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► To cite this version:

Chunfei Chen, Jin-Xiang Huang, Stephen Foley, Zaicong Wang, Frédéric Moynier, et al.. Compositional and pressure controls on calcium and magnesium isotope fractionation in magmatic systems. *Geochimica et Cosmochimica Acta*, 2020, 290, pp.257-270. 10.1016/j.gca.2020.09.006 . insu-03029807

HAL Id: insu-03029807

<https://insu.hal.science/insu-03029807>

Submitted on 29 Nov 2020

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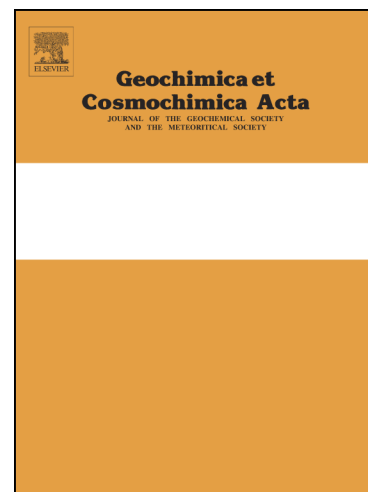
PII: S0016-7037(20)30557-3
DOI: <https://doi.org/10.1016/j.gca.2020.09.006>
Reference: GCA 11912

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 11 December 2019
Revised Date: 14 August 2020
Accepted Date: 7 September 2020

Please cite this article as: Chen, C., Huang, J-X., Foley, S.F., Wang, Z., Moynier, F., Liu, Y., Dai, W., Li, M., Compositional and pressure controls on calcium and magnesium isotope fractionation in magmatic systems, *Geochimica et Cosmochimica Acta* (2020), doi: <https://doi.org/10.1016/j.gca.2020.09.006>

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Compositional and pressure controls on calcium and magnesium isotope fractionation in magmatic systems

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Abstract:

Stable isotope fractionation in magmatic systems depends on equilibrium isotope fractionation between different phases. However, current equilibrium stable isotope theory mostly assumes ideal crystal structures and simple chemical compositions, but it is unclear how the pressure and complex compositional variations in natural microscopic mineral structures affect inter-mineral stable isotope fractionation and thus control stable isotope fractionation in macroscopic magmatic systems. Here, we calculate the Ca-O and Mg-O bond lengths controlled by pressure and compositional variations of coexisting garnet (Grt) and clinopyroxene (Cpx) in the Roberts Victor eclogites from the Kaapvaal Craton and use these data as a proof of concept to interpret their inter-mineral Ca and Mg isotopic compositions ($\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and $\Delta^{26}\text{Mg}_{\text{Grt-Cpx}}$). Our results show that the Ca-O difference between Grt and Cpx ($\Delta\text{Ca-O}_{\text{Grt-Cpx}}$) shows a significant increase with CaO content from 3.4 to 13.6 wt.% in Grt and with pressure from 2.9 to 6.9 GPa. $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ has an excellent negative correlation with inter-mineral Ca isotope fractionation corrected for temperature effect ($\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} \times T^2/10^6$), indicating that inter-mineral Ca isotope fractionation is controlled by pressure and compositional variations of the Grt through effects on the bond

lengths. Inter-mineral Mg isotope fractionation corrected for temperature effect ($\Delta^{26}\text{Mg}_{\text{Grt-Cpx}} \times T^2/10^6$) in these eclogites shows a negative correlation with pressure but no obvious correlations with the mineral compositions, suggesting the dominant role of pressure effect in addition to temperature. The Mg-O bond length of Grt increases by about 0.02 Å with increasing CaO content in Grt of these eclogites, implying a mild compositional effect on inter-mineral Mg isotope fractionation. The results suggest that pressure and compositional variations in minerals control the equilibrium stable isotope fractionation between minerals. Utilizing the Ca isotope fractionation factor controlled by crystal chemistry of garnet, our modelling indicates that partial melting of eclogite in the mantle could not significantly fractionate Ca isotopes and, therefore, that low $\delta^{44/40}\text{Ca}$ values in previously reported basalts cannot be attributed to the involvement of eclogite in their sources. This suggests that crystal chemistry exerts major controls on isotope fractionation in magmatic systems in addition to temperature.

Keywords: stable isotopes, pressure, compositional variations, eclogites, magmatic systems

1. Introduction

The stable isotopes of major elements such as Fe, Si, Mg and Ca have been widely used to understand the origin and evolution of terrestrial planets and to trace crust-mantle recycling (e.g., Bourdon et al., 2018; Chen et al., 2018; Huang et al., 2011; Huang and Jacobsen, 2017; Valdes et al., 2014). The stable isotope geochemistry of magmatic processes during the formation and evolution of terrestrial planets is controlled by equilibrium stable isotope fractionation among different phases. To quantitatively interpret isotopic data, the equilibrium stable isotope fractionation factors between phases must be known and this has been the focus of a multitude of studies in the last twenty years (e.g., Schauble, 2004; Young et al., 2015). Equilibrium isotope fractionation factors have been primarily determined by theoretical modelling that calculates isotope fractionation between minerals with ideal crystal structures and simple chemical compositions (Huang et al., 2013; Schauble, 2011), which have shown that temperature and chemical bond lengths exert the major control on the distribution of the isotopes, with heavy isotopes tending to be concentrated in minerals with shorter bonds (e.g., Schauble, 2004).

Although some recent calculations predicted significant effects for CaO and K₂O contents on inter-mineral stable isotope fractionation of Ca and K isotopes, respectively (Antonelli et al., 2019; Feng et al., 2014; Li et al., 2019; Wang et al., 2017a; Wang et al., 2017b), modelling results cannot easily explain large and variable isotope differences between minerals in natural samples (Antonelli et al., 2019; Liu et al., 2011; Wang et al., 2017b). A possible reason is that natural minerals have complex chemical compositions and that bond lengths are controlled by chemical compositions and pressure (Nestola et al., 2008; Novak and Gibbs, 1971; Yang and Ghose, 1995). Very few theoretical models have investigated the effect of pressure (Huang et al., 2013) or the combined effect of pressure and chemical compositions on equilibrium isotope fractionation factors. It is unclear how the pressure and compositional variations in natural microscopic mineral structures affect the equilibrium stable isotope fractionation between minerals and thus control the stable isotope geochemistry of macroscopic magmatic systems.

The ideal pathway for the investigation of inter-mineral equilibrium isotope fractionation is the direct measurement of isotope differences between minerals in natural samples with a range of equilibrium temperatures (and/or pressures) and chemical compositions, provided that equilibrium between the minerals can be demonstrated. These isotopic data can be compared to bond lengths that are controlled by pressure and compositional variations. Here we present Ca isotopic measurements for garnet (Grt) and clinopyroxene (Cpx) with variable chemical compositions separated from a series of well-characterized eclogite xenoliths from the Kaapvaal craton (Gréau et al., 2011; Huang et al., 2016; Huang et al., 2012), and combine them with previously reported Mg isotope measurements (Huang et al., 2016). We calculate the Ca-O and Mg-O bond lengths of the Grt and Cpx in these eclogites and establish their relationship to inter-mineral stable isotope fractionation. Finally, we investigate how pressure and compositional variations control stable isotope fractionation in magmatic processes.

