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Using Triple Oxygen Isotopes to Reveal the Origin and Evolution of Mantle Eclogite

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USING TRIPLE OXYGEN ISOTOPES TO REVEAL THE ORIGIN AND EVOLUTION OF MANTLE ECLOGITE

BY

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THESIS

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USING TRIPLE OXYGEN ISOTOPES TO REVEAL THE ORIGIN AND EVOLUTION OF MANTLE ECLOGITE

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Bachelor of Science, Geology, University of South Florida, 2018

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Abstract

Triple oxygen isotope (TOI) measurements of mantle eclogite from the Orapa kimberlite pipe have reconstructed bulk rock $\delta'^{18}O$ values from 4.587 to 9.542‰ (vs. VSMOW) and $\Delta'^{17}O$ from -0.075 to -0.044‰ (vs. VSMOW, λ ~0.528). TOI values show increasing $\delta'^{18}O$ with decreasing $\Delta'^{17}O$, overlapping with modern measured altered oceanic crust. Orapa eclogite xenoliths with alkali enrichments show variable mantle-like and heavy $\delta^{18}O$, consistent with subduction of seafloor altered basalt. Na# (Na/Na+Ca) in clinopyroxene for some xenoliths pairs with mantle-like oxygen, variable and extreme LREE enrichment, elevated Mg# and lower jadeite contents. These samples preserve records of eclogite melting, mantle interaction and recrystallization at lower temperatures with clinopyroxene having a pyroxenitic chemistry. $\Delta^{18}O_{cpx\text{-}gnt}$ of most eclogites reflect disequilibrium in clinopyroxene rather than garnet, which is possibly an artifact of pyroxenite formation. This suggests metasomatism by fluids having mantle-like oxygen isotope compositions interacted within the lithosphere prior to kimberlite entrainment and eruption.

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Introduction

Kimberlite-erupted eclogite xenoliths remain enigmatic in their genesis (Jacob, 2004). The basaltic chemistry of mantle eclogite underlies a subduction-relict origin, a hypothesis intrinsic to the bi-mineralic constituents, pyrope garnet and omphacitic clinopyroxene present within the assemblage (Ringwood & Green, 1966). Global oxygen isotope variation within eclogite xenoliths is distinguished by high and low values outside of the upper mantle (~5.2‰, vs. VSMOW), and remains as strong evidence for their surface origin as seawater-altered oceanic crust (MacGregor & Manton, 1986; Mattey et al., 1994; Ongley et al., 1987). Despite their emplacement sourced from deep, cratonic, subcontinental lithospheric mantle (SCLM), eclogite xenoliths preserve an artifact of temperature-dependent oxygen isotope fractionation from alteration on the seafloor. A direct alternative to the surface-altered hypothesis is that mantle eclogite has a cumulate origin (O'Hara & Yoder, 1967) involving eclogite formation by crystallization from a deep-seated, mantle-derived melt. In this scenario, wide oxygen isotope variation is ascribed to metasomatic overprinting of cumulates containing δ^{18}O values less than the average mantle, by fluids with heavy δ^{18}O values (Gréau et al., 2011).

A complicating aspect of tracing the genetic oxygen isotope history of mantle eclogite xenoliths as sea floor altered protoliths is recognized globally in strong modes at mantle-like oxygen isotope values (N. M. Korolev et al., 2018). A protracted evolution from initial seafloor alteration (subduction modification, sub-continental lithosphere emplacement, and kimberlite entrainment) presents the inevitable possibility of overprinting of original protoliths values (Aulbach & Massuyeau, 2020). Thus, the interpretation of oxygen isotope variation in mantle eclogite xenoliths poses important implications for their origins and includes a record of craton evolution since their emplacement.

The application of triple oxygen isotopes can provide a unique interpretation on the two main hypotheses for the origin and evolution of mantle eclogite xenoliths. The contribution of the least abundant isotope (^{17}O) was previously considered invaluable for terrestrial samples owing to the lack of precision necessary for discrimination from the inherited terrestrial fractionation of oxygen from the bulk silicate earth (Sharp et al., 2018a). More recently, technological advancements have allowed extraction lines to be assembled for high-precision analyses, promoting refined understanding of earth processes which result in mass-dependent fractionations.

Based on published interpretations of eclogite xenoliths, this method is relevant for investigating the existing hypotheses focused on explaining the varied oxygen isotope compositions as well as the metasomatic processes which act to overprint their preexisting record of formation (Aulbach et al., 2017; Aulbach & Massuyeau, 2020). In this work the application of triple oxygen isotope analysis is used to evaluate the origins and evolution of eclogite xenoliths from the Orapa AK1 kimberlite pipe. To do this, pristine garnet and clinopyroxene mineral separates are measured and used to evaluate the bulk rock evolution of a suite of samples that have been previously analyzed geochemically, including major and trace element analyses. The Orapa pipe was particularly chosen for its marginal location on the edge of the Zimbabwe Craton, where it may have been strongly affected by fluid interaction during multiple craton forming and destructive events (Aulbach et al., 2017).

Methods

Sample Preparation

Orapa eclogite xenoliths were provided by Sonja Aulbach of Goethe University, Frankfurt and Fanus Viljoen of the University of Johannesburg as both clean mineral separates and bulk rocks. Where clean separates were not provided, the bulk rock samples were crushed with mortar and pestle, sieved, cleaned through several ultrasonic baths, and distilled to remove intermediary veined material surrounding grains. The samples were dried in a heated oven for 12+ hours to remove all residual water prior to mineral separation. Clean separates of garnet and clinopyroxene were picked fresh under a binocular microscope, where special attention was taken to choose only the most pristine samples, free of inclusions.

Triple Oxygen Isotope Analyses

Oxygen isotope measurements were conducted at the Center for Stable Isotopes (CSI), University of New Mexico using the laser fluorination technique of (Sharp, 1990) modified for high precision analysis. Approximately 2mg of an in-house San Carlos olivine standard and hand-picked garnet and clinopyroxene separates were loaded into a 44-well nickel plate, where each sample and standard contained its own well. The plate was loaded into the sample chamber 24 hours prior to analysis and evacuated while heated under an external halogen lamp. A 30-minute pre-fluorination of BrF_5 gas was made exposed prior to analysis to react any remaining residual water in the fluorination vacuum line introduced during loading.

For each analysis, a sample was heated with a CO_2 laser in the presence of 100 mBar of BrF_5 gas to generate O_2 from the sample. The oxygen was then separated by freezing all unreacted BrF_5 with liquid nitrogen (LN), and purified through a salt trap to ensure complete removal of any remaining condensable phases. The extracted O_2 was condensed in a zeolite trap at LN temperatures followed by its' passage within a helium stream through a 6-foot 1/8" diameter 13x molecular sieve gas chromatograph (GC) specifically modified to filter out traces of NF_3 that can have an isobaric interference (NF^+ vs $^{16}O^{17}O$) at mass 33. Each sample was measured for the three isotopes of oxygen in a MAT 253 Isotope Ratio Mass Spectrometer using a reference gas calibrated to VSMOW and SLAP (Wostbrock et al., 2020). Each sample run consisted of 30 iterations, where each iteration consisted of a 26s collection time separated by a 15s delay between the reference and sample gas allowing for high precision triple oxygen isotope values to be obtained.

Solving for delta and 'Big' delta values

$\delta^{17}O$ and $\delta^{18}O$ values are defined as:

$$\text{Equation 1: } \delta^{x}O = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1{,}000$$

R is the $^{18}O/^{16}O$ or $^{17}O/^{16}O$ ratio for triple oxygen isotopes. All triple oxygen values here use a linearized form of delta notation (Miller, 2002):

$$\text{Equation 2: } \delta' = 1{,}000 \ln\left(\frac{\delta^{x}O}{1{,}000} + 1\right)$$

The terrestrial fractionation line (TFL) is the best-fit line in $\delta'^{17}O$- $\delta'^{18}O$ space for terrestrial samples not affected by photochemical effects:

$$\text{Equation 3: } \delta'^{17}\text{O} = \lambda \times \delta'^{18}\text{O} + \gamma$$

where λ is the empirically defined best-fit slope and γ is the y-intercept, taken as zero. Small differences from the TFL can be defined in 'big' delta notation where:

$$\text{Equation 4: } \Delta'^{17}\text{O} = \delta'^{17}\text{O}_{\text{measured}} - \lambda \times \delta'^{18}\text{O}_{\text{measured}}$$

In this work, a λ of 0.528 is used to calculate the $\Delta'^{17}O$ value (Sharp et al., 2018b).

