



Multiple S isotope studies of the Stillwater Complex and country rocks: An assessment of the role of crustal S in the origin of PGE enrichment found in the J-M Reef and related rocks

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Abstract

The J-M Reef in the Stillwater Complex of Montana is the highest grade Pd deposit in the world, averaging approximately 14 ppm Pd. One suggestion for the origin of the enrichment centers on the sequestration of metals in staging chambers via immiscible sulfide liquids that formed in response to the addition of crustal S. Because $\delta^{34}\text{S}$ values alone are often insufficient to document in igneous rocks the assimilation of S from Archean sedimentary rocks, a combined study of both $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values, and computed $\Delta^{33}\text{S}$ values, was undertaken. $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values of cordierite-bearing hornfels, as well as massive sulfides in the metasedimentary rocks of the contact aureole can be divided into two populations. One is characterized by anomalous positive $\Delta^{33}\text{S}$ values from 0 to 0.32‰ and $\delta^{34}\text{S}$ values from 0.5 to -1.6 ‰, whereas the other is characterized by anomalous negative $\Delta^{33}\text{S}$ values from 0 to -0.22 ‰ and $\delta^{34}\text{S}$ values from 1.5 to 5.8‰. $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values for rocks from the Basal Series of the Complex range from -0.9 to 3.0‰ and 0.01 to 0.18‰, respectively; the anomalous S isotope ratios indicate that for some samples at least 50% of their S was of crustal origin. In contrast, most of the rocks from the J-M Reef are characterized by $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values between -1.3 and 1.8‰ and -0.06 to 0.06‰, respectively. These values deviate only slightly, if at all, from those thought to be representative of mantle S, and suggest that (i) contamination was not an important process for PGE enrichment in the Complex, (ii) the contaminant was also characterized by near 0 $\Delta^{33}\text{S}$ values, or (iii) S isotopic exchange in the staging chambers was an important process. Upgrading of PGE values via reaction between sulfide in the chamber and uncontaminated mantle-derived magma may also have resulted in the conversion of S isotopic ratios that may have been indicative of crustal S addition, to mantle-like values. Rare $\delta^{34}\text{S}$ values up to 7.2‰ in the J-M Reef and 8.2‰ in chromitite from the Ultramafic Series provide strong evidence for localized assimilation of crustal S which did not experience isotopic homogenization. The S isotopic ratios of the J-M Reef are non-unique in terms of a specific genesis as they may be interpreted in either a downward, sulfide collection model, or an upward fluid transport model. © 2017 Elsevier Ltd. All rights reserved.

Keywords: Stillwater complex; Multiple sulfur isotopes; Crustal contamination; PGE enrichment

1. INTRODUCTION

The ~ 2.7 Ga Stillwater Complex, located in the Bear-tooth Mountains in southwestern Montana, contains the

highest Pd grade reef-style PGE deposit in the world. The J-M Reef averages ~ 14 ppm Pd and 5 ppm Pt (Stillwater Mining Company report, 2012). Most of the Pd occurs within pentlandite, whereas Pt occurs within minerals such as Pt-Pd sulfides, Pt-Fe alloys and Pt-Pd tellurides (e.g., Zientek and Oscarson, 1986; Polovina et al., 2004; Godel

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et al., 2006; Godel and Barnes, 2008; Li and Ripley, 2006). The sulfide content of the Reef is low, ranging between 0.1 and 3 volume%. The origin of PGE-rich reefs in layered intrusions in general (e.g., Merensky Reef in the Bushveld Complex as well as the J-M Reef) has been the subject of considerable debate over the past 40 years. Two principal models have emerged: one centered on the collection of PGEs from a silicate magma by immiscible sulfide liquids and downward accumulation (e.g., Campbell et al., 1983), and the other focused on the importance of upward moving late magmatic fluids that remobilized S and PGEs (e.g., Boudreau and McCallum, 1986, 1992; Boudreau, 1999; Boudreau and Meurer, 1999; Meurer et al., 1999). Barnes and Campbell (1988) proposed that hydrothermal fluids interacted with sulfides that had originated via downward accumulation of sulfide liquid. Both models stress the importance of S in the sequestration of PGEs, fortified by the strong correlation between S and PGEs throughout the J-M Reef (e.g., Zientek et al., 2002). Models of immiscible sulfide liquid accumulation (Campbell et al., 1983; Barnes and Naldrett, 1985) have included the process of mixing of two magmas to promote sulfide saturation at very high R-factors (ratio of silicate melt to sulfide liquid). The ‘R-factor’ expression of Campbell and Naldrett (1979), derived from a closed system, two-component mass balance, illustrates important variables in the evaluation of PGE deposits formed in this manner:

