Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: a review

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Abstract

The halogens (F, Cl, Br, I) form an important suite of tracers of igneous processes, and may be used to track magmas from their point of origin, through their differentiation, evolution, saturation in vapour and escape to the Earth's atmosphere and hydrosphere. This review summarises the current state of the field, starting with an analysis of what is, and what is not, known about the distribution of halogens in Earth's interior reservoirs, and the principal controls on their behaviour during partial melting, crystallisation and degassing. With recent advances in measurement techniques, there is now a new opportunity to improve the inventories of halogen emissions from the open-vent, continuously-degassing systems that dominate the background contribution of volcanoes to the atmosphere. The different approaches to estimating the fluxes of HCl and HF to the atmosphere from arc and global volcanism are converging, and can now be used to place important constraints on the global cycling of halogens through subduction-zone systems. Arc-related volcanic emissions of halogens dominates the global halogen degassing budgets. Our current best estimates of halogen degassing fluxes from arc volcanoes are 4.3 (±1) Tg/a (HCl), 0.5 (±0.2) Tg/a (HF), 5 – 15 Gg/a (HBr) and 0.5 – 2 Gg/a (HI).

Keywords.

Volcanic degassing, halogen geochemistry, subduction-zone magmatism.

1. Introduction

The halogen elements are a suite of reactive elements that comprise Group VII of the periodic table (Table 1). The halogens are rarely found in nature in their free elemental states, and are more usually combined as halide ions (X-) in salts, solutions and gases. Compounds of fluorine and chlorine are relatively abundant in crustal rocks (at mean concentrations of ca. 550 ppm and 240 ppm, respectively; Table 2); while those of bromine and iodine are much less abundant (< 1 ppm in the crust). The fifth, and heaviest, halogen element is astatine (At), one of the least abundant naturally-occurring elements in nature which exists only transiently within the decay chains of the ^{235}U and ^{238}U decay series. Many halogen-bearing compounds are volatile (e.g. the halogen halides, HX, and halocarbons), while others are soluble in aqueous fluids. As a consequence, the halogens are distributed between the various terrestrial geochemical reservoirs at the present day (Table 2), with distribution patterns that have been influenced by transport between these reservoirs over geological time.

Volcanic activity and associated processes play a key role in chemical exchanges between different Earth system reservoirs. The role of volcanism in mediating halogen fluxes between these reservoirs is important for reasons associated both with the effects of the halogens themselves, as well as their role in the transport of other elements (e.g. in ore-forming processes, e.g., Williams-Jones and Heinrich, 2005). After water, carbon dioxide and sulphur species, hydrogen chloride is often the most abundant species in high-temperature volcanic emissions (Symonds et al., 1994). Volcanic HCl emissions have been shown to have detrimental effects on local soils and ecosystems (Delmelle et al., 2001; 2003), play a key role in terms of trace metal transport from the magma to the atmosphere (Symonds et al., 1992), contain useful information about subsurface processes in terms of volcanic hazard assessment (Edmonds et al., 2001; Allard et al., 2005) and have recently been implicated in stratospheric ozone losses following an Icelandic eruption (Hekla, 2001; Millard et al., 2006; Rose et al., 2006). Volcanic HF emissions accompanying major ash-forming eruptions are also implicated in the environmental impacts which may accompany volcanic eruptions: HF is now considered to be an important reagent in volcanic plumes, in particular due to its involvement in the reaction and dissolution of volcanic glass (Woelff-Boenisch et al., 2004; Delmelle et al., 2007), while the deposition of water-soluble halides to agricultural land is considered a major factor in fluorosis in grazing animals affected by eruptions (Cronin et al., 2003). With the recent discovery of bromine monoxide in volcanic plumes (Bobrowski et al., 2003), and improved techniques for the analysis of direct samples of volcanic plumes allowing detection of HBr and HI (Aiuppa et al., 2005), the fluxes and atmospheric consequences of the less abundant halogens bromine and iodine are just beginning to be understood.

While there have been several attempts at quantifying and understanding volcanic halogen emissions to the atmosphere in recent decades (e.g. Symonds et al., 1988; Halmer et al., 2002; Wallace, 2005; Fischer, 2008), many uncertainties remain both in terms of quantifying rates of volcanic emission to the atmosphere, as well as in terms of understanding the global geochemical cycles of the halogens (e.g. their origin in magmatic systems), and their fate, once released to the environment. In this paper we critically, but briefly, review the state of current knowledge concerning the distribution of halogens in volcanic rocks, and the volcanic degassing fluxes of halogens to the atmosphere and oceans. In the remainder of the paper, when we refer to the ‘halogens’ generally, the reader should be aware that in fact there is a great deal of disparity in terms of what is known about the different halogen elements themselves. So while the behaviour of chlorine in volcanic systems is well characterised and that of fluorine is moderately well characterised, there are far fewer constraints on the behaviour of bromine and iodine.

2. Halogens in terrestrial reservoirs and the behaviour of halogens during partial melting.

2.1 Halogens in terrestrial reservoirs

Little progress has been made in quantifying the distributions and concentrations of halogens in the Earth's major geochemical reservoirs since the formative work in the late 1970's to early 1990's (Unni and Schilling, 1978; Schilling et al., 1978; 1980; Ito et al., 1983; Deruelle et al., 1992; Wedepohl 1995; Jambon et al., 1995). In part, this reflects the challenges of analysing species (such as Br, I) which are only present in very low concentrations (ppb) in the Earth's mantle. In addition, it reflects the difficulty of constraining whole-earth budgets of volatile species with low nebular condensation temperatures (700 – 900 K; Wasson, 1985): not only are the Earth's starting conditions in terms of halogen content not well known; the degassing history of halogens is also not well constrained. There is the prospect of improving on this in the future, for example from noble gas models (e.g. Pepin and Porcelli 2006) which may, at least, place constraints on outgassing histories of iodine (^{129}Xe is a stable daughter of the short-lived ^{129}I).

Current estimates of the halogen contents of primitive and MORB-source mantle, crust and other terrestrial reservoirs are summarised in Table 2, along with estimates of other selected elements. There are considerable uncertainties in many of these estimates which partly reflect the poor quantitative control on the global budgets of the halogen species (in particular, Br, I), and partly reflects the complexities of assessing the halogen contents of some reservoirs (for example, those species concentrated into minerals and fluids within inaccessible parts of the continental crust; e.g. Cl). In addition, some of the variance between estimates of, for example, halogen contents of the depleted MORB-source mantle, reflects the sensitivity of these estimates to different assumptions about how chemically-enriched or depleted the asthenospheric mantle might be, and to assumptions about the extent of partial melting in the source region. Despite the uncertainties, the most notable features about which there is general agreement are that, as expected, the halogens are strongly concentrated in Earth's differentiated crust, sediments and hydrosphere. In terms of the Earth's outer reservoirs (crust, oceans and atmosphere and MORB-source mantle), the greater proportion of both Cl and Br reside in the oceans (ca. 73% and 51% respectively, Kramers, 2003); the budget of I is dominated by iodine associated with organic sediments in the bulk continental crust (ca. 60%), with < 1% dissolved in the oceans, while the budget of F is dominated by the MORB-source mantle.

2.2 Partitioning behaviour of the halogens during partial melting

The gross distributions of the halogens between mantle and crustal reservoirs reflect, as a primary control, the incompatibilities of the halogens during partial melting and differentiation. While there are no direct experimental measurements of the partitioning behaviour of halogen species between melt and crystals relevant to mantle melting, the large ionic radii of Cl^-, Br^- and I^- (Table 1) mean that they are expected to be highly incompatible during partial melting of peridotite (Schilling et al., 1980; Deruelle et al., 1992). Fluoride, on the other hand, is a much smaller ion, capable of substituting for OH^- into the major rock-forming minerals, whether hydrous or nominally-anhydrous. Consequently F^- is expected only to be moderately incompatible during partial melting.

