

Pt, Au, Pd and Ru partitioning between olivine and silicate liquid. V. Malavergne^{1 and 2}, J. Jones³, A.J. Campbell⁴, M. Perronnet³, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, ² Laboratoire des Géomatériaux, Université de Marne-La-Vallée, 5 Boulevard Descartes, 77454 Marne la Vallée Cedex, France, ³ KR, NASA Johnson Space Center, Houston, TX 77058, ⁴ Department of Geophysical Sciences, University of Chicago, 5734 S Ellis Av., Chicago, IL 60637.

Introduction The highly siderophile elements (HSE) are important tracers of early planetary processes such as accretion and core formation. Consequently, their typically low abundances (ppb to ppt range) belie their importance to planetary geochemistry. In the case of the Earth for example, chondritic relative abundances of the HSE in some mantle xenoliths have led to the concept of the “late veneer” as a source of volatiles (such as water) and siderophiles (e.g., [1]).

Unlike the Earth, we have no samples of the martian mantle, so inferring the bulk silicate siderophile element contents of Mars is more difficult. Consequently, it is not known for certain if Mars also acquired a late veneer. Silicate crystal/liquid fractionation is responsible for most, if not all, the HSE variation in the martian meteorite (SNC) suite and Pt is the element least affected by these fractionations ([2]). Therefore, in terms of reconstructing mantle HSE abundances for Mars, Pt becomes a very important player, and it is necessary to understand its geochemistry much better. A detailed understanding of the olivine-melt partition coefficient of siderophile elements provides the necessary data to evaluate the role of this mineral in controlling the distribution of the HSE during melting and solidification. In the present study, we have tried to determine the abundances of Pt, Au, Ru and Pd in olivine and quenched silicate melt from high temperature experiments with variable redox conditions.

Experimental and analytical procedures. The starting materials used for the present work were a basaltic glass (termed Eg by [3]) plus a mixture of (Au, Pt, Pd and Ru) metals. This silicate composition has olivine on the liquidus around 1290°C with low-Ca pyroxene appearing around 1250°C [4]. Experiments were performed using a vertical tube furnace which allows control of the fO_2 by gas mixing (CO/CO₂), and a rapid drop quench. A Pt-Rh thermocouple (Type B), calibrated against the melting point of gold, was used to monitor the temperature of the experiments. The oxygen fugacity of the samples was checked by using a remote zirconia oxygen probe. We performed experiments under air, pure CO₂, and around QFM. The samples were held in open crucibles fabricated from San Carlos olivine monocrystals. The crucibles were suspended in the furnace with Pt wires. The time-

temperature evolution over the experiment was designed to allow the growth of large olivine crystals from the silicate melt (Fig. 1). First, the samples were held at 1350°C for one day. Secondly, olivine growth was promoted by cooling to 1275°C at 1°C/h and holding the final temperature at least 24 h. Finally, the sample was drop-quenched into water.

Initial evaluation of experiments was performed using the JSC JEOL JSM-5910LV Secondary Electron Microscope (SEM) and the JSC Cameca SX-100 electron microprobe to determine the homogeneity of phases and to perform major/minor element analyses on crystals selected for Pt, Au, Ru and Pd analysis. Trace elements were measured using two different laser ablation inductively coupled plasma mass spectrometers (LA-ICP-MS): the first one (a Fisons Instrument with a Nd:YAG laser operating at 266 nm) at the University of Clermont-Ferrand (France), and the second one (a CETAC LSX-200 LA peripheral with a magnetic sector ICP, the Finnigan Element) at the University of Chicago. In Clermont-Ferrand, a typical time-resolved analysis involved around 20s of background acquisition followed by laser ablation for 100s. In Chicago, the LA-ICP-MS analyses were performed using techniques similar to those described by [5]. With both machines, the standards employed were NIST 610 and 612, and laser spot sizes ranged from 80 to 100 μm.

Results. A typical view of the recovered samples is shown in Fig. 1. Large crystals of olivine grew during the experiments, while two different metallic alloys have formed in each sample (Fig. 2). The major alloy is generally Au-Pt-rich with 71-80 wt.% Au and 15-27 wt.% Pt. The highest concentration of Pd is 5.4 wt.%, whereas Ru is always below 0.5 wt.%. The second metallic phase is a Pt-Ru alloy, where Au is always below 1 wt.% and Pd less than 2.2 wt.%. These observations are in good agreement with the thermodynamic properties of Pt-Au-Pd-Ru (e.g. [6]). Compared to previous studies, which gave solubility values of these elements in silicate glasses, we are not working with pure noble metal Au, Pt, Pd or Ru. Therefore the present system is more complicated in term of metallic phases. The partition coefficients of Ca, Mn and Fe between olivine and the silicate glass have been calculated and are in good agreement with previous studies [7, 8, 9]. This

