

## Volatiles in subduction zone magmatism

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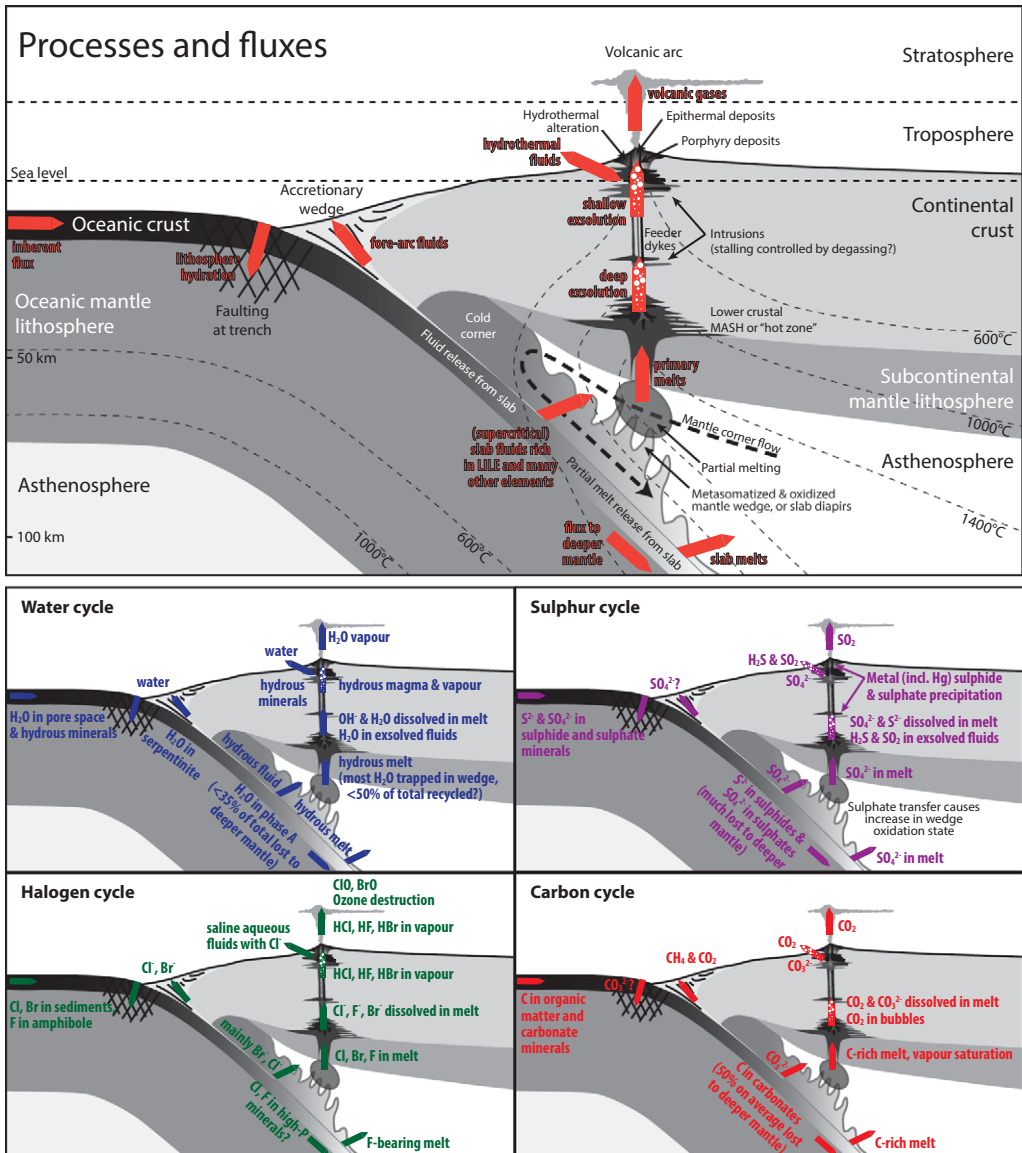
**Abstract:** The volatile cycle at subduction zones is key to the petrogenesis, transport, storage and eruption of arc magmas. Volatiles control the flux of slab components into the mantle wedge, are responsible for melt generation through lowering the solidi of mantle materials, and influence the crystallizing phase assemblages in the overriding crust. Globally, magma ponding depths may be partially controlled by melt volatile contents. Volatiles also affect the rate and extent of degassing during magma storage and decompression, influence magma rheology and therefore control eruption style. The style of eruptions in turn determines the injection height of environmentally sensitive gases into the atmosphere and the impact of explosive arc volcanism. In this overview we summarize recent advances regarding the role of volatiles during slab dehydration, melt generation in the mantle wedge, magmatic evolution in the overriding crust, eruption triggering, and the release of some magmatic volatiles from volcanic edifices into the Earth's atmosphere.

In contrast to mid-ocean ridge magmatism, where upwelling and adiabatic decompression of the mantle is the primary cause of melt generation, subduction zone magmatism is triggered by the depression of the mantle solidus due to influx of volatiles (dominantly H<sub>2</sub>O) from the dehydrating subducting slab (Grove *et al.* 2012). Although the details of melt generation in the mantle wedge are complex (for recent studies, see Grove *et al.* 2009; England & Katz 2010*b*; Grove *et al.* 2012) and remain controversial (England & Katz 2010*a*; Grove *et al.* 2010), there is some consensus in the following. (1) At shallow depths close to the trench, free H<sub>2</sub>O is expelled from the subducting slab by sediment compaction and porosity collapse that occurs when the upper oceanic crust reaches temperatures between 200 °C and 400 °C (Hyndman & Peacock 2003). (2) The fore-arc mantle becomes hydrated through release of aqueous fluids from the subducting slab, generated by progressive breakdown of hydrous minerals under increasing pressures and temperatures. Serpentine and/or chlorite dominate the assemblage in this cold fore-arc corner, which extends down to *c.* 60–80 km depth (Hyndman & Peacock 2003; Grove *et al.* 2009). Young and hot subducting slabs may dehydrate almost completely in the fore-arc, while older and colder slabs can carry significant amounts of H<sub>2</sub>O in their gabbro and peridotite sections into the deeper mantle (Schmidt & Poli 1998; Ranero *et al.* 2003; Van Keken *et al.* 2011). (3) Corner flow advects hydrated mantle as

the sinking slab drags the overlying material downwards. Dehydration reactions occur at the vapour-saturated mantle solidus and release H<sub>2</sub>O that is then available for hydrous melting. Hydrous melts likely infiltrate and permeate much of the overlying mantle wedge (e.g. Grove *et al.* 2006).

There is ongoing debate about the processes that form extractable melts of the hydrated mantle wedge. One model suggests that efficient melt extraction requires a degree of melting of the wedge so large that melts are generally extracted at or above the 1300 °C isotherm, that is, close to the anhydrous solidus (Kushiro 1987; Schmidt & Poli 1998). The advective flux of heat carried by this melt then perturbs the location of the anhydrous solidus upwards (England & Katz 2010*b*), and melts eventually penetrate the lithosphere and enter the crust by hydrofracture and dyking. Alternatively, melting is dominated by decompression in slab and mantle diapirs that may rise upwards through the wedge (Behn *et al.* 2011).

Here, we address volatile cycling from the dehydration of the subducting slab to arc volcanic degassing into the atmosphere (Fig. 1). A product of subduction is the output of volatiles as volcanic gases; another is the sinking of the slab containing 'residual' volatiles into the deep mantle. Volcanic gases in arcs are rich in H<sub>2</sub>O, chlorine, bromine and iodine compared to gases at rift and ocean island settings, which directly reflects the influence of slab-derived fluids on primary melt compositions



**Fig. 1.** Processes and fluxes in subduction zones, with individual panels showing volatile cycles for water, sulphur, halogens and carbon. Arrows indicate fluxes in a general direction. See text for discussion.

(Pyle & Mather 2009; Kutterolf *et al.* 2013; Kendrick *et al.* 2014a, b). Arc magmas are in general far richer in sulphur than their oceanic counterparts, reflecting the higher oxygen fugacity characteristic of arc melts and their enhanced capacity to carry dissolved sulphate (Wallace & Edmonds 2011). There is little direct evidence that primary arc melts are inherently richer in  $\text{CO}_2$  than ocean island basalts, although it has been suggested that deep and

pervasive  $\text{CO}_2$  gas fluxing is prevalent in many arc settings (Blundy *et al.* 2010) and might be an important process in the creation of some lower crustal granulites (e.g. Janardhan *et al.* 1979; Cameron 1988). It is likely that sulphur, chlorine and carbon in arc magmas are in large part sourced from subducted altered oceanic crust ( $\pm$  subducted sediment) and subcrustal serpentinite, ultimately from seawater during hydrothermal interaction close to the

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ridge (Alt 1995; de Leeuw *et al.* 2007; Sharp *et al.* 2007; Barnes *et al.* 2008, 2009a, b; Barnes & Straub 2010; Alt *et al.* 2012, 2013).

Available data suggest that up to about one-third of the subducted H<sub>2</sub>O may be returned to the deep mantle for the coldest slabs (Rüpke *et al.* 2004); much less is returned for hotter slabs, where dehydration may begin in the fore-arc (Kerrick & Connolly 2001b). The cycling of carbon is not as well understood; some arcs are vastly more efficient at returning carbon to the atmosphere than others, which may be largely dependent on the thermal structure of the slab (Kerrick & Connolly 2001b), but also on sediment input (Plank & Langmuir 1998). Evidence from carbon isotopes suggests that carbonated oceanic crust may be transported to the lower mantle before being returned to the surface via mantle plumes (Walter *et al.* 2011). The Central American arc is thought to return only 14–18% of carbon contained within the slab to the atmosphere through outgassing, compared to a global average of c. 50% (Shaw *et al.* 2003; de Leeuw *et al.* 2007). These studies are based on comparisons between the flux and composition of fumarolic gases from arc volcanoes and the age, thermal structure and composition of subducting slabs (Hilton *et al.* 2002).

Plumes of volcanic gases outgassed during eruptions consist of c. 90% H<sub>2</sub>O. The remaining c. 10% is made up of a mixture of sulphur, halogen and carbon gases. There are also minor amounts of noble gases, light lithophile elements (lithium, boron), nitrogen species and metals. Proportions of these species may change with the style of volcanic activity. Studies of deep cycling processes focus on quantifying the proportions of CO<sub>2</sub> relative to the He-isotope ratio for example, which constrains the extent of crustal contamination overprinting a mantle source signature (Nishio *et al.* 1998; van Soest *et al.* 1998; Hilton *et al.* 2002). Studies of outgassing seeking to elucidate eruption processes tend to target fluxes of the primary gas species SO<sub>2</sub>, CO<sub>2</sub> and HCl, which, due to their contrasting solubility behaviours, may allow constraints to be placed on gas segregation depths and yield a better understanding of the controls on eruption style (e.g. Aiuppa *et al.* 2002; Burton *et al.* 2003; Edmonds *et al.* 2010, cf. Fig. 1).

