

SMP006-01

Room:303

Time:May 25 14:45-15:00

## Diversity of silicic crust in the IBM arc and Izu collision zone: constraints from zircon and whole-rock geochemistry

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The Izu-Bonin-Mariana (IBM) arc system is an intra-oceanic arc, where silicic to intermediate middle crust is being generated through subduction zone magmatism. A characteristic tectonic feature is that the IBM arc has been colliding end-on with the Honshu arc at the Izu collision zone (ICZ) for the past 15 million years. As a result of this collision, voluminous granitic rocks are exposed in the ICZ (ICZ granitoids), previously interpreted to represent an exposed deep crustal section of the IBM arc. The collective understanding of silicic crust formation in modern intra-oceanic arcs and their successive modification during arc-arc collision is important, as they may be the modern analogue for continental crust formation during the early Earth history.

Despite their importance, the granitic rocks in the IBM arc and ICZ have not been well characterized geochronologically and geochemically to understand their petrogenesis. In this study, comprehensive zircon U-Pb and Lu-Hf isotopic compositions, together with whole-rock major/trace element and Sr-Nd-Pb isotopic compositions, were acquired for granitic rocks from the IBM arc and ICZ.

The zircon ages obtained from the IBM arc granitoids range from ca. 50 Ma to <1 Ma, showing that silicic crust formation in IBM arc was initiated at the earliest stage of arc magmatism and has continued to the present. Episodic Eocene crustal formation is suggested from the zircon ages of the granitic rocks exposed in the IBM forearc and Kyushu-Palau Ridge, possessing distinctive Pb, Hf, and Nd isotopic compositions from other volcanic rocks erupted in the history of the IBM arc. These results suggest that the Eocene silicic crust is derived from a distinctive proto-IBM crust. Furthermore, the IBM middle crust layer displays geochemical and petrological across-arc variation that range from granodiorite to tonalite composition not consistent with the previously believed monolithologic layer of tonalitic rocks.

Zircon dating of the ICZ granitoids reveals that all of these plutons were syncollisional, formed after the onset of IBM arc collision with the Honshu arc. This implies voluminous and rapid granitic magma formation during the arc-arc collision. ICZ granitoids show marked influence of the mature sediments from the Honshu arc during their syncollisional magma formation, which is most compellingly documented by whole-rock Pb isotope, as well as the zircon and whole-rock Th/Nb ratios. The ICZ granitoids show clear spatial distribution in terms of ages and geochemistry, with respect to the E-W Tonoki-Aikawa Tectonic Line (TATL). The plutons north of TATL are older (ca. 16 to ca. 13 Ma) and enriched in incompatible elements, whereas plutons south of TATL are younger (ca. 9 to ca. 4 Ma) and depleted in these elements. These geochemical spatial variations among the ICZ granitoids may reflect the compositional diversity that existed in the primary IBM lower crust that sourced these granitic magmas.

SMP006-02

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## Evidence for contrasting magmatic conditions of A-type granitoids from the Emeishan large igneous province (SW China)

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The Emeishan large igneous province contains a diverse assemblage of igneous rocks including mildly peralkaline granitic rocks of A-type affinity. The granitic rocks from the Panzhihua, Baima and Taihe plutons are temporally, spatially and chemically associated with layered mafic-ultramafic intrusions. Electron microprobe analyses of the major and accessory minerals along with major and trace element data were used to document the magmatic conditions of the three peralkaline plutons. The amphiboles show magmatic/subsolidus trends and are primarily sodic-calcic in composition (i.e. ferrichterite or richterite). Sodic (i.e. riebeckite-arfvedsonite) amphiboles are restricted to the Panzhihua and Taihe plutons. The amphiboles from the Panzhihua and Taihe granites are very similar in composition whereas amphiboles from the Baima syenites have higher MgO wt% and lower FeO wt% and  $\text{TiO}_2$  wt%. Whole-rock Zr saturation temperature estimates indicate the initial average magma temperatures were  $\sim 940 \pm 21$  °C for the Panzhihua pluton,  $\sim 860 \pm 17$  °C for the Baima pluton, and  $\sim 897 \pm 14$  °C for the Taihe pluton. The initial  $F_{\text{melt}}$  (wt%) values were calculated to be  $1.1 \pm 0.1$ ,  $0.8 \pm 0.1$  and  $1.1 \pm 0.1$  wt% for the Panzhihua, Baima and Taihe plutons, respectively. The estimated  $F_{\text{melt}}$  (wt%) values are higher than what can be accounted for in the Panzhihua and Taihe plutons and indicate that they may have lost F during crystallization. In contrast the  $F_{\text{melt}}$  (wt%) value for the Baima pluton can be accounted for. The presence of titanite + magnetite + quartz in the Baima syenites indicates oxidized  $f_{\text{O}_2}$  conditions whereas the presence of aenigmatite and ilmenite in the Panzhihua and Taihe granites indicate that they were relatively reducing. Although the A-type granitoids formed by the same processes (i.e. fractional crystallization of mafic magmas), their differences in major element and mineral chemistry are likely related to a combination of initial bulk magma composition and magmatic oxidation state.

