Volatile (H$_2$O, CO$_2$, Cl, S) budget of the Central American subduction zone

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Abstract

After more than a decade of multidisciplinary studies of the Central American subduction zone mainly in the framework of two large research programmes, the US MARGINS program and the German Collaborative Research Centre SFB 574, we here review and interpret the data pertinent to quantify the cycling of mineral-bound volatiles (H$_2$O, CO$_2$, Cl, S) through this subduction system. For input flux calculations, we divide the Middle America Trench into four segments differing in convergence rate and slab lithological profiles, use the latest evidence for mantle serpentinization of the Cocos slab approaching the trench, and for the first time explicitly include subduction erosion of forearc basement. Resulting input fluxes are 40-62 (53) Tg/Ma/m H$_2$O, 7.8-11.4 (9.3) Tg/Ma/m CO$_2$, 1.3-1.9 (1.6) Tg/Ma/m Cl, and 1.3-2.1 (1.6) Tg/Ma/m S - (bracketed are mean values for entire trench length).
Output by cold seeps on the forearc amounts to 0.625-1.25 Tg/Ma/m H₂O partly derived from the slab sediments as determined by geochemical analyses of fluids and carbonates. The major volatile output occurs at the Central American Volcanic Arc (CAVA) that is divided into 10 arc segments by dextral strike-slip tectonics. Based on volcanic edifice and widespread tephra volumes as well as calculated parental magma masses needed to form observed evolved compositions, we determine long-term (10⁵ years) average magma and K₂O fluxes for each of the 10 segments as 32-242 (106) Tg/Ma/m magma and 0.28-2.91 (1.38) Tg/Ma/m K₂O - (bracketed are mean values for entire CAVA length). Volatile/K₂O concentration ratios derived from melt inclusion analyses and petrologic modelling then allow to calculate volatile fluxes as 1.02-14.3 (6.2) Tg/Ma/m H₂O, 0.02-0.45 (0.17) Tg/Ma/m CO₂, 0.07-0.34 (0.22) Tg/Ma/m Cl. The same approach yields long-term sulfur fluxes of 0.12-1.08 (0.54) Tg/Ma/m while present-day open-vent SO₂-flux monitoring yields 0.06-2.37 (0.83) Tg/Ma/m S.

Input-output comparisons show that the arc water fluxes only account for up to 40% of the input even if we include an "invisible" plutonic component constrained by crustal growth. With 20-30% of the H₂O input transferred into the deeper mantle as suggested by petrologic modeling, there remains a deficiency of, say, 30-40% in the water budget. At least some of this water is transferred into two upper-plate regions of low seismic-velocity and electrical-resistivity whose sizes vary along arc: one region widely envelopes the melt-ascent paths from slab-top to arc, the other extends obliquely from the slab below the forearc to below the arc. Whether these reservoirs are transient or steady remains unknown.
Keywords:

subduction input, forearc dewatering, arc magmatism, subduction fluids

1. Introduction

The fluxes of volatiles and fluids into, and out of, subduction zones are a major component of the global volatile elemental exchange between lithosphere, hydrosphere and atmosphere that affects long-term changes in climate and environmental conditions for the biosphere and relates to questions such as the permanence of the ocean through geologic time.

Troposheric through stratospheric emissions of volcanic gases can have a variety of severe environmental impacts on regional to global scales (Delmelle et al. 2002; Robock 2000; Metzner et al. this volume; von Glasow et al. 2009; Kutterolf et al. 2013). Volcanic CO2 emissions are particularly important for the evolution of the atmosphere's composition over geological time scales (Hansen and Wallmann 2003). Moreover, fluxes of fluids and of mineral-bound volatiles associated with mechanical and metamorphic transformation processes change rheological and thermodynamic properties in the subduction system and ultimately pre-determine the frequency and intensity of geohazards such as earthquakes and explosive volcanic eruptions.

Subduction zones and mid-ocean ridges are the major sites of material exchange between the deeper mantle and the lithosphere and surface, where the exchange of volatile components is particularly important for the biosphere. In order to understand to what extent the output at mid-ocean
ridges is balanced by return flux into the deeper mantle at subduction zones, the budget between subduction input and output needs to be determined for each volatile species. In one of the first attempts to budget global subduction fluxes, Peacock (1990) estimated that only 10% of subducted H₂O and CO₂ returns to the surface via arc magmatism. More recently, comprehensive analyses of modern subduction zones by Jarrard (2003), Hacker (2008) and van Keken et al. (2011) revealed large regional differences in subduction fluxes of volatile components. Return fluxes of H₂O into the deep mantle have been estimated by advanced thermal and petrologic modeling of slab dehydration (Rüpke et al. 2004; Hacker 2008; van Keken et al. 2011; Faccenda et al. 2012) while various approaches were used to quantify the global arc-volcanic volatile outputs (e.g., Marty and Tolstikhin 1998; Hilton et al. 2002; Straub and Layne 2003; Wallace 2005; Fischer 2008; Ruscitto et al. 2012). However, considerable uncertainties remain in these budgets due to quite incomplete knowledge of subduction input conditions and the mass fluxes at the arcs. While the serpentinization of subducted mantle (Peacock 2001) has been considered in the most recent studies (Hacker 2008; van Keken et al. 2011; Halama et al. this volume), the extent of serpentinization at individual subduction zones is mostly poorly constrained. None of the budgeting studies has considered subduction-erosion of forearc crust (von Huene and Scholl 1991) as an input component. Thus there is a continued demand for comprehensive analyses of individual subduction zones.

The Central American subduction system, and in particular the Costa Rican and Nicaraguan segments, has been a focus of multi-disciplinary research
during the past decade, led by two major research programmes: the German Collaborative Research Center SFB 574 and the US MARGINS program. The combination of offshore and onshore geophysical observations, submarine investigations of forearc fluid venting, petrological analyses of subduction-zone metamorphic complexes over the whole range of P-T conditions, volcanological/geochemical studies of arc magmatism and advanced geodynamic numerical modelling allow us to constrain the sources and sinks of volatiles, and the fluxes between them. In this paper we review the present knowledge about the fate of volatiles (H₂O, CO₂, Cl, S) in the Central American erosive subduction zone which is transitional from an oceanic nature in the south to a continental nature in the north. We attempt to calculate volatile budgets whereby the recognition of serpentinization of slab upper mantle, the quantification of subduction-erosion rates, and the comprehensive determination of arc-magma fluxes are particularly important factors. A companion paper (Völker et al. this volume) summarizes data on the accretionary, continental subduction zone of southern Chile.

2. The Central American subduction zone

The oceanic Cocos plate subducts beneath the Caribbean plate along the Middle America Trench (MAT) that is paralleled on land by the Central American Volcanic Arc (CAVA) extending from Costa Rica to Guatemala (Fig. 1). The Cocos plate from Nicaragua to Guatemala, northwest of the triple-junction trace, is composed of normal MORB produced at the East Pacific Rise but Cocos plate offshore Costa Rica stems from the Cocos-Nazca spreading center when it was close to the Galapagos hotspot (Mann et al.
This part of the Cocos plate is straddled by numerous seamounts in a northern stripe, followed by the Cocos Ridge to the south (Fig. 1). The Cocos Plate subducts at 62 to 78 km/Ma and its sub-arc dip varies widely from ~44° at southern Costa Rica through ~65° at Nicaragua to ~55° at Guatemala (Syracuse and Abers 2006); consequently sub-arc depth to the slab top is largest at Nicaragua. The volcanic front, which assumed its present position about 8 Ma ago (Ehrenborg 1996), is divided into 10 segments (Fig. 1) by dextral strike-slip tectonics caused by slightly oblique subduction (Carr 1984; DeMets 2001). Arc magmatic compositions vary systematically with latitude in response to changing subduction conditions (Carr et al. 2003, 2007; Feigenson et al. 2004; Hoernle et al. 2002; Patino et al. 2000) as well as arc-parallel mantle flow (Hoernle et al. 2008; Rabbel et al. 2011). The upper-plate crust gets as thin as 30 km in Nicaragua while it is around 38 km in northern Costa Rica with a largely basaltic composition; the crust thickens through El Salvador to 43 km in Guatemala while changing to a felsic, continental composition (Lücke this volume; Kim et al. 1982; Carr 1984; Walther et al. 2000; MacKenzie et al. 2008).

3. Input into the subduction zone

In this section we investigate the H₂O, CO₂, Cl, and S fluxes associated with each of the lithological units of the subducting slab in order to determine the total input fluxes. The volatile components are transported both dissolved in pore water and structurally bound in mineral phases. The pore water, which is most abundant in the marine sediments, is largely expelled by tectonic compression during the first few kilometers of subduction to escape through...
the prism toe and forearc (Jarrard 2003; Saffer 2003; Hensen and Wallmann 2005; Saffer and Tobin 2011). Here we ignore pore water and its dissolved components and determine input fluxes only for the mineral-bound volatile components in the different subducted lithologies: sediments, igneous oceanic crust, serpentinized oceanic mantle, and eroded upper-plate crust.

In the following we determine the input volatile mass fluxes ($F_V$) per unit length of the subduction zone by the volatile concentration ($C_v$) in each rock unit, the thickness ($H$) and density ($\rho$) of that unit adjusted for pore space ($\varepsilon$), and the subduction rate ($V_c$) as

$$F_V = C_v H (1-\varepsilon) \rho V_c.$$ 

Table 1 summarizes the calculation parameters and results for the different slab lithologies.

3.1. Sediments

Jarrard (2003) has quantified the volatile input by subducted sediments at Central America updating earlier work by Plank and Langmuir (1998). DSDP site 495 and ODP site 1039 show that sediment on the incoming plate from Guatemala to Costa Rica comprises about 150 m hemipelagic clays underlain by about 250 m pelagic carbonates; thus carbonate contents vary vertically between 1 to 87% (Li and Bebout 2005). Large variations in clay and carbonate thicknesses occur on the topographically rough seafloor off Costa Rica (Spinelli and Underwood 2004). Jarrard (2003) calculated the weight fractions in the total sediment pile of pore water (48.7 wt%), mineral-bound
water (4.59 wt%), and CO₂ (26.55 wt%). He also estimated chloride contents in pore water assumed to have seawater composition. However, chloride dissolved in pore water or stored in soluble salts will be quickly lost from the subduction system with the expelled pore water. We prefer insoluble mineral-bound chloride concentrations measured by ion chromatography after pyrohydrolysis of DSDP site 495 sediment samples (for analytical procedures see John et al. 2011), giving 810-2273 ppm Cl in the overlying clays and 82368 ppm Cl in the underlying carbonates. The depth-averaged concentration of insoluble mineral-bound Cl is 805 ppm. The average sulfur content of pelagic clay at ODP site 1039 is 5320 ppm whereas there is virtually no sulfur in the underlying carbonate (Kimura et al. 1997); the average sulfur content over the entire sediment column is thus 1900 ppm.

