A review of sulfur to selenium ratios in magmatic nickel–copper and platinum-group element deposits

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ABSTRACT

Deviations in the sulfur to selenium ratios (S/Se) from mantle values in magmatic Ni–Cu–Platinum Group Elements (PGE) sulfide deposits have been widely used to constrain the ore forming processes. Basically, S/Se ratios greater than mantle values are interpreted to be the result of contamination of the mantle derived magma by S-rich sedimentary rocks, whereas S/Se ratios lower than mantle values are thought to be the result of S loss during post-crystallization. However, there are many other processes involved in producing a deposit and it is possible that these may be also important in controlling S/Se ratios. In order to investigate the relative importance of these processes, we have compiled a data base of S, Se, $\delta^{34}S$ and metal values from Ni–Cu–PGE sulfide deposits. This compilation shows that processes affecting S/Se ratios can be divided into two main classes: the magmatic processes and the late- to post-magmatic processes.

1) Magmatic processes include the well-known addition of S from sedimentary rocks, variations in the sulfide to silicate liquid ratio (R-factor), depletion of the silicate magma in Se by early segregation of the sulfide liquid, and the moderate incompatibility of Se into the first sulfide minerals to crystallize from a sulfide liquid, the monosulfide-solid-solution (MSS). This incompatibility results in a change in S/Se ratio between the Fe-rich and Cu-rich zones of magmatic sulfide ores. The fractionation of Se during crystallization of sulfide liquids has not previously been appreciated.
2) Late- to post-magmatic processes include: hydrothermal alteration, high-grade metamorphism, serpentinization and supergene weathering. Some metamorphosed Cu-deposits have low S/Se ratios suggesting S-loss by breakdown of sulfide minerals during a high-grade metamorphic event. However, the effectiveness of this process remains unclear and alternative models exist. The preferential remobilization of S relative to Se during hydrothermal alteration, serpentinization and supergene weathering leads to a moderate decrease of S/Se ratios values and can mask the initial S/Se ratio.

1. Introduction

Following the pioneering compilation work of Eckstrand (unpublished data, 1988), S/Se ratios have been used in many studies of magmatic Ni–Cu–PGE deposits as a petrogenetic indicator of ore forming processes (e.g., Eckstrand et al., 1989; Eckstrand and Cogulu, 1986; Hinchey and Hattori, 2005; Maier et al., 2008; Peck and Keays, 1990; Ripley, 1990; Thériault and Barnes, 1998). S/Se ratios in magmatic Ni–Cu sulfide or PGE deposits vary from 100 to 100,000. The S/Se ratio of the mantle was estimated at between 2850 and 4350 by Eckstrand and Hulbert (1987). Later studies indicate average mantle values of 3333 (McDonough and Sun, 1995), 3300 (Hattori et al., 2002) and 3150

(Lorand et al., 2003). Most igneous rocks have a S/Se ratio close to the mantle value, as in the case of Merensky Reef of the Bushveld Complex (Barnes and Maier, 2002; Godel et al., 2007), which suggests that the S that saturated the mafic magma had a mantle origin. S/Se ratios greater than mantle values have been interpreted to signify that a large S contribution from the country rock has occurred, (e.g., Lesher and Burnham, 2001; Maier and Barnes, 2010). In contrast, S/Se ratios less than the mantle values are taken to indicate a S-loss such as the Heazlewood River, the Lac des Iles Complex or the PGE-rich reef of the Penikat intrusion (Barnes et al., 2008; Hinchey and Hattori, 2005; Peck and Keays, 1990). It has been suggested that S/Se ratios can also be affected by: 1) Preferential retention of Se during partial melting (Hattori et al., 2002); 2) Refertilization of mantle lithosphere by metal-rich sulfide melts (Lorand and Alard, 2010); 3) Changes in the silicate to sulfide liquid ratio, i.e. the R-factor (Thériault and Barnes, 1998); 4) Early

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segregation of the sulfide liquid (Barnes et al., 2009); 5) Partial desulfur-ization caused by a S-undersaturated fluid (Godel and Barnes, 2008).

Despite the utility of S/Se ratios and the large amount of data determined in many deposits, no study has been dedicated specifically to considering the relative importance of these processes and their implications on the interpretation of the S/Se ratio. We have compiled S, Se, δ^{34}S, metals (Pt, Pd, Ni, Cu) data and interpretations available in the literature up to 2013 on the use of S/Se ratio applied on magmatic Ni–Cu–PGE sulfide deposits. Furthermore, we have added few new data from Voisey's Bay deposit. The objectives of this review are: a) characterizing the deposits, b) considering the effects of a wider range of processes than have been discussed in the past and, c) provide recommendations on the use of the S/Se ratio. The behavior of S/Se ratio will be analyzed at each step involved in the formation of a Ni–Cu or PGE sulfide deposit: 1) Partial melting; 2) S-saturation and the contribution from the country rocks, especially the S-rich sedi-ments; 3) Interaction between sulfide and silicate liquid (i.e. R-factor); 4) Collection of the sulfide liquid; 5) Fractional crystallization of sulfide liquid; and 6) Post-cumulate processes. An important conclusion not previously noted is that fractional crystallization within the sulfide liquid affects the S/Se ratio.

