

## Electromagnetic detection of partial melts and volatiles across the Middle America Trench offshore Nicaragua

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In April 2010 we conducted a large-scale marine electromagnetic (EM) experiment along a 280 km profile across the Middle America Trench offshore Nicaragua in order to image the electrical conductivity of the incoming plate and asthenosphere before and during the early stages of subduction. The 50 seafloor EM stations were deployed onto the Cocos plate extending from the abyssal plain, across the trench and continental rise and onto the shelf. The instruments recorded controlled-source electromagnetic (CSEM) and magnetotelluric (MT) data that are sensitive to crustal and upper mantle structure, respectively. We inverted the data for 2D electrical conductivity using nonlinear regularized inversion implemented with a newly developed adaptive finite element forward algorithm; this code employs unstructured grids to readily handle the rugged seafloor bathymetry and uses automatic adaptive mesh refinement to ensure numerical accuracy.

The MT data were inverted to yield the triaxially anisotropic resistivity tensor aligned with the trench axis, revealing the existence of a 30 km thick, horizontally extensive low-resistivity layer that extends from the trench outer rise to 200 km into the interior of the plate. The onset of this layer is consistent with seismically observed lithosphere-asthenosphere boundary (LAB) depths. The layer resistivity (4-6 ohm-m) is 2 times more conductive in the direction of plate motion than perpendicular to it. While the low resistivity is compatible with both hydrous olivine and partial melt, we rule out hydrous olivine as it requires unrealistic mantle water contents to account for our observed resistivity. The solidus of wet peridotite suggests that a low degree of partial melt is stable, while the layer anisotropy suggests it is being actively sheared, such that the lithosphere is being decoupled from the deeper mantle over a 30 km depth interval.

The CSEM data image a resistive oceanic crust beneath the abyssal plain, but which decreases by a factor of 2-4 directly with the onset of bending faults at the trench outer rise. A strong azimuthal anisotropy is observed only on the densely faulted outer rise, with crustal conductivity highest in the trench parallel direction. The observed resistivity decrease and anisotropy can be explained by a porosity increase along vertical fault planes, which we interpret as evidence that the bending faults provide fluid pathways allowing for the deeper serpentinization of the uppermost mantle. We infer that the width of the faulting region and the density of fractures are primary controls on the extent of upper mantle serpentinization prior to subduction. Hence, the heavily faulted outer rise offshore Nicaragua is the culprit of the anomalously wet slab. By comparison, other sections of the Middle America Trench contain fewer bending faults and thus lower degrees of serpentinized upper mantle, perhaps resulting in a direct impact on arc volcanism.

## Mantle tomography and dynamics of the Western-Pacific subduction zones

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We used multiscale seismic tomography to determine the detailed 3-D seismic velocity structure of the crust and mantle under the Western-Pacific subduction zones and the East-Asia continental regions. The subducting Pacific and Philippine Sea (PHS) slabs are imaged clearly from their entering the mantle at the oceanic trenches to their reaching the mantle transition zone and finally to the core-mantle boundary (CMB). High-resolution local tomography of NE Japan has imaged the shallow portion of the slab from the Japan Trench down to about 200 km depth under Japan Sea. The 3-D  $V_p$  and  $V_s$  structures of the forearc region under the Pacific Ocean are constrained by locating suboceanic events precisely with sP depth phases. Strong structural heterogeneity is revealed in the megathrust zone under the forearc region, and there is a good correlation between the heterogeneity and the distribution of large thrust earthquakes. A joint inversion of local and teleseismic data imaged the subducting Pacific slab down to 670 km depth under the Japan Islands and the Japan Sea. We found that the PHS slab under SW Japan has subducted aseismically down to 460 km depth. A mantle upwelling is found under SW Japan that rises from about 400 km depth right above the Pacific slab up to the PHS slab. Regional and global tomography revealed the Pacific slab that is stagnant in the mantle transition zone under East Asia. A big mantle wedge (BMW) has formed in the upper mantle above the stagnant slab. Convective circulations in the BMW and deep dehydration of the stagnant slab may have caused the intraplate volcanoes in NE Asia. Global tomography shows pieces of fast anomalies in the middle and lower mantle as well as in the D" layer above the CMB, suggesting that the stagnant slab finally collapses down to the lower mantle and CMB. Prominent slow anomalies are also revealed in the mantle under the subducting slabs, which may represent either mantle plumes or upwelling flows associated with the deep subduction of the slabs.

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## The pattern of fluid release from the subducting slab and the migration of fluids in the mantle wedge

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In this study, we use numerical models to quantify the pattern of fluid release from the subducting slab and the migration path of aqueous fluids in the mantle wedge in subduction zones. The release and uptake of H<sub>2</sub>O by dehydration and hydration reactions, respectively, are calculated using a subduction zone thermal model and thermodynamic calculations based on Perple\_X. To date, most studies of fluid flux in subduction zones have assumed a uniform distribution of mineralogically bound H<sub>2</sub>O within given lithologies in the incoming plate. However, geological and geophysical observations and thermo-mechanical models indicate that the distribution of hydrous phases in the lower crust and upper mantle can be highly localized due to fault-controlled fluid migration and hydration. Our modeling results show that for a given bulk H<sub>2</sub>O content, localized hydration results in shallower H<sub>2</sub>O release compared to uniform hydration, and that the H<sub>2</sub>O flux off the subducting slab beneath the forearc and arc regions can be almost twice as large from a locally hydrated slab as from a uniformly hydrated slab. Hydration of the overlying mantle in the flowing part of the wedge leads to downdip transport of bound water by the flowing mantle and delays the liberation of H<sub>2</sub>O, but the volume of H<sub>2</sub>O absorbed in the mantle is small compared to that released from the subducting slab. We model the migration of the released aqueous fluids in the hot flowing part of the mantle wedge excluding the cold stagnant wedge corner. Mineral grain size affects grain-scale permeability of the mantle and fluid migration. Our thermal model coupled with a laboratory-derived grain size evolution model predicts a large spatial variation in grain size in the flowing part of the wedge; grain size increases from 10–100 microns in the shallowest part of the region beneath the forearc to a few cm in the hottest part of the mantle beneath the arc. By incorporating the grain size distribution into a fluid migration model, we find that aqueous fluids that migrate into the shallow fine-grain-size region become trapped in the downgoing mantle due to low permeability and are dragged downdip until permeability becomes high enough for the fluids to migrate upward. Thus, the grain size distribution can play an important role in controlling the location of upward fluid migration. A number of processes in subduction zones, such as arc magma generation, earthquakes, and mantle flow, depend strongly on the availability of aqueous fluids at depth. Using our modeling results, we explore the implications of the predicted fluid distribution on various subduction zone processes.

## **Behavior of subducted water and its role on the arc magma genesis in the NE Japan arc: A combined geophysical and geochemical approach**

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Subducted water is carried by downgoing oceanic plate slab and is released by dehydration/melting of the slab in prograde metamorphism. The released water migrates upwards and contributes melting of the mantle wedge to form primary arc magmas. The water is then captured by the arc magmas and eventually solidify/erupt to form arc crust and volcanoes. Water, either in fluids or melts in both the slab and the mantle, promotes dissolution and mobilization of elements truncating material transfer in the subduction factory. Water also affects physical properties of the sub-arc slab and the mantle accelerating/decelerating mantle convection and seismicity. We in this paper try to demonstrate a coherent model that may explain the geophysical and geochemical roles of the water beneath the NE Japan arc. We investigate the dehydration profile of the downgoing slab based on the seismic/geophysical/geochemical data and examine the role of the slab water to form geochemical variations found in the Quaternary magmas erupted on the arc. Arc Basalt Simulator version 4 (ABS4), a petrological/geochemical model developed for to describe the mass balance between the subduction slab inputs and the arc magma outputs, examines the subduction zone processes including behaviors of the water and 33 major/trace elements and Sr-Nd-Hf-Pb isotopes. Intensive/extensive parameters that govern those petrogenetic processes are also estimated by the model calculations and are compared with the geophysical observations. The combined approach between geophysics and geochemistry provides new perspectives in both element behaviors and geophysics in the subduction factory.

## Sr-Nd-Pb isotope compositions of frontal arc stratovolcanoes in Northeast Japan arc

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We present new Sr-Nd-Pb isotope compositions along with major and trace element compositions for representative NE Japan frontal arc stratovolcanoes, at which calc-alkaline and tholeiite rock series coexist. We selected Hakkoda and Akitakomagatake volcanoes from the northern segment of the arc, Nasu and Takahara volcanoes from the southern segment. About twenty lava samples in each volcano were analyzed for this study. Coupled with the previously published data for Zao and Azuma volcanoes in the central segment, we examined the isotopic characteristics of the two rock series from the six volcanoes. It has been proposed that the tholeiitic basalt magmas from isotopically enriched source are produced by anatexis of the lower crustal amphibolite caused by the underplating of calcalkalic basalt magmas derived from isotopically depleted mantle source for central segment. In the northern segment, mantle-derived magmas are low-K tholeiitic basalts from depleted sources. The calc-alkaline andesites from the segment are isotopically similar to the basalts with contamination of slightly enriched source materials indicating derivation from the basalts. In the southern segment, medium-K and low-K tholeiite basalts coexist. The medium-K basalts are isotopically distinct from the low-K basalts. Therefore, compositionally distinct sources should be necessary for the basalts. The calc-alkaline andesite-dacite magmas of the same K suites have the same isotopic compositions with the basalts and can be derived from the coeval tholeiitic basalt of the same K suite by remelting and internal mixing processes. The source rocks of the NE Japan arc lavas are systematically enriched in terms of Sr-Nd-Pb isotopes from north to south as has been reported elsewhere. In addition to this, we newly found remarkable features that each the volcano has distinct quasi-linear isotopic trends on Pb-Pb and Nd-Pb isotope systematics showing positively and negatively inclined arrays, respectively. These features clarified that mixing of two source compositions basically form the isotopic trends in each volcano. The extrapolations of the isotopic trends towards the depleted endmember (unradiogenic Pb) source appear to converge at one point plot within the Indian MORB-type mantle compositional field. The extrapolations towards the radiogenic Pb diverge and point to the fields of the subducted sediment and of the lower crust. Although the isotopic trends differ between volcanoes, the trends in the same segment are similar. Moreover, the isotopic compositions of the rear arc volcanoes show similar spatial variation as observed in the frontal arc volcanoes although they plot close to the depleted ends of the mixing arrays found in the frontal arc volcanoes. These features suggest that (1) the isotopic composition of the depleted mantle source is uniform, whereas (2) systematic along arc variation exists in the subducted sediment or in the lower crust, or both.

## Variable time lags between fluid addition and mantle melting in subduction zones

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The large excesses in  $^{238}\text{U}$  and  $^{226}\text{Ra}$  measured in some arc magmas are taken as evidence for addition of slab-fluids to the mantle wedge shortly (hundreds to thousands of years) before eruption, suggesting a direct spatial and causal relationship between fluid fluxing and mantle melting beneath the arcs. A large proportion of arc magmas are, however, in or close to  $^{238}\text{U}$ - $^{230}\text{Th}$  equilibrium. This is generally interpreted as resulting either from aging of the magmas in the crust or buffering of the young slab-fluid U-series signal by an older sediment component in secular equilibrium. Alternatively this may indicate that significant time lags (>350 kyr) between slab-fluid addition and mantle melting are common.

Our work on Volcan de Colima, Mexico, demonstrate that arc magmas in  $^{238}\text{U}$ - $^{230}\text{Th}$  equilibrium can have large  $^{231}\text{Pa}$  and  $^{226}\text{Ra}$  excesses, a situation likely to apply to most arc magmas in or near  $^{238}\text{U}$ - $^{230}\text{Th}$  equilibrium, which rules out aging of the magmas in the crust as the cause of equilibrium. Arc Volcanoes in or near  $^{238}\text{U}$ - $^{230}\text{Th}$  equilibrium include magmas showing limited geochemical evidence for sediment addition to the mantle wedge and magmas with significant contributions from sediments. Quantitative metasomatism and melting models further indicate that addition of sediment melts to a depleted mantle wedge cannot compensate the  $^{238}\text{U}$  excesses induced by recent addition of fluids derived from the altered oceanic crust. Addition of sediment melts cannot account for the characteristically high proportion of arc magmas in  $^{238}\text{U}$ - $^{230}\text{Th}$  equilibrium in the event of systematic addition of slab-fluids to the mantle wedge shortly before melting and eruption. Melting of sources that have returned to secular equilibrium after metasomatism by the slab-derived components appears to be a common situation in arc setting. The absence of U-Th fractionation during melting most certainly depicts higher  $f\text{O}_2$  of arc sources compared to MORB sources that yield magmas with  $^{230}\text{Th}$  excesses.

Overall, the global U-Th array is best explained in terms of the time lag between metasomatism and melting varying from less than few hundred years to more than 350 kyr for magmas in or near U-Th secular equilibrium. This implies that in some cases mantle melting has a close temporal and spatial relationship to fluid fluxing, while in other cases significant delays occur potentially allowing downward transport of the hydrated mantle to the loci of melting beneath the arc.

## Effects of water on the oxidation state of iron in hydrous rhyolites

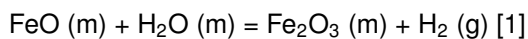
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Understanding the interaction of water with silicic magmas is of key importance in the assessment and prediction of volcanic hazards. Magmas produced by partial melting of the sub-arc mantle undergo significant degassing and crystallization near the earth's surface. This also makes it difficult to use eruptive products to estimate the oxidation state of sub-arc mantle, because components such as H<sub>2</sub>O, are themselves volatile oxide components with acid-base properties that affect oxidation states such as Fe(III)/Fe(II).

The effect of H<sub>2</sub>O on Fe oxidation state is still unclear. Some theoretical arguments have suggested that shallow degassing leads to increasing Fe<sup>3+</sup>/ΣFe as a result of preferential diffusion of H<sub>2</sub> out of the melt:



However understanding redox behaviour must take account of the overall acid-base properties of the hydrous melt. In particular, the dominantly basic behaviour of FeO the amphoteric behaviour of Fe<sub>2</sub>O<sub>3</sub> and changes in melt basicity relating to dissolution of H<sub>2</sub>O, can explain increasing Fe(III/FeII) with increasing H<sub>2</sub>O. Similar arguments might lead us to predict that dissolution of CO<sub>2</sub> should show the opposite effect, i.e. decreasing melt Fe(III/FeII) The predicted amphoteric behavior of H<sub>2</sub>O itself has been shown by NMR spectroscopy with even dominantly acidic behaviour observed, as predicted, in diopside rich melts.

Recent measurements by XANES of Fe(III/FeII) in rhyolitic obsidian hydrated in gold capsules in cold-seal apparatus, show a positive correlation between Fe<sup>3+</sup>/ΣFe and the H<sub>2</sub>O content of the glass. The observed increase in Fe oxidation state with increasing a(H<sub>2</sub>O) in these acidic melts is consistent with the addition of H<sub>2</sub>O as a predominantly Lux-Flood basic oxide. Hydrogen species in an oxide melt include molecular H<sub>2</sub>O, OH. OH<sup>-</sup> and hydroxylated silicate anions. The H<sub>2</sub> fugacity in [1] is defined thermodynamically by reactions involving water and the oxide/silicate melt and is likely to be low. Moreover it is experimentally well-known that the oxidation state of redox ions in silicate melts increases with addition of basic oxides at constant fO<sub>2</sub>. H<sub>2</sub> loss is thus unnecessary as a driver of oxidation change in these systems. As with the addition of other basic oxides, e.g. Na<sub>2</sub>O, the Fe(III/FeII) in hydrous acid melts adjusts along with activities of other components, including those containing hydrogen, as the result of acid-base equilibria in the melt at constant fO<sub>2</sub>.

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## **Thermodynamic and molecular approaches to physical-chemical evolution of high-temperature volatiles**

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There are two parts of common physics having common aims and tasks, but very different in methods of researches – thermodynamics and molecular physics. Thermodynamics operates with empirical data (macrofunctions and macroconditions) and ignores the gist of processes on molecular level. Contrariwise molecular physics analyses the gist of processes on molecular level, but has difficulties with processing of complex macrosystems. If systems macroparameters are known, thermodynamics guarantees precise quantitative estimations for macroreactions and macroprocesses in system. Molecular physics discovers qualitative gist of molecular processes in system. So thermodynamics and molecular physics must be used together if we want to understand the gist of natural processes. However scientific mainstream is thermodynamics methods in geosciences now, molecular physics is not used. It isn't correct. In endogenous geology the sense of quantitative thermodynamical methods decreases according to increasing of the number of parameters having unknown values. Molecular physics may be very useful in this case, as its methods well describe the gist of some endogenous processes (for example, physical-chemical evolution of high-temperature volatiles, genesis of oil and ore deposits).

The liquid–gas phase transitions play an important role in the evolution of endogenous fluids. When high-temperature gas mixture cools and reaches the critical temperature for one of components, it separates to form a gas–liquid interface. These processes lead to the formation of a high-temperature condensate, which accumulates excess components with the highest critical temperature. Based on elementary molecular-chemical concepts, we can trace possible evolution of gas phase of endogenous fluids and distinguish three geochemical fields of practical importance, which are listed below (from higher to lower temperature fields). (1) Zone of sulfur condensation is of great significance for the formation of many ore deposits and the formation of endogenous native sulfur deposits in zones adjacent to the water neutralization barrier. (2) Water condensation zones serve as a fluid neutralization barrier, where acid fluid flows originate. This zone has a key significance for the formation of hydrothermal, gold ore, and quartz deposits. (3) Zone of H<sub>2</sub>S and CO<sub>2</sub> condensation plays a leading role in the endogenous formation of hydrocarbon deposits.