In the absence of experimental constraints on partitioning behaviour, the systematics of halogens in suites of natural, undegassed glasses may be used to infer their incompatibility during partial melting and fractional crystallisation. From correlations observed between halogens (Cl, Br and F) and other conservative and incompatible trace elements, Schilling et al., (1980) argued that the ratios Cl/K and F/P (and F/Sr, F/Nd) appeared to be more or less invariant in basaltic rocks, suggesting that Cl and K and F, P and Nd are equally incompatible during partial melting and fractional crystallisation. Subsequent work has broadly substantiated Schilling's suggestion, with current estimates of depleted mantle Cl/K ~ 0.007-0.01 and F/P ~ 0.3 ± 0.1 (e.g. Saal et al., 2002; Salters and Stracke, 2004). During hydrous melting and crystallisation, the bulk mineral-melt partition coefficient for Cl appears to be slightly lower than those of Nb and K (Sun et al., 2007), matching observations of the similar behaviour of Cl and Nb in MORB (e.g. le Roux et al., 2006). In the case of F, undegassed submarine glasses from normal MORB, Samoa (an ocean island) and the Siquieros transform all have F/Nd ~ 21, suggesting that F and Nd have identical bulk partition coefficients during partial melting of peridotite (Saal et al., 2002; Workman et al., 2006). In terms of the other magmatic volatile species, the same approach has led to the widely adopted notions that CO_2/Nb, S/Dy and H_2O/Ce ratios are essentially invariant during partial melting of vapour-undersaturated peridotite (e.g. Michael, 1995; Saal et al., 2002; Salters and Stracke, 2004; Cartigny et al., 2008).

Evidence relating to the relative incompatibilities of Br and I are rather weaker, principally due to a lack of data. Schilling et al. (1980) argued that Br is likely to be highly incompatible, with a bulk partition coefficient close to those of Ba and Rb during partial melting of peridotite; and I is likely to be more incompatible still (Deruelle et al., 1992). These broad-brush statements are borne out by the patterns of relative enrichments of the halogens into bulk continental crust, compared to estimates of primitive mantle (Figure 1). By using the conventional ordering of elements with increasing incompatibility, and hence increasing enrichment in the bulk crust, towards the left (e.g. Hofmann, 1988), the deviations from the general trend for Br and Cl are immediately apparent. Neither Br nor Cl are as enriched as expected in the crust, since they are instead concentrated in the oceans.

2.3 Behaviour of halogens in subduction zones

As expected, the differing concentration of halogen species in different surface reservoirs leads to contrasting behaviour in subduction-related magmas: fluids in subduction zones should play a major role in recycling Br and Cl into the mantle, while organic-rich sediments should play the same role for I. The role of ocean crust recycling is, however, very poorly constrained: for example, while Matsumoto and Wedepohl (1998) argue that the ocean crust is an important repository for I, Deruelle et al. (1992) argued that the influence of the subducted oceanic crust on subduction-related magmas was not detectable. A compilation of Cl and F data from suites of mafic glasses and phenocryst-hosted melt inclusions from different tectonic settings (Figures 2a-c) shows a strong increase in Cl/K in subduction-related settings, over Hawaii, Iceland and MORB in turn, consistent with addition of a Cl-rich component in subduction zones (e.g. Ito et al., 1983), and with a contribution from recycled lithosphere to some ocean-island basalts (e.g. Simons et al., 2002; Stroncik and Haase, 2004). In contrast, F/P lies broadly in the same range in each of these settings, although showing a considerably increased variance in arcs. The variability of F/P in melt inclusions in mafic arc-related magmas (Fig. 2c) most likely reflects subduction-related (slab fluid?) controls on fluorine contents. For example, there are substantial variations in F/P of these melt inclusions both regionally within the same arc system (e.g. Central America), and between arcs (Fig. 2c), which most likely reflect variation in the composition of the slab component.

The contrasting source characteristics of F and Cl in different tectonic settings is brought out in Figure 3, which shows the systematics of mafic glass and phenocryst-hosted melt inclusions for several suites of magmas. Confirming the general pattern found by Schilling et al., 1980, F/Cl ratios are highest in (undegassed) samples of MORB (e.g. Siqueiros transform; F/Cl > 10), are lower in ocean island source regions (e.g. Azores, Schilling et al., 1980; Iceland and Hawaii, Fig. 4), and lower still in arc-related magmas (e.g. Izu, Kamchatka, F/Cl < 1). This general pattern predominantly reflects the addition of a Cl-rich component in subduction zones. Aside from this general pattern, the most striking feature of Figure 4 is the considerable range of F/Cl in Hawaiian glasses and melt inclusions. Mass ratios of F/Cl in matrix glasses from subaerial samples range from ~ 0.7 - > 7, while some melt inclusions and a portion of matrix glasses from subaqueously-emplaced samples range to very low F/Cl (<0.2). The variability might reflect contamination of some submarine samples with sea-water (rich in Cl), or sea-water-derived fluids in the crust (Davis et al., 2003); it may also reflect preferential loss of Cl during degassing of shallow-submarine and subaerial samples.

Anomalous and selective enrichments in Cl are now widely recognised in both back-arc, ocean-ridge and ocean-island settings (e.g. Michael and Schilling, 1989), and are most readily ascribed to the contamination of magmas in a range of settings by a seawater component. In submarine ocean-island and ocean-ridge settings, the Cl-enrichments might plausibly reflect interactions with deep saline brines within the oceanic crust, perhaps immediately above the axial magma chamber (le Roux et al., 2006).

In subduction zones, the Cl-rich component is most plausibly associated with the slab fluid (as shown quantitatively, for example, in the Marianas, Stolper and Newman, 1994; the Lau Basin, Kent et al., 2002; the Austral islands, Lassiter et al., 2002; and Kamchatka, Portnyagin et al., 2007), such as that produced by partial melting of hydrothermally-altered crustal components (e.g. serpentinite, Wysoczanski et al., 2006). Serpentinites are considerably enriched in chlorine with respect to unaltered peridotite, and thus must act as a major sink for seawater Cl during sea-floor alteration. Chlorine bound in serpentines is then readily available for release into the mantle wedge during subduction metamorphism (e.g. Philippot et al., 1998; Scambelluri et al., 2004). The processes and controls on Cl-uptake by the alteration products of different primary minerals (i.e. olivine and orthopyroxene) remain poorly understood (e.g. Barnes and Sharp, 2006; Bonifacie et al., 2008a). In principle, however, there is the prospect that the subduction cycle and mantle-derived fluxes of Cl might be tracked through chlorine-isotopic studies of rocks and fluids. At the moment, however, the chlorine-isotopic composition of ‘pristine’ depleted mantle and uncontaminated MORB remains unresolved (e.g. Magenheim et al., 1995; Sharp et al., 2007; Bonifacie et al., 2008a, b).

3. Global volcanic degassing fluxes of halogens.

3.1 Fluxes of halogens to the atmosphere due to volcanic activity

Halogens released to the atmosphere by volcanoes are thought predominantly to be degassed as halogen halides (Symonds et al., 1994), and the few available measurements of other trace halogen species (e.g. volcanic halocarbons, and halogen oxides) support this hypothesis (e.g. Schwandner et al., 2004; Frische et al., 2006; Bobrowski et al., 2007). Ultimately, halogen species may come from a number of sources (see section 2), both deep (associated with melt generation, evolution and exsolution of vapour and/or hydrosaline fluids prior to eruption), and shallow sources local to the volcano (e.g. revolatilisation of seawater, or other crustal fluids; thermal decomposition of hydrothermal deposits within the volcanic edifice). Understanding the balance between these different sources for halogen species is challenging, and remains a goal of continuing work. A number of different approaches have been employed with the goal of constraining the sources of halogens in magmatic systems, including isotopic studies of volcanic fluids (e.g. ^{129}I, Synder and Fehn, 2002), mass balance arguments based on analyses of submarine glasses and crystal-hosted melt inclusions (e.g. Straub and Layne, 2003) and through the interpretation of the ratios between gaseous halogen species measured in open-vent volcanic gases (Witt et al., 2008).

The two most commonly employed approaches for estimating the fluxes of halogens to the atmosphere are: (i) petrological methods (namely melt inclusion studies) on erupted products and (ii) measurement of halogen to SO_2 flux ratios combined with SO_2 flux measurements at active or degassing volcanoes. Both methods have their advantages and disadvantages.

The petrological approach, developed by Devine et al., (1984) and most recently reviewed by Wallace (2005), uses the dissolved volatile content recorded in crystal-hosted melt inclusions (MIs) in comparison with that of glass in the final degassed erupted lava and scales up to the flux using the mass of lava erupted. This is the only method routinely available for estimating the volatile emissions from past eruptions.

Although halogen species tend to be much more soluble than CO_2 or S species (increasing the likelihood that trapped melt inclusions may record the halogen content of the parental magma, unmodified by degassing), not all volcanoes produce ejecta containing crystal-hosted melt inclusions suitable for such analysis. A weakness of the petrological method is that, without experimental constraints, it is not usually possible to account for volatiles held in a coexisting pre-eruptive vapour (or hydrosaline fluid) phase (e.g. Scaillet et al., 2003; Webster, 2004). Additional uncertainties also arise from estimates of the quantity of magma erupted, and, in terms of estimating fluxes to the atmosphere, from losses of halogen species which are emitted from the magma but which do not necessarily end up in the atmosphere (e.g. scrubbing into hydrothermal systems, Symonds et al., 2001). Scaling up to global fluxes using this methodology is possible, as Wallace (2005) showed, and useful at least to establish the extent to which degassing fluxes of halogens can be supplied from erupted magma fluxes.

