Contamination of the Bushveld Complex (South Africa) magmas by basinal brines: Stable isotopes in phlogopite from the UG2 chromitite

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ABSTRACT

There is abundant evidence for significant H_2O in evolved melts from the platinum-rich UG2 chromitite and the Merensky Reef of the Bushveld Complex (South Africa), but there is no consensus about the source of H_2O. We report triple-oxygen and hydrogen isotope ratios of interstitial, late-magmatic phlogopite from three localities of the UG2 layer. The phlogopite yielded δD values of −43‰ to −23‰, which is >30‰ higher than previously known from Bushveld rocks and far above the mantle values of ∼−75‰. The phlogopite triple-oxygen isotope ratios are the first to be reported for Bushveld rocks, with values of $\Delta'^{17}O_{0.5305}$ (^{17}O excess relative to the reference line 0.5305) from −0.069‰ to −0.044‰ ($\delta^{18}O$ 5.2‰–6.2‰). The oxygen data support existing models of as much as 30%–40% contamination of mantle-derived magmas in the lower to middle crust. However, the high δD values require a second step of contamination, which we attribute to brines from the marine sediments in the Transvaal Basin at the emplacement level.

INTRODUCTION

Understanding the petrogenesis of mafic layered intrusions and their mineralization remains a huge challenge, and among many open questions is the role of H_2O in these essentially anhydrous igneous bodies (Charlier et al., 2015). The Rustenburg Layered Suite (RLS) of the Bushveld Complex (South Africa) contains the world's three largest deposits of platinum-group elements: the Upper Group 2 (UG2) chromitite and the Merensky Reef in the upper Critical Zone (CZ) in the eastern and western limbs of the complex, and the Platreef in the northern limb (Fig. 1). Crystallized melt inclusions containing phlogopite, hornblende, and Cl-rich apatite have been reported in UG2 chromite and Merensky Reef olivine, confirming a role of hydrated melts in the formation of these layers (Li et al., 2005; Schannor et al., 2018;

Smith et al., 2021). These late-stage melts crystallized interstitial phlogopite, which is closely intergrown with chromite and sulfide minerals (Smith et al., 2021). It has been suggested that interaction of hydrated, Cl-rich melts with near-solidus cumulates of the UG2 and Merensky Reef caused remelting of the latter and remobilization of fluid-mobile elements (e.g., Mathez and Mey, 2005; Boudreau, 2008). Veksler and Hou (2020) confirmed experimentally that adding 4 wt% H_2O to a B1 composition (parental melt composition for the CZ; Barnes et al., 2010) shifts the liquidus assemblage from silicate minerals to Cr-spinel. They inferred that localized H_2O additions from the floor of the Bushveld magma chamber could have remelted pyroxenite cumulates and precipitated chromite, thus forming chromitite layers like UG2.

While the evidence for late hydrous melts in the CZ is well documented, the source of H_2O is not. One option is concentration of primary, mantle-derived H_2O in residual melts by frac-