2. Roberts Victor eclogites

The eclogite samples are xenoliths from the Roberts Victor kimberlite (128±15 Ma in age (Smith et al., 1985)) in the central Kaapvaal craton (Fig. S1), in which most xenoliths are eclogites (~80%) (Macgregor and Carter, 1970). Previous studies have identified two distinct groups

(including five sub-groups) based on microstructure and geochemical compositions (Gréau et al., 2011; Huang et al., 2016; Huang et al., 2012; Macgregor and Carter, 1970; McCandless and Gurney, 1989; Schulze et al., 2000). The first group (Type I) have been interpreted as metasomatised eclogites containing subhedral or rounded Grt in a Cpx matrix. They show highly enriched incompatible element patterns and have Grt with high Na_2O (≥ 0.07 wt.%) and Cpx with high K_2O (≥ 0.08 wt.%). The second group (Type II) are primary eclogites with interlocking textures of anhedral Grt and Cpx. They show depleted incompatible element patterns, indicating that pristine Type II eclogites escaped mantle metasomatism. We estimate their equilibrium temperatures and pressures using the garnet-clinopyroxene Fe-Mg geothermometer of Krogh (1988) projected on to the local conductive geothermal gradient (Chapman and Pollack, 1977) with 40 mW/m^2 surface heat flow (Griffin et al., 2003). On the basis of equilibrium temperature and pressure, we can divide the eclogites into low-temperature and pressure eclogites (Low-TP, $810\text{--}910^\circ\text{C}$ and $2.9\text{--}3.5 \text{ GPa}$) and high temperature and pressure eclogites (High-TP, $>1050^\circ\text{C}$ and $4.4\text{--}6.9 \text{ GPa}$) (Table 1). The samples selected for Ca isotopic analysis in the present study include ten Type I eclogites (all High-TP eclogites) and ten Type II eclogites including five High-TP and five Low-TP eclogites.

3. Methods

3.1 Sample preparation

Clear and fresh Grt and Cpx were separated under a binocular microscope after processing the hand specimen by SelFrag (electrostatic disaggregation). In order to remove any possible Ca carbonate on the mineral surfaces, handpicked minerals were rinsed in milli-Q water and leached in 1 mol/L HCl at room temperature before digestion. About $5\text{--}20 \text{ mg}$ of mineral grains were dissolved using $3 \text{ ml HF} + 1 \text{ ml HNO}_3$ in 7 ml Teflon vessels on a hotplate (120°C), followed by the replenishment of the dried residue with $1 \text{ ml HNO}_3 + 1 \text{ ml HCl}$ until the solutions were clear. Finally, samples were dried and re-dissolved in $1 \text{ ml } 4 \text{ mol/L HNO}_3$ for chemical purification.

3.2 Calcium isotope analysis

Chemical purification and measurement of Ca isotopes were performed at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences,

Wuhan, China. The detailed column chemistry and measurements by MC-ICP-MS (multi-collector inductively-coupled-plasma mass-spectrometer) have been documented in previous publications (Chen et al., 2020; Chen et al., 2019; Feng et al., 2018; Li et al., 2018); here we provide a short summary. Calcium was separated from the sample matrix on micro-columns filled with Ca-selective DGA resin: unlike Ca, matrix elements such as Al, Fe, K, Ti, Na, Sr, and Mg are not retained on DGA resin in 4 mol l⁻¹ HNO₃. The Ca fraction was collected in 3 ml H₂O. High recovery (> 99%), efficient separation of Ca and a low total procedural blank of <10 ng were achieved. Calcium isotopic measurements were performed using a Nu Plasma 1700 MC-ICP-MS. The ⁴²Ca, ⁴³Ca and ⁴⁴Ca ion beams were measured using Faraday cups at L4, L2, and H2. Isotope measurements were performed using standard-sample bracketing to correct for instrumental drift over time. Calcium isotopic variations are defined using δ -notation: $\delta^{n/42}\text{Ca} = [({}^n\text{Ca}/{}^{42}\text{Ca})_{\text{sample}}/({}^n\text{Ca}/{}^{42}\text{Ca})_{\text{SRM915a}}-1]\times 1000$ where n=44 or 43. All Ca isotopic values ($\delta^{44/42}\text{Ca}$) in this study are converted to $\delta^{44/40}\text{Ca}$ using a factor of 2.048 calculated by the mass-dependent fractionation law (Heuser et al., 2016). Two standard deviations of $\delta^{44/40}\text{Ca}$ of NIST SRM 915b measured in the course of previous studies over one year were 0.14‰ (n=62) (Chen et al., 2019; Li et al., 2018), which represents the long-term external precision for this study.

Four reference materials (BIR-1, BCR-2, BHVO-2, and OKUM) and seven duplicate samples were processed as unknowns to assess accuracy and reproducibility. We obtained $\delta^{44/40}\text{Ca}$ of 0.80 ± 0.07‰ (2sd, n=4), 0.81 ± 0.10‰ (2sd, n=8), 0.80 ± 0.08‰ (2sd, n=7) and 0.86 ± 0.03‰ (2sd, n=2) for BIR-1, BCR-2, BHVO-2, and OKUM respectively (Table S1), consistent with previous studies within the analytical uncertainty (Amini et al., 2009; Amsellem et al., 2017; Feng et al., 2017; He et al., 2017; Liu et al., 2017b; Schiller et al., 2012). Seven duplicate samples show good reproducibility within the analytical uncertainty (Table 1). A three-isotope plot ($\delta^{43/42}\text{Ca}$ versus $\delta^{44/42}\text{Ca}$) is commonly used for identifying mass-independent fractionation, isobaric interference, and analytical artefacts. All measured $\delta^{44/42}\text{Ca}$ and $\delta^{43/42}\text{Ca}$ of Grt and Cpx in the eclogites and the reference materials plot on a line of theoretical kinetic fractionation with a slope of 0.506 (Heuser et al., 2016) (Fig. S2), suggesting no analytical artifacts from interferences.

3.3 Calculation of Ca-O and Mg-O bond lengths of garnet and clinopyroxene

In Grt (X₃Y₂Si₃O₁₂), X and Y cations occupy polyhedra with dodecahedral and octahedral coordination with O, respectively. Cations such as Ca²⁺, Mg²⁺, and Fe²⁺ preferentially occupy the

eight-fold coordinated X site while Al^{3+} and Fe^{3+} cations prefer the six-fold coordinated Y site ($\text{Ca}_x, \text{Mg}_y, \text{Fe}^{2+}_{3-x-y}$) ($\text{Fe}^{3+}_z, \text{Al}_{2-z}$) Si_3O_{12} (Wang, 1973). The substitution of Al^{3+} by Fe^{3+} in the Y site does not significantly change X–O bond length in Grt (Novak and Gibbs, 1971) and the Fe^{3+} content in eclogitic Grt is low, so this is not considered further in this study. As the ionic radius of Ca^{2+} (1.14 Å) is much larger than those of Mg^{2+} and Fe^{2+} (0.86 Å and 0.77 Å, respectively) (Shannon, 1976), the proportion of Ca^{2+} in the X site may largely control X–O bond length. In addition, Mg^{2+} and Fe^{2+} have similar radii, implying that the variation of Fe^{2+} content in the X site does not significantly modify the X–O bond length (Novak and Gibbs, 1971). Therefore, we would not consider the effect of the Fe^{2+} on the bond lengths. Previous ab initio calculations of the pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)–grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) solid solutions series at 1 atm indicated that the Ca–O and Mg–O bond lengths of the Grt increase almost linearly from 2.35 Å to 2.39 Å and 2.28 Å to 2.31 Å, respectively, with Ca afu (x_{Ca}) increasing from 0.12 to 1.5 in the X site (Fig. 1a) (Freeman et al., 2006). We estimate the Ca–O and Mg–O bond lengths of Grt in the Roberts Victor eclogites at 1 atm (L[Ca–O] (1 atm) and L[Mg–O] (1 atm)) by projecting x_{Ca} of Grt onto the bond lines in Fig. 1a.

