RARE EARTH ELEMENTS IN PALLASITE OLIVINES.

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Introduction: Pallasites are highly differentiated meteorites with two major phases, olivine and Fe-Ni metal (e.g., [1]). There are two explanations concerning the formation of pallasites; deeply buried formation at the core-mantle boundary in the interior of a rather large parent body (e.g.,[2]) and near-surface formation (e.g.,[3]). Pallasites are classified into two groups, main group and the other (anomalous) group, mainly on the basis of chemical composition of metal [4]. Most of the main group pallasites have oxygen isotopic compositions similar to HED meteorites and IIIAB irons [5].

Chemical compositions of metal phases have been extensively studied for pallasites and their data are used for the classification of pallasites [4]. Olivine and its accessory minerals have been studied petrologically and mineralogically for most cases but scarcely for trace element compositions. For rare earth element, only four pallasites have been analyzed; Brenham [6, 7], Thiel Mountain [7], Eagle Station [8] and Spring Water [8]. These data show V-shaped REE patterns regardless of the classification of pallasites. Experimentally, V-shaped patterns of REE in olivines were investigated. Consolmagno [9] calculated for REE patterns based on their partition coefficients between olivine and silicate melt, but could not produce V-shaped patterns. Later, Saito et al. [8] asserted that the V-shaped pattern was produced with crystallization near the liquidus temperature. In this study, we determined REE in olivines isolated from six pallasites (Brenham, Brahin, Dora, Esquel, Imilac and Mt. Vernon). Based on these data, we firstly evaluate the previously reported results of REEs in pallasite olivines and secondly discuss how the REE abundance in pallasite olivines is explained in related with the formation of pallasites.

Experimental: A lump of each pallasite sample was crushed and olivine crystals were mechanically separated from the metal. Visible metal phases were removed by using a dental grinder. Some olivine grains looked rusty and were separated by picking under an optical microscope. Olivine samples from several pallasites were washed in 1M HCl before neutron activation. Olivines grained were sealed in quartz tubes and irradiated for 100h in the JRR-3M reactor of the Japan Atomic Energy Research Institute at a thermal neutron flux of 1 x 10^{14} $cm^{-2}s^{-1}$. After activation, olivines grained were leached in 6M HCl for 20min. Both leachate and the residual grains were subjected for radiochemical separation of REEs. The REE were radiochemically purified by a combination of precipitation steps and anion and cation exchange column separation steps mainly from ^{46}Sc. Chemical yields (typically 30-60%) were obtained by ICP-emission spectrometry. A total of six REEs (La, Sm, Eu, Tb, Yb and Lu) were determined. For some meteorites only upper limit values were obtained for some of them.

Discussion: The Brenham pallasite olivine had been analyzed by Schmitt et al. [6] and Masuda [7] for REEs but their data are not consistent; absolute abundances are different by one to three orders of magnitudes and REE abundance patterns are mirror images to each other. Considering such a situation, we firstly analyzed the Brenham olivine for REEs three times. Our results are shown in Fig 1, along with REE patterns from two preceding studies. As shown in Fig. 1, heavy REE (Yb and Lu) abundances are reproducible among our three analyses and are in good agreement with those by Masuda [7]. However, the difference becomes increased with decreasing the atomic number. Samarium has the highest analytical sensitivity among REEs by NAA and yields a CI-normalized abundance of as low as 10^{-5} in our duplicate analyses, which is about three orders of magnitude lower than the Sm abundance obtained by Masuda [7]. We once tried to determine REEs both for HCl-leachate and the residual grains and their data are also plotted in Fig. 1. Interestingly, the HCl leachate shows a similar REE pattern to that reported by Masuda [7] for the Brenham olivine. We could obtain only an upper limit for La at the third experiment, when the olivine grains were extensively leached in HCl in relative sense. Considering these results obtained in this study, we suspect that the preceding studies didn't report real REE abundances in pallasite olivines.

In order to explain the REE abundance pattern observed for the HCl-leachate fraction, we assume an admixture of light REE enriched component to the pallasite olivine which has a monotonically depleted light REEs towards to La, as illustrated in Fig. 2. The added component is assumed to have similar REE abundances to those in typical crustal rocks of the earth. By mixing these two components, we can produce V-shaped REE abundance patterns reported by Masuda [7]. Thus, it seems to be highly probably that the V-shaped abundance pattern of REEs reported for pallasite olivines is not real, but is produced by terrestrial contamination.

Figure 3 summarizes REE abundance patterns

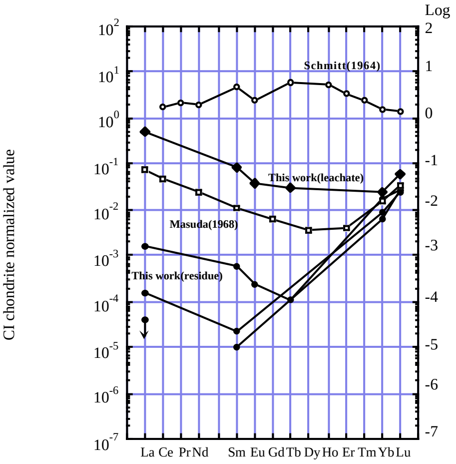

Figure 1. CI chondrite normalized REE abundances in pallasite olivine, Brenham.

