Sperrylite saturation in magmatic sulfide melts: Implications for formation of PGE-bearing arsenides and sulfarsenides

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ABSTRACT

Sperrylite (PtAs2) is one of most common Pt minerals, but the processes whereby it forms are not clearly established. Most commonly it is associated with the major-component base metal sulfide minerals (pyrrhotite, pentlandite, and chalcopyrite), which are believed to have crystallized from magmatic sulfide melts. Hence, sperrylite is thought to have formed by crystallization from a sulfide melt or by exsolution from sulfide minerals. However, sperrylite is also found associated with silicate and oxide minerals where it is thought to have formed by crystallization from the silicate magma. To investigate the conditions under which sperrylite could crystallize from a magmatic sulfide melt we investigated sperrylite saturation in Fe-Ni-Cu-S sulfide melts under controlled $f_{O2}$ and $f_{S2}$ at 910–1060 °C and 1 bar. The As and Pt concentrations in the sulfide melt at sperrylite saturation increase from 0.23–0.41 to 2.2–4.4 wt% and from 0.36–0.65 to 1.9–2.8 wt%, respectively, as the iron concentration in the sulfide melt decreases from 50 to 36 wt% at 910–1060 °C. We show that transitional metal concentrations, particular iron and nickel, as well as sulfur and oxygen fugacities influence As and Pt concentrations in the sulfide melt at sperrylite saturation. These intensive variables appear to effect sperrylite solubility by influencing the oxidation state of As in the sulfide melt. The measured concentrations of As and Pt in sperrylite-saturated sulfide melts produced in our experiments are much higher than that in most natural sulfides, implying that arsenides and sulfarsenides will not reach saturation in natural magmatic sulfide melts at high temperatures unless the magma has been contaminated with an exceptionally As-rich rock. This suggests that the observed arsenides and sulfarsenides in natural sulfide ores were not formed by crystallization from unfractionated sulfide melts at high temperatures above 900 °C, but might form at low temperatures below 900 °C.

Keywords: Sperrylite, PGE, magmatic sulfide melt, arsenide, sulfarsenide

INTRODUCTION

Arsenic is found to have a profound effect on the distribution of platinum group elements (PGE), because PGE have a stronger affinity for arsenides than for sulfides (Hanley 2007; Piña et al. 2013). The highest PGE concentration (in particular Pt and Pd) is correlated with arsenide and sulfarsenide minerals in several sulfide deposits, such as the Platreef deposit in the Bushveld Complex (Holwell and McDonald 2006), the Creighton Cu-Ni-PGE deposit in the Sudbury Igneous Complex, Canada (Dare et al. 2010), and the Aguablanca Ni-Cu-PGE deposit (SW Spain) (Piña et al. 2012a). In magmatic sulfide ore deposits, arsenides, sulfarsenides, and other semimetal-bearing platinum group minerals (PGM) generally occur in four associations: (1) as mineral inclusions within base metal sulfides (BMS) (Barnes et al. 2008; Dare et al. 2010); (2) at grain boundaries of sulfides and silicates (Barkov et al. 1999; Hanley 2007); (3) interspersed among the silicate grains (Barnes et al. 2008, 2016); and (4) within oxides (Farrow and Watkinson 1997). These textures are widely used to infer the PGM formation mechanisms (Naldrett 1969; Ger-villa et al. 1998; Li et al. 2008; Godel et al. 2012; Piña et al. 2012a; Prichard et al. 2013; Canali and Brenan 2015; Maier et al. 2015). However, textural information is not enough to infer the formation mechanism of arsenides and sulfarsenides because these phases can form either at high or low temperatures. It has been suggested that PGE-bearing arsenides and sulfarsenides form by early crystallization from a magmatic sulfide melt at high temperatures of 900–1200 °C (Hutchinson and McDonald 2008; Dare et al. 2010), by crystallization from a silicate melt (Maier et al. 2015; Barnes et al. 2016), or by crystallization from an immiscible arsenide melt at high temperatures (Hanley 2007; Piña et al. 2013). If these processes occur before the first sulfide mineral crystallizes, the As-rich melt or PGM arsenides and sulfarsenides could collect most PGE and other trace metals that have an affinity for As. If these crystals are then removed from the system (e.g., by fractional crystallization), the residual magma can become depleted in PGE (Dare et al. 2010; Piña et al. 2012b).

However, the distributions of PGE in some deposits suggest that PGE-bearing arsenides and sulfarsenides can also form at low temperatures by two different processes: (1) by direct exsolution of Pt and Pd along with As that were initially dissolved in base metal sulfides (BMS) to form As-bearing PGM at