In Cpx (XYSi_2O_6), large cations such as Ca^{2+} and Na^+ preferentially occupy the eight-fold coordinated X site while smaller cations (e.g., Mg^{2+} , Fe^{2+} , Fe^{3+} , and Al^{3+}) prefer the six-fold coordinated Y site. The variation of the Ca–O bond length in Cpx ($(\text{Ca}_x\text{Na}_{1-x})(\text{Mg}_y(\text{Fe}, \text{Al})_{1-y})\text{Si}_2\text{O}_6$) is limited: the average Ca–O bond length increases from 2.458 Å to 2.470 Å with increasing x/y from 3/4 to 1 and decreases from 2.470 Å to 2.453 Å with increasing x/y from 1 to 5/4 (Wang et al., 2017b). Furthermore, the effect of Na content on the average Ca–O bond length is also limited: the average bond length decreases by less than 0.01 Å as the jadeite proportion increases from 0 to 53% at a given pressure (Nestola et al., 2008). Variation in Cpx compositions in the Roberts Victor eclogites corresponds to a formula of $(\text{Ca}_{0.51-0.70}\text{Na}_{0.18-0.40}\text{Fe}_{0.05-0.15})(\text{Mg}_{0.41-0.80}(\text{Fe}, \text{Al})_{0.20-0.59})\text{Si}_2\text{O}_6$, indicating that the average Ca–O bond length is about 2.450 at 1 atm. Mg^{2+} , Fe^{2+} , Fe^{3+} , and Al^{3+} share the same Y site in the Cpx. Due to the poor quantitative constraints on the effect of substitution between Fe^{2+} , Fe^{3+} , Al^{3+} , and Mg^{2+} on Mg–O bond length in Cpx, we do not calculate the Mg–O bond lengths of the Cpx in the Roberts Victor eclogites.

With increasing pressure, the unit cell volumes and Ca–O bond lengths of both Grt and Cpx

decrease significantly. However, the rate of decrease of the Ca-O bond length in Cpx is larger than that in Grt (Fig. 1b). Both first principles calculations (Walker et al., 2008) and experimental studies (Levien and Prewitt, 1981) indicate that the Ca-O bond length of diopside decreases almost linearly at a rate of 0.0092-0.0089 Å per GPa (Fig. 1b). Furthermore, previous experiments (Nestola et al., 2008) indicated that the Ca-O bond lengths in jadeite ($\text{NaAlSi}_2\text{O}_6$)-hedenbergite ($\text{CaFeSi}_2\text{O}_6$) solid solutions decrease at a similar rate of about 0.0089 Å per GPa, which is independent of their compositions. For Grt, the ab initio calculation of the structural properties of grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) under pressure indicated that its Ca-O bond length decreases almost linearly at a rate of 0.0049 Å per GPa (Akhmatskaya et al., 1999), identical to the experimental studies of andradite (0.0048 Å per GPa for $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) (Fig. 1b) (Hazen and Finger, 1989). Hazen and Finger (1978) also indicated that the Ca-O bond length in grossular decreases at an average rate of 0.0040 Å per GPa but their result indicated that the bond length does not linearly decrease with increasing pressure (Fig. 1b). Therefore, we can calculate the average Ca-O bond lengths of the Grt and Cpx at their equilibration pressures (P GPa):

$$L[\text{Ca-O}] (\text{P GPa}) = L[\text{Ca-O}] (1 \text{ atm}) - 0.0048 \times P \text{ for Grt} \quad (1)$$

$$L[\text{Ca-O}] (\text{P GPa}) = L[\text{Ca-O}] (1 \text{ atm}) - 0.0089 \times P \text{ for Cpx} \quad (2)$$

4. Results

Calcium isotope compositions of Grt and Cpx in the Roberts Victor eclogites are reported in Table 1 and illustrated in Fig. 2. Major element compositions of these Grt and Cpx were reported in Gréau et al. (2011) and Huang et al. (2014). The garnet separates in the Low-TP eclogites show higher $\delta^{44/40}\text{Ca}$ values (0.80 to 1.74‰) than co-existing Cpx (-0.19 to 1.01‰) with $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values of 0.73 to 1.13‰. The Grt separates in the High-TP eclogites also show higher $\delta^{44/40}\text{Ca}$ values (0.89 to 1.35 ‰) than co-existing Cpx (0.66 to 1.04‰) except for two samples. The Grt in the two samples show lower $\delta^{44/40}\text{Ca}$ values (0.99 to 1.02 ‰) than co-existing Cpx (1.14 to 1.33‰). The Low-TP eclogites have much higher $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values than the High-T eclogites (-0.31‰ to 0.55‰) (Fig. 3). Furthermore, the $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values in both Low-TP and High-TP eclogites show excellent correlations with CaO contents of the Grt (Fig. 4). As for previously reported other eclogite xenoliths from the Kaapvaal craton (Wang et al., 2015; Wang et al., 2012),

$\delta^{26}\text{Mg}_{\text{Grt}}$ in the Roberts Victor eclogites show a positive correlation with $\delta^{26}\text{Mg}_{\text{Cpx}}$ (Fig. 3b), and their $\Delta^{26}\text{Mg}_{\text{Grt-Cpx}}$ values show a variation from -0.76 to -0.36‰ (Huang et al., 2016) (Fig. 3 and Table 1).

The garnets in the Roberts Victor eclogites have variable compositions with a formula of $(\text{Ca}_{0.27-1.09}, \text{Mg}_{0.82-1.71}, \text{Fe}_{0.86-1.25}) (\text{Al}_{1.88-1.98}\text{Fe}^{3+}_{0.02-0.12})\text{Si}_3\text{O}_{12}$; their Ca contents are projected onto the lines of the Ca-O and Mg-O bond lengths in Fig. 1a for calculated Ca-O and Mg-O bond lengths at 1 atm. The calculated Ca-O and Mg-O bond lengths for Grt in the eclogites at 1 atm vary from 2.355 to 2.380 Å and 2.28 to 2.30 Å, respectively. The Ca-O bond length of the Cpx in the eclogites are about 2.450 Å at 1 atm, independent of their chemical compositions. The Ca-O bond length difference between Grt and Cpx ($\Delta\text{Ca-O}_{\text{Grt-Cpx}}$) at 1 atm increases from -0.10 to -0.07 Å as CaO content in Grt increases from 3.4 to 13.6 wt.% (Fig. 5a). The calculated Ca-O bond lengths for the Grt and Cpx in the eclogites at their equilibration pressures vary from 2.33 to 2.35 Å and 2.39 to 2.42 Å, respectively. $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ at their equilibration pressures varies from -0.08 to -0.04 Å (Fig. 5a).