Results

Table 1 presents the triple oxygen isotope results for garnet and clinopyroxene mineral separates corrected to the San Carlos (SCO) olivine reference standards measured throughout the analyses in this work (*Table 2)*. All data are reported relative to VSMOW-SLAP for triple oxygen isotopes (Wostbrock et al., 2020). Based on 25 SCO standard analyses, the 1σ precision is 0.1 ‰ for $\delta'^{18}O$ and 0.008‰ for $\Delta'^{17}O$. Orapa samples were corrected if the standard ran prior to the analysis was outside of the 1σ value from the average $\delta'^{18}O$ and $\Delta'^{17}O$ of all SCO ran for this work ($\delta'^{18}O$ ~ 5.26‰, $\Delta'^{17}O$ ~ -0.058‰). Corrected garnet $\delta'^{18}O$ values range from 4.59 to 9.54‰ and $\Delta'^{17}O$ -0.023 to -0.080‰ and clinopyroxene $\delta'^{18}O$ values range from 4.53 to 9.25‰ and $\Delta'^{17}O$ values range from -0.045 to -0.088‰. To understand the overall bulk rock formation and evolution of the Orapa eclogite xenoliths, published mineral modes (Aulbach et al., 2017) were used to calculate reconstructed bulk rock oxygen isotope values. Where mineral modes were not determined, an assumed mode of 0.5 clinopyroxene and 0.5 garnet were used for estimating the bulk rock oxygen isotope value. Mineral modes and reconstructed triple oxygen isotope bulk rock values ($\delta'^{18}O$ 4.59 to 9.54‰, $\Delta'^{17}O$ -0.075 to -0.044‰) are presented in *Table 1*.

Table 1 Corrected Orapa eclogite mineral separate analyses

Triple oxygen mineral separates analyses ran throughout this work. Each sample consisted of one garnet, and one clinopyroxene analysis, except where n=0. Bulk values are calculated used mineral modes, published in Aulbach et al. (2017).

Sample	**Group**	**Type**	**n**	**δ^{17}O**	**1σ**	**δ^{18}O**	**1σ**	**δ'^{17}O**	**δ'^{18}O**	**Δ'^{17}O**	**1σ**	**1000lna d^{18}O CPX-GNT**	**Mode**	**Bulk δ'^{17}O**	**Bulk δ'^{18}O**	**Bulk Δ'^{17}O**
XM3	1	GNT	2	4.006	0.006	7.719	0.024	3.998	7.689	-0.063	0.006	0.119	0.50	4.027	7.748	-0.064
		CPX	2	4.065	0.078	7.838	0.123	4.057	7.808	-0.066	0.013		0.50			
766	1	GNT	2	4.139	0.011	7.979	0.039	4.130	7.947	-0.066	0.009	-0.321	0.50	4.047	7.788	-0.065
		CPX	2	3.972	0.194	7.658	0.379	3.964	7.629	-0.065	0.005		0.50			
XM26	1	GNT	2	4.230	0.101	8.139	0.172	4.221	8.106	-0.060	0.011	0.175	0.50	4.252	8.192	-0.074
		CPX	2	4.292	0.003	8.313	0.008	4.283	8.279	-0.088	0.001		0.50			
JJG891	1	GNT	2	4.610	0.099	8.866	0.194	4.600	8.827	-0.061	0.003	-0.881	0.50	4.365	8.391	-0.065
		CPX	2	4.139	0.066	7.986	0.118	4.131	7.954	-0.069	0.004		0.50			
XM67	1	GNT	2	4.986	0.161	9.588	0.302	4.973	9.542	-0.065	0.001	N/A	0.50	4.973	9.542	-0.065
		CPX	0										0.50			
800	1	GNT	2	4.302	0.135	8.298	0.266	4.292	8.264	-0.071	0.004	-0.036	0.50	4.282	8.246	-0.073
		CPX	2	4.280	0.051	8.263	0.127	4.271	8.229	-0.074	0.016		0.50			
XM30	1	GNT	2	4.452	0.055	8.588	0.128	4.442	8.551	-0.073	0.012	N/A	0.50	4.442	8.551	-0.073
		CPX	0										0.50			
XM64	1	GNT	1	4.959		9.540		4.947	9.495	-0.067		-0.248	0.50	4.881	9.372	-0.068
		CPX	1	4.826		9.292		4.814	9.249	-0.069			0.50			
790	1	GNT**	1	2.588		4.960		2.584	4.948	-0.028		0.430	0.50	2.682	5.162	-0.044
		CPX	1	2.783		5.390		2.779	5.376	-0.059			0.50			
OE79	2	GNT**	1	3.121		6.016		3.116	5.998	-0.051		-0.181	0.55	3.065	5.917	-0.059
		CPX	1	3.007		5.835		3.002	5.818	-0.069			0.45			
OE81	2	GNT**	1	2.993		5.778		2.988	5.761	-0.054		-0.069	0.55	2.968	5.731	-0.058
		CPX**	1	2.947		5.709		2.942	5.693	-0.064			0.45			
OE70	2	GNT**	1	2.437		4.663		2.434	4.652	-0.023		0.528	0.55	2.533	4.889	-0.048
		CPX	1	2.659		5.191		2.655	5.178	-0.078			0.45			
OE72	2	GNT**	1	2.653		5.119		2.649	5.106	-0.047		0.514	0.55	2.770	5.336	-0.047
		CPX**	1	2.922		5.633		2.918	5.617	-0.048			0.45			
OE86	2	GNT**	2	2.994	0.080	5.808	0.155	2.990	5.792	-0.068	0.001	-0.311	0.55	2.920	5.652	-0.064
		CPX	1	2.839		5.497		2.835	5.482	-0.059			0.45			
OE16	2	GNT**	1	2.398		4.603		2.395	4.593	-0.030		0.471	0.55	2.492	4.803	-0.045
		CPX	1	2.613		5.074		2.610	5.061	-0.063			0.45			
OE52	2	GNT	1	2.882		5.569		2.878	5.554	-0.054		-0.157	0.50	2.828	5.476	-0.063
		CPX	1	2.782		5.412		2.778	5.397	-0.072			0.50			
OE18	1	GNT	1	3.443		6.646		3.437	6.624	-0.060		-0.410	0.50	3.324	6.421	-0.066
		CPX**	1	3.217		6.236		3.212	6.217	-0.071			0.50			
789	1	GNT	1	3.005		5.835		3.000	5.818	-0.071		N/A	0.55	3.000	5.818	-0.071
		CPX	0										0.45			
OE83	2	GNT	1	2.783		5.397		2.779	5.382	-0.063		-0.066	0.50	2.768	5.350	-0.057
		CPX	1	2.760		5.331		2.756	5.317	-0.051			0.50			
787	1	GNT	1	3.100		6.032		3.095	6.014	-0.080		-0.759	0.50	2.908	5.637	-0.069
		CPX	1	2.724		5.273		2.720	5.259	-0.057			0.50			
OE34	1	GNT	1	2.412		4.655		2.409	4.644	-0.043		-0.115	0.50	2.378	4.587	-0.044
		CPX	1	2.349		4.540		2.346	4.530	-0.045			0.50			
OE71	2	GNT	1	2.738		5.301		2.734	5.287	-0.057		0.307	0.55	2.798	5.424	-0.066
		CPX	1	2.880		5.608		2.876	5.592	-0.077			0.45			
801	1	GNT	0									N/A	0.55	2.847	5.521	-0.068
		CPX	1	2.851		5.536		2.847	5.521	-0.068			0.45			
794	1	GNT	0									N/A	0.55	2.751	5.353	-0.075
		CPX	2	2.755	0.162	5.367	0.289	2.751	5.353	-0.075	0.010		0.45			
OE23	1*	GNT	1	2.673		5.170		2.669	5.157	-0.053		-0.480	0.50	2.547	4.918	-0.049
		CPX	2	2.428	0.119	4.690	0.242	2.425	4.679	-0.046	0.009		0.50			

*Sample not grouped by Aulbach (2017); **Corrected Value to AVG of all SCO; Mineral Modes and Groups from Aulbach (2017)

Table 2 San Carlos olivine standard analyses

Standards ran throughout eclogite mineral separate analyses for this work. Standards highlighted in gray fell outside of the 1σ value from the average of all SCO ran. Samples ran with these standards were corrected by the difference between the standard and average value.

Sample #	δ^{17}O	δ^{18}O	δ'^{17}O	δ'^{18}O	Δ'^{17}O
1	2.658	5.157	2.654	5.144	-0.061
2	2.661	5.156	2.657	5.143	-0.058
3	2.743	5.326	2.739	5.312	-0.065
4	2.705	5.260	2.701	5.246	-0.069
5	2.793	5.390	2.789	5.376	-0.049
6	2.717	5.260	2.713	5.246	-0.057
7	2.709	5.233	2.705	5.219	-0.050
8	2.761	5.331	2.757	5.317	-0.050
9	2.709	5.243	2.705	5.229	-0.056
10	2.728	5.278	2.724	5.264	-0.055
11	2.751	5.317	2.747	5.303	-0.053
12	2.753	5.312	2.749	5.298	-0.048
13	2.836	5.498	2.832	5.483	-0.063
14	2.709	5.243	2.705	5.229	-0.056
15	2.693	5.207	2.689	5.193	-0.053
16	2.724	5.304	2.720	5.290	-0.073
17	2.735	5.279	2.731	5.265	-0.049
18	2.739	5.278	2.735	5.264	-0.044
19	2.701	5.244	2.697	5.230	-0.064
20	2.809	5.457	2.805	5.442	-0.068
21	2.700	5.228	2.696	5.214	-0.057
22	2.664	5.199	2.660	5.185	-0.078
23	2.822	5.461	2.818	5.446	-0.058
24	2.833	5.474	2.829	5.459	-0.053
25	2.860	5.546	2.856	5.531	-0.064
Average	2.741	5.307	2.737	5.293	-0.058
SD (1σ)	0.0565	0.1068	0.0564	0.106	0.008

Characterizing Orapa Mantle Eclogites

Following the classification scheme for eclogite xenoliths used by previous workers, all samples in this work are distinguished based on the chemical classification for K_2O > 0.08wt% in clinopyroxene and Na_2O > 0.09wt% in garnet as Group I and K_2O/Na_2O values less than this threshold are considered depleted and designated Group II (Aulbach et al., 2017; McCandless, TE; Gurney, 1989; Viljoen et al., 1996) (*Figure 1a)*. Group II samples can be further distinguished as pyroxenitic rather than eclogitic using the sodium number (Na# = 100xNa/(Na+Ca)>0.2) in clinopyroxene (Aulbach et al., 2016, 2017) (*Figure 1b)*. Three total groups, Group I, Group II eclogitic, and Group II pyroxenitic will be used to evaluate the formation and evolution of Orapa eclogite xenoliths.

