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Experimental and Observational Constraints on Halogen Behavior at Depth

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ABSTRACT

Halogens are volatile elements present in trace amounts in the Earth's crust, mantle, and core. Except for fluorine, they show volatile and incompatible behavior, which makes them key tracers of fluid-mediated and/or melt-mediated chemical transport processes. Even small quantities of halogens can profoundly affect many physicochemical processes such as melt viscosity, the temperature stability of mineral phases, the behavior of trace elements in aqueous fluids, or the composition of the atmosphere through magma degassing. Experiments allow us to simulate deep-Earth conditions. A comparison of experimental results with natural rocks helps us to unravel the role and behavior of halogens in the Earth's interior.

KEYWORDS: element partitioning; volatiles; degassing; subduction;; fluid inclusions

INTRODUCTION

Halogens are present in the deep Earth as volatile trace elements. Whereas fluorine is relatively abundant in crustal rocks (~550 ppm), as is chlorine (~240 ppm), bromine and iodine are more than three orders of magnitude lower (<1 ppm). In the Earth's primitive mantle, the halogens are present in low concentrations, ranging from 7 ppb for iodine to 25 ppm for fluorine, with even lower concentrations in the depleted mantle. In contrast, the halogens are relatively enriched in the outer reservoirs of the Earth, e.g., ~2 wt% Cl in seawater and ~28 ppm iodine in marine sediments (Pyle and Mather 2009 and references therein).

The heavy halogens (chlorine, bromine, and iodine) behave incompatibly in most minerals due to their large ionic radius, and they partition preferentially into melts or fluids. Their distribution is influenced by fluid mobility, crystal fractionation, degassing, and partial melting, which makes them excellent tracers for volatile transport processes in the deep Earth. Fluorine, the lightest halogen, shows a more compatible and rather lithophile behavior due to its smaller ionic radius, which is comparable to that of an OH group. As a consequence, F and the heavy halogens decouple during fluid-mediated metamorphic reactions and magmatic differentiation. Knowledge of the behavior, abundance, and distribution of F and the heavy halogens can help us to better understand the mechanisms that control the origin, distribution, and transport of volatiles in the deep Earth and the complex processes during subduction and recycling of oceanic lithosphere.

Here, we discuss the importance of the halogens by examining experimental challenges and by reviewing pioneering studies on the halogen abundance, distribution, and behavior. This review will focus on the application of experimental studies to four topics corresponding to different halogen-

bearing reservoirs in the deep Earth: (1) the behavior of halogens in magmas; (2) the constraints on halogen transport and storage in silicate minerals; (3) halogens in fluids, with implications for their recycling in subduction zone settings; (4) halogens in metallic phases, including the first constraints on their abundance in the Earth's core.

EXPERIMENTAL CHALLENGES

Microthermometry uses a heating and cooling stage under an optical microscope. This method can characterize fluid inclusions, under the assumption that there is a constant volume that will reestablish itself to the original pressure during experimental heating. High-temperature furnaces at atmospheric pressure are used to study silicate melts, the assumption being that the effect of pressure on the studied process (e.g., melt viscosity) may be negligible (Dingwell and Hess 1998).

In contrast, the study of magmatic processes requires reproducing the pressure (P) and temperature (T) conditions relevant to those of magma chambers and conduits. Most of the experiments that study halogen partitioning between fluids, melts, and minerals, and their solubility in these magmatic phases, are performed in a large variety of high- P –high T apparatuses, such as rapid quench cold-seal pressure vessels (up to a few GPa and up to 1,200 °C; i.e., Bureau et al. 2000) or piston cylinders (0.5–5 GPa, up to 1,600 °C).

These experimental setups come with two major limitations. First, they usually last only hours or days, which is orders of magnitude shorter than natural processes. Second, experiments have to be quenched (cooled down) as fast as possible in order to preserve the volatiles (i.e., the halogens and water) and the silicates that were dissolved in the fluid phases during the experiment. It is often assumed that the halogen concentrations in a glass, which represents a quenched melt, reflects the respective equilibrium concentrations at a designated P and T . Today, we know that this approach is not accurate for the investigation of fluid properties, which requires that volatile species are monitored in situ at high- P and high- T . A new generation of experiments has been proposed that can associate specific high- P tools, such as diamond anvil cells (up to a few GPa and up to 1000 °C) and combine these with in situ characterizations (e.g., Bureau et al. 2016).