5. Discussion

5.1 Isotope equilibrium in the Roberts Victor eclogites

Chemical and isotope equilibrium between Grt and Cpx is the premise that their isotope differences reflect inter-mineral isotope equilibrium fractionation. The Roberts Victor eclogites in this study show highly variable $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values (-0.31 to 1.13‰) and uniform $\Delta^{26}\text{Mg}_{\text{Grt-Cpx}}$ values (mostly from -0.68 to -0.45‰). Here, we demonstrate that such Ca and Mg isotope differences between Grt and Cpx reflect inter-mineral equilibrium isotope fractionation rather than kinetic fractionation as found recently in metamorphic Grt (Antonelli et al., 2019). Firstly, mineral major and trace element compositions of the Grt and Cpx pairs from the Roberts Victor eclogites studied here have achieved chemical equilibrium. The Grt and Cpx have homogeneous chemical compositions with no mineral zoning nor chemical variations across individual samples (Gréau et al., 2011). The major elements SiO_2 , Cr_2O_3 , and MgO show positive correlations between Grt and Cpx (Fig. 6), indicating major element equilibrium. Furthermore, the estimated equilibrium temperatures of these eclogites by the REE-in-garnet–clinopyroxene thermobarometer are in good

agreement with the temperatures calculated by the garnet–clinopyroxene Fe–Mg thermometer (Sun and Liang, 2015), indicating that Grt and coexisting Cpx are in equilibrium in trace elements. Given that isotope equilibrium is achieved faster than chemical equilibrium (Leshner, 1990; van der Laan et al., 1994), chemical equilibrium in the Grt and Cpx pairs indicates that the Roberts Victor eclogites will have reached inter-mineral stable isotope equilibrium. Secondly, the preservation of kinetic isotope fractionation in natural samples requires rapid cooling after a disequilibrium geological event ($<10^4$ years at mantle conditions (Zhao et al., 2017)) to avoid isotope re-equilibration between minerals at high temperature. Depleted incompatible element patterns and unradiogenic Sr and radiogenic Nd–Hf isotopic compositions suggested that Type II eclogites, which have highly variable $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values, were not modified by metasomatism just before being brought to the surface by kimberlites (Gréau et al., 2011; Huang et al., 2012). Furthermore, the Type I and II eclogites have been stored in the cratonic mantle for at least 128 Ma and 1.1 Ga, respectively (Huang et al., 2012), which is sufficient time to achieve isotope re-equilibration if kinetic fractionation occurred during formation and evolution. Lastly, kinetic isotope fractionation is caused by light isotopes generally diffusing faster than heavier isotopes and should occur simultaneously for different stable isotope systems (Teng et al., 2011; Zhao et al., 2017). No correlation between $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and $\Delta^{26}\text{Mg}_{\text{Grt-Cpx}}$ values is seen in the Roberts Victor eclogites (Fig. 3a), therefore precluding kinetic isotope fractionation. Similar to the previously reported eclogite and garnet pyroxenite xenoliths with equilibrium inter-mineral Mg isotopes from Kaapvaal craton (Wang et al., 2015; Wang et al., 2012) and Hawaii (Stracke et al., 2018), the Roberts Victor eclogites in this study show a positive correlation between $\delta^{26}\text{Mg}_{\text{Grt}}$ and $\delta^{26}\text{Mg}_{\text{Cpx}}$ and fall on inter-mineral Mg equilibrium fractionation lines corresponding to the calculated result at the temperature of 850–1350 °C and pressure of 3.0–7.0 GPa from Huang et al. (2013) (Fig. 3b), indicating equilibrium inter-mineral Mg isotope equilibrium in the Roberts Victor eclogites. These lines of evidence unambiguously indicate that Grt and Cpx pairs from the Roberts Victor eclogites have reached inter-mineral stable isotope equilibrium.

5.2 Bond length variation controlled by composition and pressure

Constraining the bond length difference between minerals is essential for understanding inter-mineral isotope equilibrium fractionation. Our bond length calculations show the Ca–O and Mg–O bond lengths at 1 atm for Grt in the Roberts Victor eclogites increase from 2.35 to 2.38 Å

and 2.28 to 2.30 Å, respectively, with increasing CaO content in the Grt from 3.4 to 13.6 wt.% (Fig. 1a). Given the limited variation of Ca-O bond length of the Cpx in the Roberts Victor eclogites at 1 atm with the variation of their chemical compositions, $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ at 1 atm shows a linear increase with CaO content in the Grt, indicating the control of CaO content in Grt on the $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ (Fig. 5a). Furthermore, the variation of $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ at the equilibration pressures for these eclogites is greater than that of $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ at 1 atm, suggesting the effect of equilibration pressure (Fig. 5a). This could be attributed to a larger decrease of Ca-O bond length in Cpx as pressure increases than for Grt (Fig. 1b). Our results show that the CaO content of Grt and pressure exert the major controls on the Ca-O bond length variations in Grt and Cpx, and thus on inter-mineral Ca isotope fractionation, as discussed below.

5.3 Isotope fractionation controlled by temperature, pressure, and compositional variations

Inter-mineral equilibrium isotope fractionation is controlled by temperature and basic crystal chemical parameters such as bond strength (Huang et al., 2019; Urey, 1947; Young et al., 2015). The equilibrium constant of isotopic exchange reactions between two minerals A and B ($\alpha_{\text{A-B}}$) can be written as (Young et al., 2015):

$$\ln \alpha_{\text{A-B}} = \frac{1}{24} \left(\frac{h}{k_b T} \right)^2 \left(\frac{1}{m} - \frac{1}{m'} \right) \left[\frac{\bar{K}_{f,A}}{4\pi^2} - \frac{\bar{K}_{f,B}}{4\pi^2} \right] \quad (3)$$

where h is the Planck constant, k_b is the Boltzmann's constant, T is the temperature, m and m' are atomic masses of light and heavy isotopes, respectively, and $\bar{K}_f$ is the average force constant for the vibrational modes. This suggests that inter-mineral equilibrium isotope fractionation depends on the inverse of the square of temperature, the difference in mass between the two isotopes, and on differences in force constants for the vibrational modes in each phase (Young et al., 2015). A phase with shorter, stronger bonds has higher vibrational energy than a phase with longer bonds, and is therefore enriched in the heavier isotope (Schauble, 2004; Young et al., 2015). This implies that inter-mineral equilibrium Ca isotope fractionation between Grt and Cpx is a linear function of $1/T^2$ if the differences in force constants do not change:

$$\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} = 10^3 \ln \alpha_{\text{Grt-Cpx}}^{44/40} \sim \frac{10^3}{24} \left(\frac{1}{T^2} \right) \left(\frac{1}{m_{40}} - \frac{1}{m_{44}} \right). \quad (4)$$

The Grt separates from the Roberts Victor eclogites show higher $\delta^{44/40}\text{Ca}$ values (0.80 to

1.74‰) than co-existing Cpx (-0.19 to 1.04‰), except for two High-TP eclogites (Table 1). The $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values of the Low-TP eclogites (0.73 to 1.13‰) are higher than those of the High-TP eclogites (-0.31 to 0.55‰), indicating an effect of temperature and pressure (Fig. 4a). Given the linear relationship between $1/T^2$ and $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$, we use $T^{44/40}\text{Ca}_{\text{Grt-Cpx}} = \Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} \times T^2/10^6$ to correct for the temperature effect. An excellent negative correlation is observed between $T^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ (Fig. 5b) in the Roberts Victor eclogites, suggesting the control of bond strength on inter-mineral Ca isotope fractionation in addition to temperature. The excellent negative correlation between $T^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ indicates the propensity of heavy isotopes to concentrate where force constants are greater, and therefore in stiffer bonds (usually shorter bond lengths). Interestingly, the Grts have the same $\delta^{44/40}\text{Ca}$ as Cpx when $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ is about -0.05 Å (Fig. 5b), implying that Grt and Cpx have similar force constants or Ca-O bond stiffness at the $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ of -0.05 Å.

