PT IN SILICATE MELTS: CENTRIFUGING NANONUGGETS TO DECIPHER CORE FORMATION PROCESSES.

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Introduction: Highly siderophile elements (HSE = Au, Re, and the Pt-group elements) are key tracers of silicate / metal interactions during planetary processes. As such, they are extensively used to constrain planetary differenciation and core formation processes, as most core-formation models involve some state of equilibrium between liquid silicate and liquid metal. Understanding the partioning of highly siderophile elements (HSE) between silicate and metallic melt is a key issue for models of core/mantle equilibria and for core formation scenarios. Precise knowledge of the partition coefficients will help constrain core formation processes.

However, this task has proven challenging, due to the presence of nanometric metallic particules ("nanonuggets" – 50 to 200 nm in diameter) [1]) in silicate glasses produced at fO_2's relevant for core formation. The first partitioning experiments were analyzed with bulk techniques (INAA, ICP-MS…): nanonuggets could not be detected, and were thus included in the measured HSE concentrations [e.g. 2]. The developpement of in-situ analytical techniques (LASER-ablation ICP-MS), allowed a more accurate spatial resolution, and nuggets were widely identified in experimental HSE-bearing silicate glasses. Ablation of nuggets produces large spikes in the LA-ICP-MS spectrum [3]. From that point on, two schools of thought developed in the scientific literature: (1) nuggets are present at high-pressure and high-temperature, as equilibrium metal particles inside the silicate melt [1]. They thus play no role in the HSE concentration, and the spikes produced when encountering a nugget need to be removed from the LA-ICP-MS spectrum, or (2) nuggets represent metal dissolved in the silicate melt (presumably with a zero valency) at high pressure and high temperature [4]. The metal exsolved during quenching, so the signal produced by the nuggets needs to be included in the LA-ICP-MS spectrum.

Whether the nanonuggets are considered equilibrium or quench phases (and thus re-integrated into the bulk concentration) results in orders of magnitude of variation in partition coefficients for HSE [1]. Here we describe a series of experiments to constrain the nature and the formation mechanisms of nanonuggets, and develop new techniques for accurate determination of partition coefficients for the highly siderophile elements.

Experimental techniques: In this study, we focus on Pt as a typical example of HSE. All the experiments involve equilibration between a metal (mostly liquid Fe-Pt alloy) and a silicate glass (of basaltic composition), at a constant pressure of 1.0 – 1.2 GPa and temperatures between 1400 and 1800 °C. Oxygen fugacity varies between IW-2 and IW+2, and is set by the interaction of variably oxidized starting material with graphite containers [5]. Two kind of experiments were performed : static and dynamic. Static experiments are regular piston-cylindre experiments, using talc-graphite(Pyrex or SiO_2 glass)-MgO assemblies and graphite capsules. Dynamic experiments use the same assembly, but are run in the centrifuging piston-cylinder at ETH Zürich [6] for up to 12 h, following a first step of static equilibration. If the nanonuggets are present at high P and T, they should be centrifuged out of the silicate glass and sedimented at the bottom of the capsule. Composition of the metallic phases and the silicate glasses were measured by EPMA. Pt concentrations in all glasses were then analyzed by femtosecond LA-ICP-MS.

Fig. 1. General view of the centrifuging piston-cylinder at ETH Zurich. It is a regular non-end-loaded piston-cylinder mounted on a centrifuge, in which the sample is accelerated at the experimental conditions up to 1450 g.

Nature of nanonuggets: In the low-temperature static experiments (1400 °C), silicate melts are heterogeneous, and the LA-ICP-MS signal highly noisy, in-

