A Study of the $\Delta^{33}S$ Signature of Xenoliths from the Premier Kimberlite, South Africa

Greg Polley Geol393H

Advisors: Dr. Sarah Penniston-Dorland[1] & Dr. James Farquhar[1]

[1] University of Maryland, College Park. Department of Geology

Introduction

South Africa hosts the largest layered igneous intrusion and platinum-group element (PGE) repository in the world, the Bushveld Complex. Emplaced roughly 2.05 Ga within the Kaapvaal craton, the magma sources of this complex have been widely debated (Richardson and Shirey, 2008). Although the magma itself is thought to be derived from the mantle, previous isotopic analyses of oxygen, strontium, neodymium, and osmium suggest significant amounts of crustal contamination. Measurements of non-zero $\Delta^{33}S$ for Bushveld igneous rocks also suggest contamination (Penniston-Dorland et al., 2008). Models to explain these anomalous isotopic signatures include contamination of magma upon emplacement, sub-continental lithospheric mantle, and contamination of magma residing in a lower crustal staging chamber (Shiffries & Rye, 1989; Richardson and Shirey, 2008; Harris et al., 2004). The juvenile mantle is thought to possess a $\Delta^{33}S$ signature of zero; however, only a small suite of mantle-derived samples has been investigated for multiple sulfur isotopic composition. The Premier kimberlite pipe, located centrally within the Kaapvaal craton, hosts numerous mantle xenoliths suitable for sulfur isotopic analysis.

The hypothesis of this project is that mantle xenoliths from the Premier kimberlite have a nonzero $\Delta^{33}S$ isotopic signature.

Geologic Setting

Premier Kimberlite

•Located centrally within the Kaapvaal craton, about 50 km east of Pretoria, South Africa.

•Emplacement age of 1179 ± 36 Ma (Smith, 1983).

•Hosts numerous eclogite and peridotite xenoliths suitable for sulfur isotopic analysis.

•The mantle xenolith suite from Premier contains abundant garnet peridotites, lesser quantities of spinel peridotites, igneous textured xenoliths with hydrous minerals, eclogite xenoliths, and common Cr-poor megacrysts (Gregoire et al., 2005).

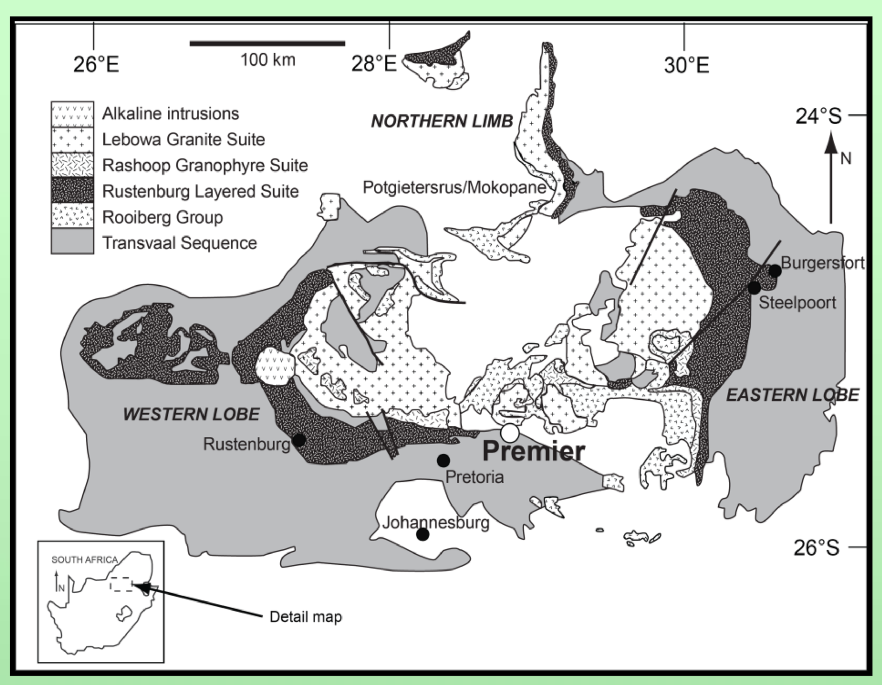
•The most common types of xenoliths from the Premier kimberlite are garnet and spinel harzburgites and garnet lherzolites.