The second method, which relies on measurements of volcanic emissions originating from high-temperature sources, has been widely applied to the relatively small number of accessible volcanoes and volcanic vents. This technique relies on measuring a ratio of halogen species to sulphur in the plume (e.g. with Giggenbach flasks (Taran et al., 1995), filter packs (F^-, Cl^-, Br^- and I^-: Zreda-Gostynska et al., 1997; Allen et al., 2000; Mather et al., 2003, Witt et al., 2008), by infra-red remote sensing techniques (HF, HCl: Mori et al., 1993; Francis et al., 1995), or with electrochemical sensors (HCl: Aiuppa et al., 2005; Shinohara, 2005)), and then scaling this ratio by the measured SO_2 fluxes determined by UV spectroscopy from the ground (e.g. COSPEC or miniDOAS; Stoiber and Jepsen, 1973; McGonigle et al., 2002; Galle et al., 2003), or satellites (e.g. TOMS, OMI; Carn et al., 2003). This method has the advantage of being a direct proxy for the atmospheric input at a given time, but since both halogen to SO_2 ratios and SO_2 fluxes can vary quite dramatically at one volcano during different phases of activity (best shown, for example, at Soufriere Hills Volcano, Montserrat; Edmonds et al., 2001, 2002) there are challenges associated with converting measurements at a given point in time to a time-averaged flux even at an individual system. This problem is exacerbated when trying to scale up to a global degassing flux, and is further complicated by contrasts in ratios of gas species during different styles of degassing.

The best example of this problem can be seen in a comparison of recent halogen emissions fluxes (compared in Table 3). Much of the variation between estimates of global halogen fluxes arise simply from the fact that the majority of halogen to SO_2 ratios have been measured at individual fumaroles, and these systems are inherently highly variable. Measurements on high-temperature fumaroles are logistically relatively straightforward, but while in some arcs (e.g. Kamchatka), high-temperature fumaroles are essentially the only sample of high-temperature emissions from volcanoes (see Taran, 2008), in other arcs, much of the sustained gas flux may come from volcanoes which lack fumaroles (e.g. Nicaragua/Central America). With care, it is possible to exclude air- and groundwater-contamination from such analyses, leading to the widely held assumption that the resultant fluid-chemical ratios represent the composition of the volatile phase escaping from the degassing magma (e.g. Taran et al., 1995; Hilton et al., 2002). It has also been established that the ratios of halogen species (e.g. Cl/Br, Cl/I) in high-temperature condensates spans the same range as measured in high-temperature volcanic plumes (e.g. Taran et al., 1995; Snyder et al., 2003; Aiuppa et al., 2005). But in general, the inevitable challenge of fumarole measurements is that it is not possible to be certain that during the passage from the magma body to the surface there has been no chemical modification of the fluid: in many situations chemical modification is unavoidable (e.g. Symonds et al., 2001), and modelling is needed to understand the link between gas emission and the magmatic source (e.g. Villemant et al., 2005). In contrast, at open-vent volcanoes (e.g. above lava lakes, such as at Masaya), while there is evidence for chemical processing of volcanic gases as they mix with air, this has no significant impact on, near-source halogen (HF, HCl, HBr) to sulphur ratios (Horrocks et al., 2003; Martin et al., 2006; Aiuppa et al., 2007; Bobrowski et al., 2007).

A second challenge is that fumarole measurements are essentially point-source measurements, which leads to the question of how should one average data from multiple fumaroles at the same volcano in order to estimate a realistic mean fluid composition?

The alternative approach to point-source sampling of fumaroles is to use remote-sensing measurements (principally FTIR, for HCl and HF; or mini-DOAS for BrO), actively-pumped gas filters (for F, Cl, Br and I), or real-time electrochemical sensor methods (thus far only for HCl) to measure gas-chemical ratios in the gas and aerosol plumes of open-vent degassing volcanoes. These techniques have been widely applied over the past decade, leading to new measurements of the ratios between halogen halide gases and sulphur dioxide at many previously un-sampled volcanoes, and more importantly, measurements at the volcanoes which actually dominate the global volcanic SO_2 emissions flux. Published measurements from these techniques are summarised in Table 4. These new sampling and measurement approaches have provided a uniquely detailed picture of both the uniformity of gas plume compositions at some long-degassing volcanoes (e.g. above the lava lakes of Erebus, Antarctica and Masaya, Nicaragua), and of the dynamical processes associated with degassing which lead to radical, and rapid, changes in gas-chemical compositions (e.g. at Etna and Stromboli; Aiuppa et al., 2004; Allard et al., 2005; Burton et al., 2007). Such measurements have led to new insights into both the relationships between magma and gas composition, and the degassing process. As Aiuppa and others have shown elsewhere (e.g. Aiuppa et al., 2007, Aiuppa, this volume), high-time resolution measurements of gas-phase species, coupled with experimentally-calibrated thermodynamic models of the partitioning of volatile species between the magmatic vapour and melt, and measurements of pre-eruptive volatiles dissolved in melt inclusions, hold great promise for improving understanding of the link between gas-chemical composition and the mechanisms of the degassing process. For example, the extent to which exsolution is an open- or closed-system process; and the extent to which gas segregated at depth subsequently interacts with shallow magmas prior to escape (e.g. Spilliaert et al., 2006a,b; Burton et al., 2007). While the melt-vapour partitioning behaviour, and transport properties, of chloride and fluoride are now fairly well known for a range of melt compositions (e.g. Métrich and Rutherford, 1992; Webster, 1997; Webster et al., 1999; Signorelli and Carroll, 2000, 2001; Alletti et al., 2007), the same is not yet true for Br and I, where there are only sparse constraints (Bureau et al., 2000; Bureau and Métrich, 2003; Musselwhite and Drake, 2003).

Figure 4 shows the comparison between compositions (HCl/SO_2 and HF/SO_2 ratios) of high-temperature fumaroles at arc volcanoes (compiled in Fischer, 2008) and vent gas measurements from arc and other volcanoes (compiled in Table 4). While there is a measure of agreement between high-temperature vent gas and fumarole compositions in arcs, the range of fumarole compositions is considerably greater than that of the plume gases, extending both to much lower and higher halogen/sulphur ratios. This compositional variation (with more than 2 orders of magnitude variation in both HF/SO_2 and HCl/SO_2) is the principal reason why previous estimates of global degassing budgets of halogens (e.g. those of Symonds et al., 1988, and Halmer et al., 2002; Table 3) have such a large uncertainties. Two other important features are apparent from Figure 4: firstly, although the data are rather sparse, it is apparent that the gases from Kilauea and Nyiragongo are distinct from those from arc settings due to their lower halogen:sulphur ratios, and their higher HF/HCl ratios. Secondly, the strongly halogen-rich gas from the Erebus lava lake, with mass ratios $HF/SO_2 > 0.2$, are clearly distinct from those measured from most other settings, presumably due to the strong control of magma composition (Erebus magma is phonolitic) on halogen and sulphur saturation and solubility (c.f. Cioni, 2000; Bureau and Métrich, 2003; Balcone-Boissard et al., 2008).

Although the global coverage of gas chemical data from degassing volcanoes compiled in Table 4 is still somewhat sparse, the samples account for emissions from volcanoes responsible for ~ 5 Tg/a of the annual passive-degassing SO_2 flux. This is about 30 - 40% of the total annual SO_2 emissions budget (of ~ 13-18 Tg SO_2 /a; Stoiber et al., 1987; Andres and Kasgnoc, 1998; Halmer et al., 2002), and is > 50% of the global emissions to the atmosphere from passively degassing volcanoes (~ 9 Tg SO_2 /a Pyle and Mather, 2003). This gives an adequate sample on which to develop an assessment of global halogen emissions from high-temperature degassing. From the compiled data in Table 4, we can determine typical halogen:sulphur ratios for the emissions which characterise arc and non-arc volcanism.