3.2. Cocos plate igneous crust

Jarrard (2003) has analyzed in detail the lithological units of extrusive and intrusive oceanic crust for their volatile-carrying capacities, mainly as a function of age. We use his Central America data to calculate pore water concentrations depth-averaged over the crustal thickness of 5 km offshore Nicaragua through Guatemala (Walther et al. 2000; von Huene et al. 1980) to 7 km offshore Costa Rica (Weinrebe and Flüh 2002). Seismic refraction data shows profoundly reduced seismic velocities within and below seamounts offshore Costa Rica (Ivandic et al. 2010), suggesting more intense hydration of crust heavily populated with seamounts compared to the smooth Cocos seafloor further north (Fig. 1) but this is yet difficult to quantify.
Jarrard’s chloride estimate is again based on pore water; we here prefer measured chlorine contents of altered MORB. Bonifacie et al. (2007) did not leach their altered MORB samples prior to analysis such that their bulk Cl contents of 240-490 ppm include Cl bound in soluble phases (salts) and Cl bound in non-soluble silicate minerals. Own analyses involving leaching of the sample-powders yielded 20-37 ppm insoluble Cl in oceanic crust offshore Guatemala (samples DSDP/67/495/48R/04W/82-84 and DSDP/67/500/19R/01W/20-27) comparable to concentrations of 12-54 ppm Cl found for Izu-Bonin and Nankai (samples ODP/185/1149B/32R/01W/60-63 and IODP/322/C0012A/57R/01W/51-56). The respective bulk chlorine contents were 65-144 ppm and 185-1189 ppm such that Cl bound in non-soluble silicate minerals only accounts for 5-30% of the total Cl subducted with the crust. Depending on when pervading fluids scavenge soluble Cl from the crustal rocks relative to metamorphic phase changes of the Cl-bearing silicates, soluble and insoluble Cl may be fractionated from each other and follow different paths through the subduction system. However, this has not yet been systematically studied and is a subject beyond the scope of this contribution. Since we are mainly concerned with a bulk subduction zone volatile budget, we use the total Cl content (soluble plus insoluble) of ocean crust estimated as 300 ppm in the flux calculations.

Sulfur contents of fresh MORB range between 800 and 1400 ppm (Wallace and Anderson 2000), and vesicular, partly degassed volcanic glasses on the Cocos ridge and associated seamounts have sulfur contents of 300-1000
ppm, in contrast to 1300-1700 ppm found in dense, undegassed hyaloclastites of the Fisher ridge offshore Costa Rica (Werner et al. 1999).

Judging from Troodos ophiolite analyses (Alt 1994), high-temperature seawater alteration of oceanic crust seems to mainly redistribute sulfur from the lower intrusives to the upper crust with little net change in the overall sulfur content while subsequent low-temperature alteration removes some sulfur from the upper extrusives. We estimate an average concentration of 1000 ppm S of the subducting Cocos plate crust but note the large uncertainty associated with this value.

3.3. Serpentinized mantle

Water

High-resolution bathymetry and seismic profiles show intense bend-faulting of the Cocos plate across the outer rise (Fig. 1) with many faults extending into mantle depths that may have provided pathways for deeply intruding water (Ranero et al. 2003; Ranero and Weinrebe 2005). Upper-mantle velocity anomalies revealed by seismic tomography, and heat-flow measurements, imply large amounts of water carried by serpentinized mantle (Abers et al. 2003; Grearemeyer et al. 2005, 2007). Subsequent studies, however, show that some of the velocity anomaly must be attributed to the presence of faults, and that the depth range of hydration is limited by the change from tensional to compressional stress conditions downward in the bending plate (Lefeldt and Grearemeyer 2008; Lefeldt et al. 2009, 2012). Moreover, seismic velocities might be influenced by anisotropy related to bend faulting although such anisotropy has not yet been clearly demonstrated by refraction profiles.
Therefore water contents derived from seismic velocity reduction should be considered maximum values. In trench-perpendicular seismic profiles offshore Nicaragua, Ivandic et al. (2008, 2010) observed an increasing extent of mantle hydration with approach toward the trench (Fig. 2), and concluded that the upper 3.5 km of the Cocos-plate mantle reaching the trench are 12-17% serpentinized, implying a bulk-rock water content of about 2 wt% H₂O. Van Avendonk et al. (2011) analyzed seismic velocity variations in the incoming plate along the trench offshore southern Nicaragua and northern Costa Rica (Fig. 2). Offshore Nicaragua they found some along-trench variation in the degree of serpentinization of Cocos plate mantle but estimate an average water content of 3.5 wt% in the upper roughly 7 km of the mantle. Offshore Costa Rica, however, where the Cocos plate crust is thickened by the Galapagos hotspot track (Cocos Ridge and seamount province; Fig. 1), slab buoyancy only allows for little bending (Ranero and Weinrebe 2005). Here, seismic refraction data provide much faster velocities (V_p=7.8 km/s) in the upper mantle north of Cocos Ridge (Walther 2003; Walther and Flueh 2002). These were supported by the recent along-trench investigations of van Avendonk et al. (2011) who show an increase in seismic velocities, interpreted as a steep decrease in upper-mantle water contents, from southern Nicaragua to central Costa Rica (Fig. 2). Other seismic refraction and wide-angle investigations on the Cocos plate along profiles normal to the margin yielded 8.1 km/s for the mantle on three sections off Costa Rica (Ye et al. 1996), 8.0 km/s northwest of Osa peninsula (Stavenhagen et al. 1998), and 8.1 km/s northwest of Nicoya peninsula (Christeson et al. 1999; Sallares et al. 2001). Using these values we estimate that the mantle offshore of Costa
 Rica is much less hydrated than offshore of Nicaragua. The degree of serpentinization might be variable, ranging from 0% to ~10% of serpentinization. Thus, bound water contents will be ≤1 wt% and limited to the uppermost 1-3 km of the mantle.

The seismological observations at Nicaragua have been used to calibrate a numerical reactive-flow model of outer-rise mantle serpentinization (Iyer et al. 2012) that uses temperature-dependent reaction rates (between 100-400°C with maximum at 270°C), plate temperature as a function of plate age, and a linear increase in porosity toward the trench simulating the effect of bend faulting. Next to reaction kinetics, plate age and convergence rate (i.e. the time from onset of bend faulting to subduction at the trench) are the major controlling factors on the degree of slab mantle serpentinization. Application of this model to Central America (K. Iyer, pers. comm. 2012) shows that the expected slab mantle water contents are very similar from Nicaragua through El Salvador to Guatemala but lower at Costa Rica as observed seismically. In our flux calculations for serpentinized mantle we use 3 wt% H₂O for Nicaragua to Guatemala and 1 wt% H₂O for Costa Rica (Table 1).

**Carbon dioxide**

The highly variable carbon contents of serpentinites are controlled by parent-rock composition, by hydrothermal alteration and, near the seafloor, by microbial activity depositing organic carbon. In ultramafic hydrothermal systems carbonate may precipitate from pure seawater, from heating of seawater and from cooling of hydrothermal fluids (Eickmann et al. 2009; Bach et al. 2011). Analyzed serpentinites from a wide range of settings and
formation conditions (but none from outer-rise bend faulting) contain 60 to 300 ppm CO₂ although veined rocks may have wt-%-contents (Delacour et al. 2008a; Alt et al. 2013). Since geophysical studies limit serpentinization to <17% at the Middle America Trench, we adopt a value of 200 ppm CO₂.

**Chlorine**

Scambelluri et al. (2004) determined 729 ppm Cl as an average value of oceanic serpentinite and showed how this concentration gradually decreases to 45 ppm Cl in high-pressure olivine-orthopyroxene rocks as a consequence of metamorphic slab dehydration. Kendrick et al. (2013) determined 990-2300 ppm Cl in 93-99% serpentinized rocks at the Guatemalan forearc but their global seafloor-serpentinites data set shows <700 ppm Cl at <60% serpentinization as expected at the Middle America Trench. The analyses of Scambelluri et al. and Kendrick et al. did not include prior thorough leaching and give bulk (soluble plus insoluble) Cl concentrations. Pre-subduction serpentinites analyzed by John et al. (2011) with prior leaching have concentrations of 120-350 ppm of insoluble, silicate-bound Cl. Serpentinites from the Hess Deep contain 900-5100 ppm (average 2524 ppm) water-soluble chloride stored in salt minerals in addition to 300-1200 ppm (average 535 ppm) insoluble Cl stored in other minerals (Barnes and Sharp 2006).

Obviously there is a wide margin of uncertainty in estimating the Cl concentration of serpentinite subducted at the Middle America Trench and, as discussed for ocean crust in chapter 3.2, the fate of soluble versus insoluble Cl as the serpentinite dives to high pressures and temperatures remains unclear. Kendrick et al. (2012) argue that a significant fraction of Cl in
serpentinite is subducted beyond sub-arc depths. In the flux calculations we use 1000 ppm Cl as a conservative estimate of the bulk Cl content but it may also be considered as an upper bound of insoluble Cl content.

**Sulfur**

The combined data of serpentinized harzburgites from the Hess Deep at the western end of the Cocos-Nazca spreading center (Alt and Shanks 1998) and the Mariana forearc (Alt and Shanks 2006) show sulfur contents similar to fresh harzburgite (<200 ppm) at <50% serpentinization; up to 860 ppm S are only reached at higher degrees of serpentinization. Oceanic serpentinites formed at slow-spreading centers may even reach 1 wt% sulfur concentration (Alt and Shanks 2003; Alt et al. 2013; Delacour et al. 2008b). Here we assume an average concentration of 200 ppm S (similar to little altered harzburgite; Puchelt et al. 1996) for the only moderately serpentinized uppermost mantle of the subducting Cocos plate.

