

Genesis of carbonatite melt by partial melting of COH-bearing peridotite

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On the Earth's surface, nutrients are one of the most important factors to hosting life.

The nutrients (C,O,N,P...) have to be supplied sustainably and enough. Carbon, oxygen and nitrogen can be supplied from the atmosphere, but phosphorus must be supplied from the interior of the Earth.

A potential source of phosphorus will be carbonatites, because carbonatites have the highest phosphorous concentrations among igneous rocks on the Earth. The genesis of carbonatites will be a key to understand possible mechanism for supplying phosphorus from the interior to the surface of the Earth.

The most popular theory for the origin of carbonatites is that carbonated silicate liquids generated by deep melting of carbonated mantle materials rises through the mantle and separates immiscibly into silicate melt and carbonatite melt. Veksler et al. (2011) experimentally investigated partitioning behavior of 42 elements between synthetic silicate melt and immiscible carbonate melt. They suggest that phosphorus concentrated to carbonate melt under hydrous conditions much more than under anhydrous conditions. Brooker (1998) experimentally determined the maximum extent of the silicate-carbonate immiscible field in a multicomponent system, and found that under CO₂-saturated condition the silicate-carbonate immiscible field is wider than under CO₂ undersaturated condition, leading more concentration of phosphorus to carbonate melt. However, it is still unclear whether immiscible separation of silicate and carbonate melt will occur within mantle-derived melt.

In this study, we performed high-pressure melting experiments on primitive mantle + CO₂ + H₂O in order to examine the possibility of liquid immiscibility in mantle-derived melt and the behavior of phosphorus between those melts.

We packed synthetic KLB-1 peridotite with ~10wt% oxalic acid dehydrate within a Au-Pd capsule, and performed melting experiment at 2.5GPa and 1100 °C for 26 hours using an end-loaded piston cylinder apparatus. The run product contains MgO-rich, SiO₂-poor partial melt.

The composition of the melt is not plotted within the silicate-carbonate immiscibility field in the (SiO₂+Al₂O₃+TiO₂)-(Na₂O+K₂O)-(CaO+MgO+FeO) pseudoternary system of Brooker (1998), so it is not likely that the melt itself will separate immiscibly into silicate and carbonate melts during ascending in the mantle. However, crystal fractionation of olivine in the melt will lead the composition more alkali rich, which may cause immiscible separation into silicate and carbonate melts.

It is possible to produce carbonatite melt from mantle-derived melt. A further study should be conducted on what conditions are needed to generate immiscible carbonatite melt on the early Earth.

Keywords: phosphorus, carbonatites, partial melting, liquid immiscibility, the early Earth

Determination of precise age corrected Sr-Nd-Pb-Hf isotope ratios of the clinopyroxene from Raivave OIB samples

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In Sr-Nd-Pb-Hf isotope analyses of whole rock samples, the leaching technique is used for removing the effect of secondary alteration and contamination from outside environments. Especially for the rock samples collected from sea area, the leaching is indispensable to eliminate the effect of seawater alteration. However, even if the strong leaching condition is applied, it is difficult to remove the altered components completely. In order to overcome this problem, clinopyroxene (CPX) was paid attention because of its early crystallization phase and its high resistibility against alteration. It is expected that the CPX preserve more primitive isotope signature than the leached whole rock samples. Using the CPX sample from ocean island basalt (OIB), Hanyu and Nakamura (2000) and Jackson et al. (2009) revealed the Sr and Nd isotope signature of OIB source mantle. Hanyu et al. (2011; 2014) also analyzed Sr and Nd isotopes as well as Pb and Hf isotopes of CPX to investigate the mantle end-members in the OIB samples from Polynesia and St. Helena.

Parent/daughter (P/D) ratios such as Rb/Sr, Sm/Nd, U/Pb, Th/Pb, and Lu/Hf were used for determining the age-corrected isotope ratios (initial ratios) of Sr, Nd, Pb, and Hf isotopes. The most suitable method for correction is using P/D ratios determined from the same CPX aliquot used for each of the isotope measurements. However, due to the limitation of the decomposition method used for the Pb isotope analysis in our laboratory, there was difficulty in determining the U/Pb and Th/Pb ratios from the CPX aliquot used for the Pb isotope. Therefore, Hanyu et al. (2011) determined the U/Pb and Th/Pb ratios from the whole rock U, Th, and Pb concentrations and partition coefficients, although the Rb/Sr, Sm/Nd, and Lu/Hf ratios were determined from the same CPX aliquot used for the Sr, Nd, and Hf isotope analyses. To overcome the uncertainty using partition coefficients, Hanyu et al. (2014) determined the U/Pb and Th/Pb ratios using the U, Th, and Pb concentrations of the CPX aliquot used for the Sr, Nd, and Hf isotope measurements, although the uncertainty of inhomogeneity in the CPX separates still remained.

