



# The formation of nuggets of highly siderophile elements in quenched silicate melts at high temperatures: Before or during the silicate quench?



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## ABSTRACT

The Highly Siderophile Elements (HSE) are powerful tracers of planetary differentiation. Despite the importance of their partitioning between silicate and metal for the understanding of planetary core formation, especially for the Earth and Mars, there is still a huge discrepancy between conclusions based on different high temperature (HT) experimental studies. These disagreements may be due to the presence of HSE micro and nanonuggets in HT experiments. The formation of these nuggets is still interpreted in different ways. One hypothesis is that these HSE nuggets formed during the quench of the silicate melt, while another hypothesis supposes that these nuggets formed before the quench and represented artefacts of HT experiments. The goal of this work is to clarify whether the presence of HSE nuggets in silicate melts is linked to a quench effect or not. Understanding the formation of these HSE nuggets represents thus a necessary step towards the resolution of the Earth's core formation scenarios. We performed new HT experiments (1275–2000 °C) at different oxygen fugacities ( $f_{O_2}$ ), between ambient air up to  $\sim 5$  log units below the Iron-Wüstite buffer [IW-5], for two different silicate compositions (synthetic martian and terrestrial basalts) mixed with a metallic mixture of Pt–Au–Pd–Ru. Our 1275–1600 °C experiments were contained in either olivine, diopside or graphite crucible; experiments at 2000 °C were performed using a levitation method, so no capsule was necessary. Our samples contained quenched silicate melts, minerals (olivine, pyroxene, spinel depending on the run), a two-phase metallic bead and nano and micro-nuggets of HSE. Our samples underwent fine textural, structural and analytical characterizations. The distribution of the nuggets was not homogeneous throughout the quenched silicate melt. HSE nuggets were present within crystals. Dendritic textures from the quenched silicate melt formed around HSE nuggets, which could be crystallized, showing that the nuggets acted as nucleation sites during the quench. Thus they predated the quench. Finally, these nuggets also had strong heterogeneities suggesting at least a two-stage formation process under reducing conditions. Consequently, our observations clearly show that these HSE nuggets formed before the quench in the silicate melt. Our results agreed with previous studies, which concluded that HSE abundances in the Earth's mantle require the late accretion of chondritic material subsequent to core formation. However, the effects of metallic Si, O, H, or the effect of pressure on the HSE partitioning are still not fully understood. Further work to constrain these effects is to be encouraged to understand the Earth's core formation.

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## 1. Introduction

The Platinum Group Elements belong to the family of the Highly Siderophile elements (HSE). Due to their highly siderophile character, HSE partition strongly into metal during core segregation. In the case of the Earth for example, chondritic relative abundances of the HSE in some mantle xenoliths have led to the concept of a “late veneer” as a source of volatiles (such as water) and highly siderophiles (e.g., Chou, 1978; O'Neill et al., 1995; Holzheid et al., 2000; Becker et al., 2006; Ertel et al., 2006). Additionally, it is possible that a hybrid model considering both high pressure and high temperature (HP-HT) equilibrium of metal and silicate with an overprint by late accretion is necessary to explain terrestrial abundances of HSE (Righter, 2005; Mann et al., 2012). As the partition coefficients of these elements  $D_{\text{metal-silicate}}^{\text{HSE}}$  between metal and silicate are very high ( $D_{\text{metal-silicate}} \sim 10^4\text{--}10^{15}$ , e.g., Borisov and Palme, 1994, 1995, 1997; Ertel et al., 1999, 2006, 2008; Walker, 2009; Brenan et al., 2003, 2005; Brenan and McDougough, 2009; Mann et al., 2012; Cottrell and Walker, 2006; Laurenz et al., 2010, 2013; Righter et al., 2000, 2005, 2008; Yokoyama et al., 2009; Bennett et al., 2014; Médard et al., 2015), their concentrations in silicates are very low (ppb to ppt range). Therefore, the  $D_{\text{metal-silicate}}^{\text{HSE}}$  and the  $D_{\text{mineral-silicate melt}}^{\text{HSE}}$  are among the most challenging  $D$ 's to obtain precisely. But such coefficients are indeed necessary to model planetary differentiation.

The analytical difficulty of such measurements is increased by the presence of HSE-rich-nuggets in quenched silicate melts (e.g., Lindstrom and Jones, 1996; Ertel et al., 1999, 2001, 2006; Cottrell and Walker, 2006; Fortenfant et al., 2006; Yokoyama et al., 2009; Bennett et al., 2014; Médard et al., 2015). These tiny (nano or micro sized) HSE nuggets complicate the interpretation of measured HSE concentrations in quenched silicate melts of high temperature (HT) and high pressure (HP) experiments. If the HSE micro-nuggets are just experimental artefacts (e.g., Ertel et al., 2006; Fortenfant et al., 2006; Médard et al., 2015), then their contributions have to be removed before calculating the final silicate concentration. On the other hand, if they are produced during the quench (Cottrell and Walker, 2006), then they should be included in the analysis. To summarize, the origin of HSE nuggets in previous experimental studies remains a crucial question, as their presence is still not well characterized or understood.