Bushveld Complex

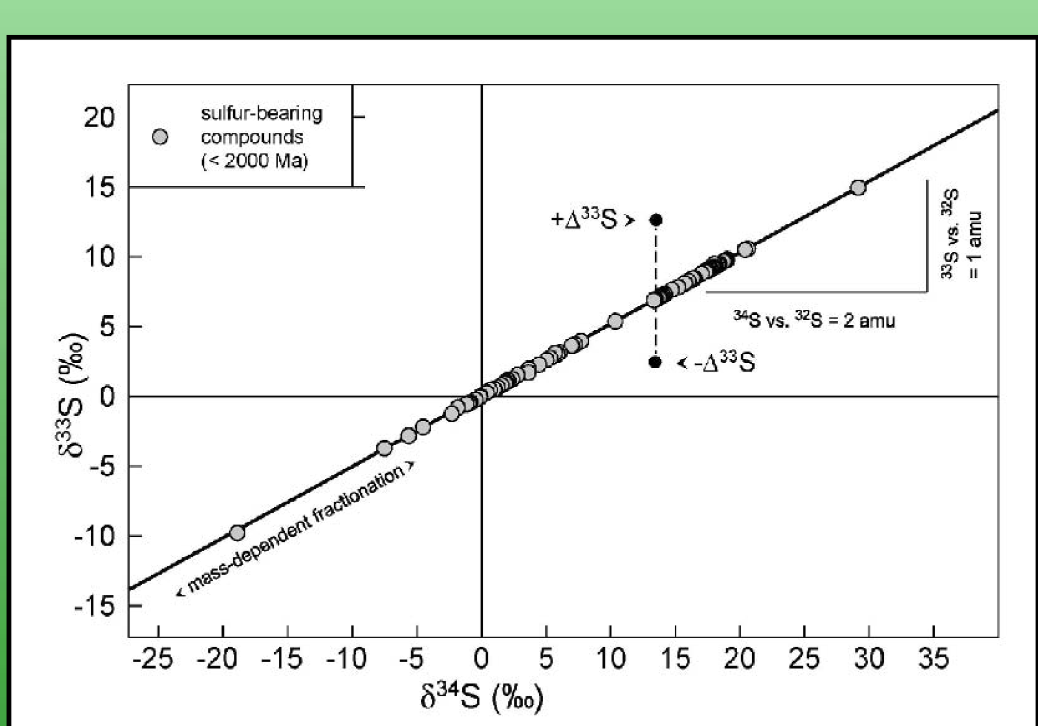
•The Bushveld Complex in South Africa is the world's largest mafic-ultramafic layered igneous intrusion covering an area of nearly 66,000 km^2.

•The origin of the unusual characteristics of the Bushveld Complex is still ambiguous, whether they are related to crustal contamination or partial melting of enriched mantle lithosphere, and whether the complex was formed by intrusion and solidification of multiple pulses of magma or was one open system through which magmas passed to the surface (Hatton & Sharpe, 1989; McCandless et al., 1999; Maier et al., 2000). Three models have been proposed to explain the anomalous characteristics of the Bushveld, and are discussed in a separate section.

The Premier kimberlite is both spatially and temporally associated with the Bushveld Complex . The Premier kimberlite pipe intrudes the Bushveld Complex in the south, and the ages of the xenolith samples as acquired from Re-Os depletion techniques are about 2.05 billion years old, approximately the same age as the Bushveld (Carlson et al., 2000). This implies that these xenoliths sample the original Bushveld mantle source.



Sulfur Isotope Notation



$$\Delta^{33}S = \delta^{33}S - 1000 \times \left(1 + \delta^{34}S/1000\right)^{0.515}$$

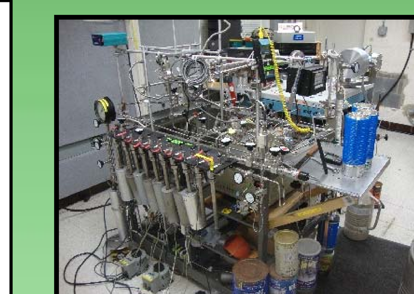
The variations in $^{33}S/^{32}S$ ratio of a sample will be about half that of $^{34}S/^{32}S$ because fractionation is proportional to the relative differences in masses

This linear fractionation trend is known as "mass-dependent fractionation". Mass-independent fractionation, on the other hand, is reflected by non-linear variations in isotopic fractionation with mass.