Since the gas chemical ratios span a wide range (e.g. HCl/SO_2 ranges from < 0.2 to > 1), we estimate the ‘typical’ halogen:sulphur ratio in two ways: by determining the geometric mean of the data (which is a better measure of central tendency than the arithmetic mean for such data), and by calculating a flux-weighted mean, which accounts approximately for the typical contribution of each volcano to the global volcanic SO_2 budget. Both calculations can be performed straightforwardly for HCl and HF (Table 5); however, data for HI and HBr are simply too sparse to do anything else other than make a simple extrapolation to an estimated global flux. From this analysis, and assuming an arc SO_2 flux of ~ 15 Tg/a, we estimate the global annual arc volcano degassing fluxes of HF to be ~ 0.5 (±0.2) Tg/a, and of HCl to be ~ 4.3 (±1) Tg/a (Table 3). These values are not radically different from the most recent estimates (Fischer 2008), although they are based on a completely different dataset. The coherence between the two datasets verifies that the assumption that high temperature fumaroles are an adequate sample of magmatic gas composition is appropriate, given a sufficiently large sample size and appropriate statistical treatment. Neither dataset, however, includes the flux of Cl in hot springs (as opposed to fumaroles) which, in some arcs, may be significant (e.g. Kamchatka, Taran, 2008). It is also worth noting that the higher arc-HF flux that we estimate here is influenced strongly by the measurements of a high HF/SO_2 ratio at Lascar, Chile (Mather et al., 2004): this is a volcano where the gas plume is a mixture of high-temperature gases from a pit crater/lava dome, augmented by strong fumarolic emissions from the crater walls. The estimate of global fluxes of HI and HBr from arc volcanoes are constrained only by two measurements of gas plumes, from volcanoes in the Central American arc (Witt et al., 2008). These emissions are remarkably iodine-rich (compared, for example, to emissions from Etna), consistent with studies of ^{129}I in Central American arc fluids (Snyder and Fehn, 2002), and our scaling up to a global arc HI flux yields an estimate which is also consistent with this prior work (Table 3). However, it remains to be seen whether the HI-rich nature of Central American arc gases is a regional effect, controlled by the iodine-rich nature of the subducted sediment component to this arc, or whether it is a general feature of subduction-related volcanoes from around the world.

Fluxes of halogens to the atmosphere from non-arc volcanoes are less well-constrained than those for arc volcanoes, since there are fewer available measurements (Table 4). Of the systems that have been well-characterised, Etna is both the best constrained, and one of the strongest point sources of continuous gas emission to the atmosphere. Halogen to sulphur ratios (HF/SO_2 ~ 0.06; HCl/SO_2 ~ 0.3; Table 4) are close to the average arc compositions (Table 5) and, given a time-averaged SO_2 flux of ~ 2 Tg/a, Etna accounts for an additional flux of ~ 0.1 Tg HF/a and 0.6 Tg HCl/a. In contrast, HF and HCl fluxes from Nyiragongo and Kilauea are at least an order of magnitude smaller than this, due to the lower halogen:sulphur ratios of gases in these systems.

3.2 Fluxes of halogens to the oceans due to volcanic activity

In addition to the fluxes of halogens and other gases released to the atmosphere by subaerial volcanoes, there is a volcanic flux of fluids released to the oceans by submarine volcanic activity. While this submarine gas flux is hard to quantify, due to the challenges of determining appropriate undegassed magmatic compositions (e.g. Marty and Tolstikhin, 1998; Saal et al., 2002), it is also likely that the halogen degassing flux from submarine volcanism is small. Unni and Schilling (1978) argued that F and Cl systematics of mid-Atlantic ridge basalts suggested that chlorine-loss by volcanic degassing only became important for samples erupted under less than ~ 500 m water depth (~ 5 MPa confining pressure). Based on present-day ridge-axis bathymetry, <1% of ocean-ridge samples are erupted at a sufficient low confining pressures to degas halogens in any quantity. In terms of global magma fluxes, the time-averaged amount of non-arc submarine basalt which would lose halogens by degassing is ~ 0.2 km^3/a; about a tenth of the subaerial magma flux in arc settings. While ridge-axis volcanism is negligible in terms of direct degassing of halogen-rich fluids to the oceans, the role played by ocean-ridge processes (e.g. hydrothermal alteration, brine-formation and exchange with seawater; e.g. German and von Damm, 2003; Gillis et al., 2003; Sharp and Barnes, 2004) is of considerable importance to the global halogen cycles, due to the role played by the ocean crust in volatile recycling in subduction zones. The loss of fluids in the forearc of subduction zones may represent a significant additional flux of halogens to the oceans (see section 3.3), however this flux is very poorly constrained (Jarrard, 2003; Wallace, 2005). The fraction of, and timescale over which, volcanic halogens emitted to the atmosphere are processed into the oceans (for example by wet or dry deposition, or from run-off from land masses) is also poorly constrained.

3.3 Fluxes of halogens through subduction zones

Subduction zones are important conduits for the transport of chemical species between the crust, mantle, oceans and atmosphere, and emissions from the associated volcanism dominates the global subaerial flux, accounting for 70-80% of global time-averaged volcanic SO_2 fluxes. One obvious question to resolve is to what extent are halogens (and other gases) recycled in subduction zones, and is there a material balance between inputs (subducted slab and associated fluids) and outputs (whether fluids escape in the forearc; fluid loss to the overriding plate, and fluxes related to arc volcanism: volcanic gases, fluids and intrusive and extrusive volcanic rocks). In terms of the overall halogen balance, if the outputs exceed the inputs then the mantle is still outgassing, and there will be an accumulation of halogens in surface reservoirs such as the ocean. If the converse is true, then over geological time halogens should accumulate in Earth's interior. The relative stability of halogen levels in the oceans over geological time suggests that neither of these situations prevail and in fact halogens are effectively recycled through subduction zones with inputs equal to the outputs (Wallace, 2005). There have been a number of attempts to evaluate the chlorine cycle in subduction zones on both global and regional scales (e.g. Ito et al., 1983; Jarrard, 2003; Straub and Layne, 2003; Figure 5), and there is a measure of agreement that chlorine is fairly efficiently recycled through subduction zones. The few existing data for iodine and ^{129}I suggest that fluxing of I into subduction zones is also very important for the global I budget: this mechanism both sustains the I content of the depleted mantle, and explains the elevated levels of ^{129}I in arc-related magmas (Deruelle et al., 1992; Snyder and Fehn, 2002). On the whole however the inputs to and outputs from subduction zones are too poorly constrained in terms of Br and I to say anything definitive in terms of the efficiency of their recycling.

As the melt inclusion data reveal (Fig. 2), the Cl contents of subduction zone magmas appear to be strongly influenced by the addition of a hydrous slab component. The same is probably true for F in most arcs, although the estimated contribution of a fluid-slab component to F budgets is highly variable (e.g. < 30% in the Kermadec arc, Wysoczanski et al., 2006; > 50% in the Izu arc, Straub and Layne, 2003). Much work remains to be done to define the compositional systematics of the halogen-bearing slab component since it appears to be spatially highly variable, both between and within arcs (e.g. Portnyagin et al., 2007); a reflection, presumably, both of source compositions, and the conditions of fluid release and halogen transport at depth.

Qualitatively, the extent to which all halogen species require a supply from a subduction-related 'slab' component can be seen from Fig. 6. Figure 6 summarises the global arc-related degassing fluxes for HCl, HF, HBr and HI, assuming an annual arc-related SO_2 flux of 15 Tg/a. The horizontal dashed lines indicate the *minimum* supply of halogens (both dissolved in magma and degassed) that would be supplied to the crust through volcanism, assuming that all volatiles (S, Cl, F, Br, I) are supplied *only* from partial melting of a depleted mantle component. Since F and Cl are only partially degassed during magma emplacement and eruption, much of this halogen flux will be trapped in the shallow crust in intrusive bodies, or will remain dissolved in the quenched erupted lavas. Even without accounting for the magma-hosted halogen contents, it is clear from Fig. 6 that melting of the depleted mantle alone cannot account for the observed arc-degassing fluxes of HCl, HBr and HI, confirming that each must be sustained by a significant slab-related fluid component. The same conclusion probably holds for HF, given the high solubility of F in magmas down to low pressures (Aiuppa, this volume), and the documented importance of subduction-related slab components of F shown by the systematics of arc-related mafic melt inclusions (Fig. 2).

4. Closing remarks.

The measurement, interpretation and understanding of halogens in volcanic systems is at an exciting stage. As chemical tracers of magma source regions, and monitors of degassing processes, the halogens have an important complementary role to play in extending the armoury of the modern igneous petrologist. However, before this point can be reached, we need to have a more complete understanding of the basics: for example, what are the concentrations of halogens in the solid earth reservoirs, and what are the principal controls on their behaviour during partial melting, crystallisation and degassing? In terms of the evidence trail left in erupted volcanic products, much will be gained with the further application of quantitative micro-analytical tools to measure halogens in parallel with their non-volatile trace element proxies in volcanic glasses and melt inclusions, in order to unravel the coupled complexities of magmatic differentiation, vapour saturation and degassing, and thereby to open a window on the source regions of magmas.

