LA-ICP-MS 2D MAPPING AND TRACE ELEMENT ANALYSIS OF OSCILLATORY ZONED OLIVINES IN IMILAC PMG.

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Introduction: Pallasites are stony-iron meteorites that are composed of nearly equal parts of metal, derived from the molten metal core of a differentiated planetesimal, and a mantle-derived olivine counterpart along with a number of accessory minerals (including chromites, sulfides, phosphides, and phosphates). The majority of pallasites originate in a single parent body and are classified accordingly as Main Group Pallasites (PMG). Despite their simple mineralogy, relatively little data are available on their geochemistry and the lateral elemental distribution in individual olivines.

Reliable bulk determination of many vital elements in pallasite olivine has proven difficult as a result of their protracted annealing history inside their parent body, which led to extreme depletion of incompatible elements. It is further complicated by ubiquitous non-olivine inclusions (*e.g.* metal) and terrestrial contamination. This is best exemplified by determination of REEs in olivine, when analytical techniques relying on bulk digestion result in higher REE concentrations and strikingly different REE-patterns [1–3], when compared with *in situ* analytical approaches [4,5]. Moreover, it was revealed that pallasite olivines exhibit zoning within a few hundred micrometers of the metal-olivine rim for a range of elements, such as Fe, Mg, Ca, Mn, and Cr [6,7].

Methods: To obtain detailed major and trace element distribution 2D maps and single line scan "bulk" analyses of the pallasite olivines, a Teledyne CETAC Technologies Analyte G2 laser ablation system, equipped with a Helex double volume ablation cell was coupled to a Thermo Scientific Element XR sector field ICP-MS unit. In the LA-ICP-MS analytical approach presented, quantitative major to trace elemental data are achieved based on oxides 100 wt% sum normalization, and in contrast to bulk analytical methods, laterally resolved mapping technique allows to discriminate non-olivine inclusions mathematically. The approach addresses non-divalent element relationships which involve charge-balancing.

Results: The element distribution maps obtained reveal complex zoning in pallasite olivines, which can be explained as (i) diffusion gradients formed during olivine cooling, (ii) crystal chemistry of element substitution due to the required charge-balancing, and iii) inherited features of olivine before the metal-olivine mixing, e.g. oscillatory zoning of Cr and Al in a single olivine of Imilac (Fig. 1).

Concentrations of the trace elements Cr and Al were found to be correlated both within single olivines and between olivines of different pallasites, forming a 1:1 linear trend (Fig. 1). This is likely the result of a spinel type charge-balancing substitution mechanism in pallasite olivine. It is important that coupled substitution decreases the diffusion rate of the elements involved by increasing the energy barrier, taking the elements involved longer to equilibrate. It also suggests that significant part of Cr in pallasite magma was present in a 3+ state.
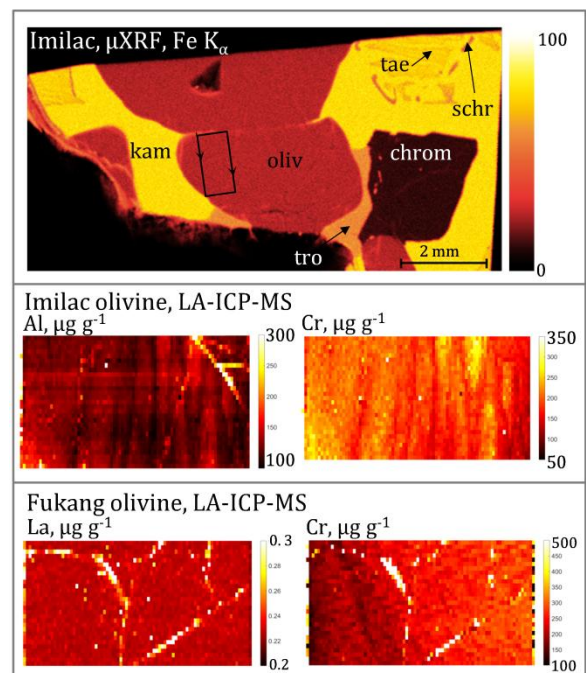
Oscillatory zoning of the Imilac olivine. Only few

Fig 1. Fe K_α intensity μXRF map of Imilac and quantitative LA-ICP-MS maps of Imilac and Fukang PMG olivines. The maps are measured using 20x20 μm laser spot scanning in the direction from the olivine-metal rim to the olivine core (left to right on the maps). Each LA-ICP-MS map is 1450 μm long and 600 μm wide.