Another challenge is the analysis of heavy halogens in small experimental samples. Conventional analytical methods require crystal sizes with a diameter of at least several tenths of micrometers. This can be achieved with the addition of small crystal nuclei to the starting material (Dalou et al. 2012), slow cooling (Beyer et al. 2012), or deliberate temperature-cycling around the target temperature. Potential methods to assess, if these crystals were in equilibrium with the surrounding

melt are (1) euhedral, monocrystalline, and inclusion-free crystal shapes; (2) a homogeneous major-element distribution between crystals and melts; (3) partition coefficients that are identical at varying crystal growth rates (Joachim et al. 2015).

HALOGENS IN MAGMAS

The Role of Halogens in Crustal Magmatic Systems

Fluorine and chlorine were the first halogens to be analyzed in volcanic glasses and rocks because of their relatively high abundances. They have been the subject of numerous studies since the 1980s. During the last two decades, the role of bromine and iodine in magmatic processes has also been studied thanks to methodological advances, including in situ chemical analyses and satellite monitoring. Over the last few decades, databases that can correlate halogen concentration and distribution with depth in the Earth have been established (see Pyle and Mather 2009). Experimental studies of the role of the halogens in magmatic processes include determining their solubilities in melts; their partitioning behavior between fluids, silicate melt, and mineral phases; chemical differentiation during mineralization; and their effects on the physical properties of magmas.

Experimental constraints on halogen properties in silicate melts

The term *solubility* refers to the maximum amount of halogens that can be dissolved in a silicate melt that is saturated with an immiscible aqueous fluid + brine assemblage at a given set of conditions (Carroll 2005) (FIG 1A). Partitioning is defined by the Nernst-type partition coefficient D between two phases, for example between an aqueous fluid (f) and a melt (m) ($D_{\text{halogen}}^{f/m}$). Halogens also fractionate into minerals from melt during crystallization. Vapor–liquid immiscibility processes have been observed at magmatic conditions, mostly for Cl (FIG. 1B). Indeed, depending upon the bulk halogen concentration, a silicate melt can coexist with variable phases: a low-density aqueous phase (vapor); a vapor–liquid mixture; solid salts; and a liquid, also called a high-density hydrous phase or a hydro-saline liquid.

Many studies have measured the solubility of chlorine in hydrous felsic melts at pressures and temperatures relevant for crustal conditions (e.g., Webster 1997; Carroll 2005 and references therein). Both, Cl and F solubilities in magmatic melts depend on the Al content, Na/Si ratio, and on network-modifier alkalis (FIG. 1A). Whereas chlorine is mainly associated with the network-modifying cations Al, Na, and K, fluorine forms complexes with Al and Na. Dissolved water has a strong effect on the silicate melt structure. The solubility of F increases with increasing water content, while the solubility of Cl decreases (FIG. 1B) (Dalou and Mysen 2015).

Solution mechanisms established for Cl are also found for Br (Bureau and Métrich 2003), and their solubilities are comparable in felsic melt compositions (FIG. 1A). Iodine shows a similar solubility despite its larger ionic size (Leroy et al. 2019), which opposes the expectation that the four halogens exhibit a systematic change in solubility in chemically identical melts depending on their ionic radii. In fact, the three heavy halogens have the capacity to be incorporated at similar concentrations in hydrous silicate melts (FIG. 1A). Fluorine, the smallest halogen, is the most compatible in silicate melts and has the highest solubility (e.g., Dalou and Mysen 2015 and references therein).

Several experimental observations illustrate that the effect of F and Cl in petrogenesis. For example, the presence of ≥ 1 wt% F in a diopside melt causes a depression of the liquidus temperature that is of similar magnitude to that of dissolved water, and the addition of F to depolymerized liquids increases that liquid's viscosity (Dingwell and Hess 1998). In polymerized peraluminous or peralkaline melts, the extent to which dissolved water decreases viscosity is suppressed due to the presence of dissolved F and Cl (Baasner et al. 2013 and references therein). Small amounts of dissolved chlorine can lower the liquidus temperature of basaltic melts. Chlorine also forms complexes with Fe, and perhaps Mg and Ca, in basaltic melts, which increases silica activity and stabilizes pyroxene against olivine (Filiberto and Treiman 2008).