The technical challenges for the future are to establish procedures for the quantitative micro-analysis of glasses and melt inclusions for the full spectrum of halogens (F, Cl, Br, I) their non-volatile ‘proxies’ (e.g. P, Nb, Nd, Rb, Ba) and the isotopic signatures of key light element tracers (e.g. δ^{7}Li, δ^{11}B, δ^{34}S), whether by proton-induced X-ray or gamma-ray emission (PIXE, PIGME; e.g. Mosbah et al., 1991; Bureau and Métrich, 2003), synchrotron micro-XRF (e.g. Alletti et al., 2007), secondary ion mass spectrometry (e.g. Hauri 2002; Layne et al., 2004; Bouvier et al., 2008), or even laser-ablation ICP MS (Boulyga and Heumann, 2005).

Our review shows that despite the challenges in terms of making appropriate measurements, and the temporal and spatial paucity of the dataset, modern estimates of the fluxes of HCl and HF to the atmosphere from arc and global volcanism appear to be converging. Despite our demonstration that there are systematic differences in the halogen to sulphur ratios between measurements at individual high-temperature fumaroles and measurements of bulk plumes, the scatter in both datasets is such that when scaled up to global fluxes there is a reasonable degree of agreement. Measurements of HBr and HI in volcanic plumes are in their infancy but more such measurements are to be strongly encouraged in order to constrain better the role of volcanic degassing in the global geochemical cycles of these species. Further measurements of halogen to sulphur ratios at non-arc volcanoes are also to be encouraged both in terms of understanding the flux they represent to the atmosphere and better to constrain the importance of subduction processes in terms of the fluxes of these heavier halogens.

The fluxes of halogens released to the oceans by degassing of submarine lavas are suggested to be negligible due to the high solubility of halogens in silicate liquids at even relatively low pressures. Other halogen fluxes to the oceans, due to expulsion of fluids in the forearc of subduction zones, or deposition of volcanic halogens to the oceans from the atmosphere via wet or dry deposition, or by run-off from the continents, remain to be adequately constrained. The role played by ocean-ridge processes (e.g. hydrothermal alteration, brine-formation and exchange with seawater) is of considerable importance to the global halogen cycles, due to the role played by the ocean crust in volatile recycling in subduction zones. Estimates to date suggest that Cl is effectively recycled through subduction zones and is thus not accumulating in either the planet’s interior or surface reservoirs. Much further work remains to be done to establish the extent to which this is also true for the other halogens.

Studies of the behaviour of halogens in igneous rocks are at an important stage: there is a new appreciation of the role that halogen species may play in the atmosphere, once released from the magma (e.g. Bobrowski et al., 2003); and the potential of volcanic plume gas measurements for contributing to an improved understanding of magma degassing processes has been demonstrated (Aiuppa et al., 2005; Allard et al., 2005). At the moment, however, understanding of the global halogen cycles associated with partial melting, magmatism and recycling at subduction zones is hindered by a lack of data. With the development of micro-analytical techniques to analyse heavy halogens in glasses and minerals, and with a targeted approach to making appropriate field measurements at selected volcanoes, the field should progress rapidly in the future.

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Figure captions.

Figure 1.

Graph showing the ratio of recent estimate of bulk continental crust composition (Rudnick and Gao, 2003) to a recent estimate of primitive mantle composition (Palme and O'Neill, 2003) for selected elements, ordered with assumed increasing incompatibility during partial melting towards the left hand side. Bulk continental crust composition does not include the reservoirs of present-day seawater and atmosphere. Cl and Br show a deviation from the general trend because substantial amounts of chlorine and bromine are accounted for by seawater. Significant quantities of I are held in crustal sediments, rather than seawater, and the strong enrichment of I in the bulk crust is consistent with its assumed highly incompatible nature during anhydrous partial melting of peridotite (e.g. Deruelle et al., 1992). The enrichment of F in the crust is consistent with evidence for the similar incompatibilities of F, Nd and Sr in MORBs (e.g. Schilling et al., 1980; Workman et al., 2006; Le Roex et al., 2006).

Figure 2.

Compilation of F/P and Cl/K ratios measured in phenocryst-hosted mafic melt inclusions from different settings. Note the broad uniformity of F/P ratios between different settings (Siqueiros, Hawaii and Iceland, Fig. 2A); the lack of evidence for strong losses of F during degassing (melt inclusion and matrix glass fields generally overlap, Fig. 2B), and the strong variability of F/P in arc settings, particularly notable for the Izu arc samples (Figs. 2A, 2C). In contrast, Cl/K increases substantially from Siqueiros through Hawaii and Iceland to subduction-related settings, pointing to fluid-related source enrichment of Cl in subduction-zone magmas. Data sources: Hawaii -

Davis et al., 2003; Stolper et al., 2004; Siqueiros transform – Saal et al., 2002; Iceland – Thordarson et al., 1996; Moune et al., 2007; Subduction zones: Kermadec – Wysoczanski et al., 2006; Izu – Straub and Layne, 2003; Central America – Wade et al., 2006, Benjamin et al., 2007, Sadofsky et al., 2008; Kamchatka – Portnyagin et al., 2007.

Figure 3.

Systematics of variation of the mass ratio F/Cl with MgO (wt%) in mafic glasses and melt inclusions from different volcanic settings. Note the high F/Cl ratio which characterises the MORB-source mantle, such as that sampled at the Siqueiros transform. Also noteworthy is the considerable range of F/Cl in Hawaiian glasses and melt inclusions: matrix glasses from subaerially-erupted samples show a narrower (high) range of F/Cl, from ~ 0.7 - > 7; some melt inclusions and a portion of matrix glasses from subaqueously-emplaced samples range to very low F/Cl (<0.2). The variability might reflect contamination of some submarine samples with sea-water, or sea-water-derived fluids in the crust; it may also reflect preferential loss of Cl during degassing of shallow-submarine and subaerial samples. Mafic samples from some arc-related systems (Kermadec (not shown), Izu) show low F/Cl, reflecting the importance of the subduction component for Cl. Melt inclusion data (e.g. for Kamchatka) show no evidence of low-pressure loss of Cl during fractional crystallisation. Data sources: Hawaii - Davis et al., 2003; Stolper et al., 2004; Kamchatka – Portnyagin et al., 2007; Izu – Straub and Layne, 2003; Siqueiros transform – Saal et al., 2002; Iceland - Thordarson et al., 1996; Moune et al., 2007.

Figure 4.

Comparison of high-temperature fumarole data for arc volcanoes (compiled in Fischer, 2008) and vent gas (plume) measurements from arc and other volcanoes (compiled in Table 3). Note the halogen-rich character of emissions from Erebus' phonolite lava lake; and the HCl/SO_2 ratios of gases from some mafic intraplate volcanoes (Nyiragongo, Kilauea).

Figure 5.

Summary of different estimates of the Cl budget in subduction zones, based on assessments of the quantities subducted (in fluids, ocean crust and sediments; the 'input' component) and the 'output' (the degassing flux, plus that accounted for in erupted and intruded magmas), with error bars shown on the 'output' estimates. Data sources: 1 – Ito et al., 1983; 2 – Jarrard, 2003; 3 – Straub and Layne, 2003; 4 – Wallace 2005; 5 – this work. The current estimate of the arc HCl degassing flux (~ 5 Tg/a) is shown for reference. Although estimates of global Cl subduction fluxes vary by over an order of magnitude, none of these authors have suggested that the inputs and outputs are not closely matched, with the implication that observed magmatic Cl-fluxes at subduction zones can be entirely accounted for by the addition of Cl associated with a subduction (slab fluid) component.

Figure 6.

Summary of global arc related degassing fluxes for HCl, HF, HBr and HI, assuming an annual SO_2 flux of 15 Tg/a. Data sources: 1 – Symonds et al., 1988; 2 – Halmer et al., 2002; 3 – this work; 4 – Bobrowski et al., 2003; 5 – Snyder and Fehn, 2002; 6 – Aiuppa et al., 2005 (estimated global flux). The horizontal dashed lines indicate the *minimum* supply of halogens (both dissolved in magma and degassed) supplied to the crust and atmosphere through volcanism, assuming that all volatiles (S, Cl, F, Br, I) are supplied only from the depleted mantle, calculated assuming 10% partial melting of a depleted mantle (spinel lherzolite) source (Salters and Stracke, 2004; Table 1 line 5), with bulk mineral-melt partition coefficients of: S (0.07), F (0.02), Cl, Br (0.0002), I (0), a basalt magma flux of 3 km^3/a, and an SO_2 flux of ca. 15 Tg/a. The point of the calculation is that while melting of the depleted mantle alone *can* account for the degassing flux of S to the atmosphere from arc volcanoes, the estimated arc degassing fluxes of HCl, HBr and HI cannot be accounted for by the observed arc magma flux. The total magmatic flux of HF is potentially significant, but only a small component is released during degassing, suggesting that a subduction-related slab component is also needed to account for observed arc HF degassing fluxes.

