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Nano-SIMS U-Pb zircons dating and geochemistry of from alnöite in Malaita, Solomon Islands

Kouki Kitajima[1], Akira Ishikawa[2], Shigenori Maruyama[3] and Yuji Sano[1]
[1]*Center for Advanced Marine Research, Ocean Research Institute, The University of Tokyo, Tokyo, Japan*
[2]*Dept. of Earth Sciences, Durham University, Durham, UK*
[3]*Dept. of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan*

Kimberlite-hosted zircons commonly occurring as a member of low-Cr megacryst suites have proven useful for U-Pb dating which is believed to provide the time of kimberlite eruption, either because of contemporaneous formation, or cooling below the closure temperature of Pb in zircon (e.g. Davis, 1977; Davis *et al.*, 1976). However, several kimberlite localities are known to have both a contemporaneous and a much older zircon population (e.g. Kinny *et al.*, 1989; Zartman and Richardson, 2005), implying that the quantification of the age distribution is the key to understand the enigmatic origin of the mantle-sourced zircon. The main impediment to obtaining large numbers of age data is the analytical difficulty associated with significantly lower U and radiogenic Pb contents than crustal zircon, which requires time-consuming task of digesting relatively large amount of zircons using highly purified chemical reagents in a clean environment. Furthermore, as is the case of crustal zircon, the conventional technique is not suited to reveal more than one history or generation preserved in a given zircon sample. Hence, use of *in-situ* analysis made by a rapid but precise secondary-ion mass spectrometric (SIMS) technique is a promising approach to detect significantly older age information.

In this study, we apply SIMS U-Pb geochronology and REE geochemistry to zircons separated from an alnöite intrusion, Malaita, Solomon Islands, known as a unique occurrence of low-Cr megacryst suite from an oceanic environment (e.g. Nixon and Boyd, 1979). Although the relationship of megacryst and host alnöite remains unclear, it has been suggested that the alnöite is the end-product of the fractionation process facilitated by the megacryst crystallization (Neal and Davidson, 1989). Two megacrystalline zircons extracted from soils and stream gravels were previously analyzed for U-Pb dating by use of conventional technique, and obtained 34 Ma has been interpreted to provide the age of alnöite eruption (Davis, 1977; Davis *et al.*, 1976). However, due to such young, low U (~4.8 ppm) zircons, the analyses were carried out on large amounts of zircon powders without additional information, thus the aim of this study is to evaluate the previous age data by the use of different technique.

Another aim of this study is to take a broad view of possible age distribution of rare oceanic zircons. Previous studies revealed that the evolutionary history of the lithosphere beneath Malaita includes the Jurassic formation (~160 Ma) of oceanic lithosphere at mid-oceanic ridge setting, and significant disturbance due to Cretaceous (~120 Ma) Ontong Java Plateau magmatism and subsequent (~44 Ma) minor alkaline basalt magmatism (Ishikawa *et al.*, 2004; Ishikawa *et al.*, 2005; Tejada *et al.*, 1996). Thus, if older generations of zircon are recognized, this may provide potential link between plateau magmatism and megacryst crystallization, or key evidence for existence of crustal heterogeneity within the source of the Ontong Java Plateau (Ishikawa *et al.*, 2007).

Method

We have separated 110 grains of submillimeter-sized zircon from 1500 g alnöite rock. Selected 23 grains were subjected to the U-Pb isotopic analyses and 11 grains were subjected to the REE analyses performed using CAMECA NanoSIMS 50 at Ocean Research Institute, The University of Tokyo, Japan.

For U-Pb dating, intensity of the O^- primary ion beam was ~10 nA, and the spot size was 10 µm in diameter. We got flat-topped peaks with a mass resolving power (MRP) of ~4100. QGNG standard zircon (1842 Ma) was using for Pb^+/UO^+ and UO_2^+/UO^+ calibration to obtain $^{238}U/^{206}Pb$ ratio. U-Pb age calculation was performed by ISOPLOT v.3, a Microsoft Excel plug-in. Analytical procedures of U-Pb isotope dating are outlined in Takahata *et al*. (2008).

Rare Earth Elements were measured at the same or nearby point of U-Pb dating spot. Spot size was 10 µm with 10 nA of O^- primary beam. REE, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{147}Sm, ^{151}Eu, ^{153}Eu, ^{155}Gd, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu were measured by six magnet scan with multi-collector mode and using energy filter, and also ^{138}Ba and ^{177}Hf were analyzed for interference correction. A 60 V energy offset was applied to the secondary beam in order to minimize molecular interference. Relative sensitivity factors (RSF) were estimated from QGNG standard zircon analyses (Sano *et al.*, 2002).