Experiments also reveal the strong affinity of Cl to form complexes with ore metals and trace elements that preferentially partition into hydrothermal fluids and are responsible for mineralization. Halogen behavior during magma degassing can be controlled either by partitioning into vapor/aqueous fluid phases or by saturation of a halogen-bearing mineral phase. Halogen behavior in immiscible brine is probably controlled by saturation processes alone (see Shinohara 2009 for Cl).

Experimental Constraints on Volcanic Degassing of Halogens

The exsolution of magmatic volatiles is a key process in volcanic systems, because it drives magma differentiation, crystallization, ascent, and eruption. Locally, it also drives hydrothermal alteration and mineralization. Because halogens are lost from magmatic melts through degassing, the best constraints on their initial melt concentrations are through the analyses of melt inclusions trapped in crystals.

The impact of volcanic degassing of halogens on atmospheric chemistry is one important justification for experimental research on halogen behavior in magmas. For example, estimates of halogen fluxes into the oceans and atmosphere are based on measurements from fumaroles and plumes, and mass-

balance calculations between melt inclusions and volcanic glasses. However, these calculations require knowledge of the partitioning behavior of halogens between silicate melts and fluids at magmatic conditions. Early experimental studies have shown that Cl partitions strongly into fluids (i.e., large $D_{\text{Cl}^{\text{f/m}}}$) (Webster and Holloway 1988). For example, in the topaz–rhyolite–H₂O ± CO₂ ± F system at 0.5–5 kbar and 725–950 °C, the $D_{\text{Cl}^{\text{f/m}}}$ ranges from 2 to 130. The $D_{\text{halogen}^{\text{f/m}}}$ may approach unity as the miscibility gap is closed between melt and an aqueous fluid (Bureau et al. 2016). Although F, the most compatible halogen in silicate melts, exhibits late degassing at shallow depths, the heavier halogens experience early degassing, which is enhanced by the presence of water (Bureau et al. 2000, 2016). In felsic melts (e.g., albitic melts), $D_{\text{halogen}^{\text{f/m}}}$ increases with increasing ionic radius at 0.2 GPa and 900 °C: 8.1 ± 0.2 for Cl, 17.5 ± 0.6 for Br, and 107 ± 7 for I (Bureau et al. 2000) (FIG. 1C). Despite their low concentrations in silicate melts, Br and I can, nevertheless, be released into the atmosphere, as confirmed by measurements from volcanic plumes.

Combining natural halogen abundances with experimentally derived partition coefficients enables the calculation of volcanic halogen input to the atmosphere. Experimentally combining fluid–melt–mineral phase equilibria at magmatic pressure–temperature conditions with in situ characterization (i.e., by synchrotron radiation X-ray fluorescence, and/or by Raman and infrared spectroscopy) is a powerful tool to understand halogen behavior in magma chambers and volcanic conduits because it avoids quench modifications (FIG. 2). This experimental approach established the extreme efficiency of water to wash out Br and I from hydrous silicate melts and their significant input to the atmosphere during magma ascent (e.g., Bureau et al. 2016 and references therein), and also applies to the study of recycling processes of volatiles in subduction zones (i.e., slab burial).

HALOGENS IN SILICATE MINERALS

Mid-ocean-ridge basalt (MORB) and ocean island basalt (OIB) can provide sources of information for the abundance and distribution of halogens in the Earth’s mantle, because they represent partial melts that originate from different mantle sources and depths. Elemental ratios (e.g., Cl/K or F/P) have long been used to determine respective halogen concentrations in different source regions and still offer a reliable and important database (Pyle and Mathers 2009 and references therein). Here, the focus is on recent experimental and analytical developments that allow the investigation of fluorine and chlorine partitioning behavior between silicate melt and residual minerals at the P – T conditions where the mantle partially melts. These provide an independent approach to estimate halogen concentrations in these mantle source regions.