tional crystallization, while the other is derivation from external, crustal sources. The latter might be suggested by long-established evidence for crustal contamination of RLS magmas from high Sr- and Os-isotope ratios (Hart and Kinloch, 1989; McCandless and Ruiz, 1991; Kruger, 1994) and from $\delta^{18}O$ values higher than the mantle composition (Schiffries and Rye, 1989; Harris et al., 2005). Benson et al. (2020) reviewed evidence for large-scale fluid generation in the thermal aureole beneath the Bushveld intrusion and used geochemical and thermal-mechanical models to show how such fluids might have affected the RLS magmas. Surprisingly few studies have addressed the source of H_2O by coupled hydrogen and oxygen isotope analysis of OH-bearing minerals, possibly because conventional methods required prohibitively large amounts of pure mineral separates given the low abundance of phlogopite. Two exceptions are studies by Mathez et al. (1994) and Willmore et al. (2002), who reported δD values of biotite from the Merensky Reef and other pyroxenite units from the CZ. There are a number of published bulk-rock values of δD, but these are harder to interpret because the mineral hosts of H_2O are unknown. We report the first co-registered H and triple-O (^{16}O, ^{17}O, and ^{18}O) isotopic ratios in late-magmatic phlogopite from the UG2 horizon at three localities spaced throughout the complete RLS (Fig. 1). Our analytical techniques require a sample mass of just a few milligrams, low enough to obtain high-purity phlogopite separates from the UG2 chromitite and also from silicate wall rocks.
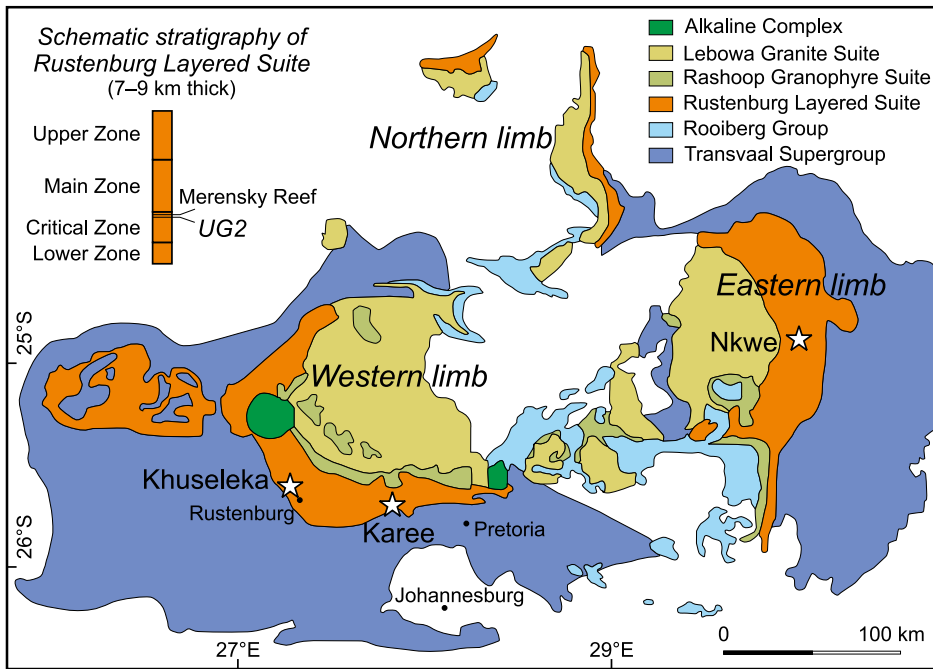
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Figure 1. Simplified geological map of the Bushveld Complex, South Africa (after Kinnaird et al., 2005), with study locations (stars) and a schematic stratigraphy of the Rustenburg Layered Suite.

SAMPLES AND METHODOLOGY

Samples were collected from industry drill cores through UG2 in the Nkwe, Khuseleka (chromitite and wall rocks), and Karee (chromitite only) mines. Details of UG2 at these mines are given by Veksler et al. (2018) and Junge et al. (2014). The spatial distribution and abundance of phlogopite in the samples were determined by micro–X-ray fluorescence element mapping on the same polished thin sections used for electron microprobe analyses. Phlogopite was separated from ~10 g of crushed, sieved rock material, and the stable isotopic ratios of hydrogen and oxygen were measured by thermal conversion elemental analyzer (TC/EA) and laser fluorination, respectively. Details of methods and analytical conditions are given in the Supplemental Material[1].

RESULTS

Phlogopite Occurrence and Composition

Phlogopite forms fresh, reddish-brown, interstitial grains (0.1–1 modal%, ~50–500 μm in size) in the UG2 chromitite and its silicate wall rocks. It is evenly disseminated in the samples, with no clustering or connectivity between grains (Fig. S1 in the Supplemental Material). Phlogopite replaces orthopyroxene in UG2 chromitite and is intergrown with chromite, plagioclase, sulfides, and platinum-group minerals (Figs. 2A and 2B). Locally, phlogo-pite is associated with myrmekitic K-feldspar–quartz intergrowths (Figs. 2C and 2D). The phlogopite within chromitite has Mg# [100 × Mg/(Mg + Fe^{2+})] of 92–97, molar K/(K + Na) of 0.81–0.97, and TiO$_2$, F, and Cl contents of 3.0–5.1, 0.1–0.6, and 0.1–0.4 wt%, respectively (Table S1, Figs. S2 and S3). Phlogopite in silicate wall rocks has a lower Mg# (71–88), higher K/(K + Na) ratio (0.97–1), and nearly the same range of TiO$_2$, F, and Cl contents.