Sample description

Separated 110 grains of zircon from Malaita alnöite are colorless to honey-yellowish color. Almost all grains have no crystal faces; they are rounded to sub-rounded shapes (Fig. 1). Rounded shapes are common in kimberlite zircon due to resorption in the kimberlite magma (Belousov *et al.*, 1998), and there are no reaction rims. Some zircons, however, preserved a prismatic, euhedral shape (upper left grain of Fig. 1). These lines of evidence suggest that not all grains are fragments of megacrysalline zircon which is commonly discovered from kimberlite. Size of separated zircons is very variable, 350 µm to 50 µm in length of long axis.

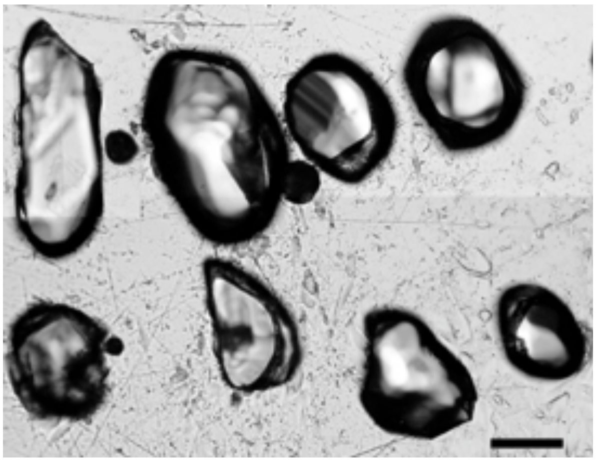

Fig.1. Photomicrograph of Malaita zircons. Scale bar is 100 µm.

Zircon U-Pb isotope ages

Obtained 23 ^{238}U-^{206}Pb ages from individual grains by NanoSIMS analysis range from 35-49 Ma and yield a weighted mean of 36.9±0.4 Ma with MSWD = 1.12 (Fig. 2). This demonstrates that our results are in agreement with the previous data, despite the slightly older mean value due to the tailing towards older value.

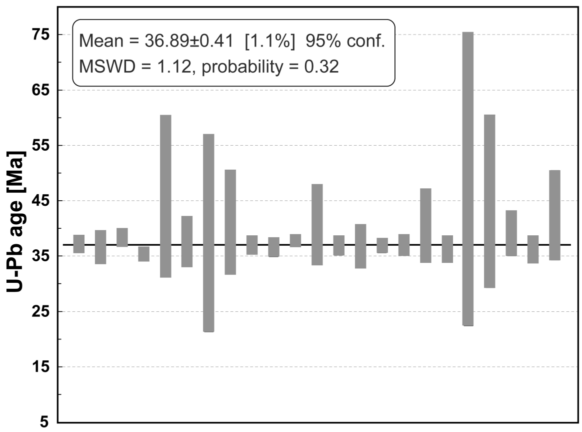

Fig. 2. Weighted mean U-Pb ages of zircon from Malaita alnöite. Gray bars display ranges of U-Pb ages. Heavy line indicates weighted mean age (36.9 Ma) of 23 analyses. Error bars are 2σ.

Rare earth elements

11 grains were selected for REE analysis by NanoSIMS in separate analytical session. The chondrite-normalized REE patterns of the Malaita zircons show variable total REE content and relatively flat heavy and middle REE patterns (Fig. 3). These patterns are similar to range of average compositions of zircon from five cratons (Kaapvaal, Siberia, Alto Paranaiba, Juina and Six-Pak) on four continents. Ratio of chondrite-normalized $(La/Sm)_N$ ranges from 0.0026 to 0.1614. Heavy REE shows relatively flat patterns, $(Gd/Lu)_N$ = 0.0629-0.8360. $(La/Yb)_N$ displays small variation (0.0002-0.0046). The REE content of Malaita zircons is extremely variable, ranges from 36 ppm to 1058 ppm. Some of them are enriched in REE than the kimberlite zircons (Fig. 3). Furthermore, REE content of most kimberlite zircons is less than 50 ppm (Belousov *et al.*, 1998). Low total REE zircons represent the Nd deficiency which was reported from other low total REE kimberlite zircons (Belousov *et al.*, 1998; Page *et al.*, 2007).