agreement is thus a good indicator of equilibrium. For the trace elements and the LA-ICP-MS analysis, conclusions are not so simple because of the formation of HSE micro-nuggets in the glass (e.g. [10]). This phenomenon appears clearly in Fig. 2, where nuggets are visible in the Pt and Ru spectra as concentration spikes. Pt and Ru spikes show a strong correlation, whereas different patterns are observed for Au and Pd spikes. Some LA-ICP-MS analyses, made in Chicago with shorter durations, appear to be nugget-free.

Discussion. The formation of the HSE micro-nuggets in our experiments complicates the interpretation of the measured concentrations. If the HSE micro-nuggets are just sample artifacts (e.g. [10]), then their contributions should be removed before the calculations. On the other hand, if they are produced during the quench [11], then they should be included in the analysis. The formations of two types of macroscopic Pt-Ru and Au-Pt alloys in our samples (e.g. Fig. 2) suggest that our nanonuggets are smaller versions of these phases. If so, then these nanonuggets are not a simple quench effect. To confirm or to invalidate this hypothesis, a Transmission Electron Microscopy study is underway. Up until now, Au and Pt, were always under the detection limit in the olivine or with nuggets in one sample. It was thus impossible to calculate partition coefficients for these two elements, but this study is still ongoing. For Ru and Pd, it was possible to calculate two partition coefficients (Fig. 3). They are in good agreement with previous work for Ru, but our datum for Pd is higher than previously found. Clearly more data are needed at lower fO_2 to understand the behavior of these elements.

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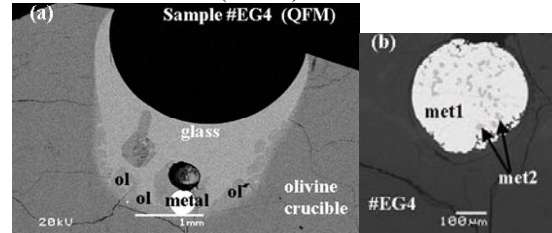


Fig. 1: SEM photos of the run #EG4 (QFM). (a) a typical view of the samples. Ol means olivine. (b) Enlargement of (a) where the two metallic phases labeled met1 and met2 can be seen.

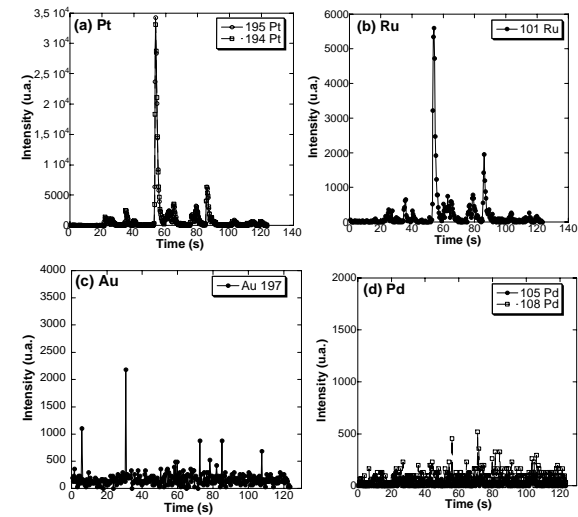


Fig. 2: LA-ICP-MS time-resolved spectra obtained in the glass of #EG4 for (a) Pt, (b) Ru, (c) Au (d) Pd.

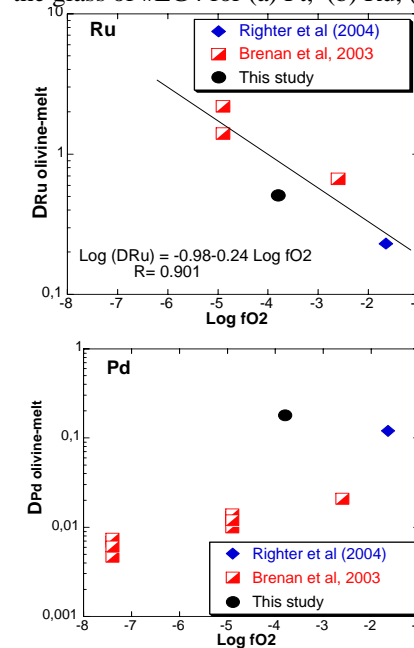


Fig. 3: $D_{\text{olivine-melt}}$ of Ru and Pd.