### Tracing volatiles from the subducting slab to the overriding crust

#### *Devolatilization of the subducting slab*

The oceanic lithosphere hosts significant amounts of volatiles (H<sub>2</sub>O, CO<sub>2</sub>, sulphur and halogens), inherently or through secondary uptake by hydrothermal and seawater circulation after its formation at the mid-ocean ridges (e.g. Staudigel *et al.* 1996;

Kerrick 2002; Alt *et al.* 2012). Seawater also pervades the slab along steep, deep-reaching faults that cut through the crust and hydrate the lithosphere up to tens of kilometres depth by bending-related faulting at the trench (Ranero *et al.* 2003; Fig. 1). Oceanic lithosphere stores volatiles in secondary hydrous phases, chief among them the serpentinite minerals (chrysotile, lizardite and antigorite) that contain significant amounts of H<sub>2</sub>O (up to 13 wt%), chlorine, carbon and sulphur (Ulmer & Trommsdorf 1995; Schmidt & Poli 1998; Straub & Layne 2003b; Barnes & Sharp 2006; Alt *et al.* 2013). Once free pore space is closed after early subduction, release or retention of volatile and other elements from the slab are controlled by a series of metamorphic dehydration reactions. Dependent on depth and host lithology (sediment v. igneous crust v. peridotite), H<sub>2</sub>O in the subducting slab principally resides in amphibole, lawsonite, epidote-zoisite, biotite, chlorite, chloritoids, phengite, paragonite and phase A (Ulmer & Trommsdorf 1995; Kerrick & Connolly 2001a; Grove *et al.* 2009; Kim *et al.* 2010), while white mica and the serpentine mineral antigorite have the capacity to transport H<sub>2</sub>O beyond arc front depths (Schmidt & Poli 1998; Schmidt *et al.* 2004). Carbonate sediments, metabasalts and carbonated peridotite carry CO<sub>2</sub> into subduction zones. CO<sub>2</sub> is principally bound in calcite, but also brucite, talc, dolomite and magnesite (Kerrick & Connolly 1998, 2001a). Sulphur is hosted in serpentinite (Alt *et al.* 2013) or sulphide minerals (Jego & Dasgupta 2014), but is also inherent to marine sediment and igneous oceanic crust in significant amounts. Fluorine is typically present as a low-level trace element in mineral phases (e.g. amphibole, Straub & Layne 2003b). Little is known about the distribution and abundance of bromine and iodine in the slab. The stability of volatile-bearing phases across the subduction interface will determine what volatile mix is recycled back to the surface via arc volcanism, and what fraction is returned to the mantle.

Reconstructing the details of slab devolatilization is clearly a complex task; the stability of volatile-bearing phases not only depends on the composition of the host lithology, but is also a function of the pressure–temperature path of the slab, which varies widely among subduction zones (e.g. Van Keken *et al.* 2011). *In situ* observations are not possible, so information is collated from various sources. These include active serpentinite mud volcanism in the shallow fore-arc region (<40 km slab depth, e.g. Fryer *et al.* 2000), the systematics of the volatiles in undegassed primitive arc magmas (Straub & Layne 2003b; Johnson *et al.* 2009; Ruscitto *et al.* 2010), experimental studies (e.g. Kessel *et al.* 2004; Jego & Dasgupta 2013; Duncan & Dasgupta 2014; Jego & Dasgupta 2014),

thermodynamic models (e.g. Van Keken *et al.* 2011) and studies of exhumed slabs (e.g. Sorensen *et al.* 1997). Metamorphic complexes that have been exposed to  $P$ – $T$  conditions up to arc-front depths provide a direct view of the effects of devolatilization on the residual slab, even through additional modifications of retrograde metamorphism (Sorensen *et al.* 1997; Bebout & Nakamura 2003). In a contribution to this book, Negulescu & Săbău (2014) report evidence for subduction-mediated alteration of eclogite lenses within the Leaota metamorphic melange complex (South Carpathians, Romania) and show that fluids carry both fluid-mobile large-ion lithophile elements (LILE) and major elements, which are extracted from the slab to depths of 75–80 km. Understanding the transfer mechanism from slab to wedge is important, as volatile elements may mimic the behaviour of non-volatile mobile elements with similar partitioning behaviour. For example, boron may serve as proxy for  $H_2O$  or neodymium as proxy for fluorine (Straub & Layne 2003a, b). Further, the nature of the transfer agent – fluid-like, melt-like or even ‘diapirs’ of low-density slab material (e.g. Behn *et al.* 2011) – affects the efficiency of element extraction from the slab, which is usually lower in aqueous fluids than in partial hydrous silicate melts or in slab diapirs.

Despite continuous progress, our understanding of slab devolatilization remains incomplete. The devolatilization of  $H_2O$  and chlorine are fairly well constrained, as their fluxes can be traced through their enrichment in calc-alkaline arc magmas (Straub & Layne 2003b). Interestingly, several studies suggest that the slab flux of  $H_2O$  is decoupled to some extent from the flux of non-volatile LILE, which supports the hypothesis of distinct fluid reservoirs within the slab (Straub & Layne 2003a; Johnson *et al.* 2009; Ruscitto *et al.* 2012). Regardless of the dominance of slab-derived  $H_2O$  and chlorine in arc magmas, however, mass-balance calculations suggest that a lesser amount of subducted  $H_2O$  and chlorine is recycled at the arc relative to the amount either trapped in the mantle wedge or returned to the deeper mantle (Straub & Layne 2003b; Sharp & Barnes 2004; Kendrick *et al.* 2011; Alt *et al.* 2012). In contrast, elemental systematics of undegassed fluorine in arc magmas suggests that fluorine is poorly mobilized in slab fluids (Straub & Layne 2003b). However, partial slab melts may be more efficient in mobilizing fluorine from the slab (cf. Fig. 1). Studies of bromine and iodine in subduction-related magma have only just begun (Kutterolf *et al.* 2013, 2014a). While some slab flux from igneous crust and serpentinite is indicated (Kendrick *et al.* 2014a), verification of subduction input is still pending.

Slab release of the climate-important species sulphur and carbon has attracted much attention.

Because undegassed abundance data are rare in arc magmas (e.g. Ruscitto *et al.* 2012), the best evidence for slab devolatilization beneath volcanic arcs is based on a combination of experimental studies, high-pressure phase equilibria considerations and mass-balance calculations (e.g. Kerrick & Connolly 1998, 2001a; Alt *et al.* 2013; Jago & Dasgupta 2013, 2014). Evidence from these studies converge on the notion that much of the subducted sulphur and carbon is returned to the deeper mantle rather than recycled, thus suggesting only moderate devolatilization at the  $P$ – $T$  conditions relevant to subduction environments (e.g. Tsuno & Dasgupta 2012; Alt *et al.* 2013; Jago & Dasgupta 2014). Despite this, however, primary arc melts are observed to contain much higher concentrations of sulphur than mid-ocean ridge basalts; this is primarily due to their more oxidized nature and higher carrying capacity when sulphur is dissolved as sulphate (Jugo *et al.* 2005; Wallace & Edmonds 2011).

#### *Compositions of the primary melts and their detection in the mantle wedge*

As a result of interactions between the mantle wedge and subducting slab, arc magmas are significantly more hydrous than melts generated beneath ocean ridges or in intraplate settings (e.g. Gill 1981; Michael 1995; Wallace 2005). Experimental petrology has provided some insights into the effect of  $H_2O$  on primary melt compositions. Hydrous melting occurs at lower temperatures than dry melting due to depression of the solidus by  $H_2O$ . Because the partitioning of magnesium and iron in pyroxene and olivine is temperature dependent, arc magmas typically have lower MgO and FeO and higher  $SiO_2$  contents compared to melts in other tectonic settings (Gaetani & Grove 1998). Nevertheless, most experiments still yield basaltic compositions at  $H_2O$ -undersaturated melting conditions (Kushiro 1972; Gaetani & Grove 1998). Only at low pressures (1 GPa) and high  $H_2O$  contents of above 7 wt% (i.e. close to saturation), when temperatures of last equilibration between the melt and the residual mineral phases are unreasonably low (<1000 °C), can high-magnesium andesitic melts be generated directly from the wedge, leaving a harzburgitic residual mineralogy (Hirose 1997; Grove *et al.* 2012). Primary arc andesite formation by hydrous melting of peridotite can therefore be considered unlikely.

However, mineral transformations in the subducting slab due to increasing pressures and temperatures do not only yield  $H_2O$ , but result in the release of several other components into the sub-arc mantle. Arc magmas are typically enriched in LILE, lead and uranium, which are fluid mobile and are thought to be carried by slab fluids. Thus,

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enrichment of mobile LILE relative to high-field-strength elements (HFSE), including the rare Earth elements (REE), is often referred to as the 'slab signature'. In addition, young arc rocks frequently display  $^{226}\text{Ra}$  excess. From a study of high-precision U–Th–Ra isotope data on global arc volcanic rocks, it is apparent that the highest  $^{238}\text{U}$  and  $^{226}\text{Ra}$  excesses are carried by samples with between 50 and 55 wt%  $\text{SiO}_2$  (i.e. by silica-rich basalts and basaltic andesites). Disequilibrium clearly declines towards more primitive basaltic compositions (Zellmer *et al.* 2005). This is consistent with the notion that the slab signature not only consists of fluid mobile elements/species (such as radium and  $\text{U}^{6+}$ ), but in addition includes major element oxides such as  $\text{SiO}_2$  (e.g. Kelemen 1995; Kelemen *et al.* 2004; Gomez-Tuena *et al.* 2007; Gómez-Tuena *et al.* 2008; Straub *et al.* 2011; Straub *et al.* 2013). Major element oxides are mobilized from the slab by fluids, as documented in this volume by the study of metamorphic assemblages within the Leaota subduction-accretion mélange complex of Negulescu & Săbău (2014), and may also be contributed to the mantle wedge by slab melts (e.g. Kay 1978; Smith *et al.* 1979; Defant & Drummond 1990). Here, it is noteworthy that some degree of partial melting of the slab is predicted to occur in even the coldest subduction zones (Plank *et al.* 2009).

Since  $\text{H}_2\text{O}$ -saturated and dehydration melting experiments of amphibolites and eclogites produce adakitic melts (Rapp *et al.* 2003), adakitic glass inclusions found in mantle xenoliths from subduction zones (Schiano *et al.* 1995) are taken as primary evidence for the occurrence of slab melting. Reaction of volatile- and  $\text{SiO}_2$ -rich slab components with the initially peridotitic mantle wedge may then produce hydrous pyroxenite veins. Such wedge pyroxenites can subsequently yield more evolved melts upon melting, with dacitic compositions being produced in the case of silica excess in the source. Volatile transfer into the wedge, which promotes the transfer of conventionally non-mobile elements, may therefore result in large chemical variations of subduction zone primary melts.

Geophysical detection of fluids and melts in the mantle wedge remains difficult despite rapid advances in spatial resolution. One issue is how to distinguish hydration of the mantle wedge by slab fluids from partial melting of the wedge, as both processes result in seismic velocity reduction. Using Rayleigh wave dispersion in the Chilean subduction system, Thorwart *et al.* (2014) show in this volume that the problem can be addressed by combining several geophysical imaging techniques: while partial melts result in reduction of resistivity and seismic velocity, hydration of the mantle wedge appears to result in seismic velocity reduction only,

with little effect on resistivity. Their results suggest that much of the mantle wedge is affected by slab fluid addition, but that melting is more spatially restricted to the upper part of the wedge.

