

SMP006-01

会場:303

時間:5月25日 14:45-15:00

伊豆小笠原マリアナ弧・伊豆衝突帯における多様な珪長質地殻形成史：ジルコン・全岩化学組成分析からの制約

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.

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

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 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_{melt} (wt%) values were calculated to be 1.1 ± 0.1 , 0.8 ± 0.1 and 1.1 ± 0.1 wt% for the Panzhihua, Baima and Taihe plutons, respectively. The estimated F_{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_{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.

キーワード: A-type granite, Peralkaline, Late Permian, Zr saturation thermometry, Ferrichterite, Aenigmatite

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

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

Anderson, A.T., 1976. *J. Volc. Geoth. Res.*, 1(1): 3-33. Muller, A., Breiter, K., Seltmann, R. and Pecskey, Z., 2005. *Lithos*, 80(1-4): 201-227. Wark, D.A., Hildreth, W., Spear, F.S., Cherniak, D.J. and Watson, E.B., 2007. *Geology*, 35(3): 235-238. Wark, D.A. and Watson, E.B., 2006. *Contrib. Min. Pet.*, 152(6): 743-754. Wiebe, R.A., 1968. *Am. J. Sci.*, 266(8): 690-703.

キーワード: quartz, rhyolite, cathodoluminescence, crystal stratigraphy

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 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% SiO₂). In most of SiO₂ 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 SiO₂ 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% SiO₂ 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.

キーワード: evolution of magma feeding system, magma chamber, mineral chemistry, magma mixing, Zao volcano, northeast Japan

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

SMP006-05

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電子線プローブマイクロアナライザーを用いたかんらん石の高精度分析 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.

キーワード: 電子線プローブマイクロアナライザー, かんらん石, プチスポット
Keywords: Electron Probe Micro Analyzer, olivine, petit-spot

SMP006-06

会場:303

時間:5月25日 16:00-16:15

海洋底かんらん岩の微量元素組成：真のマントル化学組成の追求 Trace element concentrations in ocean floor peridotites: the pursuit of real mantle signatures

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我々は、海洋底で直接採取されたサンプルを用いて、マントルの化学的特徴を明らかにすることを試みている。海洋底かんらん岩は、様々な程度で蛇紋岩化を受けていることから、局所分析による2次変質を免れた初生鉱物領域の分析が必須である。そこで、SIMS, LA-ICPMSを用いて、微量元素測定を行っている。特に、軽元素に着目すると、しばしば測定値が大きく変動する。発表では、我々が分析する上で直面している問題点と、現在わかってきた化学的特徴について簡単に紹介したい。

キーワード: 海洋底かんらん岩, 2次イオン質量分析計, レーザーアブレーション-ICPMS, フィールドエミッション電子顕微鏡

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

SMP006-07

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時間:5月25日 16:30-16:45

火山灰に含まれるナノライトから探る桜島のガス溜まりプロセス 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 ~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.

キーワード: ブルカノ式噴火, 桜島, ガス溜まり, 火山灰, ナノライト

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

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水に飽和した島弧低カリウムソレイト玄武岩マグマ：斜長石斑晶のOH含有量からの制約

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 H₂O contents, approximately 1 wt.% H₂O, based on melt inclusion analyses and phase equilibria studies. However, melting experiments of hydrous basaltic magmas require higher amounts of H₂O to crystallize Ca-rich plagioclase, which is commonly observed mineral in island arc low-K tholeiitic basalts. The estimated H₂O 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 H₂O in magma and degassing history of magma during ascent. Plagioclase is one of the NAMs which accommodates hydrogen up to hundreds of wt. ppm H₂O 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 H₂O. Three distributions of OH concentrations, 20-80 wt. ppm H₂O, 100-180 wt. ppm H₂O, and 220-300 wt. ppm H₂O, were found. Variation in the OH concentrations can be explained by the fact that plagioclase had been finally equilibrated with H₂O-saturated melt at three depths beneath the Izu-Oshima volcano; melt under almost atmospheric pressure (1 wt.% H₂O), at the 4-km deep magma chamber (3 wt.% H₂O), and the 8-10-km deep magma chamber (5 wt.% H₂O), respectively. Assuming such polybaric degassing from H₂O-saturated island arc tholeiitic basalts will explain so-called "excess SO₂ degassing", which has been proposed in many arc volcanoes, because SO₂ is preferentially partitioned into degassed H₂O bubbles. We suggest that more H₂O comes from the upper mantle in subduction zones than ever postulated that they are H₂O-undersaturated or H₂O-poor.

キーワード: 無水鉱物中の水, 島弧低カリウムソレイト, 火山フロント, Ca に富む斜長石

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

SMP006-09

会場:303

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

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 H₂O/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-/H₂O 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⁻¹), and ii) a high wave-number region, which corresponds to the OH- stretching vibrations and H₂O molecular vibrations (3100-3750 cm⁻¹). 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⁻¹. 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.

キーワード: Water speciation, Raman spectroscopy, glass, melts
Keywords: Water speciation, Raman spectroscopy, glass, melts

SMP006-10

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

キーワード: geospeedometry, MORB, seamount, dyke, magma chamber, residence time

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

SMP006-11

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時間:5月25日 17:30-17:45

Precise Sr isotope microanalysis of plagioclase by LA-MC-ICPMS and its application to the Azuma volcanic rocks, NE Japan 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 ⁸⁵Rb on ⁸⁶Sr, 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, An₉₅) 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 (An₉₂) in a lava from Azuma volcano was analyzed by using LA-MC-ICPMS and MM-TIMS. The results were ⁸⁷Sr/⁸⁶Sr = 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 ⁸⁷Sr/⁸⁶Sr 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 An₅₀.

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

SMP006-12

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紫外フェムト秒レーザーアブレーション装置の開発と元素分析へのアプリケーション

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 μm in 200 nm and 90 μm 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 ($> 300\text{ fs}$) 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 (SiO₂, TiO₂, Al₂O₃, Fe, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅) 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 μm (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.

キーワード: フェムト秒, レーザーアブレーション, 元素分析

Keywords: femtosecond, laser ablation, elemental analysis