Table 1. The halogens: summary of their key properties

	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Atomic mass	18.998	35.453	79.904	126.905	(210)
Radius of halide ion (X^-, x 10^{-12} m)	133	181	195	216	-
Stable isotopes	^{19}F	^{35}Cl, ^{37}Cl	^{79}Br, ^{81}Br	^{127}I	-
Naturally occurring radioactive isotopes, and half lives		^{36}Cl (300 ka; [a])		^{129}I (15.7 Ma; [a])	^{218}At (1.5 s), ^{219}At (56 s) [b]
50% nebular condensation T (K) at 10 Pa	736	863	690	-	-

Data sources: Greenwood and Earnshaw (1984), Railsback (2003), Wasson (1985).
a – cosmogenic nuclide; b – products of the U, Th decay series

Table 2.

Selected estimates of halogen and other volatile contents of terrestrial reservoirs (ppm, for solid reservoirs; mol/kg for aqueous fluids, ppb by volume for the atmosphere).

Reservoir	F	Cl	Br	I	H_2O	C	S	K	P	Nb	Dy	Ref
CI chondrite	58.2 *(15%)*	698 *(15%)*	3.5 *(10%)*	433 *(20%)*	1.8x10^{5} *(10%)*	32200 *(5%)*	54100 *(5%)*	544 *(5%)*	926 *(7%)*	0.247 *(3%)*	0.254 *(5%)*	1
Primitive mantle	25 *(40%)*	30 *(40%)*	0.075 *(50%)*	0.007	1080 *(20%)*	100	200 *(40%)*	260 *(15%)*	86 *(15%)*	0.588 *(20%)*	0.711 *(10%)*	2
Primitive mantle	18 *(40%)*	1.4 *(40%)*	0.0036 *(10%)*	0.001	-	-	230 *(35%)*	190 *(20%)*	66 *(20%)*	0.46 *(40%)*	0.54 *(20%)*	3
Depleted Mantle	65	7.3	0.02									4
Depleted Mantle	11 *(41%)*	0.51 *(18%)*	-	-	116		119 *(25%)*	60 *(28%)*	40.7 *(10%)*	0.21 *(35%)*	0.53 *(10%)*	5
Depleted Mantle	16 *(20%)*	1 *(50%)*	-	-	142 *(60%)*	72 *(26%)*	146 *(24%)*	100 *(20%)*	54		0.615	6, 7
Bulk Crust	553	244	0.88	0.7			404	14900	570	8	3.6	8
Upper Crust	557 *(10%)*	370 *(100%)*	1.6	1.5 *(50%)*			62 *(50%)*	23200 *(8%)*	650 *(15%)*	12 *(9%)*	3.9	8
Shale	740	180	20	19			2400	22000	700	11	4.7	9
Pelagic Clay	1300			28			2000	20700	1500	14	7.4	9
Oceans (mol/kg)	68 x 10^{-6}	546 x 10^{-3}	840 x 10^{-6}	450 x 10^{-9}			28 x 10^{-3}					10
Vent fluids (mol/kg)	16 – 39 x 10^{-6}	30 – 1245 x 10^{-3}	29–1910 x 10^{-6}									11
Troposphere (ppbv)	1.8	3.6	0.016	0.001 – 0.002		385,000	0.7					12

Bracketed numbers in italics indicate the estimated percentage error in the value, as quoted by the original source.

References:

1 – Palme and Jones, 2003; 2 – Palme and O'Neill, 2003; 3 – Lyubetskaya and Korenaga, 2007; 4 – Schilling et al., 1980; 5 – Salters and Stracke, 2004; 6 – Saal et al., 2002; 7 - Hofmann, 1988; 8 – Rudnick and Gao, 2003; 9 – Li and Schoonmaker, 2003; 10 – Bruland and Lohan, 2003; 11 - German and Von Damm, 2003; 12 – Warneck (2000).

Table 3. Estimates of volcanic halogen gas fluxes to the atmosphere.

HF (Tg/a)	HCl (Tg/a)	HBr (Gg/a)	HI (Gg/a)	
0.06 - 6	0.4 – 11			Symonds et al., 1988. Global volcanic flux.
			0.2 – 7.7	Snyder and Fehn, 2002. Global arc flux.
0.7 – 8.6	1.2 – 170	2.6 – 43.2		Halmer et al., 2002. All volcanoes, 1972-2000.
		13 (3 – 40)	0.11 (0.004 – 6.6)	Aiuppa et al., 2005. Global volcanic flux.
	4 – 7			Wallace, 2005. Global arc flux.
0.24	5.6			Fischer 2008. Global arc flux.
0.5 (± 0.2)	4.3 (± 1)	5 - 15	0.5 – 2	This work, global arc flux.

Table 4.

Plume measurements of high-temperature halogen to SO_2 ratios associated with volcanic systems emitting a high SO_2 flux.

Volcano	Mean mass ratio				SO_2 flux* (Mg day^{-1})	Method and comments	Ref.
	HF/SO_2	HCl/SO_2	HBr/SO_2	HI/SO_2			
Erebus, Antarctica						*High-temperature lava lake degassing*	*Intraplate phonolite*
December 1986	0.52±0.31	0.90±0.58			21±11	Filter pack	Zreda-Gostynska et al., 1997
December 1988	0.23±0.08	0.56±0.15			27±9	Filter pack	Zreda-Gostynska et al., 1997
December 1989	0.48±0.30	0.92±0.77			52±21	Filter pack	Zreda-Gostynska et al., 1997
January 1991	0.23±0.13	0.51±0.28			71±20	Filter pack	Zreda-Gostynska et al., 1997
1997	0.27±0.08	0.42±0.19			70±10	Chemical traps	Wardell et al., 2008
1999	0.34±0.06	0.76±0.10			70±10	Chemical traps	Wardell et al., 2008
2000	0.18±0.05	0.45±0.22			70±10	Chemical traps	Wardell et al., 2008
December 2004	0.32	0.56				Filter packs	Oppenheimer and Kyle, 2008
2004	0.28	0.28				FTIR	Oppenheimer and Kyle, 2008
Erta' Ale, Ethiopia						*High-temperature lava lake degassing*	*Rift Basalt*
March 2003	0.006	0.20	-	-	112	Filter packs	Allard et al., 2004
October 2005	0.0055±0.0002	0.044±0.006			60±15	FTIR	Sawyer et al., 2009
Etna, Italy						*Open-vent degassing and sporadic flank eruptions*	*Intraplate Alkali Basalt*
2004	0.11	0.49	9×10^{-4}	8×10^{-6}	Up to >4000 (during eruption)	NE crater mean	Aiuppa et al., 2005
2004	0.01	0.19	4×10^{-4}	1.3×10^{-5}		Voragine crater mean	Aiuppa et al., 2005
May 2001	0.035	0.196	-	-	-	NE crater FTIR eruptive plume	Burton et al., 2003
	0.064	0.385	-	-	-	SE crater	Burton et al., 2003
	0.124	0.654	-	-	-	SE crater lava flow	Burton et al., 2003

	0.035	0.196	-	-	-	Central craters	Burton et al., 2003
	0.034	0.196	-	-	1500	Bulk plume	Burton et al., 2003
July 2001	0.122	0.678	-	-	-	Valle de Leone fissure	Burton et al., 2003
	0.046	0.177	-	-	7245	Bulk summit plume	Burton et al., 2003
2000	-	0.19	-	-	-	Bulk equilibrium degassing	Allard et al., 2005
	-	0.23	-	-	-	Summit crater	Allard et al., 2005
	-	0.06	-	-	-	Lava fountain	Allard et al., 2005
	-	0.32	-	-	-	Overflowing lava	Allard et al., 2005
1997	0.031	0.142	-	-	5440-5700	FTIR mild activity	Francis et al., 1998
Sept 1994		0.11-0.19	-	-	5000-6000	Open-vent degassing	Francis et al., 1995
Kilauea, Hawaii						*Degassing associated with basaltic lava emission*	*Intraplate Basalt*
2004-2005	0.01±007	0.017±0.007	-	-	1500	FTIR, quiescent degassing	Edmonds and Gerlach, 2007, Edmonds et al., 2008.
Lascar, Chile						*High-temperature lava dome fumaroles*	*Arc Andesite*
2003	0.16	0.35	-	-	2420	Filter packs	Mather et al., 2004
Masaya, Nicaragua						*High-temperature open vent degassing*	*Arc Basalt*
2006		0.17	3×10^{-4}	3×10^{-5}	650-1700	Filter packs	Witt et al., 2008
2003	0.03	0.27	-	-	220	Filter packs	Mather et al., 2006
Dec 2001	0.01	0.22	-	-	346	Filter packs	Mather et al., 2006
May 2001	0.045	0.310	-	-	-	Filter packs and diffusion tubes	Allen et al., 2002
April 2001	0.007	0.124	-	-	346	FTIR before small explosion	Duffell et al., 2003
2000	0.079	0.335	-	-	950	FTIR	Duffell et al., 2001
1998/1999	0.04	0.34	-	-	-	FTIR	Horrocks et al., 1999 Burton et al., 2001 Burton et al., 2000
Miyakejima, Japan						*Degassing associated with eruptive activity which then declined*	*Arc Basalt*
2000/ 2001	-	0.05-0.07	-	-	27000-42000	FTIR June 2000 eruption	Notsu et al., 2002