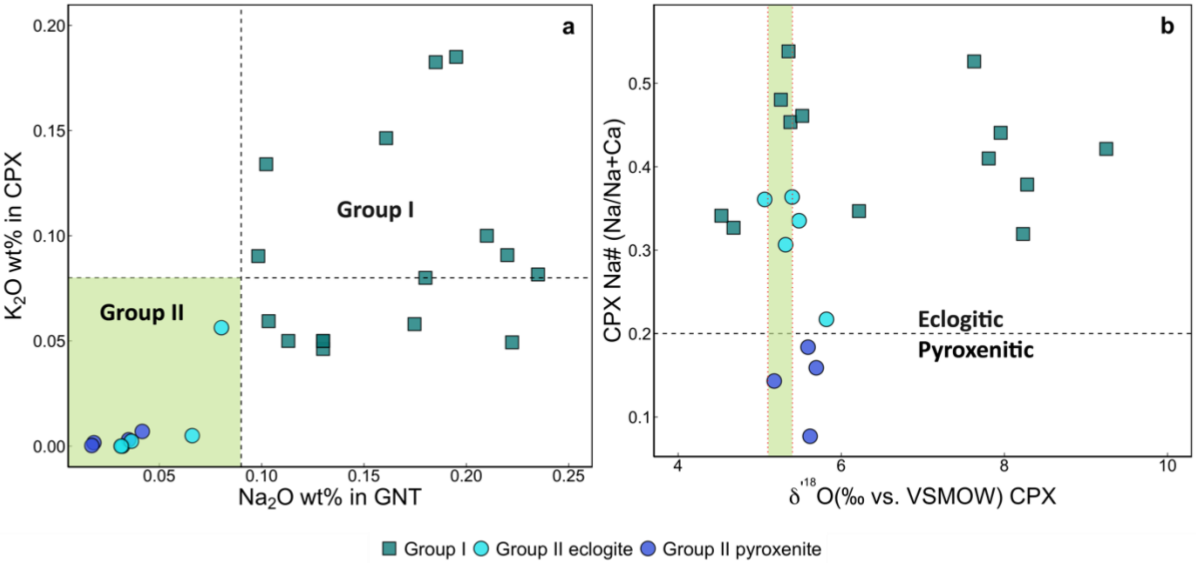

Figure 1 Classification of Orapa eclogite xenoliths

a. Orapa eclogite xenoliths classified as Group I and Group II based on the chemical classification of 0.08wt% K_2O in clinopyroxene and 0.09wt% Na_2O in garnet for a single, bimineralic eclogite sample (McCandless, TE; Gurney, 1989). **b.** Na# (Na/(Na+Ca)) verses $\delta'^{18}O$ in clinopyroxene used to distiguish eclogitic (Na#>0.2) and pyroxenitic (Na# <0.2) types, primarily in Group II samples (Aulbach et al., 2017). Vertical lines represent the mantle from San Carlos olivine standards ran in this work. Major element data published in (Aulbach et al., 2017). Oxygen isotope values are from this work.

Figure 1 also presents ^{18}O data, where Group I samples are varied, from ~4.8-9.3‰ (vs. VSMOW), while all Group II samples are within the mantle range (~4.8-5.5‰ vs. VSMOW).

Reconstructed bulk rock chondrite-normalized trace element patterns show distinct trends between groups (Aulbach et al., 2017) (*Figure 2*). Group I are variably LREE depleted relative to MORB while Group II are depleted and enriched in LREE, with the greatest enrichments in pyroxenitic types.

Temperatures of equilibration based on Mg-Fe partitioning between garnet and clinopyroxene were determined at 4.5 GPa for Orapa eclogite xenoliths (*Figure 3)* (Aulbach et al., 2017; Krogh, 1988; Viljoen et al., 1996). Temperatures of equilibration for Group I samples are between 1000 to 1400°C while Group II eclogites and pyroxenites are between 800 to 1000°C.

Overall, Group I samples are enriched in alkalis (Na_2O and K_2O), depleted in REE compared to MORB, have equilibration temperatures >1000°C and mantle-like to elevated δ^{18}O values. Group II eclogites equilibrated at <1000°C and are depleted in alkalis. Specifically, Group II pyroxenitic clinopyroxenes are depleted in jadeite contents, have elevated Mg# (100xMg/(Mg+Fe)) and Cr_2O_3 (wt%), light rare earth element (LREE) enrichment (Ce/Yb), and mantle-like oxygen isotope values.

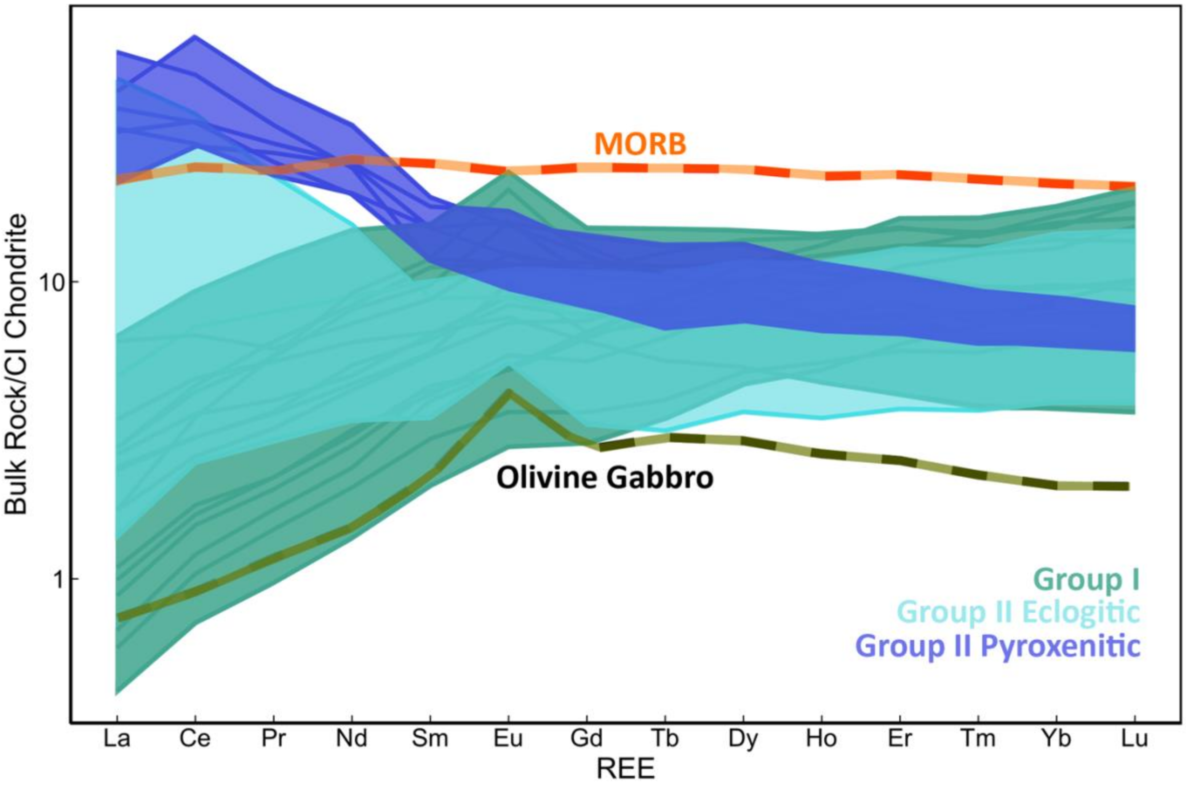

Figure 2 Bulk-rock chondrite normalized trace elements

Reconstructed bulk rock rare earth element values normalized to CI Chondrite (Sun & McDonough, 1989) for Orapa eclogite xenoliths. Orapa garnet and clinopyroxene trace element data and mineral modes are published in (Aulbach et al., 2017; Aulbach & Massuyeau, 2020). Values for MORB are from (Gale et al., 2013) and the olivine gabbro is from the Southeast Indian Ridge (Hart et al., 1999) as presented in (Aulbach & Massuyeau, 2020).

