoxic zone (when calculating the ratio (only works if Ni is present)).

Note the how the diagrams discriminate between the clustered black shales and the Getino Beds (particularly apparent in graph C).
Figure 8.7.13.4: Geochemical environmental reconstruction, using the ratios Rb/K, Th/U and Si/Al, displaying data from the Sena de Luna section (all 79 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents freshwater to brackish, whereas 0.006 fully marine developed environment. Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic (Fertl, 1979). There is no U within a select few of the coarser grained siltstone horizons/Getino Beds (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input 'detrital influx' therefore rising sea-level or basin subsidence.

Note the how the diagrams discriminate between the clustered black shales and the Getino Beds (particularly apparent in graph C).
1.7.14 Cyclicity

Figure 8.7.14.1: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Sena de Luna section, 69 samples (Sena 11 – Sena 79). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the U ppm values from the base (sample No. 1) to the middle (sample No. 69) of the lower member, cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of <0.01 (upper line) and <0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.014706 (highest intensity)</td>
<td>= 1/(0.014706/22099 yrs)</td>
<td>1.5 Myr</td>
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<tr>
<td>0.036765</td>
<td>= 1/(0.036765/22099 yrs)</td>
<td>601.08 Kyr</td>
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<tr>
<td>0.066176</td>
<td>= 1/(0.066176/22099 yrs)</td>
<td>333.94 Kyr</td>
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<tr>
<td>0.10294</td>
<td>= 1/(0.10294/22099 yrs)</td>
<td>214.67 Kyr</td>
</tr>
<tr>
<td>0.13603</td>
<td>= 1/(0.13603/22099 yrs)</td>
<td>162.45 Kyr</td>
</tr>
<tr>
<td>0.22059</td>
<td>= 1/(0.22059/22099 yrs)</td>
<td>100.18 Kyr</td>
</tr>
<tr>
<td>0.35662</td>
<td>= 1/(0.35662/22099 yrs)</td>
<td>61.96 Kyr</td>
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<tr>
<td>0.38971</td>
<td>= 1/(0.38971/22099 yrs)</td>
<td>56.7 Kyr</td>
</tr>
<tr>
<td>0.42462</td>
<td>= 1/(0.42462/22099 yrs)</td>
<td>52.04 Kyr</td>
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</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the Sena de Luna section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.7.14.2: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Sena de Luna section, 69 samples (Sena 11 – Sena 79). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) to the middle (sample No. 69) of the lower member, cyclicity is apparent in the V values, b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually, the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.018382 (highest intensity)</td>
<td>1/(0.018382/22099 yrs)</td>
<td>1.2 Myr</td>
</tr>
<tr>
<td>0.060662</td>
<td>1/(0.060662/22099 yrs)</td>
<td>364.29 Kyr</td>
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<tr>
<td>0.12684</td>
<td>1/(0.12684/22099 yrs)</td>
<td>174.22 Kyr</td>
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<tr>
<td>0.17096</td>
<td>1/(0.17096/22099 yrs)</td>
<td>129.26 Kyr</td>
</tr>
<tr>
<td>0.22059</td>
<td>1/(0.22059/22099 yrs)</td>
<td>100.18 Kyr</td>
</tr>
<tr>
<td>0.47794</td>
<td>1/(0.47794/22099 yrs)</td>
<td>46.23 Kyr</td>
</tr>
</tbody>
</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the Sena de Luna section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
1.8 Villanueva Section

The following section documents all geochemical results for the Villanueva section. The Villanueva section consists of 111 samples; all 111 are representative of the basal Formigoso Fm. (Bernesga Mb.). The sampling interval within the Bernesga Mb. was set at 25cm, as is the case for all other sampling locations (other than the Aralla HR field analysis). Please also refer to the Villanueva log section (showing the sample location in regards to the log section) in the Results Chapter and the results tables in Appendix B (part 2).
1.8.1 **Major Elements**

Figure 8.8.1.1: All major element variation curves for the Villanueva log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
1.8.2 Trace Elements

Figure 8.8.2.1: Trace element variation curves for the Villanueva log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
Figure 8.8.2.2: Trace element variation curves for the Villanueva log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
Figure 8.8.2.3: Trace element variation curves for the Villanueva log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
Figure 8.8.2.4: Trace element variation curves for the Villanueva log section. Each sample number represents a 25cm sampling interval, only the basal Bernesga Mb. of the Formigoso Fm. was apparent at the locality.
1.8.3 Elemental cross-plots

Figure 8.8.3.1: Showing the cross-plots of $\text{Al}_2\text{O}_3$ to $\text{K}_2\text{O}$, $\text{TiO}_2$, $\text{MgO}$, $\text{Rb}$, $\text{Cr}$ and $\text{Zr}$ for the Villanueva section (111 samples). All show positive correlations except for $\text{Zr}$, a negative correlation in the basal organically enriched shales (the lower the enrichment of $\text{Zr}$ (detrital influx) the higher the $\text{Al}_2\text{O}_3$ concentrations).

Figure 8.8.3.2: Cross-plots of $\text{Al}_2\text{O}_3$ vs. $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ for the Villanueva section (111 samples), all showing negative correlations indicating the presence of clay minerals. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ cross plot indicates the maturity of the shales.
**Figure 8.8.3.3:** Showing the geochemical ratios of Cr/V and Ni for the Villanueva section (111 samples). The ratios can be compared between localities to determine environment differences/changes laterally (redox states, redox sensitive elements). Plots a + b display the ratios plotted against stratigraphy. Cr, Ni and V are redox sensitive elements. Hence the enrichment shown in the V vs. Cr cross plot towards the organically enriched anoxic shales. The V vs. Cr cross plot shows a strong positive correlation (the higher the V values the higher the Cr values).

**Figure 8.8.3.4:** Showing grain size (SiO$_2$/Al$_2$O$_3$ and Rb/K$_2$O) and redox state (Cu/Zn) for the Villanueva section (111 samples), indicating the maturity of the Formigoso Fm., the lower the silica content, smaller the grain size.
Figure 8.8.3.5: Harker type major element variation diagrams for the Villanueva section (111 samples). The CaO readings were just above the detection limit.
Figure 8.8.3.6: Cross plots of Al₂O₃, U, Th, Cs and Ba vs. K₂O for the Villanueva section (111 samples), all showing positive correlations. The U cross plot showing the organically enriched basal shales, the higher the U content, the higher the total organic carbon (TOC), using U as a proxy for organic content and redox indicator.

Figure 8.8.3.7: MgO cross plots of Fe₂O₃, MnO, (Cr+Ni) and V for the Villanueva section (111 samples), all showing positive correlations.
Figure 8.8.3.8: Showing Cr/Rb, V/Rb, Th/U, Ba/Rb and Zr/Rb ratios for the Villanueva section (111 samples). The values are normalised to Rb as it is inert with respect to biogenic processes unlike Al₂O₃ and SiO₂. The Th/U ratio can be used as a redox proxy.
Figure 8.8.3.9: TOC cross-plots for the Villanueva section (all 111 samples); trace elements of 'strong euxinic affinity' (Algeo & Maynard, 2004) a) U, b) V, c) Zn and d) Pb all of the trace elements are Al normalized (x10^-4). Trace elements of 'weak euxinic affinity' e) Cu, f) Ni and g) Cr again all Al normalized (x10^-4).
Figure 8.8.3.10: Selected major element vs. Al\textsubscript{2}O\textsubscript{3} variation diagrams for the Formigoso Fm. (Bermesga Mb.) at Villanueva (a + b), displaying all 111 samples. The ranges of K\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} ratios in K-feldspars and clays (plot (b)) after Cox et al., 1995. Selected trace element vs. Al\textsubscript{2}O\textsubscript{3} variation diagrams (c-e).

f) Th vs. Th/U plot (McLennan et al., 1993) for the Villanueva samples (all 111 samples). Dashed lines: Th/U ratio and Th content of UCC; circle: PAAS (Taylor and McLennan, 1985); fields for depleted mantle sources and Australian shales (AS) from McLennan et al., 1993. Arrows indicate direction of trends for weathering (U loss) and enrichment (U gain).