## **Metasomatism within the mantle wedge inferred from NaCl equivalent content of aqueous fluid inclusions in sub-arc mantle peridotites from the Kamchatka arc**

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Hydrated oceanic lithosphere supplies aqueous fluids to the mantle wedge through dehydration processes, i.e., progressive metasomatism, of the subducted slab, and such aqueous fluids can dissolve various components, especially LILE (large-ion lithophile elements). The aqueous fluids could also contain Cl as an important component controlling the solubility of Si, Al, Ca, alkalis and other elements [1]. Such saline fluids derived from the subducting oceanic lithosphere have a role of transporter of such elements to and within the mantle wedge. Salinity of the aqueous fluids is changeable through the interaction with the surrounding rocks and possibly provides us with the information how they reach there from the source.

We determined the NaCl equivalent content of aqueous fluid inclusions in minerals in Avacha peridotite xenoliths (8 samples), derived from the mantle wedge beneath the volcanic front of the southern Kamchatka arc, by using Linkam THM600 heating-freezing stage at Kyoto University. The peridotite xenoliths are spinel harzburgites and of residual origin after a high degree of mantle melting assisted by slab-derived aqueous fluids/melts [2]. In addition, multi-stage metasomatic events by several agents are recorded in those samples [2,3]. A typical metasomatic event observed in the Avacha peridotites is silica addition: the formation of secondary orthopyroxenes replacing olivine. We can observe two types of secondary orthopyroxenes, Opx II-1 and Opx II-2, and they thought to be involved with silica-rich aqueous fluids and H<sub>2</sub>O-rich silicate melts, respectively [2]. Among the 8 samples, the amount of secondary metasomatic orthopyroxenes is variable from <1 to 20 vol.%, and some of them contain silica-rich glasses as interstitial film, associated with Opx II-2, or as inclusions in chromian spinel. Estimated NaCl equivalent contents of aqueous fluids in harzburgites containing Opx II-2 are lower than those in harzburgites containing Opx II-1: 0.4-5.0 wt% in the former and 1.0-15 wt% in the latter. On the other hand, the NaCl equivalent contents are rather high (1.4-17 wt%) in aqueous fluid inclusions in harzburgites with low modal amount of secondary orthopyroxenes (Opx II-1) relative to the more intensely metasomatized harzburgites (total Opx II > 2 vol.%). These results probably imply the differences in degree of interaction of the aqueous fluids with surrounding mantle wedge peridotite as well as in the source of NaCl-bearing aqueous fluids, and convince us of the multiple (or constant) metasomatic events within the mantle wedge, especially in the sub-frontal mantle.

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## The mantle water valve: A melting feedback on arc magma water concentrations

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Arc magmas vary widely in the concentration of chemical tracers derived from the subduction zone, with the notable exception of H<sub>2</sub>O. Nearly all arc volcanoes are sourced with mafic magmas that contain 2 to 6 wt% H<sub>2</sub>O, based on the least degassed melt inclusions from each volcano. The average for each arc varies even less, from 3.2 (for the Cascades) to 4.5 (for the Marianas), with a global average of 3.9 wt% H<sub>2</sub>O [1]. A modulating process, either in the crust or mantle, is likely responsible for the restricted range in the H<sub>2</sub>O contents of arc melt inclusions. Although stalling of magma in the upper crust may affect some arc magma water contents, we describe here a mantle control, caused by a negative feedback in the melting process driven by water itself. A strong relationship between the water content of the source, H<sub>2</sub>O(o) and the degree of melting (F) can maintain a nearly constant water content in the melt for a restricted range in mantle temperature. This is because water is at once a highly incompatible element in mantle minerals, and a major element with a large cryoscopic effect (i.e., freezing point depression). Thus H<sub>2</sub>O(o) contents drive high F, keeping H<sub>2</sub>O in the melt similar to what would result from lower H<sub>2</sub>O(o) at low F. Magmas with 3 to 4 wt% H<sub>2</sub>O can be generated at about 50C below the dry solidus for a wide range in F and H<sub>2</sub>O(o). This result can be derived from the cryoscopic effect. 3.5 wt% H<sub>2</sub>O in the melt depresses the melting temperature of peridotite or the olivine-saturated basalt liquidus by about 110C [2,3]. On the other hand, F of 10 to 20% (typical for arc magmas) requires an increase in temperature 40 to 80C above the dry solidus, and so the two effects together lead a net depression of 30 to 70C below the dry solidus. Thus the ultimate cause of the limited range in the water contents of parental arc magmas is a combination of the negative melting feedback, and a restricted range in mantle wedge temperatures, as predicted from recent numerical models that hold upper mantle potential temperature constant [4]. Like the nearly uniform thickness of the oceanic crust, the small range in the water contents of arc magmas may be another reflection of a planet with a background uniform potential temperature of 1400 C. The characteristic mean and range of H<sub>2</sub>O contents of arc magmas has implications for both the volatile fuel for explosive eruptions and the mass balance of H<sub>2</sub>O recycled through subduction zones. References. (1) Plank, et al. (2013) EPSL, in press. (2) Hirschmann, PEPI, 2010. (3) Medard and Grove, CMP, 2008. (4) Syracuse et al., PEPI, 2010.

## **Influence of pre-eruptive volatile contents on eruptive style at scoria cones: the case of Pelagatos volcano, Sierra Chichinautzin, central Mexico**

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Volatiles dissolved in magmas impact greatly on volcanoes eruptive style. Their concentration in the melt and mode of exsolution control the ascent velocity of the magma, and hence the eruption intensity. Complex feedbacks exist between the rate and extent of volatile exsolution at shallow levels and groundmass crystallization. This in turn affects the mixture rheology and extent of fragmentation producing important shifts in eruption style (explosive to effusive). Melt inclusions contained in crystals potentially record the volatile content and composition of melts at various stages of the evolution of the magma during its ascent providing important insights on the degassing-crystallization processes at shallow crustal levels. In this work, we present new melt-inclusion data from Pelagatos scoria cone, to characterize magma ascent and eruption processes at monogenetic volcanoes. Pelagatos is a small, young (less than 14 000 years B.P) monogenetic volcano which is part of the Sierra Chichinautzin volcanic field located in the central portion of the Trans Mexican Volcanic Belt (south-east of Mexico City). Petrological and textural data from previous work by Guilbaud et al. (2009) indicate that Pelagatos magma was initially hot (over 1200 °C), gas-rich (up to 5 wt% H<sub>2</sub>O), crystal-poor (about 10 vol% Fo<sub>90</sub> olivine phenocrysts) and thus poorly viscous (40-80 Pa s) producing rapid magma rise. This in turn delays degassing and cooling-induced crystallization up to shallow levels, driving the violent Strombolian eruptive style that is indicated by the morphology and structure of the proximal pyroclastic deposits. However, the water-content estimate of Guilbaud et al. (2009) was indirect and based on models calibrated by experimental work, and melt-inclusion analyses of similar magmas elsewhere. To better constrain eruptive processes during the Pelagatos eruption, we constrained the pre-eruptive volatile content of the magma by analyzing major element composition and volatile content (H<sub>2</sub>O, CO<sub>2</sub>, Cl, S) in olivine-hosted melt inclusions from 4 different tephra layers within the scoria cone stratigraphy. Olivine hosts for the melt inclusions are Fo<sub>83-90</sub>. The melt inclusions are basaltic andesite to andesite in composition, with 1.84 - 6.02 wt% MgO, 51.95 - 59.21 wt% SiO<sub>2</sub> and 0.64 - 1.55 wt% K<sub>2</sub>O. The H<sub>2</sub>O vary from 0.5 to 4.3 wt% whereas CO<sub>2</sub> vary from below detection limit up to 976 ppm. Sulfur content varies from 35 to 1451 ppm, showing a decrease with increasing MgO content as expected from crystallization induced degassing. Furthermore, Cl content, which varies from 900 to 1267 ppm, shows no correlation with MgO or K<sub>2</sub>O. The new data combined with existing whole-rock and matrix glass data indicate that the melt inclusions represent melt quenched after various degrees of differentiation in the conduit. Hence, olivine growth and melt-inclusion entrapment were shallow and syn-eruptive, pointing to a very dynamic conduit system.

## Noble gas and halogen recycling at the Izu-Ogasawara subduction zone

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Recent findings of subducted halogens and noble gases with seawater and sedimentary pore-fluid signatures in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan [1,2], as well as seawater-derived heavy noble gases (Ar, Kr, and Xe) in the convecting mantle [3], challenge a popular concept that the water flux into the mantle wedge is controlled only by hydrous minerals in altered oceanic crust and sediment. Serpentinized lithosphere of the subducting oceanic plate may transport noble gases and halogens acquired from pore-water in the overlying sediment [1,2,4]. To verify whether and how such subduction fluids modify the composition of the mantle beneath subduction zones, we determined noble gas and halogen compositions of olivines in arc lavas collected from 10 localities of the northern Izu-Ogasawara subduction zone and 11 IODP sediments and basalts recovered from northwestern margin of the Pacific plate.

MORB-like <sup>3</sup>He/<sup>4</sup>He and halogen ratios of the Izu olivines indicate insignificant contributions to the mantle wedge of radiogenic <sup>4</sup>He and pore fluid-like halogens, both of which are observed in the subduction fluids in the Sanbagawa samples exhumed from a depth ranging from 40 to 100 km [1,2]. On the other hand, a systematically higher contribution of atmospheric Ar in volcanic front lavas relative to rear-arc lavas suggests progressive decrease in the flux of subducted Ar from the slab with increasing distance from the Izu-Ogasawara Trench. The distinct halogen and heavy noble gas elemental ratios of altered oceanic basalts indicate their minor contributions to the Izu arc magma and the Sanbagawa subduction fluids. In contrast the I/Cl ratios of the Sanbagawa subduction fluids are elevated above sedimentary pore fluid values [1] and can most simply be related to the high I/Cl ratios of pelagic clays and radiolarian cherts.

The significantly smaller contributions of subducted noble gas and halogen in the Izu-Ogasawara arc relative to those in the Sanbagawa belt may result from a difference in the P-T condition of the subducted slabs. A hotter mantle wedge than those characteristic of mature subduction zones is proposed for the Sanbagawa subduction system [5], in contrast the Izu subducting slab is relatively cold and would therefore lose relatively little water at equivalent depths to other slabs [6]. This implies a relatively small amount of the pore water subduction fluids would be released from the Izu slab at a sub-arc depth (150-200 km) resulting in further subduction of halogens, heavy noble gases and potentially water, to great depths in the mantle.

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## Fluorine and chlorine as tracers of magma-fluid and magma-crust interactions

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Fluorine and chlorine are halogen elements present as minor or trace elements in basaltic magmas. During magma formation and evolution, they behave as incompatible volatile elements and preferentially partition into the melt or gas/fluid phases. Similar to H<sub>2</sub>O, they are enriched in the outer layers on Earth (atmosphere, hydrosphere and crust) compared to the mantle. Unlike H<sub>2</sub>O, however, they are mostly undegassed in basaltic systems. Thus halogens can be used to assess the nature of the source and magmatic interactions with crustal reservoirs and fluids. We will show examples from two contrasting tectonic settings: mid-ocean ridge spreading centers and subduction zones.

At oceanic spreading centers, rapid quenching and confining water pressure during submarine eruptions prevents most volatiles from degassing, allowing us to use Cl, F, H<sub>2</sub>O and S contents dissolved in the glasses to study magma evolution. The Cl/Nb in submarine basalts is usually used as tracer for seawater contamination. We identify 4 out of 20 glass samples analyzed from the equatorial Mid-Atlantic ridge with high Cl/Nb, suggesting seawater contamination. These 4 samples are the most depleted of the area ((La/Sm)<sub>N</sub> down to 0.27), indicating that depleted samples are more sensitive to contamination than enriched ones. These 4 samples are also characterized by more reduced iron oxidation stages ( $Fe^{3+}/Fe_{total}=0.13\pm 0.005$ ) compared to the uncontaminated ones ( $Fe^{3+}/Fe_{total}=0.16\pm 0.01$ ). Such characteristics cannot be generated by seawater contamination only. We suggest the participation of a seawater-derived depleted lithology either in the source or a secondary contaminant during magma evolution. The selective depletion of F compared to Cl could be used to differentiate the effect of seawater from the effect of other contaminants or variations in the mantle source.

In subduction zones, arc basalts are enriched in F and Cl compared to mid-oceanic ridge basalts (MORB), due to the input of H<sub>2</sub>O-rich slab components to their mantle source. F/Cl ratios measured in melt inclusions can be used to identify the nature of the slab-derived components. We apply this approach to mafic lavas from Mt. Shasta (Cascades Arc, USA). The selective enrichment of the melt inclusions in Cl, F and other fluid-mobile elements as well as their contrasting  $\delta^{11}B$  show the imprints of two distinct slab-derived components C1 and C2. Using trace element ratios, we modeled the compositions of these two H<sub>2</sub>O-rich components (C1 with Cl/F of 1.1 is rich in both in high field strength elements and incompatible trace elements; whereas C2 with Cl/F of 4.0, is poorer in trace elements) and show that they represent a mixing between sediment melts and dehydration fluids from the altered oceanic crust.

## Tracing He, N, Ar and C isotopes in the hydrothermal system of Tatun Volcanic Group, Taiwan

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Tatun Volcanic Group (TVG) is a part of the northern Taiwanese volcanic zone produced by the subduction of the Philippine Sea Plate under the East Asian continent. TVG is composed of more than 20 Quaternary volcanoes distributed along the NE-SW Chinshan older than 0.2 Ma. Fumaroles and hot springs located along Chinshan fault indicate that 1) TVG is still active and 2) there is a link between the major fault and the TVG volcanic hydrothermal activity. In this study, we present preliminary results of He, N, Ar and C isotopic compositions from hot springs and bubbling gases of Tatun Volcanic Group. This gives important constrains on the origin and formation of this volcano-hydrothermal system, and may help in forecasting volcanic eruptions or large seismic events.

The <sup>3</sup>He/<sup>4</sup>He ratios show two distinct groups ranging between (A) 5.32Ra and 5.57Ra, and (B) between 2.80Ra and 4.94Ra, with group B affected by assimilation of crustal helium compared to group A. Importantly, this variation of helium isotopic compositions is largely correlated with Vp/Vs anomalies observed under TVG (Wen et al., 2012). The samples of group A are located where the Vp/Vs anomalies are low, which is evidence for a mantle-derived He (from the TVG fluids) connected to the magmatic-hydrothermal activity. This has important implications on the potential hazards. The  $\delta^{15}\text{N}$  data are also divided in two groups, ranging from  $-1.8\pm 0.8\%$  to  $2.2\pm 0.7\%$  for group A and from  $0.4\pm 0.7\%$  to  $-0.4\pm 0.7\%$  for group B. The ratios <sup>40</sup>Ar/<sup>36</sup>Ar and N<sub>2</sub>/<sup>36</sup>Ar of our TVG samples vary from  $279\pm 11$  to  $331\pm 14$  and from  $3.2\times 10^4$  to  $5.3\times 10^4$ , respectively. The low <sup>40</sup>Ar/<sup>36</sup>Ar values clearly indicate the importance of atmospheric-derived nitrogen. The corrected  $\delta^{15}\text{N}$  (from the atmospheric component) data show the implication of sediment-derived nitrogen for group A, but only little contribution for group B. The  $\delta^{13}\text{C-CO}_2$  values ( $-9.62\pm 0.8\%$  to  $-4.66\pm 0.19\%$ ) are negatively correlated with CO<sub>2</sub>/<sup>3</sup>He ( $2.77\times 10^9$  to  $2.59\times 10^{10}$ ), which is explained by fractionation and crustal assimilation. If we exclude these fractionation and crustal effects, the high  $\delta^{13}\text{C-CO}_2$  values (ca.  $-5.5\%$ ) from TVG bubbling gases seem to represent the original magmatic signature, which is described here in terms of a mixture of three components: limestones, MORB and organic sediments.