### 3.4. Subduction erosion

Subduction erosion, i.e. the subduction of material scraped off the base of the overlying plate, occurs at a large fraction of the global subduction-zone length (von Huene and Scholl 1991) and is another process introducing volatile components into the subduction system. Subduction erosion mainly operates underneath the continental slope promoted by hydrofracturing caused by overpressured water released from the subducted sediments (Ranero et al. 2008). Modeling suggests that subduction erosion occurs when forearc sediments have high rheological strength, i.e. are less weakened by fluids
(Gerya 2011; Gerya and Meilick 2010). Subduction erosion occurs along the entire Central American subduction zone but the detailed processes and rates vary (Ranero and von Huene 2000; Ranero et al. 2000). Where the smooth Cocos plate ocean floor subducts beneath Guatemala (Fig. 1), Vannucchi et al. (2004) determined an erosion rate of about 12 km$^3$/Ma/km. In contrast, where the Cocos ridge and seamount province subduct beneath Costa Rica (Fig. 1), subduction erosion is much more efficient with 113 km$^3$/Ma/km for about the past 6.5 Ma (Vannucchi et al. 2003). For the time span back to 17 Ma, the average erosion rate was 35 km$^3$/Ma/km (Vannucchi et al. 2001). The dramatic increase in erosion rate thus roughly coincides with the Pliocene onset of subduction of the Cocos Ridge (Hoernle et al. 2002).

The nature of the material subducted by erosion is difficult to determine. Based on geophysical evidence and ODP drilling results, Vannucchi et al. (2001) conclude that the forearc basement eroded off Costa Rica corresponds to the geological structure of the Nicoya peninsula, which is formed by a basement of accreted and brecciated ocean crust overlain by marine sediments of Late Cretaceous through Eocene age. Similarly, Azema et al. (1982) interpreted seismic profiles to show stacked ophiolitic slabs forming the forearc basement off Guatemala. Walther et al. (2000) identified accreted oceanic crust as the forearc basement offshore Nicaragua. Ages of accreted complexes range from 20 to 70 Ma (Hoernle et al. 2002). Thus the material subducted by erosion from Costa Rica through Guatemala seems to have a dominant composition similar to strongly altered oceanic crust. As an approximation, we thus estimate mineral-bound volatile contents as 3.57 wt%
H₂O and 0.54 wt% CO₂ (mean values for 20-70 Ma old oceanic crust after Jarrard 2003). We estimate 300 ppm Cl and 1000 ppm S in the eroded material as in Cocos plate crust (see 3.2).

3.5. Input fluxes along the subduction zone

The average calculated subduction input fluxes of the mineral-bound volatiles at Central America are 53 Tg/Ma/m H₂O, 9.3 Tg/Ma/m CO₂, 1.6 Tg/Ma/m Cl, and 1.6 Tg/Ma/m S (Table 1), such that the typical composition of the bulk subducted volatile mass is approximately 81% H₂O, 14% CO₂, and 2.5% Cl and 2.4% S (ignoring other volatiles such as F, Br, N, etc.). The input fluxes of mineral-bound water, CO₂, Cl and S gradually increase from Guatemala to Nicaragua mainly in response to increasing convergence rate since there is no indication of major changes in subducted lithology (Fig. 3). Toward Costa Rica, however, H₂O and Cl input fluxes drop because the Cocos plate mantle is very little serpentinized (Fig. 3). In contrast, thicker Cocos Plate oceanic crust, high rates of subduction erosion and faster convergence cause an increase in S and CO₂ subduction.

The input of mineral-bound water is dominated by serpentinized mantle (Fig. 4a), except at Costa Rica where ocean crust and subduction-erosion are the main water carriers. For comparison, published globally averaged distributions of water fluxes across the lithologies are shown by arrows in Fig. 4a; while our data for Costa Rica are similar except for the stronger role of subduction erosion, our results for Nicaragua through Guatemala suggest that mantle serpentinite is much more important than igneous crust as a water carrier.
More than 60% of subducted CO$_2$ is carried by the sediments (Fig. 4b) while ocean crust delivers another 20-30%. The crust also carries about 20% of subducted chlorine but the Cl input is clearly dominated by about 80% riding with the serpentinite (except at Costa Rica). This is distinctly different from Jarrard (2003) who had the sediments as the major carrier of chlorine (Fig. 4c) because he considered chlorine in pore water rather than mineral-bound chlorine as done here, and he did not consider serpentinized mantle as a chlorine carrier.

The subduction input of sulfur is largely dominated (>70%) by the subducted ocean crust (Fig. 4d). Thus the uncertainties that most affect the flux estimates are those of water contents in crust and serpentinite, CO$_2$ contents in sediments, chlorine contents in serpentinite, and sulfur contents in the crust. Uncertainty in the nature of material eroded from the forearc plays a role at Costa Rica but is less important along the remaining subduction zone. These potential errors in volatile concentrations translate directly into relative errors in the flux calculations and are larger than relative uncertainties in the physical subduction parameters.

4. Output at the forearc

Fluid seepage at the Central American forearc is focussed at a variety of structures such as mud volcanoes, mud domes, faults, and scarps formed by seamount subduction. High-resolution bathymetric, geophysical and geochemical studies as well as video observations have identified more than 100 fluid seep sites at the forearc of Costa Rica and Nicaragua, which are typically concentrated at mid-slope depths (Fig. 5; Sahling et al. 2008; Ranero
et al. 2008). Discharging fluids are generally rich in methane feeding bacterial
and other organic vent communities that act as a benthic filter limiting
methane outflow into the ocean bottom water (Linke et al. 2005; Karaca et al.
2010, this volume; Suess this volume). Measured CH$_4$ fluxes vary significantly
over time scales of months to years (Mau et al. 2006, 2007, this volume).
Moreover, geologic records show that the seepage activity of mud mounds
varies spatially and temporally on time scales of $10^3$ to $10^5$ years (Liebetrau et
al. this volume; Mörz et al. 2005; Kutterolf et al. 2008). The largest outflow
rates have been determined for seep sites at seamount-subduction scarps
offshore Costa Rica (Mau et al. this volume) but the density of seeps is larger
offshore Nicaragua (Fig. 5).
Seismic profiles show that mounds and other cold seeps are underlain by
relatively undeformed slope sediment and likely fed by fault-controlled fluid
pathways which may originate at the plate boundary several kilometers below
the seafloor (Ranero and von Huene 2000; Hensen et al. 2004; Schmidt et al.
2005). Fluid movement near the plate boundary and through the forearc is
associated with pore pressure change (Saffer 2003) and may cause seismic
swarm activity which was indeed observed offshore Nicaragua (Thorwart et al.
this volume). Emanating fluids are diluted with respect to seawater by mixing
with freshwater derived from smectite to illite transformation as shown by
$\delta^{18}$O-$\delta^D$ systematics of fluid endmembers (Hensen et al. 2004) and
thermogenically formed CH$_4$ in the mound fluids (Schmidt et al. 2005). The
most likely source of that freshwater is the subducted hemipelagic sediment,
because it is rich in detrital smectite (Spinelli and Underwood 2004) from
terrestrial weathering, other than at high-latitude margins where authigenic
smectite yields a more limited freshwater reservoir (Scholz et al. 2013).

Moreover, temperatures of 60-150°C required for the smectite to illite
transformation are typically not reached inside the continental slope but within
the sediments at the plate boundary (Fig. 5; Ranero et al. 2008). Elevated
δ¹⁸O values of mound carbonates indicate that the supply of deep-seated
fluids is a long-term process (Han et al. 2004; Mavromatis et al. this volume;
Liebetrau et al. this volume; Suess this volume). However, expelled fluids
have a geochemical signature that shows also evidence for various types of
fluid-rock interaction processes during the ascent. Thus, the ¹²⁹I/I fluid ages of
≥25 Ma (Lu et al. 2007) are inconsistent with the fluid directly derived from the
subducting sediments but rather require an additional source such as iodine
released from old sediments of the wedge.

The average density along the Costa Rica - Nicaragua margin is one seep
every 4 km. Based on seep-flux measurements, Ranero et al. (2008)
estimated an average fluid flow rate per seep/mound of 0.5-1.0 cm/yr that
corresponds to an average present-day discharge of 2500-5000 m³/yr per 4
km equivalent to 0.625-1.25 Tg/Ma/m (per unit trench length). Saffer (2003)
investigated porosity and pore pressure variations at the Costa Rica forearc
and deduced a dewatering rate of underthrust sediment of 8 Tg/Ma/m across
the first 1.6 km of subduction, corresponding to 65% of subducted sediment
pore water. Moore et al. (2011) show that this rate of pore water drainage for
the erosive Costa Rican margin is much more rapid than at the accretionary
Nankai margin. Moreover, this flux is 6-13 times the flux estimated from
measurements at the mid-slope seeps some 20-30 km from the trench, but
much of it is typically lost by bedding-parallel backflow and hence, would not
be available as a source for seep fluids. The 0.625-1.25 Tg/Ma/m seep flux would account for 58-116% of the input flux of mineral-bound water in the sediment but a significant fraction of mineral-bound water must be retained in the sediments because high-pressure metasediments typically contain OH-bearing minerals up to pressures and temperatures well beyond the sub-forearc (Domanik and Holloway 1996; Bebout et al. 2007; Hacker 2008). Hence, while containing freshwater from the smectite to illite transformation, a significant fraction of the seep flux must derive from pore water of subducting sediment and/or, more likely, the overlying forearc wedge. Nevertheless, even ignoring the contribution of pore water, the seep output of 0.625-1.25 Tg/Ma/m only accounts for ≤2% of the total mineral-bound water input with the subducting slab.