Keywords: A-type granite, Peralkaline, Late Permian, Zr saturation thermometry, Ferrichterite, Aenigmatite

## Magma chamber dynamics in a silicic LIP revealed by quartz zoning

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Crystal zoning of different mineral species represents a response to changing crystallisation conditions and has been used to gain insight into the history of magmas (e.g. Anderson 1976). Growth zones define a crystal stratigraphy (Wiebe 1968) which yields information on the variations of intensive parameters and the relative timing of magmatic processes. Thanks to the development of modern microanalytical techniques, quartz is being increasingly used as a source of petrological information (e.g. Muller et al. 2005; Wark et al. 2007). The main advantages of quartz in comparison with other minerals are its chemical stability and physical strength.

This study is focussed on the characterisation of quartz populations in the Mesoproterozoic Gawler Range Volcanics (GRV) and Hiltaba Suite (HS) granite of South Australia on the basis of texture, cathodoluminescence (CL), and trace element content. The volcano-plutonic province (Gawler SLIP) is a silicic-dominated large igneous province emplaced in an intracontinental setting. The study involves a wide array of quartz occurrences in different, but genetically associated, volcanic and intrusive rocks (lavas, ignimbrites, shallow and deeper intrusions).

Primary (syn-crystallisation) CL textures in quartz are better preserved in rapidly cooled volcanic and hypabyssal units than in slowly cooled granite samples. Intersection relationships of CL textures indicate episodes of growth and resorption. The dykes have homogeneous quartz populations, and CL zones can be correlated among quartz phenocrysts within single dykes. The volcanic units contain multiple quartz populations coexisting in the same sample. Each of these populations records a complex history of crystallisation and resorption events. Both the dykes and the volcanic units contain quartz crystals with CL-bright, Ti-rich rims that truncate internal growth textures (reverse zoning).

CL zones are characterised by different trace element (Al, Ti, Fe) content, and CL brightness is correlated with Ti content. Because of the relation between Ti content of quartz and crystallisation temperature (Ti-in-quartz geothermometer; Wark and Watson, 2006), CL can be used as a proxy for temperature. Based on Ti content, crystallisation temperature of dykes and volcanic units can be estimated in the range 740-870°C. Significant variations in Ti content between adjacent zones were measured (?80 ppm), corresponding to  $\Delta T \approx 180^\circ\text{C}$  in crystallisation temperature. The largest variations were measured between the bright rim and the core in volcanic units.

The homogeneity of quartz populations in single dykes is interpreted as evidence that quartz crystals shared the same crystallisation history and probably crystallised largely after isolation of these small magma batches in separate intrusions. The volcanic units tapped a larger part of the magma characterised by a dynamic regime which resulted in juxtaposition of different quartz populations, each with different crystallisation histories. Alternating events of crystallisation and resorption, reverse zoning, and partially melted granite enclaves in volcanic units are consistent with non-monotonous thermal evolution of the GRV-HS magma and suggest the occurrence of different thermal pulses. The described textural features are best explained by re-heating and convective stirring of the magma chamber (self-mixing; Couch et al. 2001). Heat input represented both the engine for convection and the cause of re-melting of previously crystallised magma, and was possibly supplied by underplating of mafic magma.

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Keywords: quartz, rhyolite, cathodoluminescence, crystal stratigraphy

SMP006-04

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## Several patterns of evolution course of magma feeding system in Zao volcano newest stage, NE Japan

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### 1. Introduction

Based on chemical and textural data of phenocrystic minerals coupled with volcanic stratigraphy, we revealed several patterns of magmatic evolution course in the Zao newest stage. Eruptive products of the newest stage are classified into Komakusadaira agglutinate (ca. 33-12.9 ka), Umanose agglutinate (ca. 7.5-4.1 ka), and Goshikidake pyroclastic rock (ca. 2.0-0.4 ka). Komakusadaira agglutinate is further divided into Komakusadaira pyroclastics, Kumanodake agglutinate, and Kattadake pyroclastic rocks. In this study we will show the case of the Komakusadaira pyroclastics, whose activity is divided into five periods (1-5).