## Estimation of sulfur and halogen fluxes at mid-ocean ridges deconvolving contributions from vesicle and solid components of MORB glasses

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Though sulfur (S) and halogens (fluorine (F) and chlorine (Cl)) form various compounds on the Earth's surface and significantly affect the environment, their geochemical cycles are not well understood. Fluxes of S and halogens at MORs (Mid-Ocean Ridges) have been estimated based on compositions of glassy rims of MORBs (MOR Basalts) which retain those of magmas derived from the upper mantle. However, they may be overestimated, and plausible estimations based on compositions of both silicate melts and fractions released as hydrothermal fluids are needed. We determined compositions of hydrothermal fluid and melt components retained respectively in vesicles and solids of MORB glasses and estimated MOR fluxes of S and halogens to constrain the evolutionary history of the Earth's surface. We analyzed glasses of MORBs collected at 2 sites on the East Pacific Rise, 2 sites on the Mid-Atlantic Ridge and 2 sites on the Central Indian Ridge. After volatiles in vesicles were extracted using the frozen crushing method, concentrations of helium-3 (<sup>3</sup>He) were measured using a noble gas mass spectrometer (VG-5400) and those of S and halogens were measured using an ion chromatography (ICS-2100). Concentrations of S and halogens in solids were measured using a secondary ion mass spectrometer (NanoSIMS 50). We calculated relative molar ratios of S and halogens to <sup>3</sup>He (S/<sup>3</sup>He, F/<sup>3</sup>He and Cl/<sup>3</sup>He) and estimated MOR fluxes of S and halogens calibrating against the known <sup>3</sup>He flux (527 mol/yr). Using molar ratios, it is not necessary to discuss variations of volatile concentrations due to differences in porosities of each sample. <sup>3</sup>He concentrations in vesicles were (1.8-6.3)×10<sup>-15</sup> mol/g. Global averages of S/<sup>3</sup>He, F/<sup>3</sup>He and Cl/<sup>3</sup>He were calculated. For vesicle components, they are (4.2±1.6)×10<sup>7</sup>, (1.4±0.7)×10<sup>6</sup> and (2.6±1.0)×10<sup>7</sup>, respectively. For bulk compositions, they are (0.3-1.2)×10<sup>10</sup>, (1.6-6.5)×10<sup>9</sup> and (0.7-3.0)×10<sup>9</sup>, respectively. Using these ratios and the known <sup>3</sup>He flux at MORs, MOR fluxes were estimated to be (2.2×10<sup>10</sup>-6.6×10<sup>12</sup>) mol/yr for S, (7.1×10<sup>8</sup>-3.4×10<sup>12</sup>) mol/yr for F and (1.4×10<sup>10</sup>-1.6×10<sup>12</sup>) mol/yr for Cl. Mass balances were discussed comparing MOR fluxes in this study with arc fluxes, influxes at subduction zones and rates of accretion to the continental crust. When we assume the continuous degassing with the low MOR fluxes estimated using vesicle (hydrothermal fluid) compositions, the amount of S accumulated on the Earth's surface are calculated to be 50 times lower than its surface inventory, and halogens are calculated not to be accumulated on the Earth's surface because of dominant influxes. This implies a possibility that the most part of surface S and halogens were degassed in the early Earth.



## Halogens in normal- and enriched-basalts from Central Indian Ridge (18-20°S): testing the E-MORB subduction origin hypothesis

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Basalts erupted along oceanic ridges have often been subdivided into two categories: the N-MORB and the E-MORB, the latter is anomalously enriched in highly incompatible elements. Donnelly et al. (2004) proposed that the formation of enriched sources is related to two stages of melting. The first one occurs in subduction zones where the mantle wedge is enriched by the addition of low-degree melts of subducted slab. The second stage of melting occurs beneath ocean ridges. Because of their incompatibility in basalt minerals, their relatively high concentrations and distinct elemental compositions in surface reservoirs, the halogens are good tracers to detect the slab contribution in E-MORB sources.

However, the halogen systematics in mantle reservoirs remains poorly constrained mainly because of their very low abundance in materials of interest. The innovative halogen analytical technique, involving neutron irradiation of samples to convert halogens to noble gases, provides detection limits unmatched by any other technique studies. For the first time Cl, Br and I can now be determined in appropriate samples.

We focus on the content of halogens in the glassy margins of basalts erupted along the CIR (18-20°S). Our set of samples contains both N- and E-MORB. The halogen concentration range is between 10 and 140 ppm for Cl, 30 and 520 ppb for Br, 1 and 11 ppb for I. The concentrations are not related to superficial processes such as fractional crystallisation and degassing. The strong correlation that exists between the halogens and other incompatible elements also excludes seawater assimilation prior to and during eruption as a means of supplying halogens and water. Therefore, concentrations can be directly linked to melting and mantle source features. Estimates of halogen abundances in the source of CIR depleted-mantle with 10% of partial melting, are 1.1 ppm Cl, 3.4 ppb Br and 0.1 ppb I.

Furthermore, the halogen elemental ratios show no significant variations along the ridge:  $Br/Cl=0.00336\pm0.00003$ ,  $I/Cl=0.000076\pm0.000018$  and  $I/Br=0.023\pm0.006$ . This similarity between N-MORB and E-MORB can be explained by a common mantle source and therefore, it is not consistent with subduction as a source of halogen enrichment.

The CIR samples display a mean K/Cl value of  $26.7\pm7.2$  ( $12.5\pm1.0$  for global MORB). The chlorine enrichment is also well correlated with water content. The fractionation of K/Cl ratio can be caused by metasomatic enrichment via small degree partial melts, such as those that may form between the wet and dry solidi of the mantle peridotite near ridges (Galer and O'Nions, 1986). The breakdown of accessory phases in peridotite at wet solidus will control the amount of water and halogens. The very low degree melts formed at the volatile-present solidus then mixes with higher degree melts formed directly beneath the ridge.

## Do fluorine and chlorine follow water and carbon dioxide fluid in magma?

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Fluorine and chlorine are commonly considered as volatile elements in volcanic system, together with hydrogen, carbon, and sulfur. This is because molecular species of these elements were found in volcanic gasses. We have been examining potentials of using these elements as tracers of magmatic processes, especially to serve as an alternative to major degassing elements such as hydrogen and carbon. Based on glass and melt inclusion data both newly acquired and extensively compiled from previous publications, we report geochemical systematic fluorine and chlorine. First, fluorine and chlorine do not correlate with H<sub>2</sub>O and CO<sub>2</sub> among degassed volcanic glasses, suggesting these halogens are inefficient in degassing, fractionate during that process. While this finding is consistent with several previous studies, this implies that there is a potential that these halogen elements can infer volatile abundance in magma even for the quenched material that has experienced degassing. Therefore, these elements are suitable for detecting volatile fractionation and transport processes before an eruption. For example, trace element ratios of F/Nd and Cl/Nb are higher in primitive melt inclusions from arcs than in those from MORB and OIB. Because these ratios are thought to fractionate so little during their melting and mineral fractionation processes, these element ratios reflect the nature of volatile element abundance at the time of magma formation. Specifically, F/Nd in some arc samples ranges from comparable values to dry mantle samples to values higher by an order of magnitude. On the contrary Cl/Nb of all arc samples are higher than dry mantle samples. Given F is weakly soluble in aqueous fluid compared to Cl, in presence of amphibole, mica and humites, the enrichment of Cl without an enrichment of F suggest the volatile addition to the source via fluid. On a contrary, the simultaneous F-Cl enrichment trends in arc magmas are consistent with the addition of volatile to arc magma via melt derived from slab. Further trace element systematics is examined to determine to constrain the quantity of fluorine and chlorine added to the source. With combination of previous phase relation data, the abundances of H<sub>2</sub>O and CO<sub>2</sub> are potentially constrained as well.

## The effect of water on fluorine and chlorine solubility and solution mechanisms in aluminosilicate melts at high pressure and high temperature

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The influence of water on F and Cl solubility and structural complexing in silicate melts is important to understand the difference in fractionation of F and Cl during hydrous mantle melting. This is illustrated in a recent study of Mt Shasta melt inclusions (Le Voyer et al. 2010) shows two distinct Cl/F ratios. These two ratios can be modeled by the melting of a peridotite that had been metasomatized by low or high amount of aqueous fluid, using F and Cl partition coefficients between a peridotite and hydrous basaltic melts (Dalou et al, in review).

Here, we address, therefore, the effect of water on the solution behavior of F and Cl by combining solubility measurements of F and Cl, and Raman data of F or Cl-bearing peralkaline aluminosilicate glasses (quenched melt). Six compositions along the join  $\text{Na}_2\text{Si}_3\text{O}_7\text{-Na}_2(\text{NaAl})_3\text{O}_7$  were used, keeping a constant NBO/T and varying Al/(Al+Si). Starting materials were doped with 5 wt% Cl in the form of  $\text{PdCl}_2$  or 10 wt% F in the form of  $\text{AgF}_2$ , which release gaseous  $\text{F}_2$  or  $\text{Cl}_2$ , respectively, during an experiment. Starting material was loaded together with 2 to 10 wt% of water, in order to maintain water undersaturation content (Mysen and Cody, 2004). Samples were synthesized at 1400 °C and 1.5 GPa.

The F solubility increases from 1.4 to 5.2 wt% (4.5 to 7.8 mol%) with increasing water from 2 to 10 wt% , in the Al-bearing melt system (5 mol%  $\text{Al}_2\text{O}_3$ ).

The Cl solubility decreases from 3.4 to 2.1 wt% (5.7 to 3.4 mol% )with water increasing from 2 to 10 wt% , in the Al-free melt system. Increasing Al content (5 to 10 mol% ) reduces the effect of water on Cl solubility.

In F-bearing glasses (quenched melt), a peak around 870-910  $\text{cm}^{-1}$  in their Raman spectra is assigned to Si-F bonding. This peak is absent in spectra of anhydrous F-bearing glasses, but integrated area, and, therefore, concentration of Si-F bonds, increases with increasing water. In anhydrous Al-free glasses, solution of F is in the form of NaF-type complexes, whereas in hydrous silicate glasses water may exist as NaOH-bearing and SiF-bearing complexes. When Al is added to the hydrous system, AlF-bearing complexes appear, in addition to the SiF-bearing complexes. This suggests, therefore, that the OH-complexing governs F solubility mechanism in silicate melts. In Cl-bearing glasses on the other hand, there is no indication in the Raman spectra of changes of Cl speciation as water is dissolved in aluminosilicate melt.

Here we show that F and Cl solution behaviors depend strongly on the amount of water dissolved in the melt, which has profound effect in melt structure. These data are consistent with changes of F and Cl partition coefficients with water during hydrous melting and explain why Cl/F ratios in arc magmas can be produced by variable amounts of water involved in magma genesis.

## Fluorine and the emplacement of extensive felsic lavas (flood rhyolites)

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Volatile components are known to fundamentally affect the eruption behaviour of magmas. The melt viscosity, a parameter that affects magma ascent through the crust and its extrusion, is primarily controlled by the amount of H<sub>2</sub>O and F dissolved, as well as temperature and bulk composition of the magma (1). Further, decompression-driven saturation and exsolution of volatile components (H<sub>2</sub>O, Cl, H<sub>2</sub>S...) can cause vesiculation and trigger explosive eruptions. However, because of their very nature, volatile components tend to be lost during degassing and subsequent alteration and weathering, leaving little or no evidence in the rock record. Thus their importance on the eruption behaviour can be easily overlooked when studying ancient volcanic successions.

The ca. 1590 Ma old Gawler Range Volcanics (GRV) and the ca. 2060 Ma Rooiberg Group are part of intracratonic silicic large igneous provinces that include extensive (several tens to a few hundred km) felsic lava units (2, 3). The two igneous provinces share similar anhydrous parageneses, and several lines of evidence indicate that in both cases, magmas had relatively high F contents and high temperatures. Evidence includes melt inclusion analyses (F up to 1.3 wt.pc, Cl up to 0.3 wt.pc, EPMA tot 98 wt.pc for the GRV), water content estimates based on paragenesis (H<sub>2</sub>O = 1 - 2 wt.pc (4)), and thermometric estimates based on two-pyroxene thermometry and zircon and apatite saturation (new data and (4)). We propose that high concentrations of de-polymerising F, coupled with large magma volume, created favourable conditions for the eruption of extensive, large-volume felsic lavas. The low water contents caused low degrees of vesiculation, precluding explosivity during eruption.

These characteristics are dictated by the tectonic setting in which these magmas were produced and erupted. In an intraplate setting, melting is believed to occur because of mantle rise and decompression. These mantle movements cause a geotherm uprise, and as a consequence, the decompression-triggered melts have high temperatures (5). Intraplate magmas have generally lower total volatile compositions in comparison to magmas produced at convergent margins, and tend to have higher F/Cl and F/H<sub>2</sub>O (6). Similar combinations of high F, water-undersaturated compositions and high magmatic temperatures might have been important in the emplacement of other extensive felsic lavas and strongly rheomorphic ignimbrites in similar tectonic environments (Snake River Plain-Yellowstone, Keweenaw Midcontinent Rift volcanic units, Etendeka Igneous Province).

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## Atmospheric CFCs and geogenic HCFCs in gas discharges from Mt. Etna and Vulcano Island (Italy)

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Significant concentrations of light hydrocarbons mainly pertaining to the alkane alkene and aromatic groups typically characterize fluids discharged from volcanic hydrothermal systems.

Halogenated species are of great interest due to their strong environmental impact and health effects since they play a key role as primary agents of tropospheric ozone depletion.

The recent increase of halocarbon concentrations in air especially that of chlorofluorocarbons (CFCs) is commonly ascribed to anthropogenic activities. Halocarbons are naturally produced from biogenic activity in soils from biomass combustion and from oceans and are reported to occur in volcanic plumes and gas emissions related to hydrothermal reservoirs. Although volcanic halocarbons were interpreted as related to an atmospheric source although recent studies reported geochemical evidence supporting the idea of a geogenic origin for halocarbons.

In the present study CFCs and HCFCs geochemistry in fumarolic gases discharged from Mt. Etna and Vulcano Island (Southern Italy) was investigated in order to elucidate the possible sources and processes controlling the emission of these organic species in a volcanic environments.

Halocarbon concentrations in gas discharges from these two volcanic systems were compared to those expected when the fraction of air present in our gas samples calculated on the basis of their Ar concentrations is considered. Such a detailed evaluation of halocarbon contribution due to background air values was carried out to assess if these gas compounds might have been generated in volcanic fluids from a geogenic source to check the efficiency of genetic

processes such as halogenation of methane and alkenes at hydrothermal conditions.

Our calculations evidence that the concentrations of most hydrogenated halocarbons in gases from both Etna and Vulcano are up to three orders of magnitude higher than those expected considering air as their unique source implying that these compounds have a geogenic origin.

Abundances of CFCs appear to be consistent with background air suggesting that processes of complete halogenation of organic compounds in natural environments are not efficient.

## Reactive Halogen Chemistry in Volcanic Plumes

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A decade ago the discovery of reactive bromine in a volcanic plume was published for the first time. Since then many measurements and modeling have been undertaken to understand the radical chemistry in volcanic plumes, in particular, the interaction between volcanic gas species, released under strongly reduced conditions, and the oxidizing atmosphere.

Technical advances have lead to more continuous data acquisition with enhanced frequency, in particular, with relatively easy to use remote sensing techniques, e.g. DOAS and FTIR. In open conduit volcanoes, acquired data sets provide new possibilities to investigate volcanic volatile compositions with a good temporal resolution partly even during explosive eruptions.

Many halogen containing molecules are non-inert gas molecules; therefore, care has to be taken in volcanological interpretations. It is, for instance, of great importance to link the measurements of halogen oxides (which are often easy to measure) and gaseous hydrogen halides to the total emission flux of the halogen species in order to estimate the pristine composition of gases exsolved from magmas. In particular, it is important to better understand the effects of meteorological conditions on the formation and measurements of halogen oxides, but as well the influences on measurements of hydrogen halides which are often considered as stable. Only with this knowledge we can relate changes of the measured gas ratios to the volcanic fluids emitted by the underlying magma and can interpret the data as signals, which describe the evolution of magmatic bodies inside the Earth.

A summary of the current knowledge and the most important improvements made during the last decade will be presented, focusing on bromine and chlorine and to a minor extend on iodine. We will present an overview of measurement data including new unpublished results from in-situ and remote sensing measurements. The formation process of BrO, ClO and OCIO in volcanic plumes will be discussed showing measurements from close proximity to the crater up to a distance of several km or tens of km away from the emission point at several volcanic sites (among others: Etna, Nyiragongo, Masaya, Popocateptl, Gorely). The variation on the order of a factor of 3 in bromine monoxide to sulfur dioxide ratios will be shown to depend on plume age, and meteorological influences as long as we exclude measurements at crater rims. Beside these variations there are changes of the ratios of a factor up to 8 most probably caused by changes in volcanic activity. Also, improvements and uncertainties of the determination of total halogen contents due in-situ sampling (alkaline trap sampling) will be mentioned and discussed.

## **P-wave velocity in the subducting crust of the Pacific plate: Role of aqueous fluids on seismogenesis**

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It is considered that the low-velocity oceanic crust exists at the uppermost part of the oceanic lithosphere. Water produced by dehydration reactions of hydrous minerals is considered to weaken the strength of faults by increasing pore-fluid pressure and facilitate seismic activity in the oceanic crust. Therefore, it is important to reveal the spatial variation in seismic velocity to understand where fluids are trapped and where dehydration reactions occur in the oceanic crust. However, it is generally difficult to obtain the detailed velocity variation in the oceanic crust, because the direct P- and S-waves from intraslab earthquakes tend to propagate in a short distance in the crust.

It is known that P-to-S converted phases at the plate interface are often observed in seismograms of intraslab earthquakes. Matsuzawa et al. (1986) examined arrival times and amplitudes of PS-converted phases, and suggested the existence of a low-velocity layer at the top of the slab down to a depth of at least 150 km. Here, we follow the strategy of Matsuzawa et al. (1986), and estimate the spatial variation in P-wave velocity in the oceanic crust beneath northeastern (NE) Japan using arrival times of PS-converted waves.

