

**EVIDENCE FOR METAL ANIONS IN SILICATE MELTS: IMPLICATIONS FOR PT PARTITIONING, NANONUGGETS AND CORE FORMATION.** E. Médard<sup>1</sup>, M. W. Schmidt<sup>2</sup>, A. M. Martin<sup>3</sup>, J. A. van Orman<sup>3</sup>, M. Wälle<sup>2</sup>, J.-L. Devidal<sup>1</sup>, A. Lanzirroti<sup>4</sup>, M. Newville<sup>4</sup>, D. Günther<sup>5</sup>, <sup>1</sup>Laboratoire Magmas et Volcans, Université Blaise Pascal - CNRS - IRD, OPGC, 5 rue Kessler, 63038 Clermont-Ferrand, France (E.Medard@opgc.univ-bpclermont.fr); <sup>2</sup>Institut für Geochemie und Petrologie, ETH Zürich, Clausiusstrasse 25, CH-8092 Zürich, Switzerland; <sup>3</sup>Department of Earth, Environmental and Planetary Sciences, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, OH 44106, USA; <sup>4</sup>Center for Advanced Radiation Sources, University of Chicago, 5640 S. Ellis, Chicago, Illinois 60637, USA; <sup>5</sup>Laboratory of Inorganic Chemistry, ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland.

**Introduction:** Highly siderophile elements (HSE = Au, Re, and the Pt-group elements) are tracers of silicate / metal interactions during planetary processes. Since most core-formation models involve some state of equilibrium between liquid silicate and liquid metal, understanding the partitioning of highly siderophile elements (HSE) between silicate and metallic melts is a key issue for models of core / mantle equilibria and for core formation scenarios.

However, this task has been proven challenging, due to the presence of nanometric metallic particules (“nanonuggets” - 50 to 200 nm in diameter, [1]) in silicate glasses produced at oxygen fugacities ( $fO_2$ ) relevant for core formation. Two schools of thought developed in the scientific literature: (1) nuggets are present as equilibrium metal particles inside the silicate melt [1], and thus play no role in the HSE concentration, or (2) nuggets represent metal dissolved in the silicate melt (presumably with a zero valence) at high pressure and high temperature that exsolved during quenching [2]. Whether the nanonuggets are considered equilibrium or quench phases results in orders of magnitude of variation in partition coefficients for HSE [1].

We performed high-pressure, high-temperature experiments at 1.2-2.0 GPa, 1360-2100 °C, and oxygen fugacities between IW-7 and IW+2 (where IW is the oxygen fugacity of the iron-wüstite buffer) to investigate the partitioning of Pt, one of the HSE, between a silicate melt and a metallic melt [3]. Our experiments indicate that nanonuggets encountered in previous experiments are experimental artifacts. They form at high temperature by oversaturation caused by high oxygen fugacity during the initial stages of an experiment. Our experiments also strongly suggest that Pt is dissolved in an anionic form (likely a platinide anion Pt<sup>-</sup>) at oxygen fugacities at or below the IW buffer, a behavior that was previously hidden by data dispersion caused by formation of nanonuggets at the low oxygen fugacity relevant for core formation processes.

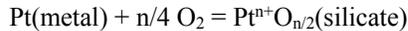
**Experimental and analytical techniques:** Most experiments involve equilibration between a metallic melt (Fe-Pt alloy containing C or Si) and a silicate melt

(of basaltic composition) in graphite capsules. A few experiments were run in Al<sub>2</sub>O<sub>3</sub> or MgO capsules.  $fO_2$  varies between IW-7 and IW+2, and is set by the interaction of variably oxidized starting materials with graphite containers [4]. Experiments were mostly performed in static piston-cylinders at CWRU and ETH, with a few experiments being performed in the centrifuging piston-cylinder at ETH [5]. Composition of the metallic phases and the silicate glasses were measured by EPMA. Pt concentrations in all glasses were then analyzed by LA-ICP-MS. We are also currently investigating the valence and speciation of Pt in silicates and metals using X-ray Absorption Near-Edge Spectroscopy (XANES) on the 13ID-E beamline at the Advanced Photon Source (Argonne National Labs).

**Origin of nanonuggets:** No evidence for nanonuggets was found in most of the experiments, and results are identical for static as well as dynamic experiments. Nanonuggets have previously been encountered in all the studies using Fe-free systems. A comparison between our data and the Fe-free data of [6] under similar conditions strongly suggest that Fe plays a key role in nanonuggets formation/dissolution.

Two experiments were performed at 1400 °C with an oxidized starting material enriched in Pt. Contrary to all our other experiments, one static experiment yielded charges full of nanonuggets, whereas the amount of nanonuggets was partially reduced in the other experiment run at high acceleration. This indicates that nanonuggets can easily be produced by Pt oversaturation. All nanonuggets-bearing experiments in the literature are reduction experiments: the final experimental  $fO_2$  is systematically lower than the initial  $fO_2$  of the starting material. Since Pt solubility decreases with decreasing  $fO_2$ , any Pt that is present in the glass at the beginning of the experiment, or that dissolves in the glass at the initially high  $fO_2$  will result in Pt-oversaturation in the silicate melt and subsequent precipitation of equilibrium nanonuggets. Nanonuggets can be removed by gravity at high acceleration [3], by using initially reduced starting materials [3, 7], or through wetting effects [8].