### 2. Mixing origin of the products

The rocks are calc-alkaline, medium-K mixed basaltic andesite to andesite (55-59% SiO<sub>2</sub>). In most of SiO<sub>2</sub> variation diagrams, data are plotted on linear trends, which is suggesting basically two end-members mixing origin. Based on chemical and textural data, phenocrystic minerals are classified into three groups: (1) felsic end-member derived, (2) mafic end-member derived, and (3) intermediate. The intermediate phenocrysts are considered to be crystallized in mixed magmas. These phenocrysts in most of periods show quenched texture and are small in size, but those in period 2 do not show such texture and the size is similar to that of group 1 phenocrysts.

3. Temporal change of chemical compositions of phenocrystic minerals and whole rock In periods 1 and 5 samples, groups 1 and 2 phenocrysts are dominant and the amount of the latter ones increase toward upper part. In periods 3 and 4, groups 1 and 2 phenocrysts are also dominant but the Mg# or An% of the group 1 phenocrysts gradually increase toward upper part. In period 2, intermediate phenocrysts are dominant with minor amount of groups 1 and 2 phenocrysts in the lower part, and the amount of group 2 and 3 phenocrysts get higher in upper part. Generally, bulk SiO<sub>2</sub> and incompatible elements contents decrease with time in each period: 58->56, 56.2->55.7, 58->56.2, 58->56.3 and 59->57.8% SiO<sub>2</sub> in periods 1 to 5, respectively.

### 4. Three patterns of magma evolution course of Zao newest activity

Examining above mentioned petrologic features, following three courses of magma evolution have been defined. (1) Basal portion of the colder and high crystallinity felsic magma was withdrawn by the forced injection of the mafic magma and these were mixed in the conduit (periods 1 and 5). The ratio of mafic magma involved in the mixing would increase with time. (2) Intermediate magma formed by the mixing between infused mafic magma and felsic magma at the base of shallow chamber, ascended buoyantly to the chamber top. The intermediate magma erupted, thereby withdrawing felsic magma in upper part of the chamber. The percentage of the intermediate magma involved in the eruptions decreased with time, which corresponds to the increased percentage of the mafic magma which would reactivate the felsic magma (period 2). (3) By repeated injection of mafic magma, the shallow felsic chamber gradually changed in composition toward intermediate (periods 3 and 4). The mixed magma erupted intermittently after the repeated injections.

Keywords: evolution of magma feeding system, magma chamber, mineral chemistry, magma mixing, Zao volcano, northeast Japan

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## High precision olivine analysis using Electron Probe Micro Analyzer

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Concentrations of minor elements Ni and Mn in olivine phenocrysts enable the degree of fractional crystallization to be calculated using bulk volcanic rock geochemistry. This then allows the primary magma compositions of the magma that the olivines have crystallized from to be reconstructed (e.g., Tatsumi et al., 1983; Takahashi, 1986; Machida et al., 2008). Furthermore, high precision Mn and Fe concentrations in olivine allow the contribution from recycled lithosphere to magma genesis to be estimated (Sobolev et al., 2007). Ni and Mn can be routinely analyzed by an Electron Probe Micro Analyzer (EPMA) together with major elements using an accelerating voltage of 15kV and a probe current of 12 nA. However, under these conditions Ni and Mn concentrations have a large uncertainty. In contrast, while a high accelerating voltage (20kV) and probe currents (300 nA) with long counting times (more than 90 seconds on peak) provide precise Ni and Mn data, this set up usually results in over estimations of the major elements. This is related to the choice of primary standard used in the calibration of the EPMA. Rather than using wollastonite for Si, magnesium oxide for Mg, and hematite for Fe, the use of natural olivine standards, such as San Carlos olivine (Jarosewich et al., 1980), allow major and minor elements in olivine to be measured contemporaneously under the conditions for high precision analysis. After applying this analytical protocol to the analysis of olivines in basalts from petit-spot, it is suggested that recycled lithosphere derived-melt contributes generally makes up more than 90% of the source of petit-spot magmas.

Keywords: Electron Probe Micro Analyzer, olivine, petit-spot

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## Trace element concentrations in ocean floor peridotites: the pursuit of real mantle signatures

