

Diffusion-driven isotopic fractionations in olivine in laboratory and natural settings

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Our previous *in situ* measurements of a zoned olivine from Kilauea Iki lava lake revealed large and negatively-coupled Mg-Fe isotopic fractionations [1]. We estimated the relative diffusivities of the isotopes of Mg and Fe in olivine, scaled as $D_1/D_2 = (m_2/m_1)^{\beta}$, with $\beta_{Fe} \sim 0.25$ and $\beta_{Mg} \sim 0.15$ for an olivine zoned from Fo₈₀ to Fo_{83.6}.

Olivine diffusion experiments were run with the goal to quantify β -values and to compare them with the values estimated from the natural sample. In each experiment, crystallographically oriented Fo₁₀₀ (synthetic) and Fo₀ (Rockport fayalite) crystals were placed in an alumina crucible, held together by gravity, and the rest of the crucible was hand-packed with FeO powder. A total of six crucibles were placed together in the hot spot of a gas-flowing furnace at the Université de Lille 1. Each pair of crucibles were quenched at a time by moving them to a cold spot in the furnace after 10 and 20 days; all crucibles were taken out of the furnace after 30 days. Contacts were made across some Fo₁₀₀-Fo₀ and all Fo₁₀₀-FeO interfaces. The Fo₁₀₀-Fo₀ profiles were fitted using the diffusion equation of [2], while that of Fo₁₀₀-FeO required slower diffusion coefficients.

The longest profile (Fo₁₀₀-Fo₀, 30 days, diffusion along c-axis) was analyzed for its Mg isotopic compositions using SIMS (IMS 1280) at CRPG, Nancy. Matrix standards (Fo# 6, 16, 64, 76, 79, 85, 90, and 95) were previously measured by solution for their $\delta^{26}Mg$, and were used to monitor matrix effects. We find that matrix correction is critical in obtaining accurate β -values and that more matrix standards may be required. Our preliminary data shows > 10% fractionation in $\delta^{26}Mg$, which suggests a β_{Mg} of about 0.1 or less in olivine.

We are currently analyzing more experimental samples and investigating the cause of the apparent discrepancy of the β -value.

[1] C.K. Sio *et al.*, GCA, (in revision). [2] R. Dohmen and S. Chakraborty, (2007). Phys Chem Min. 34, 597-598.

Experimental study of the system Mg₄Si₄O₁₂-Mg₃Cr₂Si₃O₁₂ at 12-25 GPa and 1600 °C

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Pyrope-rich garnets of the ultrabasic paragenesis widely abundant as inclusions in diamonds are characterized by significant admixture of the knorringite, Mg₃Cr₂Si₃O₁₂, end-member. Such garnets often contain majoritic component, (Ca,Fe,Mg)SiO₃, which is an indicator of the sub-lithospheric mantle conditions. Although both components are important for barometry of mantle mineral associations, high-pressure phase relations in the system MgSiO₃-Mg₃Cr₂Si₃O₁₂ have been not studied yet. In this study we report the first results of experiments on the majorite-knorringite join at 12–25 GPa and 1600 °C aimed on investigation of conditions of the formation, structural peculiarities, and evolution of the composition of Cr-bearing majoritic garnets.

We investigated the full range of starting compositions with steps of 10–20 mol% and 2–3 GPa in multi-anvil experiments, which allowed us to plot the preliminary phase diagram for the system MgSiO₃-Mg₃Cr₂Si₃O₁₂ and synthesize garnets of a wide compositional range. The phase assemblages for majorite-rich starting materials (<30 mol % knorringite) include garnet, enstatite, and eskolaite (Cr₂O₃). With the increase of knorringite content in the starting composition, garnet + eskolaite association is formed. Typically synthetic garnets contain significant portion of majorite (>15 mol %) even for pure Mg₃Cr₂Si₃O₁₂ starting composition. The stability of garnet on the phase diagram is limited by pressure: MgSiO₃ ilmenite containing up to 7 wt% Cr₂O₃ appears together with eskolaite at $P > 20$ GPa. Single-crystal X-ray diffraction studies carried out on the produced garnets demonstrated their cubic symmetry in the studied compositional range and allowed us to study structural peculiarities of garnets. The lattice parameter of garnet (in parentheses) linearly increases with increasing the Mg₃Cr₂Si₃O₁₂ component: 11.4725(4) Å (Mg_{3.88}Cr_{0.24}Si_{3.88}O₁₂), 11.5187(6) Å (Mg_{3.58}Cr_{0.84}Si_{3.58}O₁₂), 11.5445(5) Å (Mg_{3.38}Cr_{1.24}Si_{3.38}O₁₂), and 11.5718(1) Å (Mg_{3.21}Cr_{1.58}Si_{3.21}O₁₂).