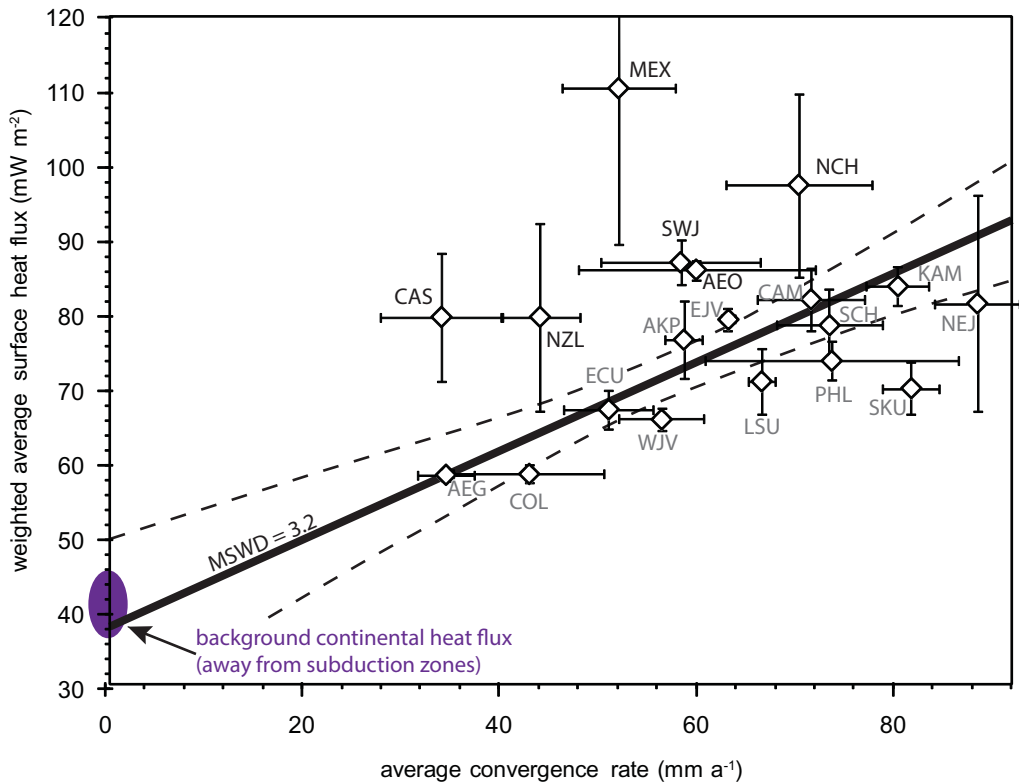
### *Effect of volatiles on magma differentiation and ascent*

The generation of arc magmas at temperatures close to the dry mantle wedge solidus, typically well above 1250 °C (England & Katz 2010b), has important implications for the dynamics of hydrous melt ascent and crustal evolution. Hydrous melt liquids lie well below 1200 °C, and hydrous arc magmas therefore leave their source crystal-free and with extremely low viscosities, resulting in intermittent release and upward migration of small melt batches from the wedge beneath the volcanic front (cf. Zellmer & Annen 2008). Their ascent through the cooler, upper part of the mantle wedge and the overriding crust may be very rapid if conduits are available. Extremely rapid ascent of some arc magmas from great depths to the surface (within a few days) has for example been suggested on the basis of seismic studies (Blot 1972; Fedorov *et al.* 1983) and the preservation of reactive ultramafic hornblende-peridotite mantle xenoliths in their host magmas (Blatter & Carmichael 1998). Slower magma ascent times of months to years from the mantle and through the crust have been derived from nickel diffusion profiles in olivines at Irazu volcano, Costa Rica (Ruprecht & Plank 2013).

If melts stall in the deep crust, their volatile content may have important implications for the phases crystallizing at depth. Adakitic magmas, initially believed to be unequivocally diagnostic of slab melting, can for example also be generated from parental basalts by fractionation of phases such as amphibole and garnet at typical lower crustal pressures and moderate  $\text{H}_2\text{O}$  contents (Müntener *et al.* 2001; Alonso-Perez *et al.* 2009). Several studies have advocated adakite petrogenesis through fractional crystallization of primary basaltic mantle melts at relatively high lower crustal pressures (1 GPa, or more, e.g. Garrison & Davidson 2003; Macpherson *et al.* 2006; Zellmer *et al.* 2012). It has also been shown that dissolved magmatic  $\text{H}_2\text{O}$  plays a role in the differentiation pathways of arc magmas in the deep overriding crust (e.g. Sisson & Grove 1993; Langmuir *et al.* 2006; Zellmer *et al.* 2014c).

Melt ascent through the overriding crust to subvolcanic ponding levels in the shallower crust may also be significantly affected by melt volatile contents. The higher the initial volatile contents, the earlier decompression-induced degassing will commence during melt ascent. In this volume, for example, Bégué *et al.* (2014) discuss volatile



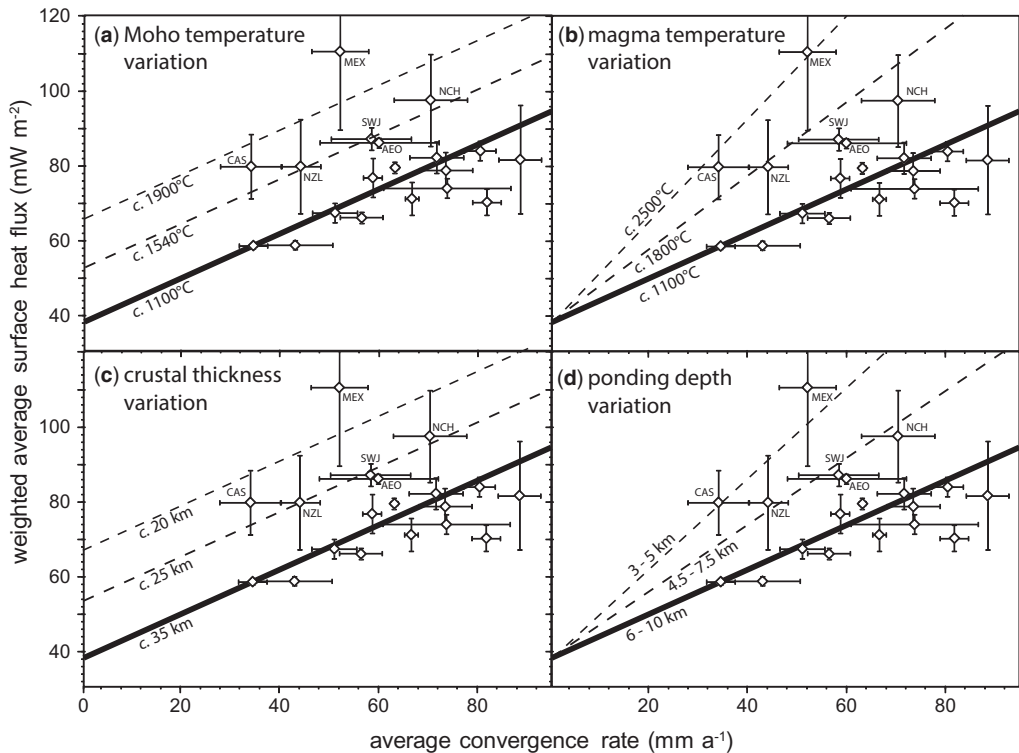


**Fig. 2.** Variation of average surface heat flux with average convergence rates for global continental to transitional volcanic arcs, compiled from Zellmer (2008). Weighted average surface heat flux with  $1\sigma$  uncertainties due to along- and across-arc heat flux variations are based on the global surface heat flux model of Shapiro & Ritzwoller (2004). Average convergence rates with  $1\sigma$  uncertainties due to along-arc variations in convergence rates are based on the global plate boundary model of Bird (2003). Arc acronyms: AEG, Aegean Volcanic Arc; AEO, Aeolian Volcanic Arc; AKP, Alaska Peninsula; CAM, Central American Arc; CAS, Cascades Volcanic Arc; COL, Colombia; ECU, Ecuador; EJV, Eastern Java; KAM, Kamchatka and Northern Kurile Arc; LSU, Lesser Sunda Arc; MEX, Mexican Volcanic Belt; NCH, Northern Chile; NEJ, Northeast Japan; NZL, New Zealand; PHL, Philippine Arc, SCH, Southern Chile; SKU, Southern Kurile Arc; SWJ, Southwest Japan and Northern Ryukyu Arc; WJV, Western Java. For a detailed list of volcanoes included in each segment, see Zellmer (2008). Best-fit line with uncertainty envelope is calculated using the program Isoplot (Ludwig 2008), taking into account all data points with their respective  $1\sigma$  uncertainties, and passes through the background continental heat flux away from subduction zones (Shapiro & Ritzwoller 2004).

concentrations in melt inclusions from Taupo Volcanic Zone rhyolites, and show that variations can be linked to variable depths of degassing. Degassing at variable depths is a consequence of differences in initial volatile contents of the parental melts, which may ultimately reflect variations in along- and across-arc slab fluid flux beneath New Zealand. In general, efficient degassing will ultimately result in crystallization and concomitant viscosity increase of ascending magmas (Sparks *et al.* 2000; Cashman 2004), hindering further ascent and promoting ponding in subvolcanic magma reservoirs. Melts with initially high volatile contents may therefore be expected to stall deeper, on average, than melts with lower volatile contents (cf. Zellmer 2009).

There remains some controversy about the origin of relatively low variability of melt inclusion  $H_2O$  contents in arc magmas. As outlined by Plank *et al.* (2013), the  $H_2O$  content of melt inclusions in arc magmas may either be controlled through the melting process or by equilibration of magmas within crustal storage regions if ponding depths are relatively invariable. On the other hand, there is some data that support the notion of volatile control on magma ponding depth. Average crustal ponding levels in typical subduction zones may be between 6 and 10 km depth (cf. Hammarstrom & Zen 1986; Hollister *et al.* 1987; Anderson & Smith 1995). Potential variations in magma ponding levels between different arcs may be assessed by

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**Fig. 3.** Exploring ways to explain excess heat flux in Mexico, the Cascades, New Zealand, Southwest Japan and Northern Chile. The effects of varying (a) Moho temperature, (b) magma temperature, (c) crustal thickness and (d) magma ponding level, assuming heat conduction through the crust and heat advection by rising melts. Modelled temperatures, thicknesses and depths are based on attribution of values reasonable for continental subduction zones to the best-fit baseline derived in Figure 2. Increasing Moho temperature or decreasing crustal thickness results in an elevation of surface heat flux that is independent of magma flux (cf. parallel dashed contour lines). In contrast, magma temperature and ponding level variations result in heat flux variations that are dependent on the magma flux (cf. non-parallel dashed contour lines tied at zero convergence rate). Arc acronyms as in Figure 2, but omitted here for most arcs for clarity. See text for discussion.

comparing surface heat flux variations of global subduction zones. Figure 2 shows average surface heat flux v. plate convergence rates for a number of continental to transitional arcs, using previously compiled data (Zellmer 2008) sourced from published convergence rates and a global surface heat flux model (Bird 2003; Shapiro & Ritzwoller 2004). It is evident that all arcs display an average surface heat flux greater than the background continental heat flux away from subduction zones. A line of best fit (MSWD = 3.2) is constrained by those arcs with low along-arc surface heat flux variations, has a positive slope and passes through the background continental heat flux at zero convergence rate. Our interpretation of this best-fit line is that surface heat flux is influenced by advected magmatic heat, the rate of which would increase with increasing magma production rate, which in turn is

linked to plate convergence rate (cf. Cagnioncle *et al.* 2007).

However, several arcs plot significantly above this best-fit line, apparently displaying excess surface heat flux. Potential causes for such excess are explored in Figure 3. Neither variations in Moho temperature (Fig. 3a) or in magma temperature (Fig. 3b) can explain the magnitude of observed heat flux excess of these arcs, because the temperatures required are unreasonably high for subduction environments on Earth. Crustal thinning may be a reason for the excess heat flux observed in New Zealand (cf. Fig. 3c), where intra-arc rifting takes place (Bird 2003). However, crustal thinning clearly cannot be called upon when considering the thickness of overriding crusts of Northern Chile (Yuan *et al.* 2002), where crustal-scale convection may contribute to the high observed heat flux (Babeyko

*et al.* 2002), or the Cascades (Das & Nolet 1998), the Mexican volcanic belt (Perez-Campos *et al.* 2008) and SW Japan (Oda & Ushio 2007; Ueno *et al.* 2008). These subduction zones are all built on thick to very thick continental crust.