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Ocean floor peridotites are usually variably serpentinized and weathered, resulting in a wide range of modifications in both major and trace element abundances and isotopic compositions (e.g., Morishita et al., 2009 *J. Petrol.* 50, 1299-1325, and references therein). Serpentine acts as an important sink for H<sub>2</sub>O and fluid-mobile elements and, therefore, is crucial for global geochemical cycling. On the other hand, elemental mobilization during serpentinization of peridotite masks mantle geochemical signatures. In-situ chemical analysis of minerals is required to obtain geochemical characteristics of primary mantle minerals. Optical microscope observation of thin sections permits investigation of heterogeneity within grains such as zoning, exsolution and presence of inclusions, alterations and etc. Light elements (Li, Be, B: LE hereafter) are potentially powerful geochemical tracers of fluid fluxes during metamorphism, metasomatism and partial melting, particularly at ARC setting (e.g., Bebout et al., 1999 *EPSL* 171, 63-81). However, in-situ determination of LEs in common minerals is not an easy task because of their low-abundances. Secondary ion mass spectrometry (SIMS) is currently the widely used technique for the in situ determination of trace element compositions in geological minerals. In SIMS analysis, the analytical time is relatively long, and complex matrix-related interference corrections are often required to obtain accurate results. In the last decade, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become a powerful and flexible analytical technique for in-situ elemental and isotopic determination of solid materials. The latest generation of high sensitivity ICP-MS is capable of detecting LEs at trace levels with laser ablation sampling (Tiepolo et al., 2005 *Geostand. Geoanal. Res.*, 29, 107-122). In fact, many laboratories have analyzed LE abundances in minerals with LA-ICP-MS (Lee et al., 2008 *G3*, doi:10.1029/2008GC002078). A significant difference between SIMS and LA-ICP-MS is the volume of material sampled during an analysis, with laser-ablation consuming significantly more material than SIMS. We have been examining the similarities and differences in petrological and mineralogical characteristics of ocean floor peridotites between mid-ocean ridge (MOR) and forearc (F-ARC) settings using SIMS and LA-ICPMS methods. We sometimes found a wide range of variation in some trace element compositions (particularly in LEs) of nominally unaltered minerals. In the presentation, we would like to introduce some example of uptake for some elements in minerals with high-resolution FE-EPMA observations, and show our preliminary results on real mantle geochemical signatures.

Keywords: Ocean floor peridotite, SIMS, LA-ICPMS, FE-EPMA



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## Nanolites in volcanic ash: a clue to understand gas pocket processes in the on-going Sakurajima eruption

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Our understanding of magma ascent processes has been greatly improved by focusing on the dehydration-induced crystallization of microlites in volcanic rocks. In the magmas underwent extensive undercooling at low pressure, the microlite crystallization is followed by appearance of sub-micron scale acicular crystals. The presence of those minute crystals in the groundmass of relatively slowly-cooled magmas has long been known through optical microscopic observation as cryptocrystalline texture. Sharp et al (1996) explicitly defined the pyroxene and plagioclase crystals with width  $< 0.6$  micrometer in the Ben Lomondo rhyolite lava dome as "nanolites". In this study, we report occurrence of nanolites in the juvenile micropumices erupted from Vulcanian explosions of Sakurajima volcano, Kyushu Japan, and propose that they may be a clue to clarify the processes in the "gas pockets" in shallow conduit, which is central to the mechanisms of Vulcanian explosion.

We investigated the volcanic ashes erupted from the Showa crater on February 16, 2010. Besides the highly oxidized and hydrothermally altered lithic fragments, three types of grains were identified in the ashes: (A) vesicular, light-colored micropumices, (B) less-vesicular dark-colored pumices and (C) dense lava fragments. Because their groundmass compositions are almost the same, all the three types are concluded to be juvenile. The groundmass crystallinity increases in the order from A to C. (FE-)SEM observations revealed that acicular pyroxene crystals with length of a few to 10 micrometers and widths from hundreds nanometers to  $\sim 1$  micrometer are in particular responsible for the increase in the crystallinity and decrease in the sample brightness. Such pyroxene "nanolites" are rich in the Tschermack component, suggesting that they rapidly crystallized under large supercooling. Considering that effusions of such grains had occurred continuously for the period, a few times a day, we assume that their crystallization was driven by undercooling caused not by cooling but by dehydration of the hydrous melt in the shallow conduit (A and B- types) and lava caps (C-type) in the Showa crater. The observed eruption interval may constrain the timescale of nanolites crystallization from the supercooled melt and limit the temperature range. Existence of vesicular materials at low pressure and high-temperature environment indicates that the gas pocket was formed in the shallow conduit, as has been required in terms of the explosion dynamics.

In order to understand the crystallization conditions of the nanolites quantitatively, we have started annealing experiments of the vesicular pumice samples. As a starting material, we have used the pumice clasts erupted in the Plinian eruption in 1914. Its bulk-chemical and ground compositions approximate those of the on-going eruption. The water content in the groundmass glass is ca. 0.5 wt. %. The experiments are carried out in the air and in evacuated silica glass tubes with NNO buffer at a temperature ranging from 1000 to 400 degree C for 0.5 to 8 hours. In the run products of preliminary experiments at 1000 degree C, systematic increase in the amount of Al-rich pyroxene nanolites was observed. We are conducting further experiments to find temperature and time conditions that reproduce the chemical composition, shape and number density of the natural nanolites in the ashes from the Showa crater.