The major residual minerals that remain in the mantle after partial melting are olivine and pyroxene. Temperature strongly affects the partitioning behavior of halogens between olivine (ol) and a silicate melt ($D_{\text{halogen}}^{\text{ol/m}}$). As an example, $D_{\text{F}}^{\text{ol/m}}$ increases by about two orders of magnitude from ~ 0.003 at $1,350^\circ\text{C}$ (Beyer et al. 2012) to ~ 0.3 at $1,600^\circ\text{C}$ (Joachim et al. 2015). The $D_{\text{F}}^{\text{ol/m}}$ also increases linearly with increasing dissolved water in the silicate melt (Joachim et al. 2017), which is not the case for $D_{\text{Cl}}^{\text{ol/m}}$. The effect of pressure on fluorine and chlorine partitioning behavior seems to be negligible in the upper mantle. Halogen partition coefficients between the pyroxenes and silicate melt are usually greater than those between olivine and a melt. Fluorine partitioning between orthopyroxene and melt seems to be largely independent of the crystal chemistry and correlates positively with increasing melt polymerization, whereas initial results suggest that the increase of a jadeite component ($\text{NaAlSi}_2\text{O}_6$) in orthopyroxene and the increase of a calcium tschermakite (CaAlAlSiO_6) component in clinopyroxene can promote Cl incorporation (Dalou et al. 2012). These experimentally derived halogen-partitioning data allow the concentrations of halogens in MORB and OIB mantle source regions to be calculated based on a simple batch melting model, which neglects degassing of halogens during ascent and eruption of the basalts because of the relatively low volatile concentrations in MORBs and OIBs (Beyer et al. 2012; Joachim et al. 2015, 2017).

A comparison of the halogen concentrations in the MORB source region with primitive mantle estimates indicates that the upper mantle is degassed and relatively homogeneous with respect to fluorine and chlorine. In contrast, the fluorine and chlorine concentrations in the OIB source region are heterogeneous and show a significant enrichment in fluorine relative to the primitive mantle, which indicates substantial fluorine recycling and partial separation between fluorine and the heavy halogens during the subduction of oceanic lithosphere into deeper mantle regions.

Serpentinization and deserpentinization of peridotite play a crucial role for volatile transport of the heavy halogens in subduction zones. After deserpentinization, most of the heavy halogens are likely to be transported via fluids (and through melts if supersolidus temperatures are reached) to the overriding mantle wedge due to their hydrophilic nature. Fluorine will more likely be transported in mineral phases because of its lithophile behavior. An important fluorine- and water-bearing mineral in subducting oceanic crust is amphibole, which can retain significant quantities of fluorine in the solid residue, so leading to substantial F/Cl fractionation during partial melting (Van den Bleeken and Koga 2014). Other minerals that may lead to halogen recycling into the mantle through subduction and a partial fluorine- heavy halogen separation in the subducting slab are olivine, humite group minerals, garnet, apatite, lawsonite, phlogopite, and phengite.

In the Earth's mantle, potentially important hosts for the halogens are the hydrous minerals apatite and humite, although their abundance can be limited by available concentrations of phosphorus and titanium, respectively. Nominally anhydrous minerals (NAMs) are another potentially important host due to their large modal abundance. An example is olivine, which is the most abundant mineral in the upper mantle. Experimental results show that olivine may contain hundreds of ppm of Cl (170 ppm) (Dalou et al. 2012). A combination of high P -high T experiments and first-principle calculations shows that fluorine and water are clumped and associated with Si vacancies in the crystal structure of forsterite, resulting in fluorine solubilities of up to $\sim 1,715$ ppm at 2 GPa and 1,250 °C (Crépeau et al. 2014). This implies that significant amounts of associated F and OH have the potential to be stored in the upper mantle and can be recycled into deeper mantle regions in the peridotite layer at the bottom of subducting plates. At depths of the transition zone (410–670 km), which represents the zone between the upper and lower mantle, olivine becomes unstable and is transformed into wadsleyite (Wd) and ringwoodite (Rw), whose fluorine solubilities decrease with increasing water concentrations. These minerals may not only store significant amounts of fluorine but also up to 200 ppm (Wd) and 113 ppm (Rw) chlorine in hydrous systems (Roberge et al. 2017). This implies that the transition zone can be a significant repository for fluorine and the heavy halogens in the Earth's mantle. Bridgmanite (Brg) is another potential host for fluorine in the deep Earth, having a solubility of $>8,000$ ppm in aluminous and water-bearing systems at 1,800 °C and 25 GPa. However, in Al-free and water-free systems, Brg exhibits fluorine contents below 50 ppm at identical P - T conditions (Yoshino and Vazhakuttiyakam 2018).