Freshened fluids emanating at the slope most likely originate from subducting sediments but have become strongly modified by fluid-rock interactions during passage through the forearc wedge (Suess this volume) which make it impossible to derive quantitative estimates for slab-sediment-derived fluxes of CO₂, S and Cl through the forearc. Methane and CO₂ are likely to be produced in the subducting sediments within the temperature window of the smectite to illite transformation as suggested by findings of thermogenic methane in seep fluids (Schmidt et al. 2005). However, typically components from biogenic and thermogenic sources are mixed (C. Hensen, unpublished data) such that exact quantities are difficult to assign. Carbon stored in carbonates is stable at P-T-conditions of subducting sediments below the forearc and cannot contribute to C-fluxes to the forearc. Similarly, pyrite and
other Fe-sulphides are also stable at these conditions such that mineral-bound sulfur will not be lost. Moreover, a loss of pore-water sulphate to the forearc is also unlikely as it is quantitatively reduced by anaerobic oxidation of methane (Hensen and Wallmann 2005) and subsequently precipitated as iron sulphides. The net loss of Cl to the forearc wedge through seepage is difficult to assess as it depends on the mixing ratio between available pore water at depth and clay-mineral derived water. Since pore water of normal salinity may be taken up elsewhere along the flow path, the initial concentration of Cl cannot be reconstructed. However, compared to the large loss of Cl with pore water due to tectonic compression close to the deformation front, the contribution from mineral-bound (soluble or insoluble) chlorine can most likely be neglected.

5. Output at the volcanic arc

The volcanic arc is the major site of volatile output of the subduction zone. Silicate melts originating in the mantle wedge metasomatized by slab-derived fluids carry dissolved volatiles into crustal levels where they become partly stored in plutonic rocks but mostly exsolve during magma storage and during eruptions, and are largely transferred into the atmosphere. In the following, we apply two approaches to estimate volatile fluxes from the mantle wedge to the volcanic front: (1) long-term average fluxes based on erupted magma volumes and associated melt compositions, and (2) present-day fluxes based on measurements at continuously degassing volcanoes.
5.1. Long-term magma and volatile fluxes

Magma fluxes

In order to determine volatile fluxes from the arc via volcanic eruptions, both the erupted magma masses and the respective volatile concentrations need to be known. Carr (1984) and Carr et al. (1990, 2007) obtained long-term average magma fluxes from CAVA volcanoes by measuring the volumes of the volcanic edifices and constraining their age. Kutterolf et al. (2008) extended that work by also including the magma masses stored in the widely dispersed tephras formed by highly explosive eruptions, which account for about half of the calculated total magma mass output of the arc. Erupted magmas span a wide range in compositions from basalt through rhyolite, with the widespread tephras mostly having evolved magmatic compositions. The parental magma masses needed to form the observed differentiated compositions by fractional crystallization can be calculated by geochemical mass balance and are included in the total magma production of volcanic activity. Kutterolf et al. (2008; their Fig. 6) show how the resulting magma fluxes vary between individual volcanic centers along the volcanic front. Here we simplify that data by calculating the long-term average magma flux for each of the 10 tectonic segments of the arc (Fig. 1).

Volatile concentrations

Volatile concentrations in about 2500 melt inclusions and matrix glasses of tephra samples collected along the entire CAVA have been determined by a variety of methods in SFB 574. It is generally assumed that melt inclusions represent the pre-eruptive volatile contents of melts while matrix glasses
contain the volatiles remaining after degassing to atmospheric pressure, such
that the concentration difference between both gives the volatile fraction
degassed into the atmosphere. This is a minimum assumption for poorly
soluble volatiles (CO₂, S) because they may have formed a separate fluid
phase already during entrapment of the melt inclusions.
Water contents were measured by ion probe and FTIR in melt-inclusion and
matrix glasses, and calculated from plagioclase-melt equilibrium compositions
after Putirka (2008) and Lange et al. (2009) as well as from amphibole
compositions after Ridolfi et al. (2010). CO₂ contents of primitive melt
inclusions have been measured by ion probe (Wehrmann et al. 2011) while S
and Cl contents have been mostly analyzed by electron microprobe.

Volatile/K₂O ratios
The more soluble volatiles (H₂O, Cl) are typically enriched like incompatible
elements during differentiation of magmas from basaltic to more evolved
compositions. Since potassium also behaves as an incompatible element in
the CAVA magmas (except in rare alkali feldspar-bearing rhyolites in
Guatemala), we have corrected for the fractionation effect by determining the
volatile/K₂O mass ratios. Using mass-weighted average bulk-rock K₂O
contents for each volcano, we have converted the erupted magma mass
fluxes along the arc to the respective K₂O mass fluxes which, when multiplied
by the respective volatile/K₂O mass ratios, yield the magmatic volatile mass
fluxes from the mantle to the surface. In the following, we investigate along-
arc variations in volatile/K₂O in order to derive the parameterizations used for
volatile flux calculations; typically these are upper envelopes of observed data
based on the assumption that reduced volatile/K$_2$O values in any magmatic system result from volatile exsolution.

Water

In their study of primitive melt inclusions in basalt-hosted olivines along the CAVA, Sadofsky et al. (2008) found H$_2$O contents to systematically increase with Ba/La, a geochemical slab signature. H$_2$O/K$_2$O values measured in primitive melt inclusions (Sadofsky et al. 2008; Wehrmann et al. 2011) reach values up to 20 in Nicaragua but only up to 4.5 in Guatemala and 3.5 in Costa Rica (Fig. 6a). The high values in Nicaragua come from samples of Cerro Negro, Nejapa and Granada which are all very K-poor (avg. 0.19 wt% K$_2$O resulting in avg. H$_2$O/K$_2$O=6.1), while maximum water concentrations exceed those of other mafic CAVA suites by only up to 1 wt%. In contrast, samples from Masaya have avg. 1.47 wt% K$_2$O and H$_2$O/K$_2$O=1 which is more compatible with the range observed in central Nicaraguan felsic rocks.

H$_2$O/K$_2$O values in mafic melt inclusions of Guatemala and Costa Rica fit the values of evolved tephras there. The fact that mafic compositions reach higher maximum H$_2$O/K$_2$O values than felsic tephras is due to buffering of dissolved H$_2$O at the saturation limit in many of the felsic compositions as shown by the occurrence of aqueous fluid inclusions and thermobarometric constraints. We therefore use an upper envelope of the H$_2$O/K$_2$O along-arc variation (Fig. 6a) to calculate the magmatic water fluxes from the mantle to the arc.

Carbon dioxide
CO₂ contents of primitive melt inclusions reach maximum values (≤1800 ppm) at Nicaragua and drop off towards Costa Rica and Guatemala (≤500 ppm); in contrast to H₂O contents, CO₂ contents do not vary systematically with geochemical slab signatures such as Ba/La (Wehrmann et al. 2011). Felsic melt inclusions have CO₂ concentrations below detection limits. CO₂/K₂O values are much higher for Nicaragua than for other parts of the volcanic front (Fig. 6b). This is certainly partly due to the K-poor nature of primitive melt inclusions there, as discussed above for H₂O. In contrast to H₂O, which in Nicaragua reaches only 1.4 times the maximum concentrations of adjacent regions, the highest CO₂ contents of mafic melt inclusions in Nicaragua are 3 times those in the other parts of the arc such that relatively higher CO₂/K₂O than H₂O/K₂O values are to be expected. On the other hand, most of the K-poor, more MORB-like samples (cf. Sadofsky et al. 2008) come from the Nejapa and Granada volcanic systems, which contribute little to the overall magma and K₂O fluxes of the east-Nicaraguan arc segment (cf. Walker et al. 1990; Freundt et al. 2006; Avellan et al. 2012) such that using the largest CO₂/K₂O values would strongly bias the volatile flux calculations for Nicaragua. However, the melt inclusion data define both water-rich and water-poor degassing paths in CO₂ vs. H₂O space which indicate that all melts had exsolved CO₂ at pressures ≤500 MPa prior to melt-inclusion entrapment, with more extensive exsolution for melt compositions with high slab contributions (Wehrmann et al. 2011). Thus all measured CO₂ contents yield minimum estimates of magmatic CO₂ flux. As a conservative estimate we calculate the arc CO₂ fluxes using the envelope of CO₂/K₂O values indicated in Fig. 6b but emphasize that uncertainties remain particularly large for CO₂.
Chlorine

Chlorine contents in felsic rocks are higher than in mafic rocks, and maximum chlorine contents in the felsic rocks decrease northward probably as an effect of increasing apatite fractionation associated with the change from dacite to rhyolite as the most evolved composition. Cl/K₂O ratios decrease from maximum values at Nicaragua towards Costa Rica and Guatemala in both mafic and evolved volcanic rocks, and we use a parameterization of along-arc variation as shown in Fig. 6c to estimate magmatic chlorine fluxes.

Sulfur

Sulfur contents do not show a systematic variation along the arc in mafic rocks. Felsic melts are all strongly depleted in sulfur relative to mafic compositions. The along-arc variation of S/K₂O in mafic-rock melt inclusions is shown in Fig. 6d.

Volatile fluxes

Figure 7 and Table 2 summarize the along-arc variations in long-term average mass fluxes (per unit arc length) of magma, K₂O and the volatile species for the tectonic segments of the volcanic front. The spreadsheet provided as electronic supplement is an extension of Table 2 of Kutterolf et al. (2008) that includes the detailed volatile flux calculations. The largest source of error in the magma fluxes (that translates into all other fluxes) are uncertainties in the age of volcanoes; with a mix of well and poorly constrained ages on each segment we estimate a typical error for segment-wise fluxes of ±20%.
Considering uncertainties in the parameterization of volatile compositions (Fig. 6) the total error on volatile fluxes may be about ±40% (Fig. 7). The unsteady but overall northward increase in magma and K$_2$O fluxes largely controls a similar pattern in the H$_2$O fluxes while Cl fluxes remain roughly constant along the arc. Particularly large fluxes of CO$_2$ and sulfur result for Nicaragua. For the whole arc, the volatile fluxes from the mantle to the volcanic front are 6.18 Tg/Ma/m H$_2$O, 0.17 Tg/Ma/m CO$_2$, 0.54 Tg/Ma/m S, and 0.22 Tg/Ma/m Cl. The CO$_2$ flux is smaller than the value of 0.67 Tg/Ma/m calculated by Wehrmann et al. (2011) using the Nicaraguan maximum CO$_2$/K$_2$O values for the entire volcanic front (cf. Fig. 6b). These mass fluxes indicate a long-term average composition of volatiles delivered from the mantle source to the arc volcanoes of 87% H$_2$O, 2.5% CO$_2$, 7.5% S and 3% Cl (ignoring other volatile species). Compared to the average subduction input composition, the average output composition has almost the same proportions of H$_2$O and Cl but is depleted in CO$_2$ and enriched in S.