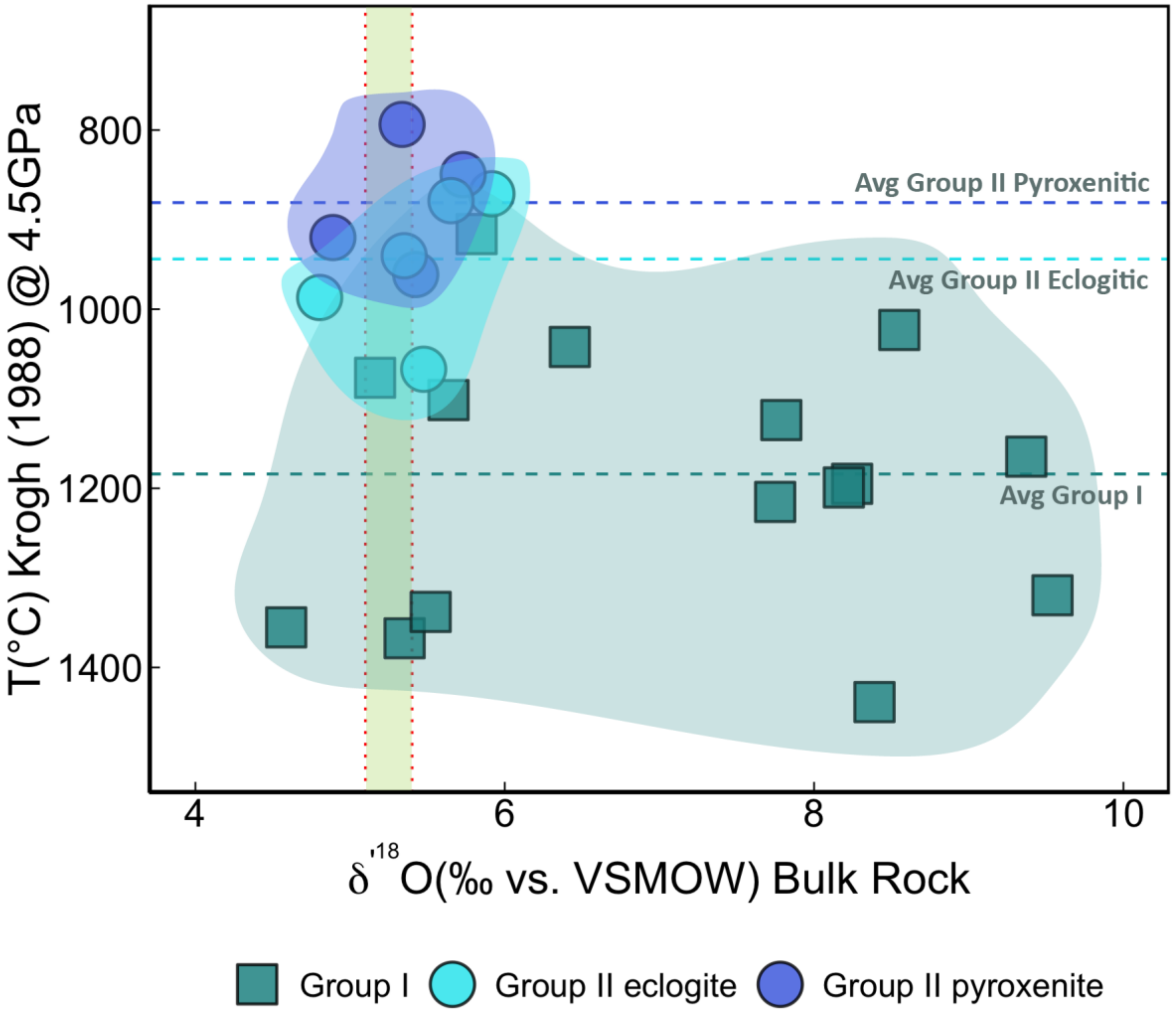

Figure 3 Krogh (1988) calculated equilibrium temperatures versus $\delta^{18}O$

Temperatures of equilibration for touching garnet and clinopyroxene pairs (Krogh, 1988) evaluated by (Aulbach et al., 2017) versus bulk rock $\delta'^{18}O$. Dashed horizontal lines are averages for each group. Mantle $\delta'^{18}O$ value denoted by shaded green region. *Note: y-axis is flipped.

Discussion

Historical recognition of widely varied oxygen isotope values of mantle eclogites has been primarily attributed to basalt alteration on the seafloor at low and high temperatures (Muehlenbachs, 1986). Alternative hypotheses have also been put forth suggesting eclogite xenoliths may have formed as mantle cumulates, altered by an exotic, $\delta^{18}O$ metasomatic fluid (Gréau et al., 2011). To discern the origin and evolution of oxygen isotope heterogeneity in mantle eclogites, the Orapa eclogite suite is considered using new triple oxygen isotope values in conjunction with previous geochemical data and experiments.

Altered Oceanic Crust Origin

The original model for alteration of oceanic crust proposed a mechanism of fluid-rock alteration at variable high and low temperatures during on-axis spreading and off-axis cooling (Muehlenbachs, 1986; Alt et al., 1986). Oxygen isotope measurements of an obducted, intact portion of ocean crust, first recognized from the Samail ophiolite, subsequently identified a high-porosity, low temperature altered section near the surface and a deeper, low-porosity, high temperature altered portion (Gao et al., 2012; Gregory & Taylor, 1981). Overall, the oxygen isotope variation within a depth-section of oceanic crust reflects the incursion of seawater at variable fluid rock ratios and temperatures, facilitated through downwelling within porous basalt and transitioning to deep incursion along fracture zones within the sheeted dike system (J.C. Alt et al., 1996). In essence, $\delta^{18}O$ values of altered oceanic crust (AOC) record the temperature dependent fractionations between mineral phases and seawater. As a result, low temperature alteration values are greater than the mantle, while high temperatures are less (Muehlenbachs, K; Clayton, 1972).

Previous oxygen isotope measurements of altered oceanic crust have only measured the $\delta^{18}O$ variation. Recently, triple oxygen isotope composition of modern measured IODP and DSDP drill core sections of low and high temperature altered oceanic crust from the East Pacific Rise and Caribbean Arc have been determined (McGunnigle et al., 2022). These values are directly compared to Orapa eclogite from this work (*Figure 4*). Modern AOC values are increasing in $\delta'^{18}O$ while decreasing $\Delta'^{17}O$, extending from ocean water and passing through the accepted mantle range (Cano et al., 2020; McGunnigle et al., 2022). From this comparison, Orapa reconstructed bulk rock values directly overlap with the range seen in modern, mostly low temperature altered oceanic crust. These results strongly suggest the oxygen isotope variation may be preserved from seafloor alteration.

Within the sample set, Groups I and II can be broadly interpreted based on their temperature and extent of alteration. Group I, alkali-enriched samples have mantle-like to high $\delta^{18}O$ and low $\Delta^{17}O$ values, signifying low-temperature alteration. Group II xenoliths contain strictly mantle-like oxygen isotope compositions and may have a distinct seafloor origin explained by $\delta^{18}O$ values inherited from a position in the oceanic crust where seawater alteration is minimal, or where the $\delta^{18}O$ temperature-dependent fractionation between the major phases present and seawater is ~5.2‰, leading to a mantle-like value. No samples from Orapa exhibit high temperature alteration which would be exhibited by $\delta^{18}O$ values less than the mantle. Because there is little to no sampling of the deep oceanic crust where fluid rock alteration is minimal, i.e., unaltered gabbro, distinguishing the origins of Group II eclogites is not possible currently. However, it is concluded that because the eclogite values fall within the range of AOC, seafloor preservation cannot be ruled out as the source of their oxygen isotope values.