Hydrogen and Oxygen Isotopic Ratios

The total range of δD for phlogopite within chromitite is −38‰ to −23‰ (Table S2; Fig. 3), and the average values from each locality are nearly identical (Nkwe: −30‰ ± 4‰, n = 6; Khuseleka: −33‰ ± 1‰, n = 6; Karee: −29‰ ± 3‰, n = 8). Phlogopite from silicate rocks is similar in terms of range (−43‰ to −26‰) and average values (Nkwe: −33‰ ± 7‰, n = 4; Khuseleka: −32‰ ± 5‰, n = 3). All separates yielded stoichiometric H$_2$O contents (3–4 wt%). This, combined with the lack of correlation between δD and H$_2$O (Fig. S4) and the stoichiometric contents of 9 wt% K$_2$O + Na$_2$O rules out significant chloritization. We estimated the magmatic δD range as −37‰ to −16‰ using the compositionally dependent $\Delta D_{phlogopite\text{-}water}$ ($\delta D_{phlogopite}$ − δD_{water}) equation at 800 °C (Table S2; Suzuoki and Epstein, 1976), based on the chromite-plagioclase O-isotope closure temperature from the Nkwe UG2 (Schannor et al., 2018), 750 °C for F-Cl-OH exchange between phlogopite and apatite (Willmore et al., 2000), and 850 °C for Ti thermometry of zircon associated with phlogopite from the UG2 foot-wall (Zeh et al., 2015).
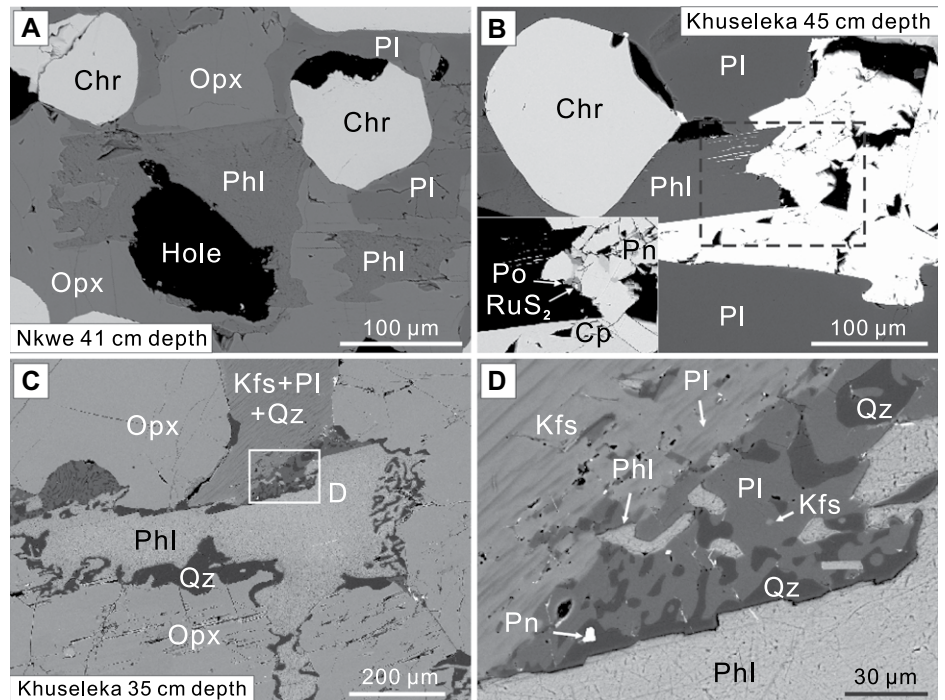
Figure 2. Microtextures of interstitial phlogopite in the UG2 chromitite and silicate wall rocks of the Bushveld Complex (South Africa) (backscattered electron images). (A) Phlogopite (Phl) in chromitite replacing orthopyroxene (Opx). (B) Phlogopite in chromitite with plagioclase (Pl), chromite (Chr), and ore minerals (inset: Cp—chalcopyrite; Pn—pentlandite; Po—pyrrhotite; RuS$_2$—laurite). (C,D) Phlogopite in pyroxenite with granophyric quartz (Qz), K-feldspar (Kfs), and plagioclase.