As discussed in Section 5.2, the variation of $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ depends on pressure and CaO content in Grt, suggesting that pressure and compositional variation significantly modify equilibrium Ca isotope fractionation between Grt and Cpx. The corrected $T^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ for the Low-TP Roberts Victor eclogites are still systematically higher than those of the High-TP eclogites, pointing to a pressure effect (Fig. 4b). We estimate the equilibrium isotope fractionation factors between Grt and Cpx for Grt with 5 wt.% CaO at 3 GPa and 4.5 GPa, based on the $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ of low-T and high-T eclogites, to be (Fig. 7):

$$\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} = 0.96 \times 10^6/T^2 \text{ (at 3 GPa)} \quad (5)$$

$$\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} = 0.66 \times 10^6/T^2 \text{ (at 4.5 GPa)} \quad (6)$$

The difference in slope between equations 5 and 6 may indicate the control of pressure (Fig. 7). Here, we attribute the pressure effect to the difference of variation of Ca-O bond lengths in Grt and Cpx with pressure (Fig. 1b). Due to a larger rate of decrease of the Ca-O bond length in Cpx than that in Grt with increasing pressure (Fig. 1b), the $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ at 4.5 GPa is larger than that at 3 GPa and thus $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ at 4.5 GPa is smaller than at 3 GPa for a given temperature.

One of the most remarkable findings is that both Low-TP eclogites and High-TP eclogites show good correlations between $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ (and temperature-corrected $T^{44/40}\text{Ca}_{\text{Grt-Cpx}}$) and the CaO content of Grt (Fig. 4) but do not correlate with temperature or Cpx composition (Figs. S3-4), indicating a strong compositional effect on the isotopic fractionation in Grt. Our bond length

calculations suggest that Ca-O bond length in Grt at 1 atm is positively correlated with CaO content for both Low-TP and High-TP eclogites, and increases from 2.355 to 2.38 Å (Fig. 1a). Given the limited variation in Ca-O bond length of Cpx in the Low-TP and High-TP eclogites, the increase of Ca-O bond length in Grt results in a decrease in the difference in Ca-O bond lengths between Grt and Cpx (Fig. 1a). This could explain the negative correlation between $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and CaO content of Grt. A similar correlation between temperature effect-corrected $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values and CaO content of Grt was also observed in low-temperature (479-872 °C) Dabie eclogites and peridotites (Fig. 4b) (Wang et al., 2019). The absence of a correlation between $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values and Cpx composition (e.g., jadeite proportion and CaO content in Cpx, Fig. S4) in both Low-TP and High-TP eclogites suggests that inter-mineral Ca isotope fractionation is not affected by the jadeite component in Cpx speculated by Wang et al. (2019), which also agrees well with the limited variation of Ca-O bond lengths with increasing Jd and CaO content in these Cpx. We estimate the equilibrium isotope fractionation factor between Grt and Cpx for Grt with 12.7 wt.% CaO at ~3 GPa (Fig. 7):

$$\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} = 0.45 \times 10^6 / T^2 \text{ (at 3 GPa)} \quad (7)$$

The difference in slope between equations 5 and 7 may be controlled by CaO content in Grt (Fig. 7). Furthermore, the temperature-corrected $T^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ in the High-TP eclogites shows a more significant decrease with increasing CaO in Grt (the slope of -0.13) than that of the Low-TP eclogites (the slope of -0.089) (Fig. 4b). The Low-TP eclogites show similar equilibrium pressure, whereas the equilibrium pressure of the High-TP eclogites ranges from 4.4 to 6.9 GPa (Table 1), indicating that the slope difference in Fig. 4b is most likely due to the additional pressure effect on the inter-mineral Ca isotope fractionation in the High-TP eclogites in addition to the compositional effect (Fig. 7).

The positive trend between $T^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and $T^{26}\text{Mg}_{\text{Grt-Cpx}}$ ($= \Delta^{26}\text{Mg}_{\text{Grt-Cpx}} \times T^2/10^6$) indicates that, like Ca isotopes, inter-mineral Mg isotope fractionation in the Roberts Victor eclogites is also modified by pressure and/or compositional variation in addition to temperature (Fig. 8a). The negative trend between $T^{26}\text{Mg}_{\text{Grt-Cpx}}$ and pressure in the Roberts Victor eclogites and previously reported eclogite xenoliths from Kaapvaal craton (Wang et al., 2015; Wang et al., 2012) (Fig. 8b) may indicate the pressure effect on inter-mineral Mg isotope fractionation, consistent with the trend predicted by theoretical calculations (Huang et al., 2013). Our calculations show that the

Mg-O bond length of Grt in the Roberts Victor eclogites increases by about 0.02 Å with increasing CaO content in the Grt (Fig. 1a), implying a mild compositional effect on inter-mineral Mg isotope fractionation. However, no obvious correlation between $T^{26}\text{Mg}_{\text{Grt-Cpx}}$ and CaO content in Grt or Cpx compositions is found (Fig. S5). A possible reason is that any such compositional effect is much less than the pressure effect or the Mg-O bond length of Cpx could also be slightly modified by their compositional variations.