g+h) Zr/Sc vs. Th/Sc plots (McLennan et al., 1993) for (a) Formigoso Fm. at the Villanueva section (all 111 samples); (b) modern muds from trailing edge (TE, passive margin), continental arc (CA), and forearc (FA) settings (McLennan et al., 1990). Solid line connecting stars B (basalt) and F (felsic volcanic rock), illustrates the trend expected in first-cycle sediments due to magmatic evolution from mafic to felsic end members; star G is the average granite (Condie, 1993). UCC and PAAS from Taylor and McLennan (1985), the arrow illustrates the trend produced by zircon concentration during sedimentary sorting and recycling.
Figure 8.8.3.11: Geochemical plots for the Villanueva section (all 111 samples utilised). a) Showing V/(V+Ni) vs. TOC; the higher the TOC values the lower the sedimentation rate (V/(V+Ni) values have to be above 0.5 in order for the organic carbon to be preserved (not oxidised, Rimmer, 2004), the sedimentation rate indicator taken after Arthur & Sagemann, 1994). b) Represents the TOC values vs. stratigraphy (every data point is equivalent to 25cm). b,c & d) the selected geochemical indices for the Villanueva section (all 111 samples).
Figure 8.8.3.12: Utilising all geochemical data from the Villanueva section (all 111 samples). a) shows Zr/Ti ratios used as a provenance proxy; high Zr/Ti ratios point towards granitic rocks (G1 granite: Zr/Ti is 0.14) or clastic sediments (average phanerozoic quartz arenite: Zr/Ti is 0.13; Boryta and Condie, 1990). Lower Zr/Ti ratios around 0.067 represent the composition of the average upper crust (Taylor and McLennan, 1985). The ‘North American shale composite’ (NASC) has a Zr/Ti ratio of 0.043. Lower Zr/Ti ratios are indicative of basic igneous rocks; Andean volcanic rocks yield Zr/Ti ratios between 0.024 for basalts and 0.034 for andesites (Ewart, 1982). Lowest Zr/Ti ratios around 0.01 represent primitive magmas of OIB’s and MORB’s (Bonn, 2004). b) Signifies palaeosalinity (using Rb/K ratios), the dashed line values were taken from Campbell & Williams, 1965. c-f) palaeo-redox indicators; the ratio lines are documented in the table. g) Th/U Ratios for Villanueva, any value <2 implies anoxic (Fertl, 1979), organically rich black shale genesis.
Figure 8.8.3.13: Geochemical data representative of the Villanueva section (all 111 samples) a) V/Al vs. stratigraphy and b) correlation of V with TOC.

Figure 8.8.3.14: Geochemical data from the Villanueva section (all 111 samples). a) Scatter plot showing heavy mineral indicating element vs. major component. b) TOC values vs. stratigraphy. c + d) Fe$_2$O$_3$ vs. stratigraphy and Fe$_2$O$_3$/Al$_2$O$_3$ (normalised with Al) vs. stratigraphy. e + f) V and Zn vs. TOC.
Figure 8.8.3.15: All data from the Villanueva section (111 samples); a) SiO₂ vs. Al₂O₃ concentrations are plotted relative to the idealized composition of the observed minerals. The majority of the variation in composition may be related to variations in quartz and clay minerals-muscovite (Cullers & Podkovyrov, 2000). b) Fe₂O₃ total vs. Al₂O₃ concentrations plotted relative to the composition of the observed minerals, again much of the variation in composition may be accounted for by variations in quartz and clay minerals-muscovite.

Figure 8.8.3.16: Representing all data from the Villanueva section (111 samples). Redox sensitive elements (V and Cr) showing positive correlations with TOC values; a) Cr (ppm) vs. TOC, b) V (ppm) vs. TOC, c) Cr (wt %) vs. TOC and d) V (wt %) vs. TOC.
Figure 8.8.3.17: Representing all data from the Villanueva section (111 samples). Al₂O₃ bivariate diagrams of major element composition along with estimated elemental mineral compositions (Descourvieres et al., 2011).
Figure 8.8.3.18: Cross-plots showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. The plots represent sample data from the Villanueva section (all 111 samples). Th/U is used as a redox indicator; the dashed black line representing a Th/U ratio of 2, less than 2 indicates anoxic after Fertil, 1979. Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction); high values reflect coarse grained units, lower values in clay stones and shales. (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values found in samples with little carbonate.

Figure 8.8.3.19: Cross-plot of Ni vs. Cr representing all data from the Villanueva section (111 samples).
Figure 8.8.3.20: Representing all data from the Villanueva section (111 samples). The ratios Ni/V and V/Cr (Jones and Manning, 1994) are redox indicators.

Figure 8.8.3.21: Geochemical data from the Villanueva section (all 111 samples). Selected elements and ratios plotted vs. Stratigraphy.

Figure 8.8.3.22: Representing the relationship between Al2O3 and Ba for all Villanueva data (111 samples).
Figure 8.8.3.23: Representing all data from the Villanueva section (111 samples). a) Plot of U/Pb ratios vs. U concentrations (ppm). Samples generally reflect elevated U concentrations relative to North American Shale Composite (Condie, 1993). b) TOC (wt.%) vs. U concentrations (ppm). The U content of NASC is plotted for reference (samples are enriched in U relative to the NASC composite). U and TOC exhibit a perfect correlation as TOC values were generated using the U (ppm) values as a proxy, from Fertl & Chillingar (1988).

Figure 8.8.3.24: All diagrams represent the data from the Villanueva section (111 samples). a) Th vs. Sc (in log scale) and b) Th vs. U diagrams (modified after McLennan et al., 1990, and Luchi et al., 2003). c) Fe₂O₃/K₂O vs. SiO₂/Al₂O₃ d) log SiO₂/Al₂O₃ vs. log (Fe₂O₃/K₂O) of Herron (1986). e) Th/Sc vs. Zr/Sc (log scale) diagram after McLennan et al., (1993), reflecting reworking through Zr/Sc and upper crust felsic input through Th/Sc. Numbers identify the mean values for 1, OIA, 2, CIA, 3, ACM and 4, PM following Bathia and Crook (1986). f) TiO₂ vs. Ni, fields for acidic and basic source materials after Floyd et al., (1989).
Figure 8.8.3.25: Displaying all data from the Villanueva section (111 samples). Th/Sc vs. Zr/Sc plot (Mongelli et al., 2006), the samples depart from the compositional trend, indicating zircon addition suggestive of a recycling effect.

Figure 8.8.3.26: Representing all data from the Villanueva section (111 samples). Zr versus SiO$_2$, a positive relationship is apparent, indication that the Zr is indeed associated with the Quartz (heavy fraction).
Figure 8.8.3.27: TiO₂ vs. Ni bivariate plot for shale samples from the Villanueva section (all 111 samples), fields after Floyd et al., 1989.

Figure 8.8.3.28: Representing all data from the Villanueva section (111 samples). The trace elements are normalised to Al and then multiplied by 10⁻⁴. As, Cr, Cu, Ni, V, Zn vs. Stratigraphy.
Figure 8.8.3.29: Geochemical classification (Pearce et al. 2010) based on the criteria listed in Table b (above) for the Villanueva dataset (all 111 samples). The geochemical classification values (y-axis of plot a)) reflect the following: Score of 4 = floodplain mudstone, Score of 7 = brackish water or lacustrine, Score of 10 = marginal marine mudstone, Score of 13 or 16 = marine mudstone (= marine band). If a sample has a very high Zr/U value (above 65), it is presumed to contain abundant heavy minerals and is awarded a final score of 2. If a sample comes from a coal, it is awarded a default score of 0, modified (Pearce et al., 2010).

Mo and P₂O₅ values for the Villanueva section are near/below detection limits.