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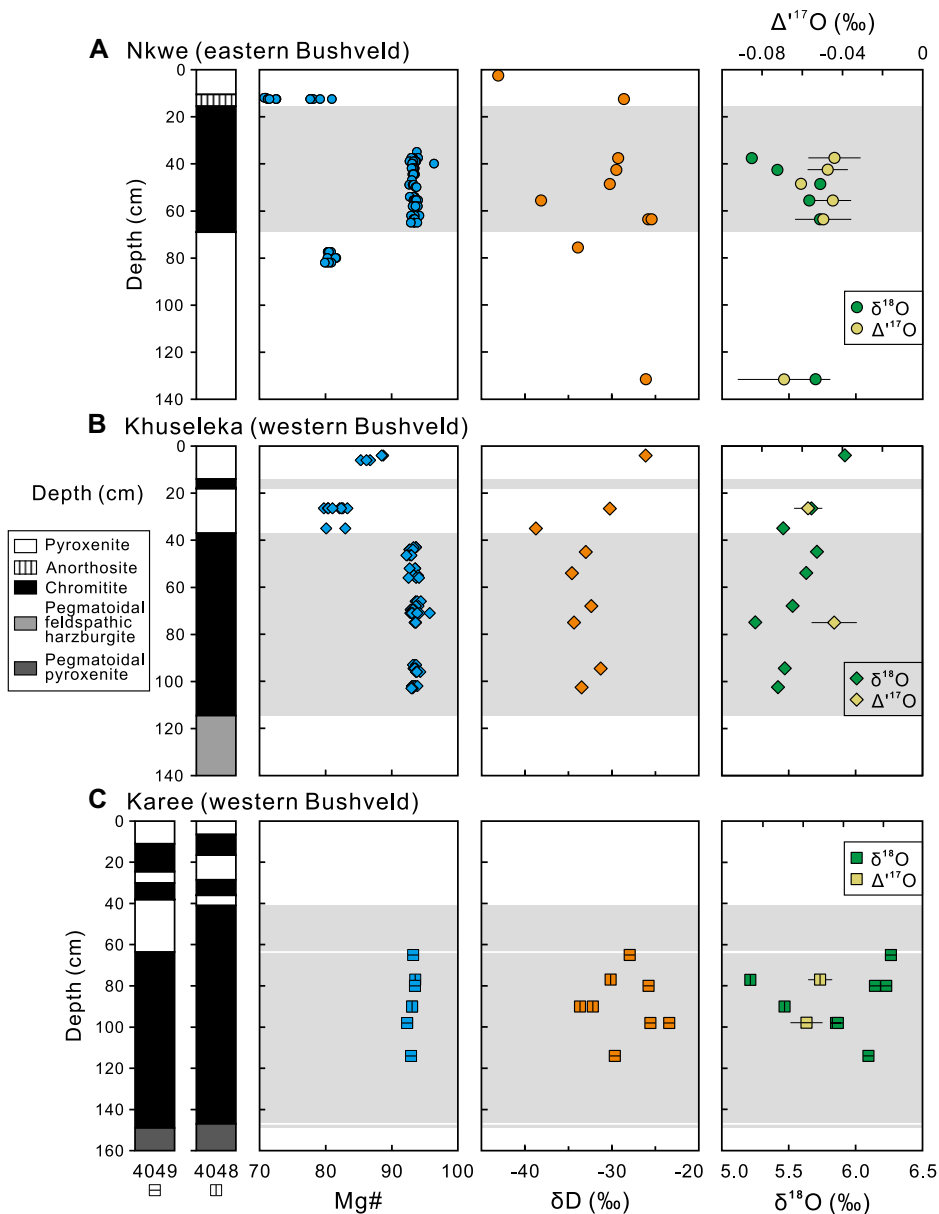
Figure 3. Variation of Mg# [100 × Mg/(Mg + Fe²⁺)], δD, δ¹⁸O, and Δ′¹⁷O (error bars at 1 standard deviation) in phlogopite from the three UG2 chromitite (Bushveld Complex, South Africa) localities studied. Light gray zones across each of the plots represent chromitite layers. For Karee, two drill cores (4048 and 4049) are shown in the same plots.