One option is a systematic variation in magma ponding depths between different arcs (Fig. 3d). If typical ponding depths of hydrous arc melts range from 6 to 10 km, shallower but still reasonable average ponding levels down to 3 km may be called upon to explain the heat flux excess in some arcs. For example, lower-than-average magmatic H<sub>2</sub>O content has been revealed in SW Japan through plagioclase hygrometry (Zellmer *et al.* 2012, 2014c), linked to dehydration beneath the fore-arc in western Honshu and/or upwelling of sub-slab asthenospheric mantle at the leading edge of the young Philippine Sea slab or through a slab tear. Here, the lower-than-usual initial H<sub>2</sub>O content may result in shallower levels of decompression-induced degassing and thus shallower ponding levels, leading to excess heat flux compared to many other arcs. Work is in progress to assess potential evidence for relatively shallow ponding levels and low H<sub>2</sub>O contents of magmas from the Mexican Volcanic Belt and the Cascades. We note that slab window or edge effects on primary melt compositions have been already been called upon in both of these arcs (Beaudoin *et al.* 1996; Ferrari *et al.* 2001; Calmus *et al.* 2003).

### The role of volatiles in subvolcanic processes and eruption triggering

Magmatic volatiles are fundamental in controlling the behaviour of magmas in the arc crust. H<sub>2</sub>O-bearing mafic melts have the capacity to evolve to H<sub>2</sub>O-rich intermediate compositions in the deep crust through fractional crystallization, and to induce partial melting of the crust by hydrous fluxing (Annen *et al.* 2006). Volatile exsolution results in pressure increase within subvolcanic magma reservoirs, which may trigger eruptions. Exsolution of volatiles requires nucleation of bubbles, and it has been shown previously on the basis of theory and experiment that magnetite crystals constitute prime bubble nucleation sites for exsolving gases (e.g. Hurwitz & Navon 1994; Cluzel *et al.* 2008). In this volume, using mafic enclaves from Montserrat in the Lesser Antilles as an example, Edmonds *et al.* (2014a) for the first time confirm that this process is indeed relevant in natural systems. The notion of bubble-crystal aggregates in recharging mafic magmas has implications for mixing and mingling processes and the generation of hybrid magmas. Due to the lower buoyancy of these bubble-crystal aggregates over single bubbles, accumulation of

vapour at magma interfaces, such as at the base of andesite or rhyolite bodies, may not be favoured. Instead, the aggregates might promote whole-scale magma overturn, allowing mafic and silicic magmas to mingle at higher levels in the system.

Quantifying exsolved vapour at depth is a great challenge. The presence of vapour has only very subtle petrological consequences, and very little record of it exists in the erupted lavas. A vital component of any observational study is the measurement of the mass of emitted gases during eruption in comparison to the amount of erupted magma. In this volume, Christopher *et al.* (2014) present an 18-year time series of SO<sub>2</sub> emissions from Soufriere Hills Volcano. The time series highlights that gas and magma fluxes are decoupled, and that gas emissions continue and are often highest when the volcano is not erupting. Christopher *et al.* (2014) identify two cycles in the SO<sub>2</sub> emission rate time series that they relate to pressure changes in a dual reservoir system in the crust, with limited connectivity between the two magma reservoirs; this model is constrained independently by ground deformation (Elsworth *et al.* 2008; Melnik & Costa 2014). One of the periods identified is independent of lava extrusion, because lava cannot respond on timescales of 4–5 months due to its yield strength. A timescale of *c.* 2 years is common to both lava and gas emission, and relates to pressure changes caused by magma supply into the deep reservoir.

Recharge by hot mafic melts into the subvolcanic upper crust causes partial melting and remobilization of long-lived, almost ‘locked’, crystal-rich mushes associated with the influx of volatile-rich fluids (Bachmann & Bergantz 2006). These episodes of mafic recharge with periodic magma overturn and mingling are thought to be integral to the process of generating crystal-rich andesites (e.g. Humphreys *et al.* 2009; Kent *et al.* 2010) and also for charging the magmatic system with volatiles, the ‘fuel’ for eruption. The resulting magma bodies can sustain long-duration eruptions that are characterized by switches in the style of activity between vulcanian explosions and lava flow and dome emplacement. In upper crustal magma reservoirs, it is likely that most magmas exist with a substantial fraction of exsolved vapour. Crystal-rich andesites are perhaps particularly well-suited to ‘gas trapping’ due to the effect of crystals on impeding bubble rise through melts (Belien *et al.* 2010) and the high viscosity of their melts. This fraction of exsolved vapour present in a magma body has important implications for eruption style, magnitude and duration (Huppert & Woods 2002). The vapour fraction makes the magma compressible and the vapour phase is able to grow or contract in response to pressure changes. Injection of magma from depth might cause an increase in magma chamber pressure



for example, which might act to cause both volatile resorption and contraction of the vapour phase to buffer the pressure change. The result is that systems with a high proportion of exsolved vapour have a greater capacity for magma recharge without eruption and, once they begin to erupt, will typically have longer eruptions due to the effect of volatile expansion to restore pressure in the reservoir syn-eruption (Huppert & Woods 2002; Rivalta & Segall 2008; Edmonds *et al.* 2014a).

Melt inclusions and volatile-bearing phenocrysts allow a forensic reconstruction of degassing processes. For example, **Cigolini *et al.*** (2014) used melt inclusions from eruption products of Stromboli in the Aeolian arc, Italy, to probe the physicochemical conditions (including volatile concentrations) in different parts of the vertically protracted upper crustal magma reservoir and conduit root-zone of this volcano. They show that an exponential decrease in long-term SO<sub>2</sub> degassing following the 2007 major eruption is consistent with the gradual release of elastic strain accumulated within the chamber and the response and gradual depletion of a co-existing volatile phase, which allows constraints to be placed on magma chamber volume (1–2 km<sup>3</sup>).

Melt inclusion studies also provide useful insights into the links between magmatic volatile contents and eruptive style. For example, **Roberge *et al.*** (2014) use the geochemical composition of melt inclusions to infer that a late explosive phase of activity at the Pelagatos monogenetic cone in central Mexico was driven by the influx of mafic magma into a shallow, small, short-lived crustal reservoir. They surmise that the style of activity at this kind of small volcanic centre is controlled by the balance between magma influx and reservoir size, with stored magmas dominating effusive activity and primitive gas-rich magmas driving the more explosive phases.

As magmas ascend from shallow reservoirs towards the surface, their volatiles exsolve in response to decompression. It is this stage of degassing that controls eruption dynamics and style through the development of porosity and permeability. Recent studies have shown that slowly ascending magmas degas efficiently, causing an increase in their bulk viscosity by up to 5–6 orders of magnitude, due to both H<sub>2</sub>O loss from the melt and degassing-induced crystallization (Sparks *et al.* 2000; Cashman 2004). Development of overpressure caused by the viscous retardation of bubble growth in the upper parts of the conduit system in these highly viscous magmas is typically the trigger for lava dome destruction and explosive eruption (e.g. Melnik & Sparks 2002). Switches in style occur rapidly with only minor changes in reservoir pressure (Melnik & Sparks 1999), making arc volcanoes the most hazardous of all.

In a case study of eruption sequences of the 2010 eruption of the Gunung Merapi stratovolcano in central Java, **Genareau *et al.*** (2014) use rapidly diffusing volatile species (lithium and hydrogen) to investigate the degassing processes during the final stages of magma ascent through the conduit at the onset of eruption. They find that lithium is exsolving from deeper parts of the magmatic system, accumulates in the shallow conduit system and contributes to the development of system overpressure immediately prior to the initial explosive eruption. Later lavas extruded within the eruption sequence are fully degassed upon exiting the conduit.

### Volatiles in magmatic-hydrothermal systems, ore deposits and volcanic degassing

To date, little is known about how exactly ascending arc melts interact with subvolcanic hydrothermal systems. However, recent evidence shows that when melts reach upper crustal levels, interaction with subvolcanic hydrothermally altered material does indeed occur: in some instances, uptake of hydrothermally altered crystals into fresh arc magmas is revealed from combined <sup>238</sup>U–<sup>230</sup>Th and <sup>234</sup>U–<sup>238</sup>U disequilibria of crystals in a fresh groundmass that is in <sup>234</sup>U–<sup>238</sup>U equilibrium (Zellmer *et al.* 2014a; Zellmer *et al.* In press). In the present volume, using electron and ion microbeam techniques, **Zellmer *et al.*** (2014b) provide microanalytical evidence for hydrothermal alteration of olivines in fresh arc basalts from western Honshu, and argue that these crystals are sourced from a partially altered mush zone that disaggregated into the melt at the onset of eruption. Clearly, if a significant amount of hydrothermally altered material is taken up into the ascending melt, the volatile budget of the melt may be affected by this interaction; this needs to be taken into account when the balance of volatile input and output of the subduction factory is considered.

The gases exsolved from arc volcanoes are typically rich in H<sub>2</sub>O, CO<sub>2</sub> and chlorine, derived ultimately from the subducting slab. The composition of gases may be used to investigate a range of processes from source to surface. There have been numerous observational studies which use the fluxes and compositions of gases from arc volcanoes to infer mechanisms of magma storage, transport and eruption, as well as the environmental impact of subduction volcanic eruptions (e.g. Giggenbach 1980; Burton *et al.* 2000; Edmonds *et al.* 2001; Shinohara 2008; Werner *et al.* 2012; Kutterolf *et al.* 2013). A widespread observation is that the fluxes of volatiles from oxidized arc systems are in general far higher than can be accounted for by the concentrations of volatiles in melt inclusions, scaled up to

erupted volumes (Wallace 2001). For carbon and sulphur it is likely that partitioning into an exsolved fluid phase occurs at high pressures in the crust (cf. Fig. 1).  $\text{CO}_2$  is only weakly soluble in melts, and for mafic melts in arcs the initial volatile phase involved in bubble nucleation will be rich in carbon. Under conditions of high  $f\text{O}_2$ , sulphur partitions strongly into vapour even at high pressures (Scailliet & Pichavant 2003); this has the result that for evolved melts stored in the upper crust, the bulk of the sulphur may be stored as vapour (Wallace & Gerlach 1994; Wallace & Edmonds 2011). Alternatively, or perhaps in addition for some systems, mafic magma underplating supplies volatiles through a process of 'gas sparging' (Bachmann & Bergantz 2006) or quench crystallization, vesiculation and mingling (Edmonds *et al.* 2014*b*). The result of these vapour-dominated processes is that, in order to understand the magnitude of the sulphur and carbon budgets of arc magmas, it is necessary to measure their fluxes as gases at the surface. Increases in  $\text{CO}_2$  flux days to weeks prior to eruptions of Mount Etna illustrate the value of this approach for eruption forecasting (Aiuppa *et al.* 2008).

In contrast, halogen gases and  $\text{H}_2\text{O}$  exsolve dominantly at much shallower pressures in the crust and their fluxes may be proportional to magma flux (Edmonds *et al.* 2002; Fig. 1). Chlorine degassing from arc volcanoes may be substantial (Symonds *et al.* 1992; Shinohara 1994; Edmonds *et al.* 2002) and it is becoming increasingly clear that chlorine, along with bromine, may play a role in dynamic heterogeneous chemistry in volcanic plumes that may destroy ozone either locally in the troposphere (Lee *et al.* 2005) or in the stratosphere during large explosive eruptions (Kutterolf *et al.* 2013).