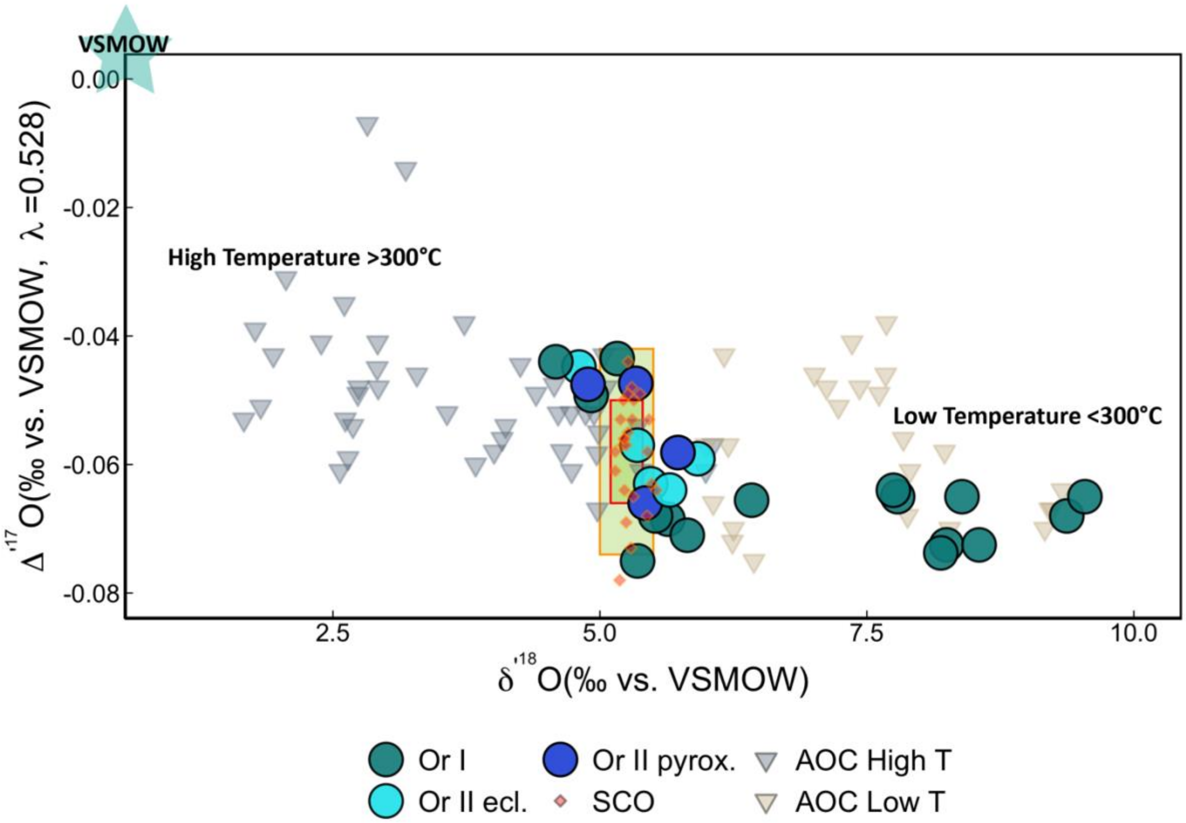

Figure 4 Triple oxygen isotopes of Orapa eclogite xenoliths and modern altered oceanic crust

Reconstructed bulk rock triple oxygen isotope values of Orapa eclogite xenoliths and modern altered oceanic crust from drilled IODP and DSDP cores of the Carribean Arc and East Pacific Rise (McGunnigle et al., 2022). See text for details on bulk rock calculations. The shaded green region oulined in red and orange represent the 1σ (red) and 2σ (orange) variation of San Carlos olivine (SCO) measurements (Average $\delta'^{18}O$= 5.293‰ and $\Delta'^{17}O$=0.058‰). Actual measured SCO values are shown (orange diamonds: n=25), where all except one fall within the 2σ variation for $\Delta'^{17}O$.

Cumulate Origin

A cumulate origin for mantle eclogite was originally proposed from partial melting experiments where fractionated mantle melts of peridotite produce a basaltic composition of pyrope garnet and diopside at elevated temperatures ~ 1600°C (O'Hara & Yoder, 1967). Theoretical triple oxygen isotope fractionations between diopside-forsterite and grossular-forsterite can also be used to evaluate equilibrium fractionation and crystallization of eclogitic phases from a mantle melt (*Figure 5*) (Schauble & Young, 2021). For this model, an initial melt value is taken from the average SCO of this work (δ'^{18}O ~ 5.3‰, Δ'^{17}O ~ -0.058‰). The oxygen isotope fractionation between forsterite-grossular increases slightly with decreasing temperature (~1300 to 500°C) from 5.32 to 5.37‰ in δ^{18}O and -0.058 to -0.057‰ in Δ^{17}O. Forsterite-diopside fractionations are greater, increasing from 5.61‰ to 6.44‰ in δ^{18}O and 0.057‰ to -0.056‰ in Δ^{17}O. The Δ^{17}O fractionation is near 0‰ between an eclogite assemblage and forsterite over this temperature range, suggesting that equilibrium fractionation from a mantle melt at elevated and low mantle temperatures does not explain the variation in Orapa Group I samples. Further, Group I samples are typically considered diamondiferous containing elevated K_2O and Na_2O contents, both representative of a high-pressure, low temperature crystallization of subducting lithosphere (McCandless and Gurney; Jacob 2004). Consequently, Group II samples with mantle-like oxygen isotope values are more relevant for the cumulate model, except for the elevated jadeite contents in eclogitic types and enriched LREE in pyroxenitic types. Both exceptions are counterintuitive to direct crystallization from cumulate melts in consideration of element partitioning between the melt and crystalizing phases. Therefore, Orapa samples cannot be associated strictly with cumulate formation, as the expectation would include mantle-like oxygen isotope values and depletions in fluid-mobile elements if the melt is in equilibrium with the mantle.

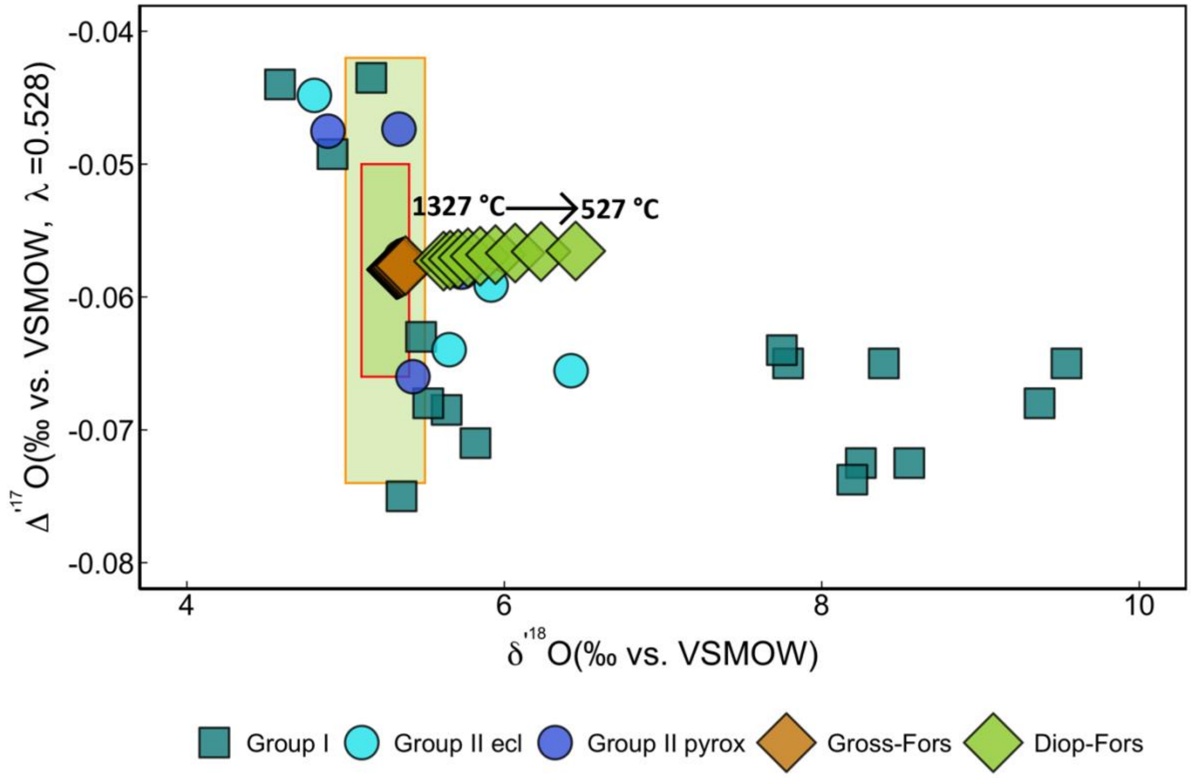

Figure 5 Theoretical triple oxygen isotope equilibrium fractionation, grossular/diopside-forsterite

Orapa bulk rock triple oxygen isotope values relative to theoretical equilibrium fractionations, diopside-forsterite and grossular-forsterite, from 527 to 1327°C. Theoretical values are the expected triple oxygen isotope composition of grossular and diopside in equilibrium with the bulk upper mantle assumed to have a forsteritic composition of $\delta'^{18}O$ and $\Delta'^{17}O$ values of 5.2 and -0.054‰, respectively (Schauble & Young, 2021). Increasing $\delta'^{18}O$ pairs with decreasing temperature, and little to no change in $\Delta'^{17}O$, apparent in diopside but not grossular.

Constraints on Mantle Metasomatism and Heterogenous SCLM Reservoirs

While Orapa Group I samples with heavy $\delta^{18}O$ values reflect seawater alteration of mid ocean ridge basalt, the effect of metasomatism via an exotic $\delta^{18}O$ fluid must also be discussed (Gréau et al., 2011). A recent study modeled closed and open system equilibration of fluids percolating through mantle material and have concluded that this metasomatic process may only shift the $\delta^{18}O$ of a mantle rock by ~2‰ when considering elevated, temperature-dependent fractionations (Riches et al., 2016). Group I samples extend to 9‰ in $\delta^{18}O$, thus cannot be explained by metasomatic alteration if the original value was mantle-like or less. In essence, a fluid passing through the mantle at elevated temperatures (where fractionations are minimal) and maintaining its' exotic oxygen isotope composition is inconsistent owing to interaction and buffering by the rock through which it passes. The nature of the metasomatic hypothesis is inadvertently depicted by the exact mechanism presented by seawater infiltration of mid ocean ridge basalt (MORB), except for the distinction of low temperatures during hydrothermal seafloor alteration (0 to ~500°C) and a continuous flux of ocean water for millions of years. It is emphasized here that passage of a fluid within rock, both with contrasting oxygen, will converge towards the value of the far-larger mantle oxygen reservoir, where this reservoir will show little to no change.