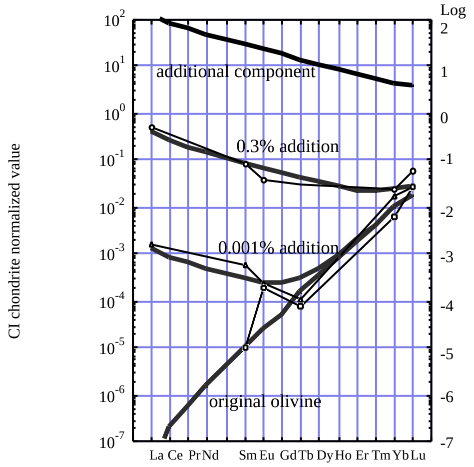

Figure 2. Conparison of observed REE patterns in Brenham, pallasite olivine and an additional model.

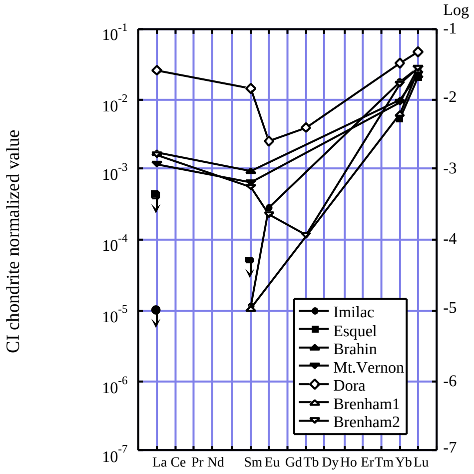

Figure 3. CI chondrite normalized REE abundances in pallasite olivine

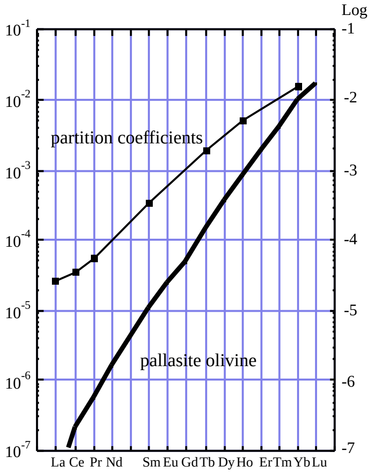

Figure 4. REE patterns in pallasite olivine and REE partition coefficients of olivine/melt (Beattie, 1994)

obtained for olivine grains separated from six pallasites. As noticed in Fig. 3, Yb and Lu abundances for these meteorites are less variable except for Dora. The Dora olivine grains remain brownish after HCl leaching, suggesting heavy weathering. Relatively high abundance of REEs with a V-shape pattern for Dora seems to be linked with such an appearance, confirming out suggestion for a relationship between V-shaped REE abundance patterns and terrestrial contamination. Samarium abundances vary from 10^{-2} to 10^{-5} as CI-normalized values among six pallasite olivines analyzed in this study. However, it may be noted that both Brenham and Imilac (and possibly Esquel) yield a similar abundance of 10^{-5}, which is the lowest value obtained. The lowest value of Sm for Imilac may be related with an observation that the Imilac olivine looks unaffected by terrestrial weathering, being furthest from the Dora's. REE abundances for the remaining pallasites (Brahin and Mt. Vernon) are between two extremes and are likely affected by a different degree of terrestrial contamination.

Partition coefficients of REEs between olivine and melt have been measured [8, 10, 11]. Their values of the latter study are completely different from those of the former two studies. In Fig. 4, partition coefficients of REEs of olivine determined by Beattie [11] are compared with a REE abundance pattern assumed for the pallasite olivine in this study. Apparently, pallasite olivine cannot be produced by a single stage differentiation from the starting material with an unfractionated REE abundance pattern. Thus, the simplest model to explain the observed REE pattern in pallasite olivine needs two steps; the light REE-enriched phase is removed at first and the olivine crystal is formed as a cumulate later. Davis and Olsen [12, 13] observed high REE abundances in Ca and Mg phosphates in nonmetallic fraction of several pallasite samples by using SIMS. They proposed a model to explain the REE abundance pattern for the Eagle Station whitlockite. According to their model, REE abundances in the Eagle Station olivine are controlled by three steps; metal-silicate separation, cumulative separation of olivine and a formation of phosphate at the olivine-metal boundaries. Their estimated REE patterns for the Eagle Station olivine before and after the phosphate separation seem to have gentler and steeper inclinations, respectively, than the pattern deduced in this study. Thus, it is not certain whether the presence of phosphate can explain the REE abundance of pallasite olivine in general.

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