**Platinum speciation at low oxygen fugacity:** The dissolution of metals in silicate melts is often assumed to occur through formation of a metal oxide. The valence of a dissolved metal can then be estimated from the partitioning as a function of  $fO_2$  as follows [9]:



where  $n$  is the valence of dissolved Pt. The equilibrium constant of this reaction is given by:

$$K = \frac{a_{PtO_{n/2}}^{\text{silicate}}}{a_{Pt}^{\text{metal}} \cdot f_{O_2}^{n/4}} = \frac{1}{D_{\text{metal/silicate}}^{Pt} \cdot f_{O_2}^{n/4}}$$

By plotting the partition coefficient as a function of  $fO_2$  in log units, all other parameters (temperature, pressure, melt composition) being kept constant, one can solve for the valence of dissolved platinum (the slope of the line should be equal to  $-n/4$ ). Results from a series of experiments performed at 1900 °C and 1.2-2.0 GPa are plotted in figure 1.

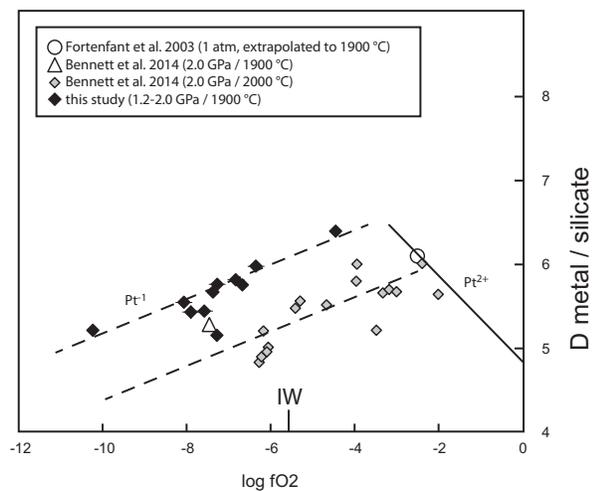
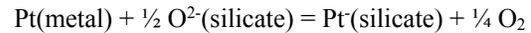


Fig.1. Variation of the metal / silicate partition coefficient for Pt (activity units) as a function of  $fO_2$  at 1900 °C and 1.2-2.0 GPa. Data at 2000 °C from Bennett et al. are given for comparison. Data below IW+2 show a positive trend, with a slope consistent with presence of a Pt- anion.

Contrary to expectations, for the investigated range of oxygen fugacities, the slope is positive, and very close to 0.25, as expected for a -1 valence. A similar behavior was also suggested by [7]. This slope indicates that the dissolution reaction for Pt metal in silicate melts at  $fO_2$  of IW-7 to IW+1 produces oxygen. Although some complex-forming reactions could produce oxygen together with Pt-(CO), Pt-Si or Pt-S complex-

es, the most likely species is the platinide anion  $Pt^-$ , an anion already known to exist in a few binary compounds [10]:



The presence of another metallic anion,  $Au^-$ , in silicate melts, was already suggested in the earliest HSE studies by [11], for oxygen fugacities around or below IW. The transition between  $Pt^{2+}$  and  $Pt^-$  would be around IW+2. Dissolution of Au and Pt in anionic form in silicate melts at low oxygen fugacities is not surprising, since these elements have the highest electronegativities of all the transition metals, and their anions would be stabilized by favorable electronic structures and relativistic effects. Pt concentrations in our experiments are high enough to be investigated by X-ray spectroscopy on synchrotron. XANES investigations on the Pt L-edge are currently being performed in order to confirm the exact nature and valence of the Pt species.

Assuming an average oxygen fugacity of IW-2 during core formation processes [12], at least Pt and Au (and possibly other highly siderophile elements) would have been in an anionic form in silicate melts during core segregation processes. This fact has been previously hidden by the presence of nanonuggets in experiments under the relevant oxygen fugacities. The decrease in partition coefficient at low  $fO_2$  caused by the negative valence can provide a partial solution to the excess-siderophile problem, although addition of a late veneer is likely still required to explain the HSE concentration in the Earth's mantle.

**References:** [1] Ertel W. et al. (2008) *Chem Geol*, 248, 119-139. [2] Cottrell E. and Walker D. (2006) *GCA*, 70, 1565-1580. [3] Médard E. et al. (2015) submitted to *GCA*. [4] Médard E. et al. (2008) *Am Min*, 93, 1838-1844. [5] Schmidt M.W. et al. (2005) *Science*, 5780, 1646-150. [6] Ertel W. et al. (2006) *GCA*, 70, 2591-2602. [7] Bennett N. R. et al. (2014) *GCA*, 133, 422-442. [8] Brenan J. M. and McDonough W. F. (2009) *Nat. Geosci.*, 2, 798-801. [9] Borisov A., Palme H. and Spettel B. (1994) *GCA*, 58, 705-716. [10] Karpov A., Konuma M., and Jansen M. (2006) *Chem. Commun.*, 2006, 838-840. [11] Borisov A. and Palme H. (1996) *Mineralogy and Petrology*, 56, 297-312. [12] Wade J. and Wood B.J. (2005) *EPSL* 236, 78-95.