Nyiragongo						*High-temperature lava lake degassing*	*Intraplate Alkali-Basalt*
2005-2007	0.007	0.03	-	-	1990-3280	FTIR	Sawyer et al., 2008
Popocatépetl						*Dome building eruption*	*Arc Andesite*
Feb 1997	0.015-0.019	0.11-0.13			2700-13000	FTIR	Love et al., 1998
Sakurajima						*Degassing associated with ongoing explosive activity*	*Arc Andesite*
1999	0.02-0.03	0.13-0.18	-	-	1000-3000	FTIR persistent activity	Mori and Notsu, 2003
Satsuma-Iwojima						*High-temperature lava dome fumaroles*	*Arc Rhyolite*
1996	0.009-0.015	0.14-0.33	-	-	560	FTIR	Mori et al., 2002
Soufriere Hills, Montserrat						*Dome building eruption*	*Arc Andesite*
1996	0.077	12.63	-	-	-	Filter packs	Allen et al., 2000
1999-2000	-	0.34-6.80	-	-	40-2000	FTIR (higher ratios and fluxes associated with higher extrusion rate)	Edmonds et al., 2001, 2002
Stromboli, Italy						*High-temperature open vent degassing*	*Arc Basalt*
2000-2002	-	0.38-0.57	-	-	-	FTIR, quiescent degassing	Burton et al., 2007
2000-2002	-	0.12-0.23	-	-	-	FTIR, during explosions	Burton et al., 2007
June 1993	0.03	0.4	-	-	340	Filter packs, medium eruptive activity	Allard et al., 2000
July 1994	0.02	0.3	-	-	820	Filter packs, high eruptive activity	Allard et al., 2000
June 1997	0.01	0.3	-	-	170	Filter packs, low eruptive activity	Allard et al., 2000
Telica, Nicaragua						*Fumarolic degassing around filled crater*	*Arc Andesite*
2006		0.26	4×10^{-4}	11×10^{-5}	-	Filter packs	Witt et al., 2008
Unzen, Japan						*Dome building eruption*	*Arc Dacite*
1992	-	0.32-0.81	-	-	-	FTIR	Mori et al., 1993
Villarrica, Chile						*High-temperature open vent degassing*	*Arc Basalt*
2004	0.03	0.17	-	-	-	Filter packs	Shinohara and Witter, 2005
2003	0.07	0.34	-	-	320	Filter packs	Mather et al., 2004
2001	0.03	0.22	-	-	-	Filter packs	Witter et al., 2004

Yasur, Vanuatu						*High-temperature open vent degassing*	*Arc Andesite*
2005	-	0.28	-	-	-	FTIR, quiescent degassing	Oppenheimer et al., 2006
2005	-	0.02	-	-	-	FTIR, during explosions	Oppenheimer et al., 2006

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[*] SO_2 fluxes are only quoted when measurements were available made at the same time as the ratio measurements; or when long-term averages based on multiple measurements were available (Erebus, Kilauea).

Table 5. Estimates of averaged halogen: sulphur dioxide mass ratios for arc volcanoes.

	HF/SO_2	HCl/SO_2
Geometric mean	0.036 $({}^{+0.014}/_{-0.01})$	0.29 (±0.06)
SO_2-flux weighted mean	0.039	0.33

Figure 1.

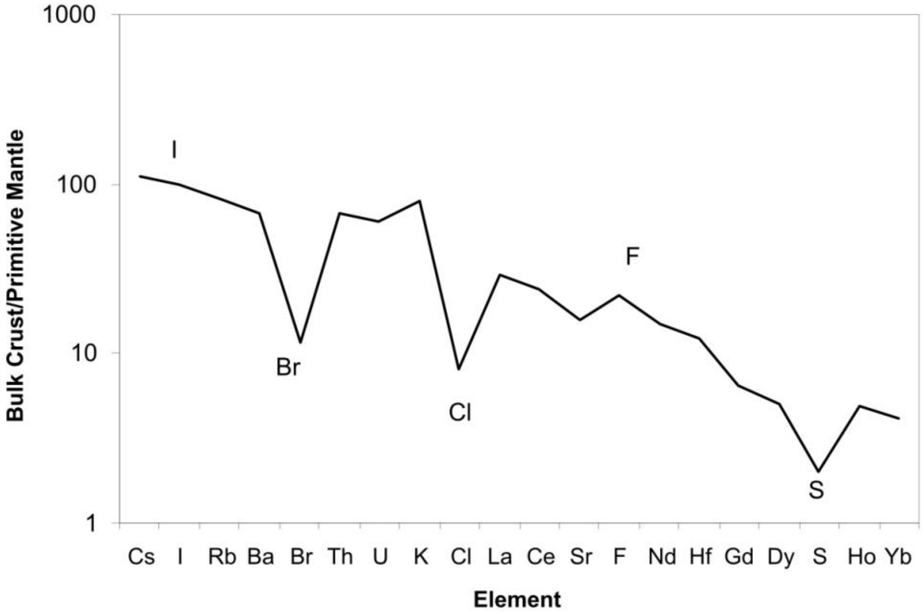
1000
100
10
1
Bulk Crust/Primitive Mantle
I
Br
Cl
F
S
Cs
I
Rb
Ba
Br
Th
U
K
Cl
La
Ce
Sr
F
Nd
Hf
Gd
Dy
S
Ho
Yb
Element

Figure 2.

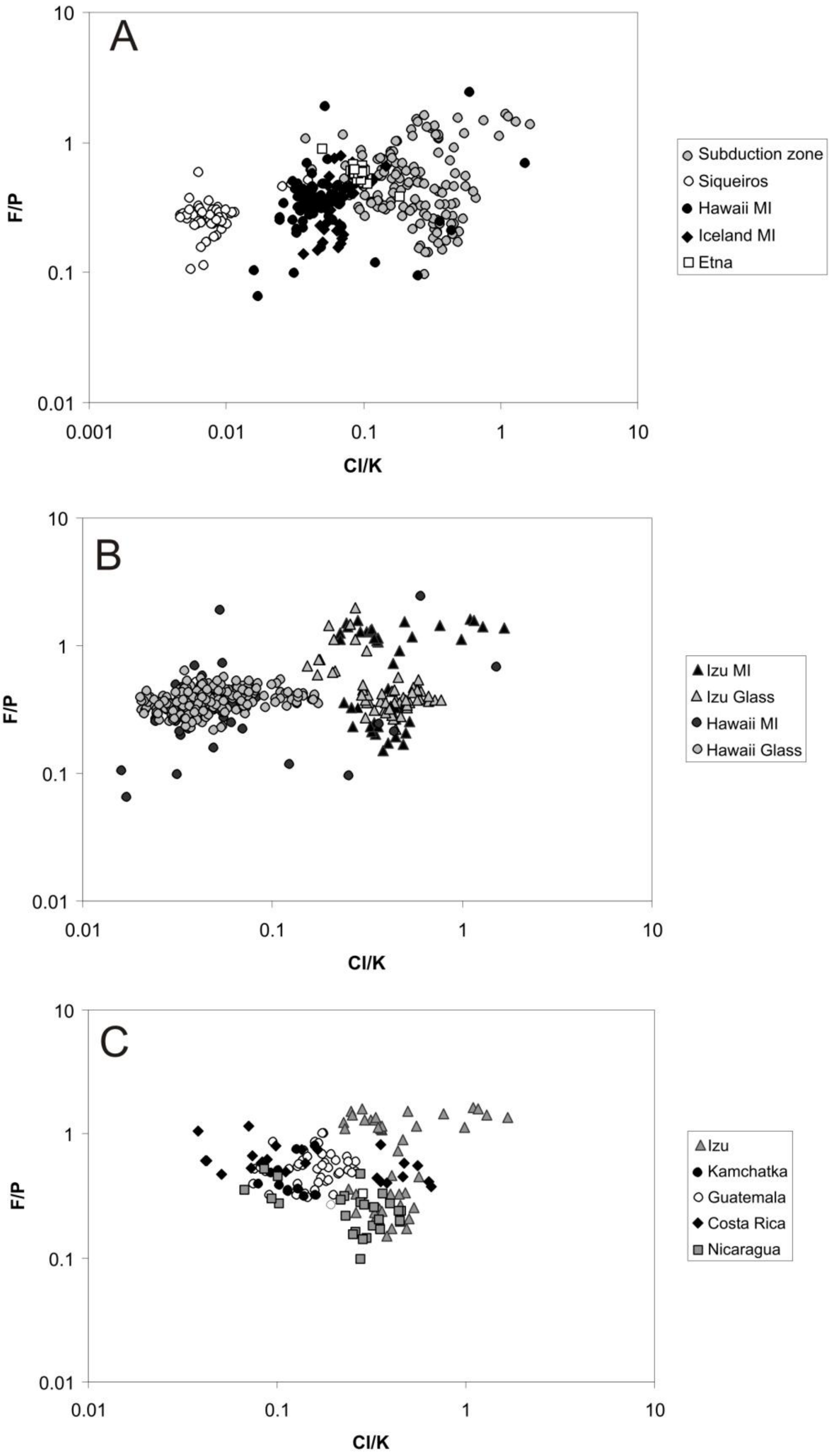
A
F/P
Cl/K
10
1
0.1
0.01
0.001
0.01
0.1
1
10
Subduction zone
Siqueiros
Hawaii MI
Iceland MI
Etna
B
F/P
Cl/K
10
1
0.1
0.01
0.01
0.1
1
10
Izu MI
Izu Glass
Hawaii MI
Hawaii Glass
C
F/P
Cl/K
10
1
0.1
0.01
0.01
0.1
1
10
Izu
Kamchatka
Guatemala
Costa Rica
Nicaragua