On a plot of one isotopic ratio to another, such as $d^{33}S$ against $d^{34}S$, samples that have undergone mass-dependent fractionation would fall along a line known as a mass-fractionation line, the slope of which corresponds to the relative mass difference between the two ratios. Deviations from this line reflect mass independent fractionation processes

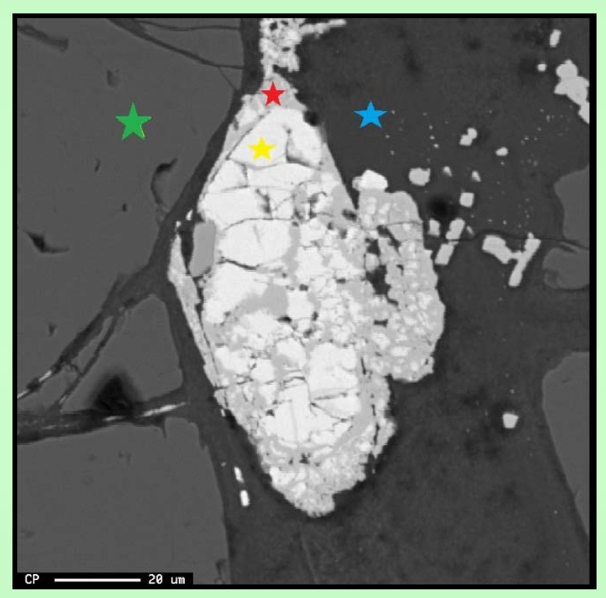
Analytical Methods

1. Cutting and Pulverization
   *Samples will be cut to a desired mass using a rock saw, then crushed into fine powder using a steel mortar and pestle



2. Chemistry (CRS extraction)
   *Both elemental sulfur and sulfur from sulfide phases will be reduced and extracted using HCl and chromium reducing solution
3. (Spectrophotometry)
   *This step will only be for initial extraction of xenoliths, to determine sulfur concentration
4. Fluorination
5. Mass Spectrometry

Samples

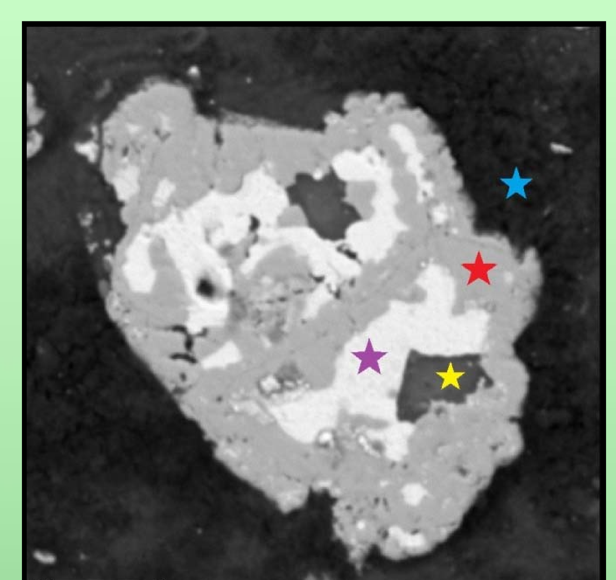


(left) BSE image of sample FRB 1659 shows pentlandite (yellow star), along with associated phases olivine (green star), serpentine (blue star), and iron oxide (red star). Scale bar of 20 um shown at bottom left corner of image

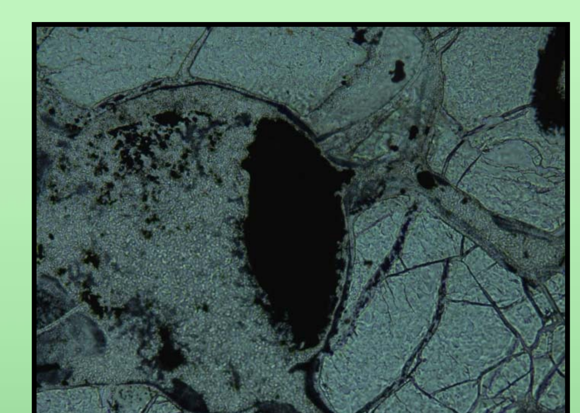
(right) Chart of samples organized by rock type and mass