If substantial amounts of halogens are recycled from the surface and stored in the Earth's upper mantle, the transition zone, and perhaps the lower mantle, these may have an effect on physicochemical properties. For example, the presence of fluorine has the potential to increase the stability of mineral phases, such as clinohumite, to higher temperatures (Grützner et al. 2017). Fluorine-rich phlogopite may produce electrical anomalies in the upper mantle, thus challenging the assumption that high electrical conductivity zones are always related to the presence of partial melts, aqueous fluids, saline fluids, graphite, or sulfides (Li et al. 2016).

HALOGENS IN MANTLE FLUIDS

Chlorine is observed in arc volcanic gasses as a form of hydrochloric acid, with an abundance that follows water, carbon dioxide, and sulfur dioxide/hydrogen sulfide. The enrichment of alkaline, alkaline earth elements, and Pb is characteristic for subduction-zone basalts compared to MORB and has been attributed to "slab-derived components". Chlorine, present in aqueous fluids in the form of

(Na, K)Cl, has a strong effect on the partition coefficient of these enriched elements between aqueous fluid and andesitic melt. This was first shown by quench experiments (Keppler 1996) and later verified in situ using an externally heated diamond-anvil cell combined with synchrotron radiation X-ray fluorescence (FIG. 2) (Kawamoto et al. 2014). The partition coefficient of Pb between saline fluid and melt increases by more than one order of magnitude compared to that between pure H₂O fluid and melt (FIG. 3A). A similar effect is observed for alkaline elements (Rb) and the alkaline earth elements (Sr), which show enhanced partitioning into saline fluids. Geochemical systematics suggest that the ingredients of arc magmas are a mantle peridotite component, a slab-derived aqueous fluid component, and a slab-derived melt component (FIG. 3B). FIGURE 3A and 3B indicate that slab-derived fluids are saline fluids that contain Pb, alkaline, and alkaline earth elements, whereas slab-derived melts contain the fluid-insoluble elements Th, Ta, P, Zr, Hf, Y, and the rare earth elements.

Fluid inclusions are locally observed in mantle peridotite xenoliths and high-pressure metamorphic rocks (Kawamoto et al. 2013; Kawamoto et al. 2018). Raman microscopy shows that the fluid inclusions are composed of aqueous solutions and vapor bubbles. Findings of magnesite-bearing saline fluid inclusions in tremolite-bearing harzburgite xenoliths from Mount Pinatubo Volcano (Philippines) suggest the presence of H₂O–CO₂–NaCl fluids at high-pressure and high-temperature conditions. This discovery led to the hypothesis that seawater-like saline fluids are present in the mantle wedge beneath the Philippine volcanic arc (FIG. 3C) (Kawamoto et al. 2013). The presence of tremolite indicates *P–T* conditions of <830 °C at 0.9 GPa, which is above the temperature stability of serpentine minerals and talc and below the solidus temperature of H₂O-saturated mantle peridotite. Thus, the *P–T* conditions that stabilize tremolite allow excess H₂O to exist as aqueous fluids in the mantle wedge.

Microthermometry on fluid inclusions in mantle xenoliths and metamorphic rocks from various arcs allows an estimate of the NaCl equivalent concentrations in the entrained rock: 5.1 ± 1 wt% in the harzburgite beneath Mount Pinatubo Volcano; 3.7 ± 1 wt% in lherzolite beneath Ichinomegata Volcano; 4.5 ± 1 wt% in jadeitite and jadeite-bearing rocks in the suprasubduction zone of the Dominican Republic; and 3–7 wt% in the high-pressure metamorphic rocks of the southwest Japan arc (e.g., Kawamoto et al. 2013; Kawamoto et al. 2018) (FIG. 4). This suggests that subduction-zone fluids are slightly more saline than present seawater (3.5 wt% NaCl). Rare-gas and heavy-halogen systematics show that the fluid inclusions in mantle xenoliths from Mount Pinatubo have chemical features similar to sedimentary pore-fluids and to serpentinite, both of which are enriched in iodine through the decomposition of subducted organic materials (Kobayashi et al. 2017). This implies that

subduction-zone fluids are probably produced through hydration and dehydration processes during seawater–oceanic plate interactions and inherit their sedimentary signature possibly through the dehydration of serpentinites.

