

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 H₂O) 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 H₂O 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 H₂O 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 H₂O 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 H₂O, 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

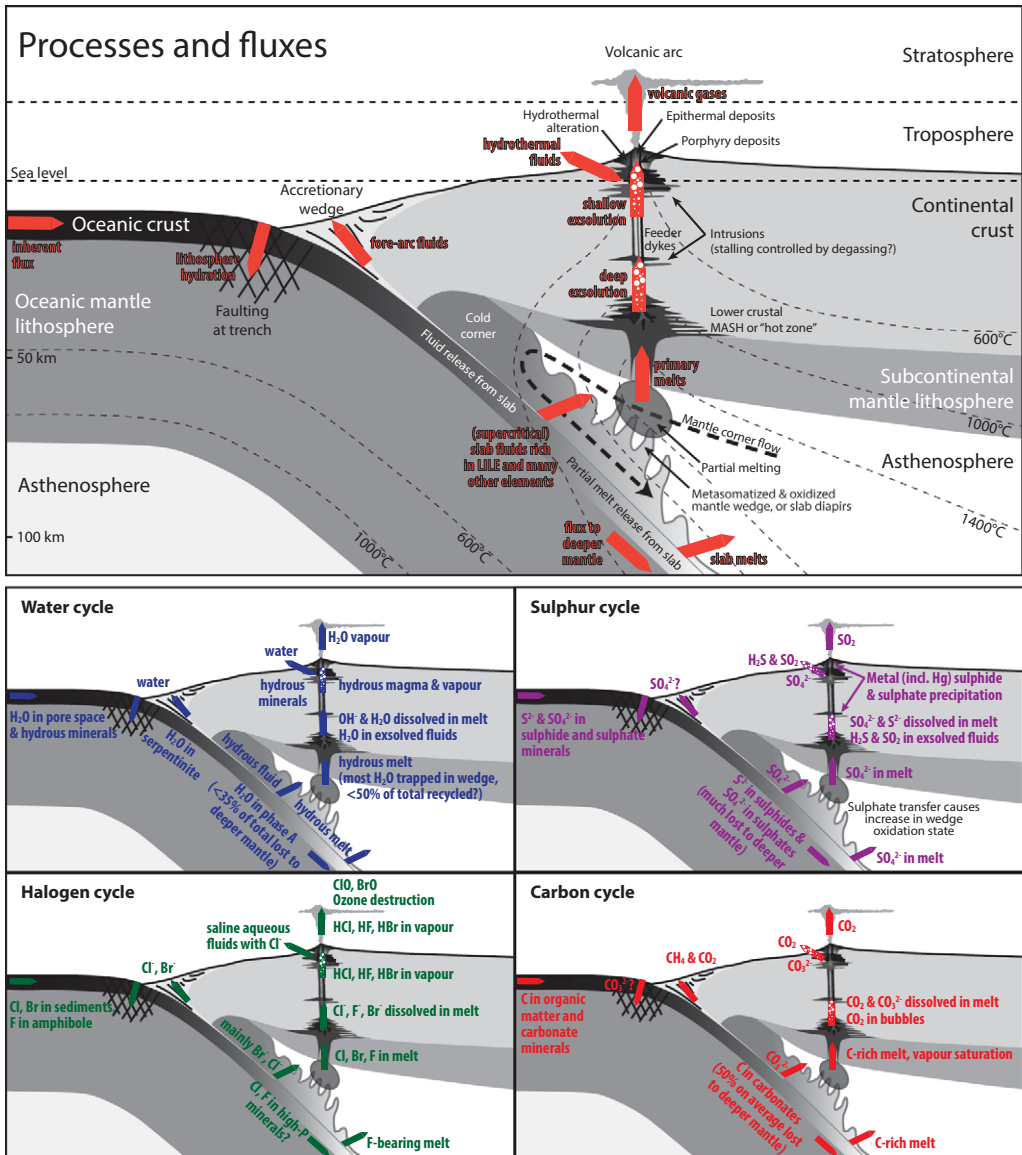


Fig. 1. Processes and fluxes in subduction zones, with individual panels showing volatile cycles for water, sulphur, halogens and carbon. Arrows indicate fluxes in a general direction. See text for discussion.

(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 CO₂ than ocean island basalts, although it has been suggested that deep and

pervasive CO₂ 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 H₂O 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% H₂O. 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 CO₂ 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 SO₂, CO₂ 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 (H₂O, CO₂, 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 H₂O (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), H₂O 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 H₂O beyond arc front depths (Schmidt & Poli 1998; Schmidt *et al.* 2004). Carbonate sediments, metabasalts and carbonated peridotite carry CO₂ into subduction zones. CO₂ 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,

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}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}U and ^{226}Ra excesses are carried by samples with between 50 and 55 wt% SiO_2 (i.e. by silica-rich basalts and basaltic andesites). Disequilibrium clearly decline 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 U^{6+}), but in addition includes major element oxides such as 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 H_2O -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 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 H_2O 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 H_2O 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