Sample ID	Rock Type	Mass
FRB 1656*	Garnet harzburgite	60.1 g
PHN 5239	Garnet harzburgite	60.0 g
FRB 1318	Garnet harzburgite	55.9 g
FRB 1657*	Garnet harzburgite	50.0 g
FRB 1352	Garnet lherzolite	66.5 g
FRB 1309*	Garnet lherzolite	58.0 g
FRB 1370	Phlogopite dunite	65.6 g
FRB 1331.3	Spinel dunite	60.1 g
FRB 1375	Spinel-graphite-phlogopite harzburgite	55.0 g
FRB 1659*	Spinel harzburgite	82.2 g
FRB 1655*	Spinel harzburgite	61.4 g
PHN 5247	Spinel harzburgite	48.8 g

*Samples accompanied by thin section



(left) BSE image of sample FRB 1656 shows sulfide phase millerite (purple star) in association with phases calcite (yellow star), serpentine (blue star), and iron oxide (red star). Scale bar of 10 um shown at bottom left corner of image.



(left) Sample FRB 1657 in plane polarized light at 20x magnification (field of view ~ 1 mm); opaque phase determined to be sulfide phase (pentlandite)

References

Carlson et al.,2000, GSA Today, 10, 1-7.

Farquhar et al., 2000, Science, 289, 756-758.

Farquhar et al.,2002, Science, 298, 2369-2372.

Gregoire et al., 2005, Lithos, 84, 185-205.

Harris et al., 2005, Journal of Petrology, 46, 579-601.

Hatton & Sharpe, 1989, Unwin Hyman, London, pp. 174-208.

Hiebert & Bekker, 2010, Ontario Geological Survey, 269, 1-4.

James et al., 2001, Geophysical Research Letters, 28, 2485-2488.

Kruger, 1994, South African Journal of Geology, 97, 393-398.

Maier et al., 2000, Contributions to Mineralogy and Petrology, 140, 316-327.

Maier et al., 2005, South African Journal of Geology, 108, 413-428.

McCandless et al., 1999, Geochemica et Cosmochimca Acta 63, 911-923.

Penniston-Dorland et al., 2008, Geology, 36, 979-982.

Richardson & Shirey, 2008, Nature, 453, 910-913.

Smith, 1983, Unpublished PhD thesis, University Witwatersrand, Johannesburg, South Africa.

Thomassot et al., 2009, Earth and Planetary Science Letters, 282, 79-90.

Vaughan, David J., ed. Sulfide Mineralogy and Geochemistry. Vol. 61. Chantilly, VA: Mineralogical Society of America, 2006. Print.

Acknowledgements

•Dr. Sarah Penniston-Dorland
•Dr James Farquhar
•Smithsonian Museum of Natural History
•Sorena Sorensen and Leslie Hale
•Dr. Phil Piccoli
•Daniel Eldridge

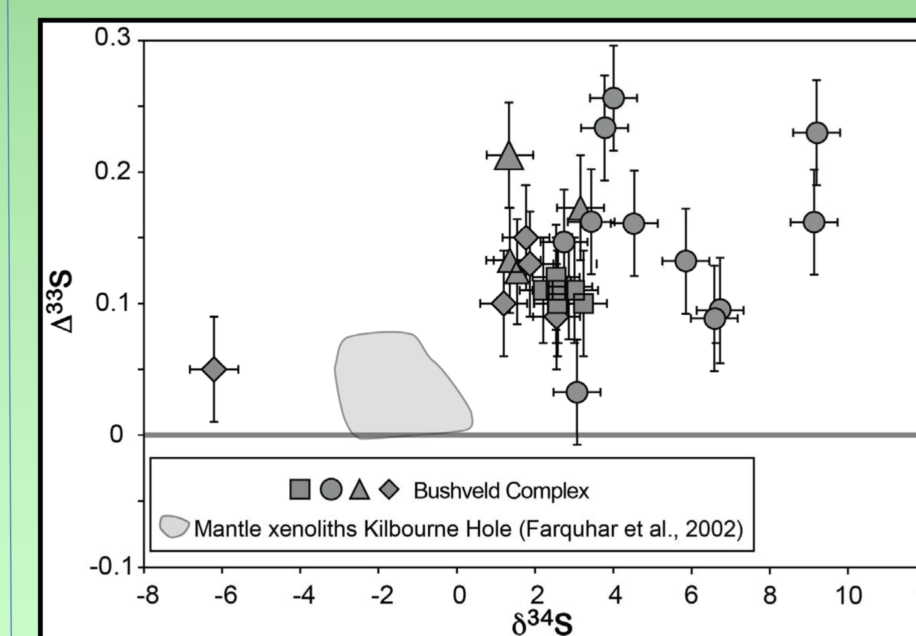
UNIVERSITY OF MARYLAND
DEPARTMENT OF GEOLOGY

Future Work

By the end of the semester, I plan to fluorinate and send the three xenolith samples that have already been reduced to mass spectrometry and collect multiple sulfur isotope measurements. I will be working on mineral characterization, reading the literature, and possibly work on my xenolith samples through mass spec over the summer. I plan to have all 12 samples finished at some point next semester, so we may then start working on sulfur extraction of eclogite xenoliths.