Using a global compilation, Taran & Zelenski (2014) show that the highest-temperature gases preserve the H-isotope signature and chlorine concentrations typical of a slab-derived volatile phase. However, most gas mixtures emitted from lava domes and island arc volcanoes have been affected by shallow hydrothermal processes such as seawater or meteoric water addition, or are the result of protracted and prolonged degassing of lava at the surface (cf. Fig. 1).

As well as the primary volcanic gas species, arc volcanoes are also responsible for the outgassing of a whole range of metals. Arcs are the sites of large gold-copper porphyry deposits, whereby mafic melts supply sulphur and chalcophile elements (Hattori & Keith 2001; Fig. 1). Through a global review of copper porphyries, it has been shown that copper sulphide accumulations are most significant in arcs with thick overriding plates and with magmas exhibiting strong calc-alkaline (iron depletion) trends; this suggests that plate thickness exerts a first-order control on magma differentiation and

metal segregation (Chiaradia 2014). At Merapi volcano, Indonesia, metals and sulphur outgas in the same proportions as found in sulphide minerals contained in minerals as inclusions, suggesting that entrainment of sulphide and its subsequent dissolution is the source for outgassing metals (Nadeau *et al.* 2010). In this volume, Bagnato *et al.* (2014) show that volcanoes are also significant sources of mercury released into the atmosphere, perhaps accounting for up to one-quarter of natural atmospheric emissions.

## Concluding remarks and outlook

An overview has been provided here of the wide range of studies undertaken to elucidate the complex and important role that volatiles play in the genesis, evolution and ascent of arc magmas; what their effects are on subvolcanic processes leading to volcanic eruptions; and what insights their release into the atmosphere may provide, both with regards to understanding magmatic systems in particular and volatile cycling through subduction zones in general. Studies range from metamorphic petrological work on exhumed subduction-accretion complexes, through geophysical studies of the mantle wedge, to a wide variety of geochemical approaches, including microanalytical techniques on erupted rocks and remote sensing of volcanic gases. A clear focus on the most abundant volatile species of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{SO}_2$  is apparent and undoubtedly due to the major influence that these volatiles play in the magmatic processes operating at subduction zones. However, trace species such as lithium and mercury clearly provide supplementary insights that cannot be gained from the major volatile compounds alone.

Future studies on these topics will help to further refine and quantify the details of the volatile cycle for a range of compounds. The study of exhumed subduction zones offers insights into the slab input, and the integration of such work with observations on arc output will be paramount in assessing the amount of volatiles recycled through arc volcanism v. the amount returned to the deeper mantle. Ever-improving spatial resolution in geophysical studies may eventually provide a better image of the spatial distribution of fluids and melts in the mantle wedge, allowing us to gain real insights into the detailed melt generation processes operating in the mantle rather than having to make inferences on the basis of arc output alone.

Magma ascent through the overriding crust leading up to volcanic eruptions at the surface is key to the development and improvement of hazard mitigation strategies, and the number of studies focusing on the volatile control on subvolcanic magmatic

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processes reflects the importance of this issue. The range of different types of arc volcanoes reveals differing petrogenetic regimes under which they operate. These apparently lie between two extremes: (1) dissolved volatiles in melts rapidly ascending from great depths towards the surface promote attainment of superliquidus conditions so that any crystal cargo, disaggregating into the rising melt from crustal magmatic mush zones, will be in the process of dissolving; and (2) volatiles exsolving from melts in middle–upper crustal sections promote attainment of subliquidus conditions with concomitant magma crystallization, viscosity increase and ponding, and the establishment of one or more ephemeral subvolcanic magma reservoirs that may modulate both eruptive behaviour and magma degassing. Future work will have to address which of the above petrogenetic scenarios is more prevalent, and/or how magmatism evolves or varies between these extremes during the lifetime and progressive growth of individual volcanic edifices.

Finally, studying volcanic volatile release from open- and closed-vent volcanoes is beginning to provide important clues to subvolcanic magmatic processes and remains important for understanding the volatile cycle as a whole (Fig. 1). In particular, the budget of volcanically released CO<sub>2</sub> into the atmosphere (which to date has been difficult to address due to the relatively high atmospheric CO<sub>2</sub> background; Burton *et al.* 2013) requires further attention.

In summary, volatiles provide important insights into arc magmatic processes; at the same time, the volatile cycle is itself intimately dependent on these processes. Volatile cycling and subduction zone magmatism are two aspects of the same system, and one cannot be understood without the other. The study of volatiles in ancient and young subduction zones therefore remains a very active area of research. This area has in the past been a key to understanding arc volcanism, and will likely continue to deliver important results for both fundamental and applied research topics in this field.

We would like to acknowledge all colleagues who have contributed to the many advances in our understanding of the role of volatiles in the genesis, evolution and eruption of arc magmas over the last few decades. We thank P. Leat for editorial handling of this chapter, which has benefited from the constructive comments of two anonymous reviewers, and T. Anderson and A. Hills for administrative support throughout our guest-editorial work on this volume. GFZ acknowledges support through a Massey University Research Fund.

## References

- AIUPPA, A., FEDERICO, C., PAONITA, A., PECORAINO, G. & VALENZA, M. 2002. S, Cl and F degassing as an

- indicator of volcanic dynamics: the 2001 eruption of Mount Etna. *Geophysical Research Letters*, **29**, 1159.
- AIUPPA, A., GIUDICE, G. *ET AL.* 2008. Total volatile flux from Mount Etna. *Geophysical Research Letters*, **35**, L24302.
- ALONSO-PEREZ, R., MÜNTENER, O. & ULMER, P. 2009. Igneous garnet and amphibole fractionation in the roots of island arcs: experimental constraints on andesitic liquids. *Contributions to Mineralogy and Petrology*, **157**, 541–558.
- ALT, J. C. 1995. Subseafloor processes in mid-ocean ridge hydrothermal systems. In: HUMPHRIS, S. E., ZIERENBERG, R., MULLINEAUX, L. S. & THOMSON, R. E. (eds) *Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions*. AGU Geophysical Monograph Series, **91**, 85–114.
- ALT, J. C., GARRIDO, C. J. *ET AL.* 2012. Recycling of water, carbon, and sulfur during subduction of serpentinites: a stable isotope study of Cerro del Almirez, Spain. *Earth and Planetary Science Letters*, **327–328**, 50–60.
- ALT, J. C., SCHWARZENBACH, E. M. *ET AL.* 2013. The role of serpentinites in cycling of carbon and sulfur: seafloor serpentinization and subduction metamorphism. *Lithos*, **178**, 40–54.
- ANDERSON, J. L. & SMITH, D. R. 1995. The effects of temperatures and fO<sub>2</sub> on the Al-in-hornblende barometer. *American Mineralogist*, **80**, 549–559.
- ANNEN, C., BLUNDY, J. D. & SPARKS, R. S. J. 2006. The genesis of intermediate and silicic magmas in deep crustal hot zones. *Journal of Petrology*, **47**, 505–539.
- BABEYKO, A. Y., SOBOLEV, S. V., TRUMBULL, R. B., ONCKEN, O. & LAVIER, L. L. 2002. Numerical models of crustal scale convection and partial melting beneath the Altiplano-Puna plateau. *Earth and Planetary Science Letters*, **199**, 373–388.
- BACHMANN, O. & BERGANTZ, G. W. 2006. Gas percolation in upper-crustal silicic crystal mushes as a mechanism for upward heat advection and rejuvenation of near-solidus magma bodies. *Journal of Volcanology and Geothermal Research*, **149**, 85–102.
- BAGNATO, E., TAMBURELLO, G. *ET AL.* 2014. Mercury fluxes from volcanic and geothermal sources: an update. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online August 1, 2014, <http://dx.doi.org/10.1144/SP410.2>
- BARNES, J. D. & SHARP, Z. D. 2006. A chlorine isotope study of DSDP/ODP serpentinized ultramafic rocks: insights into the serpentinization process. *Chemical Geology*, **228**, 246–265.
- BARNES, J. D. & STRAUB, S. M. 2010. Chlorine stable isotope variations in Izu Bonin tephra: implications for serpentinite subduction. *Chemical Geology*, **272**, 62–74.
- BARNES, J. D., SHARP, Z. D. & FISCHER, T. P. 2008. Chlorine isotope variations across the Izu-Bonin-Mariana arc. *Geology*, **36**, 883–886.
- BARNES, J. D., PAULICK, H., SHARP, Z. D., BACH, W. & BEAUDOIN, G. 2009a. Stable isotope ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ,  $\delta^{37}\text{Cl}$ ) evidence for multiple fluid histories in mid-Atlantic abyssal peridotites (ODP Leg 209). *Lithos*, **110**, 83–94.