At surface pressure conditions, the solubilities of H$_2$O, CO$_2$ and S in silicate melt are very small (e.g., Blank et al. 1993; Behrens et al. 2004; Botcharnikov et al. 2004; Carroll 2005; Dixon et al. 1995; King and Holloway 2002; Papale 1999) such that the fluxes of these volatiles into the atmosphere can be assumed equal to their fluxes into the volcanoes, although a minor fraction may remain stored in the crust (in hydrous minerals, crustal fluids). However, this is not true for chlorine because, on average, about half the initial Cl content is retained in the matrix glasses of the volcanic rocks.
Another approach to assess mass fluxes at the volcanic arc makes use of the monitored degassing of SO$_2$ at active volcanoes. We have compiled data from optical remote sensing of gas plumes at 17 Central American volcanoes (others are not monitored or not presently degassing) that was obtained during the last 25 years (Mather et al. 2006; Hilton et al. 2002; Zimmer et al. 2004; Andres and Kasgnoc 1998) and own unpublished data obtained in the SFB574 and NOVAC (Network for Observation of Volcanic and Atmospheric Change) projects (Frische et al. 2006; Galle et al. 2012; Bo Galle, pers. comm. 2012). The measured SO$_2$ fluxes range from 15 to 1540 tons per day (averages of the temporally varying monitoring data for each volcano). Adding up available average fluxes of the volcanoes, the resulting sulfur fluxes per unit arc length for each arc segment are of comparable magnitude to those determined from magma masses (Fig. 8a), although they are derived from only 17 compared to 71 volcanoes (note that no SO$_2$ flux data are available for the east-Guatemalan and central-Salvadorian segments). In fact, when summing up for the entire volcanic front, the present-day open-vent sulfur flux from the 17 volcanoes (0.84 Tg/Ma/m) is 1.4 times larger than the sulfur flux derived from the long-term magma fluxes at the 71 volcanoes; it is also larger than previously published open-vent flux values ($\leq$0.66 Tg/Ma/m; see Fig. 12 below). We note that monitoring open-vent degassing may only capture part of the total degassing; Shinohara (2013) found that diffuse soil and spring degassing in Japan accounts for 16% of total S output (and for 39% H$_2$O, 44% CO$_2$, 58% Cl).
The magma mass fluxes required to feed the observed open-vent SO$_2$ fluxes can be calculated using typical mafic-melt sulfur concentrations (Sadofsky et al. 2008; Wehrmann et al. 2011), and are compared with the long-term erupted magma fluxes for those volcanoes in Fig. 8b. The magma fluxes differ by less than a factor of ten for 11 out of the 17 volcanoes. The major reason why mass-flux estimates from the two approaches differ significantly is probably their greatly differing time scales of observation ($10^1$ versus $10^5$ years), because both volcanic magma emission rates and open-vent degassing rates vary over wide ranges of time scales. Another difference is that quiescent degassing may derive from magmas that never erupt whereas the long-term approach based on erupted magma masses does not capture intrusive magmas that never made it to the surface. The "intrusive" component of arc magmatism certainly remains the major factor of uncertainty in the estimation of magma and volatile mass fluxes.

5.3. Arc output versus subduction input

Here we focus on the arc output versus trench input comparison because fluid emissions through the forearc are comparatively very small (chapter 4). For water and chlorine the outputs at the arc account for about <26% and <20% of the respective inputs at the trench. The relative output of CO$_2$ (0.1-2.3%) is an order of magnitude lower compared to H$_2$O and Cl except at Nicaragua where it reaches 5% (Fig. 9). On the other hand, the relative sulfur outputs derived from both long-term magma fluxes (9-82%) and present-day open-vent monitoring (3-197%) significantly exceed the relative outputs of the other volatiles (Fig. 9). Recycling efficiencies determined by Ruscitto et al. (2012)
using magma fluxes of Sadofsky et al. (2008) and input fluxes including
mantle serpentinization of van Keken et al. (2011) are similar to our values for
H₂O, Cl and S but about 10 times larger for CO₂ (Fig. 9). We will later discuss
the significance of the different input-output relationships but at this point the
comparison serves to emphasize the imbalance between input and output
volatile fluxes. Since the output at the arc only accounts for a minor fraction of
the input particularly for H₂O - which is the dominant volatile component by
mass - we clearly need to look for other sinks in the subduction system.

6. Other volatile reservoirs in the subduction system

In the following we review information on additional volatile reservoirs in the
subduction system. We focus on Costa Rica and Nicaragua where the most
detailed geophysical studies of subduction zone structure are available.

6.1. Upper-plate geophysical anomalies

Seismic tomography has identified strongly reduced Vₚ, and increased Vₚ/Vₛ,
in the mantle below the arc down to the subducting slab at Nicaragua; this
anomaly (A4 in Fig. 10) is strongest below the Concepción-Maderas
volcanoes but diminishes through northern to central Costa Rica (Dinc et al.
2011, 2010). It is plausible to assume that this anomaly reflects fluids and
melts in the subarc mantle, and its southward diminishing qualitatively
correlates with magma production rates decreasing from Nicaragua to Costa
Rica (Fig. 7), decreasing geochemical slab signals (e.g., Ba/La) in arc-magma
compositions (Carr et al. 1990), and a change from extensional to
compressional tectonic stresses (Walther et al. 2000; Marshall and Anderson
1995; La Femina et al. 2009). Only in the lower half of the subarc anomaly at Nicaragua (approximately from 200 to 100 km depth, about 50 km cross-arc width) do mantle temperatures exceed the wet peridotite solidus (e.g., Peacock et al. 2005; Rüpke et al. 2002) such that volatiles may be withdrawn via ascending melts. Elsewhere in the anomaly volatiles are trapped in hydrous minerals formed in the mantle.

Another seismic velocity anomaly lies in the upper-plate lithosphere, where it extends from the contact to the subducting slab at 30-50 km depth towards the Nicaraguan volcanic arc (A1 to A2 in Fig. 10; Dinc et al. 2011). This is interpreted as a sub-forearc hydrated zone that accumulates fluid that is released from the slab at greater depths and migrates upward along the steeply (c.80°) dipping slab. The further transport of fluids from near the slab toward the arc is probably facilitated by extensional faulting (Dinc et al. 2011). However, the discovery of northwestward trench-parallel flow in the mantle wedge (Hoernle et al. 2008; Rabbel et al. 2011) also suggests a lateral component of volatile transport that may add to the observed reservoirs.

The strongest negative velocity anomaly at Costa Rica comprises the forearc to about 20 km depth (A5 in Fig. 10), probably reflecting strong hydration facilitated by intense fracturing of the forearc by seamount subduction (Arroyo et al. this volume; Dinc et al. 2010). A seismic velocity anomaly at the tip of the mantle wedge (A6 in Fig. 10) is also observed at central Costa Rica but is less well developed compared to Nicaragua. This anomaly has been interpreted to result either from hydration of the mantle tip (Dinc et al. 2010) or from underplating by eroded forearc material (Arroyo et al. 2009; this volume).
No such anomaly at the mantle wedge has been detected at northern Costa Rica (DeShon et al. 2006; Dinc et al. 2010) suggesting limited or absent mantle-wedge hydration. Below the volcanic arc of Costa Rica there is only a very small negative velocity anomaly in the uppermost crust (A7 in Fig. 10).

A magnetotelluric profile across northern Costa Rica basically supports the seismic anomalies there as zones of high electrical conductivity due to hydration (Brasse et al., 2009; Worzewski et al. 2011). By reviewing global magnetotelluric subduction zone data, Worzewski et al. (2011) concluded that a hydrated region (their low-resistivity anomaly G, projected as A3 into Fig. 10) at 20-40 km depth and 20-40 km in front of the volcanic arc exists in many mature subduction zones around the globe.

The geophysically observed anomalies are snapshots of present conditions; they cannot reveal volatile fluxes but they can be interpreted in terms of stored water masses. These can be determined by measuring the volume per unit arc length enclosed by the $\Delta V_p$ isolines, and estimate water contents in the anomaly volumes from the simple relation

$$H_2O \ (\text{wt\%}) = -0.31 \times \Delta V_p \ (%)$$

(Carlson and Miller 2003) ignoring P-T dependencies that are insignificant compared to other uncertainties. Here we obtain minimum estimates for the stored water masses by just considering the $\Delta V_p=-4\%$ volumes with the water concentration corresponding to that value (i.e., ignoring lower water contents
outside and higher water contents inside these volumes). In order to understand the instantaneous distribution of water in the subduction system, we also calculate the mass of water (per unit arc length) introduced into the system during the time the slab takes to descend from the trench to sub-arc depth (229 Tg/m at Nicaragua, 103 Tg/m at Costa Rica), to then determine the fractions of the total water stored in each reservoir.

The amount of water stored in the Nicaraguan sub-arc anomaly A4 (2000 km$^3$/km volume per unit arc length, 74.4 Tg/m) then would correspond to 21 wt% of the total water in the subduction system. The large anomaly A1 to A2 (1400 km$^3$/km, 52.1 Tg/m) would account for another 15 wt% of water. The water content in the low-resistivity anomaly G (A3 in Fig. 10) as determined by Worzewski et al. (2011) would be barely 1 wt% of the total, hence an insignificant fraction compared to A1-A2 with which it overlaps. At Costa Rica, no significant hydration below the arc has yet been detected, partly due to insufficient spread of seismic profiles across the arc. The anomaly A6 at the tip of the mantle wedge is small (150-375 km$^3$/km; Dinc et al. 2010; Arroyo et al. this volume), making up 1-5 wt% of the total water. We do not include the large Costa Rican forearc anomaly A5 (Dinc et al. 2010) in this budget because this is probably mostly fed by expelled pore water rather than mineral-bound water.