Results

Sample / STDV	$\delta^{33}S$	$\delta^{34}S$	$\delta^{36}S$	$\Delta^{33}S$	$[S]_{avg}$
BHTV1.1 (GP)	0.853	1.413	2.540	0.125	11.1 ppm
1 σ (GP, DE)	0.011	0.011	0.230	0.011	-
BHTV1.1 (PD)	0.820	1.339	2.830	0.131	-
1 σ (PD)	0.148	0.286	0.548	0.013	-



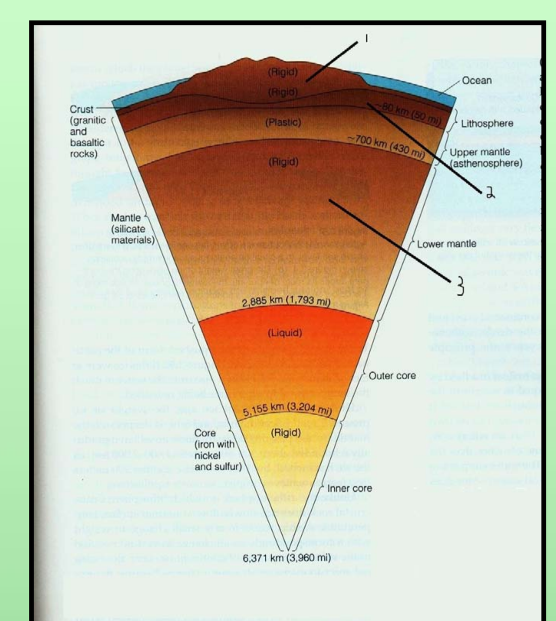
Previous measurements made by Penniston-Dorland et al. indicate slightly elevated Δ33S values in Bushveld igneous rocks.
By conducting multiple sulfur isotope analyses on mantle-derived xenoliths, this will provide insight into whether this anomalous signature is mantle derived or if it is reminiscent of crustal contamination.

If the samples report $\Delta^{33}S$ values approximately equal to zero, then we can conclude that the mantle source of the Bushveld Complex is pristine in regards to composition, and therefore contamination must have occurred during staging, ascent, or emplacement of magma

The BHTV1.1 sample that I had reduced and sent through to mass spectrometry yielded very similar results to those measured by Dr. Penniston-Dorland. These measurements demonstrate feasibility of the project; by acquiring isotope values from a standard, I have successfully shown that I can process samples all the way to mass spectrometry and obtain results that are consistent with previously measured values.

Three xenolith samples have been cut and crushed into fine powder, and 1 g of each sample has been reduced using CRS . Each sample yielded enough product for suitable fluorination and mass spectrometry results. This not only demonstrates feasibility of the project, but also indicates that there is enough sulfur in these xenoliths. These samples will be finished by the end of the semester, and the first collection of multiple sulfur isotope data will occur.

Current Models



1. Contamination Upon Emplacement

2. Lower Crustal Magma Staging Chamber
   Magma becomes contaminated with Bushveld wall rock while in chamber

3. Sub-Continental Lithospheric Mantle
   Magma within mantle already maintains anomalous signature, possible from ancient recycling of crust via subduction

Significance

Large Layered Igneous Intrusions
- By understanding the possible magma sources of the Bushveld Complex, this will add valuable information in regards to how layered igneous intrusions form

PGE Mineralization
- Concentration of PGE is much higher in sulfide melt than in silicate melt, making sulfide a potent agent for collection and segregation of PGE from magmas

Ancient Sulfur Cycle
- If the underlying mantle source is inferred to have an anomalous $\Delta^{33}S$ signature in contrast to pristine mantle values, then this may imply mechanisms of recycling, such as subduction of crust that contains the anomalous signature

First study on $\Delta^{33}S$ of Premier xenoliths