At first, we identified PS-converted waves in seismograms of intraslab earthquakes and obtained 2,798 arrival times of PS converted waves from 305 earthquakes. Before estimating P-wave velocity structure in the oceanic crust, we applied tomographic inversion method of Zhao et al. (1992) to arrival-time data of the direct P and S waves, and estimated 3D seismic velocity structures beneath the entire region of NE Japan. We then relocated earthquakes with the obtained 3D velocity model and determined P-wave velocity in the oceanic crust using arrival-time data of PS-converted waves.

The obtained results show that P-wave velocity in the oceanic crust varies across the arc, with  $V_p$  of 6.5-7.5 km/s in the fore arc and 7.5-8.5 km/s in the back arc. P-wave velocity at depths of < 100 km is much lower than the values derived from MORB model beneath NE Japan (Hacker et al., 2003), suggesting the existence of aqueous fluids in the oceanic crust. High seismic activity at depths of 70-90 km (Kita et al., 2006) is located in areas of abundant aqueous fluids. The enhanced pore-fluid pressures and the resultant reduced effective normal stress weaken the strength of the faults sufficiently to bring the system into the brittle regime. Fluid-related embrittlement is probably working for the genesis of crustal earthquakes. Another important observation to be noticed here is that the observed P-wave velocity is almost consistent with the prediction of MORB model at depths of >100 km. This suggests that aqueous fluids in the crust should be released to surroundings at depth of 100 km, and the fluids thus liberated may contribute to metamorphic reactions in the overlying mantle wedge.



## A three-dimensional electrical conductivity model in the subduction zone of Tohoku district, northeastern Japan

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We acquired magnetotelluric (MT) data at 65 sites in Tohoku district, northeastern Japan for the aim of three-dimensional (3-D) electrical conductivity distribution in the wedge mantle. Typical observation duration were three months at each site, and MT response functions from 10 to 20000 s in period have successfully collected with fine quality. The site location was arranged with ca. 20 km distance. We integrated the MT data observed on the seafloor in Japan Sea using the ocean bottom electromagnetometers (OBEM) (Toh et al., 2006) into these inland data, and estimated a conductivity model.

The MT phase response functions at some sites show over 90° longer than 5000 s period and suggest that 3-D conductivity distribution beneath those sites. The distribution of phase tensor ellipses (Caldwell et al., 2004) shows more clearly the degree of lateral heterogeneity or dimensionality. The phase tensor ellipses of the sites in Akita and Iwate Prefectures have major axes aligned with NW direction. The direction is almost parallel to the Pacific plate motion. On the other hand, the major axes around Naruko and Kitakami river have random directions and the ellipticity of the phase tensor ellipses is very large (>10).

We carried out the 3-D inversion using WSINV3DMT code (Siripuvaporn et al., 2005) and gave a prior model composed of subducting slab ( $10^{-4}$  S/m) and seafloor bathymetry. The plate boundary information by Kita et al. (2010), Nakajima et al. (2009) and Nakajima and Hasegawa (2006) was used. Before inverting the observation data, simple checker board resolution tests were performed to estimate a resolution. We tested the three models composed of cubes with the same size (60, 40 and 20 km on side) and 1 S/m conductivity in the wedge mantle of 0.01 S/m. Each cube with 40 and 60 km on side was imaged using the synthetic data, while the adjacent cubes sticking together were imaged in the model composed of cubes with 20 km on side. Furthermore, any cubes beneath no observation site were not imaged at all using the synthetic data. The east-west profile (across the Japan Arc) of the obtained model shows that conductive region appears from 20 km to just above the subducting slab beneath Tohoku backbone range. This image is well consisted with the seismic tomographic model (Nakajima et al., 2001), provided that conductive and low velocity zone should corresponds with each other. Obtained the final 3-D model, we plan to estimate the mantle geotherm and fluid distributions in the wedge mantle using seismic tomographic and electrical conductivity images.

### 3D Imaging of crustal fluids under the NE volcanic arc

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Magnetotelluric (MT) method can image the crustal and mantle structure in terms of resistivity, which is sensitive to the existence and connectivity of fluids and melts. Previous MT studies in NE Japan have successfully imaged fluid/melt distribution under the seismically active regions (Ogawa et al., 2001; Mitsuhashi et al., 2001) and volcanic zones (Mishina, 2009; Asamori et al., 2010). However, these studies were restricted to two-dimensional modeling along profiles.

We have carried out wideband MT measurements in order to map the deep crustal fluids and melts under the volcanic arc in the NE Japan around the Naruko volcano. The area has several Quaternary calderas, such as Naruko, Onikobe, Sanzugawa and Mukaimachi calderas. The area has also high shallow seismicity and has one of the largest intraplate earthquakes, M7.0, in 2008 near the Kurikoma volcano. Thus the area is thought as a good test field to study the relation of fluids and volcanoes and intraplate earthquakes. We have 224 sites in total with average site spacing of 5km. From the three-dimensional modelling we have imaged (1) subvertical conductors which shallows towards the active volcanic zones under Onikobe, Naruko and Sanzugawa calderas, and (2) seismic activities over the resistive zones above the crustal conductors, which implies earthquake triggering by fluid migration into the brittle crust.

## Generation of TH and CA suite magmas in the Quaternary NE Japan arc

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Tholeiitic (TH) and Calc-alkaline (CA) suite lavas frequently coexist at the Quaternary volcanos in the NE Japan arc. Recent works suggested that the origin of some low-K TH basalt was melts produced by high-degree melting of a lower crustal amphibolite (Nekoma volcano: Kimura et al., 2002; Zao volcano: Tatsumi et al., 2008; Azuma volcano: Takahashi et al., 2012). We examined the generation process of the TH/CA suite lavas over the NE Japan arc including volcanic front lavas from Osore, Hakkoda, Iwate, Akita-koma (North group), Zao, Azuma (Central group), Nasu, Takahara (South group) and rear-arc lavas from Chokai using bulk rock Sr-Nd-Pb-Hf isotope compositions and Sr-Pb isotope compositions of plagioclase phenocrysts analyzed by in-situ micro-analytical techniques.

The TH/CA suite lavas at the volcanic front were classified into three groups by the isotopic compositions. The North group lavas are derived from depleted source with narrow variations (e.g.  $87\text{Sr}/86\text{Sr}$ : 0.7038-0.7042), and the variations between TH and CA sites are narrow. The Central group lavas have wide isotopic compositions (e.g.  $87\text{Sr}/86\text{Sr}$ : 0.7036-0.7062) with relatively enriched source for the TH lavas than that for CA. The South group lavas have enriched source composition (e.g.  $87\text{Sr}/86\text{Sr}$ : 0.7043-0.7062) with the TH lavas usually from depleted source than for CA, although both the TH and CA lavas show a continuous isotopic trend when their isotopic compositions plot against element abundances. The Rear-arc TH/CA suite lavas have the most depleted source among others (e.g.  $87\text{Sr}/86\text{Sr}$ : 0.7029-0.7034), and TH lavas are from slightly enriched source than for CA.

Tatsumi et al. (2008) and Takahashi et al. (2012) argued that the Central group TH basalt formed by melting of the lower crustal amphibolite, whereas CA lavas of the same group formed by magma mixing between a mantle-derived basalt and a felsic magma from the crust or fractionated felsic magmas from TH basalt. The rear-arc Chokai lavas have affinities with the TH/CA at Zao and Azuma. Therefore, the Chokai lavas can be explained by the same model for the Central group lavas. However, the melting conditions and geochemical composition of the source mantle and the lower crust amphibolite should differ from those for the Central group lavas. In contrast, North and South group lavas indicate that the parental basalt for both the TH and CA suites is common. The TH suite lavas were derived from the basalt by fractional crystallization, whereas the CA suite lavas formed by magma mixing between the basalt and felsic magmas from enriched crustal source. Moreover, the isotopic contrasts between the mantle and the crustal source rocks are smaller in the North group than that for the South group lavas. These results indicate that the genetic processes and the source materials of the TH/CA suite vary considerably for the Quaternary NE Japan arc and, therefore, any unique model cannot account for the origin of TH/CA series.

## **Sr, Nd, Pb, and Hf isotopic composition of the Cretaceous to Paleogene plutonic rocks from the Asahi, Ashio, and Abukuma Belts, southern part of the NE Japan Arc**

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The Cretaceous to Paleogene plutonic rocks are widely distributed of the NE Japan Arc. The igneous activity in the subduction zone of a NE Japan Arc, in order to solve the origin and evolution of magma, it is necessary to consider participation of a basement rock. Kagami (2005) arranged Sr and Nd isotopic compositions of the granitic rocks in the NE Japan Arc, and performed isotope zone division as compared with the isotope feature of the granitic rocks of the SW Japan Arc. The North zone (N-zone) is the lower crust to upper mantle origin, which is low epsilon Sr and high epsilon Nd values. The South zone (S-zone) is differ from N-zone isotope character and the partly mixing of early to middle Proterozoic and sedimentary rocks. The Transitional zone (T-zone) has N-zone, S-zone, and intermediate isotope character. The Sado zone is a unique value of the epsilon Nd value (-6 -7) neighborhood on a mantle array. This study aims at the isotope data acquisition, verification of isotope zone division, and the elucidation of the origin of plutonic rocks.

Southern NE Japan Arc is classified into the Asahi, Ashio, and Abukuma Belts by a geotectonic division. The Abukuma and the partly Ashio Belt are N-zone, the southern Ashio Belt is S- and T-zones, the northern Ashio Belt is Sado-zone or unclassified, and the Asahi Belt is unclassified. Plutonic rocks of the Asahi Belt are composed of gabbro (Gb), quartz diorite (Qd), granodiorite (Gd), and granite (Gr). The Abukuma Belt is mainly composed of Qd and Gd. The Ashio Belt is mainly composed of Gr and Gd. Although all of the rock chemical composition shows similar, the Ashio Belt have tendency of high SiO<sub>2</sub> and K<sub>2</sub>O values compared with the Abukuma Belt. Each of the REE patterns has settled comparatively. The Ashio Belt have clearly Eu negative anomaly compared with the Abukuma Belt, because degree of magmatic differentiation is probably different. The new isotopic data was plotted to the epsilon diagram. The Abukuma belt is plotted together with the N-zone, the Ashio Belt has widely composition range which is plotted to Sado- and T-zones, and the Asahi Belt is S- and T-zones. The northern Ashio belt has the special isotope feature that clearly also from the new data in this study.

On the other hand, considering the crust contamination to Quaternary volcanic rock magma, the present value of the granitic crust becomes the key. In an epsilon Nd-Sr (0Ma) diagram, the domain of the Abukuma Belt and the Ashio Belt is distinguished clearly. Although the composition range as an Ashio Belt is wide, regionality is recognized to some extent. The epsilon Hf-Nd diagram shows the narrow extent, and are distinguished more clearly. About some samples of Ashio belt that is classified into N-zone, it turned out that epsilon Hf value differs from the Abukuma Belt. Thus, the reclassification of isotope zone division by Hf isotope composition is possible.

## Contrasting magmatic processes producing two coexisting rock series at Hakkoda, northern Honshu, Japan

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Two coexisting series of high Fe/Mg (referred to as TH) and low Fe/Mg (referred to as CA) lavas occur in Hakkoda volcano, northern Honshu, Japan. Two distinct trends intersect at an oblique angle on the SiO<sub>2</sub> vs. FeO/MgO diagram (Miyashiro diagram): one, TH (tholeiitic) group, is characterized by a pronounced increase in FeO/MgO with increasing SiO<sub>2</sub> and the other, CA (calcalkalic) group, by a modest increase in FeO/MgO. The bifurcating trends are also distinct on the MgO - K<sub>2</sub>O diagram. Many rocks of the CA group preserve records of open system magmatic processes as complex intracrystalline textures and as chemically disequibrated mineral assemblages, involving coexistence of reversely-zoned pyroxenes with normally-zoned pyroxenes and of magnesian olivine with quartz phenocrysts, and various kinds of dissolution textures (e.g. dusty zones) in plagioclase, quartz, and pyroxenes. On the other hand, phenocrysts in the rocks from TH group exhibit simple normal zoning, implying crystallization during a simple magmatic process. The most plausible process that produced the CA group rocks is mixing between basaltic magma of TH group and a felsic CA endmember magma. The CA felsic endmember is not a simple derivative of TH magma by crystallization differentiation because the endmember composition is far from the liquid lines of descent. Referred to studies on some volcanoes in the region, it is most likely that the source of the CA felsic endmember is different from that of TH series rocks. Stratigraphy at northernmost cones suggests that erupted magma chronologically evolved in the order: differentiated TH basalt (lower North-Hakkoda basalt), felsic CA andesite (Tamoyachidake lavas), mixed magmas that chemically fluctuated from low-silica TH basalt to felsic CA andesite (Narusawa Lavas), and felsic CA andesite (Ohkuzure Lavas). This evolution implies that the TH series basalt magma and the CA felsic endmember magma contemporaneously existed beneath the cones. The chemical fluctuation during the eruptive period of Narusawa Lavas was caused by the temporal variation of mixing ratio between TH basalt and CA felsic endmember magmas. Regardless of rock series and degree of differentiation or mixing ratio, <sup>87</sup>Sr/<sup>86</sup>Sr(0.7040), <sup>143</sup>Nd/<sup>144</sup>Nd (0.51290), <sup>206</sup>Pb/<sup>204</sup>Pb(18.4), <sup>207</sup>Pb/<sup>204</sup>Pb(15.584), <sup>208</sup>Pb/<sup>204</sup>Pb(38.54), <sup>176</sup>Hf/<sup>177</sup>Hf (0.28316) isotopic ratios are nearly constant. This isotopic homogeneity of magma implies the isotopic similarity of source rocks of TH basalt and CA felsic endmember. It is considered that their sources are lithologically different (e.g. peridotite vs. gabbro) but isotopically similar. Solidified TH series magma is a possible source of the CA felsic endmember.

## Coexistence of mantle- and crust-derived island-arc tholeiites with associated calc-alkaline magma at Akita-Komagatake volcano, Northeast Japan arc

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Akita-Komagatake volcano is located in the Sengan geothermal field of the Northeast Japan arc. The volcanoes in this field are characterized by predominant low-K tholeiitic magmas with co-existing minor medium-K calc-alkaline magma. This is contrastive to the general tendency of the coexisting two magma types in the frontal arc volcanoes of the Northeast Japan arc, at which calc-alkaline magma erupted predominantly. Akita-Komagatake volcano consists of the main stratocone with a caldera in the south and several parasitic cones at the summit. The main stratocone collapsed and the caldera formed at about 13 ka, associated with a pyroclastic flow. Magmatic eruption history in the post-caldera stage is divided into two sub-stages by a dormancy of activity between 7 and 4ka. Summit parasitic cones in the northern area were built in the earlier sub-stage (13-7 ka), whereas parasitic cones in the southern area developed during the later sub-stage (post 4 ka). This study examines the spatial-temporal variations of the magma types and the compositional variations in each magma type. Genetic relationships among the magma types were examined by analyzing elemental and isotopic compositions. Low-K tholeiitic magmas have been the dominant rock type throughout the post-caldera stage. The early sub-stage (13 ka) began with eruptions of the low-K tholeiitic andesites, and was followed by low-K tholeiitic basalts to andesites. Calc-alkaline andesites erupted only episodically in the later sub-stage after 4 ka. During this later sub-stage low-K tholeiitic magma was still dominant with the first eruption of an andesite followed shortly afterwards by low-K tholeiitic basalts to basaltic andesites. Low-K tholeiitic andesite was erupted during the most recent eruption.

The calc-alkaline andesite indicates incorporation of large amount of crustal materials (crustal assimilation), whereas low-K tholeiitic basalts are more likely derived from the sub-arc mantle. This model is consistent with the previous works on the genesis of low-K tholeiitic and calc-alkaline magmas. Even so, two types of isotopically distinct low-K tholeiitic andesites are present. One low-K tholeiitic andesite type shows involvement of isotopically enriched crustal source material which is more enriched than the contemporaneous calc-alkaline andesite. The other low-K tholeiitic andesite type is derived from depleted mantle source by fractional crystallization unaffected by crustal assimilation.

Plausible genetic relationships among the magmas at Akita-Komagatake are summarized as follows: (1) basaltic low-K tholeiitic magmas was generated immediately by the mantle and simply crystallized to form LTH basaltic andesites, (2) calc-alkaline magma was the mixture between basaltic low-K tholeiitic magmas and a felsic magma of crustal melt in origin, and (3) the low-K tholeiitic andesite with enriched (crustal) source might have been generated by a high degree of melting of an amphibolitic crust.