Keywords: Vulcanian eruption, Sakurajima, gas pocket, volcanic ash, nanolite

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## Polybaric degassing of island arc low-K tholeiitic basalt recorded in OH concentrations of Ca-rich plagioclase

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Among hydrous magmas in subduction zones, island arc low-K tholeiitic basalts have been characterized by low H<sub>2</sub>O contents, approximately 1 wt.% H<sub>2</sub>O, based on melt inclusion analyses and phase equilibria studies. However, melting experiments of hydrous basaltic magmas require higher amounts of H<sub>2</sub>O to crystallize Ca-rich plagioclase, which is commonly observed mineral in island arc low-K tholeiitic basalts. The estimated values of H<sub>2</sub>O content of low-K tholeiitic magma by different approaches are not consistent. Hydrogen in nominally-anhydrous minerals (NAMs) can be an alternative indicator of dissolved H<sub>2</sub>O in magma and degassing history of magma during ascent. Plagioclase is one of the NAMs which accommodates hydrogen up to hundreds of wt. ppm H<sub>2</sub>O in it. The speciation of hydrogen in volcanic plagioclase is demonstrated to be structural OH. In this study, we analyzed OH concentration in Ca-rich plagioclase from the summit eruptions of Izu-Oshima volcano, a frontal-arc volcanic in Izu arc and issues island arc tholeiitic basalt, during 1986 and 1987. The OH concentrations of plagioclase were analyzed by polarized infrared spectroscopy, which ranged from 20 to 300 wt. ppm H<sub>2</sub>O. Three distributions of OH concentrations, 20-80 wt. ppm H<sub>2</sub>O, 100-180 wt. ppm H<sub>2</sub>O, and 220-300 wt. ppm H<sub>2</sub>O, were found. Variation in the OH concentrations can be explained by the fact that plagioclase had been finally equilibrated with H<sub>2</sub>O-saturated melt at three depths beneath the Izu-Oshima volcano; melt under almost atmospheric pressure (1 wt.% H<sub>2</sub>O), at the 4-km deep magma chamber (3 wt.% H<sub>2</sub>O), and the 8-10-km deep magma chamber (5 wt.% H<sub>2</sub>O), respectively. Assuming such polybaric degassing from H<sub>2</sub>O-saturated island arc tholeiitic basalts will explain so-called "excess SO<sub>2</sub> degassing", which has been proposed in many arc volcanoes, because SO<sub>2</sub> is preferentially partitioned into degassed H<sub>2</sub>O bubbles. We suggest that more H<sub>2</sub>O comes from the upper mantle in subduction zones than ever postulated that island arc low-K tholeiitic basalt is H<sub>2</sub>O-undersaturated or H<sub>2</sub>O-poor.

Keywords: water in nominally-anhydrous mineral, island arc low-K tholeiite, volcanic front, Ca-rich plagioclase



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## Water speciation in silicate melts investigated by Raman spectroscopy: implication for volcanic process

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In addition to temperature, pressure and main chemical components, volatiles exert a strong influence on the physical properties of magmas. In particular, water plays a fundamental role in the dynamics and evolution of magmas in the deep interior and during volcano eruption. However, water speciation in silicate melts is not fully understood. Infrared and NMR spectroscopy had provided some valuable information about the H<sub>2</sub>O/OH- speciation. We already know that this speciation is a function of temperature, pressure, and water contents of melts. However, some issues still remain unsolved about the OH-/H<sub>2</sub>O linkage to the silicate network.

Raman spectroscopy already allows quantifying the proportion of water dissolved in an aluminosilicate melt. Raman spectra are composed of i) a low wave number region that corresponds to vibrations of the silicate network (0-1500 cm<sup>-1</sup>), and ii) a high wave-number region, which corresponds to the OH- stretching vibrations and H<sub>2</sub>O molecular vibrations (3100-3750 cm<sup>-1</sup>). We have performed a first set of in situ experiments using a micro-furnace at ambient atmosphere. An evolution of the high wave-number region in function of the time and temperature of the experiments is observed. New Raman peaks can be distinguished, particularly near 3650-3700 cm<sup>-1</sup>. In this communication, we will present our first results on this subject and then discuss them in term of relation between water and silicate network in melts.

Keywords: Water speciation, Raman spectroscopy, glass, melts

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## Rates and processes of crystallization in on-axis and off-axis MOR basaltic melts