$$C(s) = C(\text{sil})D(R + 1)/(R + D)$$

where C(s) is the concentration of the PGE in the sulfide, C(sil) is the initial concentration of the PGE in the silicate magma, D is the partition coefficient defined as C(PGE–sulfide)/C(PGE–silicate), and R is the silicate liquid/sulfide liquid mass ratio. D values have been determined both empirically and experimentally and have been shown to be very large for PGEs. Recent experimental work by Mungall and Brenan (2014) illustrated that D values for Pd may be as high as 5×10^5 . Using the average Pd content of the J-M Reef of 14 ppm and a S content of ~2000 ppm, the Pd content, or tenor, of the sulfide is ~2550 ppm. Keays et al. (2012) suggested that the Pd content of basaltic magmas that may have been parental to rocks of the Stillwater Complex was ~15 ppb. The Pd contents of dikes and sills beneath the Stillwater Complex are in the 5–15 ppb range (Zientek et al., 1985). With a silicate magma Pd content of 10 ppb, the computed R factor necessary to produce the high Pd tenor sulfides exceeds 10^5 . The maximum tenor of the sulfide liquid is limited by the D value, and processes that cause a magma to become saturated in sulfide liquid (e.g. Ripley and Li, 2013) can produce such high R factors only for the first increments of sulfide saturation. As either additional sulfide liquid exsolution or crystallization of the silicate liquid proceeds, the extremely high R factors cannot be maintained. In addition, the height of a magma column (with 10–15 ppb Pd) from which sufficient Pd to produce a 1 meter thick JM Reef (14 ppm Pd) would have been derived must have exceeded ~1400 m. Campbell et al. (1983) suggested that high R factors were produced when sulfide saturation was attained due to magma mixing and small sulfide droplets stirred through the necessary volume of magma as a result of turbulent magma injection. The production and preservation of

very high R factors and the generation of the J-M Reef via settling through a thick magma column have been contentious topics.

One alternative to an in situ process of PGE enrichment involving very high R factors and a thick magma column has been the suggestions that the PGE concentration of the silicate liquid must have been enriched by open system processes. Vermaak (1976) and von Gruenewaldt (1979) suggested that PGE-enriched interstitial melt fractions were expelled from deeper chambers. Keays and Lightfoot (2002), Kerr and Leitch (2005), Li et al. (2009) and Naldrett et al. (2009) proposed models for the production of PGE-enriched magmas that involved the interaction of multiple magmas with sulfide in deep chambers. The extremely high D values for PGEs (Mungall and Brenan, 2014) ensured that small amounts of sulfide remaining in the chamber, in part the result of sulfide dissolution by PGE-bearing but sulfide undersaturated magmas, was PGE-enriched. Keays et al. (2012) proposed that assimilation of crustal S promoted PGE sequestration in staging chambers, and the emplacement of such PGE-enriched magmas accounted for the generation of the J-M Reef. PGEs may have been transported as part of sulfide droplets (sulfide xenomelts; e.g., Lesher and Campbell, 1993) or potentially dissolved as PGE–S complexes.

In order to further evaluate the role of externally derived S in staging chambers and ultimately in the production of the J-M Reef, and to determine the extent of potential S assimilation throughout the Stillwater Complex, we have measured both $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values of rocks within the Reef as well as those above and below. In addition, sulfur isotopic compositions have been determined for pelitic country rocks that occur beneath the Complex. The measurement of multiple sulfur isotope ratios has proven to be very useful in determining the extent of assimilation of Archean S by mafic magmas (e.g., Penniston-Dorland et al., 2008; Bekker et al., 2009; Fiorentini et al., 2012; Ding et al., 2012; Ripley and Li, 2017). Measurements of both $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ are particularly important for detecting the importance of Archean S in mafic igneous rocks because many Archean sedimentary rocks do not show $\delta^{34}\text{S}$ values that differ significantly from mantle values that are near 0‰. The restricted $\delta^{34}\text{S}$ values in Archean sedimentary rocks are often attributed to relatively low sulfate concentrations in Archean oceans (e.g. Canfield and Raiswell, 1999) which resulted in the inability of sulfate reducing bacteria to generate large S isotope fractionation between sulfide and sulfate. Farquhar et al. (2010) and Farquhar and Wing (2003) showed that during the Archean photochemical processes in an oxygen-deficient atmosphere produced anomalous ^{33}S – ^{34}S fractionation (thought to be produced via ‘‘mass-independent fractionation (MIF)’’ with either positive or negative deviation from a Reference Line in $\delta^{33}\text{S}$ - $\delta^{34}\text{S}$ space defined by mass dependent fractionation with a slope of ~0.515) that were recorded in sedimentary rocks. The deviation from the Reference Line is referred to as $\Delta^{33}\text{S}$; the working premise is that magmas that may have assimilated sedimentary rocks with either positive or negative $\Delta^{33}\text{S}$ values may themselves be characterized by anomalous $\Delta^{33}\text{S}$ values. The work compliments

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