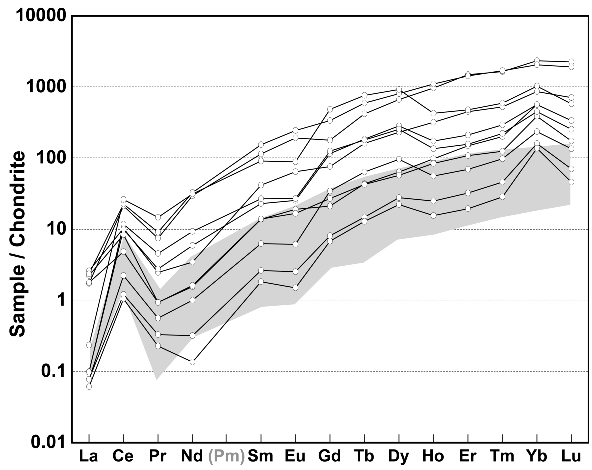

Fig.3. Chondrite-normalized REE patterns of zircons from Malaita alnöite. Shaded area shows the range of average compositions of kimberlite zircons from five cratons on four continents (Page *et al.*, 2007).

Discussion

Despite the significant error in individual spot analyses, there is a possibility that age variation of the Malaita zircons is varying with their REE concentration (Fig. 4). They can be subdivided into two groups: one is high REE content (ΣREE >300 ppm) with younger age (<38 Ma); another is low REE content (ΣREE <300 ppm) with older age (>38 Ma). Alternatively, both groups may follow a single trend on increasing ΣREE with decreasing age value. If this correlation is significant, our data may demonstrate that zircon U-Pb age reflect the timing of formation rather than temperature-drop due to the host eruption, as suggested for kimberlite zircon based on their low Ti temperatures (Page *et al.*, 2007). In this scenario, the U-Pb ages of zircon record the timing of crystallization from a single evolving magma, whose REE concentrations increased temporally. If this is the case, slightly younger age obtained for megacrystalline zircons can be attributed to their crystallization from highly evolved magma. However, more likely explanation is that they resided in significantly deeper mantle than where smaller zircons crystallized. Ti thermometry may prove this possibility.

It is interesting to note that the oldest age obtained in this study is very similar to the eruption age of alkaline basalts [Maramasike Volcanic Formation (MVF): ~44 Ma], spatially associated with alnöite intrusions. Based on REE modeling, Neal and Davison (1989) invoked that megacrysts in the Malaita alnöite are the product of crystal fractionation from 'proto-alnöite', which is an alkali basalt character. If it possible that the studied zircons are recording the temporal evolution of the magma stored within the lithospheric mantle beneath the Malaita.

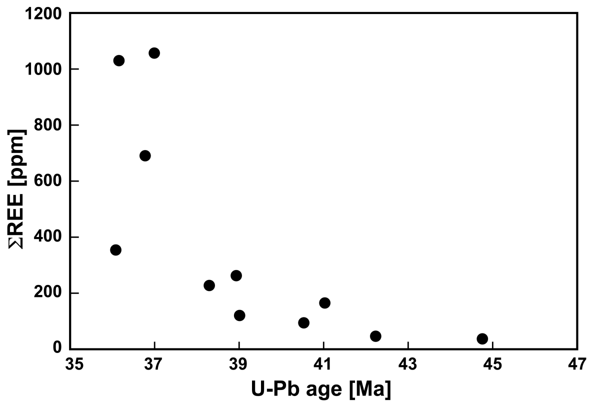

Fig. 4. Relationship between Total REE (ΣREE) concentration and U-Pb age of selected Malaita zircon.

Conclusions

1. We obtained a weighted mean U-Pb isotope age of 36.9±0.4 Ma by ion microprobe (NanoSIMS) from zircon separated from alnöite in Malaita, Solomon Islands. This age is slightly older than previously reported age (34 Ma) for megacrysytalline zircons.

2. Chondrite-normalized REE patterns of alnöite zircons similar to those of continental kimberlite zircons which have flat HREE patterns. Some of alnöite zircons have higher REE concentration, up to 1058 ppm than kimberlite zircons.

3. The correlation between zircon U-Pb age and total REE content might reflect temporal evolution of magma that crystallized zircons. This magma is likely to be "proto-alnöite" magma that stored in lithospheric mantle at least between 45 Ma and 36 Ma.

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