Based on the criteria above the depositional environment of the Formigoso Fm. at the Villanueva section is classified as borderline; brackish water or Lacustrine - marginal marine mudstone (which fits with the Rb/K ratios for palaeosalinity).
Figure 8.8.3.30: Representing all data from the Villanueva section (111 samples). A) SiO$_2$/Al$_2$O$_3$ vs. TOC and B) Zr/Rb vs. TOC. The SiO$_2$/Al$_2$O$_3$ and Zr/Rb ratios are renowned grain size proxies, plotted against TOC (Total Organic Carbon) values. The zones for hydrocarbon potential (TOC cut off values) based on Bordenave et al., (1993). The TOC values for the basal shales act independently of the grain size values, the grain size remains consistent yet the TOC levels vary; this is most likely due to changes in the redox state.
Figure 8.8.3.31(a): Plots representing data from the Villanueva section (all 111 samples), showing the relationship between Al₂O₃, selected trace elements and Fe₂O₃. The plots show the relationship between the Cantabrian formations (predominantly the Formigoso Fm.) trace element:Al₂O₃ ratios and the World Shale Average (WSA, plotted as star, taken from Gromet et al., 1984), the Zr vs. Al₂O₃ also includes the Upper Crust (UC) and North American Shale Composite (NASC).
Figure 8.8.3.31(b): Plots representing data from the Villanueva section (all 111 samples). The plots show the relationship between various trace elements within the Cantabrian formations (predominantly the Formigoso Fm).

Figure 8.8.3.32: Representing data from the Villanueva section (all 111 samples). a) Chemical classification, after Herron, 1986. b) Plot of discriminant functions 1 and 2 for shales (after Roser and Korsch (1988). Discriminant function 1 = ($-1.773 \times TiO_2\% + (0.607 \times Al_2O_3\% + (0.76 \times Fe_2O_3T\% + (-1.5 \times MgO\% + (0.516 \times CaO\% + (0.509 \times Na_2O\% + (-1.22 \times K_2O\% + (-9.09)$. Discriminant function 2 = $(0.445 \times TiO_2\% + (0.07 \times Al_2O_3\% + (-0.25 \times Fe_2O_3T\% + (-1.142 \times MgO\% + (0.432 \times Na_2O\% + (1.426 \times K_2O\% + (-6.861)$. Provenance fields are after Roser and Korsch (1988). P1 = mafic and lesser intermediate igneous provenance; P2 = intermediate igneous provenance; P3 = felsic igneous provenance and P4 = recycled-mature polycyclic quartzose detritus. c) Distribution of K and Rb relative to a K/Rb ratio of 230 (= main trend of Shaw, 1968).
Figure 8.8.3.33: Representing all Zr vs. Cr data from the Villanueva section (111 samples). Variations in the Zr and Cr values are likely to reflect changes in the sediment provenance.

Figure 8.8.3.34: Cross plot of Mo (ppm) and TOC (wt%) values from the Villanueva section (all 111 samples). Evidently the Mo concentrations are near/below the detection limit.
Figure 8.8.3.35: Representing data from the Villanueva section (all 111 samples). a) V/Cr used as a palaeoredox proxy. b) V/Cr ratio vs. TOC. c) Mo/Al ratio vs. TOC (Mo values are near/below the detection limit).

Figure 8.8.3.36: Representing all data from the Villanueva section (111 samples). a + b) plots of the detrital parameter Th vs. Zr and Th vs. Ti. c + d) Cross plots of Th as detrital monitor vs. authigenic uranium (U-aut) and V (ppm).
Figure 8.8.3.37: Representing all data from the Villanueva section (111 samples). a) Scatter plot of V/(V + Ni) vs. degree of pyritization (DOP), displaying average shale (Turekian & Wedepohl, 1961) and average continental crust. b) DOP vs. stratigraphy; the lines representing DOP values are from Wignal, 1994. c) Represents an idealized plot of a uniform DOP with increasing TOC, (a+c).

Figure 8.8.3.38: Displaying all data from the Villanueva section (111 samples), provenance and source signature diagrams. a) Th vs. Sc, Th is an incompatible element that is enriched in silicic rocks, and Sc is a compatible element that is enriched in mafic rocks. Th/Sc ratios near unity express the upper continental crust (UC) the Th/Sc ratios near 0.6 suggest a more mafic component, modified (Totten et al., 2000). b) Th/Sc vs. Cr/Th the samples lie upon a curve consistent with mixing of a continental source enriched in incompatible elements (Th) and a more mafic source enriched in compatible elements (Cr, Sc). The values for UC, Granites and mid-oceanic-ridge-basalts (MORB) are given for comparison, (Totten et al., 2000). c) Th vs. Sc relation and d) Th/Sc vs. Cr/Th.
Figure 8.8.3.39: Representing all data from the Villanueva section (111 samples). MgO/Al₂O₃ vs. K₂O/Al₂O₃ cross plot including the fields of kaolinite, illite/K-feldspar and chlorite (clay typing) (Turgeon + Brumsack, 2006).
Figure 8.8.3.40: Representing all data from the Villanueva section (111 samples). Diagrams used for discriminating the differing lithologies (basal shales; lower member and the sand/silt intercalations; upper member).

Figure 8.8.3.41: Showing all data from the Villanueva section (all 111 samples). a) cross-plot of SiO$_2$ vs. Al$_2$O$_3$ shows an enrichment of SiO$_2$ over Al$_2$O$_3$ in comparison to the World Average Shale (WSA) of Turekian & Wedepohl, 1961. b + c) TOC vs. Al$_2$O$_3$ and SiO$_2$, showing that the TOC values vary as the Al$_2$O$_3$/SiO$_2$ content remain consistent.
Figure 8.8.3.42: Representing all data from the Villanueva section (111 samples). Plot of total organic carbon (TOC wt.%) against authigenic uranium content (U$_{auth}$). The correlation between TOC and total U would be 1:1 as the TOC values have been generated by using U as a proxy. Yet the U$_{auth}$ values use Th values in order to correct for detrital uranium.

Figure 8.8.3.43: Representing all data from the Villanueva section (111 samples). Elemental Sr/Al, Mn/Al, Si/Al, Ba/Al, Zr/Al ratios plotted against TOC and stratigraphy.
1.8.4 $\text{Na}_2\text{O}$ plots

**Figure 8.8.4.1:** Displaying data from the Villanueva section (all 111 samples). a) Provenance discrimination diagram for shales (after Roser and Korsch, 1988). Discriminant Discriminant function 1 $= (-1.773 \times \text{TiO}_2\%) + (0.607 \times \text{Al}_2\text{O}_3\%) + (0.76 \times \text{Fe}_2\text{O}_3\%) + (-1.5 \times \text{MgO}%) + (0.616 \times \text{CaO}%) + (0.509 \times \text{Na}_2\text{O}%) + (-1.22 \times \text{K}_2\text{O}%) + (-9.09)$. Discriminant function 2 $= (0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\%) + (-1.142 \times \text{MgO}%) + (0.432 \times \text{Na}_2\text{O}%) + (1.426 \times \text{K}_2\text{O}%) + (-6.861)$. b) Bivariate $\text{SiO}_2$ wt.% vs. $(\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O})$ wt.% palaeoclimate discrimination diagram, fields after Suttner and Dutta (1988). c) $\text{SiO}_2/\text{Al}_2\text{O}_3$ vs. $\text{K}_2\text{O}/\text{Na}_2\text{O}$ after Kampunzu et al., 2005. d) Discriminant function diagram after Roser and Korsch (1988); Discriminant function I $= (-1.773 \times \text{TiO}_2\%) + (0.607 \times \text{Al}_2\text{O}_3\%) + (0.76 \times \text{Fe}_2\text{O}_3\%) + (-1.5 \times \text{MgO}%) + (0.616 \times \text{CaO}%) + (0.509 \times \text{Na}_2\text{O}%) + (-1.224 \times \text{K}_2\text{O}%) + (-9.09)$; Discriminant function II $= (0.445 \times \text{TiO}_2\%) + (0.07 \times \text{Al}_2\text{O}_3\%) + (-0.25 \times \text{Fe}_2\text{O}_3\%) + (-1.142 \times \text{MgO}%) + (0.438 \times \text{CaO}%) + (1.475 \times \text{Na}_2\text{O}%) + (1.426 \times \text{K}_2\text{O}%) + (-6.861)$. e) Akul'shina (1976) + Kiipli et al., (2012): $\text{Al}/\text{Ti}$ ratio and climate: $\text{Al}_2\text{O}_3/\text{TiO}_2 <20$ for humid, $20–30$ for semi-humid and semi-arid, and $>30$ for arid climate.
1.8.5 Histograms (major elements & redox ratios)

Figure 8.8.5.1: Histograms and cumulative frequency representing the major oxides a) SiO\textsubscript{2} values b) Al\textsubscript{2}O\textsubscript{3} values c) K\textsubscript{2}O values and d) TiO\textsubscript{2} values, using all sample data (111 samples) from the Villanueva section. Wt% vs. frequency for the histograms and cumulative frequency for the curve.