Experimental studies suggest that saline (i.e., halogen-bearing) fluids not only enhance the dissolution of metals but also that of carbonate (Newton and Manning 2002). For example, 10 wt% NaCl-bearing fluids can dissolve more than double the amount of carbonate at 800 °C and 1 GPa. This shows the importance of being salty in subduction zone fluids for the enhancement of elemental transfer. Experiments and natural observations indicate the presence of H₂O–CO₂–NaCl fluids in the mantle wedge (e.g., Kawamoto et al. 2013), although CO₂ is less common in fluid inclusions in the high-pressure metamorphic rocks that originate from subduction channels, the interplate boundary layers composed of oceanic crust and serpentinites at the base of the mantle wedge (e.g., Kawamoto et al. 2018). Isotopic investigation of the carbon in magnesite found in fluid inclusions within mantle xenoliths may be useful for understanding the transfer of carbon in subduction channels and the mantle wedge.

HALOGENS IN METALLIC PHASES

During core formation, which occurred early in Earth's history during the ~100 My interval after the initial solar nebula processes, the partitioning behavior between Earth's silicate mantle and crust and the metal core controlled the elemental distribution between these reservoirs. Whereas chlorine seems to be largely lithophile and remains in the silicate melt, iodine exhibits mildly siderophile behavior, indicating that the core could be a significant iodine reservoir containing up to 82% of the bulk Earth's budget (Armytage et al. 2013 and references therein).

FUTURE PERSPECTIVES

To date, available studies strongly indicate that the transport of water and halogens into the deep Earth are closely linked, either through halogen-bearing aqueous and/or fluids or through the combined incorporation of OH groups and halogens in hydrous or nominally anhydrous minerals. This implies that a better understanding of the halogen behavior and distribution in the solid Earth is of fundamental importance for understanding the deep volatile cycle and its effects on physicochemical processes. This, in turn, will give a deeper insight into the role of halogens during the origin and evolution of our planet.

Carefully designed experiments to identify the key halogen-carrier phases in the crust, subducting slab, and mantle, are needed to better understand the halogen-incorporation mechanisms in

minerals and melts, halogen speciation in fluids and melts, and to quantify their distribution, mobility, and release through partitioning or degassing at depth. The unquenchable properties of deep fluids/melts will require the novel use of in situ characterization techniques (i.e., infrared spectroscopies, X-ray characterization) combined with either laser-heated diamond anvil cells or any optical or X-ray-transparent high-pressure devices. These experimental strategies must be associated with new analytical tools, such as synchrotron X-ray fluorescence using nanoscale beams. Conventional setups will remain relevant to investigate processes and properties in the Earth's mantle, such as the solubilities of halogens in mineral phases, and mineral–melt partitioning of the heavy halogens. These will require the development of analytical techniques that allow for the precise analysis of Cl, Br and I down to the parts-per-billion level with high spatial resolution to analyze them in individual phases.

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FIGURE CAPTIONS

FIGURE 1 (A) Representative solubility data for Cl, Br, and I versus (A/CNK)/Si [molar ($\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2$)] determined using similar experimental protocols at water saturation (except for I): 0.1–0.4 GPa and 900–1,400 °C for felsic (open symbols) and mafic (closed symbols) melts. Blue triangles = Cl; red squares = Br; orange circles = I. Data for Br and I are limited; nevertheless, the diagram illustrates that Cl, Br, and I have a similar solubility mechanism in felsic melts at a comparable range of pressures and temperatures. In mafic melts (i.e., basalts), Cl (closed blue triangles) may have a higher solubility compared to I. **(B)** Phase relations in the silicate melt–water–Cl system between 800 °C (low temperature, LT) and 1,700 °C (high temperature, HT). The curves delimit isobaric solubilities of saturated magmatic volatile phases and silicate melts. They show that small quantities of Cl have a dramatic effect on volatile phase exsolution. The curves designate the H_2O and Cl solubilities and delimit the stability of silicate melt, melt-plus-vapor (or low-density gas), melt-plus-liquid (or brine), and melt-plus-vapor-plus-liquid. The light curves express the volatile solubilities and phase relations at comparatively lower temperatures. The H_2O solubility varies only minimally as the melt composition changes from felsic to mafic at constant pressure. The Cl solubility in H_2O -poor melts increases by an order of magnitude. The strong relationship between melt composition and Cl solubility implies that the chemical evolution of magma from mafic to more felsic composition enhances the role of Cl in driving volatile phase exsolution. The dotted red curve represents the Cl in a haplogranite (HGR solubility curve at 0.05 GPa, illustrating the strong pressure effect on Cl solubility). **(C)** Fluid/melt partition coefficients ($D^{f/m}$, where D = partition [i.e., distribution] coefficient, f = fluid, m = melt) of halogens versus their ionic radius in the albite–water system at 900 °C and 0.2 GPa. REFERENCES FOR DATA IN ONLINE SUPPLEMENT.

