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Solubility of platinum-arsenide melt and sperrylite in synthetic basalt at 0.1 MPa and 1200 °C with implications for arsenic speciation and platinum sequestration in mafic igneous systems

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Abstract

To better understand the Pt-As association in natural magmas, experiments were done at 1200 °C and 0.1 MPa to measure the solubility of Pt and Pt-arsenide phases (melt and sperrylite, $PtAs_2$), as well as to determine the oxidation state, and identify evidence for Pt-As complexing, in molten silicate. Samples consisting of synthetic basalt contained in chromite crucibles were subject to three experimental procedures. In the first, platinum solubility in the synthetic basalt was determined without added arsenic by equilibrating the sample with a platinum source (embedded wire or bead) in a gas-mixing furnace. In the second, the sample plus a Pt-arsenide source was equilibrated in a vacuum-sealed fused quartz tube containing a solid-oxide oxygen buffer. The third approach involved two steps: first equilibrating the sample in a gas-mixing furnace, then with added arsenide melt in a sealed quartz tube. Oxygen fugacity was estimated in the latter step using chromite/melt partitioning of vanadium.

Method two experiments done at high initial arsenic activity (PtAs melt + $PtAs_2$), showed significant loss of arsenic from the sample, the result of vapour transfer to newly-formed arsenide phases in the buffer. Method three experiments showed no loss of arsenic, yielding a uniform final distribution in the sample. Analyses of run-product glasses from experiments which did not show arsenic loss reveal significant increase in arsenic concentrations with fO_2, varying from ~10 ppm (FMQ-3.25) to >10,000 ppm (FMQ + 5.5). Despite very high arsenic loadings (>1000 ppm), the solubility of Pt is similar in arsenic-bearing and arsenic-free glasses. The variation in arsenic solubility with fO_2 shows a linear relationship, that when corrected for the change in the activity of dissolved arsenic with the melt ferric/ferrous ratio, yields a solubility-fO_2 relationship consistent with As^{3+} as the dissolved species. This result is confirmed by X-ray absorption near edge structure (XANES) determination on run-product glasses.

Levels of arsenic required for Pt-arsenide saturation are 50–500 ppm over the fO_2 range of most terrestrial basalts (FMQ to FMQ-2), >100× higher than the arsenic concentrations typical of such magmas, indicating significant enrichment of arsenic is required if Pt-arsenide saturation is to occur. In contrast, the level of dissolved Pt required to saturate in sperrylite is >8× lower than for pure Pt, suggesting that arsenic enrichment could lead to Pt removal at concentrations much less than required for pure metal saturation.

Keywords: Arsenic; Platinum; Sperrylite; Solubility

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1. INTRODUCTION

Although sulfur has long been implicated as an important ligand in the concentration of the platinum group metals (PGE) at the magmatic stage, there is evidence to suggest that arsenic could also play a significant role in some cases. For example, close textural relations between relatively PGE-depleted base metal sulfide and coexisting PGE-rich arsenide phases (NiAs, nickeline; $Ni_{11}As_8$, maucherite; NiAsS, gersdorffite), interpreted to have been coexisting immiscible sulfide and arsenide melts, have been reported in the magmatic sulfide segregations within the Ronda and Beni Besoura peridotite bodies (Gervilla et al., 1996; Pina et al., 2013), the Kylmakoski (Finland) Ni-Cu deposit (Gervilla et al., 1998) and komatiite-hosted base metal sulfide mineralization (Dundonald Beach South, Ontario (Hanley, 2007); Rosie Ni Prospect, Western Australia (Godel et al., 2012)). Recent work on samples from Creighton Mine, Sudbury (Dare Sarah et al., 2010) have shown that the base metal sulfides are not the dominant hosts for some PGE, and that Ir, Rh, Pt occur as arsenic-rich discrete platinum group minerals (PGMs; i.e., irarsite-hollingsworthite, IrAsS-RhAsS; sperrylite, $PtAs_2$), possibly crystallizing before or with early-formed magmatic sulfide minerals (e.g., monosulfide solid solution, or MSS). Detailed chemical imaging has also revealed textural evidence favouring the direct crystallization of Pt-Fe alloy along with sperrylite from the magma that formed the orthopyroxenite section of the Monts de Cristal Complex (Gabon; Maier et al., 2015; Barnes et al. 2016).