Figure 3.

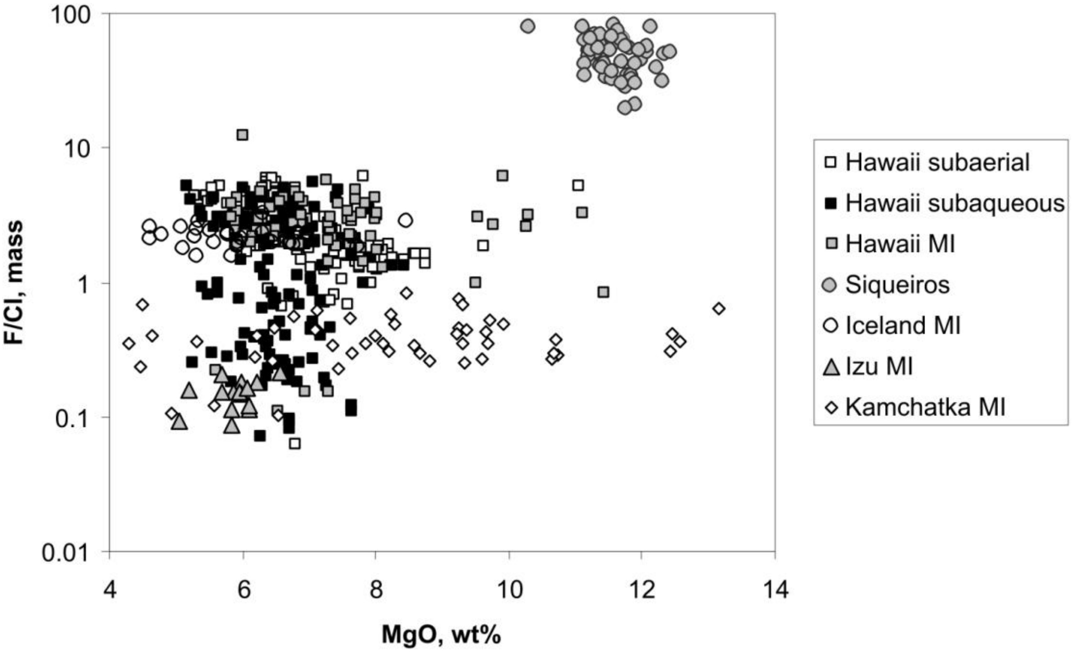

Figure 4.

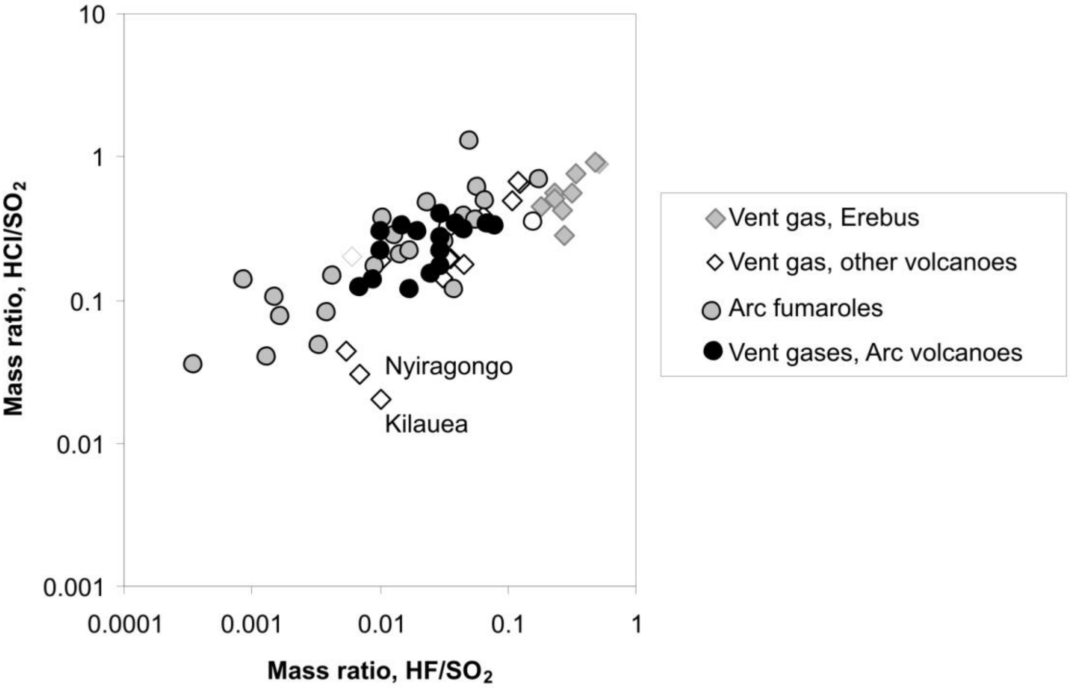

Figure 5

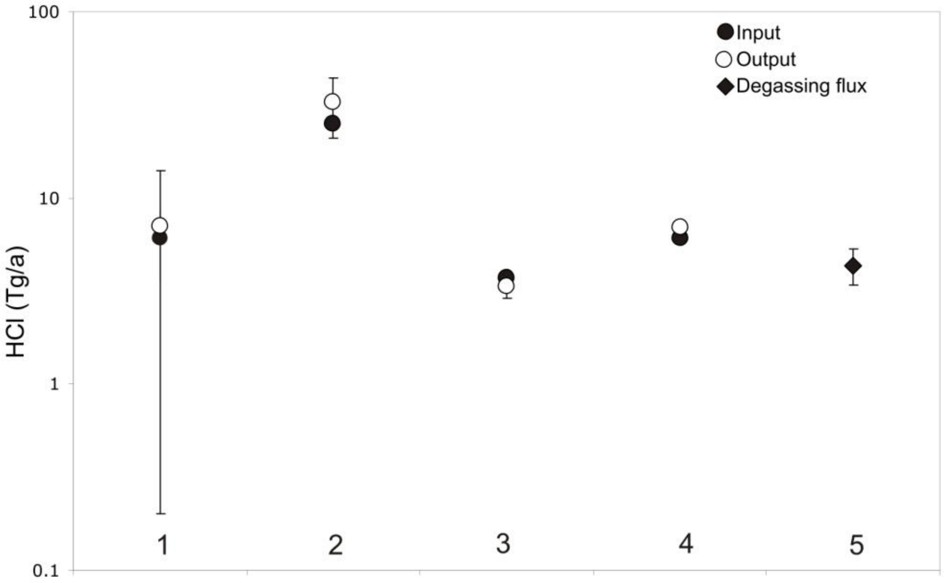

Figure 6