- BARNES, J. D., SHARP, W. D., FISCHER, T. B., HILTON, D. R. & CARR, M. 2009b. Variations in chlorine stable isotopes along the Central American volcanic front. *Geochemistry Geophysics Geosystems*, **10**, Q11S17.
- BEAUDOIN, B. C., GODFREY, N. J. *ET AL.* 1996. Transition from slab to slabless: results from the 1993 Mendocino triple junction seismic experiment. *Geology*, **24**, 195–199.
- BEBOUT, G. E. & NAKAMURA, E. 2003. Record in metamorphic tourmalines of subduction-zone devolatilization and boron recycling. *Geology*, **31**, 407–410.
- BÉGUÉ, F., GRAVLEY, D. M., CHAMBEFORT, I., DEERING, C. D. & KENNEDY, B. M. 2014. Magmatic volatile distribution as recorded by rhyolitic melt inclusions in the Taupo Volcanic Zone, New Zealand. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online August 1, 2014, <http://dx.doi.org/10.1144/SP410.4>
- BEHN, M. D., KELEMEN, P. B., HIRTH, G., HACKER, B. R. & MASSONNE, H. J. 2011. Diapirs as the source of the sediment signature in arc lavas. *Nature Geosciences*, **4**, 641–646.
- BELIEN, I. B., CASHMAN, K. V. & REMPEL, A. W. 2010. Gas accumulation in particle-rich suspensions and implications for bubble populations in crystal-rich magma. *Earth and Planetary Science Letters*, **297**, 133–140.
- BIRD, P. 2003. An updated digital model of plate boundaries. *Geochemistry Geophysics Geosystems*, **4**, 1–52.
- BLATTER, D. L. & CARMICHAEL, I. S. E. 1998. Hornblende peridotite xenoliths from central Mexico reveal the highly oxidized nature of subarc upper mantle. *Geology*, **26**, 1035–1038.
- BLOT, C. 1972. Volcanisme et séismes du manteau supérieur dans l'Archipel des Nouvelles-Hébrides. *Bulletin of Volcanology*, **36**, 446–461.
- BLUNDY, J., CASHMAN, K. V., RUST, A. & WITHAM, F. 2010. A case for CO<sub>2</sub>-rich arc magmas. *Earth and Planetary Science Letters*, **290**, 289–301.
- BURTON, M. R., OPPENHEIMER, C., HORROCKS, L. A. & FRANCIS, P. W. 2000. Remote sensing of CO<sub>2</sub> and H<sub>2</sub>O emission rates from Masaya volcano, Nicaragua. *Geology*, **28**, 915–918.
- BURTON, M. R., ALLARD, P., MURÈ, F. & OPPENHEIMER, C. 2003. FTIR remote sensing of fractional magma degassing at Mount Etna. In: OPPENHEIMER, C., PYLE, D. M. & BARCLAY, J. (eds) *Volcanic Degassing*. Geological Society, London, Special Publication, **213**, 281–293.
- BURTON, M. R., SAWYER, G. M. & GRANIERI, D. 2013. Deep carbon emissions from volcanoes. In: HAZEN, R. M., JONES, A. P. & BAROSS, J. A. (eds) *Carbon in Earth*. MSA Reviews in Mineralogy & Geochemistry, **75**, 323–354.
- CAGNIONCLE, A.-M., PARMENTIER, E. M. & ELKINS-TANTON, L. T. 2007. Effect of solid flow above a subducting slab on water distribution and melting at convergent plate boundaries. *Journal of Geophysical Research*, **112**, B09402.
- CALMUS, T., AGUILLÓN-ROBLES, A. *ET AL.* 2003. Spatial and temporal evolution of basalts and magnesian andesites ('bajaites') from Baja California, Mexico: the role of slab melts. *Lithos*, **66**, 77–105.
- CAMERON, E. M. 1988. Archean gold: relation to granulite formation and redox zoning in the crust. *Geology*, **16**, 109–112.
- CASHMAN, K. V. 2004. Volatile controls on magma ascent and eruption. In: SPARKS, R. S. J. & HAWKESWORTH, C. J. (eds) *The State of the Planet: Frontiers and Challenges in Geophysics*. AGU Geophysical Monograph, **150**, 109–124.
- CHIARADIA, M. 2014. Copper enrichment in arc magmas controlled by overriding plate thickness. *Nature Geoscience*, **7**, 43–46.
- CHRISTOPHER, T., EDMONDS, M., TAISNE, B., ODBERT, H., COSTA, A., HARDS, V. & WADGE, G. 2014. Periodic sulphur dioxide degassing from the Soufrière Hills Volcano, related to deep magma supply. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online September 5, 2014, <http://dx.dio.org/10.1144/SP410.11>
- CIGOLINI, C., LAIOLO, M. & COPPOLA, D. 2014. Revisiting the last major eruptions at Stromboli volcano: inferences on the role of volatiles during magma storage and decompression. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online August 6, 2014, <http://dx.doi.org/10.1144/SP410.3>
- CLUZEL, N., LAPORTE, D., PROVOST, A. & KANNEWISCHER, I. 2008. Kinetics of heterogeneous bubble nucleation in rhyolitic melts: implications for the number density of bubbles in volcanic conduits and for pumice textures. *Contributions to Mineralogy and Petrology*, **156**, 745–763.
- DAS, T. & NOLET, G. 1998. Crustal thickness map of the western United States by partitioned waveform inversion. *Journal of Geophysical Research*, **103**, 30021–30038.
- DE LEEUW, G. A. M., HILTON, D. R., FISCHER, T. P. & WALKER, J. A. 2007. The He–CO<sub>2</sub> isotope and relative abundance characteristics of geothermal fluids in El Salvador and Honduras: new constraints on volatile mass balance of the Central American Volcanic Arc. *Earth and Planetary Science Letters*, **258**, 132–146.
- DEFANT, M. J. & DRUMMOND, M. S. 1990. Derivation of some modern arc magmas by melting of young subducted lithosphere. *Nature*, **347**, 662–665.
- DUNCAN, M. S. & DASGUPTA, R. 2014. CO<sub>2</sub> solubility and speciation in rhyolitic sediment partial melts at 1.5–3.0 GPa – implications for carbon flux in subduction zones. *Geochimica et Cosmochimica Acta*, **124**, 328–347.
- EDMONDS, M., PYLE, D. & OPPENHEIMER, C. 2001. A model for degassing at the Soufriere Hills Volcano, Montserrat, West Indies, based on geochemical data. *Earth and Planetary Science Letters*, **186**, 159–173.
- EDMONDS, M., PYLE, D. M. & OPPENHEIMER, C. 2002. HCl emissions at Soufrière Hills Volcano, Montserrat, West Indies, during a second phase of dome building, November 1999 to September 2000. *Bulletin of Volcanology*, **64**, 21–30.
- EDMONDS, M., AIUPPA, A. *ET AL.* 2010. Excess volatiles supplied by mingling of mafic magma at an andesite



## VOLATILES IN SUBDUCTION ZONE MAGMATISM

- arc volcano. *Geochemistry Geophysics Geosystems*, **11**(4), <http://dx.doi.org/10.1029/2009GC002781>
- EDMONDS, M., BRETT, A., HERD, R. A., HUMPHREYS, M. C. S. & WOODS, A. 2014a. Magnetite-bubble aggregates at mixing interfaces in andesite magma bodies. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online August 14, 2014, <http://dx.doi.org/10.1144/SP410.7>
- EDMONDS, M., HUMPHREYS, M. C. S. ET AL. 2014b. Pre-eruptive vapour and its role in controlling eruption style and longevity at Soufrière Hills Volcano. In: WADGE, G., ROBERTSON, R. E. A. & VOIGHT, B. (eds) *The Eruption of Soufrière Hills Volcano, Montserrat from 2000–2010*. Geological Society, London, Memoirs, **39**, 291–315.
- ELSWORTH, D., MATTIOLI, G., TARON, J., VOIGHT, B. & HERD, R. 2008. Implications of magam transfer between multiple reservoirs on eruption cycling. *Science*, **322**, 246–248.
- ENGLAND, P. C. & KATZ, R. F. 2010a. Global systematics of arc volcano position. *Nature*, **468**, E6–E7.
- ENGLAND, P. C. & KATZ, R. F. 2010b. Melting above the anhydrous solidus controls the location of volcanic arcs. *Nature*, **467**, 700–703.
- FEDOROV, S. A., GOREL'CHIK, V. I., STEPANOV, V. V. & GARBUZOVA, V. T. 1983. The development of the Great Tolbachik Fissure Eruption in 1975 from seismological data. In: FEDOTOV, S. A. & MARKHININ, Y. K. (eds) *The Great Tolbachik Fissure Eruption*. Cambridge University Press, Cambridge, England, 189–203.
- FERRARI, L., PETRONE, C. M. & FRANCALANCI, L. 2001. Generation of oceanic-island basalt-type volcanism in the western Trans-Mexican volcanic belt by slab rollback, asthenosphere infiltration, and variable flux melting. *Geology*, **29**, 507–510.
- FRYER, P., LOCKWOOD, J. P., BECKER, N., PHIPPS, S. & TODD, C. S. 2000. Significance of serpentinite mud volcano in convergent margins. In: DILEK, Y., MOORES, E. M., ELTHON, D. & NICOLAS, A. (eds) *Ophiolites and Oceanic Crust: New Insights from Field Studies and the Ocean Drilling Program*. Geological Society of America, Boulder, Colorado, Special Paper, **349**, 35–51.
- GAETANI, G. A. & GROVE, T. L. 1998. The influence of water on melting of mantle peridotite. *Contributions to Mineralogy and Petrology*, **131**, 323–346.
- GARRISON, J. M. & DAVIDSON, J. P. 2003. Dubious case for slab melting in the Northern volcanic zoned of the Andes. *Geology*, **31**, 565–568.
- GENAREAU, K., CRONIN, S. J. & LUBE, G. 2014. Effects of volatile behaviour on dome collapse and resultant pyroclastic surge dynamics: Gunung Merapi 2010 eruption. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online August 1, 2014, <http://dx.doi.org/10.1144/SP410.6>
- GIGGENBACH, W. F. 1980. Geothermal gas equilibria. *Geochimica et Cosmochimica Acta*, **44**, 2021–2032.
- GILL, J. B. 1981. *Orogenic Andesites and Plate Tectonics*. Springer Verlag, Heidelberg.
- GOMEZ-TUENA, A., LANGMUIR, C. H., GOLDSTEIN, S. L., STRAUB, S. M. & ORTEGA-GUTIERREZ, F. 2007. Geochemical evidence for slab melting in the trans-Mexican volcanic belt. *Journal of Petrology*, **48**, 537–562.
- GÓMEZ-TUENA, A., MORI, L., RINCÓN-HERRERA, N. E., ORTEGA-GUTIÉRREZ, F., SOLÉ, J. & IRIONDO, A. 2008. The origin of a primitive trondhjemite from the Trans-Mexican Volcanic Belt and its implications for the construction of a modern continental arc. *Geology*, **36**, 471–474.
- GROVE, T. L., CHATTERJEE, N., PARMAN, S. W. & MÉDARD, E. 2006. The influence of H<sub>2</sub>O on mantle wedge melting. *Earth and Planetary Science Letters*, **249**, 74–89.
- GROVE, T. L., TILL, C. B., LEV, E., CHATTERJEE, N. & MÉDARD, E. 2009. Kinematic variables and water transport control the formation and location of arc volcanoes. *Nature*, **459**, 649–679.
- GROVE, T. L., TILL, C. B., LEV, E., CHATTERJEE, N. & MÉDARD, E. 2010. Grove ET AL. reply. *Nature*, **468**, E7–E8.
- GROVE, T. L., TILL, C. B. & KRAWCZYNSKI, M. J. 2012. The role of H<sub>2</sub>O in subduction zone magmatism. *Annual Review of Earth and Planetary Sciences*, **40**, 413–439.
- HAMMARSTROM, J. M. & ZEN, E.-A. 1986. Aluminum in hornblende: an empirical igneous geobarometer. *American Mineralogist*, **71**, 1297–1313.
- HATTORI, K. H. & KEITH, J. D. 2001. Contribution of mafic melt to porphyry copper mineralization: evidence from Mount Pinatubo, Philippines, and Bingham Canyon, Utah, USA. *Mineralium Deposita*, **36**, 799–801.
- HILTON, D. R., FISCHER, T. P. & MARTY, B. 2002. Noble gases and volatile recycling at subduction zones. In: PORCELLI, D., BALLENTINE, C. J. & WIELER, R. (eds) *Noble Gases in Geochemistry and Cosmochemistry*. MSA Reviews in Mineralogy and Geochemistry, **47**, 319–370.
- HIROSE, K. 1997. Melting experiments on Iherzolite KLB-1 under hydrous conditions and generation of high-magnesian andesitic melts. *Geology*, **25**, 42–44.
- HOLLISTER, L. S., GRISSOM, G. C., PETERS, E. K., STOWELL, H. H. & SISSON, V. B. 1987. Confirmation of the empirical correlation of Al in hornblende with pressure of solidification of calc-alkaline plutons. *American Mineralogist*, **72**, 231–239.
- HUMPHREYS, M. C. S., CHRISTOPHER, T. & HARDS, V. 2009. Microlite transfer by disaggregation of mafic inclusions following magma mixing at Soufrière Hills volcano, Montserrat. *Contributions to Mineralogy and Petrology*, **157**, 609–624.
- HUPPERT, H. E. & WOODS, A. W. 2002. The role of volatiles in magma chamber dynamics. *Nature*, **420**, 493–495.
- HURWITZ, S. & NAVON, O. 1994. Bubble nucleation in rhyolitic melts: experiments at high pressure, temperature and water content. *Earth and Planetary Science Letters*, **122**, 267–280.
- HYNDMAN, R. D. & PEACOCK, S. M. 2003. Serpentinization of the forearc mantle. *Earth and Planetary Science Letters*, **212**, 417–432.