In this study, we reexamined our analytical method, especially for the determination of U/Pb and Th/Pb of the CPX separates. We determined the Rb/Sr, Sm/Nd, and Lu/Hf ratios from the CPX aliquot used for the Sr, Nd, and Hf isotope measurements (Sr-Nd-Hf aliquot) and the U/Pb and Th/Pb ratios from the CPX aliquot used for the Pb isotope measurement (Pb aliquot) to determine the precise age-corrected Sr-Nd-Pb-Hf isotope ratios of the CPX sample from the Raivavae OIB samples. Comparisons between the Sr-Nd-Hf and Pb aliquots showed inhomogeneity in the U, Th, and Pb concentrations and revealed 0.34 and 0.88 of $\Delta U/Pb$ and $\Delta Th/Pb$, in maximum. These $\Delta U/Pb$ and $\Delta Th/Pb$ yielded 1052, 61, and 448 ppm in the $\Delta^{206}Pb/^{204}Pb$, $\Delta^{207}Pb/^{204}Pb$, and $\Delta^{208}Pb/^{204}Pb$ when the age correction used was 6 Ma. These $\Delta^{206}Pb/^{204}Pb$ and $\Delta^{208}Pb/^{204}Pb$ were beyond the analytical uncertainty of the standard samples. Therefore, using P/D ratios determined from the same CPX aliquot used for each of the isotope measurements is an important factor for the determination of precise age-corrected Sr-Nd-Pb-Hf isotope ratios of the Raivavae CPX sample.

Keywords: Sr-Nd-Pb-Hf isotopes, CPX, Raivavae, Age correction, P/D ratio

Laser-ablation Sr isotopic analyses of small glass samples using MC-ICPMS

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An analytical protocol was developed for correcting Kr baseline-induced bias and Rb isobaric overlap factors to analyze Sr isotope ratios for small glass samples using laser ablation (LA) with a desolvating nebulizer dual-intake system and MC-ICP-MS. The combined use of a low-oxide interface setup along with high-gain Faraday amplifiers with a $10^{12} \Omega$ resistor enabled precise determination of Sr isotope ratios from 50-100 μm diameter craters using 10 Hz laser repetition rate. Residual analytical biases of $^{84}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios induced from Kr baseline suppressions (Kimura et al., 2013), were found to be nonlinear, but the correction method was applicable to 50-200 $\mu\text{m}/10$ Hz craters. We also found that the $^{85}\text{Rb}/^{87}\text{Rb}$ overlap correction factor changed with time with a change in the surface condition of sampler-skimmer cones. The correction factor of $^{85}\text{Rb}/^{87}\text{Rb}$ was thus determined at least once per five unknown measurements using the nebulizing intake line. We determined $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from MkAn anorthite (Sr = 305 ppm, Rb = 0.07 ppm), BHVO-2G, KL2-G, ML3B-G (Sr = 312-396 ppm, Rb = 5.8-9.2 ppm), and BCR-2G (Sr = 337 ppm, Rb = 48.5 ppm) basalt glasses using a 50-100 $\mu\text{m}/10$ Hz crater. The results agree well with their reference values determined by thermal ionization mass spectrometry, even with the high Rb/Sr ratio (0.14) in the BCR-2G glass. The internal/intermediate precisions were ± 0.0002 (two-standard deviation: 2SD) for 100 μm craters and ± 0.0005 for 50 μm craters. The new instrument settings and analytical protocol improved the precision by a factor of two compared to the previous report using LA-(sector field)-ICP-MS and enables the analysis of sample volumes that are ten times smaller than those used in previous LA-MC-ICP-MS analyses with equal precision.

Keywords: Sr isotope, geological glasses, LA-MC-ICP-MS, Kr baseline-induced bias, Rb overlap correction