Multiple sulfur isotopes reveal a magmatic origin for the Platreef platinum group element deposit, Bushveld Complex, South Africa

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INTRODUCTION

The Platreef ore horizon of the Bushveld Complex, South Africa, is the third largest platinum group element ore deposit in the world, but the origin of its ore remains enigmatic. A complex contact relationship between the igneous and footwall rocks of the Bushveld Complex, coupled with evidence for widespread late-stage hydrothermal processing, obscures the original mineralization history of the Platreef. We constrain the parental magmatic origin of the Platreef by exploiting multiple sulfur isotope contrasts across Bushveld Complex contact zones in order to see through the effects of postmineralization hydrothermal activity. We report S isotope measurements made on samples collected along two profiles through the Platreef into underlying metapelitic and metacarbonate footwall rocks. In both profiles, igneous rocks far from the contact have low Δ33S values (average Δ33S = 0.15%), whereas metasedimentary rocks far from the contact have high Δ33S values (Δ33S to 5.04%) with a smoothly varying profile between the two end members. The midpoint in both isotope profiles is displaced into the footwall, defining a classic advective-dispersive tracer geometry. This geometry is not present in the associated Δ34S values. The displacement of the Δ33S front suggests fluid transport and advection of S into the country rocks; this was accompanied by back diffusion of the S isotope tracer into the Platreef. The Platreef magma was apparently S saturated prior to emplacement and, counterintuitively, lost S during the formation of the present Platreef ore horizon.

SULFUR ISOTOPES

The Bushveld Complex in northern South Africa is the world’s largest layered igneous intrusion, and contains the world’s three largest platinum group element (PGE) ore horizons: the UG2 Chromitite, Merensky Reef, and Platreef (Cawthorn, 1999). The layered mafic-ultramafic Rustenberg Layered Suite of the Bushveld Complex intruded into the Transvaal Supergroup sedimentary rocks (Fig. 1) ca. 2.06 Ga (Buick et al., 2001).

A general model for the formation of the Platreef (e.g., Naldrett, 2004) suggests that an immiscible PGE-rich sulfide melt separated from silicate melt when the mafic magma became saturated with respect to S. Experimental studies (e.g., Mavrogenes and O’Neill, 1999) suggest that for an undersaturated mafic magma to reach S saturation it must either incorporate wall rock or mix with a more felsic melt. Some researchers have postulated that S derived from the underlying footwall rocks was added to the Platreef (e.g., Buchanan et al., 1981; Gain and Mostert, 1982; Sharman-Harris et al., 2005), triggering S saturation. In contrast, processes leading to mineralization in the Merensky Reef and UG2 Chromitite are believed to be purely magmatic in origin (e.g., Campbell et al., 1983; Naldrett et al., 1986; Cawthorn, 2005).

Traditional S isotope compositions {δ34S; δ33S=(33S/32S) sample/(33S/32S) V-CDT − 1} values are shown to be referenced to Vienna Canyon Diablo Troilite (V-CDT), expressed in ‰ of sulfides in the Platreef (Buchanan et al., 1981; Buchanan and Rouse, 1984; Manyeruke et al., 2005; Sharman-Harris et al., 2005) range from ~−3‰ to 10‰, higher than the range of ~−0.6‰ to 3.5‰ measured in unmineralized Bushveld Complex rocks (Buchanan et al., 1981), with the higher values attributed to incorporation of material from footwall rocks (δ34S from ~−12‰ to 29‰). Holwell et al. (2007) defined a narrower range of δ34S values associated with texturally defined primary sulfides (~0.7‰ to 2.6‰) along with a wider range of values associated with secondary and basement sulfides (~1.9‰ to 11.1‰). They developed a complex genetic model for the Platreef including both magmatic and footwall-derived S. Here we show how the addition of Δ33S measurements provides further insight into the mineralization processes affecting the Platreef.

Our research tests the hypothesis that S saturation and subsequent ore formation were triggered by S derived from the underlying footwall rocks during emplacement of the magma. We use mass-independently fractionated sulfur isotopes {Δ33S measurements; Δ33S = δ33S − 1000 × [(1 + δ34S/1000)1/0.515 − 1]} to track the sulfur source in the Platreef. This approach represents a new application of a recently developed isotopic tracer. Sedimentary rocks with a depositional age older than 2.45 Ga, such as those underlying the Platreef, may record mass-independent (nonzero) values of Δ33S, which would contrast with the Bushveld Complex magma (Δ33S ~ 0). The juxtaposition of two reservoirs of S (parental magma and footwall rock) that had distinctly different S isotopic compositions provides a setting where the transport and sources of S can be evaluated.