In summary, reservoirs outside the subducting slab hold between 12 wt% (at Costa Rica) and 35 wt% (at Nicaragua) of the total water presently stored in the subduction system. We do not know, however, if these reservoirs are in a transient state, shrinking or swelling, or in a steady state where water influx and outflux are balanced.
6.2. Volatile fluxes beyond subarc depths

Numerical modeling based on experimental investigations of the metamorphic dehydration of subducting slabs predicts that the cooler (i.e., older and faster-sinking) the slab the larger the fraction of water that is retained in the slab to beyond sub-arc depths (Schmidt and Poli 2003; Rüpke et al. 2004; Hacker 2008). Also, cooler slabs are expected to store more water initially particularly in serpentinized uppermost mantle (Iyer et al. 2012) such that absolute and relative fluxes of water into the deep mantle increase with slab age. For Central America with slab ages of 15-20 Ma, Rüpke et al. (2004) predicted that <10% of the initial water content are retained beyond sub-arc depths mainly by the serpentinized slab mantle. Recent modeling by van Keken et al. (2011) applied to Central America, which considers three scenarios of no, 20% or full serpentinization of uppermost slab mantle, shows that water flux with the slab decays to <60% of the input at 150 km depth, and <30% at 230 km depth. Sub-arc depths to the slab top range from 78-106 km at Guatemala through 118-148 km at Nicaragua to 80-120 km at Costa Rica (Syracuse and Abers 2006), and fluid released between 150-230 km may flow updip into the sub-arc region (cf. Tsuno et al. 2012) so that it is difficult to define the depth where flux into deep mantle may be determined. Faccenda et al. (2012) identified a stress-controlled process of fluid transport in the slab even without involving high-pressure hydrous minerals, and they conclude from their model that water transfer into deep mantle remains <20% of the input. Global modeling over geologic time scales constrained by sea-level changes suggests that about 40% of subducted water reach the deeper mantle (Parai
and Mukhopadhyay 2012). In summary, a minimum of 20-30% of water input into the Central American subduction system may be lost to mantle reflux.

7. Discussion

7.1. Comparing input fluxes

Almost all studies investigating subduction zone volatile input have focussed on water, and some have considered only selected lithologies of the downgoing slab. Figure 11 compares results for total slab H\textsubscript{2}O input either for Central America or globally, where global data have been recalculated to 44,000 km total subduction zone length. Obviously input fluxes based on sediment and crust compositions alone are lower than those which also consider serpentinized mantle. Where serpentinized mantle is included in the budget, flux estimates vary widely due to large uncertainties in the extent of serpentinization (cf. Rüpke et al. 2002, 2004, and van Keken et al. 2011). Our results for Central America make use of the latest geophysical observations that now include both across- and along-trench profiling but focus on Costa Rica and Nicaragua such that much greater uncertainty remains for El Salvador and Guatemala. Apart from our study here, only Hacker (2008) explicitly included the effect of subduction erosion on the water input.

Compared to the more recently estimated global average input fluxes of water (Rüpke et al. 2004; Hacker 2008; van Keken et al. 2011; Parai and Mukhopadhyay 2012) our estimates for Central America are about two times higher (Fig. 11) confirming earlier observations that the subducting Cocos plate is unusually wet largely due to mantle serpentinization (e.g., Abers et al. 2003). Lateral variations in input flux along the 1265 km long Middle America
trench, as well as those along the 1480 km long Chile trench (Völker et al.,
this volume), are wider than the ranges of individual global estimates.

Subduction fluxes of other volatiles than water have been rarely investigated. Previously estimated global average input fluxes of CO$_2$ are 5 Tg/Ma/m (Peacock 1990), 5-23 Tg/Ma/m (Bebout 1996) and 3.4 Tg/Ma/m (Jarrard 2003). Jarrard's value for Central America of 8.6 Tg/Ma/m is similar to our average value of 9.3 Tg/Ma/m (where the range over subduction segments is 7.8-11.4 Tg/Ma/m) while Li and Bebout (2005) calculated a lower value of 5.7 Tg/Ma/m CO$_2$. The chlorine input fluxes determined by Jarrard (2003) of 0.47 Tg/Ma/m (average global input) and 0.66 Tg/Ma/m (Central America), and by Straub and Layne (2003) for the Izu subduction zone of 0.1 Tg/Ma/m, are significantly lower than our average value of 1.62 Tg/Ma/m Cl (range 1.27-1.85 Tg/Ma/m). Alt et al. (2013) estimate a global average sulfur subduction rate of ~1.8 Tg/Ma/m similar to our 1.6 Tg/Ma/m for Central America.

### 7.2. Comparing arc output fluxes

The range of water output fluxes along the Central American volcanic arc (CAVA) is almost as wide as the range of previously estimated arc water fluxes (Fig. 12). Only Carmichael's (2002) water fluxes based on the Crisp (1984) arc volcanic plus plutonic magma fluxes are significantly higher. Water fluxes of the Chilean Southern Volcanic Zone are typically lower than at Central America except for one segment between the Valdivia and Chiloé fracture zones (Völker et al. 2011, this volume). We have also included in Fig. 12 the modeled water flux released from the slab to 150 km depth according
to van Keken et al. (2011) for the cases of no serpentinization, 20% serpentinization and full serpentinization of the uppermost 2 km of slab mantle. The seismological studies discussed in section 3.3 suggest that the depth of serpentinization offshore Nicaragua is probably greater than in the 20%/2 km assumption of van Keken et al. and their corresponding H$_2$O input flux of 28 Tg/Ma/m is only half our value of 62 Tg/Ma/m for Nicaragua, which is actually similar to their input flux for full serpentinization (60 Tg/Ma/m). We therefore think that van Keken et al. underestimated the depth of serpentinization and, as a compromise, their modeled release flux of water from the slab for the full-serpentinization scenario may be compared to our arc output fluxes. This water-release flux of about 24 Tg/Ma/m is significantly larger than the output fluxes of 6-8 Tg/Ma/m that we calculate for the Nicaraguan arc segments. Since slab-derived water is also distributed into upper-plate reservoirs apart from the arc (see section 6.1), modeling results and our observation-based calculations do at least qualitatively agree.

Our CO$_2$ flux from the CAVA, which is based on melt-inclusion analyses, is considerably lower than fluxes derived from hydrothermal and gas emissions (Fig. 12). In order to obtain similar fluxes with our method, we would have needed, for example, to assume melt CO$_2$/K$_2$O≥1 along the entire arc (cf. Fig. 6b). This underlines that the petrological method strongly underestimates poorly soluble magmatic volatiles such as CO$_2$.

However, this may not necessarily be true for sulfur, because our petrologically estimated sulfur fluxes of the CAVA straddle the upper limit of published fluxes derived from open-vent degassing (Fig. 12). On the other
hand, our review of recent open-vent degassing rates yields a still much
deeper arc sulfur flux and suggests that previous calculations based on less
abundant monitoring data have underestimated true fluxes. Most segments of
the Chilean Southern Volcanic Zone yield sulfur fluxes much less than at
Central America except for the segment between the Valdivia and Chiloë
fracture zones (Völker et al. this volume).
As for H₂O, our chlorine emission fluxes along the CAVA largely cover the
range of previously estimated fluxes (Fig. 12). On average the CAVA chlorine
fluxes are somewhat higher than at the Southern Volcanic Zone in Chile but
the along-arc variation is larger there.

7.3. Output vs. input: sources and sinks of volatiles

Water

Figure 9 compares the outputs at the arc to the inputs at the trench; we
neglect here the emissions at the forearc because they are minor for water
and we assume that they are also minor for Cl and S. While there are along-
arc variations, on average the water output at the arc accounts for roughly
10% of the water input at the trench. This is similar to 13% estimated by
Straub and Layne (2003) for Izu arc and 4-8% for Chile (Völker et al., this
volume); Jarrard's (2003) calculations yield much higher 27-81%, Parai and
Mukhopadhyay (2012) modeled 53%, and Wallace (2005) concluded that
input and output fluxes of water are roughly balanced but Jarrard and Wallace
both did not consider water input by serpentinized mantle.
Our arc magma fluxes include an "intrusive" component insofar as we have also considered the masses of primitive magma required to generate the masses of evolved magma that had actually erupted (cf. Kutterolf et al. 2008). We now extend that approach by also considering a "plutonic component" that never forms a trace at the surface. Using plate-kinematic constraints, Phipps Morgan et al. (2008) argued that an intrusion rate of 90-180 km$^3$/Ma/km would be required to half or fully balance crustal extension at the arc. Clift and Vannucchi (2004) calculated intrusion rates around 100 km$^3$/Ma/km to allow for crustal growth in the presence of subduction erosion. Thus total magma intrusion into the arc crust may be as large as 234-468 Tg/Ma/m (cf. Fig. 7) such that our volcanic mean-CAVA magma flux of 106 Tg/Ma/m would account for 45-23 wt% of total arc magma production. We note with caution, however, that the rate of crustal growth is averaged over a time frame of 1.5x10$^7$ years compared to the ~10$^5$ years time window of our magma flux estimates. Moreover, intrusion rates may have varied laterally along the arc. Hence, the ratio between "volcanic" and "plutonic" rates may vary temporally and spatially but here we assume a constant ratio. In addition, we make the assumption that the hidden plutonic magmas followed the same along-arc compositional variations that we derived from the volcanic rocks (Fig. 6). Then the volatile output/input percentages (Fig. 9, Table 2) would have to be approximately multiplied by a factor of 2-5 and the segment-wise variation of relative water output would range from 9-98% with a mean CAVA value of about 40%. Allowing 20-30% of the input to be carried to beyond sub-arc depths (see section 6.2), we still have 40-30% not accounted for. In section 6.1 we have estimated that the upper-plate low-velocity anomalies hold 12%
(Costa Rica) to 35% (Nicaragua) of the present instantaneous distribution of water in the subduction system. Thus, if we assume the highest plutonic/volcanic ratio for Nicaragua where there is the greatest crustal extension (Phipps Morgan et al. 2008), we achieve an almost closed water budget: 40% transfer from mantle to arc, 20% in subarc velocity anomaly A4, 15% in anomaly A1 to A2, A3 (Fig. 10), and 20-30% into the deeper mantle seem to satisfy a closed budget. For Costa Rica, however, even allowing generous 30% transfer to the arc and 12% into the "seismic anomalies", we fail to account for more than half the input. The slab crust as the main carrier of water (Fig. 4) is thicker than at Nicaragua to Guatemala, and additional igneous ocean-crust material is subducted by forearc erosion. Particularly the gabbroic crust may keep its water to beyond sub-arc depths (van Keken et al. 2011). We speculate that the relative water flux into the deep mantle is larger at Costa Rica than farther north and may account for about (or more than?) half the input flux.