- JANARDHAN, A. S., NEWTON, R. C. & SMITH, J. V. 1979. Ancient crustal metamorphism at low P H<sub>2</sub>O; charnockite formation at Kabbaldurga, South India. *Nature*, **278**, 511–514.
- JEGO, S. & DASGUPTA, R. 2013. Fluid-present melting of sulfide-bearing ocean-crust: experimental constraints on the transport of sulfur from subducting slab to mantle wedge. *Geochimica et Cosmochimica Acta*, **110**, 106–134.
- JEGO, S. & DASGUPTA, R. 2014. The fate of sulfur during fluid-present melting of subducting basaltic crust at variable oxygen fugacity. *Journal of Petrology*, **55**, 1019–1050.
- JOHNSON, E. R., WALLACE, P. J., DELGADO-GRANADOS, H., MANEA, V. C., KENT, A. J. R., BINDEMAN, I. N. & DONEGAN, C. S. 2009. Subduction-related volatile recycling and magma generation beneath central Mexico: insights from melt inclusions, oxygen isotopes and geodynamic models. *Journal of Petrology*, **50**, 1729–1764.
- JUGO, P. J., LUTH, R. W. & RICHERDS, J. P. 2005. An experimental study of the sulfur content in basaltic melts saturated with immiscible sulfide or sulfate liquids at 1300 °C and 1.0 GPa. *Journal of Petrology*, **46**, 783–798.
- KAY, R. W. 1978. Aleutian magnesium andesites: melts from subducted pacific ocean crust. *Journal of Volcanology and Geothermal Research*, **4**, 117–132.
- KELEMEN, P. B. 1995. Genesis of high Mg# andesites and the continental crust. *Contributions to Mineralogy and Petrology*, **120**, 1–19.
- KELEMEN, P. B., HANGHOI, K. & GREENE, A. R. 2004. One view of the geochemistry of subduction-related magmatic arcs, with an emphasis on primitive andesite and lower crust. In: HOLLAND, H. D. & TUREKIAN, K. K. (eds) *Treatise on Geochemistry*. Elsevier-Pergamon, Oxford, **3**, 593–659.
- KENDRICK, M. A., SCAMBELLURI, M., HONDA, M. & PHILLIPS, D. 2011. High abundances of noble gas and chlorine delivered to the mantle by serpentinite subduction. *Nature Geoscience*, **4**, 807–812.
- KENDRICK, M. A., ARCULUS, R. J., DANYUSHEVSKY, L. V., KAMENETSKY, V. S., WOODHEAD, J. D. & HONDA, M. 2014a. Subduction-related halogens (Cl, Br and I) and H<sub>2</sub>O in magmatic glasses from Southwest Pacific Backarc Basins. *Earth and Planetary Science Letters*, **400**, 165–176.
- KENDRICK, M. A., JACKSON, M. G., KENT, A. J. R., HAURI, E. H., WALLACE, P. J. & WOODHEAD, J. 2014b. Contrasting behaviours of CO<sub>2</sub>, S, H<sub>2</sub>O and halogens (F, Cl, Br, and I) in enriched-mantle melts from Pitcairn and Society seamounts. *Chemical Geology*, **370**, 69–81.
- KENT, A. J. R., DARR, C., KOLESZAR, A. K., SALISBURY, M. J. & COOPER, K. M. 2010. Preferential eruption of andesite magmas through recharge filtering. *Nature Geoscience*, **3**, 631–636.
- KERRICK, D. M. 2002. Serpentinite seduction. *Science*, **298**, 1344–1345.
- KERRICK, D. M. & CONNOLLY, J. A. D. 1998. Subduction of ophiicarbonates and recycling of CO<sub>2</sub> and H<sub>2</sub>O. *Geology*, **26**, 375–378.
- KERRICK, D. M. & CONNOLLY, J. A. D. 2001a. Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature*, **411**, 293–296.
- KERRICK, D. M. & CONNOLLY, J. A. D. 2001b. Metamorphic devolatilization of subducted oceanic metabasalts: implications for seismicity, arc magmatism and volatile recycling. *Earth and Planetary Science Letters*, **189**, 19–29.
- KESSEL, R., ULMER, P., PETTKE, T., SCHMIDT, M. W. & THOMPSON, A. B. 2004. A novel approach to determine high-pressure high-temperature fluid and melt compositions using diamond-trap experiments. *American Mineralogist*, **89**, 1078–1086.
- KIM, Y., CLAYTON, R. W. & JACKSON, J. M. 2010. Geometry and seismic properties of the subducting Cocos plate in central Mexico. *Journal of Geophysical Research*, **115**, B06310.
- KUSHIRO, I. 1972. Effect of water on the composition of magmas at high pressures. *Journal of Petrology*, **13**, 311–334.
- KUSHIRO, I. 1987. A petrological model of the mantle wedge and lower crust in the Japanese island arcs. In: MYSEN, B. O. (ed.) *Magmatic Processes: Physico-chemical Principles*. The Geochemical Society, Special Publications, **1**, 165–181.
- KUTTEROLF, S., HANSTEEN, T. H., APPLE, K., FREUNDT, A., KRÜGER, K., PÉREZ, W. & WEHRMANN, H. 2013. Combined bromine and chlorine release from large explosive volcanic eruptions: a threat to stratospheric ozone? *Geology*, **41**, 707–710.
- LANGMUIR, C. H., BEZOS, A., ESCRIG, S. & PARMAN, S. W. 2006. Chemical systematics and hydrous melting of the mantle in back-arc basins. In: CHRISTIE, D. M., FISHER, C. R., LEE, S. M. & SHARON GIVENS, S. (eds) *Back-Arc Spreading Systems – Geological, Biological, Chemical, and Physical Interactions*. AGU Geophysical Monograph, **166**, 87–146.
- LEE, C., KIM, Y. J. *ET AL.* 2005. High ClO and ozone depletion observed in the plume of Sakurajima volcano, Japan. *Geophysical Research Letters*, **32**, L21809.
- LUDWIG, K. R. 2008. Isoplot version 3.70, A Geochronological Toolkit for Microsoft Excel, Berkeley Geochronology Center Special Publication No. 4.
- MACPHERSON, C. G., DREHER, S. T. & THIRWALL, M. F. 2006. Adakites without slab melting: high pressure differentiation of island arc magma, Mindanao, the Philippines. *Earth and Planetary Science Letters*, **243**, 581–593.
- MELNIK, O. & SPARKS, R. S. J. 1999. Nonlinear dynamics of lava dome extrusion. *Nature*, **402**, 37–41.
- MELNIK, O. & SPARKS, R. S. J. 2002. Dynamics of magma ascent and lava extrusion at Soufrière Hills Volcano, Montserrat. In: DRUITT, T. H. & KOKELAAR, B. P. (eds) *The Eruption of Soufrière Hills Volcano, Montserrat, from 1995 to 1999*. Geological Society, London, Memoirs, **21**, 153–171.
- MELNIK, O. E. & COSTA, A. 2014. Dual chamber-conduit models of non-linear dynamics behaviour at Soufrière Hills Volcano, Montserrat. In: WADGE, G., ROBERTSON, R. & VOIGHT, B. (eds) *The Eruption of Soufrière Hills Volcano, Montserrat from 2000 to 2010*. Geological Society, London, Memoirs, **39**, 61–69.
- MICHAEL, P. 1995. Regionally distinctive sources of depleted MORB: evidence from trace elements and

## VOLATILES IN SUBDUCTION ZONE MAGMATISM

- H<sub>2</sub>O. *Earth and Planetary Science Letters*, **131**, 301–320.
- MÜNTENER, O., KELEMEN, P. B. & GROVE, T. L. 2001. The role of H<sub>2</sub>O during crystallization of primitive arc magmas under uppermost mantle conditions and genesis of igneous pyroxenites: an experimental study. *Contributions to Mineralogy and Petrology*, **141**, 643–658.
- NADEAU, O., WILLIAMS-JONES, A. E. & STIX, J. 2010. Sulphide magma as a source of metals in arc-related magmatic hydrothermal ore fluids. *Nature*, **3**, 501–505.
- NEGULESCU, E. & SĂBĂU, G. 2014. Fluid-mediated alteration of eclogite lenses in subduction complexes: a case from the Leaota Massif (South Carpathians). In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online September 3, 2014, <http://dx.doi.org/10.1144/SP410.10>
- NISHIO, Y., SASAKI, S., GAMO, T., HIYAGON, H. & SANO, Y. 1998. Carbon and helium isotope systematics of North Fiji Basin basalt glasses: carbon geochemical cycle in the subduction zone. *Earth and Planetary Science Letters*, **154**, 127–138.
- ODA, H. & USHIO, T. 2007. Topography of the Moho and Conrad discontinuities in the Kyushu district, Southwest Japan. *Journal of Seismology*, **11**, 221–233.
- PEREZ-CAMPOS, X., KIM, Y. H. ET AL. 2008. Horizontal subduction and truncation of the Cocos Plate beneath central Mexico. *Geophysical Research Letters*, **35**, 18303.
- PLANK, T. & LANGMUIR, C. H. 1998. The geochemical composition of subducting sediments and its consequence for the crust and mantle. *Chemical Geology*, **145**, 325–394.
- PLANK, T., COOPER, L. B. & MANNING, C. E. 2009. Emerging geothermometers for estimating slab surface temperatures. *Nature Geosciences*, **2**, 611–615.
- PLANK, T., KELLEY, K. A., ZIMMER, M. M., HAURI, E. H. & WALLACE, P. J. 2013. Why do mafic arc magmas contain ~4 wt% water on average? *Earth and Planetary Science Letters*, **364**, 168–179.
- PYLE, D. M. & MATHER, T. A. 2009. Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: a review. *Chemical Geology*, **263**, 110–121.
- RANERO, C. R., PHIPPS MORGAN, J., MCINTOSH, K. & REICHERT, C. 2003. Bending-related faulting and mantle serpentinization at the Middle America trench. *Nature*, **425**, 367–373.
- RAPP, R. P., SHIMIZU, N. & NORMAN, M. D. 2003. Growth of early continental crust by partial melting of eclogite. *Nature*, **425**, 605–609.
- RIVALTA, E. & SEGALL, P. 2008. Magma compressibility and the missing source for some dike intrusions. *Geophysical Research Letters*, **35**, L04306.
- ROBERGE, J., GUILBAUD, M. N., MERCER, C. N. & REYES-LUNA, P. C. 2014. Insight into monogenetic eruption processes at Pelagatos volcano, Sierra Chichinautzin, Mexico: a combined melt inclusion and physical volcanology study. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online September 12, 2014, <http://dx.doi.org/10.1144/SP410.12>
- RÜPKE, L. H., PHIPPS MORGAN, J., HORT, M. & CONNOLLY, J. A. D. 2004. Serpentine and the subduction zone water cycle. *Earth and Planetary Science Letters*, **223**, 17–34.
- RUPRECHT, P. & PLANK, T. 2013. Feeding andesitic eruptions with a high-speed connection from the mantle. *Nature*, **500**, 68–72.
- RUSCITTO, D. M., WALLACE, P. J., JOHNSON, E. R., KENT, A. J. R. & BINDEMAN, I. N. 2010. Volatile contents of mafic magmas from cinder cones in the Central Oregon High Cascades: implications for magma formation and mantle conditions in a hot arc. *Earth and Planetary Science Letters*, **298**, 153–161.
- RUSCITTO, D. M., WALLACE, P. J., COOPER, L. B. & PLANK, T. 2012. Global variations in H<sub>2</sub>O/Ce: 2. Relationships to arc magma geochemistry and volatile fluxes. *Geochemistry Geophysics Geosystems*, **13**, Q03025.
- SCALLET, B. & PICHAVANT, M. 2003. Experimental constraints on volatile abundances in arc magmas and their implications for degassing processes. In: OPPENHEIMER, C., PYLE, D. M. & BARCLAY, J. (eds) *Volcanic Degassing*. Geological Society, London, Special Publications, **213**, 23–52.
- SCHIANO, P., CLOCHIATTI, R., SHIMIZU, N., MAURI, R. C., JOCHUM, K. P. & HOFMANN, A. W. 1995. Hydrous, silica-rich melts in the subarc mantle and their relationship with erupted lavas. *Nature*, **377**, 595–600.
- SCHMIDT, M. W. & POLI, S. 1998. Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. *Earth and Planetary Science Letters*, **163**, 361–379.
- SCHMIDT, M. W., VIELZEU, D. & AUZANNEAU, E. 2004. Melting and dissolution of subducting crust at high pressures: the key role of white mica. *Earth and Planetary Science Letters*, **228**, 65–84.
- SHAPIRO, N. M. & RITZWOLLER, M. H. 2004. Inferring surface heat flux distributions guided by a global seismic model: particular application to Antarctica. *Earth and Planetary Science Letters*, **223**, 213–224.
- SHARP, Z. D. & BARNES, J. D. 2004. Water-soluble chlorides in massive seafloor serpentinites: a source of chloride in subduction zones. *Earth and Planetary Science Letters*, **226**, 243–254.
- SHARP, Z. D., BARNES, J. D., BREARLEY, A. J., CHAUSSIDON, M., FISCHER, T. B. & KAMENETSKY, M. B. 2007. Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. *Nature*, **446**, 1062–1065.
- SHAW, A. M., HILTON, D. R., FISCHER, T. P., WALKER, J. A. & ALVARADO, G. E. 2003. Contrasting He-C relationships in Nicaragua and Costa Rica: insights into C cycling through subduction zones. *Earth and Planetary Science Letters*, **214**, 499–513.
- SHINOHARA, H. 1994. Exsolution of immiscible vapor and liquid phases from a crystallizing silicate melt: implications for chlorine and metal transport. *Geochimica et Cosmochimica Acta*, **58**, 5215–5221.

