

Trace element composition in zircons from A-type granitoids in the Cape Ashizuri, SW Japan: Implications for new source rock index using zircon

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Trace element composition in zircon is expected to be an important indicator of composition of host magma, especially of Hadean detrital zircons (e.g. Grimes et al., 2007). Some Hadean detrital zircons are suggested to be formed in continental crustal magma (e.g. Valley et al., 2005; Grimes et al., 2007), however, detail composition of host magma is still unveiled. Recent discoveries of granitic clast in meteorites in Early Solar System (lunar, HED and LL meteorite) showing anhydrous, alkali-rich A-type granitic affinities (e.g. Warren et al., 1983; Bonin et al., 2002; Terada and Bischoff, 2009) implies that A-type granitic rocks were present in the Hadean Earth (Bonin et al., 2007). Therefore, it is important to know trace element characteristics in zircons from A-type granite for exploring evidence of the ancient A-type granitic rocks.

To obtain primary features of trace element composition in zircons from A-type granite, we conducted *in-situ* LA-ICP-MS trace element analysis for 47 zircon grains from 4 samples of rapakivi granite, Qtz-syenite and melanocratic syenite in the Ashizuri complex. These alkalic granitoids in Ashizuri complex have characteristics of A-type granite (Loiselle and Wones, 1979) and within-plate granite (Pearce et al., 1984), and is suggested to be formed dominantly by crystal fractionation process from OIB-type basaltic magma (Stein et al., 1996).

Zircons from the Ashizuri A-type granitoids show oscillatory zoning, homogeneous dark core, disturbed texture and patchy texture in Cathodoluminescence images. Based on the typical igneous REE patterns (HREE enrichment, negative Eu anomaly and positive Ce anomaly) and its similarity each other in zircons from rapakivi granite and Qtz-syenite, it is suggested that the trace element composition of the zircons reflect those of the host magma. On the other hand, some zircons in melanocratic syenite show large variations of REE pattern and include obvious inherited cores, which imply contamination of surrounding rocks to host magma. To clarify characteristics of zircons crystallized from A-type granitic magma, we only use data from the rapakivi granite and the Qtz-syenite for comparison with previous data from other type (S-, I-, M-type) granitic rocks.

The magmatic zircons from the Ashizuri A-type granitoids show large Eu negative anomalies ($Eu/Eu^* = <0.004 - 0.070$), high Nb contents (2.85 -236 ppm), relatively high Y (423 -13520 ppm) and U contents (171 -7908 ppm), and relatively low Sr contents (0.08 -2.38 ppm). These trace element feature in the zircons probably reflect high HFSE, low Eu and Sr concentration in the host A-type granitic magma. The geochemical characteristics of the zircons from Ashizuri complex become more distinct in Eu/Eu^* , Nb/Sr, U/Sr, Y/Sr cross-plot diagram, showing lower Eu/Eu^* , higher Nb/Sr, U/Sr and Y/Sr ratio compared to those in zircons from other type granitic rocks. Previous trace element data in zircons from A-type granitoids in Delamerian Orogen, South Australia (Pankhurst et al. 2013) is also plotted on similar area to the Ashizuri A-type granitoids in Eu/Eu^* vs. Nb diagram. Because high HFSE, low Eu and Sr contents are common feature in the A-type granitic rocks, these diagrams are probably useful for distinguish zircons crystallized in A-type granite from those in other granitic rocks.

Keywords: Zircon trace element composition, A-type granite, LA-ICP-MS, the Cape Ashizuri, SW Japan