The $\delta^{18}O$ values of chromitite-hosted phlogopite are practically the same in all localities (5.7‰ ± 0.3‰, $n = 19$; Table S2; Fig. 3), and this is also true for phlogopite in silicate rocks (5.7‰ ± 0.2‰, $n = 4$). The corresponding magmatic values are 6.6‰ ± 0.3‰ based on $\Delta^{18}O_{\text{phlogopite-basalt}}$ of −0.9‰ at 800 °C (Zhao and Zheng, 2003). Not all samples yielded enough phlogopite for combined D/H and triple-O measurements, so the latter are fewer in number (Fig. 3). The $\Delta'^{17}O$ values, expressing ¹⁷O excess relative to the reference line 0.5305, are calculated as: $\Delta'^{17}O = \delta'^{17}O - 0.5305 \times \delta'^{18}O$, where $\delta'^{17,18}O = 1000 \times \ln(\delta^{17,18}O/1000 + 1)$. They range from −0.069‰ to −0.044‰ and are similar in all localities (Nkwe: −0.053‰ ± 0.009‰,

$n = 6$; Khuseleka: −0.051‰ ± 0.007‰, $n = 2$; Karee: −0.054‰ ± 0.003‰, $n = 2$). These $\Delta'^{17}O$ values can be considered equivalent to magmatic values given the negligible difference in $\Delta'^{17}O$ between magma and minerals at high temperatures (Bindeman, 2021). There are no correlations of either $\delta^{18}O$ or δD with the chemical composition of phlogopite (Figs. S5 and S6).

DISCUSSION

Comparison with O-H Isotope Data from the Bushveld Complex

The triple-O isotopic ratios reported here are the first published for the Bushveld Complex. Our average $\delta^{18}O$ values for UG2 phlogopite (5.7‰ ± 0.3‰) are similar to biotite data from

CZ pyroxenites (5.6‰–5.7‰; Willmore et al., 2002), and both data sets suggest a magma composition of 6.6‰ ± 0.3‰, which is consistent with the RLS range (6.8‰–7.1‰; Schiffries and Rye, 1989; Harris et al., 2005). In contrast, the δD values of phlogopite from UG2 at all three localities studied (−43‰ to −23‰) are distinctly higher than previously reported for the RLS (Fig. 4A), although there are no published data from the UG2 layer. The range of δD values for phlogopite or biotite from the Merensky Reef, other CZ rocks, and the Platreef (−88‰ to −49‰; Mathez et al., 1994; Harris and Chaumba, 2001; Willmore et al., 2002; Pronost et al., 2008) is similar to the bulk-rock range for the entire RLS (−99‰ to −53‰; Mathez et al., 1994; Harris et al., 2005). The authors cited above suggested a magmatic source of H₂O because the δD values are similar to those of mantle rocks (−75‰ ± 12‰; Loewen et al., 2019). A late-magmatic origin of phlogopite in UG2 is indicated by textures (e.g., interstitial grains with no connection outside the layer; intergrowths with chromite, sulfide minerals, and feldspar–quartz microgranophyre) and chemical composition (e.g., high TiO₂, stoichiometric K₂O and H₂O contents). Therefore, we consider the phlogopite δD values to reflect those of the magma. Our estimate of δD for the UG2 magma based on phlogopite (−37‰ to −16‰) is at least 30‰ higher than the mantle value.

The Origin of High δD in UG2

In principle, high magmatic δD can be source related or related to processes of magma evolution including mixing and assimilation. Source-related D/H enrichment in the mantle has been attributed to subduction-related metasomatism (Loewen et al., 2019), and indeed, a link between Bushveld parental magmas and subduction-related boninites has been suggested (e.g., Willmore et al., 2002). However, if the high δD values in UG2 were source related, they should be found throughout the RLS, which is not the case. Processes that enrich D/H during magma evolution include degassing, crystallization of abundant hydrous minerals, and contamination with external, high-δD material. Degassing cannot be ruled out for the shallow-level Bushveld intrusion, but there is no reason why this process should affect UG2 more than other layers of the RLS, so it is discounted. Enrichment of D/H in residual magma due to crystallization of hydrous minerals is unlikely because all but the latest, interstitial phases are anhydrous. The same argument rules out post-cumulus equilibration of interstitial melts with the surrounding, anhydrous cumulus minerals. Therefore, contamination of the UG2 magma seems the only likely explanation.