dicating the presence of nanonuggets, as observed in previous static experiments [3,4]. In contrast, the bulk of the dynamic samples show a very smooth LA-ICP-MS signal without any evidence for nanonuggets and much lower time integrated concentrations. Nuggets only persist on the bottom and sometimes the sides of the sample capsules. Nanonuggets are thus not formed upon quench, but are present at high temperature and can effectively be sedimented out of the silicate melt.
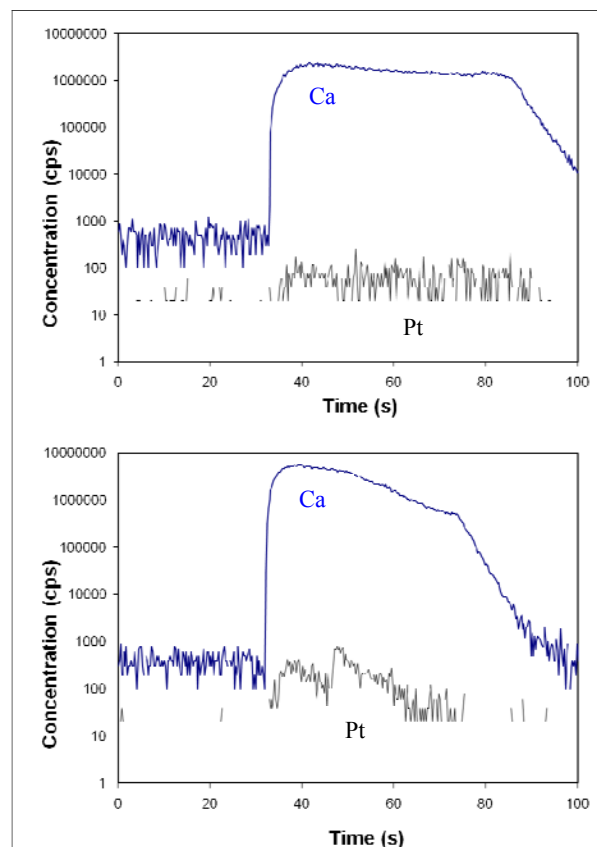

Fig.2. LA-ICP-MS ablation spectra for the middle (a) and the bottom (b) of sample Z164 (1.0 GPa / 1400 °C / centrifuged at 1450 g). Nuggets are only present on the bottom of the capsules, and sometimes on the sides. Ca is used as an internal standard.

At higher temperature (experiments at 1600 to 1800 °C), nanonuggets are not observed anymore, and there is no more difference between the dynamic and the static experiments.This suggests that the nanonuggets forming process is temperature dependant. Previous experimental series using a fixed oxygen fugacity indicate that nuggets are more abundant at low temperature and low HSE concentration [1]. Our experiments indicate that HSE concentration is not the controlling factor, since no nanonuggets were observed at

temperatures ≥ 1600 °C, even with Pt concentrations below the detection limit. In agreement with [7], we suggest that nanonuggets are formed at the beginning of the experiments, probably as a consequence of initial variations in oxygen fugacity. Once formed, metallic particles can only be removed by dissolution-reprecipitation or by sedimentation. Calculations using Stokes law indicate that in static experiments, sedimentation is way to slow to have any effect on nanonuggets that are 50-100 nm in diameter [e.g., 3]. Dissolution-reprecipitation is a temperature-depend process, and would be too slow at the lowest temperatures to efficacely remove nanonuggets. Moreover, for metallic particles, the dissolution process likely involves a redox reaction, since most metals are dissolved as oxidized species in silicate melts [1]. Nuggets-removal is thus expected to be more efficient in melts containing elements with multiple valence states (for e.g. Fe in our experiments) than in pure CMAS melts. This is confirmed by the absence of nuggets above 1600 °C in our experiments, whereas they persist up to 1900 °C in experiments using Fe-free silicate melts [7]. We do not exclude, however, that some "nuggets" may be formed by different processes. For example, the reappearance of nuggets at 1900-2400 °C in Fe-bearing experiments [4] does not fit with our observations. One hypothesis that we are currently testing is that "nanonuggets" is a catchall word, and that under some conditions, there may also be a different kind of quench-related nanonuggets.

Constraints on Pt partitioning: Our dynamic technique allows to measure accurate "true" (or "chemical") partition coefficients for Pt, which are in reasonable agreement with the lowest average solubilities defined by the nanonugget-corrected data of [1]. However, the centrifuging technique gives uncertainties that are an order of magnitude lower (e.g., 37 +- 4 ppb instead of 86 +- 67 ppb under similar conditions). Dynamic experiments are thus a powerfull tool for HSE partitioning, particularly under conditions where the lowest concentrations are expected.

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