## **Geochemistry of potassic minerals in the Xiaogulihe-Keluo-Wudalianchi-Erkeshan volcanic rock belt, NE China and their geological implications**

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Xiaogulihe-Keluo-Wudalianchi-Erkeshan potassic volcanic rock belt in northeastern China, one of the well preserved volcanic clusters from Pleistocene to Holocene epoch in China, was characterized by the high contents of potassium, alkali and high  $K_2O/Na_2O$  ratios in their rocks. They were high potassium peralkaline volcanic rocks with total alkali contents generally ranging from 7.81 wt.% to 10.56 wt.%. Some phlogopite-bearing iherzolit xenoliths and typical potassic mineral of leucites were found through field investigation work and under microscopic work. On the basis of comprehensive geochemistry research work relating the compositions of the whole rocks, crystallization condition of potassic minerals (especially phlogopites, leucites) in hosted volcanic rocks and mantle peridotite xenoliths with the magma component and its source, the authors suggested that the hidden rift in northeastern China and lithospheric extension in the study region should be responsible for the low-degree decompression melting of phlogopite-bearing iherzoliths in the mantle and the potassic magma source had experienced leucites crystallization in shallow crust. As magma evolved, the magma tended to be Na-rich and xenomorphic nepheline and sodalite were observed in matrix glass after the crystallization of lots of potassic minerals. The volatile-rich minerals as leucite, aptite, nepheline, sodalite and phlogopite occurred in volcanic rocks and mantle xenoliths also provided the evidence of high abundance of  $H_2O$ , F, Cl and P in the magma prior to eruption.

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## Recycling and melting of a dehydrated oceanic crust in the stagnant slab in back-arc mantle: Constraints from Cenozoic alkaline basalts in eastern China

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Cold oceanic plates, which include igneous and sediment layers, start sinking along subduction zones. The layers dehydrate and melt as they undergo subduction, which feeds slab components to arc magmas. After the subduction, the remaining slab stagnates in the mantle transition zone (at depths of 400 – 660 km), where the minerals undergo pressure-induced transformation, and the resulting density turnover prevents further slab penetration. Recent experimental study predict that igneous layer of the stagnant slab could partially melt due to conductive heating from the ambient mantle, although relevant geochemical evidence of melting of the stagnant slab has not yet been found from igneous rocks above the stagnant slab. We present evidence that suggests that melts from the igneous layer in the stagnant Pacific slab have contributed to the source composition of basalts in eastern China.

Within the Late Cenozoic basalts of eastern China, primitive basalts with extremely Fe-rich (>13 wt%) and Si-poor (<43 wt%) features only occur in the area surrounded by 117 – 121 °E and 30 – 43 °N, which is ~2000km to the west of the trench of the Pacific Plate. Multi trace element plots (normalized to the primitive mantle) of these basalts show that they commonly have convex-up patterns with depletions in Rb, Ba, Pb relative to other large ion lithophile elements and light rare earth elements, and to a lesser extent, depletions in Zr and Hf relative to middle rare earth elements. The peridotite xenoliths reported from eastern China commonly show positive Rb, Pb, and Sr anomalies, which is definitely not characteristic of the plausible source mantle of the basalts. Instead, these trace element features are similar to those of the OIBs with HIMU isotopic signatures, suggesting that their source material was modified by a subduction dehydration process. Source mantle of the basalts has, however, much less radiogenic Pb than the OIBs with HIMU isotopic signatures. Sr–Nd–Pb isotope compositions of the extreme basalts in China are similar to those of mid-oceanic-ridge basalt and have Nd–Hf isotope composition akin to the igneous layer in the Pacific slab. None of high-pressure melting experiments on peridotite have reproduced melt with the high FeO \* (>13 wt%) and low Al<sub>2</sub>O<sub>3</sub> (<12 wt% at MgO ~12 wt%), whereas partial melts with such major element characteristics can be generated by the melting of carbonated eclogite.

Taken together, these geochemical characteristics of these basalts help us to conclude that these basalts have received a significant contribution from dehydrated carbonate-bearing oceanic crust in the stagnant slab, without a long time-integrated ingrowth of Sr–Nd–Hf–Pb isotope systems, almost at the leading edge of the stagnant Pacific slab.

## Melting of clinopyroxene + magnesite and its role on the formation of CO<sub>2</sub>-rich magmas

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The assemblage clinopyroxene Ca(Mg,Fe)Si<sub>2</sub>O<sub>6</sub> (cpx) + magnesite (Mg,Fe)CO<sub>3</sub> (mc) has been observed in ultra-high pressure metamorphic rocks from Dabie (China) (Zhang and Liou 1994). This suggests that this mineral association can be stable at high pressure in a subducted slab and/or at the interface between a slab and the mantle wedge. It has been proposed that the rarity of this assemblage at the Earth's surface results from its destabilization during the transfer from the slab to the mantle or during the path to the surface (by tectonic exhumation or magmatic eruption). Kushiro et al (1975) and Brey et al (1983) show experimental evidence for the stability of the iron-free cpx + mc assemblage from 2 to 5 GPa at subduction zones temperatures. This assemblage, however, is destabilized when temperature increases in contact with the mantle wedge. It reacts to form orthopyroxene MgSiO<sub>3</sub> (opx) + dolomite CaMg(CO<sub>3</sub>)<sub>2</sub> (dol) above 950 °C at 3 GPa. According to Wyllie and Huang (1976) and Eggler (1978), the opx + dol assemblage also transforms into cpx + forsterite Mg<sub>2</sub>SiO<sub>4</sub> (fo) + CO<sub>2</sub> (V) below 3 GPa if the temperature increases to the mantle adiabat. Eggler suggested that a melting reaction that would consume dol, di and V to form fo and melt should occur at 1275 °C at 1.8 GPa. The presence of iron in the cpx + mc assemblage could lower its melting temperature and produce a carbonate-silicate melt which may metasomatize the mantle. Martin et al (2012) show experimentally that an iron-bearing assemblage cpx + mc is stable at 6 GPa and subduction zones temperatures. However, the role of iron content and fO<sub>2</sub> variations on the fate of cpx + mc in portions of the mantle away from subducted slabs has not been constrained. Therefore, we performed piston-cylinder experiments at 1.8 and 3 GPa and temperatures corresponding to the Earth mantle adiabat using a starting mixture of diopside CaMgSi<sub>2</sub>O<sub>6</sub> and magnesite MgCO<sub>3</sub>. The role of iron and of fO<sub>2</sub> was investigated by replacing magnesite by siderite FeCO<sub>3</sub> or by adding either C graphite or Fe metal to the system. We show that melt forms in equilibrium with olivine, clinopyroxene and iron oxides (Martin and Righter 2013). Moreover, the presence of ferrous or metal iron decreases the liquidus temperature and favors the melting of cpx + mc deeper in the mantle. The produced silicate-carbonate melts (10-46 wt% CO<sub>2</sub>, 0.1-31 wt% SiO<sub>2</sub>, 11-55 wt% CaO, 1.9-18 wt% MgO and 0.01-37 wt% FeO) could play a role in the generation of CO<sub>2</sub>-rich magmas (e.g., carbonatites or kimberlites). They could also metasomatize the mantle and modify the petrology (e.g., by increasing the olivine fraction and producing graphite) and chemistry (fO<sub>2</sub>, trace elements and REE) of the source of subduction magmas.

## Global variation in Fe-isotopic composition of arc basalts indicate a variably oxidised mantle wedge source?

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We present new Fe-isotope data on >80 mainly basaltic samples from the currently active global network of arcs and use this data to investigate systematic variation in Fe isotopic compositions that may reflect differing oxidation and water content of different arc's mantle wedges. Differences between the melting conditions of different sub-arc mantle wedges may reflect critical tectonic factors such as the rate of subduction. Some models predict that wetter and hence more oxidised mantle wedge peridotite will produce basaltic melts with systematically heavier Fe-isotopic composition.

It is established that magmas in subduction-related arc systems have significantly more water than those of other tectonic settings. Recent XANES studies of melt inclusions using have established good positive correlations between the water content of primitive un-degassed melts and their oxidation state (expressed as  $Fe^{3+}/Fe_T$ ). Global arc magmas have elevated  $Fe^{3+}/Fe_T$  values in the range >0.1 to 0.5 (our data set has a mean of ~0.35), compared to MORB with values in the range 0.1-0.2. Studies of peridotite from sub-arc mantle wedges have also revealed elevated oxidation states compared to non-arc mantle samples. In spite of the peridotite evidence, the site of the oxidised state of arc magmas remains controversial. Arguments based on redox-sensitive trace element ratios such as V/Sc or Zn/ $Fe_T$  imply that oxidation of arc magmas is a process associated with differentiation after the melts have left the mantle wedge source and that the mantle wedge has  $fO_2$  values as reduced as the source of MORB.

Our  $\delta^{57}Fe$  data span a range from -0.2 to +0.2 ( $\pm 0.04$ ), with a mean of +0.05. This is lighter than MORB and BABBs (+0.10). Arc data sets do trend towards heavier values for more fractionated samples. This may reflect a mantle wedge that is more depleted than MORB. Some key relations in our data set include; positive correlations between  $\delta^{57}Fe$  and Pb- or Sr-isotope ratios, and with  $Fe^{3+}/Fe_T$ . There is also a weak correlation between  $\delta^{57}Fe$  and age of subducting crust (positive). As the trend towards heavier iron in more oxidized samples is not coupled with any correlation with MgO content, this cannot be fractionation driven by olivine or pyroxene.

Our interpretation is that our data reflects difference in the oxidation state of the wedge between different arcs because  $Fe^{3+}$  mineral sites have heavier Fe-isotopic and  $Fe^{3+}$  is more incompatible during melting. We take the positive correlation with Pb- and Sr-isotopes as a measure of slab input to the wedge, and with slab age to indicate that cold, old slab subduction delivers more oxidation capacity to the wedge.

## Estimation of slab-derived fluid contributions to arc magmas: a study of across-arc and along-arc variations of trace elements and isotopes of volcanic rocks from Java island, Sunda arc

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We compiled a dataset of chemical composition of volcanic rocks from Java island, Sunda arc, for the purpose of understanding material transfer process in subduction zones. The analyzed samples are basalt to basaltic andesite in composition to avoid the effect of crustal contamination. We observed across and along arc variation of slab-derived fluid contributions to arc magmas, both from sediment (SED) and from altered oceanic crust (AOC) by examining ratios of fluid-mobile elements to HFS (High Field Strength) elements (e.g. B/Nb, B/Zr, Ba/La). Lateral Nb depletion along this island, which characterizes arc magmas, is also evaluated by using Nb/HFSE (e.g. Nb/Ta, Nb/Zr) ratios. To estimate the contribution of SED and AOC to arc magma source, Sr-Nd isotopes were determined as well.

Based on volcano distribution and tectonics, Java island is divided into western, central and eastern sections. Our result shows lavas from this island are distinguished by LILE and LREE enrichment, which is accompanied by negative anomalies of Nb and Ti. The values of Nb/HFSE ratios are evenly low along the island, with distinct increasing trend toward back arc in central and eastern sections, which implies particular mantle source enrichment in these parts. The ratios of B/HFSE and Ba/HFSE across the western section show very little variation, whereas they significantly decrease from volcanic front toward back arc in the central and eastern sections. This negative correlation between incompatible elements ratio and the depth of Wadati-Benioff zone suggests a recognizable influence of slab-derived fluid along this island. However, the decreasing trends of these ratios, particularly in central and eastern sections, positively indicate a reduced influence of slab-derived fluid from volcanic front toward back arc. In terms of isotopic ratios, samples from all sections are shifted from Indian Ocean MORB field toward higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and lower  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. The back arc alkaline lavas from central and eastern sections exhibit relatively low values of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, which confirm particular back arc source enrichment in these sections. On the other hand, some volcanic front samples from central section are plotted overlapping with Indian Ocean sediment values. This isotopic ratio pattern suggests involvement of slab fluid in all sections of this island, including the back arc mantle source of central and eastern sections.

These findings suggest that even though observed all along the island, the greatest enrichment of subduction components is found in central section, which implies strongest slab-derived fluid contributions in this section. It raises questions of (1) the main factor that controls different magma characteristics of the three sections, (2) the responsible hydrous phase in this arc, and (3) the mechanism of slab fluid-mantle interaction that results in such variation.

## Insights into subduction-zone melting processes from across-arc and down-slab variation in thermal and chemical parameters

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Arc magmatism is sustained by fluids released into the overlying mantle at subduction zones. Simulations of melting processes suggest significant variability both within and between arcs in the depth and rate of fluid release, dependent on the thermal structure of the downgoing slab. These models are not well tested against eruption products. By examining primitive volcanic rocks in across-arc profiles, a better understanding can be obtained of the processes of fluid release at the slab interface, and of melt generation and transport processes in the intervening mantle wedge.

Here, we investigate the melt-inclusion chemistry of a suite of primitive volcanic rocks from across the southern Chilean arc, ranging from picrites to high-magnesium basalts. These rocks preserve the chemical signature of a systematic down-slab gradient in fluid chemistry. The chemical gradient is consistent with predictions from modelling, geothermometry and experiments, and suggests that the fluid escaping from the slab changes from a water-rich fluid to one dominated by hydrous sediment melt, over an across-arc distance of a few kilometres. This change is due to the thermal regime of the slab in this particular arc, where the wet-sediment solidus is crossed in the zone of fluid release feeding the sub-arc melting region. Thus, the material driven off the slab is a mix of aqueous fluid and sediment melt, whose proportions follow opposite trends as slab temperature increases. This same gradient appears to influence major element compositions (K<sub>2</sub>O-SiO<sub>2</sub> trends) of volcanic rocks throughout the arc, and therefore exerts a first-order control on magma chemistry. Our observations also imply that discrete melt paths are maintained through the mantle wedge, without focussing or mixing of separate melts in an across-arc direction.

## Estimation of slab-derived fluids using olivine-hosted melt inclusions collected from volcanoes in Kyushu, SW Honshu arc, Japan

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Olivine-hosted melt inclusions from four Quaternary volcanoes from Kyushu, located in the volcanic front of SW Honshu arc, were used to estimate primitive magma compositions and slab-derived fluid compositions. Small scoria samples were collected from Nakadake and Ojodake peaks of Aso volcano, Hiijidake peak of Kuju volcano, Ohachi peak of Kirishima volcano, and Kaimondake tephra of Kaimon volcano.

Major and minor elements of olivine-hosted melt inclusions and of minerals (host olivine, Fe-Ti oxides) were determined using an electron probe micro analyzer. H<sub>2</sub>O and CO<sub>2</sub> concentrations in melt inclusions were determined by Fourier transform infrared spectroscopy (FTIR). The compositions of melt inclusions were corrected for post-entrapment modifications including diffusive Fe loss, H<sub>2</sub>O loss due to iron oxidation and magnetite formation, and olivine crystallization. All melt inclusions, except those from Aso Nakadake, have high volatile concentrations (2.9–4.8 wt.% H<sub>2</sub>O, 450–780 ppm CO<sub>2</sub>, 0.09–0.19 wt.% S, 0.06–0.10 wt.% Cl). This indicates that there was little or no degassing prior to melt entrapment.

Primitive magma composition, which is in equilibrium with mantle olivine, was calculated using olivine additions to melt compositions. TiO<sub>2</sub>, a fluid immobile element, was used to estimate the degree of partial melting, which was then used to estimate the compositions of slab-derived fluid components. Estimated compositions of slab-derived fluids beneath Kyushu frontal arc have a wide variation, but the range of fluid compositions are similar to those from other volcanic arcs. Positive correlation was found between estimated degree of partial melting and H<sub>2</sub>O contents in mantle source. K<sub>2</sub>O contents in Aso and Kuju primitive magmas are higher than those from Kirishima and Kaimon and from other volcanic arcs. Dehydration processes controlled by phengite-bearing eclogite is a possible mechanism to create high K<sub>2</sub>O primitive magmas, when considering the deeper location of subducted slab beneath these volcanoes.

## Hydrogen concentration in plagioclase as a hygrometer of arc basaltic melts: approaches from melt inclusion analyses and hydrous melting experiments

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The hydrogen in nominally anhydrous minerals (NAMs) can be an indicator of H<sub>2</sub>O activity in silicate melts if the partitioning coefficient of hydrogen between NAMs and melts is known. Although plagioclase is one of the most common NAMs in arc basaltic rocks, few studies have been performed to constrain partitioning and solubility of hydrogen in plagioclase.

Here, we determined the partition coefficient of hydrogen between plagioclase and basaltic melt by two approaches. For the first part of this study, plagioclase-hosted melt inclusions in mid-ocean ridge basalt were analyzed. The hydrogen concentration in plagioclase is less than 60 wt. ppm water, and the average H<sub>2</sub>O concentration in melt inclusions is 0.3 wt.%. Therefore, the apparent partition coefficient of hydrogen between plagioclase and melt is approximately 0.01 on a molar basis. For the second part of this study, hydrous melting experiments of basaltic magma were performed at 0.35 GPa using an internally-heated pressure vessel. A grain of Ca-rich plagioclase (1 mg) and 10 mg of powdered basaltic glass with 0.8-5.5 wt.% H<sub>2</sub>O were sealed in a AuPd alloy capsule, and then kept at near the crystallization temperature of plagioclase as a liquidus phase to attain an equilibrium of hydrogen between plagioclase and melt. Combining the results of these two parts of the study, we formulated two linear equations to correlate the hydrogen concentration in plagioclase and H<sub>2</sub>O concentration in basaltic melt. When H<sub>2</sub>O in melt is  $\leq 1$  wt.%,

hydrogen in plagioclase (wt. ppm water)  $\approx 80 \times$  H<sub>2</sub>O in melt (wt.%).

When H<sub>2</sub>O in melt is  $\geq 4$  wt.%,

hydrogen in plagioclase (wt. ppm water)  $\approx 40 \times$  H<sub>2</sub>O in melt (wt.%).