In the present study, we have performed different kinds of HT experiments followed by a finely detailed structural and textural study of HSE (micro- and nano-) nuggets in order to clarify whether the presence of HSE nuggets in silicate melts is linked to a quench effect or not. As several points have been invoked in the literature (Cottrell and Walker, 2006 and Mann et al., 2012) as key parameters to promote the formation or the absence of PGE nuggets, we explored the effect of:

(i) *The silicate and metal compositions.* We used two Fe-bearing basaltic silicate glasses as starting materials for our HT, HT-HP experiments. Indeed, previous studies (e.g., Cottrell and Walker, 2006; Laurenz et al., 2013) proposed that the Fe-free silicates used in most previous studies were too far from pertinent terrestrial compositions. Moreover, basaltic melts are known to avoid complications due to quench textures, yet still enable Fe-bearing compositions that are relevant to natural systems. Finally, the use of mixed alloy compositions would help to understand the phase relations for mixed HSE alloys and also fix HSE component activities below 1, at more similar levels to natural systems. Therefore, we decided to perform experiments on basaltic compositions using a mixture of Pt, Pd, Ru and Au as HSE.

(ii) *Redox conditions.* Because of the analytical difficulties of obtaining HSE partitioning data (due to the extremely low concentration of HSE in silicates and the regular presence of HSE nuggets in the silicates), most of the previous experiments were designed

to optimize the HSE concentrations in silicates, with the risk that experimental conditions would be far from the range applicable to the Earth or Mars. For example, some studies were performed at very oxidized oxygen fugacities well above those of the differentiating Earth. Cottrell and Walker (2006) and Bennett et al. (2014) underlined this point as a potentially important problem for the understanding of PGE nugget formation. Thus, our experiments covered a wide range of  $fO_2$  (from air down to 5 log units below the iron wüstite buffer). Finally, HSE nuggets have been seen to precipitate as a result of redox gradients that form during the growth of mineral phases that sequester ferric iron (e.g. Finnigan et al., 2008). These results highlight the fact that multiple processes may be at work to generate HSE nuggets.

(iii) *Temperature and pressure.* One of the most important and relevant arguments of Cottrell and Walker (2006) in favor of the formation of PGE nuggets during the quench was that they had reached very high temperatures (up to 2500 °C at 2.2 GPa). To assess potential experimental P-T problems, the P-T conditions of our experiments varied between 1275 and 2000 °C at atmospheric pressure or at 1 GPa.

All the samples were investigated at high magnification and characterized with complementary methods, which has rarely been systematically done before (e.g. Fortenfant et al., 2006; Finnigan et al., 2008; Righter et al., 2015).

## 2. Experimental and analytical procedures

The starting materials used for the present work were a terrestrial synthetic glass (called BT hereafter in the text) and a synthetic martian basaltic glass (called EG hereafter in the text) (Table 1), a mixture of (80 wt.% Au, 10 wt.% Pt, 5 wt.% Pd and 5 wt.% Ru) metals, and in some samples a small amount of powdered minerals (olivine, diopside or spinel). These powders were used as seeds to help mineral crystallization at HT. Experiments were performed using three different procedures.

I. The first HT technique used was a vertical tube furnace, which allowed control of the  $fO_2$  by gas mixing (CO/CO<sub>2</sub>) or by using a pure gas (air, CO<sub>2</sub>, Ar). Experiments were carried out at JSC (Houston, USA), at LGE (Paris Est-Marne la Vallée, France), and at ENS (Paris, France). 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 ( $fO_2$ ) of the samples was measured using a remote zirconia oxygen cell. We performed experiments under air, pure CO<sub>2</sub>, near quartz fayalite magnetite (QFM) buffer, near two log units below the iron wüstite buffer (IW-2) and under pure Ar (Table 2). The samples were held in open crucibles fabricated from graphite, diopside or San Carlos olivine monocrystals. The crucibles were suspended in the furnace with Pt wires. The samples were held at HT (at superliquidus conditions) for several hours or days in order to reach equilibrium, then the samples were drop-quenched into water. Two experiments (#EG4 and #EG5, see Table 2) followed a different heat treatment: (i) these samples were maintained for 24 h at 1350 °C, (ii) olivine growth was promoted by cooling to 1275 °C at 1 °C/h, and (iii) holding the final temperature at least 24 h, (iv) finally the samples were drop-quenched into water. This quench was very rapid as the temperature of the sample decreased from its final furnace temperature to the water temperature (~30 °C) in less than 30 s.

II. The second HT procedure used a levitation apparatus associated with CO<sub>2</sub> laser heating. This free-container technique used a conical nozzle enabling the diffusion of a regulated gas flow below the sample. The sample was slightly lifted inside the nozzle eliminating completely any contact between sample and container and thus, preventing any contamination. Powders of EG glass and PGE mixtures were used as starting material. The powders were

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