Harris et al. (2005) compiled new and existing isotopic data showing a narrow range of magmatic $\delta^{18}O$ values throughout the RLS
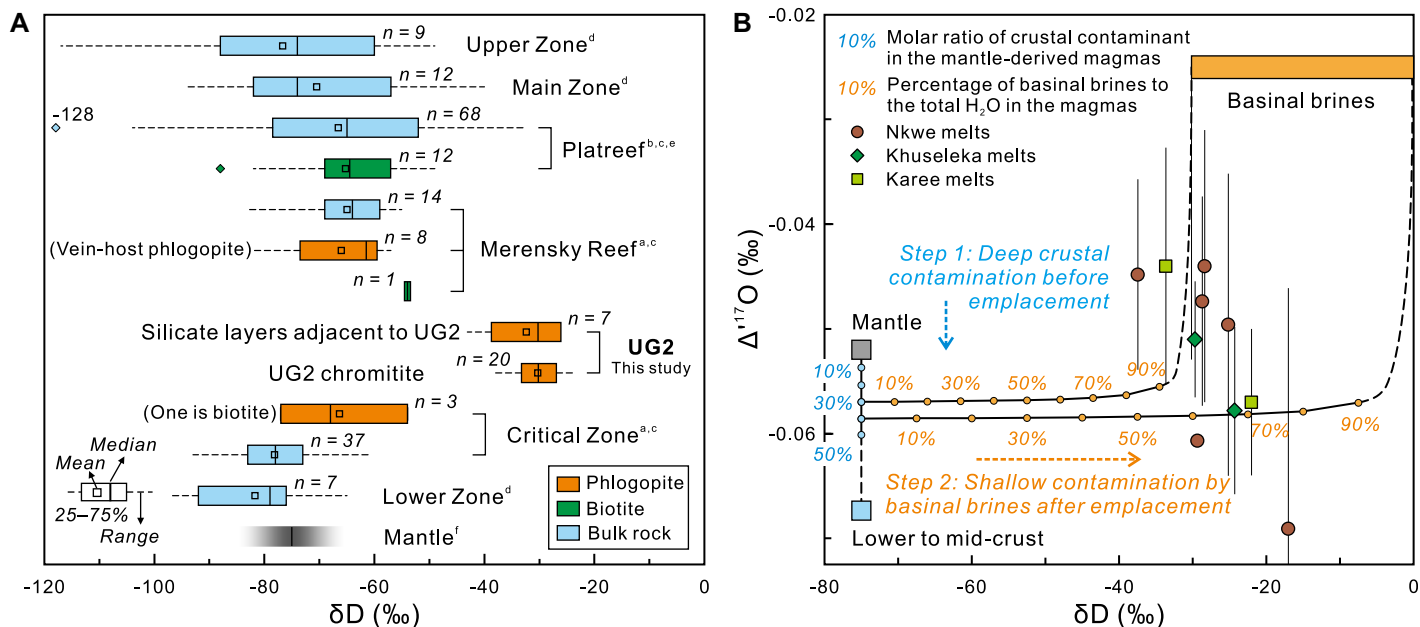
Figure 4. (A) Statistical summary of all available δD values from the Rustenburg Layered Suite (RLS, South Africa). Sources: a—Mathez et al. (1994); b—Harris and Chaumba (2001); c—Willmore et al. (2002); d—Harris et al. (2005); e—Pronost et al. (2008); f—Loewen et al. (2019). **(B)** Δ'[17]O–δD plot showing two-step mixing model. Δ'[17]O is shown with 1 standard deviation; see the Supplemental Material (see footnote 1) for data sources and model details. Step 1 (following Harris et al., 2005) is contamination of mantle-derived magmas with Archean rocks (orthogneiss, high-grade metapelites) in lower to middle crust; step 2 is shallow emplacement of contaminated RLS magmas into Transvaal Basin and incorporation of basinal brines (connate seawater) into UG2 melts.