Probably most magmatic water reaching the arc is derived from the subducted slab because primitive melt H\textsubscript{2}O contents correlate positively with geochemical slab signatures (e.g., Ba/La; Sadofsky et al. 2008; Ruscitto et al. 2012) and magmatic H\textsubscript{2}O/K\textsubscript{2}O ratios distinctly exceed those of both N- and E-MORB type mantle (Fig. 6a; Michael 1988). A source distribution such as in the global modeling of Parai and Mukhopadhyay (2012), with only 3% of the water emitted at the volcanic arcs originally stemming from the mantle wedge but 97% being derived from the subducting slabs, probably also applies to the Central American subduction system.
Carbon dioxide

The volcanic CO$_2$ output determined by our petrologic method is typically <2% of the input but reaches 5% at Nicaragua. Both closed- and open-system CO$_2$-degassing was common in these magmas (Wehrmann et al. 2011) such that CO$_2$ contents are petrologically underestimated. Arc CO$_2$ outputs derived from hydrothermal and gas emissions are higher (Fig. 12) but still only account for 6-24% of the input. He-CO$_2$ and $\delta^{13}$C relationships of Central American hydrothermal and gas emissions indicate that the provenance of CO$_2$ released along the volcanic front is dominated by subducted marine carbonates ($L=76\pm4\%$) and organic sediments ($S=14\pm3\%$), with the mantle wedge ($M$) contributing only 10±3% to the total carbon flux (Shaw et al. 2003; de Leeuw et al. 2007). These geochemical observations seem to contradict petrological studies implying that carbonate phases are stable to beyond subarc depths in limestone (Kerrick and Connolly 2001), serpentinized mantle (Kerrick and Connolly 1998) and carbonated ocean crust (Molina and Poli 2000), and released fluids are very CO$_2$-poor (except for unusual high-T low-P conditions). This apparent contradiction may be resolved in two ways:

1. Aqueous fluids from the lower lithological units of the slab may react with carbonate in the metasediment layer if percolation is pervasive rather than channeled to produce a CO$_2$-rich fluid entering the mantle wedge (Kerrick and Connolly 2001; Schmidt and Poli 2003). Gorman et al. (2006) modelled CO$_2$ release from the sediment and upper crust of the slab by either channelized or pervasive flow of fluid from underlying lithologies for the Nicaraguan subduction conditions. The CO$_2$ flux from the slab is about an order of
magnitude greater for pervasive than channelized flow, but for both CO₂ liberation occurs at sub-forearc rather than subarc depths. Carbonate veins in subduction-zone metamorphosed rocks are quite common, demonstrating mobilization of C (e.g., Cartwright and Barnicoat 1999; Sadofsky and Bebout 2004), and C-O isotopic compositions of these veins indicate a slab derivation of C from both inorganic marine/hydrothermal and organic sources (van der Straaten et al. 2012). Thus, while veins have been abundantly observed in high-pressure metamorphic rocks (e.g., John et al. 2008; Gao et al. 2007; van der Straaten et al. 2012), geochemistry of the hydrothermal and gas emissions seems to suggest that pervasive flow is required to liberate substantial amounts of carbon from the source lithologies.

(2) An alternative explanation of sub-arc CO₂ transfer makes use of the modeled ascent of metasediment diapirs at temperatures of 500-850°C that serves to introduce fluid-insoluble slab elements into the mantle wedge (Behn et al. 2011). Tsuno et al. (2012) show experimentally that near-solidus melting of Al-poor carbonated pelite at P≥5 GPa produces alkali-rich carbonatite melt. They propose that immiscible carbonatite melt formed at 220-250 km depth rises updip to sub-arc depth and then via metasediment diapirs into the mantle wedge. This model can explain both geochemical signals (e.g. high Ba/La) and high CO₂ flux at Nicaragua.

Chlorine

The close similarity between chlorine and water in terms of input and output flux variations along the subduction zone, relative importance of input lithologies, and input-output flux ratio (Figs. 3, 4, 7, 9) suggests that both
volatiles may behave similarly during the various metamorphic and magmatic processes. Scambelluri et al. (2004) showed that Cl contents decrease strongly from oceanic serpentinites to high-pressure serpentinites and anhydrous olivine-orthopyroxene rocks representative of prograde slab metamorphism of ultramafic rocks and conclude that Cl quantitatively enters the slab-derived fluid. Kendrick et al. (2012), on the other hand, argue that serpentinite retains a significant fraction of Cl beyond sub-arc depths. Still most of the Cl contained in the arc-volcanic rocks would be derived from the slab. Cl/K$_2$O values of the volcanic melt inclusions (Fig. 6c) are significantly higher than in N- or E-MORB type mantle (e.g., Kent et al. 2002) and are largest at Nicaragua where other geochemical signatures suggest maximum slab contribution (e.g., Carr et al. 1990). In contrast, Barnes et al. (2009) interpreted chlorine isotope compositions of Central American arc rocks to support a slab-source dominance only at Nicaragua while favoring a mantle-source dominance for Costa Rica and El Salvador/Guatemala. However, later work (John et al. 2010) showed that the chlorine isotope compositional range of subducted sediment is wider than previously thought such that it overlaps completely with the arc rock compositions. Noting wide ranges of Cl/H$_2$O in arc magmatic compositions, Wallace (2005) argued that Cl and H$_2$O become strongly fractionated while processed through the subduction zone. The observation by Straub and Layne (2003) that Izu-arc Cl output makes good for 77% of the input, but water only for 13%, seems to support such fractionation but they did not consider slab mantle serpentinization in their budget. Our observation that the relative outputs of Cl and H$_2$O are roughly correlated need not contradict Cl-H$_2$O fractionation at the local process scale but
suggests that over larger spatial and time scales such fractionations balance out to some correlated behavior.

### Sulfur

The output-input ratio for sulfur is much larger than for the other volatiles, a result shown by both the long-term fluxes based on melt inclusion analyses and the present-day fluxes based on open-vent monitoring (Fig. 9). The S/K₂O values of Nicaraguan melt inclusions, which have the least evolved compositions, are near the value for primitive mantle (Fig. 6d; McDonough and Sun 1995). However, S-concentrations up to 2500 ppm in Central American primitive melt inclusions (Sadofsky et al. 2008) would require about 400-500 ppm S in the mantle source (cf. de Hoog et al. 2001), i.e. roughly twice the concentration of 250 ppm S expected in fertile mantle (McDonough and Sun 1995). Moreover, rocks and glasses from the Mariana and Japan arcs have elevated $\delta^{34}$S isotope values which suggest slab-derived additions to the mantle source (Alt et al. 1993; Ueda and Sakai 1984). To our knowledge, the fate of S-bearing minerals in sediment during high-P slab metamorphism has not yet been systematically studied. Recently Jego and Dasgupta (2013) showed experimentally that partial melts of subducted MORB would be very S-poor (<50 ppm) but coexisting fluids would be very S-rich (10-15 wt%) and could remove almost half the sulfur from the slab crust. Hattori and Guillot (2007) determined ≤5 ppm S in Alpine and Cuban high-pressure serpentinites originally formed from abyssal peridotites, and Alt et al. (2013) conclude that significant fluid escape of sulfur is delayed until the transformation from antigorite serpentinite to chlorite harzburgite. We
tentatively conclude that contributions of S from the slab are complemented
by S originally hosted in the mantle wedge in order to explain why the arc
output / trench input ratio is much larger for sulfur than for the other volatiles.

8. Conclusions

We have reviewed the presently available information on the Central American subduction zone in order to constrain a budget of volatiles (H$_2$O, CO$_2$, Cl, S) carried into, processed through, and expelled out of the system.

Regarding the input into the subduction zone by the downgoing slab, we have extented earlier approaches by considering mineral-bound rather than pore-water chlorine, by including sulfur in the budget, and by explicitly including volatile subduction fluxes via serpentinized slab mantle and the removal of forearc basement (typically accreted oceanic crust) by subduction erosion.

While volatile input fluxes gradually increase from Guatemala to Nicaragua, there is a jump in input-flux values toward Costa Rica because of a strong change in subduction lithologies: thicker ocean crust, stronger subduction erosion but little mantle serpentinization. We find that H$_2$O and Cl fluxes are mainly controlled by serpentinized mantle, CO$_2$ fluxes by subducted sediment which includes carbonates, and S fluxes by subducted oceanic crust including accreted crust removed by subduction erosion. The range of input fluxes along the Middle America Trench covers a large part of the total range of published global volatile input-flux estimates.

Analyses of fluid and carbonate compositions and flux measurements at cold seeps along the Central American forearc allow to estimate that about 2 wt%
of mineral-bound H$_2$O subducted at the trench is expelled through the forearc, probably mostly derived from subducted sediment. Mixing of seep fluids with seawater and biogenic in addition to thermogenic methane production mask any emission of other volatiles (CO$_2$, Cl, S) from the slab through the forearc.

The major output of volatiles is their transfer from the slab through the mantle wedge to the arc crust, and finally into the exosphere, by arc magmatism. We have used an extensive data set of geochemically and petrologically determined melt volatile concentrations in combination with volcanologically determined long-term (~$10^5$ years) average magma fluxes which consider both proximal, edifice-forming deposits and widely dispersed tephras as well as the intrusive masses required to produce the observed evolved compositions, in order to calculate the volatile fluxes to the arc. As an alternative approach, we have also used present-day open-vent gas-flux measurements to determine sulfur and associated magma fluxes. While both approaches yield similar along-arc variations, they greatly differ in the time scales of observation of transient processes. Our volcanological and geochemical data set for Central America, which is probably one of the most detailed records worldwide, defined the along-arc variations in magma and volatile fluxes that we then extrapolated to the hidden plutonic magma flux that has been derived from crustal growths rates of the past 15 Ma (Clift and Vannucchi 2004; Phipps Morgan et al. 2008). This extrapolation led to 2-5 times higher mantle-to-crust volatile fluxes compared to the purely volcanic rates.
The along-arc variations of water and chlorine fluxes cover a large fraction of the range of global arc flux estimates. While our sulfur fluxes tend to be higher than published estimates, our petrological approach underestimates CO\textsubscript{2} fluxes compared to gas and hydrothermal He-CO\textsubscript{2} relationships. Even though the thermal state of the Cocos slab intermediate between "hot" and "cold" extremes should provide optimum conditions for sub-arc fluid release (Ruscitto et al. 2012), the volatile (H\textsubscript{2}O, CO\textsubscript{2}, Cl) transfer through the arc only accounts for a fraction of the volatile input at the trench, even if we consider "invisible" intrusions as required by crustal growth. For sulfur, however, the output flux at the arc may approximately balance the input flux at the trench. Recent numerical models simulating the stability of hydrous mineral phases under the pressure-temperature conditions in slab lithologies subducting at Central America found that 20-30\% of the water input may be transferred beyond subarc depths into the deeper mantle (Rüpke et al. 2004; van Keken et al 2011). Such mantle reflux plus the mantle-wedge to arc flux still leaves a deficiency of 30-40\% of the input. We conclude that at least some of this deficiency corresponds to the water stored in upper-plate regions identified as anomalies of low seismic velocities and/or electrical resistivities: a lithospheric to asthenospheric subarc region widely enveloping melt ascent pathways, and a lithospheric region extending from the slab below the forearc to below the arc. We have estimated the present, static distribution of water into these anomalies but do not know if they are temporally variable. However, the fact that the static distribution is very similar to the flux distribution expected from the overall water budget, we suspect that these water reservoirs may be in a near-steady state where input and output fluxes are roughly balanced.
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(*) marks SFB 574 contributions