Hydrogen concentration in plagioclase lies between two equations when H<sub>2</sub>O in melt ranges from 1 to 4 wt.%. In accordance with these two formulations, the partition coefficients of hydrogen between plagioclase and basaltic melt switches from  $0.01 \pm 0.005$  under H<sub>2</sub>O-poor conditions to  $0.005 \pm 0.001$  under H<sub>2</sub>O-rich conditions. Such switches of hydrogen partitioning can be related to change of the atomic site for hydrogen in the crystal structure of plagioclase.

The hydrogen concentration in Ca-rich plagioclase from the 1986 summit eruption of Izu-Oshima volcano, a frontal-arc volcano in Izu arc, shows variation ranging from <50 through 300 wt. ppm H<sub>2</sub>O as a result of polybaric degassing (Hamada et al., 2011 *Earth Planet. Sci. Lett.*). Our present study confirms that plagioclase with 300 wt. ppm H<sub>2</sub>O can be in equilibrium with melt dissolving about 6 wt.% H<sub>2</sub>O, which also confirms presence of H<sub>2</sub>O-rich magmas beneath arc volcanoes.



## Replenishment of volatiles into a degassed chamber driving mixing and eruption of Tungurahua volcano

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In July and August of 2006, and May of 2010, multiple 'boiling over' pyroclastic flow-forming eruptions occurred at Tungurahua volcano, Ecuador. These eruptions marked increased explosivity compared to the low-energy events that characterized most of Tungurahua's volcanic behavior between when activity reinitiated in 1999, and 2006. Volatile (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl) and major-element concentrations of 39 melt inclusions hosted within olivine and pyroxene phenocrysts were analyzed from these events in order to reconstruct the magmatic conditions present before these eruptions as a means to understanding the 'boiling over' process. Heterogeneity within melt inclusions indicate two distinct magma bodies are being preserved, one volatile rich (water ~4.0 wt.% and sulfur ~1800 ppm) within more primitive olivine-hosted melt inclusions and a secondary population of relatively degassed magma from more evolved pyroxene-hosted inclusions. The degassed magma contains water concentrations ~1.0 wt.% and sulfur concentrations between 100 and 500 ppm. The interaction of these two magma batches preserved by melt inclusions is consistent with the model that the 2006 eruption was the result of mafic recharge into a shallow, degassed chamber, and subsequent mixing. Melt inclusions from the 2006 and 2010 eruptive products have similar volatile concentrations and major elemental compositions, indicating that both magma bodies are sampled in both years. We propose that these 'boiling over' pyroclastic flows are the result of the recharge of a volatile saturated magma into a more evolved, degassed magma body.

## Use of attenuated total reflectance (ATR) FTIR spectroscopy to measure H<sub>2</sub>O and CO<sub>2</sub> in silicate glass

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Petrologists have long sought simple, rapid, and inexpensive techniques to quantify the amounts of H<sub>2</sub>O and CO<sub>2</sub> dissolved in volatile-bearing silicate melts. We recently developed a calibration for Attenuated Total Reflectance (ATR) micro-FTIR that requires only a singly polished sample and applies to compositions ranging from basalt to rhyolite. A Ge ATR accessory makes direct contact with the sample to measure evanescent wave absorption within the hydrous glass. Absorbance at 3450 and 1630 cm<sup>-1</sup> showed high correlation ( $r^2 = 0.98$ ) with measured H<sub>2</sub>O concentration in the glasses as determined by manometry and transmission FTIR spectroscopy. The calibration permits determination of H<sub>2</sub>O concentration in singly polished glass samples with spot size down to 15 micrometers (for H<sub>2</sub>O-rich samples) and detection limits of 0.1 wt.% H<sub>2</sub>O. Accuracy is 6% relative at 1 wt.% H<sub>2</sub>O and 3% relative at 6 wt.% H<sub>2</sub>O (one sigma). Precision based on replicate analyses is similar. Results for basaltic and basaltic andesite glasses of known H<sub>2</sub>O concentrations fall along a density-adjusted calibration, indicating that ATR spectra are relatively insensitive to glass composition. The technique can also be used to quantify dissolved carbonate in basalts with >100 ppm CO<sub>2</sub>. We are still evaluating whether quantification of dissolved CO<sub>2</sub> in rhyolite (2350 cm<sup>-1</sup>) is feasible.

The ATR micro-FTIR technique is less sensitive than transmission FTIR, but requires only a singly polished sample for quantitative results, thus minimizing time for sample preparation. Compared with specular reflectance, it is more sensitive and better suited for imaging of H<sub>2</sub>O variations in heterogeneous samples such as melt inclusions. One drawback is that the technique can damage fragile samples and we therefore recommend mounting of unknowns in epoxy prior to polishing. Our calibration should hold for any Ge ATR crystals with the same incident angle (31°). Use of a different crystal type or geometry would require measurement of several H<sub>2</sub>O-bearing standard glasses to provide a crystal-specific calibration.

## Determining molar absorption coefficients for rhyolitic glass

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The objective of this research project is to determine robust molar absorption coefficients to be used in the measurement of H<sub>2</sub>O and CO<sub>2</sub> in silica-rich glasses by Fourier Transform Infrared spectroscopy (FTIR). Compositionally dependent molar absorption coefficients are required to calculate H<sub>2</sub>O and CO<sub>2</sub> contents from FTIR spectra. However, while the coefficients are reasonably well established for basaltic glasses, paradoxically for silica-rich glasses they are poorly constrained, despite such compositions being typically associated with more explosive eruptions driven by volatiles (primarily H<sub>2</sub>O and CO<sub>2</sub>). A sample of Ben Lomond rhyolite from the Maroa Centre in the Taupo Volcanic Zone of New Zealand was crushed and glass particles with minimal microvesicle contents were hand-picked for density determination. Random sample densities ranged from 2288-2350 kg/m<sup>3</sup> while the hand-picked sample density was 2397kg/m<sup>3</sup>, reflecting the significant impact of microvesicularity. Microdrilled rhyolite cores were hydrated in an internally heated autoclave at the Institut des Sciences de la Terre d'Orleans, CNRS - Universite d'Orleans to a range of nominal water contents from 0.5 to 5 wt%. The samples were analysed by micro-FTIR at Massey University using a Nicolet Continuum microscope and 6700 bench. Spectra were collected using a globar source, KBr beam splitter and MCT detector. Absorbances of water peaks in the near-IR region, caused by the combination of stretching and bending of H<sub>2</sub>O mol at 5200 cm<sup>-1</sup> and Si-OH and Al-OH vibrations at 4500 cm<sup>-1</sup>, were measured in thick wafers. The wafers were then thinned to allow absorbances in the mid-IR region, caused by the fundamental OH-stretching vibration at 3500 cm<sup>-1</sup> (for total H<sub>2</sub>O) and bending of H<sub>2</sub>O mol at 1600 cm<sup>-1</sup>, to be measured. Splits of the same samples were also analysed at the Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine Earth Science and Technology (JAMSTEC) using a Varian FTS Stingray 7000 Micro Image Analyzer spectrometer. Absorbances of peaks in the near-IR region were measured in spectra from thick wafers using the same set up as before, and the same spots were then analysed again using the optimal set up for measurements in the near-IR region, a halogen source, CaF<sub>2</sub> beam splitter and MCT detector, in order to compare results. Finally, in order to check for homogeneity in the experimental charges, FTIR imaging was performed on both thick and thin wafers using a focal-plane array (FPA) detector and both KBr and CaF<sub>2</sub> beam splitters with a globar source. Independent measurements of water content are currently being made by Differential Thermal Analysis/Differential Scanning Calorimetry (DTA/DSC) at Massey University in order to independently determine total H<sub>2</sub>O contents, and thus allow molar absorption coefficients to be constrained for each of the peaks.

## Cogenetic distributions of deep fluids and earthquakes in Japan arc: Implications for slab fluid processes

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Very saline, CO<sub>2</sub>-bearing and 18O-shifted springs are found in Japan. Those springs naturally occur at various places along active faults, tectonic lines and close to volcanoes. Here, we show the spatial distribution of these deep fluids and discuss crustal fluid processes by showing the areal relationships between chemistry and hypocenters of earthquakes (deep low frequency (DLF) and shallow micro-earthquakes).

The waters of Cl concentration higher than 200 mg/l are selected to classify into three origin groups: seawater, fossil seawater, and deep fluid (including magmatic fluid) using Li/Cl ratios, water chemistry and hydrogen and oxygen isotope ratio. Deep fluid is defined here as originated neither from meteoric water nor from fossil seawater in isotopic composition and with the feature showing high Li/Cl ratio (>0.001 in wt. ratio), which is an indicator of a deep hydrothermal origin.

The DLF earthquakes are well determined for hypocenter having feature of very deep (20-40km depth) and thought to be related with hydrothermal fluids. Characteristic feature of spatial distribution of the DLF earthquakes are as follows; type-1) found along 1000 km of the SW Japan arc on the upper part of subducted Philippine Sea Plate, type-2) occurs close to Quaternary volcanoes, and type-3) occurs as non-volcanic clusters.

The deep fluids found along the Median tectonic line (MTL) through Shikoku-Kinki-Tokai district (close to type-1) have a mixing end-member with isotopic composition of water similar to magmatic water, highly saline and free CO<sub>2</sub> gas. These fluids are likely originated from dehydrated water from the Philippine Sea slab since there are no mantle above the slab beneath the MTL. The deep fluids close to type-2 DLF events are neutral to a little acidic in pH, and never have low pH like the volcanic fluids degassed from shallow magmas. Amounts of the free CO<sub>2</sub> with salts would never come from shallow degassing magmas but likely from fluids released when basalts are solidified at the lower crust. The type-3 DLF earthquake clusters are found at non-volcanic areas especially in Chugoku-Kinki at forearc area and Tohoku-Hokkaido regions at rear-arc area. The deep fluids related to type-3) in forearc area may be directly come from slab, and those in rear-arc area are possibly related to solidifying basaltic magmas at the lower crust like the type-2.

Spatial distribution of the deep fluids is found to relate to that of the shallow micro earthquakes. This evidence suggests that either earthquake makes a fault as fluid path for the deep fluids ascent or the deep fluid itself makes a fault to occur earthquakes. Recent studies on seismic tomography reveal that fluids are inhomogeneously existed in the crust and our distribution of the deep fluid is consistent with those geophysical observations. Therefore, the crustal deep fluids are NaCl-CO<sub>2</sub>-type water originated directly from the slab or released from a solidified magma at lower crust.

## **CO<sub>2</sub> and methane flux from the submerged Wakamiko Crater in Aira Caldera of Kagoshima Bay, southern Kyushu, Japan**

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Vigorous fumarolic activity in the submerged Wakamiko Crater, which is one of the active craters of Aira Caldera, southern Kyushu, Japan, has been recognized since at least fifty years ago. Carbon dioxide is a main constituent of the discharged gas and its carbon isotopic signature indicates that the gas is derived from magma below the seafloor. Gas bubbles of a part of the discharged gas reach to the sea surface through overlying seawater about 200 m thick from seafloor vents. Such significant amount of fumarolic gas discharge has been expected an useful proxy for monitoring of magma activity of the caldera. Since 2007, we sampled seawater one or two times every year and measured total dissolved inorganic carbon and methane concentrations in the seawater samples. Occupied seawater in the caldera is overturned in early spring every year, it means that vertical mixing of water bodies is occurred. After the mixing stagnant bottom water body is developed lower than about 100 m in water depth due to salinity and temperature stratification, then carbon dioxide and methane discharged from the fumaroles start to accumulate in the bottom water. Therefore, we can estimate the flux of carbon dioxide and methane from the increasing rate of those gases in the bottom water. The estimated flux of carbon dioxide is ranging from c.138 to c. 362 billion g·y<sup>-1</sup> during 2007 ~ 2012 (maximum at 2011), while methane flux is estimated c. 11 to 40 million g·y<sup>-1</sup> during 2010 ~ 2012 (maximum at 2010).

Adjacent subaerial active volcanoes, Sakurajima and Kirishima-Shinmoedake, have been significantly activated recently. Frequency of explosive eruptions have been increasing significantly since 2007 for Sakurajima and 2011 for Shinmoedake volcanoes. Magma chamber expected lying below Aira Caldera is considered to connect and supply magma to another magma chamber developed below Sakurajima continuously. Carbon dioxide flux of Aira Caldera shows maximum values at 2011, it means that we need to accumulate further data of the flux and observe carefully the relationship with those adjacent volcanoes.

## Large contribution of the magmatic water to the seafloor hydrothermal fluid at the Wakamiko hydrothermal field and its associated mineralization in Aira Caldera, southern Kyushu, Japan

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Active hydrothermal venting from shallow seafloor (200-m depth) with talc chimneys has been discovered at the Wakamiko Crater floor in the Aira Caldera, southern Kyushu, Japan. The major chemical composition of the fluids suggests that the fluids are supplied from a single reservoir. Silica and alkaline geothermometers indicate that the fluid-rock interaction in the reservoir occurs in the temperature range of 230 to 250 °C. The fluid is characterized by a high alkalinity and high ammonium and dissolved organic carbon concentrations, indicating interaction of the fluid with organic matter in sedimentary layers. The fluid is also characterized by a low chloride concentration relative to seawater, suggesting that boiling of hydrothermal fluid occurs below seafloor and/or that the source of the fluid contain both seawater and meteoric water which is derived from the surrounding land mass. In addition, a low  $\delta D$  and a high  $\delta^{18}O$  values of the fluid also imply that the fluid is mixed with andesitic water and that the proportion of andesitic water may reach 50 %. Such abundant magmatic input may be supported by the significant occurrence of As, Sb, and Hg minerals in the chimneys and crater-floor sediment. The graben-fill and/or caldera-fill sediments that include abundant organic matter and volcanoclastics deposited under bay conditions in this area are expected to provide a reservoir and medium for water-rock interaction. At least three hydrothermal vents have been observed in the crater. Two of them have similar cone-shaped chimneys. The chimneys have a unique mineralogy and consist dominantly of talc (kerolite and hydrated talc) with lesser amounts of carbonate (dolomite and magnesite), anhydrite, amorphous silica, and stibnite. The precipitation temperature estimated from  $\delta^{18}O$  values of talc was almost consistent with the observed fluid temperature (c. 200 °C). Geochemical modeling calculations also support the formation of talc and carbonate upon mixing of the endmember hydrothermal fluid with seawater and suggest that the talc chimneys are currently growing from venting fluid.

## **Subvent hydrothermal mineralization and rare metal accumulation within the unconsolidated sediments of Wakamiko submarine crater in Aira Caldera, southern Kyushu, Japan**

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On the seafloor off northeast Sakurajima volcano in the Kagoshima bay, south Kyushu, Japan, an active volcano "Wakamiko" is located, and the volcano is characterized by vigorous fumarolic and hydrothermal activity. The "Wakamiko" volcano is considered one of the active craters of Aira caldera, which occupied the bay head area, and is formed small depression of 200 m in depth deeper than the caldera floor of about 140 m in depth. In the depression, i.e., Wakamiko crater, hydrothermal vents have been identified and maximum temperature of emitting fluids reach 200°C. In addition several hydrothermal fluid shimmering sites have been found in the crater.

The coastal line is close to the crater, therefore, much clastic sediments include volcanoclastics emitted from surrounding volcanoes and its self are filled the crater. The unconsolidated sediments in the crater is considered to reach up to 80 m by seismic observation. The venting and shimmering hydrothermal fluids penetrate the unconsolidated sediment layer, then several commercially important elements, it means rare metals, have been expected to precipitate and condense in the sedimentary layer.

Sediment core samples obtained in 2008 and 2012 were provided for this study and use to study pore water chemistry, clay mineral compositions, and bulk elemental analysis. Bulk elemental analysis was applied neutron activation analysis (NAA) and was carried out at Kyoto University Research Reactor Institute.

From the core (total length of 330 cm) collected in the vicinity of the active hydrothermal field where high temperature fluid (T = 200°C) venting, two types of smectite were dominantly observed as hydrothermal alteration minerals. While montmorillonite was found all over the core except for the surface, saponite (Mg-rich smectite) was found only in sediment from 270 to 300 cmbsf of the core, where relative amount of the saponite gradually increase downwards in replacement of the montmorillonite decrease. Profiles of the pore fluid chemistry indicated that the saponite layer corresponds to the boundary between sediment occupied with pore fluid of seawater composition (from 0 to 270 cmbsf) and of the hydrothermal component (from 300 to 330 cmbsf).

In, Se, V, Mn, Au and so on in addition to As, Sb and Hg, which are previously reported anomalous condensation in this area, were detected by NAA. As, Sb, Hg and Au were condensed at the layer where present contribution of hydrothermal fluid was obvious. On the other hand, condensation of Mn, V and In was observed at about 50 cm depth below seafloor from the both core samples.

As, Sb and Hg are expected to precipitate directly from the hydrothermal fluid, while Mn, V and In were even condensed at the hydrothermal fluid-free layer. It may suggests that Mn, V, and In are precipitated from the bottom seawater containing hydrothermal components once emitted from the vents under suitable physicochemical condition.



