Supplementary material

Title: THE HOROMAN PERIDOTITE COMPLEX, JAPAN: THE UPPER MANTLE VARIATIONS IN ONE PLACE

By Tomoaki MORISHITA and Eiichi TAKAZAWA

SUPPORTING RESULTS OF THE HOROMAN PERIDOTITE COMPLEX

Textural development of symplectite texture of the Horoman Peridotite

The vermicular intergrowths of the Horoman symplectites have attracted considerable interest, particularly with regard to the reaction kinetics governing their formation. Obata (1997) conducted quantitative digital image analysis and statistical correlation methods, following the framework established by Morishita and Obata (1995), to characterize symplectite microstructures; this approach led to a structural evolution model, that elucidates the observed heterogeneity in grain size, morphology, and spatial mineral distribution. Morishita (1998) introduced a stochastic cellular automata framework designed to reconstruct the kinetic evolution of lithological textures, effectively parameterizing spatial and temporal information. To validate the stochastic model, Morishita (1998) analyzed the textural maturation of Horoman symplectites, employing a statistical comparison based on normalized spatial correlation formalisms and the scaling properties of cluster-size distributions.

The symplectite minerals in the Horoman MHL lherzolite appear to be three-dimensionally continuous based on observations using SEM and micro-CT images (Morishita, 2000b; Morishita et al., 2003b). SEM-EDS study confirmed that the symplectite minerals exhibit systematic crystallographic topotaxial relationships, where the (100) and (010) planes and axis of both orthopyroxene and clinopyroxene are nearly identical, and these planes align closely with the {111} and {101} planes of spinel, respectively (Odashima et al., 2008). The observation that the symplectite is enclosed within a fine-grained (100–200 μm) mineral aggregate (lenticular seam) indicates a two-stage decompression history. An initial slow, diffusion-controlled reaction under low supersaturation formed the fine-grained aggregate. This seam subsequently prohibited direct garnet-olivine contact, maintaining a relict garnet core. The final formation of the symplectite was likely triggered by subsequent deformation thinning the seam, leading to a rapid, high-supersaturation transformation of the relict garnet. See Odashima et al. (2008) for more details.

Comprehensive geochemical results from the Bozu Section samples

Since Takazawa et al. (1992) reported the results of samples collected from the Bozu section, these samples have been used for further analysis. Here, we briefly introduce the geochemical results from the Bozu section.

Lai et al. (2015) performed Mg and Li isotope analyses. Mg isotopic compositions remain stable among samples, δ^{26}Mg = 0.23 ± 0.04 ‰ (2SD, n = 17), despite variable degrees of partial melting and local metasomatism. The observed constancy of δ26Mg suggests that chemical change by melt infiltration were insufficient to induce detectable Mg isotope fractionation (exceeding the external

precision of 0.03 ‰). This value is consistent with the estimated values for the primitive mantle and the Bulk Silicate Earth.

Normal-type samples constrain the Li isotopic composition of the fertile upper mantle to an average of δ^{7}Li = 3.8 ± 1.4 ‰ (2SD, *n*=9), with an average Li concentration of 1.1 ± 0.3 ppm. The consistency of this value with previous estimates from xenoliths and N-MORB provides strong reassurance regarding the reliability of the estimated mantle δ^{7}Li reservoir.

This study also confirmed spatially localized areas coinciding with incompatible element enrichment (Takazawa et al., 2000) that exhibit anomalously low δ^{7}Li values -0.2 ‰ to 1.6 ‰). This signature can be explained by kinetic isotopic fractionation where the lighter isotope, ^{6}Li, preferentially diffused faster than ^{7}Li from high-[Li] metasomatic agents into the host peridotite mineral. Diffusion modeling suggests that the preservation of local low δ^{7}Li signature would be erased by continued diffusion, requiring the infiltration of metasomatic agent to have been a late-stage event. Based on diffusion modeling, the maximum cooling duration of the massif from the assumed peak metasomatic temperature (950°C) to the Li closure temperature (700°C) is approximately 0.3 Ma, indicating the rapid emplacement rate and uplift history of the Horoman Peridotite Complex.

Anguelova et al. (2022) performed Ti isotope analyses. The Bozu HML samples exhibit a vast range in δ^{49}Ti values, spanning 2.07 ‰ (from −1.523 ±0.029‰ to 0.547 ± 0.015‰). This variation in Ti isotope demonstrates significant small-scale Ti isotope heterogeneity within the Bozu section, contradicting the narrow range typically observed in most primitive mantle-derived magmas. Continental crust-like heavy Ti isotope compositions observed in the Bozu HML samples (up to 0.547 ‰) are negatively correlated with Nb/Th and are likely induced by metasomatism. This suggests that isotopically heavy Ti was inherited from subducted terrigenous sediments. Highly refractory harzburgites with low Ti contents exhibit anomalously light Ti isotope compositions (δ^{49}Ti down to −1.523 ± 0.029 ‰). These light signatures are attributed to kinetic diffusion-driven isotope fractionation during fluid/melt percolation, where lighter Ti isotopes preferentially diffuse into the peridotite. Significant Ti isotope fractionation is found between coexisting clinopyroxene and orthopyroxene (Δ^{49}Tiopx-cpx =0.16 ‰−0.29 ‰). This inter-mineral disequilibrium can be explained by non-equilibrium fluid/melt-rock interaction (e.g., preferential diffusion of light Ti isotopes into clinopyroxene).

Micro Platinum-Group minerals: Implications for “nuget effect”

Kogiso et al. (2008) conducted microbeam synchrotron radiation X-ray fluorescence (SR-XRF) analysis on a MHL lhezolite and identified nine grains of PGM microphases ranging from approximately 1 μm to 10 μm in maximum dimension within a single thin section. All detected PGM microphases were located near or within Fe-Ni-Cu sulfides and the Cu-rich rims of the base-metal sulfides. The identified microphases exhibited combinations including Os-Ir-Pt, Os-Ir, Pt-Bi, Pt-Au, and Au. This was the first report of Pt-Au alloys in peridotites. This micro-scale heterogeneity is demonstrated to be the likely cause of the well-known "nugget effect" in whole-rock PGE analyses, operating at the centimeter scale in the Horoman MHL lherzolite.

Copper-bearing phases and Cu isotopic composition

Kitakaze et al. (1998, 2008, 2011) reported three new Cu-Fe-Ni sulfide minerals—sugakiite [$Cu(Fe,Ni)_8S_8$], horomanite [$(Fe,Ni,Co,Cu)_9S_8$], and samaniite [$Cu_2(Fe,Ni)_7S_8$]—within the MHL lherzolite. Native copper is intimately associated with these minerals.

Ikehata and Hirata (2012) performed copper isotope analyses. Primary native copper grains and the corresponding whole-rock sample (MHL plagioclase lherzolite) yield homogeneous δ^{65}Cu values between –0.03 and 0.14 ‰ (whole rock average: 0.05 ± 0.07 ‰). The whole-rock copper concentration (25 ppm) falls within the typical range for the Earth's mantle. The observed isotopic homogeneity between the primary native copper and the whole-rock sample suggests that copper isotope fractionation does not occur significantly during magmatic processes recorded in the Horoman peridotites. In contrast to the primary native copper, secondary native copper grains exhibit significantly lower δ^{65}Cu values (–0.67 to –0.41 ‰). These secondary grains are texturally linked to replacement by Fe oxide, serpentine, and carbonate minerals during serpentinization. This isotopic depletion in secondary copper grains indicates the possibility that selective preferential leaching of the heavier copper isotope (^{65}Cu) occurred during the serpentinization.