Figure 8.8.5.2: Histograms and cumulative frequency curves representing all sample data for the Villanueva section. a) Showing the calculated degree of pyritization (DOP): A= Anaerobic (0-0.4); R = Restricted (0.45-0.75); I = Inhospitable (0.55-1) ranges from Raiswell et al.,1988. b + c) palaeo-redox proxies V/(V + Ni) and V/Cr. Ranges for inferred bottom-water conditions for V/Cr, <2 oxic, 2-4.25 dysoxic, >4.25 suboxic-anoxic from Jones and Manning (1994); ranges for V/(V + Ni), <0.46 oxic, 0.46-0.6 dysoxic, 0.54-0.82, suboxic-anoxic, >0.84 euxinic (Hatch and Leventhal (1992)).
1.8.6  $K$, $Th$ and $U$ bubble plots

Figure 8.8.6.1: Bubble plot displaying $K_2O$, $Th$ and $U$ concentrations for the Villanueva section, representing all sample data (111 samples). $K_2O$ and $Th$ and $U$ contents were analysed by X-Ray Fluorescence (XRF) whole rock analysis, the bubble size is proportional to $U$ content.
### 1.8.7 Ternary diagrams

**Figure 8.8.7.1:** Ternary diagram showing relative proportions of major shale/mud rock components; $\text{SiO}_2$ (quartz), $\text{Al}_2\text{O}_3$ (clays) and $\text{CaO}$ (carbonates) (Ross & Bustin, 2009) displaying data from the Villanueva section (all 111 samples). The Key for the expanded plot is shown to the left of the figure, the key for the inset ternary (top right); diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the ‘Average shale’ also shown as star (after Wedepohl, 1971).

**Figure 8.8.7.2:** Villanueva section (all 111 samples) ternary $10\text{Al}_2\text{O}_3 - 200\text{TiO}_2 - \text{Zr}$ plot, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).
Figure 8.8.7.3: Villanueva section (all 111 samples) ternary $15\text{Al}_2\text{O}_3 - 300\text{TiO}_2 - \text{Zr}$ (Mongelli et al., 2006) plot, diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the star - Post-Archean Australian Shale (PAAS); Taylor and McLennan (1985).

Figure 8.8.7.4: TOC–S–Fe relationships for the Villanueva section (all 111 samples). The diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.8.7.5: TOC–TS10–Fe ternary diagram for the Villanueva samples (all 111). The diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The construction and principles of the diagram based on Dean and Arthur (1989) and Arthur and Sageman (1994).

Figure 8.8.7.6: Degree of pyritization of sediments from the Villanueva section (all 111 samples) in the Fe(x) - total organic carbon (TOC) - S2 (following stoichiometry of pyrite-FeS$_2$) system (relative weight ratios). Reactive Fe (Fe(x)) is calculated with Fe(x) = Fe – 0.25 × Al (Mosher et al., 2006). The diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the data point for pyrite is also shown.
Figure 8.8.7.7: Al–Mg–Ca (Garnier et al., 2008) diagram showing the distribution of the shales from the Formigoso Fm at Villanueava (all 111 samples were used). Inset ternary (top left); diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the domains of evaporites and meta-evaporites, and of platformal marls and shales are from Moine et al., (1981). The key for the expanded plot is towards the right of the figure.
Figure 8.8.7.8: The ternary diagrams top right (inset); (A) Ternary plot of \((\text{Cu+Co+Ni}) \times 10 \) – Fe – Mn (Bonatti et al., 1976 and Mohapatra 2009) showing various generic fields, displaying all data (111 samples) from the Villanueva section (B) Chemical composition of the formation at the Villanueva section (all 111 samples) in terms of components Fe – Mn – Al+Si. The arrow indicates the decreasing clastic input. The key for the expanded plots is found towards the upper left of the figure.
Figure 8.8.7.9: Th – (Cr + Ti)/1000 – Zr/10 ternary plot showing all 111 samples from the Villanueva section. The key for the upper left ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.8.7.10: Al₂O₃, MgO and Fe₂O₃ ternary plot representing data from the Villanueva section (all 111 samples). The key for the upper left ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.8.7.11: Al₂O₃, MgO * 10 and Fe₂O₃ - (expanded plot of previous (Figure 8.8.7.10)) representing data from the Villanueva section (all 111 samples). The diagonal crosses representing the basal Formigoso Fm. (Bernesga Mb.).

Figure 8.8.7.12: Fe₂O₃, Al₂O₃ and MnO ternary plot; represents data from the Villanueva section (all 111 samples). The key for the upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key for the expanded plot is seen towards the upper left of the figure.
Figure 8.8.7.13: Distribution of Fe$_2$O$_3$, Al$_2$O$_3$ and SiO$_2$ within the Villanueva section (111 samples). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), compared with several ideal clay minerals, including chamosite (Chm), berthierine (Ber) thin/long rectangle to represent variable compositions, kaolin and muscovite (Ka/Mu), nontronite (Non), illite thick/long rectangle and glauconite (Gla) (Konhauser et al., 1998, Konhauser & Urrutia, 1999 and Eickmann et al., 2009) The key for the expanded plot is seen towards the left of the figure.

Figure 8.8.7.14: Distribution of K$_2$O, Al$_2$O$_3$ and SiO$_2$ from the Villanueva section (all 111 samples analysed). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.) compared to several ideal clay minerals, including, kaolin (Ka), muscovite (Mu), illite (ill) long rectangle (representing varying compositions) and glauconite (Gla) are labelled (Konhauser et al., 1998 & 1999). The key for the expanded plot is seen towards the left of the figure.
Figure 8.8.7.15: Th, As/10 and U ternary plot, representing data from the Villanueva section (all 111 samples). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.8.7.16: Major geochemical components Al₂O₃ x 5 - SiO₂ - CaO x 2 (relative weight ratios) for the Villanueva section (All 111 samples shown). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the data points for average shale (Wedepohl, 1971, 1991), kaolinite and K-feldspar are shown for comparison (Hetzel et al., 2011).
Figure 8.8.7.17: Ternary plot for Fe$_2$O$_3$, K$_2$O and Al$_2$O$_3$/10, showing all samples from the Villanueva section (111 samples). The upper right ternary; diagonal crosses – basal Formigoso Fm. (Bernesga Mb.), the key towards the left of the figure is for the exploded diagram.

Figure 8.8.7.18: Ternary plot for SiO$_2$/Al$_2$O$_3$, TiO$_2$ and MgO, expressing all samples from the Villanueva section (111 samples). Diagonal crosses representing the basal Formigoso Fm. (Bermesga Mb.). The figure shows a possible maturity trend within the basal organically rich shales.
Figure 8.8.7.19: Ternary plot for U*20, Zr and Sr, expressing all samples from the Villanueva section (111 samples). The diagonal crosses represent the basal Formigoso Fm. (Bernesga Mb.), the ‘hot’ shales trend towards uranium enrichment.

Figure 8.8.7.20: Ternary plot for K2O, Th and U, showing all samples from the Villanueva section (111 samples). The ternary plot (upper right); diagonal crosses – basal Formigoso Fm. (Bernesga Mb.). The key towards the left of the figure is valid for the exploded diagram. Note that a select few of the basal shales appear highly enriched in U and the coarser silt horizons show U depletion.
Figure 8.8.7.21: Ternary plot representing all data for the Villanueva section (111 samples) showing the relationship between $K_2O*5$, Th and U as previously (Figure 8.5.7.20) yet a higher factor for $K_2O$ values. The Majority of the shale/silts cluster towards the $K_2O$ enrichment, $K_2O$ resides mostly within the detrital fraction.