2. Methodology

The available S/Se or Se data for the Ni–Cu–PGE deposits of the world (Fig. 1) are listed in Table 1 where they are classified by magma type according to Naldrett (2004). Some sub-economic, non-economic and occurrences are presented in this study because these deposits provide insight into the processes governing the S/Se ratio. The geometric mean (geomean), although very close to the arithmetic mean in most cases, was used with the aim of overcoming variations generated by the extreme values in the concentrations of chalcophile elements, as well as for S/Se ratio values. In some publications, the S/Se ratio is presented as whole rock data but in others it is normalized to 100% sulfides. Some

recalculation methods appear to introduce systematic errors, therefore whenever possible we calculated the S/Se ratio based on the whole rock data. To estimate the Pt + Pd concentrations in 100% sulfides (Pt + Pd$_{100\% S}$), we have applied the formula of Barnes and Lightfoot (2005):

$$C_{(100\% sul)} = C_{wr} \times 100/(2.527 \times S + 0.3408 \times Cu + 0.4715 \times Ni) \quad (1)$$

where $C_{(100\% sul)}$ is the concentration of an element in 100% sulfides, C_{wr} is the concentration of the element in the whole rock and S, Cu, Ni are the concentration in wt.% of these elements in the whole rock.

To complete the database, four samples of massive ore from the Ovoïd Zone of the Voisey's Bay deposit were analyzed for S and Se. Sulfur was determined by infrared spectrometry carbon–sulfur analyser (HORIBA EMIA-220 V) according to the method of Bédard et al. (2008). Selenium was determined by Instrumental Neutron Activation Analysis (INAA) after irradiation for 90 min (neutron flux of 4.63 to 5.58 × 10^{11} n cm^{-2} s^{-1}) in the SLOWPOKE reactor at École Polytechnique, Montréal, using the method of Bédard and Barnes (2002).

One of the reasons for our lack of a detailed understanding for the variations in S/Se ratios in magmatic ore deposits is that the concentra-tion of Se in the country rocks that are thought to contaminate the mafic magmas is poorly known. In part because very few studies determine Se in the country rocks to the deposits and in part because until recently it was difficult to determine Se in sediments due to the very low Se concentrations and matrix effects (Fitzpatrick et al., 2009; Hall and Pelchat, 1997; Savard et al., 2009). Consequently, Se concentrations in country rocks are very close to the detection limit of some older analyt-ical methods, which results in unreliable S/Se values. During the build-ing of the database, particular attention was paid to evaluating the quality of Se measurements. Accordingly, some deposits were excluded from this study to limit the risks associated with older, imprecise or inaccurate Se measurements.
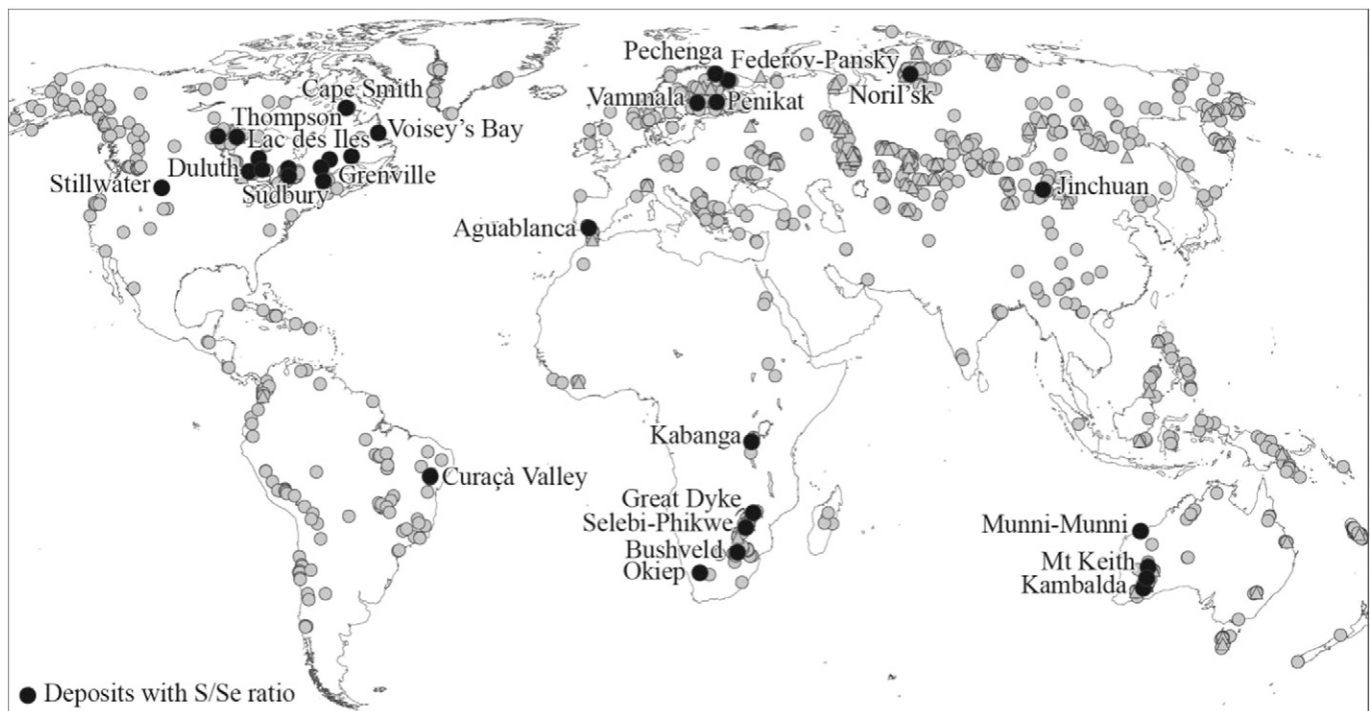

Fig. 1. Location of Ni–Cu–PGE deposits where S/Se ratios or Se data are available. As indicated by solids dots, only few major deposits have been studied using the S/Se ratio. This map includes all types of magmatic Ni–Cu–PGE deposits with at least 100,000 tons of ore (modified from Eckstrand and Hulbert (2007).