occurrences of oscillatory zoned olivine have been described in other asteroidal and planetary bodies of the Solar System, including the Moon [8], Mars [9] and some chondrites [10]. Several scenarios may be invoked to explain formation of oscillatory zoning structures in the PMG olivine. (1) Stepped zoning as a result of physicochemical variations in the magma, such as magmatic recharge. (2) Convection of growing olivine in compositionally or thermally gradient magmatic reservoir. A global magma ocean in relatively small parent bodies may contain an internal convective layer [11], which can repeatedly transfer growing olivine crystals from the core-mantle boundary to the cooler regions of the parent body near the surface and back. (3) Alternatively, the oscillatory zoning can be a peculiar case of olivine growth kinetics under specific magmatic conditions. Oscillatory zoning of a crystal as a result of competition between the interface kinetics and chemical diffusion in specific magmatic conditions is well known for plagioclase feldspar [12]. However, no quantitative kinetic model has been developed for such structures in olivine so far - a result of extremely rare observation of oscillatory zoning in natural olivines. The oscillatory zoning is strong evidence that this particular olivine is not a restite of partial melting, but has crystallized from the magmatic melt. Additionally, it hints towards a mantle origin of this olivine, rather than cumulate at core-mantle boundary.

REEs in PMG olivines. Numerous efforts have been made to measure REE concentrations of olivine in pallasites. The principal challenge of such measurements is the extremely low abundances of these incompatible elements, sensitive to terrestrial contamination. For example, olivine-melt distribution coefficients of [13] predict REEs concentrations $10^{-5} – 10^{-1}$ of chondrite. Fig. 2 demonstrates CI-normalized REE patterns of PMG olivines measured *in situ* in this work and found in literature, compared to the REE patterns of the predicted olivine-melt distribution coefficients and literature data of various terrestrial olivines. Earlier studies of REE distribution in PMG olivine, which relied on bulk analytical approaches found V-shaped REE patterns of PMG olivine, with enriched light and heavy REEs and with minimum at Eu. It was previously suggested that such REE pattern of PMG olivine could be formed as a result of olivine formation at temperatures near the liquidus of olivine-silicate melt [1]. However, such patterns disagree with olivine-melt distributions, predicted for REEs at magmatic conditions (1250-1495 °C) [13]. In addition to the specific V-shaped REE pattern, bulk analytical methods result in 1-2 orders of magnitude higher contents, compared to the results demonstrated by *in situ* analytical methods. Observation of P-rich veinlets, likely of terrestrial
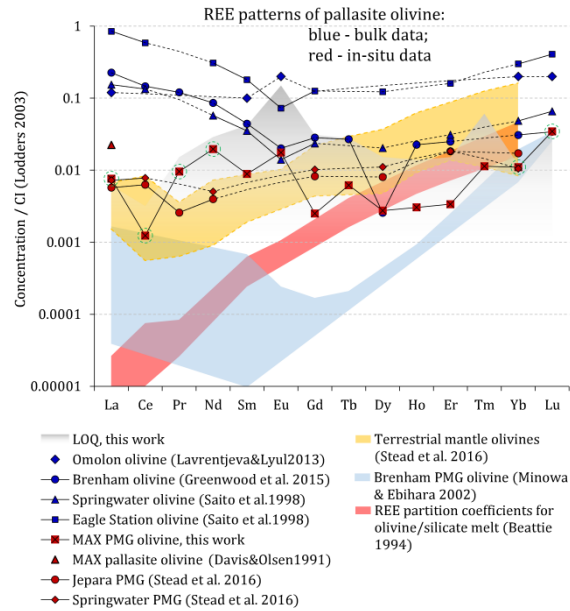

Fig. 2 REE patterns of olivines of pallasites. Blue markers - bulk analytical methods, [1–3], LA-ICP-MS – red markers [4,5]. Olivine-melt distribution coefficients [13]; REE patterns of terrestrial olivines [5]. REE concentrations in olivine of Brenham after leaching [14].

weathering origin, enriched in La and Cr inside the olivine of Fukang in this work (Fig. 1) is strong evidence that the V-shaped REE pattern of PMG olivines, reported previously, is a result of terrestrial contamination. Very careful cleaning and leaching of PMG olivine, combined with sensitive bulk analytical method, such as INAA [14] might be an alternative, but risk of artificial alteration of the pattern due to preferential leaching of light REEs should always be considered (Fig. 2).

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