Past experimental work to explore the arsenic-PGE magmatic association has largely focused on behaviour related to the crystallization of sulfide liquid. The existence of S-bearing but arsenic-rich liquids is described by Sverjensky and Williams (1976) who measured an extensive two-liquid field in the system Pd-As-S at 1000 °C and 0.1 MPa. Helmy et al. (2013) showed that similar phase relations extend into systems with Fe and Ni, with Pd-As-rich liquids stable to 770 °C (and possibly below) at 0.1 MPa, with a strong preference of Ni over Fe relative to coexisting sulfide melt. Experiments on the Pt-As-S system (Sverjensky and Williams, 1976; Mackovicky et al., 1990, 1992) document extensive solid solution between As-S melts, and that sperrylite is a possible early-formed phase, although the minimum As content of the As-S liquid coexisting with sperrylite at 1000 °C is quite high (several wt%). Helmy et al. (2013) showed that the addition of Fe (and Ni) to this system significantly reduces the solubility of sperrylite in the sulfide melt to values ranging from 9400 ppm at 1150 °C to 6200 ppm at 770 °C. Consistent with this are the results of Bai et al. (2017) who report arsenic levels of 2,300–44,000 ppm in sperrylite-saturated Fe-Ni-S melts at 910–1060 °C at controlled fO_2-fS_2 conditions. Similarly, Helmy et al. (2013) determined that the arsenic content of sulfide melt coexisting with Pd-Ni-rich arsenide melts varies from 37,800 ppm at 1150 °C to ~400 ppm at 770 °C. Such high As solubility in molten sulfide would suggest that sperrylite or Pd-Ni-As bearing melt is not likely to form early in the magmatic sulfide crystallization sequence unless the system has acquired unusually high As levels. Synukova and Kosyakova (2012) investigated the conditions of formation for the Ir and Rh-bearing sulfarsenides of the irarsite-hollingsworthite series in dynamic crystallization experiments, indicating these phases can form near the sulfide liquidus, although detailed information on the As concentrations required for saturation were not provided. Empirical observations (Hanley, 2007; Pina et al., 2013) suggest that the PGEs will be preferentially concentrated in the arsenide phase. Pina et al. (2013) reconstructed sulfide and arsenide liquid compositions in samples from the Beni Bousera magmatic Cr-Ni mineralization (Morocco), and determined values of $D^{AsLiq/SulfLiq}$ of ~100 for the PGEs. Hanley (2007) estimated relative arsenide-sulfide partitioning by comparing concentrations (on a 100% sulfide basis) between an As-rich high grade lens, with lower grade As-poor segregations, occurring in a series of mineralized komatiite flows. The arsenic-rich high grade lens was found to be enriched by ~7–60× for Pt and Pd.

In contrast to the body of experimental and empirical work on sulfide systems, comparatively little information is available to evaluate the conditions for saturation in PGE-bearing arsenide phases in molten silicate. Preliminary measurements of the solubility of molten Fe-As-S in basalt melt at 1200 °C and 1 GPa ($fO_2 \leq$ FMQ buffer; summarized in Brenan et al., 2016, section entitled "Role of the chalcogens (Se, Te, As, Bi, Sb)) have revealed values of 1100 and 3300 ppm, for silicate melts with ~19 and ~13 wt% FeO, respectively. How much these values change with other intensive parameters, such as oxygen fugacity and temperature, is unknown. Moreover, there is a complete lack of information on the conditions for direct crystallization of arsenic-bearing minerals, such as the irarsite-hollingsworthite series, and sperrylite. Such information is essential, however, to fully evaluate the possible role of these phases in the early sequestration of the PGEs, as well as to understand how these elements may become fractionated from each other. In this paper, the results of experiments to measure the As and Pt content of synthetic basalt at saturation in various Pt-As phases (Pt-As melt and sperrylite) is presented. The effect of oxygen fugacity on this behaviour is explicitly evaluated, with results providing information on the speciation of arsenic in silicate melt, as well as the conditions required for magmatic crystallization of sperrylite.

2. EXPERIMENTAL METHODS

2.1. Overview

The goal of the experiments was to saturate synthetic basalt with a Pt-arsenide-bearing phase assemblage over a range of fO_2, so as to establish solubility systematics that could be applied to natural magmatic systems. A fundamental challenge to the arsenic-bearing experiments is the volatility of arsenic at high temperature, met in this case through the use of fused quartz ampoules to contain samples. In that approach, initial experiments involved the use of internal solid oxide buffers to fix oxygen fugacity. Owing to loss of arsenic from the sample to the buffer, subsequent experiments were done without the buffer, but