An increasing number of first-principles calculations have been used to investigate the effect of the compositional variation (especially for large ionic radius elements such as Ca^{2+} and K^{+}) on inter-mineral stable isotope fractionation (Antonelli et al., 2019; Li et al., 2019; Wang et al., 2017a; Wang et al., 2017b). Wang et al. (2017b) and Antonelli et al. (2019) indicated that $\Delta^{44/40}\text{Ca}_{\text{Opx-Cpx}}$ decreases from 0.45 to 0.10‰ as $\text{Ca}/(\text{Ca}+\text{Mg})$ in Opx ranges from 2/16 to 1/64 at 800-1100 °C. However, these calculated results cannot easily explain large and variable isotope differences between minerals in natural samples, such as -0.48‰ to 1.25‰ for $\Delta^{44/40}\text{Ca}_{\text{Opx-Cpx}}$ for mantle peridotites (Chen et al., 2019; Huang et al., 2010; Kang et al., 2016; Zhao et al., 2017). This could be attributed to (1) isotopic disequilibrium between natural minerals (Antonelli et al., 2019; Chen et al., 2018); (2) compositional differences between natural minerals and theoretical calculation; (3) the poorly investigated effect of pressure in most first-principles calculations. Interestingly, the Opx in natural peridotites with high $\Delta^{44/40}\text{Ca}_{\text{Opx-Cpx}}$ ($> 0.5\text{‰}$) have extremely low Ca/Mg ratios (0.0082–0.010), lower than 1/64 (Chen et al., 2019; Huang et al., 2010; Kang et al., 2016), which has not been investigated in previous first-principles calculations (Antonelli et al., 2019; Wang et al., 2017b). This study presents a comprehensive investigation of the effect of the pressure and compositional variation on the bond length, and thus equilibrium stable isotopes, highlighting that both pressure and compositional variation could modify inter-mineral isotope fractionation (Fig. 7). The combined effect of pressure and chemical composition may help to explain inter-mineral Ca isotope differences in some natural spinel peridotites. Antonelli et al. (2019) indicated that the effect of Ca concentration is significant on $\Delta^{44/40}\text{Ca}_{\text{Grt-Diopside}}$ (from 0.56‰ to 0.33‰) from pyrope with Ca/Mg of 1/23 to grossular at 850 °C and 1 atm. However, the calculated result is smaller than for the natural eclogites in this study, for which $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ decreases from about 0.76‰ to 0.36‰ as CaO content in Grt increases from 5.0 to 12.7 wt.% at 850 and 3 GPa (Fig. 7). This is probably attributable to the ideal crystal structures and simple mineral compositions and/or the

poorly investigated effect of pressure in first-principles calculations. In addition, the calculations of Huang et al. (2019) predicted 0.44‰ for $\Delta^{44/40}\text{Ca}_{\text{Grossular-Diopside}}$ at 850 °C and 1 atm, higher than that of Antonelli et al. (2019) (0.33‰) (Fig. 7). Given the limited and inconsistent theoretical data on Ca isotope fractionation between Grt and Cpx, more theoretical work in the future may provide a clearer and more comprehensive picture for the compositional and pressure effects on inter-mineral Ca isotope fractionation.

5.4 The control of stable isotope geochemistry in magmatic systems

Stable isotope variation during partial melting and magmatic differentiation depends on isotope fractionation between minerals. The present study suggests that pressure and compositional variation in minerals significantly affect isotope fractionation between minerals, indicating that the stable isotope geochemistry of magmatic systems is controlled by pressure and compositional variation in minerals. In the following section, we explore how garnet crystal chemistry controls Ca isotope fractionation during partial melting of eclogite, which could provide important insights into the petrogenesis of the basalts.

The involvement of eclogite in the source of basalts has been invoked to explain much lower $\delta^{44/40}\text{Ca}$ values in basalts (as low as 0.65‰) than that of the mantle ($0.94 \pm 0.10\%$, 2sd, Chen et al., 2019; Kang et al., 2017) because partial melting of eclogite was speculated to significantly fractionate Ca isotopes in previous studies (Dai et al., 2020; Kang et al., 2019; Wang et al., 2019). The speculated Ca isotope fractionation during partial melting of eclogite originated from significant inter-mineral Ca isotope fractionation between Grt and Cpx. Due to poor constraints on equilibrium stable isotope mechanism, the isotope fractionation factor between Grt and Cpx has been assumed to be constant (Kang et al., 2019) or was speculated to be controlled by the Jd content of Cpx (Wang et al., 2019) in previous calculations. Utilizing our new knowledge that the Ca isotope fractionation between Grt and Cpx is controlled by pressure and compositional variation of garnet, we revisit Ca isotope fractionation during partial melting of eclogite and modify previous interpretations about the low $\delta^{44/40}\text{Ca}$ values of basalts. We quantitatively modelled the behaviour of Ca isotopes during partial melting of eclogite using an incremental batch melting model in which the fractionation factors between melt and residue were recalculated at each step (Williams and Bizimis, 2014; Zhang et al., 2018). Details are given in *supplementary*

information and Table S2. Since there is no measurable calcium isotopic fractionation during the crystallization of Kilauea Iki basalts, the Ca isotopic fractionation factor between Cpx and basaltic melt ($\alpha_{\text{Cpx-melt}}$) was suggested to be close to 1 at about 1 atm (Zhang et al., 2018). Furthermore, the MORB-like Ca isotope compositions of cumulate websterites and spinel clinopyroxenites at high-pressure (>1.2 GPa and <3 GPa) from the Balmuccia peridotite massif in the Italian Alps suggested that $\alpha_{\text{Cpx-melt}}$ is close to 1 at high pressure (Chen et al., 2019). Therefore, we speculate that there is no significant variation in $\alpha_{\text{Cpx-melt}}$ with increasing pressure. $\alpha_{\text{Cpx-melt}}$ is taken to be 1 in this modelling calculations and the $\alpha_{\text{Grt-melt}}$ is estimated from inter-mineral isotope fractionation between Grt and Cpx from this study. According to the high temperature (>1050 °C) and pressure (>3 GPa) (Klemme et al., 2002) melting conditions and isotope fractionation factors controlled by compositional variation, the isotope fractionation factors between Grt and Cpx for the modelling calculation should be a function of CaO content of the residual Grt and can be estimated from $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ of the High-TP eclogites in this study (Fig. 3a). In order to compare with previous results, we also modelled Ca isotope fractionation during partial melting of eclogite using the constant isotope fractionation factor from $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ of the eclogites from the central Siberian craton in Kang et al. (2019) (Fig. 9). Our modelled results indicate a negligible Ca isotope difference between melts and residual eclogites using isotope fractionation factors controlled by compositional variation in garnet (Fig. 9). This contrasts with the results using the assumption from previous studies that low $\delta^{44/40}\text{Ca}$ values occur in the melts. This indicates that partial melting of eclogite could not induce significant Ca isotope fractionation, consistent with mantle-like $\delta^{44/40}\text{Ca}$ of $0.90 \pm 0.04\%$ for OIB basalts whose source involves eclogites (Valdes et al., 2014). Therefore, our study indicates that low $\delta^{44/40}\text{Ca}$ values in basalts do not reflect the involvement of eclogite in their sources but may instead be the result of the recycling of crustal carbonates into the mantle (Amsellem et al., 2020; Huang et al., 2011; Liu et al., 2017a). These observations suggest that pressure and compositional variation in mineral structures at the microscopic scale exert major controls on Ca isotope fractionation in macroscopic magmatic systems which is of critical importance to understand the origin and evolution of terrestrial planets using stable isotope data.

6. Conclusions

In order to investigate the effect of pressure and compositional variations in natural microscopic mineral structures on the stable isotope fractionation of macroscopic magmatic systems, this study presents inter-mineral Ca and Mg isotopic fractionation ($\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and $\Delta^{26}\text{Mg}_{\text{Grt-Cpx}}$) of garnet and clinopyroxene from a series of well-characterized Roberts Victor eclogites from the Kaapvaal craton and calculates the Ca-O and Mg-O bond lengths of the Grt in these eclogites. The results demonstrate that the Ca-O bond length difference between Grt and Cpx ($\Delta\text{Ca-O}_{\text{Grt-Cpx}}$) show a significant increase with increasing CaO content from 3.4 to 13.6 wt.% in Grt and with pressure from 2.9 to 6.9 GPa. This is consistent with the systematically higher corrected $T^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ ($\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} \times T^2/10^6$) for the Low-TP Roberts Victor eclogites relative to those of High-TP eclogites, and with the negative correlation between CaO content of garnet and $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values. Inter-mineral Mg isotope fractionation corrected for temperature shows a negative correlation with pressure, indicating a significant pressure effect on inter-mineral Mg isotope fractionation in addition to temperature. These observations suggest that stable isotope fractionation between Grt and Cpx is controlled by pressure and compositional variations of garnet. Using inter-mineral equilibrium Ca isotope fractionation factors constrained by the Roberts Victor eclogites, we quantitatively model the behaviour of Ca isotopes during partial melting of eclogite. Results show that stable isotope fractionation by pressure and compositional variations in minerals exerts major controls on isotope fractionation in magmatic systems. Partial melting of eclogite could not significantly fractionate Ca isotopes and thus is not the cause of low $\delta^{44/40}\text{Ca}$ values in previously reported basalts.