(7.1‰ ± 0.5‰) that are higher than the mantle composition (5.7‰ ± 0.2‰; Ito et al., 1987; Bindeman, 2008) and indicate significant crustal contamination. They argued that the uniformity in $δ^{18}O$ requires that contamination took place before emplacement and at a deep level, proposing 30%–40% contamination by Archean basement (with $δ^{18}O = 9.2‰–9.6‰$) in the lower to middle crust. In terms of $δ^{18}O$, the UG2 magma appears to be no different than that of other layers of the RLS, and can be explained by the contamination model of Harris et al. (2005). The new Δ'[17]O values from this study (−0.069‰ to −0.044‰) are also consistent with this model (Fig. 4B), although we note that the triple-O isotope composition of potential contaminants is poorly constrained (see the Supplemental Material for more discussion). However, the distinctly high δD values of UG2 imply that the magma was affected by a separate (and presumably later) process that was capable of increasing δD without causing a significant shift in $δ^{18}O$. Mass-balance considerations suggest an aqueous fluid with high δD as the most likely contaminant, and the fact that RLS magmas intruded unmetamorphosed marine sedimentary rocks of the Transvaal Supergroup makes it likely that this contamination took place at the emplacement level. Benson et al. (2020) modeled the consequences of contact metamorphism and dehydration of the Transvaal sediments and showed how fluids could have been introduced into the overlying RLS by a combination of footwall diapirism and localized overpressure-driven channels.

We suggest that seawater-derived basinal brines in the Transvaal Supergroup sediments would have appropriately high D/H ratios to raise the magmatic δD substantially without affecting oxygen isotope ratios. Furthermore, saline brines provide an alternative to subduction fluids for explaining the high Cl contents found in interstitial phlogopite and apatite from the CZ (Willmore et al., 2000, 2002). Support for this suggestion comes from a study by Gleason et al. (2011), who proposed that Mississippi Valley–type mineralization around the Bushveld Complex was related to basinal brine circulation caused by the intrusion. Estimates of the δD values of Proterozoic seawater are 0‰ ± 20‰ (Pope et al., 2012; Zakharov and Bindeman, 2019). Schiffries and Rye (1990) reported −34‰ δD for fluid inclusions from the Bushveld aureole, which might represent such brines. Figure 4B and Figure S7 explore the two-step contamination scenario we propose (see the Supplemental Material). The first-step scenario follows Harris et al. (2005) as discussed above. For the second step, we assumed a range of −30‰ to 0‰ for δD in Transvaal Basin brines based on the arguments above. We used 0.3 wt% H_2O for the initial magma based on chemical analyses of B1-type sills (Barnes et al., 2010) and −75‰ for δD from average RLS values. The curves shown for $δD_{brine} = −30‰$ to 0‰ match the UG2 δD at 50%–90% mixing (brine to total dissolved H_2O), with negligible shifts of $δ^{18}O$ (−0.1‰) or Δ'[17]O (+0.001‰). Melt inclusions in Merensky Reef chromite contain 2.6 wt% H_2O (Li et al., 2005). If we assume a

similar concentration for H_2O in the late-stage UG2 melts and 0.3 wt% for initial B1 magma, then ~90% of the H_2O in these hydrous melts is externally derived, which is in agreement with the mixing model.

In summary, a two-step contamination process is proposed to explain the distinctive O-H isotope composition of the UG2 magma (Fig. 4B). The first step took place well below the emplacement level and involved the bulk of RLS magmas, raising their $δ^{18}O$ values to ~7‰ without much effect on δD (median RLS values: −80‰ to −70‰; Fig. 4A). The second step took place at the emplacement level, where thermal metamorphism and loading at the floor of the intrusion caused large-scale release of basinal brines from sediments of the Transvaal Supergroup. Injection of overpressured brine into the magma, possibly as proposed by Benson et al. (2020), led to an increase in δD. While this model can explain the O-H isotopic composition of late-magmatic phlogopite from UG2, there are still open questions. From the scant H-isotope data available, it appears that the Merensky Reef, although it also hosts phlogopite and hydrated melt inclusions, does not share the high-δD signature of UG2. Without more δD data from other layers of the Bushveld Complex, it is premature to speculate if and why external brines might have played a particular role in the development of UG2. We conclude by suggesting that phlogopite δD has proven value in distinguishing fluid sources in the Bushveld magmas and should be more widely applied.

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