The existence of a low $\delta^{18}O$ reservoir preserved from primordial mantle heterogeneity has been considered a source of low $\delta^{18}O$ values in mantle melts that could effectively metasomatize SCLM rocks. This reservoir has been characterized based on "pristine" komatiites from the 3.27 Ga Weltevreden Formation of the Barberton greenstone belt (Byerly et al., 2017). The komatiite samples are considered pristine and unaltered based on olivine crystallization control lines. However, ion microprobe analyses of the komatiitic olivine's recognizes partial serpentinization and it is considered here that hydrothermal surface alteration may have influenced the measured, low $\delta^{18}O$ oxygen isotope values. If this is the case, the komatiites do not preserve heterogenous mantle reservoirs from the Archean, but instead have interacted with ^{18}O-depleted surficial fluids during serpentinization.

Xu et al., 2021 measured oxygen isotope heterogeneity of olivine grains within kimberlitic material using secondary-ion mass spectrometry (SIMS). They suggested the crystallization of macrocrystic, low-Mg olivine grains with light oxygen isotope values from kimberlite which had previously assimilated metasomatized lithosphere. These authors further suggest assimilation of heterogenous, metasomatized SCLM containing light rather than heavy values based on analyses of two phlogopite-ilmenite-clinopyroxene (PIC) xenoliths from the Orapa cluster. Based on the occurrence of mainly light values, only PIC metasomatic phases are concluded as the source of assimilated material while eclogitic reservoirs are considered unlikely because heavy oxygen isotope values would also have been assimilated.

The presence of light oxygen isotope reservoirs within the Southern African lithosphere are thus broadly interpreted, and it is put forth here that the possibility of hydrothermal alteration throughout kimberlitic intrusion or post-emplacement should also be considered for the specifically light variation noted in various olivine-dominated lithologies. In fact, low-temperature alteration of kimberlitic material is widely documented and explored at a variety of locations (Afanasyev et al., 2014; Sheppard & Dawson, 1975; Stripp et al., 2006). Future studies should explore the triple oxygen isotope variation from serpentinization of the kimberlite and xenolithic material to fully understand whether this process is responsible for the light oxygen isotope variation in mantle-derived materials or if this is a true artifact of heterogenous reservoirs in the South African SCLM.

An Alternative Model for Group II Pyroxenitic Type Eclogites

While the overall bulk rock oxygen isotope values of Orapa eclogite infers fractionation and alteration at low temperatures on the seafloor and overlaps with measured modern AOC, Group II pyroxenitic samples not only lack oxygen isotope variation and thus a direct seafloor origin cannot be inferred, but also contain paradoxical chemistry (i.e., enriched LREE, Cr_2O_3, Mg#, and low jadeite in clinopyroxenes) to an exact cumulate origin, making their interpretation relatively unique to eclogitic xenoliths.

Previous work seeking to discern the origin of pyroxenitic samples has suggested a hybridization model between eclogitic and peridotitic lithologies (Aulbach et al., 2017; N. Korolev et al., 2021). The hybrid geochemical characteristics of Orapa pyroxenites is thought to be carried by a carbonated, ultramafic metasomatic fluid or melt (Aulbach & Massuyeau, 2020), which is typical of kimberlitic melts which crystallize megacryst assemblages within lherzolites (Bussweiler et al., 2018). The hybridization process is geochemically assessed by comparing experimental mixtures of carbonated MORB partial melts and fertile mantle (garnet peridotite). To simulate reactive infiltration, the experiment mixed basaltic andesite (BAC) and alkali basaltic (ABC) melt compositions with ~2.6 and 11.7 wt.% CO_2, respectively, with garnet peridotite (Mallik & Dasgupta, 2013). Calculated clinopyroxene-garnet cumulates (assuming 0.45 CPX, 0.55 GNT) have been shown to overlap with Orapa Group II pyroxenites of various major element compositions (Aulbach et al., 2017) *(Figure 6*). This work recognizes the significance of two compositionally distinct endmembers forming pyroxenitic eclogite assemblages: a MORB eclogite partial melt and peridotite with some fraction of CO_2 present in the reaction.

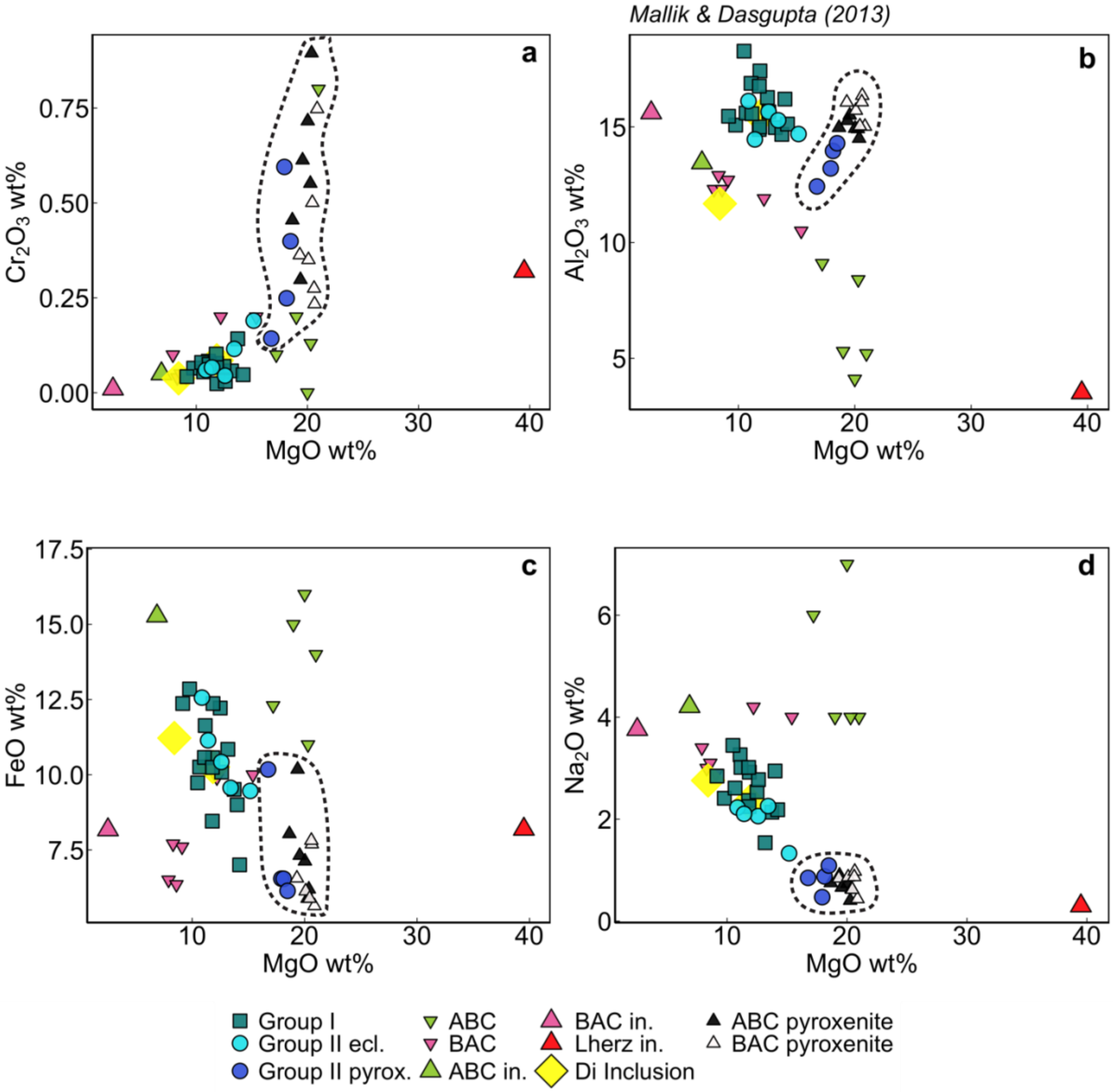

Figure 6 Orapa eclogite compared to experimental data from Mallik & Dasgupta (2013)

Orapa eclogite and reconstructed eclogite diamond inclusion compositions (Aulbach et al., 2017) (Robinson et al., 1984) compared to carbonated eclogite + peridotite reactive melt hybridization experiments from (Mallik & Dasgupta, 2013). Two endmember eclogitic melt products BAC (pink, white) and ABC (green, black) with 2.6 and 11.7 wt% CO_2 were mixed with a garnet peridotite (red) to simulate reactive infiltration of a siliceous partial melt from carbonated eclogite with fertile mantle peridotite. Pyroxenites and diamond inclusions were reconstructed assuming 0.45 clinopyroxene and 0.55 garnet bulk rock compositions. Pyroxenite compositions can be explained by the crystallization product of each experimental melt.