Geochemistry of monazite in granitic rocks from Japanese island arc

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Monazite is a one of rare earth element (REE)-rich phosphate mineral and commonly occurs in pelitic metamorphic rocks and peraluminous igneous rocks (Williams et al., 2007). Geochemistry of metamorphic monazite has been intensively investigated using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS) and its REE pattern, especially Eu negative anomaly ($[Eu/Eu^*]_N$) and heavy REE (HREE) depletion ($[Gd/Lu]_N$), is linked to the crystallization condition (e.g., Rubatto et al., 2006). In contrast, the geochemical investigation of igneous monazite has been mainly carried out using electron-microprobe analysis (EMP) (e.g., Kelts et al., 2008). Hoshino et al. (2012) analyzed the monazites in granites and pegmatites from Japan by EMP. They found that the ratios of light REE (LREE) to middle REE (MREE) on the monazites are different between ilmenite- and magnetite- series granitic rocks, which was interpreted to reflect the different degree of differentiation. Yet, the determination of Eu and HREE abundances have not been carried out due to the interference and low-concentrations during EMP analysis. In this study, we have used LA-ICP-MS to measure Eu and HREE abundances in the monazites and examined whether Eu anomaly and HREE depletion exhibit consistent variations with LREE or not. The results of monazite REE analysis using LA-ICPMS shows distinct REE patterns between the monazites from ilmenite-series and magnetite-series granitic pegmatites. The Eu negative anomalies of the igneous monazites were significantly large ($[Eu/Eu^*]_N < 10^{-3}$) relative to those of metamorphic monazites. This feature may be used as indicator to distinguish between a monazite in pegmatite and a one in metamorphic rock. Among the monazites of the two series, the $[Eu/Eu^*]_N$ values of ilmenite-series monazites are larger by one or two orders of magnitude than those of magnetite-series monazites. The REE patterns of monazites in ilmenite-series rocks display moderate decrease from La to Gd relative to those of monazites in magnetite-series rocks; in contrast, the monazite REE patterns of ilmenite-series rocks show prominent decrease from Gd to Lu relative to those of magnetite-series rocks. These different features in REE patterns between monazites from ilmenite-series and magnetite-series would reflect the degree of differentiation and imply that the formation of ilmenite-series rocks is attributed to not only assimilation of sediments but also crystal fractionation, especially the fractionation of minerals incorporating HREEs relative to MREEs. The relatively enriched MREE and depleted HREE abundances in ilmenite-series monazite cannot be explained simply by assimilation of subducted sediments, which are enriched in both MREE and HREE (Plank and Langmuir, 1998). This inference is consistent with the differences of O, Sr and Nd isotopic features between two-series granitic rocks (Takagi, 2004). We consider that fractional crystallization of the minerals enriched in HREE relative to MREE (e.g., garnet) subsequent to sedimentary assimilation defines the characteristic monazite REE patterns of the magnetite-series and ilmenite-series granitic rocks in Japanese island arc.

Keywords: REE, trace element, LA-ICP-MS

Highly siderophile element variations in the Ontong Java Plateau basalts

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The Early Cretaceous Ontong Java Plateau is widely recognized as a product of the largest igneous activity on the Earth, and its formation and evolution has been investigated by multidisciplinary approaches in order to understand large igneous provinces (LIPs) in general. Recent geochemical studies suggest that the Ontong Java Plateau has sampled a near-primitive, less degassed deep mantle reservoir that has remained isolated from convecting upper mantle shortly after the formation of the Earth. Since such primitive reservoir is possibly only available at the base of lower mantle in the modern Earth, the plateau-forming lavas may have characteristic compositions of highly siderophile elements reflecting the deep-plume source likely influenced by core formation or core-mantle interaction. Here we report comprehensive dataset of Re-Os isotopes and highly siderophile element (HSE: Os, Ir, Ru, Pt, Pd and Re) concentrations for all three distinct geochemical types of the Ontong Java Plateau basalts. They are comprised of 11 samples of the less evolved Kroenke-type lavas (>8 wt.% MgO) from two deep sea drill sites (ODP Sites 1185 and 1187), 22 samples of the more dominant Kwaimbaita-type basalts (<8 wt.% MgO) from three drill sites (ODP Sites 1183, 1185 and 1186) and on-land exposure in Malaita, Solomon Islands and 22 samples of less voluminous Singgalo-type basalts (<8 wt.% MgO with a few exceptions) forming younger cover on the Kwaimbaita-types lavas at an ODP Site 807 and Malaita. All of Kroenke- and most of Kwaimbaita-type basalt data yield a linear array on the Re-Os isochron diagram corresponding to an age of 121.5 ± 3.1 Ma and initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1304 ± 0.0049 , almost identical to those reported in previous studies. Singgalo-type basalts tend to show variably radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ ratios, indicating contributions of enriched components either derived from surficial environments or from radiogenic pyroxenitic source. Significant contributions of pyroxenitic source is inferred from the observation that Singgalo-type lavas have distinctively lower platinum-group element (PGE) abundances when compared with similarly evolved Kwaimbaita-type basalts, although sulfide-fractionation may have played a role on their depletions. The chondrite-normalized HSE patterns of Kroenke- and Kwaimbaita-type basalts show broadly similar IPGE-depleted and PPGE-enriched patterns typical of sulfur-undersaturated tholeiitic basalts. However, the two types can be distinguished by contrasting Os and Ru abundances (Kroenke: high, Kwaimbaita: low) probably reflecting the different degrees of olivine/spinel fractionation. Since the observed HSE fractionation trend (particularly Ir variation) is significantly different from those identified for Hawaiian picrites or Archean komatiites, further constraints on HSE behavior during magma evolution are clearly required for estimating HSE compositions of primitive magma and source mantle.