APPLICATION OF MULTIPLE SULFUR ISOTOPES

Measurements of sulfur isotopes from samples younger than ca. 2.0 Ga form a well-defined array with δ33S ~ 0.515 × δ34S (see GSA Data Repository Fig. DR1; Hulston and Thode, 1965; Farquhar and Wing, 2003). The close covariation between values of δ33S and δ34S reflects the strong dependence of fractionation on the mass difference between the isotopes. Since Δ33S values quantify the deviation of a sample datum from this reference fractionation array, the close covariation is also the reason that samples of this age define near zero Δ33S values with 95% of the samples being between ~−0.11‰ and 0.20‰ (Farquhar et al., 2000, 2002). The small deviations of Δ33S values from zero for this data set may reflect biogeochemical cycling of S in low-temperature environments (Johnston et al., 2005).

Large-magnitude (mass independent) variations for Δ33S values are observed in the more ancient parts of the geologic record (Fig. DR2).
Sulfur multiple isotope compositions of Platreef footwall rocks are characterized by relatively high $\Delta^{33}S$ values ranging up to 5.04‰, and a broad range of $\delta^{34}S$ values, from $-14.5$‰ to 8.1‰. The $S$ multiple isotope composition of five relatively pristine whole-rock samples chosen as proxies for the parental Platreef magma are characterized by $\Delta^{33}S$ values ranging from 0.11‰ to 0.21‰ with a narrow range of $\delta^{34}S$ values, from 1.3% to 3.2%, consistent with previous estimates (Sharman-Harris et al., 2005; Holwell et al., 2007). Sulfur multiple isotope compositions of Platreef ore horizon rocks are characterized by $\Delta^{33}S$ values that range from 0.03‰ to 0.55‰ and measured $\delta^{34}S$ values that range from 2.7‰ to 11.4‰ (Table DR1).

Samples from detailed profiles along the length of two cores drilled through the Platreef into underlying footwall rock were analyzed; one core had carbonate footwall (SS315) and the other had pelitic footwall (TN190D1) (see Fig. 1 for locations). In both cores the measured $\Delta^{33}S$ values are relatively low in the Platreef far from the contact (upper parts of the cores), with values that are below or within error of the range of the measured values for relatively pristine igneous rocks from the Bushveld Complex (Figs. 2 and 3). In both cores the measured $\Delta^{33}S$ values are relatively high in the footwall rock far from the contact (lower parts of the cores) with values of $\Delta^{33}S$ that range up to 0.93‰ in TN190D1 and to 5.04‰ in SS315. The initial transition downward through both cores is a smooth profile with increasing $\Delta^{33}S$ values into the footwall rock with a midpoint in the isotopic profile located in the footwall. Measured values of $\delta^{34}S$ do not have the same consistency in end-member compositions, and they do not record a similar smooth profile (Figs. DR3 and DR4).

In the carbonate core (SS315) there are measured $\Delta^{33}S$ values in the lower part of the Platreef $<5$ m from the contact with the footwall rock that are above the range of values from samples that represent parental Platreef magma ($\Delta^{33}S$ values range up to 0.55‰). All measured compositions in the Platreef in core TN190D1 are below or within error of the range of parental Platreef magma.

DISCUSSION

There are two striking results of the present study. The first is the preservation of smoothly varying profiles of $\Delta^{33}S$ values, despite a discontinuous distribution of $\delta^{34}S$ values, into the Platreef footwall. We explain this observation using the chemically conservative behavior of $\Delta^{33}S$ values in high-temperature geologic environments. The profile of $\Delta^{33}S$ values represents the initial signature of interaction between the Platreef magma and its footwall, while later isotopic exchange has modified the associated profile in $\delta^{34}S$ values. The second remarkable
observation is that the $\Delta^{33}S$ profiles are not symmetric about the Platreef-footwall contact, but are displaced into the rocks of the footwall. This counterintuitive feature implies that the Platreef magma has isotopically dominated the S isotope signal present in the rocks of the Platreef footwall. Both of these results can be validated within the framework of tracer mass transport (Bickle and McKenzie, 1987).

A solution to the mass-continuity equation including advection, diffusion and/or dispersion, and local fluid-mineral equilibrium has been fit to the profiles from both of the detailed core traverses (e.g., Bickle et al., 1997). Figures 2 and 3 show the S isotope compositions along with the modeled fits for both traverses. The results are similar for the two profiles, suggesting that the processes are not overly sensitive to the nature of the wall rock. The best fits suggest roughly similar advective distances ($z^*$) of the S iso- tope front (16 m for SS315 and 27 m for TN190D1) into the footwall rocks and roughly similar distances of diffusive and/or dispersive exchange of S ($D^* \times t$) where $D^*$ is effective diffusivity, and $t$ is the duration of diffusion) for the two cores (6.3 m for SS315 and 8.9 m for TN190D1). The modeled profile represents a first-order explanation of the isotopic systematics, as other factors (e.g., sedimentary heterogeneity) have likely affected the isotopic variability of the system.