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We obtained FE-EPMA elemental maps and LA-ICPMS-derived Sr profiles of over 60 plagioclase crystals from MOR basalts erupted from ultra-slow to fast spreading ridges (Gakkel, JdF, Gorda, EPR). Besides on-axis lava flow samples, the sample set includes two samples from the JdF Axial Seamount, one from a young off-axis seamount of the JdF Southern Cleft segment, and two from EPR off-axis flows. We derive equilibration times for the relatively rapidly diffusing Sr of the order of months to a few years. Most crystals preserve diffusive disequilibria of strontium. Crystal residence times at MORB magmatic temperatures are thus significantly shorter, of the order of days to a few months at most, precluding prolonged crystal storage in axial magma chambers and instead pointing to rapid crystal growth and cooling (up to about 1 deg. C per hour) shortly prior to eruption of these samples. Crystal growth is therefore inferred to occur mostly during dike injection. However, there are clear differences between different samples: At the fast spreading EPR, on-axis samples yield residence times of mostly < 5 weeks, while off axis samples cluster between 5 and 10 weeks, similar to on axis samples at intermediate spreading rates. One slightly more evolved JdF axial MOR lava yields residence times of mostly > 10 weeks, while for the JdF off-axis seamount, ages > 6 months dominate. In conjunction with the crystal morphological observations, these results provide insights into differences in the tectonomagmatic environments in which these rocks were generated.

Keywords: geospeedometry, MORB, seamount, dyke, magma chamber, residence time

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## Precise Sr isotope microanalysis of plagioclase by LA-MC-ICPMS and its application to the Azuma volcanic rocks, NE Japan

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Sr isotope system is widely applied as a tracer and chronometer in geochemical studies. Variations in Sr isotope ratios recorded in chemical zoning of plagioclase crystals of volcanic rocks provide important information on the magma generation process. In-situ Sr isotope microanalysis on plagioclase by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) has been an effective tool. However its accuracy and precision have been limited mainly by (1) high gas blank from Kr, (2) isobaric overlap of <sup>85</sup>Rb on <sup>86</sup>Sr, and (3) matrix dependent mass bias. We have overcome these problems by applying (1) on peak background subtraction of Kr signal, (2) solution (ARIDUS II)-laser aerosol dual intake system for an accurate overlap correction factor and mass bias factor determinations, and (3) use of an in-house plagioclase external standard (Miyakejima anorthite megacryst, An<sub>95</sub>) with standard-sample bracketing analytical method. We have confirmed that the anorthite standard is chemically and Sr isotopically very homogeneous using EPMA and micro milling (MM)-TIMS methods. All the LA-MC-ICPMS analyses were performed using a 193nm excimer LA system coupled to a MC-ICPMS (Thermo Fisher Scientific NEPTUNE). The spot size used was 200micrometer in both diameter and depth. The same andesite plagioclase phenocryst (An<sub>92</sub>) in a lava from Azuma volcano was analyzed by using LA-MC-ICPMS and MM-TIMS. The results were <sup>87</sup>Sr/<sup>86</sup>Sr = 0.70618±/-.28 (2SE) and 0.70614±/-.36 (2SE), respectively. With the use of above analytical protocols and the matrix-matched external standard, accuracy of an unknown plagioclase improved from +/- 0.0001 to +/- 0.00004 levels in <sup>87</sup>Sr/<sup>86</sup>Sr ratios. We observed systematic discrepancy in the analytical results between solution (SRM987)-based and matrix-matched external corrections. This improvement is due to closer match of the concomitant matrix element between the plagioclase sample and the anorthite standard. Such the mass bias occurs during high mass loading to the ICP plasma by a large volume laser ablation. Use of the anorthite standard is valid for various plagioclase crystals with different An content at least up to An<sub>50</sub>.

Keywords: LA-MC-ICPMS, Sr isotope microanalysis, plagioclase

SMP006-12

Room:303

Time:May 25 17:45-18:00

## Instrumental development on ultraviolet-femtosecond-laser ablation (UV-Fs-LA) and its elemental analysis application

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We have developed a 266/200 nm wavelength ultraviolet-femtosecond-laser ablation (UV-Fs-LA) system using frequency tripled and quadrupled near infrared (800 nm) Fs Ti-sapphire regenerative amplifier LA source (Spectra Physics, Solstice). Laser focusing optics was optimized using a high-power UV objective lens (ThorLab) for 200 nm and an aspherical objective lens (Edmond Optics) for 266 nm in order to compensate Gaussian energy profile of the laser beam. Maximum crater sizes were 30  $\mu\text{m}$  in 200 nm and 90  $\mu\text{m}$  in 266 nm depending on laser fluence threshold on silicates ( $\sim 10\text{J}/\text{cm}^2$ ). Flat bottom crater was not achievable by single spot analysis due to interference of the ultra-short pulse laser. Circular or line raster analysis by moving sample stage improved crater shape and thus signal stability for 60 to 120 sec. Ablation quality becomes comparable to homogenized excimer or Nd-YAG nanosecond lasers. Ultra-short pulse ( $> 300$  fs) combined with UV wavelength minimizes formation of coarse ablation aerosols, thus minimizes aerosol deposition around craters and stabilizes signals detected in mass spectrometer. Combined with a sector field (SF)-ICPMS (Thermo Fischer Scientific, Element XR) with high-sensitivity and wide-dynamic range (up to  $T(10^{12})$  cps) enabled simultaneous analysis of more than 43 elements including major (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>) and trace (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, U) elements from craters 20-50 by 20-50  $\mu\text{m}$  (diameter vs. depth) in size. Analytical precision is normally better than 3% in wt.% to sub-ppm levels. Accuracy is usually within 5%, when matrix matched standard is used (e.g., BCR-2G analysis using BHVO-2G), if not within 15 % (e.g., BCR-2G analysis using SRM612 glass). Accurate analysis of all major elements enables perfect correction of ablation efficiency different between samples. This realizes stand-alone analysis of UV-Fs-LA-SF-ICPMS without assist of electron probe micro analyzer (EPMA) in determining internal standard composition used for ablation efficiency correction. Furthermore, this internally consistent simultaneous major element correction eliminates errors propagated from different sampling volume between the two analytical methods. This advantage can be extended to metal analysis as ultra-short pulse dramatically improves stoichiometric sampling from metallic samples.