Keywords: Large Igneous Provinces, basalt, Platinum-group elements

Os isotope ratios and PGE abundances of the Pitcairn basalts: Implication for the EM-1 source

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It is widely known that subduction recycled materials are involved in producing the chemical and isotopic heterogeneities observed in oceanic island basalts (OIB). The type of recycled material present in the Enriched Mantle 1 (EM-1) source, which have radiogenic Sr, unradiogenic Nd, and unradiogenic Pb isotope compositions compared to those of depleted mantle source, has been widely debated. Oceanic crust with pelagic sediment (e.g., Chauvel et al., 1992), delaminated subcontinental lithospheric mantle (SCLM) (e.g., Hauri and Hart, 1993), subducted oceanic plateaus (Gasperini et al., 2000) and just single melting process involving pristine mantle (Collerson et al., 2010) have all been invoked as the EM-1 source. The rocks from Pitcairn hotspot are well known to have a strong EM-1 flavor. Recently, Garapic et al. (2015) suggested that the high Ti abundances in the Pitcairn basalts are possibly related to recycled pyroxenites in the Pitcairn mantle source. We have measured Os isotope ratios and major and trace element abundances including the platinum group elements (PGE) in the basalts from Pitcairn Island to elucidate the origin of the EM-1 signature of these basalts.

The Os isotope ratios for the samples with Os > 20 pg/g range from 0.135 to 0.152 and are similar to those measured in previous studies on EM-1-type basalts (~0.150 for samples with Os > 50 pg/g and ~0.180 with Os > 20 pg/g from Reisberg et al., 1993; Eisele et al., 2002; Garapic et al., 2015). The Os, Ir and Ru concentrations of the Pitcairn basalts are roughly correlated with MgO and Ni contents and tend to be lower than those of other OIB such as Hawaii and Canary Islands. Whereas Pd and Re concentration are similar to those for other OIBs. The chondrite-normalized PGE patterns of studied samples show systematic variation with or against the degree of the EM-1 flavor (e.g., decreasing of the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios). Since crustal materials normally show large fractionation between I-PGE and P-PGE and the crustal materials have higher Os isotope ratios than mantle, the simple assimilation of crustal materials cannot explain our data. We carefully try to make an assumption of the source magma components to explain the genesis of Pitcairn Island basalts based on our data combined with previous studies.