Acknowledgments:

We thank Prof. Yu Ye, Dr. Fei Wu, Sarath Patabendigerada, Dr. Yoann Gréau, and Prof. Dorrit E. Jacob for discussion. We also thank Prof. Qiao Shu for discussion during designing this study. SFF and CFC are funded by ARC grant FL180100134. This research is co-supported by NSFC (41530211), the 111 Project (BP0719022), MOST Special Funds of the State Key Laboratory of Geological Processes and Mineral Resources (MSFGPMR01). We thank Prof. Fangzhen Teng and

Prof. Jeffrey G. Catalano for editorial handling and three anonymous reviewers for constructive comments, which greatly improved the manuscript.

Journal Pre-proofs

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Figure captions

Figure 1. (a) Average Ca-O (black solid line) and Mg-O bond lengths (grey dotted line) in the pyrope–grossular garnet solid solutions with the variation of Ca content at 1 atm from ab initio calculations (x represents atoms per formula unit ($\text{Ca}_x, \text{Mg}_y, \text{Fe}_{3-x-y}$) $\text{Al}_2\text{Si}_3\text{O}_{12}$) (Freeman et al., 2006). Garnets in Roberts Victor eclogites are plotted on the lines for calculation of Ca-O and Mg-O bond lengths. Ca-O bond lengths of Cpx in the Roberts Victor eclogites are shown for comparison (grey band: 0.450 to 0.460 Å). (b) Variation of Ca-O bond lengths in garnet and clinopyroxene with increasing pressure from theoretical calculations and experiments. Green, red, and purple lines represent Cpx with variable Jd contents (Nestola et al., 2008). The Ca-O bond lengths of diopside (Di) obtained by first principles and experiments are from Walker et al. (2008) and Levien and Prewitt (1981), respectively. Ca-O bond lengths of grossular obtained by ab initio calculation and experiment are from Akhmatkaya et al. (1999) and Hazen and Finger (1978), respectively. The Ca-O bond length of the andradite obtained by the experiment is from Hazen and Finger (1989). The numbers on the lines represent the rate of decrease of bond length as increasing pressure. The decrease of the bond length in Cpx is more significant than in grossular.

Figure 2. Calcium isotope compositions of the garnets and clinopyroxenes in the Roberts Victor (RV) eclogite xenoliths. Filled symbols = garnets (Grt) and open symbols = clinopyroxenes (Cpx). The eclogite xenoliths from the central Siberian craton (Kang et al., 2019) and orogenic eclogites and peridotites from the Dabie orogen (Wang et al., 2019) are shown for comparison. The estimated $\delta^{44/40}\text{Ca}$ of the mantle (light green band) is from Chen et al. (2019) and Kang et al. (2017).

Figure 3. (a) Inter-mineral Ca isotope fractionation and Mg isotope fractionation (Huang et al., 2016) in the Roberts Victor eclogites. The uncertainties of $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ and $\Delta^{26}\text{Mg}_{\text{Grt-Cpx}}$ are calculated by propagating the analytical errors on both garnet (Grt) and clinopyroxene (Cpx). (b) $\delta^{26}\text{Mg}_{\text{Grt}}$ versus $\delta^{26}\text{Mg}_{\text{Cpx}}$ for the Roberts Victor eclogites in this study, previous reported Kaapvaal eclogites and garnet peridotites (An et al., 2017; Wang et al., 2015; Wang et al., 2012), orogenic eclogites from the Dabie orogen (Li et al., 2011), and garnet pyroxenite xenoliths from Hawaiian

(Stracke et al., 2018) and Hannuoba (Hu et al., 2016). Equilibrium Mg isotope fractionations for different temperatures are calculated from Huang et al. (2013) at 3 (grey solid line) and 7 GPa (grey dotted line). The grey arrow implies the trend of inter-mineral Mg isotope disequilibrium, as indicated by Wang et al. (2015) and Hu et al. (2016).

Figure 4. (a) Plots of CaO content versus inter-mineral Ca isotope fractionation between coexisting garnet and clinopyroxene in eclogites from Roberts Victor (this study) and the central Siberian craton (Kang et al., 2019). Orogenic eclogites and peridotites from the Dabie orogen (Wang et al., 2019) are shown for comparison. (b) Plots of CaO content versus inter-mineral Ca isotope fractionation corrected for temperature effect. The uncertainty of $T^2/10^6 \times \Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ is calculated by propagating the errors on temperature (50 K) and $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$.

Figure 5. (a) CaO content in Grt versus Ca-O bond length difference between Grt and Cpx ($\Delta\text{Ca-O}_{\text{Grt-Cpx}}$) at their equilibration pressures and 1 atm in the Roberts Victor eclogites. (b) $\Delta\text{Ca-O}_{\text{Grt-Cpx}}$ at their equilibration pressures versus inter-mineral Ca isotope fractionation corrected for temperature effect ($\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} \times T^2/10^6$). The uncertainty calculation is as Fig. 4b.

Figure 6. Plots of SiO_2 (a) and Cr_2O_3 (b) contents in the garnets versus those in the clinopyroxenes from the Roberts Victor eclogites. Positive correlations of major elements SiO_2 and Cr_2O_3 indicates that chemical equilibrium has achieved.

Figure 7. Equilibrium Ca isotope fractionation between garnet and clinopyroxene in the Roberts Victor eclogites. Blue lines represent equilibrium Ca isotope fractionation at about 3 GPa and CaO content of garnet of 5 and 12.7 wt.%, respectively. Red lines represent equilibrium Ca isotope fractionation at 4.4-6.9 GPa and CaO content of garnet of 5 and 13.6 wt.%, respectively. The blue and red equilibrium fractionation lines were obtained from the $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ values in the Low-TP and High-TP eclogites, respectively. First-principles calculations about Ca isotope fractionation between grossular (Grs), pyrope (Pyr) with Ca/Mg of 1/23 and diopside (Di) at 1 atm are shown for comparison (Antonelli et al., 2019; Huang et al., 2019). The blue dotted arrow indicates the effect of increasing CaO content in garnet on equilibrium Ca isotope fractionation. The black

dotted arrow indicates the effect of increasing pressure on equilibrium Ca isotope fractionation. The red dotted arrows indicate the effect of increasing pressure and CaO content of garnet. The uncertainty of $T^2/10^6$ is calculated by propagating the error on temperature (50 K).