Keywords: femtosecond, laser ablation, elemental analysis

SMP006-P01

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## Matrix effect and calibration strategy in trace element analysis of geological glasses using 193 nm excimer LA-ICP-MS

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Quantifying trace elements of solid samples by LA-ICP-MS is usually based on external calibration using a reference material (typically, NIST synthetic glasses SRM 612 and 610) and a predetermined major element composition for correction of ablated mass of the sample and calibration standard. However, chemical and physical properties difference between sample and standard may result in considerable bias, thereby compromise analytical accuracy. Short wavelength and short pulse width of the laser beam (i.e. recently developing trend towards DUV and femto-second laser systems) are supposed to be superior in reducing such matrix biases. Using a 193 nm argon fluoride (ArF) excimer laser ablation system coupled to quadrupole type-ICP-MS, we investigated the elemental responses of various standard glasses ranging from synthetic (SRM 612) to naturally-sourced chemical compositions (GSD-1G, BHVO-2G, and BCR-2G basalt glasses). Our results showed a clear matrix effect affecting on the accuracy of measured trace elements including REEs and HFSEs. Calibration against SRM 612 introduced analytical bias of about 20% from preferred values for the basalt glasses and natural minerals. Accuracies were improved when chemically matched standards were used for calibration. This was also demonstrated by analyzing a set of MPI-DING naturally-sourced glasses. The MPI-DING basalt, andesite and komatiite glasses were accurately determined by using BHVG-2G and BCR-2G basalt standards. Neither SRM 612 glass nor basalt glass standards were appropriate for the MPI-DING rhyolite, although the former gave better results perhaps due to similarly high silica contents. Difference in plasma mass loading of major element from different sample matrices would explain the above observations. It appears that the more silica fraction was introduced into the plasma, the higher the sensitivity enhancement of easily ionized elements occurred. This plasma loading effect greatly affects relative elemental responses, and it is hard to be corrected. Laser fluence apparently influences less on the relative elemental responses. Our results suggest that use of matrix-matched standard is one of the most practical means to achieve accurate analysis of trace elements in geological samples by 193 nm excimer LA-ICP-MS. Glass standards with natural composition (MPI-DING and USGS glass standards) cover a wide compositional range for geological applications (basalt, andesite, rhyolite, komatiite etc.). However, concentrations of some elements are too low for precise calibration. Use of trace element-doped natural rock-based standards potentially improves calibration precision. A caveat in using such the standard is its non-natural elemental abundances, which may additionally introduce unusual interferences on some elements.

Keywords: LA-ICP-MS, trace elements, matrix effect

SMP006-P02

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## Multitple magmatic activities recorded in the mafic and ultramafic xenoliths in the Shingu alkali basaltic dike,SW Japan