To assess the possibility of carbonated-ultramafic melt metasomatism resulting in compositional changes in Orapa eclogite, indices of metasomatism suggested from previous work (bulk rock Mg#, Ce/Yb, Cr_2O_3, and CPX jadeite) are compared to $\delta^{18}O$ values (Aulbach & Massuyeau, 2020) (*Figure 7*). No change in $\delta^{18}O$ is recognized for any indices, which suggests the affected samples retained mantle-like values from their protoliths, or fully equilibrated in the mantle with the infiltrating fluid. For the first scenario to be true, this suggests that the origin of Group II pyroxenites may have been Group II eclogites with mantle-like oxygen isotope values. On the other hand, full equilibration suggests the starting $\delta^{18}O$ value could have been within 2‰, where high fluid rock ratios shifted the values back towards the mantle, resulting in complete re-equilibration of the coexisting phases. In this case, the original protolith cannot be determined. The garnet-clinopyroxene equilibrium status can thus be used to assess the origins and evolution of Orapa samples.

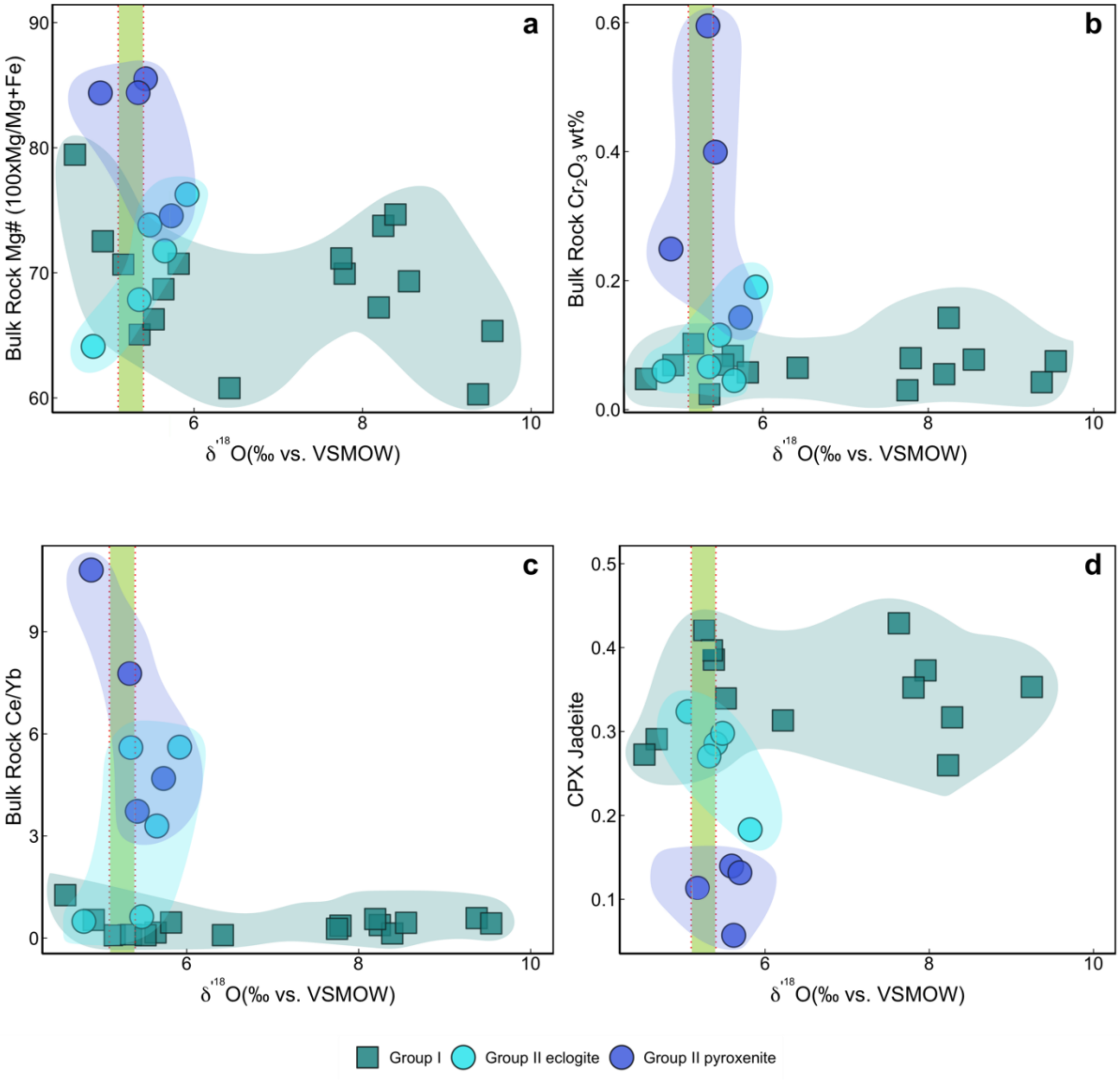

Figure 7 Indices of metasomatism versus $\delta^{18}O$

Indices of mantle metasomatism as indicated by (Aulbach & Massuyeau, 2020) include **a.** Bulk-rock Cr_2O_3 (wt%) **b.** Bulk-rock Mg# (100xMg/Mg+Fe) **c.** Chondrite-normalized bulk-rock light-rare earth element contents (LREE) indicated by Ce/Yb (Sun & McDonough, 1989) and **d.** Jadeite contents of clinopyroxene. Major and trace elements for mineral separates and bulk rocks are from (Aulbach et al., 2017). Green band denotes the 1σ variation $\delta'^{18}O$ for the mantle from San Carlos olivine measured in this work.

Garnet-Clinopyroxene Oxygen Isotope Equilibrium Fractionation

Equilibrium fractionation between clinopyroxene and garnet ($\Delta^{18}O_{CPX\text{-}GNT}$) have been calculated as ~0.2 to 0.4‰ at 1000°C (Zheng, 1993) (Schauble & Young, 2021). When the two phases form in equilibrium at this temperature, clinopyroxene will be heavier by ~0.3‰, with an increasing difference as temperature decreases. Figure 8 shows the temperatures of equilibration (based on Fe/Mg partitioning between garnet and pyroxene) versus the $1000ln\alpha_{\text{Diopside-Garnet (Di-Gt)}}$ or $_{\text{(CPX-GNT)}}$ for samples analyzed in this study. Only pyroxenitic types are in oxygen isotope equilibrium. All other samples have near-zero or negative $1000ln\alpha_{\text{Di-Gt}}$ values. *Figure 9* presents a 1:1 relationship of garnet versus clinopyroxene $\delta^{18}O$ also including previously published Orapa samples showing similar results (Viljoen et al., 1996). Samples preserving oxygen isotope values from surface alteration would be expected to have formed in equilibrium, while metasomatized samples affected by infiltrating fluids would not. The most likely scenario to explain the disequilibrium in eclogitic samples is that they have undergone a shift in either garnet or clinopyroxene, where the latter is more susceptible and thus more likely.

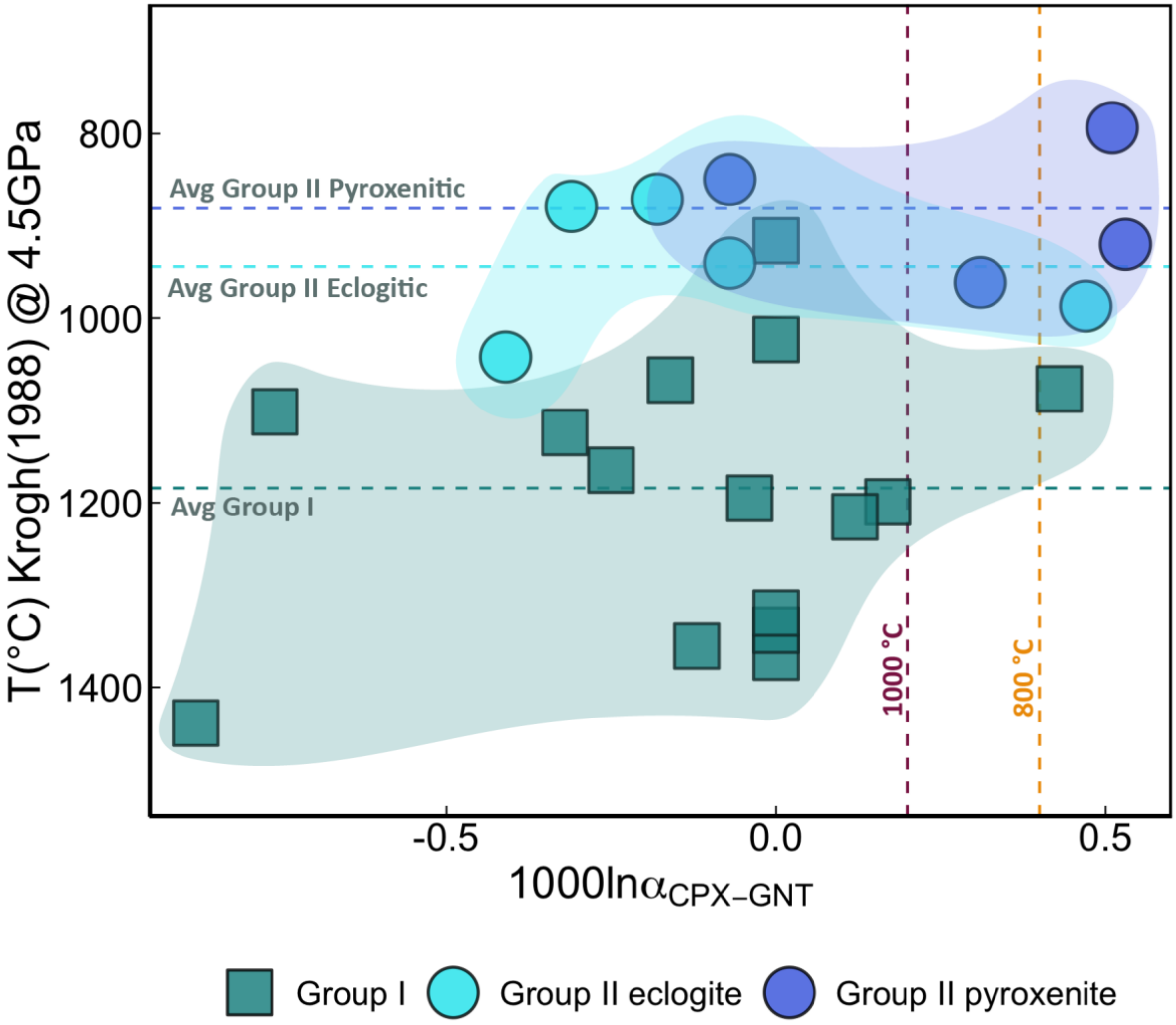

Figure 8 Krogh (1988) calculated equilibrium temperatures versus 1000ln$\alpha_{CPX-GNT}$