Figure 8.8.7.22: Ternary plot representing all data for the Villanueva section (111 samples) showing the relationship between the heavy elements; Zr, Cr and Ni. The diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.).
Figure 8.8.7.23: Ternary plot representing samples from the Villanueva section (all 111). Cross-plot constructed to characterise between the Shales (differing subunits) and the sands/silts.

Figure 8.8.7.24: Ternary diagram $\text{Fe}_2\text{O}_3$ – MgO – SiO$_2$/Al$_2$O$_3$ representing data from the Villanueva section (all 111 samples). The upper right ternary; diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.). The expanded plot shows a clear maturity trend.
Figure 8.8.7.25: CIA ternary diagram, Al₂O₃ – CaO + Na₂O – K₂O (after Nesbitt and Young, 1982), displaying data from the Villanueva section (all 111 samples). The diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.).

Figure 8.8.7.26: Al₂O₃ – (CaO + Na₂O + K₂O) – (Fe₂O₃ + MgO) ternary diagram after Hayashi et al., 1997, representing data from the Villanueva section (all 111 samples). The diagonal crosses represent – basal Formigoso Fm. (Bernesga Mb.).
1.8.8 **Index of Compositional Variation (ICV)**

![Figure 8.8.8.1](image)

**Figure 8.8.8.1:** a) $K_2O/Al_2O_3$ ratio for the Villanueva section (in order to discriminate K-feldspars and clay minerals). The stars represent values for specific minerals indicated, data from Deer *et al.*, 1966, overlay from Cox, 1995. b) expanded plot of the original (a). c) Index of Compositional Variation (ICV); $(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3$, for the Villanueva section, the stars represent values for specific minerals indicated, the arrows show the range of values for the particular mineral group, data from Deer *et al.*, 1966, overlay from Cox, 1995. d) Expanded plot of the original 'c), cyclicity apparent within the ICV values.

$K_2O/Al_2O_3$ - range of Bernesga Mb. (shales) at Villanueva: 0.1021-0.1696

$K_2O/Al_2O_3$ - average of Bernesga Mb. (shales) at Villanueva: 0.1325

ICV - range of Bernesga Mb. (shales) at Villanueva: 0.3953-0.5871 (0.8128 inc. Fe spike)

ICV - average of Bernesga Mb. (shales) at Villanueva: 0.4664
Figure 8.8.9.1: Representing data from the Villanueva section (all 111 samples). The ‘Chemical Index of Alteration’ (CIA) (Nesbitt and Young, 1982, Taylor and McLennan, 1985) is a well-established parameter for determining the degree of weathering and is the most accepted of the available weathering indices (Bahlburg & Dobrzinski, 2009). During the degradation of feldspars, Ca, Na, and K are removed and clay minerals with a higher fraction of Al are formed. The CIA is estimated from the proportion of $\text{Al}_2\text{O}_3$ vs. the weathering-prone oxides (after Mosher et al., 2006). This index measures the degree of feldspar decomposition to secondary clay products, where CIA values of about 50 indicate fresh bedrock (no chemical weathering), and values of 75-100 indicate complete conversion of feldspars to aluminous clay minerals (intense chemical weathering; see Fedo et al., 1995):

$$\text{CIA} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \times 100$$

A) Kaolinite has a CIA value of 100 and represents the highest degree of weathering. Illite is between 75 and c. 90, muscovite at 75, the feldspars at 50. Fresh basalts have values between 30 and 45, fresh granites and granodiorites of 45 to 55 (Nesbitt and Young, 1982; Fedo et al., 1995), after Bahlburg, 2009. B) Expanded plot, focusing within the Illite Zone (muscovite line also shown).

The average CIA value for the Bernesga Mb. (black shales) at Villanueva: 84.85
Figure 8.8.9.2: Representing all data from the Villanueva section (111 samples), the ‘Plagioclase Index of Alteration’ (PIA; Fedo et al., 1995).

PIA = \[
\frac{\text{Al}_2\text{O}_3 - \text{K}_2\text{O}}{\text{Al}_2\text{O}_3 - \text{K}_2\text{O} + \text{CaO} + \text{Na}_2\text{O}}\] * 100

High CIA and PIA values (i.e., 75–100) indicate intensive weathering in the source area whereas low values (i.e., 60 or less) indicate low weathering in source area. The high variations in CIA and PIA values may, however, be due to the low concentrations (sometimes below or near detection limits) of the alkalis and alkaline earth elements rather than variable degrees of source area weathering, from Osae et al., 2006.

A) Displays the PIA values for the Villanueva section, and B) Expanded plot of the PIA values, PIA calculation from Moosavirad et al., 2011.

The average PIA value for the Bernesga Mb. (black shales) at Villanueva: 94.94
Figure 8.8.9.3: Representing all data from the Villanueva section (111 samples), the ‘Chemical Index of Weathering’ (CIW; Harnois, 1988).

\[ \text{CIW} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O})} \times 100 \]

The CIW index increases with the degree of depletion of the soil or sediment in Na and Ca, relative to Al. The value of this index increases as the degree of weathering increases, and the difference between CIW index values of the silicate parent rock and soil or sediment reflects the amount of weathering experienced by the weathered material, from Harnois, 1988.

A) Showing the CIW values for the Villanueva section, and B) Expanded plot of the CIW values. Calculations from Moosavirad et al., 2011.

The average CIW value for the Bernesga Mb. (black shales) at Villanueva: 95.58
1.8.10 *Gamma-ray log and Total Organic Carbon (TOC)*

The following section documents the calculated gamma ray (API)/ TOC values for the Villanueva section (all 111 samples). The API values were calculated after Elis, 1987, found in the methodology chapter, the same goes for the TOC values calculated after Fertl & Chillingar, 1988, also documented in the methods chapter.
Figure 8.8.10.1: Showing whole rock K$_2$O, Th and U values for the Villanueva section (every data point represents 25cm of stratigraphy). Samples 1-111 contain the basal shales (or Bernesga Mb. of the Formigoso Fm.) coloured grey (contact with the underlying Barrios Fm. and the Getino Beds are missing ~4m of the section overgrown at base). From looking at the U and gamma values ‘compared to the complete Aralla section’ the first cycle ‘hot’ shales seem to be missing. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons. There is a significant shift in the data after the 2nd cycle (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The figure above also displays, Gamma-ray (GR), Computed Gamma-ray (CGR) and Total Organic Carbon (TOC) values for the Villanueva section. Note the cyclic behaviour of the GR and TOC values. The basal Bernesga Mb. shales (lower member of Formigoso Fm.) has been given rough age constrains at the base and top using graptolite data, suggesting a ~4Myr time span.

The GR values were calculated by converting K$_2$O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using $6.69U + 2.54Th + 10.64K2O = API$ after (http://server4.oersted.dtu.dk/research/RI/SNG/SNG-logs.html). CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: $-3.9637*LN(Uranium Values)-5.6873$. This formula was calculated after Fertl & Chilingar (1988) U vs. TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
Figure 8.8.10.2: Showing whole rock K$_2$O, Th and U values for the Villanueva section (every data point represents 25cm of stratigraphy). Samples 1-111 contain the basal shales (or Bernesga Mb. of the Formigoso Fm.) coloured grey (contact with the underlying Barrios Fm. and the Getino Beds are missing ~ 4m of the section overgrown at base). From looking at the U and gamma values ‘compared to the complete Aralla section’ the first cycle ‘hot’ shales seem to be missing. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constrains at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a time span of ~8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; the 181 shale samples from the lower Bernesga Mb. at the Aralla section can be assigned an age of ~22099yrs per sample. However, this ~4Ma time span per member does not take into account condensed horizons. There is a significant shift in the data after the 2nd cycle (traceable throughout the other localities); this is noted to be a possible tectonically induced event.

The figure above also displays, Gamma-ray (GR), Computed Gamma-ray (CGR) and Total Organic Carbon (TOC) values for the Villanueva section. Note the cyclic behaviour of the GR and TOC values. The basal Bernesga Mb. shales (lower member of Formigoso Fm.) has been given rough age constrains at the base and top using graptolite data, suggesting a ~4Myr time span.