## Three-dimensional magmatic volatile flux into the groundwater system around Kutcharo caldera, NE Hokkaido, Japan, based on measurements of helium isotopes in groundwater

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The groundwater flow system of a caldera area is greatly influenced by variation of hydrological structure due to caldera formation. As a scale of volcanic activity for a caldera forming volcano is very large, the magmatic volatiles supplied to groundwater system is supposed to be large. Kutcharo caldera located in northeast Hokkaido is the largest caldera in Japan. In this study, we estimate the fluxes of magmatic  $^3\text{He}$  and other magmatic volatiles such as C by an applied method using helium isotopes for the quantitative evaluation of influence of magmatic volatiles into the groundwater in and around the Kutcharo caldera. And, we show the three-dimensional distribution of magmatic volatiles into the groundwater system.

Magmatic  $^3\text{He}$  and C fluxes in and around the caldera have value of wide range. Three-dimensional distributions of magmatic volatile fluxes and concentrations show remarkable differences between three areas (caldera area, north and south sides from caldera). The shallow and deep groundwater inside the caldera indicate shorter residence time with low  $^4\text{He}$  concentrations and have high magmatic  $^3\text{He}$  flux of more than  $10^{-11}$  mol/m<sup>2</sup>/y with high concentrations of magmatic volatiles regardless of depth. In the north of caldera, the deep groundwater indicates long residence time with high  $^4\text{He}$  concentration, but has high magmatic  $^3\text{He}$  flux ranging from  $10^{-12}$  to  $10^{-11}$  mol/m<sup>2</sup>/y even in a place 30 km far from the caldera. In contrast, the deep groundwater in the south of caldera with longer residence time than that in the north of caldera has hardly received influences of magmatic volatiles. The magmatic  $^3\text{He}$  flux is significantly low, ranging from  $10^{-15}$  to  $10^{-13}$  mol/m<sup>2</sup>/y. As for shallow groundwater system, the high  $^3\text{He}$  flux is observed inside the caldera, and is hardly observed outside the caldera. The high flux in groundwater found inside the caldera regardless of depth would result from the highly permeable structure where fractures advanced to the depths. The anisotropic distribution of magmatic volatiles in the deep groundwater outside the caldera suggests that the groundwater flow system and/or the supply pathway of magmatic volatiles are restricted by the hydrological structures. Magmatic  $^3\text{He}$  and C fluxes inside the caldera is from one to two orders of magnitude larger than that of north area, and is from two to four orders of magnitude larger than that of south area. In conclusion, large amounts of magmatic volatiles are preferentially supplied to the groundwater inside the caldera and dispersed through the deep groundwater system to the north area.

## Synchrotron Radiation X-Ray Fluorescence Analysis of Aqueous Fluids and High-Magnesian Andesite Melt Under High-Temperature And High-Pressure Conditions

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Silicate melts and aqueous fluids are major fluids in subduction zones. Elemental partition among minerals and these fluids is a key to understand the elemental transfer from subducting slab to mantle wedge [Kawamoto et al. 2012 PNAS].

Synchrotron radiation X-ray fluorescence analysis is conducted to know elemental distribution between aqueous fluids and high magnesian andesite melt under high-temperature and high-pressure (HTHP) conditions. We put Cs, Ba, La, Sm, Gd, Ho, and Yb-doped high-Mg andesite with water or a saline solution and brought it under HPHT conditions. We achieved HTHP conditions with SPEED 1500 Kawai-type large-volume press installed at BL04B1, SPring-8, Japan. Incident X-ray is a white beam with energy ranging from 20 -150 keV. During heating at a given pressure, synchrotron X-ray radiography technique allows us to observe a melt globule surrounded by aqueous fluids through the diamond windows. SR-XRF spectra are collected from the melt globule and the aqueous fluid using an SSD detector.

A series of experiments has been carried out at pressures of 0.5-2.2 GPa. The spectra show characteristic X-ray peaks of the doped elements superimposed on a continuous X-ray background. At 1 GPa, no characteristic X-ray peak from any doped element is observed in Cl-free fluids and all the doped elements are partitioned into melts. At 1.5 GPa and greater pressures, only Cs is found in Cl-free fluids, with one exception of small X-ray peak of Ba at 2 GPa. In contrast, X-ray peaks of Cs and Ba are observed in saline solutions at 1 GPa. In addition to Cs and Ba, a small peak of La is also found in the saline solutions at 1.5 GPa and greater pressures. The other elements (Sm, Gd, Ho, Yb) are found only in melts at all conditions.

NaCl and KCl in aqueous fluids have large effects on elemental partition between melts and fluids as Keppler suggested [1996 Nature]. The present observation is qualitatively consistent with reported values in his measurement. Elliott et al. [1997, JGR] suggested two slab-derived components: a melt component and a fluid component in order to explain trace element characteristics of basalts and basaltic andesites in the Mariana arc. Both components are characterized by enrichment of alkali and alkali earth elements. The fluid component shows rare earth element abundances relatively similar to MORB, while the melt component shows more light rare earth element rich pattern. Such features can be consistent with a Cl-rich aqueous fluid and a melt that can be formed through a separation of a slab-derived supercritical fluid during its migration to the surface. Chemical fractionation of slab-derived supercritical fluids may play an important role in subduction zone magmatism.

## Mantle wedge infiltrated with saline fluids from dehydration and decarbonation of subducting slab

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Slab-derived fluids play an important role in heat and material transfer in subduction zones. Dehydration and decarbonation reactions of minerals in the subducting slab have been investigated using phase equilibria and modeling of fluid flow. Nevertheless, direct observations of the fluid chemistry and pressure-temperature conditions of fluids are few. This report describes CO<sub>2</sub>-bearing saline fluid inclusions in spinel-harzburgite xenoliths collected from the 1991 Pinatubo pumice deposits. The fluid inclusions are filled with saline solutions with 5.1 +/- 1.0 percent wt NaCl equivalent, magnesite crystals, CO<sub>2</sub>-bearing vapor bubbles, and a talc and/or chrysotile layer on the walls. The xenoliths contain tremolite amphibole, which is stable in temperatures lower than 840 degree C at 30 km depth. Pinatubo volcano is located at the volcanic front of the Luzon arc associated with subduction of warm oceanic plate. The present observation is the first report suggesting hydration of forearc mantle and the uppermost mantle by slab-derived CO<sub>2</sub> bearing saline fluids. Dehydration and decarbonation take place and seawater-like saline fluids migrate from the subducting slab to the mantle wedge. Saline fluids can dissolve more metals than pure H<sub>2</sub>O and affects on the chemical evolution of mantle wedge.

## Halogen contents and Pb isotopes of olivine-hosted melt inclusions: mantle source heterogeneity for South Tyrrhenian magmas revealed.

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Transfer of volatile elements from subducting slab to mantle beneath arc volcanoes through the mantle wedge, triggers partial melting and ultimately produces island arc lavas. However, due to scarcity of arc lavas representing primary compositions, much of the evidence for this coupled volatile enrichment/flux melting model has been derived indirectly from the compositional systematics of the end products, i.e. erupted volcanic rocks with evolved compositions. Thus, the models of arc magma genesis often depend intimately on the interpretation of compositional systematics that have been influenced by shallow-level contamination and differentiation processes. Alternatively, silicate melt inclusions trapped in early-formed phenocrysts during their growth can partly overcome this difficulty; olivine, the first liquidus phase in many basalts, may isolate early liquids which can provide direct information about primary magmas. It is now proven that H<sub>2</sub>O can diffuse out of olivine-hosted inclusions at magma chamber conditions (e.g. Hauri, 2002; Portnyagin et al., 2008; Chen et al., 2011; Gaetani et al., 2012). On the contrary, due to their higher solubility in mafic melts compared with CO<sub>2</sub> or H<sub>2</sub>O (Webster, 2004) and their late degassing during magma ascent (Spilliaert et al., 2006), F and Cl abundances often remain unchanged in melt inclusions, while H<sub>2</sub>O, CO<sub>2</sub>, and S show depletion trends (e.g. Vigouroux et al., 2008). Thus, the halogens have the potential to preserve their primitive abundances in the inclusions (Le Voyer et al., 2010; Metrich et al., 2010). We worked on nineteen olivine-hosted melt inclusions from seven volcanoes (Etna, Stromboli, Vulcano, Ustica, Alicudi, Marsili and Vavilov) from the Southern Italy region. They were analyzed for abundances of major, trace, and volatile elements, along with Pb isotope ratios (<sup>207</sup>Pb/<sup>206</sup>Pb, <sup>208</sup>Pb/<sup>206</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb). The systematics of primary volatile (in particular F and Cl) compositions and Pb isotopes identify three main geochemically distinct mantle sources for this region: (1) a component with radiogenic Pb (<sup>207</sup>Pb/<sup>206</sup>Pb = 0.780) and low volatile element abundances typified by the Etnean melt inclusions, (2) a component with moderately radiogenic Pb (<sup>207</sup>Pb/<sup>206</sup>Pb = 0.798) and high volatile abundance mainly associated with Sommata magmas, and (3) a component with moderate volatile abundances associated with a MORB-like <sup>207</sup>Pb/<sup>206</sup>Pb (0.830). Using the F/Nd-Cl/Nb systematics, we rule out the presence of recently subducted, altered oceanic crust for this radiogenic Pb source. The low F/Nd of this radiogenic component results from (i.e. is the residue of) slab dehydration processes.

## Fluorine partitioning between hydrous minerals and aqueous fluid at 1 GPa and 770 – 947 °C: A new constraint on slab flux

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Mechanisms of volatile element transfer from subducting slab to the melting region beneath arc volcanoes are probably the least understood process of arc magma genesis. Fluorine, which suffers minimum degassing in arc primitive melt inclusions, retains the information about the role of volatiles during magma genesis at the depth. Given that volatile elements play a critical role in magma evolution and eruption processes, in-depth investigations into the behavior of F in magma and associated fluid should provide a new constraint.

Experimentally determined solubility of F in aqueous fluid, and partition coefficients of F between fluid and minerals provide first order geochemical constraints about the character of the volatile-transporting agent. We report experimentally determined F solubility in fluid in equilibrium with hornblende and a humite group mineral at 1 GPa and from 770 to 947 °C, and partition coefficients among these phases. The composition of the fluid is determined by mass-balance calculation and consistency is verified by high-pressure liquid chromatography measurements of the quenched fluids. The  $D_F^{(Fl/Hb)}$  can be represented by a single value  $0.13 \pm 0.03$ . Similarly, partitioning of humite group minerals shows that F is strongly bound to the minerals,  $D_F^{(Fl/Nobergite)} = 0.01$ , and  $D_F^{(Fl/Chondrodite)} = 0.02$ . The average F concentration in the fluid is 2700 ppm for F-rich experiments and it constrains the maximum amount of F carried by fluid in the presence of amphibole. With a model accounting for F concentration in slab that is much lower than in our experiments, the increase of F concentration in the subarc mantle by fluid, in equilibrium with hornblende, is expected as no more than by a few ppm. Significant F enrichments found in arc lavas cannot be derived from aqueous fluid of subduction slab, or fluid in lower arc crust in the presence of amphibole, or humites.

## Distinguishing Shallow and Deep Sources of Halogens in Submarine Volcanic Systems

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Defining the primary volatile composition of submarine basalts from mid-ocean ridges, back-arc basins and arc-front volcanoes are key to understanding volatile cycling and the influence of volatiles on melting in the upper mantle. The volatile and halogen geochemistry of submarine volcanic glasses and melt inclusions has been the subject of an increasing number of studies that have made progress in distinguishing between secondary seawater contamination of magmas, and true melting and mantle-source variations, thus enabling observed magma compositions to be used to study the time-integrated cycling of volatiles through the upper mantle. But fewer studies have examined in detail the local-and segment-scale variations of volatiles together with trace elements and radiogenic isotopes, so that it can be understood how and where in the oceanic crust submarine magmas are contaminated by seawater-derived components.

Mid-ocean ridge basalts (MORB) are significantly affected by secondary seawater assimilation processes due to their low volatile contents. From combined CO<sub>2</sub>-H<sub>2</sub>O-Cl systematics, it is apparent that addition of seawater-derived components is enhanced in magmas that ascend more slowly through the crust, and/or erupt away from the ridge axis. Highly depleted magmas that erupt in extensional zones within transform faults (e.g. Siqueiros) show little evidence for seawater addition, due to the near absence of thick crust and hydrothermal systems in such environments. At the same time, there also exists a second tier of more subtle seawater addition that is evident as a function of the extent of differentiation in MORB, pointing to combined assimilation and fractional crystallization as an important process operating in MORB petrogenesis. In detail the geochemistry of the assimilants can vary substantially from simple seawater compositions.

Discerning seawater contamination in arc and back-arc magmas is more difficult, not only because of higher volatile concentrations but because addition of deep slab-derived fluids can often produce geochemical signatures that mimic the shallow assimilation of seawater-derived components in the crust. In these tectonic environments, deeply-trapped melt inclusions can often reveal compositions that permit distinguishing deep from shallow processes that influence the geochemistry of arc-related submarine basalts.

## Pore fluid-derived halogens and noble gases preserved in exhumed mantle wedge rocks from the subduction-type Sanbagawa metamorphic belt

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Subduction volcanism is generally considered to form a 'subduction barrier' that efficiently recycles volatile components contained in subducted slabs back to the Earth's surface [1]. Nevertheless, subduction of sediment and seawater-dominated pore fluids to the deep mantle has been proposed to account for the non-radiogenic elemental and isotopic compositions of heavy noble gases (Ar, Kr, and Xe) in the convecting mantle [2]. To verify whether and how subduction fluids preserve a seawater signature, we determined noble gases and halogens in the Higashi-akaishi peridotite and Western Iratsu and Seba eclogite from the subduction-type Sanbagawa metamorphic belt, southwestern Japan, in which relicts of slab-derived water are contained as hydrous mineral inclusions in wedge mantle rocks exhumed from depths of more than 100 km [3] and aqueous fluid inclusions in associated slab-derived eclogites and quartz veins and lenses [4,5].

The observed noble gas and halogen compositions of the peridotite [6] and eclogite samples show striking similarities with sedimentary pore fluids, involving a minor contribution from altered oceanic crust in the case of halogens in eclogites. The almost constant noble gas and halogen elemental ratios with depths of slab-derived fluid entrapment ranging from 30 to 100 km indicate flux of pore fluid-derived water is extensive in the mantle wedge, challenging a popular concept that the water flux into the mantle wedge is dominantly controlled by hydrous minerals in altered oceanic crust and sediment [e.g., 7]. These results indicate that subduction and closed system retention of marine pore fluid occurs to depths of at least 100 km, necessitating a reassessment of the dominant transport mechanism and source of water in subduction zones. Further subduction of a small amount of marine pore fluid can account for the heavy noble gas composition observed in the convecting mantle [1].

The mechanism by which the seawater-like noble gases are delivered to the convecting mantle remains to be elucidated. Serpentinized lithosphere of subducting slab is probably the best candidate, because serpentine contains significant amounts of Cl (up to 0.5 wt%). If the hydration of the lithosphere by pore fluids is operating in a closed system, subduction of the serpentinized lithosphere can transport pore-fluid derived noble gases and halogens into the deep mantle [6]. This is supported by a recent observation of pore fluid-like noble gases and halogens in exhumed serpentinites [8].

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## F and Cl release by hydrous melting of subducted oceanic crust

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In this study, we quantify the distribution of F and Cl between residual minerals and hydrous melts at upper-mantle conditions. The aim is to characterize the release of halogens upon melting of subducting oceanic crust by means of high-P-T piston cylinder experiments. Upon subduction, when the slab is sufficiently heated, slab melting will occur and transfer volatile elements to overlying arc mantle. F and Cl are potentially useful geochemical tracers of water in arc magmatic processes, but to our knowledge, no F or Cl partitioning data exists that is directly applicable to slab melting. The present study is necessary to establish F-Cl systematics as an anion-based diagnostic petrogenetic tracer for metasomatic processes and magma generation at the source of arc magmatism.

We will present results from an extensive set of equilibrium crystallization experiments on a starting composition representative of subducted hydrous metabasalt. The starting composition was enriched by addition of equilibrium liquid (based on Klimm et al., Journal of Petrology 2008) to optimize the experimental textures for SIMS and EPMA analyses. Experiments were performed in Au<sub>80</sub>Pd<sub>20</sub> double capsules and buffered by the Re-ReO or Ni-NiO equilibrium, at pressures of 1.3 to 3.0 GPa and temperatures of 750 to 1000 °C.

Mineral assemblages in equilibrium with trondhjemitic liquids vary over the P,T-range (e.g. for P = 2.5GPa we observe amphibole + clinopyroxene + garnet + epidote + rutile at 750 °C, amphibole + clinopyroxene + garnet + allanite + rutile at 850 °C, and clinopyroxene + garnet at 900 °C). We will present detailed phase assemblage and compositional data at the conference. Most significantly, we find that F partitions mainly into the silicate liquid and amphibole (with  $D_F(\text{Amph/Liq}) \approx 1.5$  and a bulk D for amphibolite of  $\approx 0.6$ , and for eclogite of  $\approx 0.11$ ). In contrast, Cl is incompatible in all minerals, and it partitions preferentially into aqueous fluid when this is present as a separate phase besides high-Si melt before quenching (i.e., at low P and T in our experiments).