Keywords: PGE abundances, Os isotope ratio, EM-1

Geochemical study of melt inclusions in Pitcairn basalts, South Pacific

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The existence of water and volatile element is important in thinking about mantle dynamics, and a lot of trials limiting volatile element content and distribution in mantle from the volcanic rock from mantle are made. In this study, we analyzed major element, trace element, volatile element, lead isotope at local site for the olivine melt inclusions that they were thought that had volatile element. As a result, we obtained a preliminary result about melt inclusions from the Pitcairn island, South Pacific. The isotope composition of the volcanic rocks of Pitcairn island show composition range to EM1 from DM. We chose two EM1-like basalt rock samples of PC-41 and PC-87A in this study, and prepared melt inclusions more than 50 μ m to analyze a local site by some analyzers. Each melt inclusion varied in a characteristic, and there were two kinds which crystallized amphibole and ilmenite and crystallized euhedral clinopyroxene in melt inclusions of PC-41. Melt inclusion of PC-87A includes homogeneous glass or dendritic clinopyroxene equally. Therefore the analysis domain set it from the mineral which crystallized to the maximum in remote glass or the foundation stone domain. Firstly we measured volatile elements (H₂O, CO₂, F, P, S, Cl) at a 30 μ m diameter and lead isotope at a 30 μ m diameter using SIMS (IMS 1280-HR). In the next place, I measured main element at 10 μ m diameter using FE-EPMA. Finally I measured about a major element and trace element at 20 μ m or a 30 μ m diameter using LA-ICP-MS. There was not the difference with PC-41 and PC-87A about lead isotope ratio, and they were in the isotope ratio range same as all rocks. However, there was difference in both about the elementary composition. Compared with MgO and other major elements, PC-87A shows in same trend as all rock composition, but PC-41 clearly shows two different trends. Because these two trends of PC-41 relate to the difference in crystallized out minerals, they separated by crystallization after melt inclusions trapped by olivine. In adding PC-41 is congruent with crystallization advancing to MgO being lower than PC-87A more in PC-41. About trace elements, PC-87A accorded for the composition of all rocks, however there was different composition from like PC-87A in PC-41. Difference of two compositions in PC-41 were not concerned with crystallization and major elements. The latter has low HREE in characteristically, this seems that the melt coexisted with garnet under high pressure flows into the magma reservoir and produces heterogeneity of the composition in magma reservoir. About volatile elements, there is remarkable difference of quantity of H₂O in PC-41 and PC-87A. PC-41 has 0.03-0.10 wt.% and a low value whereas PC-87A has 0.37-0.81 wt.% . CO₂ does not maintain original value by degassing and enrichment of the gas phase. Halogen elements is hard to relatively degass, for example Cl has high 570-1700ppm and correlates with H₂O and other trace elements, and seems reflect composition of the mantle source. In conclusion, quenched homogeneous melt inclusions such as PC-87A seems maintain information of deep mantle, and are important in estimating H₂O and volatile elements composition from melt inclusions in the mantle source. Melt inclusions crystallized out well such as PC-41, however, greatly lost H₂O in degassing and diffusive process and are difficult to estimate composition of the primary magma.

Origin of geochemical mantle reservoirs: Roles of subduction filter and thermal evolution of mantle

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Upwelling mantle melts at Mid-Ocean Ridges (MOR) to form basaltic igneous oceanic crust (IOC). IOC and overlying sediment (SED) descend into the mantle at subduction zones (SZ). The IOC, SED, and overriding mantle melt to form stable continental crust (CC) after crustal-level processing, whereas the residual slab is recycled into the lower mantle. We quantitatively explore the element re-distributions at MOR and SZ using numerical mass balance models, and we evaluate their roles in the Earth's geochemical cycle. Our models of slab residues differ from previous ones by being internally consistent with geodynamic models of modern arcs and successful explanations of modern arc magma genesis, and by including element fluxes from the dehydration or melting of each underlying slab component. We find that the upper mantle potential temperature (T_p) was 1400–1650 °C from 3.5 to 1.7 Gyr before decreasing gradually to ~1300 °C today. Hot SZs with T_p ~1600 °C have a thermal structure like modern SW Japan where high-Mg andesite is formed that is like CC. Isotopically, residual IOC from hot SZ evolves to the HIMU OIB reservoir, residual SED to EMII, the residual base of the mantle wedge to EMI, and the residual top of the mantle wedge to the subcontinental lithosphere (SCLM) reservoir, after 1.7–2.5 Gyr of storage in the lower mantle. The Common (C) or Focal Zone (FOZO) reservoir is a stable mixture of the first three residues. Older recycled residues (~2.5 Gyr) form the DUPAL anomaly in the southern hemisphere, whereas younger ones (~1.7 Gyr) are in the northern hemisphere. These ages correspond to major CC forming events. We attribute the E-W heterogeneity of the depleted upper mantle (DMM) to involvement of sub-Gondwana SCLM except in the Pacific.

Keywords: Mantle reservoir, Subduction zone filter, Thermal evolution of mantle