The GR values were calculated by converting K$_2$O, Th and U whole rock geochemical data to API (American Petroleum Institute) then combining the 3 curves, using $8U + 4Th + 16K_2O = API$ after Elis, 1987 and Doveton, 2004. CGR was formulated in the same way yet the U API values are not included. The TOC curve was generated using U ppm values and the following function: $=3.9637*\ln(\text{Uranium Values})-5.6873$. This formula was calculated after Fertl & Chillingar (1988) U versus TOC correlation curve. The dashed line (200API) for the GR values and the (3wt% TOC) for the TOC values represent the ‘hot shale’ threshold, the dashed line (120API) is the average value for the ‘lean shales’ of Luning (2000).
Figure 8.8.11.1: Bostrom (1973) diagram; the analysed sediments (all 111 samples from the Villanueva section) are compared to argillite (T) and hydrothermal (H) end members whose mixing is modelled by the H-T curve. PAAS and NASC (Gromet et al., 1984) are reported for comparison.
1.8.12 Bioproductivity Reconstruction (Barium proxy) & SEM/DOP

Figure 8.8.12.1: a) Al/Ti ratio, data from the Villanueva section, shaded region indicates approximate range in shales, pelagic clay, andesite and hydrothermal sediment, and the dashed lines representing oceanic crust & granite Al/Ti ratios after Murray & Leinen, 1996. It shows that the shales of the Formigoso Fm. are enriched in Al (as seen in the EF diagrams) giving the higher Al/Ti ratios, pushing towards the granitic composition, this fits with the bulk composition of basal granitic hinterland.

To test whether the Al enrichment is due to the granitic composition of the hinterland the Fe/Al ratio is used (b). The ranges after Gordon et al., 1996 in Murray & Leinen, 1996 (labelled a-e); if the sediment source were composed of pure granite (Al/Ti ~ 40; Taylor and McLennan, 1985), it could be the cause of the elevated Al/Ti. Upper crust (Fe/Al ~ 0.42), PAAS (~0.51), pelagic clay (~0.77), and, bulk continental crust (~0.84) (Taylor and McLennan, 1985). In granite, Fe/Al ~ 0.28, e (Taylor and McLennan, 1985). From this it can be inferred that the Formigoso Fm. basal shale composition is closest to that of a granitic source.

c) Table displaying Al/Ti ratios of modern day terrestrial source material, aeolian dust and marine sediments modified after Zabel et al., 1999, comparison of the Formigoso Fm. Al/Ti ratios to that of modern day environments (Villanueva ranging from ~22-33 sat within the deep-sea sediments ranges, yet higher range 33 comparable to that of surface sediments (equatorial pacific)).

d) TiO₂ vs. Al₂O₃ cross plot including all data from the Villanueva section (111 samples). The plot shows the correlation between TiO₂ and Al₂O₃ ($R^2 = 0.052$) indicating that the elements are associated with the clay mineralisation and that neither are enriched in relation to each other (no biogenic input). This meant that both elements could be used when calculating the primary production (or palaeoproductivity).

Hydrothermal tests were also carried out (refer to previous figure) to determine if the Formigoso Fm. had undergone any extensive alteration due to peculating hydrothermal fluids, thus, overprinting the true geochemistry (hydrothermal elements anyhow). The tests carried out suggested that the basal Bernesga Mb. of the Formigoso Fm. had not been effected by any hydrothermal overprinting however the upper Villasimpliz Mb. (sands and silts) had been effected yet not significantly (slightly more porous). Therefore, the Ba values of the Formigoso Fm. have not been significantly altered by hydrothermal activity, at least in the lower Bernesga Mb.
Figure 8.8.12.2: Representing the calibrated elemental values for the Villanueva section, all the elements and ratios are plotted against stratigraphy (Villa 1 being the oldest, Villa 111 the youngest), sampled at 25cm intervals. The sample No. X-axis of these plots are inverted in relation to all previous plots, as they are to be used in well log form. A set or averaged Ba/Al and Ba/Ti ratio is used for the calculation of the Ba_{bio} for each location, yet graphs e & f show the variation of Ba/Al and Ba/Ti ratios for the Villanueva section.
Figure 8.8.12.3: Tables displaying the global Ba/Al average values for area/materials and regions, modified after Pfeifer et al., 2004. The Ba/Al values (highlighted) for the Atlantic Ocean off West Africa (0.0045) and organic rich sediment (0.0032) are closest to the global crustal average value (0.0037) after Pfeifer et al., 2004 used in this project. The 0.0045 ratio of the African sediments is closest to that of the basal Gondwanan hinterland values.

<table>
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<tr>
<th>Area/material</th>
<th>Detrital Ba/Al ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba/Al ratios abundance of aluminosilicate detritus</td>
<td>0.005 – 0.01</td>
<td>Taylor and Mclennan, 1985; Taylor, 1964; Rosler and Lange, 1972</td>
</tr>
<tr>
<td>shale</td>
<td>0.0073</td>
<td>Turekian and Wedepohl, 1961</td>
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<td>shale</td>
<td>0.006</td>
<td>Krauskopf, 1967</td>
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<td>average pre-Archean shale crust</td>
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<tr>
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<td>Dymond et al., 1992</td>
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<td></td>
<td>0.0065</td>
<td>Bowen, 1979</td>
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<th>Region</th>
<th>Detrital Ba/Al ratio (estimated)</th>
<th>Detrital Ba/Al ratio (analysed)</th>
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</tr>
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<td>Pfeifer et al., 2001</td>
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<td>0.004(1)</td>
<td>0.0027(a)</td>
<td>(1) Gingele and Dahnke, 1994; (a) Pfeifer et al., 2004</td>
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<td>Southern Ocean</td>
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<td></td>
<td>Nümburg et al. 1997</td>
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<td>Atlantic Ocean off West Africa (Gong Fan)</td>
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<td>Rutsch et al., 1995</td>
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<tr>
<td>Eastern Mediterranean Sea:</td>
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<td>Ruten, 2001</td>
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<td>-oxic sediment</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>-organic rich sediment</td>
<td>0.0032</td>
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<td></td>
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<tr>
<td>Pacific</td>
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<td></td>
<td></td>
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<td>Northern California shelf</td>
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<td></td>
<td>Dean et al., 1997</td>
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<td>27.5°S</td>
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<td>0.0051(a)</td>
<td>(2) Klump et al., 2000; (a) Pfeifer et al., 2004</td>
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<td>0.0040(a)</td>
<td></td>
</tr>
<tr>
<td>35°S</td>
<td>0.0088(2)</td>
<td>0.0034(a)</td>
<td></td>
</tr>
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<td>Indian</td>
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<td></td>
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<tr>
<td>Arabian Sea</td>
<td>0.0035(3)</td>
<td>0.0039(b)</td>
<td>(3) Emeis, 1993; (b) Schenau et al., 2001</td>
</tr>
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Figure 8.8.12.3: Tables displaying the global Ba/Al average values for area/materials and regions, modified after Pfeifer et al., 2004. The Ba/Al values (highlighted) for the Atlantic Ocean off West Africa (0.0045) and organic rich sediment (0.0032) are closest to the global crustal average value (0.0037) after Pfeifer et al., 2004 used in this project. The 0.0045 ratio of the African sediments is closest to that of the basal Gondwanan hinterland values.
Figure 8.8.12.4: Biogenic barium or $\text{Ba}_{\text{bio}}$ (also called $\text{Ba}_{\text{bio}}(\text{excess})$ & $\text{Ba}_{\text{bio}}(\text{min})$) values calculated for the Villanueva section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) $\text{Ba}_{\text{bio}} = \text{Ba}_{\text{tot}} - (\text{Al x Ba} / \text{aluminosilicate})$ from Pfeifer et al., 2001

2) $\text{Ba}_{\text{bio}} = \text{Ba}_{\text{tot}} - (\text{Al x Ba} / \text{Ti} \text{aluminosilicate})$ from Bonn et al., 1998