Our results strongly suggest a decoupling between F and Cl as subducted slab undergoes progressive dehydration and hydrous melting. Chlorine appears to be released more readily in the subduction history, whereas F is released upon melting of the slab, with retention of significant concentrations in the solid residue as long as amphibole is stable.

## Systematic classification of kimberlites and their xenoliths using I/Br ratios

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The halogen elements (Cl, Br, I) have high partition coefficients in aqueous fluid (Bureau et al., 2000). Thus, they are enriched in pore fluid and difference in the partition coefficients results in distinct elemental ratios in seawater, pore fluid, sediment, oceanic crust and mantle. These characteristics are useful to trace water cycling in subduction zones (e.g., Fehn et al., 2003; Muramatsu et al., 2007).

Recently, subduction of seawater and marine pore fluid subducting into the mantle was suggested (Holland and Ballentine, 2006; Sumino et al., 2010). However, only a little is known about the behavior of halogen elements during subduction processes and their fate in the earth's mantle.

Kimberlite is an igneous rock originated from deep mantle. Compared to ordinary ultramafic rocks, kimberlite is rich in volatile components. In addition, studies on the noble gas isotopes in kimberlites showed that kimberlite magmas have similar noble gas characteristics to those of ocean island basalts derived from deep mantle plume (Sumino et al., 2006).

In this study, we analyzed concentrations of Cl, Br, and I in kimberlites and their mantle-derived xenoliths from six localities to investigate the halogen characteristics and their origins in the kimberlite source regions.

Samples analyzed are 35 kimberlites collected from South Africa, China, Greenland, Brazil, Russia and Canada, and 4 xenoliths collected from South Africa and Russia. For the analyses of Cl, Br and I, we used the pyrohydrolysis method (Muramatsu et al., 2008) combined with ICP-MS and ion chromatography.

The result shows that the kimberlite samples are classified into two groups with respect to I/Br ratios. The first group (Group S) shows high I/Br ratios (about  $1 \times 10^{-1}$ ), which are distinctively observed in the kimberlites from South Africa, Greenland, Canada and Brazil. The xenolith from South Africa is also classified into the Group S. The I/Br ratio of the Group S is fairly similar to that of CI chondrite (I/Br ratio: about  $1 \times 10^{-1}$ , Anders and Ebihara, 1982). These suggest that these kimberlites preserve the primordial characteristics of halogens in the mantle from which the kimberlite magmas formed. On the other hand, the other group (Group C) composed of Chinese and Russian kimberlite samples shows markedly low I/Br ratios (about  $6 \times 10^{-3}$ ). Similar low I/Br ratios have been observed in fluid inclusions in eclogites derived from seawater-altered oceanic crust (Svensen et al., 2001) and in seawater associated with halite precipitation (Zherebtsova and Volkova, 1996). This suggests an involvement of seawater-derived halogens having low I/Br ratios in the source regions of the Group C kimberlites. In Russian xenolith, one is classified into the Group S and the other two samples are Group C. This suggests the heterogeneous involvement of the Group C component in the mantle beneath this region.

## Slab-derived halogens and noble gases in mantle peridotites from subduction zones

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Halogens and noble gases are expected to provide complementary information as tracers on the origin and behavior of water in the mantle. This is because both of these groups of elements are strongly partitioned into fluids and have distinct elemental and/or isotopic compositions depending on their origin. Seawater-like noble gases in the convecting mantle are carried into the mantle via subduction of seawater or sedimentary pore fluids [1]. Halogens in mantle wedge peridotites also have a signature suggesting an origin involving sedimentary pore fluids [2]. The pore fluid-like halogens and noble gases would be incorporated into serpentine minerals in the oceanic plate derived from pore fluids in overlying sediments, and then carried into the mantle during the subduction process [2,3]. Here, we present the halogen and noble gas compositions of mantle peridotites from subduction zones to better constrain how far the influence of subducted pore water extends into the mantle.

We applied the noble gas method which converts halogens (Cl, Br and I) and other elements (K, Ca, Se, Te, Ba and U) to isotopes of Ar, Kr and Xe by neutron irradiation in a nuclear reactor [4]. This method has detection limits that are from two to five orders of magnitude lower than alternative methods and is required to determine the relatively low halogen abundances in mantle samples.

The samples studied are harzburgitic xenoliths from Avacha volcano in Kamchatka and Pinatubo volcano in the Philippines, and alpine-type peridotite from Horoman massif in Japan. Water-rich fluid inclusions have been found in mineral phases in all of these rocks [5,6,7]. The Br/Cl and I/Cl values show a contribution of subduction fluids [2] to a mantle-like component [7] with different proportions of subduction fluid in each sample locality. Noble gas compositions are also dominated by slab-derived noble gases with atmosphere-like isotopic compositions as previously reported [9,10].

The signatures of subducted halogens and noble gases observed in the mantle peridotites are strong evidence that the sedimentary pore water signature is preserved through the subduction process and survives in the mantle wedge. Transport of some of this material into the deep mantle then accounts for the same signature observed in mantle-derived gases [1].

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## Chlorine isotope variations in the hyper-acid lake system of Poás volcano, Costa Rica

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Chlorine is the most abundant halogen in volcanic systems. Its presence in interacting magmas, hydrous fluids and gases, together with its conservative behaviour, makes this element a convenient tracer of near-surface processes in active magmatic-hydrothermal settings. Available results of d37Cl analyses of fumarolic gases, crater lakes and geothermal waters from volcanoes worldwide are limited and commonly represent single or infrequent sampling at a given location. This absence of time-series data for individual volcanoes may hamper the interpretation of isotopic signatures of the fluids and their potential response to changes in activity.

We collected d37Cl time-series data for the hyper-acid crater lake of Poás volcano (Laguna Caliente) and for gas condensates from fumaroles from the composite pyroclastic cone (CPC), which are supposed to be equivalent to the gas influx into the lake-water body. The samples from Laguna Caliente cover an extended period (1985-2012), which is marked by conspicuous changes in activity and properties of the lake. New and published data from the CPC fumaroles, representing intermittent sampling between 2001 and 2012, cover periods when gas temperatures showed strong temperature differences (ca. 100 to >800 °C).

The d37Cl data from Laguna Caliente show a restricted range between -0.03 and 0.69‰(SMOC). Relatively positive values mark the samples taken during an interval of peak activity of the lake (1980-1986), when Cl concentrations (<73100 ppm) and temperatures (<65 °C) were high, pH values were <0, and its volume was strongly reduced. This elevated d37Cl is attributable to a preferential depletion of light Cl due to evaporation of HCl, or to a distinctive input flux into the lake. The fumarole condensates show a remarkable variability in d37Cl from -0.48 to 13.43‰, while even higher values were reported in a previous work. These d37Cl results exhibit an inverse relationship with Cl concentration and fumarole temperature. Near-zero or slightly negative d37Cl values at the highest temperature (763 °C) correspond to mantle values and are consistent with direct derivation of the gas from a shallow magma body. The strongly positive d37Cl at much lower gas temperatures reflects interaction with subsurface water bodies that preferentially remove and dissolve <sup>35</sup>Cl (cf. Sharp et al., 2010).

We infer that the observed chlorine isotope trends reflect temporal changes in water-gas interaction in the two-phase hydrothermal system below the lake. Although better constraints of magnitudes and controls of isotopic fractionation are necessary for detailed interpretations, the excellent correspondence between the Cl isotope signatures and independently derived fluctuations in the lake activity highlights their potential for monitoring purposes.

## Fluorine and chlorine contents of volcanic ash discharged from Minamidake, Sakurajima volcano in the sequence of its eruptive activity

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Decompression of magma by moving toward the surface causes exsolution of volatiles in magma, which provides the driving force for explosive eruptions. Degassing of volatiles from magma changes its viscosity and density drastically, and these can influence violence of a volcanic eruption.

Sakurajima is one of the most active volcanoes in the world and very close to the populated area. Its recent eruptive phase at the summit crater of Minamidake has been sustained since October 1955. At Sakurajima volcano, strombolian eruptions forerun vulcanian explosions, and vulcanian explosions are often followed by continuous ash emissions, which is the typical sequence of eruptive activity. HF and HCl are the major constituents of high temperature volcanic gas next to water. Further, F and Cl are the most abundant volatiles next to water in volcanic rocks. Hence, precise investigation on the behavior of halogens in volcanic ejecta will provide us reliable information on the change in the mode of eruption.

Volcanic ash particles react with HF and HCl in eruption plumes, which gives origin to the water-soluble F and Cl. Meanwhile, F and Cl that are not exsolved from magma are tightly sealed within the ash particles in water-insoluble forms. The F/Cl ratio in water-insoluble part of the ash samples was significantly larger than the F/Cl ratio in water-soluble part. This result demonstrates that F was fixed mainly in water-insoluble form, whereas Cl was fixed on the ash chiefly in water-soluble form. Thus, the difference in reactivity of F and Cl with silicates causes fractionation of these components through volcanic emanation. Cl contents of the ash particles ejected by strombolian eruption were sufficiently higher than those of the ash discharged by vulcanian explosion and continuous ash emission. Change in water-soluble and water-insoluble F and Cl contents of volcanic ash ejected by the eruption of Sakurajima in 1978 revealed that volatile-rich magma ascended to the top of the crater and caused strombolian eruption and the change in the mode of eruption to vulcanian explosion and continuous ash emission was due to degassing of volatile components. The F contents of the ash discharged by continuous ash emission were obviously higher than those of the others, which was probably caused by reaction of volcanic gases with silicates fragments.

## Behavior of fluorine and chlorine in the volcanic ash of the 2004 eruption of Asama volcano, Japan

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In eruption plumes, the pristine ash particles react with volcanic gases, which gives origin to the water-soluble components. Meanwhile, volatiles that are not exsolved from magma are tightly sealed within the ash particles in water-insoluble forms. Hydrogen fluoride (HF) and hydrogen chloride (HCl) are major constituents of high temperature volcanic gas, exclusive of water vapor. Further, F and Cl are the most abundant volatile components next to H<sub>2</sub>O in volcanic rocks. Water-soluble and water-insoluble F and Cl contents and the F/Cl ratio of volcanic products are good indicators for fractionation processes of these volatile components on volcanic eruption.

Asama volcano lying in central Japan has repeated violent explosions over the centuries. Although vulcanian explosions frequently occurred in the 1930s and the 1940s, the volcanic activity certainly had become in descendent since the middle of the 1950s. After the magmatic eruption in 1958, the eruptions with ascending new magma occurred only in 1961, 1973 and 2004. The eruptive activity of Asama volcano in 2004 began with violent explosion and continued for about four months. The explosions were followed by non-explosive eruption with continuous tephra emission. After the non-explosive eruptions, Asama produced eighteen vulcanian explosions.

Volcanic ash discharged by the first explosion had extremely high contents of F and Cl in water-soluble and water-insoluble forms, which was attributed to reaction with volcanic gas containing HF and HCl with in the crater in the non-eruptive period prior to this eruption. F and Cl were stabilized onto the ash mainly in water-insoluble form and water-soluble form, respectively, and these were fractionated through the prolonged alteration during non-eruptive period before the explosion. On the strombolian eruptions, volatile-rich magma filled the conduit and produced the pristine ash particles continuously. HCl and SO<sub>2</sub> in gas phase were congruently fixed onto the ash particles. Meanwhile, HF and HCl in gas phase were incongruently stabilized onto the ash particles due to the difference in reactivity. During the vulcanian explosion phase, chlorine was intensely degassed from the effused lava by progression of crystallization of the effused lava, whereas fluorine was captured on the lava through reaction with volcanic gases. F is less volatile from magma and much reactive with volcanic ash than Cl, and thus not only degassing but also reaction with volcanic gas controlled volatile contents in volcanic ash.

## Origin of halogen in hot-spring water in Joban and Hamadori area, northeast Japan, inferred from $^{129}\text{I}/\text{I}$ and $^{36}\text{Cl}/\text{Cl}$ ratios

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Japan is the second largest iodine producing country in the world, and it is produced from iodine-rich brine. The iodine-rich brine is often generated from fore-arc and back-arc basins. The half-life of long-lived radioisotope  $^{129}\text{I}$  is 15.7 Ma so that the  $^{129}\text{I}/\text{I}$  ratio could be used for the age determination of source formations for iodine. In the previous studies, iodine isotopic ratios of brine frequently showed older ages than those of host formations, however details of migration pathway of iodine had not been fully understood. Joban sedimentary basin is located at offshore of Fukushima Pref., where natural gas used to be produced from the Miocene sandstone layer. In order to understand the origin of groundwater around Joban and Hamadori area, we collected hot-spring water in Fukushima and north part of Ibaraki Pref., and determined  $^{129}\text{I}/\text{I}$ ,  $^{36}\text{Cl}/\text{Cl}$ , and  $^3\text{H}$  concentrations.

Iodine and chlorine concentrations in hot-spring waters were 0.4-8.7 mg/L and 722-15400 mg/L, respectively. Iodine concentration was higher than that of seawater, while chlorine concentration was lower than that of seawater.  $^{129}\text{I}/\text{I}$  and  $^{36}\text{Cl}/\text{Cl}$  ratios were determined using accelerator mass spectrometry.  $^{129}\text{I}/\text{I}$  ratios of hot-spring waters were almost constant at around  $0.27 \times 10^{-12}$  irrespective of iodine concentration and I/Cl ratio, except for two samples collected at Iwaki city showing  $5.8 \times 10^{-12}$  and  $1.8 \times 10^{-12}$ . These two samples were considered to be affected by anthropogenic  $^{129}\text{I}$  due to the mixing of recent shallow groundwater as indicated by measurable  $^3\text{H}$ , then these two were omitted from further discussion. Iodine ages were determined to be about 40 Ma, using  $1.5 \times 10^{-12}$  as the preanthropogenic initial  $^{129}\text{I}/\text{I}$  ratio. The homogeneity of iodine ages gives the limit for the source formation of iodine. On the other hand, age determined by  $^{36}\text{Cl}/\text{Cl}$  ratio varied widely, from about  $5 \times 10^4$  years to over 1.5 Ma (at secular equilibrium). Chlorine ages are considerably younger than those of iodine. In addition, iodine-rich water was obtained not only from sedimentary rock but also from the Early Cretaceous granite. Because of the large discrepancy between iodine and chlorine ages, migration of iodine is not accompanied with chlorine. There are two possible migration pathways of iodine: 1) iodine originates from the Paleogene layer of Joban basin, because in this case the iodine age is consistent with the sedimentation age; 2) iodine was derived from subducting marine sediments and had migrated with long time to the present location, which is supported by the fact that iodine is also found in granite area. Further investigation is needed to understand the origin of iodine.



## Concentrations of halogen elements and $^{129}\text{I}/^{127}\text{I}$ ratios in highly saline groundwaters collected in Hokkaido

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Hot springs and groundwaters with high halogen contents occur in many places in Japan. Since halogens are highly water-soluble and highly mobile, their concentrations and isotopic composition should reflect the rock formations where the fluids originated. It is known that several hot springs in Hokkaido, the northern Japanese island, contain high concentration of halogens including iodine. However, the origin of the salts in these springs is not well known. The purpose of this study is to understand the origin of high salinity groundwaters related to the geological settings of the area. In this study we analyzed I, Br and Cl concentrations in hot spring waters collected from various places in Hokkaido and compare their relative abundance. We also have analyzed  $^{129}\text{I}$  (half-life 15.7 m.y.) in the fluids in order to estimate the age of the dissolved iodine.

Analytical results obtained by ICP-MS and an ion chromatography show that the concentrations of I, Br and Cl in the fluids ranged between 0.04 - 650 microM, 0.5 - 2500 microM and 0.4 - 960 mM, respectively. Major iodine species was found to be iodide.

Relationships between Cl and I concentrations are classified as 3 types based on their regional distribution, i.e. Wakkanai area, Urausu area and other areas. In case of the relation between Cl and Br, an additional type (Ishikari area) was also observed. In Wakkanai area, concentrations of I increased exponentially with those of Cl, while in Urausu area, it increased logarithmically with Cl concentrations. Samples from the other areas should be a mixture of 3 end-members (meteoric water, seawater and hot spring water).

$^{129}\text{I}/^{127}\text{I}$  ratios determined by AMS (accelerator mass spectrometry) ranged between  $0.05 \times 10^{-12}$  and  $0.38 \times 10^{-12}$ . Samples collected from Urausu area showed a very low  $^{129}\text{I}/^{127}\text{I}$  ratios of  $0.05 \times 10^{-12}$  to  $0.1 \times 10^{-12}$ . Low values are also observed along the longitude of 141-142 deg which are markedly lower than the  $^{129}\text{I}/^{127}\text{I}$  ratios observed in iodine-rich fluids in other areas in Japan, such as Chiba ( $0.18 \times 10^{-12}$ ), Niigata ( $0.3-0.4 \times 10^{-12}$ , Tomaru et al. 2009) and Satsuma-Iwojima ( $0.78 \times 10^{-12}$ , Snyder et al. 2002). Considering the  $^{129}\text{I}$  systematics (Fehn et al. 2004), iodine age in Hokkaido samples of the lowest  $^{129}\text{I}/^{127}\text{I}$  ratios is estimated to be 60-70 Ma. This indicates that the iodine-rich fluids are likely to be derived from old marine sediment, which was later uplifted to form older rock formations in the present day coastal region of Hokkaido.