FIGURE 2 (A) Experimental setup of Synchrotron Soleil’s DIFFABS (‘diffraction/absorption’) beamline (France). The hydrothermal diamond anvil cell (DAC) is aligned to the high energy (17 keV) X-ray beam. Synchrotron radiation X-ray fluorescence (XRF) is detected with a Si-drift detector. The experiment is monitored through an optical microscope. **(B)** Diagrammatic section through the DAC during an experiment at high pressure and temperature. Globules of silicate melt are in equilibrium with an aqueous fluid in the sample chamber. Because the X-ray beam can cross the DAC, the halogen content in the melt and fluid phases can be quantified simultaneously. **(C)** Scanning electron microscope (SEM) image of the sample chamber after quenching.

FIGURE 3 (A) Partition (distribution) coefficients ($D^{\text{fluid/melt}}$) of Pb, Rb, and Sr between aqueous fluids and coexisting haplogranite (HGR) or jadeite (Jd) melts as a function of pressure. Open symbols denote a Cl-free system; filled symbols denote systems with 5 mole (Na, K)Cl/kg. (B) Schematic diagram of trace element concentrations in arc basalts normalized to mid-ocean-ridge basalt (MORB). Aqueous fluid- and melt-like components are attributed to aqueous fluids and sediment-derived melts or supercritical fluids from subducted oceanic plate, respectively. (C) Fluid inclusion composed of saline solution ($\text{H}_2\text{O}^{\text{L}}$), vapor ($\text{H}_2\text{O}^{\text{V}}$), and magnesite (Mgs) in an olivine from a tremolite-bearing harzburgite xenolith collected from a pyroclastic flow from the Mount Pinatubo (Philippines) eruption of 1991. REFERENCES FOR DATA IN ONLINE SUPPLEMENT.

FIGURE 4 Salinity map of subduction-zone fluids. Symbol: % NaCl = wt% NaCl-equivalent. Arima-Takarazuka (Japan) is a hot spring in the forearc region and is characterized by high $^3\text{He}/^4\text{He}$ ratios suggesting its deep mantle origin. Aqueous fluids with 4.5 % NaCl and 3–7 % NaCl are observed in jadeite-rich rocks formed in subduction channels of Dominican Republic and Southwest Japan arc, respectively. REFERENCES FOR DATA IN ONLINE SUPPLEMENT.