The total Ba, $\text{Ba}_{\text{bio}}$, and $\text{Ba}_{\text{bio}}(\text{min})$ values are plotted against stratigraphy Villa 1 being the oldest and Villa 111 the youngest, the sampling interval was set at 25cm. A number of ratios were selected for the aluminosilicate fraction and these were as follows:

1) $\text{Ba}/\text{Al}_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.002913

2) $\text{Ba}/\text{Al}_{(\text{min})}$ ratio (minimum Bernesga Mb. $\text{Ba}/\text{Al}$ ratio at the Villanueva section) = 0.00

3) $\text{Ba}/\text{Al}_{\text{aluminosilicate}}$ ratio (global ave.) = 0.0037

The global crustal average $\text{Ba}/\text{Al}_{\text{aluminosilicate}} = 0.0037$, from Pfeifer et al., 2004 & Pirrung et al., 2008 (0.007 is the most widely used global average crustal value from Pirrung et al., 2008 p. 7, original ref; Dymond et al., 1992; Nürnberg et al., 1997). I used 0.0037 as Gingele and Dahmke (1994) used 0.004 in; Pfeifer et al., 2001 (p. 5) they stated that sediments north of 30°S are prone to higher weathering conditions due to higher humidity (fits with my humidity proxies and Silurian global reconstructions), the 0.0037 ratio is lower than that of the global ave. 0.007 which means it pushes the data away from the negative values; it gives the most convincing results, Pfeifer et al., 2004. When comparing the 0.0037 ratio to the values shown in the previous tables (Pfeifer et al., 2004) it can be seen that it is closest to that of the African sediment; 0.0045 of Rutsch et al., 1995 and the organic rich sediment; 0.0032 of Rutten, 2001. The average $\text{Al}/\text{Ba}$ ratios for the Formigoso Fm. (0.002913) are also closest to that of the organic rich sediment of Rutten, 2001.

4) $\text{Ba}/\text{Ti}_{\text{aluminosilicate}}$ ratio (all Bernesga Mb. Formigoso Fm.; all locality shale data ave.) = 0.068156

5) $\text{Ba}/\text{Ti}_{(\text{min})}$ ratio (minimum Bernesga Mb. $\text{Ba}/\text{Ti}$ ratio at the Villanueva section) = 0.0232729

6) $\text{Ba}/\text{Ti}_{\text{aluminosilicate}}$ ratio (global ave.) = 0.126

The global crustal average $\text{Ba}/\text{Ti}_{\text{aluminosilicate}} = 0.126$, used for this study from Turekian and Wedepohl, 1961 in; Bonn et al., 1998 (0.14 average upper continental crust Wedepohl, 1995 in; Pirrung et al., 2008 p.6). The $\text{Ba}/\text{Al}_{(\text{min})}$ and $\text{Ba}/\text{Ti}_{(\text{min})}$ values for the Villanueva section were used after Babu et al., 2002 as the $\text{Ba}_{\text{bio}}$ values calculated cannot be negative. The ave. Formigoso Fm. $\text{Ba}/\text{Al}$ and $\text{Ba}/\text{Ti}$ ratios are too high, meaning that the calculated $\text{Ba}_{\text{bio}}$ values were...
negative, when using the lowest ratios in the area (Villanueva) for Ba/Al and Ba/Ti it pushes the $Ba_{bio}$ values into positive values as shown on graphs a and b. Graph c uses the global averages for Ba/Al (0.0037) and Ba/Ti (0.126) as a direct comparison.

**Figure 8.8.12.5:** Accumulation rates of the biogenic barium (AR $Ba_{bio}$ and AR $Ba_{bio(min)}$) expressed in g cm$^{-2}$ kyr$^{-1}$, calculated for the Villanueva section using the following formulas from Pfeifer et al., 2001;

1) $AR \; Ba_{bio} = Ba_{bio} \times MAR/100$ (where MAR = Mass accumulation rate in g cm$^{-2}$ kyr$^{-1}$)

2) $MAR = SR \times DBD$ (where SR = sedimentation rate in cm kyr$^{-1}$ and DBD = dry bulk density in g cm$^{-3}$)

The sedimentation rate (SR) was calculated by using graptolite age constraints of the basal shales of the Formigoso Fm. and the number of samples taken. The basal Bernesga Mb. of the Formigoso Fm. has been given rough age constraints at the base and top using graptolite/chitinozoan data (as covered in the Geological Setting chapter; The base occurs at ~440Ma (lowest of the Alargada Biozone) and the top occurs at ~ 432Ma (upper Murchisoni Biozone), meaning the Formigoso Fm. represents a timespan of ~ 8Ma in total. If the lower and upper members of the Formigoso Fm. were to equate to ~4Ma each; then the 181 shale samples from the Aralla section, lower Bernesga Mb. (sampled at intervals of 25cm) can be assigned an age of ~22099yrs per sample. The first 4 meters of the Aralla section were then analysed at a higher resolution of 1cm (age representation of ~883.97yrs per reading). From this an approximate average SR of 1.11603cm kyr$^{-1}$ was calculated, however, this average SR does not take into consideration condensed horizons within the basal Bernesga Mb.; represented by the mass accumulation horizons of monograptid graptolites within the basal section (mass graptolite zones representing starved basin conditions).

The dry bulk density (DBD) was estimated by taking the average shale density ranges 1.8 – 2.8 g cm$^{-3}$ (Glover, 2000). Both the lower range value and upper range DBD values were used in the calculations.

The two MAR values used;

1) 2.008854 g cm$^{-2}$ kyr$^{-1}$ (lowest range using 1.8 g cm$^{-3}$ DBD)

2) 3.124884 g cm$^{-2}$ kyr$^{-1}$ (highest range using 2.8 g cm$^{-3}$ DBD)

a) Represents the AR $Ba_{bio}$ & AR $Ba_{bio(min)}$, calculated using the upper and lower MAR values listed above and the $Ba_{bio}$ & $Ba_{bio(min)}$ values from the previous figure (the ave. Formigoso Fm. Ba/Al ratio and lowest Ba/Al ratio from Villanueva). b) The AR $Ba_{bio}$ & AR $Ba_{bio(min)}$, calculated using the upper and lower MAR values listed above and the $Ba_{bio}$ & $Ba_{bio(min)}$ values from the previous figure (ave. Formigoso Fm. Ba/Ti ratio and lowest Ba/Ti ratio from Villanueva). c) The AR $Ba_{bio}$, calculated using the upper and lower MAR values listed above and the $Ba_{bio}$ values from the previous figure (global ave. Ba/Al ratio).
AR $\text{Ba}_{\text{bio}}$ calculated using the upper and lower MAR values listed above and the $\text{Ba}_{\text{bio}}$ values from the previous figure (global ave. Ba/Ti ratio).

Figure 8.8.12.6: The flux of Ba to the sea floor (or $F_{\text{Ba}}$) was calculated using the following formulas from Pfeifer et al., 2001 and Bonn et al., 1998 for the Villanueva section;

1) $F_{\text{Ba}} = \frac{\text{AR } \text{Ba}_{\text{bio}}}{0.209 \log (\text{MAR}) - 0.213}$ expressed in mg cm$^{-2}$ kyr$^{-1}$

2) $\%\text{Ba}_{\text{pres}} = 20.9 \log (\text{MAR}) - 21.3$

The amount of Ba dissolved at the sediment water interface (or $F_{\text{Ba}}$) is calculated by dividing the AR $\text{Ba}_{\text{bio}}$ by the $\%\text{Ba}_{\text{pres}}$ (or % of preserved Ba). a) Shows $F_{\text{Ba}}$ and $F_{\text{Ba(min)}}$ using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Al ave. ratio and the Villanueva Ba/Al min value (calculated AR $\text{Ba}_{\text{bio}}$ and AR $\text{Ba}_{\text{bio(min)}}$ for Ba/Al ratios). b) Shows $F_{\text{Ba}}$ and $F_{\text{Ba(min)}}$ using the previously calculated upper and lower MAR values, Formigoso Fm. Ba/Ti ave. ratio and the Villanueva Ba/Ti min value (calculated AR $\text{Ba}_{\text{bio}}$ and AR $\text{Ba}_{\text{bio(min)}}$ for Ba/Ti ratios). c) shows $F_{\text{Ba}}$ using the previously calculated upper and lower MAR values and the global Ba/Al ave. ratio (global AR $\text{Ba}_{\text{bio}}$ for Ba/Al) and d) shows $F_{\text{Ba}}$ using the upper and lower MAR values and the global Ba/Ti ave. ratio (global AR $\text{Ba}_{\text{bio}}$ for Ba/Ti).
Figure 8.8.12.7: The calculation of new production or \( P_{\text{new}} \) and \( P_{\text{new(min)}} \) for the Villanueva section following the formula from Pfeifer et al., 2001 and Bonn et al., 1998;