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Miocene alkali basaltic dikes in the Shingu area, central Shikoku, brought up abundant crustal and mantle fragments that include information of the petrological structure beneath the region at a beginning of subduction of the Philippine Sea plate. Our detailed petrological examination of the xenoliths revealed that there is a larger geochemical and temporal diversity in magmatism at the east Eurasian continental margin than previously thought. Dunite, which had been probably formed as a cumulate from a basaltic magma, bears small gabbroic domains in the forms of discrete grains with a granoblastic texture (discrete-type) or fine-grained aggregates with an igneous texture (vein-type). From the gabbroic xenoliths, three groups, at least, can be distinguished: Hbl-bearing olivine gabbro (A type), oxide-bearing olivine gabbro (B type) and gabbro-norite (C type). The Hbl-bearing olivine gabbro group includes dunite, olivine clinopyroxenite and olivine gabbro and is characterized by smoky green Cpx partly replaced by reddish brown Hbl. The oxide-bearing olivine gabbro group is characterized by purplish brown Cpx and shows modal layering among olivine clinopyroxenite, clinopyroxenite and gabbro with concentrations of euhedral opaque minerals. The gabbro-norite group is characterized by an association of coarse-grained Opx and Cpx. There are two types of Cpx: Cpx1 with vermicular exsolution of Opx and Cpx2 with minor exsolution. Granular Opx and Cpx2 are followed by crystallization of interstitial Cpx2 and Pl. Mineral chemistry of Pl and Cpx in each gabbroic group shows distinct differentiation trend. This is most apparent in the K content of Pl: Or<sup>2</sup>~3.5 (A type), Or<sup>1</sup>~2 (B type), and Or<sup>3</sup>~9 (C type) in a range from An<sub>40</sub> to An<sub>60</sub>. Brown Cpx in B-type gabbro shows higher Mg# than green Cpx in A-type gabbro at a similar An content. The mineral chemistry of low K and Mg-rich A-type gabbro is in accord with that of phenocrysts in the host alkali basalt. Furthermore, Pl in vein-type gabbroic domains in dunite partly overlaps these trends and possibly represents the most undifferentiated one for three magmatic trends. Petrography and mineral chemistry of gabbros clearly show that they have different origins related to various magma processes in the crust-upper mantle. Correlation of geochemistry of mafic-ultramafic xenoliths will depict a complicate history of the crust-upper mantle evolution in the Shikoku fore-arc region.



SMP006-P03

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## Dunite and wehrlite crystal aggregates in basalts from West Zealandia Seamount, Southern Mariana Volcanic Arc

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West Zealandia Seamount, at approximately 16° 53' N, lies behind the magmatic front of the Mariana Arc. It is part of the Sarigan-Zealandia volcanic complex, a group of mostly submarine volcanoes and parasitic cones, the highest of which are the island of Sarigan (538 m above sea level), and Zealandia Bank, which comes within a few meters of sea level. West Zealandia rises from about 2750 m below sea level to a summit depth of around 750 m and is separated from Zealandia Bank by a saddle that is as deep as 1050 m below sea level. Bathymetric surveys reveal that its summit has an unusual arcuate morphology, while radial ridges that extend for about 10 km from the summit, and may represent lava flows, mark its western and southern slopes. Sampling of the northwestern slopes from 1390-1135 m with the ROV Hyper-Dolphin during NT09-08 was undertaken in June 2009 and recovered primitive basalts, with whole rock MgO and SiO<sub>2</sub> contents of 10.7 wt.% and 47.9 wt.%, respectively. These primitive basalts contain dunite and wehrlite crystalline aggregates, which have been analyzed by electron microprobe (EPMA) for major elements. These analyses paid particular attention to the Ca and Ni contents of the olivine, which can be used to determine whether the aggregates are mantle xenoliths. The NiO contents of the olivine in the aggregates are too low and the CaO contents too high to be in equilibrium with mantle olivine, suggesting that the aggregates are crustal xenocrysts. With Fo<sub>85-91</sub>, the olivines in the crystal aggregates contain 0.15 to 0.24 wt.% NiO, whereas at these Fo contents mantle olivines contain at least 0.28 to 0.36 wt.% NiO, respectively (Takahashi, 1986, Bull. Volcanol. Soc. Japan, 30, S17-S40). Mantle olivines are also characterized by CaO less than 0.1 wt.% (Simkin & Smith, 1970, J. Geol., 78, 304-325); the olivines in the West Zealandia crystal aggregates contain more than 0.15 wt.%. Even so, the high Fo contents of the olivines in the crystal aggregates indicate that they crystallized from a primitive melt, and in addition they contain silicate melt inclusions that may provide access to this melt, and determine whether or not it is primary. As a result, initially the volatile, and then the major and trace element concentrations in the inclusions are being measured by micro-Fourier-transform infrared spectroscopy (FTIR), EPMA and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), respectively. The H<sub>2</sub>O contents of the inclusions range from 3.01 to 4.47 wt.%, with the exception of one inclusion that contains 1.87 wt.%. CO<sub>2</sub> contents range from below detection limits (60 ppm) to 809 ppm. Overall the H<sub>2</sub>O-CO<sub>2</sub> systematics are generally consistent with open system degassing, although a few inclusions require closed system degassing with the initial melt in equilibrium with 5% exsolved vapor. The highest volatile contents indicate entrapment pressures of up to 296 MPa, equivalent to about 11.7 km below sea level, which, beneath West Zealandia, is around the base of the middle crust, top of the lower crust (Takahashi et al., 2007, Geology, 35, 203-206). If so, the West Zealandia crystal aggregates may represent the first ever direct samples of Mariana crust from such depths.

Keywords: olivine, clinopyroxene, crystal aggregates, melt inclusions, major elements, volatiles