Figure 1

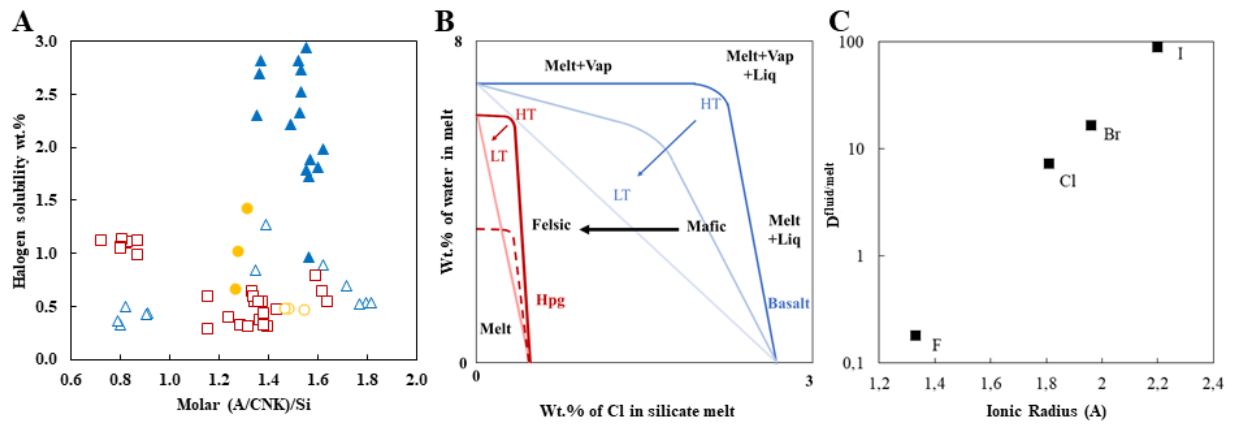


Figure 2

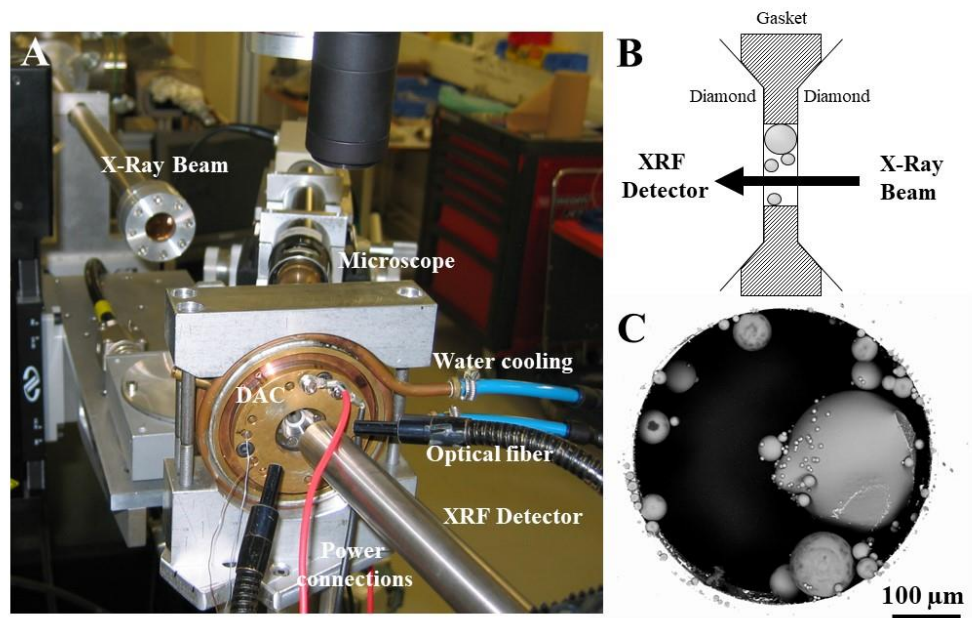


Figure 3

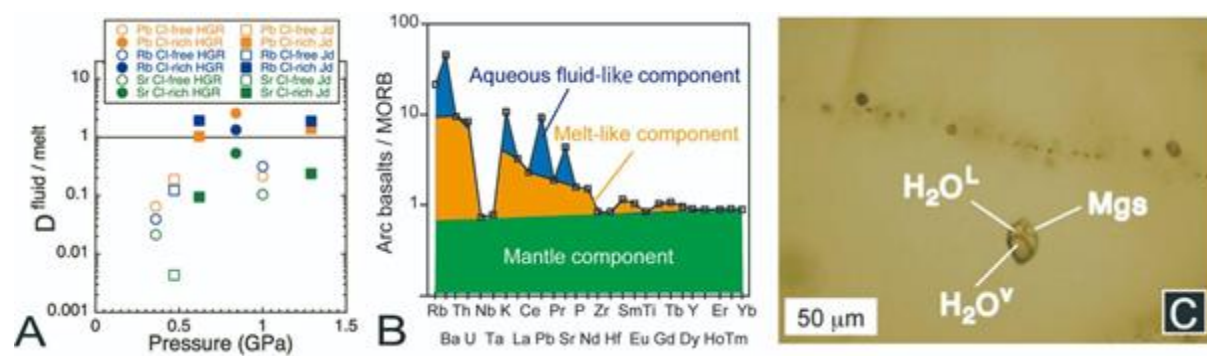


Figure 4