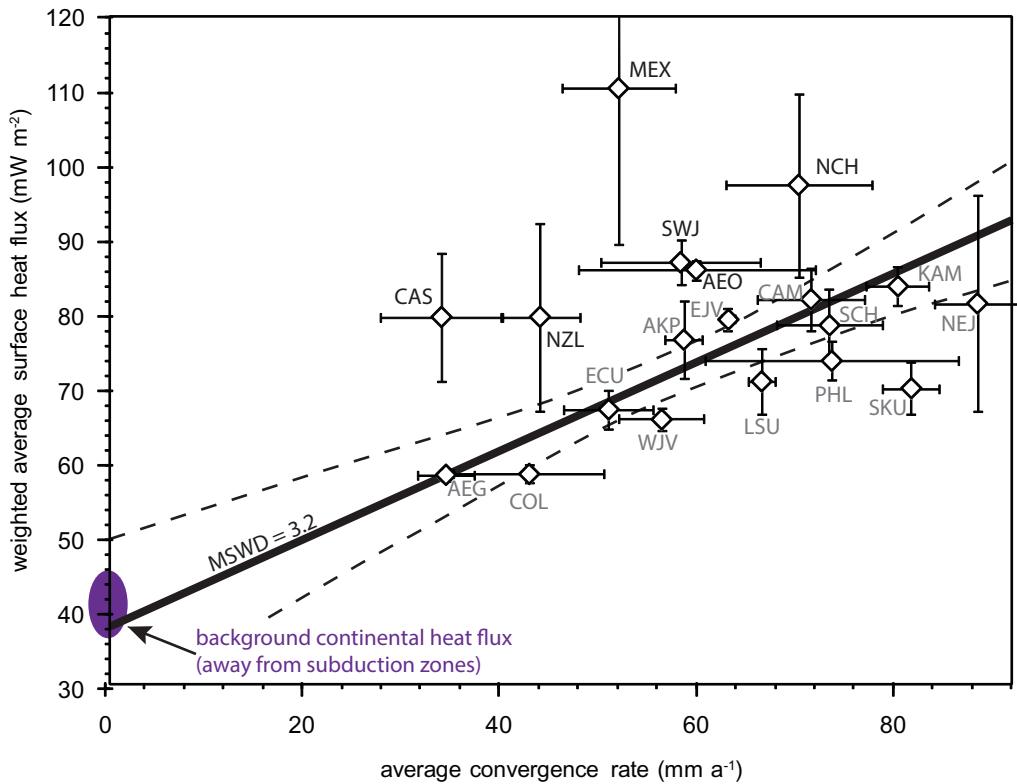


Fig. 2. Variation of average surface heat flux with average convergence rates for global continental to transitional volcanic arcs, compiled from Zellmer (2008). Weighted average surface heat flux with 1σ uncertainties due to along- and across-arc heat flux variations are based on the global surface heat flux model of Shapiro & Ritzwoller (2004). Average convergence rates with 1σ 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 1σ 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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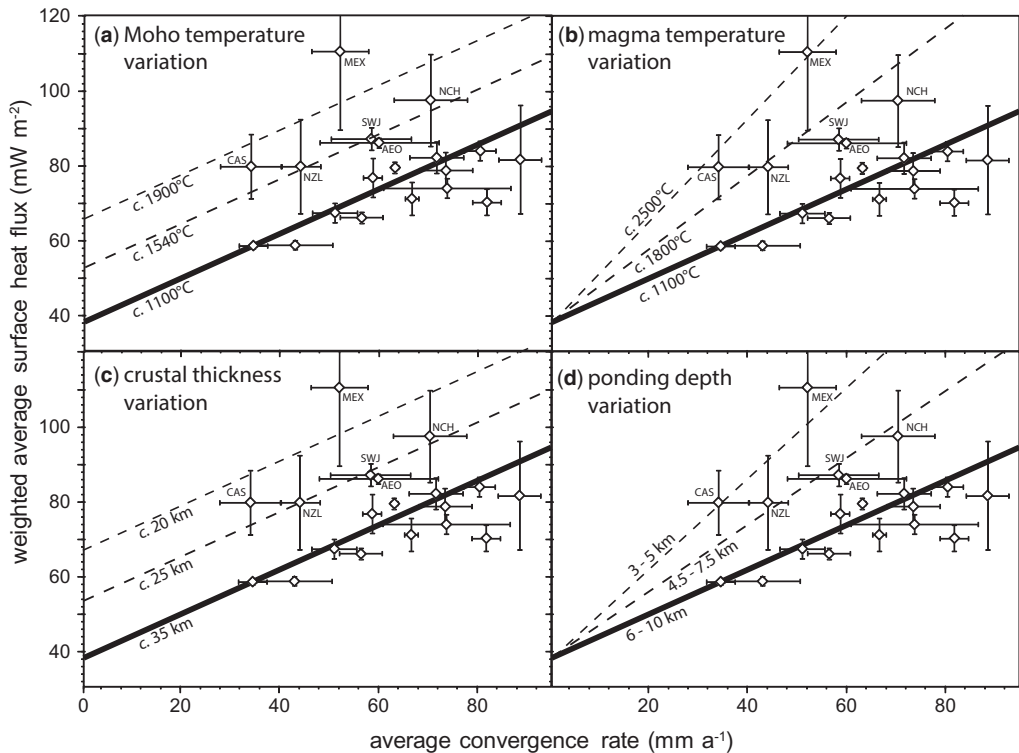


Fig. 3. Exploring ways to explain excess heat flux in Mexico, the Cascades, New Zealand, Southwest Japan and Northern Chile. The effects of varying (a) Moho temperature, (b) magma temperature, (c) crustal thickness and (d) magma ponding level, assuming heat conduction through the crust and heat advection 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 H₂O 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 H₂O 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 H₂O 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. H₂O-bearing mafic melts have the capacity to evolve to H₂O-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 SO₂ 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 SO₂ 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 SO₂ 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 km³).

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 H₂O 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 ²³⁸U–²³⁰Th and ²³⁴U–²³⁸U disequilibria of crystals in a fresh groundmass that is in ²³⁴U–²³⁸U 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 H₂O, CO₂ 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). 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 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 H_2O 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 H_2O , CO_2 and 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 CO₂ into the atmosphere (which to date has been difficult to address due to the relatively high atmospheric CO₂ 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.

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