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Figure captions
Fig. 1 Map of the Central American subduction zone. Bathymetry along the Middle America Trench shows traces of NW-SE striking bend-faults on the outer rise and seamounts and the Cocos Ridge offshore Costa Rica. The Central American Volcanic Arc (CAVA) is divided into 10 tectonic segments: WGS, CGS, EGS = west, central, east Guatemala segment; WSS, CSS, ESS = west, central, east Salvadorian segments; WNS, ENS = west and east Nicaragua segments; GCS = Guanacaste segment, CCS = Cordillera Central segment. Segment boundaries extended towards the trench parallel to the Cocos plate motion vector (arrow) serve to divide the trench into country-wise segments (GUA, ES, NIC, CR).

Fig. 2 Seismic velocity profiles along the trench - NW-SE profile drawn after Fig. 6 of van Avendonk et al. (2011) - and perpendicular to trench - SW-NE profile drawn after Fig. 4 of Ivandic et al. (2008). Red lines = MOHO; numbers give Vp [km/s]. The SW-NE profile shows how lower velocities descend below the MOHO with approach to the trench. NW-SE profile shows deeper-reaching low-velocity zones in the mantle of the Cocos plate offshore Nicaragua generated at the East Pacific Rise (EPR) compared to the plate segments offshore Costa Rica generated at Cocos-Nazca spreading center (CNS) and modified by Galapagos hotspot track.

Fig. 3 Mineral-bound volatile input fluxes for the four trench segments. See Table 1 for results. Gray inset graph shows along-trench variation in convergence rate $V_c$ after Syracuse and Abers (2006) for comparison; gray dots are average values used in calculations for each segment.
Fig. 4 Fractions of the volatile input fluxes delivered by the various lithological units. Arrows mark published global average data for comparison: H08 = Hacker (2008), vK11 = Van Keken et al. (2011); J03 = Jarrard (2003).

Fig. 5 Map of the Nicaraguan and Costa Rican segment of the Central American subduction zone modified after Ranero et al. (2008). Dashed lines mark isotherms along the plate boundary. Colored dots mark cold seeps that occur at the middle slope across the region where plate boundary temperature 60-150°C. Black dots are interplate earthquakes that occur beyond the dewatering interval at temperatures >150°C.

Fig. 6 Along-arc variations in volatile concentrations. Data from analyzed melt inclusions, water-contents from plagioclase-melt equilibria and amphibole compositions. The parameterization functions (red lines) used in flux calculations have been determined as regression functions through the (visually selected) maximum volatile/K$_2$O values along the arc. Mantle data: N-MORB and E-MORB compositions in (a) from Michael (1988), in (c) from Kent et al. (2002), primitive mantle PM in (d) from McDonough and Sun (1995).

Fig. 7 Segment-wise along-arc variation in volcanic volatile fluxes based on long-term magma fluxes converted to K$_2$O fluxes that were multiplied by volatile/K$_2$O ratios. The sum of long-term fluxes from each volcano on a segment has been divided by segment length. Typical relative errors are
estimated as ±20% for magma and K$_2$O fluxes and ±40% for volatile fluxes.

The gray bar indicates magmatic intrusion rates according to Clift and Vannucchi (2004) and Phipps Morgan et al. (2008).

**Fig. 8** (a) Along-arc variations of arc-segment sulfur fluxes derived from long-term magma fluxes and from present-day open-vent monitoring. The sum of the mean open-vent degassing rates for each monitored volcano on a segment is divided by segment length. Standard deviations around the mean vary widely but ±30-60% may be typical. (b) Comparison of long-term magma fluxes with magma fluxes calculated from open-vent degassing rates. Young volcanoes Izalco (300 yrs.) and Cerro Negro (150 yrs.) have grown at rates well exceeding the long-term magma fluxes in their neighbourhood. Error bars illustrate the standard deviation around the mean of the open-vent measurements; in some cases the standard deviation is larger than the mean value (vertical dashed lines).

**Fig. 9** Arc-volcanic volatile output fluxes as percentage of the respective input fluxes at the trench for each segment along the arc. Sulfur data: S(mi) from melt inclusions and long-term magma fluxes; S(ov) from open-vent degassing. Color-coded bars beneath R-12 show recycling efficiencies from Ruscitto et al. (2012) for comparison. Their much higher efficiency for CO$_2$ reflects the large difference in volcanic CO$_2$ flux between Hilton et al. (2002) and our data (cf. Fig. 12).
Fig. 10 Schematic illustration of anomalies in seismic velocity (cf. Dinc et al. 2010, 2011) and electrical resistivity (cf. Worzewski et al. 2011) at Nicaragua and Costa Rica.

Fig. 11 Comparison of published subduction input fluxes of mineral-bound water. Blue dots: without mantle serpentinization, green dots: with serpentinized mantle, orange dots: V-13= Völker et al. (this volume) for Chile (CL) subduction zone, red dots: this study, orange and red stars: mean values for Chile and Central America. g=global estimates (all for 44,000 km total subduction zone length). P-90= Peacock (1990); B-96= Bebout (1996); S&P-98= Schmidt and Poli (1998); R-02= Rüpke et al. (2002) for Costa Rica (CR) and Nicaragua (NI); J-03= Jarrard (2003) global (g) and Central America (CA) estimates; SL-03= Straub and Layne (2003) for Izu arc; R-04= Rüpke et al. (2004) model results for 20 Ma and 120 Ma old subducting lithosphere; H-08= Hacker (2008); vK-11= van Keken et al. (2011) for Guatemala-El Salvador (GS), Nicaragua (NI) and Costa Rica (CR) each with no mantle serpentinization (no s.), 2 wt% H₂O in topmost 2 km of mantle (2/2 s.) and full serpentinization (full s.) of topmost mantle; P&M-12= Parai and Mukhopadhyay (2012) global modeling over geologic time scales.

Fig. 12 Compilation of arc-volcanic volatile emissions. Carmichael (2002) (C-02) used DePaolo's (1983) crustal growth rate and 6 and 16 wt% H₂O to estimate global (g) arc water output. Applying the same approach to Crisp's (1984) (C-84) arc volcanic and plutonic magma flow rates yields much higher global estimates. C-02 CA and MX are Carmichael's fluxes for Central
America and Mexico. SL-03= Straub and Layne (2003) Izu arc water and
Wallace (2005) and I-83= Ito et al. (1983) global fluxes, V-13= Völker et al.
(this volume) for Chile (7 segments of Southern Volcanic Zone). vK-11= water
fluxes released from slab to 150 km depth for no or limited (20%)
serpentinization (lower data) and for full serpentinization of uppermost mantle
(upper data). Our data: star = mean CAVA, gray dots = arc segments. SW-
96= Sano and Williams (1996), H-02= Hilton et al. (2002), S-03= Shaw et al.
(2003), Z-04= Zimmer et al. (2004), M-06= Mather et al. (2006), dL-07= de
Leeuw et al. (2007), F-08= Fischer (2008), PM-09= Pyle and Mather (2009),
S-13= Shinohara (2013) all use hydrothermal and open-vent emissions to
constrain volatile fluxes globally (g), for Central America (CA), Nicaragua (NI),
Costa Rica (CR) and El Salvador (ES). For sulfur we compare our fluxes from
open-vent degassing (ov) with those from melt-inclusion compositions (mi).

Table 1 Properties of Cocos Plate lithological units and calculated volatile
input fluxes for the four segments of the Middle America Trench (Fig. 1).

Table 2 Summary of volcanic mass fluxes (per unit arc length) from the
mantle wedge to the arc for the 10 arc segments. An extended version with all
calculations is provided as electronic supplement.
Figure 4
Click here to download Figure: Fig4.eps
Figure 6
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Figure 7

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Figure 8
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(a) Sulfur flux [Tg/Ma/m] per arc segment

- ▲ from long-term magma flux
- ▲ from open-vent degassing

(b) Magma flux (open-vent degassing)

- Long-term eruptive magma flux

Distance along arc [km]
Subduction input flux per trench length of mineral-bound H$_2$O [Tg/Ma/m]

Figure 11
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Figure 12
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**Sediments**

**Cocos Crust**

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**Subduction Erosion**

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<tr>
<th>Erosion rate</th>
<th>Mass flux</th>
<th>Density</th>
<th>H₂O</th>
<th>CO₂</th>
<th>Cl</th>
<th>S</th>
<th>H₂O</th>
<th>CO₂</th>
<th>Cl</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>km³/Ma/year</td>
<td>Tg/Ma/m</td>
<td>kg/m³</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>Tg/Ma/m</td>
<td>Tg/Ma/m</td>
<td>Tg/Ma/m</td>
<td>Tg/Ma/m</td>
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<tr>
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<td>2930</td>
<td>3.57</td>
<td>0.54</td>
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**Total Volatile Composition**

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<th>Cl</th>
<th>S</th>
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<tbody>
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<td>wt%</td>
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<tr>
<td></td>
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Weighted mean entire subduction zone

<table>
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<th>Cl</th>
<th>S</th>
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<tbody>
<tr>
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<td>wt%</td>
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<tr>
<td></td>
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<td>Tg/Ma/m</td>
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<tr>
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<td>Length (km)</td>
<td>Magma (Tg/Ma/m)</td>
<td>K2O (Tg/Ma/m)</td>
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<tr>
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<td>-------------</td>
<td>-----------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Western Guatemala segment</td>
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<th>%</th>
<th>%</th>
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