Temperatures of equilibration at 4.5 GPa (Krogh, 1988) calculated and published in (Aulbach et al., 2017) versus the $\Delta\delta^{18}$O ($\delta^{18}O_{clinopyroxene}$ - $\delta^{18}O_{garnet}$) between clinopyroxene and garnet (CPX-GNT) from each sample measured in this work. Vertical lines are diopside-pyrope fractionations: 0.2 at 1000°C (purple) and 0.4 at 800°C (orange) (Zheng, 1993). Average temperatures are shown for each group (horizontal dashed lines).

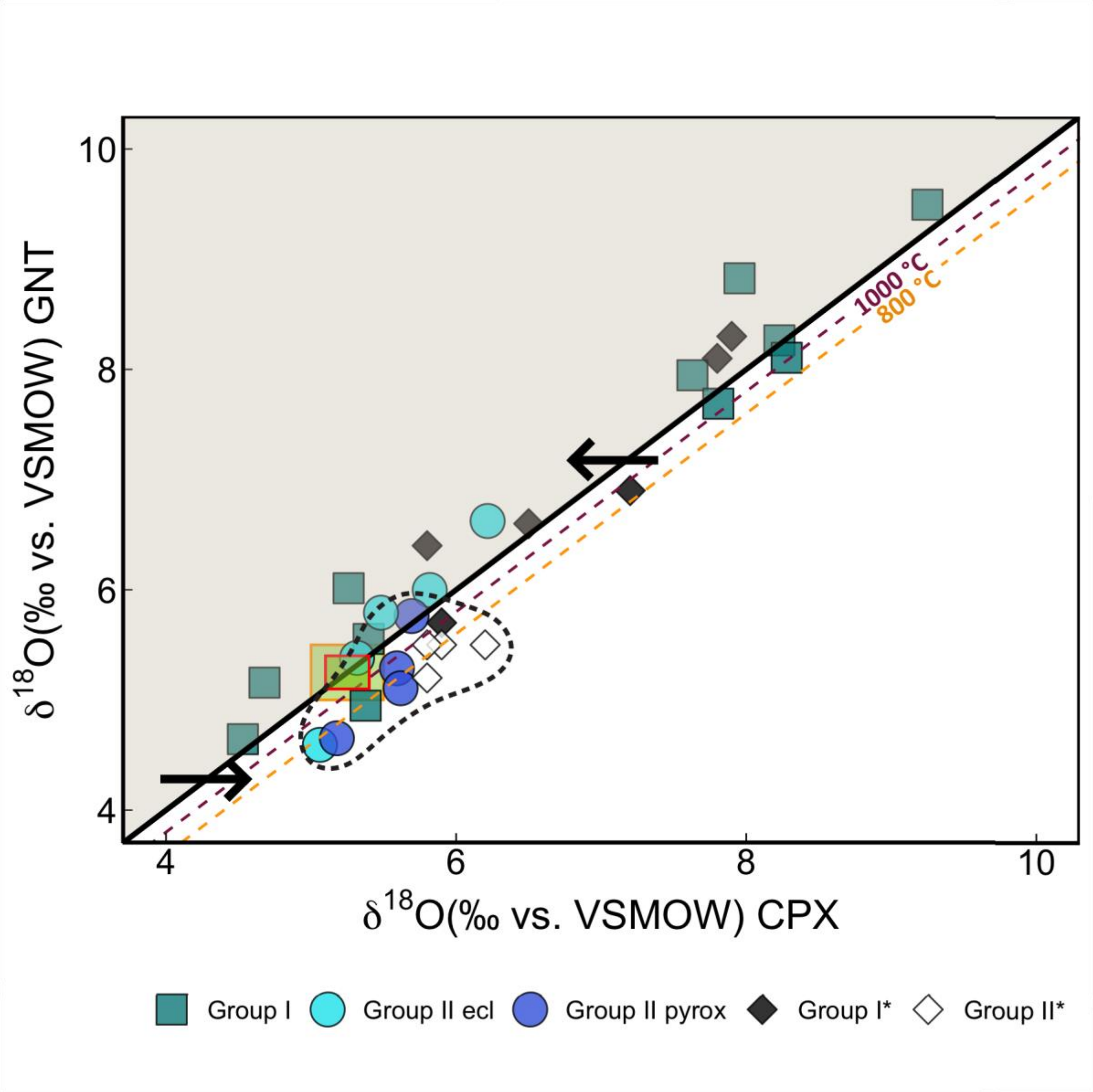

Figure 9 δ^{18}O in garnet versus clinopyroxene

δ^{18}O in garnet versus δ^{18}O in clinopyroxene. Shaded green boxes are the 1σ and 2σ variation in δ^{18}O of San Carlos ran throughout this work. Solid diagonal black line is a 1:1 comparison. Colored dashed lines represent diopside-grossular oxygen isotope fractionations of 0.2 (purple) at 1000°C and 0.4 (orange) at 800°C. The increasing equilibrium fractionation results in decreasing temperatures of equilibration. The gray shaded region represents a zone of disequilibrium. Black arrows point towards the expected change in δ^{18}O resulting from interaction with a mantle like fluid, primarily in clinopyroxene, which is supported by pyroxenite formation in equilibrium with a mantle-like composition. *Previously published Orapa samples (Viljoen et al., 1996) follow similar trends to this work, especially Group II which are also in oxygen isotope equilibrium. Two samples were measured in both works: XM3, and JJG891.

Mantle-metasomatic alteration of eclogite xenoliths has been discussed as a likely scenario affecting samples globally. To explain the disequilibrium of eclogitic but not pyroxenitic types, here it is suggested that the metasomatizing process occurred through infiltration of a fluid with a mantle-like oxygen isotope composition. The infiltration of eclogitic reservoirs has been recognized by grain boundary infiltration, fluid inclusions, and disequilibrium textures, prominent in Group I samples and previously used to explain their heavy oxygen isotope values (Huang, 2012). However, our work suggests the original values heavy oxygen isotope values (relative to the mantle) are preserved from surface alteration, but subsequently underwent interaction in equilibrium within the mantle. This process shifted clinopyroxene values towards the mantle, resulting in GNT-CPX disequilibrium. On the other hand, pyroxenitic samples are a result of eclogite melting and hybridization with mantle material, possibly recording direct crystallization from the metasomatic melt /fluid and explaining the contradictory LREE enrichment of these samples. This work suggests that all Orapa eclogite reflect altered oceanic crustal protoliths with variable metasomatic overprinting distinctly recorded in each sample.

Conclusions

The origin and evolution of mantle eclogite xenoliths from the Orapa kimberlite pipe is assessed using the triple oxygen isotope composition of pristine mineral separates and previously published geochemical data. Three groups have been distinguished based on the sodium in garnet and potassium in clinopyroxene, clinopyroxene Na#, and reconstructed bulk rock oxygen isotope compositions. Here it is shown that:

- Group I xenolith values are increasing in $\delta'^{18}O$ with decreasing $\Delta'^{17}O$, which overlaps with modern altered oceanic crust and reflects alteration of MORB on the seafloor.
- Group II eclogitic and pyroxenitic samples are indistinguishable with mantle-like triple oxygen isotope values.
- Group I and II eclogitic samples mostly record oxygen isotope disequilibrium between clinopyroxene and garnet, probably resulting from a shift in clinopyroxene oxygen isotope values from a metasomatic melt/fluid with mantle-like oxygen isotope values.
- Group II pyroxenitic samples directly record metasomatism through their resultant cumulate crystallization and mantle-like oxygen isotope equilibrium between garnet and clinopyroxene. The oxygen isotope signature resulted from melting of eclogite and evolution during interaction with mantle material.

This work concludes that all eclogitic xenoliths have altered oceanic crustal origins but may have since interacted within the mantle throughout their billion-year SCLM residence. The nature of metasomatism recorded in Orapa samples is defined by a melt/fluid with mantle-like oxygen isotope compositions , signified by a hybridized signature on SCLM reservoirs carried to the surface within the Orapa AK1 kimberlite eruption.

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