1) \( P_{\text{new}} = 1.95 \times (F_{\text{Ba}})^{1.41} \) expressed in gC m\(^{-2}\) yr\(^{-1}\);

a) Showing the \( P_{\text{new}} \) and \( P_{\text{new(min)}} \) values for the Villanueva section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the Ba/Al ratios. b) Showing the \( P_{\text{new}} \) and \( P_{\text{new(min)}} \) values for the Villanueva section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the Ba/Ti ratios. c) Showing the \( P_{\text{new}} \) values for the Villanueva section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the global ave. Ba/Al ratio. d) Showing the \( P_{\text{new}} \) values for the Villanueva section using the previously calculated upper and lower MAR values and \( F_{\text{Ba}} \) flux values using the global ave. Ba/Ti ratio.
Figure 8.8.12.8: The calculation of primary production or palaeoproductivity (PP and PP$_{\text{min}}$) for the Villanueva section using the following formula from Pfeifer et al., 2001 and Bonn et al., 1998:

1) $PP = 20 \times (P_{\text{new}})^{0.5}$ expressed in gC m$^{-2}$ yr$^{-1}$

a) Showing the PP and PP$_{\text{min}}$ values for the Villanueva section using the previously calculated upper and lower MAR values and the $P_{\text{new}}$ values using the Ba/Al ratios. 

b) Showing the PP and PP$_{\text{min}}$ values for the Villanueva section using the previously calculated upper and lower MAR values and the $P_{\text{new}}$ values using the Ba/Ti ratios.

c) Showing the PP values for the Villanueva section using the previously calculated upper and lower MAR values and the $P_{\text{new}}$ values using the global Ba/Al ratio.

d) Showing the PP values for the Villanueva section using the previously calculated upper and lower MAR values and the $P_{\text{new}}$ values using the global Ba/Ti ratio.
1.8.13 3D Environmental Reconstruction Models

Figure 8.8.13.1: General 3D plots (same data shown from differing perspectives) showing the various geochemical ratios: (Zr+Rb)/Sr, Th/U and Zr/Rb. X-Ray Fluorescence (XRF) was used for the whole-rock geochemical analysis. The plots represent all sample data from the Villanueva section (111 samples). Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic conditions after Fertl, 1979. There is no U within a select few of the coarser grained siltstone horizons (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). Zr/Rb is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in claystones and shales. The (Zr+Rb)/Sr ratio (Dypvik & Harris, 2001) reflects the balance between clastic and carbonate components (Sr is associated with CaO and MgO in carbonates), high values are generally found in samples with little carbonate.
Figure 8.8.13.2: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Si/Al, showing data from the Villanueva section (all 111 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents freshwater to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 ‘oxic’, 0.46-0.60 ‘dysoxic’, 0.54-0.82 ‘suboxic-anoxic’ and >0.82 ‘ euxinic’ (Hatch and Leventhal, 1992). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al$_2$O$_3$, TiO$_2$, and K$_2$O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.
Figure 8.8.13: Geochemical environmental reconstruction, using the ratios Rb/K, V/(V+Ni) and Zr/Rb (contrasting grain size proxy to the previous figure Si/Al), displaying data from the Villanueva section (all 111 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents fresh-water to brackish, whereas 0.006 fully marine developed environment. The V/(V+Ni) is a renowned redox indicator the values; <0.46 'oxic', 0.46-0.60 'dysoxic', 0.54-0.82 'suboxic-anoxic' and >0.82 'euxinic' (Hatch and Leventhal, 1992). The Zr/Rb ratio is used as a grain size indicator (Zr associated with quartz grains, Rb associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.
Figure 8.8.13.4: Geochemical environmental reconstruction, using the ratios Rb/K, Th/U and Si/Al, displaying data from the Villanueva section (all 111 samples). The Rb/K ratio is used as a palaeosalinity proxy, a value of 0.004 represents freshwater to brackish, whereas 0.006 fully marine developed environment. Th/U is used as a redox indicator, the dashed black line = Th/U ratio of 2, less than 2 indicates anoxic (Fertl, 1979). There is no U within a select few of the coarser grained silt stone horizons (less reducing); this explains why they fall in the anoxic zone (0 values for ratio). The Si/Al ratio is used as a grain size indicator (Si associated with quartz grains, Al associated with Al₂O₃, TiO₂, and K₂O in the clay fraction) high values reflect coarse grained units, lower values in clay stones and shales.

The data can be used to infer; the more reducing the environment the higher the salinity and lower the siliciclastic input ‘detrital influx’ therefore rising sea-level or basin subsidence.
1.8.14 Cyclicity

Figure 8.8.14.1: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Villanueva section, 111 samples (Villa 1 – Villa 111). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the U ppm values from the base (sample No. 1) to the top (sample No. 111) of the lower member, cyclicity is apparent in the U values. b) Matrix plot of the U ppm values with the sample numbers on the Y-axis and the intensity of the U ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the U ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually the sample numbers are shown on the X-axis.

<table>
<thead>
<tr>
<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.013636 (highest intensity)</td>
<td>$1/(0.013636/22099$ yrs)</td>
<td>1.62 Myr</td>
</tr>
<tr>
<td>0.060227</td>
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<td>366.92 Kyr</td>
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<tr>
<td>0.079545</td>
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<td>277.81 Kyr</td>
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<tr>
<td>0.17965</td>
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<td>123.07 Kyr</td>
</tr>
<tr>
<td>0.23295</td>
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<td>94.86 Kyr</td>
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<tr>
<td>0.28068</td>
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<td>78.73 Kyr</td>
</tr>
<tr>
<td>0.41932</td>
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<td>52.7 Kyr</td>
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</table>

Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the U values for the Villanueva section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.
Figure 8.8.14.2: Showing all shale data (Bernesga Mb. of the Formigoso Fm.) for the Villanueva section, 111 samples (Villa 1 – Villa 111). Samples were taken at 25cm intervals (each sample represents 22099yr calculated from graptolite assemblages at base and top of lower member) a) shows the V ppm values from the base (sample No. 1) to the top (sample No. 111) of the lower member, cyclicity is apparent in the V values. b) Matrix plot of the V ppm values with the sample numbers on the Y-axis and the intensity of the V ppm values expressed as colours (values to the right of plot), this plot emphasises the cyclicity. c) Represents the spectral analysis of the V ppm values, the red lines signify the lower and upper limits of p<0.01 (upper line) and p<0.05 significance levels with respect to white, uncorrelated noise and d) Short-time Fourier analysis making the higher intensity frequencies easier to pick out visually the sample numbers are shown on the X-axis.

<table>
<thead>
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<th>Frequencies (plots c and d, above)</th>
<th>Calculations of periodicity</th>
<th>Cyclicity values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.011364 (highest intensity)</td>
<td>1/(0.011364/22099 yrs)</td>
<td>1.94 Myr</td>
</tr>
<tr>
<td>0.0375</td>
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</tr>
<tr>
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<tr>
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<tr>
<td>0.16932</td>
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<td>130.51 Kyr</td>
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<tr>
<td>0.17965</td>
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<td>123.07 Kyr</td>
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<tr>
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<td>101.28 Kyr</td>
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<tr>
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<td>46.86 Kyr</td>
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<tr>
<td>0.5</td>
<td>1/(0.5/22099 yrs)</td>
<td>44.19 Kyr</td>
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</tbody>
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Table displaying the prominent frequencies determined by spectral analysis (plot c above) of the V values for the Villanueva section Bernesga Mb. The cyclicity periodicity was calculated by dividing the frequencies by the sampling interval.