- SHINOHARA, H. 2008. Excess degassing from volcanoes and its role on eruptive and intrusive activity. *Reviews of Geophysics*, **46**, RG4005.
- SISSON, T. W. & GROVE, T. L. 1993. Experimental investigations of the role of H<sub>2</sub>O in calc-alkaline differentiation and subduction zone magmatism. *Contributions to Mineralogy and Petrology*, **113**, 143–166.
- SMITH, I. E. M., TAYLOR, S. R. & JOHNSON, R. W. 1979. REE-fractionated trachytes and dacites from Papua New Guinea and their relationship to andesite petrogenesis. *Contributions to Mineralogy and Petrology*, **69**, 227–233.
- SORENSEN, S. S., GROSSMAN, J. N. & PERFIT, M. R. 1997. Phengite-hosted LILE enrichment in eclogite and related rocks: implications for fluid-mediated mass transfer in subduction zones and arc magma genesis. *Journal of Petrology*, **38**, 3–34.
- SPARKS, R. S. J., MURPHY, M. D., LEJEUNE, A.-M., WATTS, R. B., BARCLAY, J. & YOUNG, S. R. 2000. Control on the emplacement of the andesite lava dome of the Soufriere Hills Volcano by degassing-induced crystallization. *Terra Nova*, **12**, 14–20.
- STAUDIGEL, H., PLANK, T., WHITE, B. & SCHMINCKE, H. U. 1996. Geochemical fluxes during seafloor alteration of the basaltic upper oceanic crust: DSDP sites 417 and 418. In: BEBOUT, G. E., SCHOLL, D. W., KIRBY, S. H. & PLATT, J. P. (eds) *Subduction: Top to Bottom*. American Geophysical Union, Washington, 1938.
- STRAUB, S. M. & LAYNE, G. D. 2003a. Decoupling of fluids and fluid-mobile elements during shallow subduction: evidence from halogen-rich andesite melt inclusions from the Izu arc volcanic front. *Geochemistry Geophysics Geosystems*, **4**, 9003.
- STRAUB, S. M. & LAYNE, G. D. 2003b. The systematics of chlorine, fluorine and water in Izu arc front volcanic rocks: implication for volatile recycling in subduction zones. *Geochimica et Cosmochimica Acta*, **67**, 4179–4203.
- STRAUB, S. M., GOMEZ-TUENA, A., STUART, F. M., ZELLMER, G. F., CAI, Y. & ESPINASA-PERENA, R. 2011. Formation of hybrid arc andesites beneath thick continental crust. *Earth and Planetary Science Letters*, **303**, 337–347.
- STRAUB, S. M., GOMEZ-TUENA, A. *ET AL.* 2013. The processes of melt differentiation in arc volcanic rocks: insights from OIB-type arc magmas in the central Mexican Volcanic Belt. *Journal of Petrology*, **54**, 665–701.
- SYMONDS, R. B., REED, M. H. & ROSE, W. I. 1992. Origin, speciation, and fluxes of trace-element gases at Augustine volcano, Alaska: insights into magma degassing and fumarolic processes. *Geochimica et Cosmochimica Acta*, **56**, 633–657.
- TARAN, Y. & ZELENSKI, M. 2014. Systematics of water isotopic composition and chlorine content in arc-volcanic gases. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online August 7, 2014, <http://dx.doi.org/10.1144/SP410.5>
- THORWART, M., DZIERMA, Y., LIESER, K., BUHS, H. & RABELL, W. 2014. Shear-wave velocity structure of the Chilean subduction zone (39–40°S) based on Rayleigh wave dispersion: evidence of fluid release and melts in the mantle beneath the Villarrica volcano. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online August 14, 2014, <http://dx.doi.org/10.1144/SP410.9>
- TSUNO, K. & DASGUPTA, R. 2012. The effect of carbonates on near-solidus melting of pelite at 3 GPa: relative efficiency of H<sub>2</sub>O and CO<sub>2</sub> subduction. *Earth and Planetary Science Letters*, **319–320**, 185–196.
- UENO, T., SHIBUTANI, T. & ITO, K. 2008. Configuration of the continental Moho and Philippine Sea slab in southwest Japan derived from receiver function analysis: relation to subcrustal earthquakes. *Bulletin of the Seismological Society of America*, **98**, 2416–2427.
- ULMER, P. & TROMMSDORF, V. 1995. Serpentine stability to mantle depth and subduction-related magmatism. *Science*, **268**, 858–861.
- VAN KEEKEN, P. E., HACKER, B. R., SYRACUSE, E. M. & ABERS, G. A. 2011. Subduction factory: 4. Depth-dependent flux of H<sub>2</sub>O from subducting slabs worldwide. *Journal of Geophysical Research*, **116**, B01401.
- VAN SOEST, M. C., HILTON, D. R. & KREULEN, R. 1998. Tracing crustal and slab contributions to arc magmatism in the Lesser Antilles island arc using helium and carbon relationships in geothermal fluids. *Geochimica et Cosmochimica Acta*, **62**, 3323–3335.
- WALLACE, P. J. 2001. Volcanic SO<sub>2</sub> emissions and the abundance and distribution of exsolved gas in magmas. *Journal of Volcanology and Geothermal Research*, **108**, 85–106.
- WALLACE, P. J. 2005. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *Journal of Volcanology and Geothermal Research*, **140**, 217–240.
- WALLACE, P. J. & EDMONDS, M. 2011. The sulfur budget in magmas: evidence from melt inclusions, submarine glasses, and volcanic gas emissions. *Reviews in Mineralogy and Geochemistry*, **73**, 215–246.
- WALLACE, P. J. & GERLACH, T. M. 1994. Magmatic vapor source for sulfur dioxide released during volcanic eruptions: evidence from Mount Pinatubo. *Sciences*, **265**, 497–499.
- WALTER, M. J., KOHN, S. C. *ET AL.* 2011. Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions. *Science*, **334**, 54–57.
- WERNER, C., EVANS, W. C., KELLY, P. J., MCGIMSEY, R., PFEFFER, M., DOUKAS, M. & NEAL, C. 2012. Deep magmatic degassing v. scrubbing: elevated CO<sub>2</sub> emissions and C/S in the lead-up to the 2009 eruption of Redoubt Volcano, Alaska. *Geochemistry Geophysics Geosystems*, **13**, Q03015.
- YUAN, X., SOBOLEV, S. V. & KIND, R. 2002. Moho topography in the central Andes and its geodynamic implications. *Earth and Planetary Science Letters*, **199**, 389–402.
- ZELLMER, G. F. 2008. Some first order observations on magma transfer from mantle wedge to upper crust at volcanic arcs. In: ANNEN, C. & ZELLMER, G. F. (eds) *Dynamics of Crustal Magma Transfer, Storage and*

## VOLATILES IN SUBDUCTION ZONE MAGMATISM

- Differentiation*. Geological Society, London, **304**, 15–31.
- ZELLMER, G. F. 2009. Petrogenesis of Sr-rich adakitic rocks at volcanic arcs: insights from global variations of eruptive style with plate convergence rates and surface heat flux. *Journal of the Geological Society*, **166**, 725–734.
- ZELLMER, G. F. & ANNEN, C. 2008. An introduction to magma dynamics. In: ANNEN, C. & ZELLMER, G. F. (eds) *Dynamics of Crustal Magma Transfer, Storage and Differentiation*. Geological Society, London, Special Publications, **304**, 1–13.
- ZELLMER, G. F., ANNEN, C., CHARLIER, B. L. A., GEORGE, R. M. M., TURNER, S. P. & HAWKESWORTH, C. J. 2005. Magma evolution and ascent at volcanic arcs: constraining petrogenetic processes through rates and chronologies. *Journal of Volcanology and Geothermal Research*, **140**, 171–191.
- ZELLMER, G. F., IIZUKA, Y., MIYOSHI, M., TAMURA, Y. & TATSUMI, Y. 2012. Lower crustal H<sub>2</sub>O controls on the formation of adakitic melts. *Geology*, **40**, 487–490.
- ZELLMER, G. F., FREYMUTH, H., CEMBRANO, J. M., CLAVERO, J. E., VELOSO, E. A. E. & SIELFELD, G. G. 2014a. Altered mineral uptake into fresh arc magmas: insights from U–Th isotopes of samples from Andean volcanoes under differential crustal stress regimes. In: GOMEZ-TUENA, A., STRAUB, S. M. & ZELLMER, G. F. (eds) *Orogenic Andesites and Crustal Growth*. Geological Society, London, Special Publications, **385**, 185–208.
- ZELLMER, G. F., HWANG, S.-L. ET AL. 2014b. Interaction of arc magmas with subvolcanic hydrothermal systems: insights from compositions and metasomatic textures of olivine crystals in fresh basalts of Daisen and Mengameyama, Western Honshu, Japan. In: ZELLMER, G. F., EDMONDS, M. & STRAUB, S. M. (eds) *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society, London, Special Publications, **410**. First published online July 18, 2014, <http://dx.doi.org/10.1144/SP410.1>
- ZELLMER, G. F., SAKAMOTO, N., IIZUKA, Y., MIYOSHI, M., TAMURA, Y., HSIEH, H.-H. & YURIMOTO, H. 2014c. Crystal uptake into aphyric arc melts: insights from two-pyroxene pseudo-decompression paths, plagioclase hygrometry, and measurement of hydrogen in olivines from mafic volcanics of southwest Japan. In: GOMEZ-TUENA, A., STRAUB, S. M. & ZELLMER, G. F. (eds) *Orogenic Andesites and Crustal Growth*. Geological Society, London, Special Publications, **385**, 161–184.
- ZELLMER, G. F., RUBIN, K. H., MILLER, C. A., SHELLNUTT, J. G., BELOUSOV, A. & BELOUSOVA, M. In press. U–Th isotope constraints on the petrogenetic processes and ages of young effusive eruptions from Tatun Volcano Group, northern Taiwan. In: CARICCHI, L. & BLUNDY, J. D. (eds) *Chemical, Physical and Temporal Evolution of Magmatic Systems*. Geological Society, London, Special Publications.