The $\Delta^{33}S$ value of the parental Platreef magma far from the contact has been established by measurements from relatively pristine igneous rocks from the Platreef and Main Zone. These samples have S isotope compositions ($\Delta^{33}S = 0.11\%$ to $0.21\%$) that are slightly enriched in $^{33}S$ relative to inferred juvenile mantle sources ($\Delta^{33}S = 0.03\%e \pm 0.04\%e$; Table DR1; Farquhar et al., 2002). All $\Delta^{34}S$ values are positive, suggesting that the parental Platreef magma may have had a positive $\Delta^{33}S$ component. A mass-independent component could be explained by interaction of the Platreef magma with deeper-seated footwall rocks in a staging chamber (e.g., Davies et al., 1980; Harris et al., 2005). A more detailed suite of samples needs to be analyzed to characterize the S isotope composition of Platreef magma prior to emplacement.

The $\Delta^{33}S$ values distal to the contact on the footwall side of the profiles have been treated as free parameters in our fits. Both profiles exhibit heterogeneity in distal wall rock $\Delta^{33}S$ values that is outside measurement uncertainty. We attribute this to pre-emplacement or post-emplacement isotopic variability of the Platreef footwall. Although we have not attempted a quantitative reconstruction of this heterogeneity, the present distal geometry of the profiles is qualitatively consistent with modification by advection and diffusion and/or dispersion. For example, the distal wall rock in core SS315 has heterogeneous $\Delta^{33}S$ values (3.35‰ to 5.04‰). The profile for core SS315 is best fit using a $\Delta^{33}S$ value slightly higher than the highest measured $\Delta^{33}S$ value as the distal value for the wall rock. Below the maximum value, the $\Delta^{33}S$ values decrease with depth in the core, suggesting dispersive and/or diffusive modification both upstream and downstream from a maximum $\Delta^{33}S$ value. The upper profile is sharper, which reflects the contribution of upstream back diffusion against the overall advective movement of the S isotope tracer. The broader lower profile reflects the contributions of both diffusion and dispersion of the S isotope tracer acting in the downstream direction (cf. Skelton et al., 1997). The medium for outward advection and diffusion of S was likely an aqueous fluid since the sulfide mineralogy is different in the different lithologies of the footwall rocks, although the possibility of an immiscible sulfide liquid is not entirely ruled out. Concentration of sulfide phases in veinlets within the footwall rocks supports the hypothesis of outward advection of a sulfur-bearing fluid.

The $\Delta^{33}S$ profile in core SS315 shows that small but significant mass-independent S isotope compositions within the Platreef ($\Delta^{33}S$ values range up to $0.55\%e$) occur adjacent to the contact with footwall rocks (Fig. 2). This observation corroborates published suggestions, based on $\delta^{34}S$ measurements, of wall rock S in the Platreef ore horizon (Buchanan et al., 1981; Gain and Mostert, 1982; Manyeruke et al., 2005; Sharman-Harris et al., 2005; Holwell et al., 2007). Recent texturally specific $\delta^{34}S$ measurements of Platreef sulfides imply that introduction of wall rock S into the ore system postdated the main phase of Platreef mineralization (Holwell et al., 2007). The $\Delta^{33}S$ profile demonstrates, however, that the Platreef ore horizon was enriched in wall rock S during the initial emplacement of the Platreef magma; contact enrichment occurred through the process of back diffusion against an outward advection of S-bearing species from the crystallizing magma (Fig. 2).

**IMPLICATIONS**

Our multiple S isotope results suggest a different interpretation of Platreef mineralization than that reached by consideration of only $\delta^{34}S$ values. The $\Delta^{33}S$ measurements reflect a dominantly magmatic signature for S in the Platreef. This signature is obscured in $\delta^{34}S$ measurements by late-stage disequilibrium and fractionation effects likely due to hydrothermal activity. This interpretation is consistent with the results of Harris and Chaumba (2001) that suggest a large degree of fluid-rock interaction in the Platreef with a magmatic origin for the fluid. Although $\delta^{34}S$ analyses can decipher this signature when carefully linked to specific sulfide textures (e.g., Holwell et al., 2007), the chemically conservative nature of $\Delta^{33}S$ values lets us easily see through the veil of secondary processes that are mass dependent and fractionate $\delta^{34}S$, but not $\Delta^{33}S$.

Most intriguing, $\Delta^{33}S$ measurements rule out local footwall-derived S as a significant trigger for mineralization in the Platreef. The $\Delta^{33}S$ profile indicates that contact enrichment of S in the Platreef is limited to distances <5 m from the contact and is best explained by minor amounts...
of back diffusion through fluids as it is transported away from a cooling and crystallizing magma. While our data cannot definitively rule out more complex, multistep mineralization processes, it appears that, rather than being the odd exception to the rule, the Platreef forms, along with the Merensky Reef and UG2 Chromitite, a spectrum of magmatic PGE deposits hosted by layered igneous intrusions.

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