Figure 8. (a) Inter-mineral Ca isotope fractionation corrected for temperature ($\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} \times T^2/10^6$) versus inter-mineral Mg isotope fractionation corrected for temperature ($\Delta^{26}\text{Mg}_{\text{Grt-Cpx}} \times T^2/10^6$) in the Roberts Victor eclogites. (b) $\Delta^{26}\text{Mg}_{\text{Grt-Cpx}} \times T^2/10^6$ versus the equilibrium pressure in the Roberts Victor eclogites and previously reported Kaapvaal eclogites (Wang et al., 2015; Wang et al., 2012). The equilibrium temperature and pressure of the previously reported Kaapvaal eclogites are estimated using the method in this study as described in Section 2. Other published Mg isotopes of eclogites and garnet pyroxenites are omitted due to the poorly constraints on the equilibrium pressures. The uncertainty calculation is as Fig. 4.

Figure 9. Modelled $\delta^{44/40}\text{Ca}$ of basaltic melt and residual eclogite with an increasing degree of melting of eclogite. Green lines are the modelled results using the isotope fractionation factor from Kang et al. (2019). Red lines are the modelled results using isotope fractionation factor from $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}}$ of the High-TP eclogites as a function of CaO content of their garnets in this study ($\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} = -0.65 \times \text{CaO} + 0.67$). The light red and red bands represent the uncertainties of the modelled results. The uncertainties are calculated by propagating the uncertainty of the slope and intercept for $\Delta^{44/40}\text{Ca}_{\text{Grt-Cpx}} = -0.65 \times \text{CaO} + 0.67$ (0.011 and 0.077, respectively). For details of all modelling calculations see Table S2. The $\delta^{44/40}\text{Ca}$ values of oceanic island basalts (OIBs, grey area) (Valdes et al., 2014) are shown for comparison. The $\delta^{44/40}\text{Ca}$ in the starting eclogite is assumed to be 0.90‰, the average value of the Type I Roberts Victor eclogites (Table 1).

Table 1. Chemical compositions, bond lengths and Ca and Mg isotope compositions of the Roberts Victor eclogites.

[illegible]

[illegible]

								1		0		3							0		
								0		0		0							2.		
					9.		.	.	.	.								3			
RV	Hi		1	5	5	0.4	0	0.2	0	0.9	0		0			0	6	2.3	2.29		
07-	gh	II	Grt	1	1	8	4	1	9	9	7	3	-0.	.	1.0	-0.	.	9	42	6	
31	-T	B		9	.		0		0		0		15	1	8	56	0	2.			
	P			0	5	1	.	.	.				2				5	4			
			Cp		5.	0.5	0	0.2	0	1.1	0						5	2.4			
			x		5	6	5	8	7	4	9	3					0	01			
							0		0		0								2.		
					1		.	.	.									3			
					0.	0.4	0	0.2	0	1.0	1						7	2.3	2.29		
			Grt		4	9	8	2	1	1	5	3					2	39	8		
			Re				0		0		0						2.				
			pli				.	.	.								4				
RV	Hi		cat	1		0.4	0	0.2	0	1.0	0		0				5	2.3			
07-	gh	II	e	2	6		9	1	4	3	1	2	3	0.0	.	0.9	0	91			
33	-T	B		9	.		0		0		0		9	2	5						
	P			0	6	1	.	.	.				0								
			Cp		5.	0.4	0	0.2	1	0.9	1										
			x		1	5	6	0	1	1	3	3									
			Re				0		0		0										
			pli				.	.	.												
			cat			0.4	0	0.2	0	0.9	1										
			e		4	7	4	1	0	4	3										
						0		0		0								2.			
					1		.	.	.									3			
					3.	0.5	0	0.2	0	1.0	1						7	2.3	2.30		
			Grt		6	0	9	5	5	2	8	3					9	45	4		
RV	Hi			1			0		0		0		0				2.				
07-	gh	II		3	6		1		.	.	.		-0.	.	1.1		4				
34	-T	B	Cp	2	.	4.	0.6	0	0.3	0	1.3	0	31	1	8		5	2.3			
	P		x	0	9	3	5	1	2	5	3	2	3	8			0	89			
			Re				0		0		0										
			pli				.	.	.												
			cat			0.6	0	0.2	1	1.3	0										
			e			7	0	8	2	8	1	3									
							0		0		0								2.		
RV	Hi			1	4	4.	.	.	.				0				3				
07-	gh	I		0	.	2	0.5	0	0.3	0	1.1	1	0.3	.	0.8	-0.	.	5	2.3	2.28	
02	-T	A	Grt	6	5	5	8	5	3	4	9	1	3	5	1	4	54	0	7	34	6
	P		Cp	0		1	0.4	0	0.2	0	0.8	0	3	2			7	2.	2.4		

RV 07- 03	Hi gh -T P	I A <
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	P		0			5		7		9		1			0				
						0		0		0					2.				
					1	.		.		.					4				
		Cp		3.	0.3	0	0.1	1	0.6	0					5	2.4			
		x		8	3	3	9	0	7	7	3				0	10			
						0		0		0					2.				
				4.		.		.		.					3				
RV	Hi		1	7	0.5	0	0.2	0	1.1	0		0		0	5	2.3	2.28		
07-	gh	IB	4	2	4	5	6	5	1	9	3	0.3	.	0.8	-0.	8	35	7	
01	-T		6	.		0		0		0		2	1	3	51	0	2.		
	P		5	1		.		.		.		5			3	4			
		Cp		4.	0.3	0	0.1	0	0.7	1					5	2.4			
		x		1	8	6	5	5	8	2	3				0	10			
						0		0		0					2.				
				4.		.		.		.					3				
RV	Hi		1	6	0.6	0	0.3	1	1.2	1		0		0	5	2.3	2.28		
07-	gh	IB	4	8	2	8	4	2	6	7	3	0.3	.	0.9	-0.	8	35	6	
07	-T		7	.		0		0		0		5	1	8	48	0	2.		
	P		6	1		.		.		.		7			8	4			
		Cp		4.	0.4	0	0.2	0	0.9	0					5	2.4			
		x		0	5	2	3	3	1	4	3				0	09			
						0		0		0					2.				
				4.		.		.		.					3				
RV	Hi		1	5	0.6	0	0.3	0	1.3	0		0		0	5	2.3	2.28		
07-	gh	IB	4	3	6	4	6	2	5	8	3	0.5	.	0.9	8	36	6		
11	-T		5	.		0		0		0		3	0	4	2.				
	P		4	1		.		.		.		8			4				
		Cp		4.	0.4	0	0.2	0	0.8	0					5	2.4			
		x		4	0	2	1	8	3	4	3				0	11			
						0		0		0					2.				
				4.		.		.		.					3				
RV	Hi		1	8	0.5	0	0.3	0	1.2	0		0		0	5	2.3	2.28		
07-	gh	IB	4	1	9	3	0	4	1	7	3	0.5	.	0.9	8	36	7		
14	-T		7	.		0		0		0		5	0	4	2.				
	P		5	1		.		.		.		9			4				
		Cp		3.	0.3	0	0.0	0	0.6	0					5	2.4			
		x		9	2	3	8	8	6	7	3				0	10			

a: According to the equilibrium temperature and pressure, these eclogites are divided into low-temperature and pressure eclogites (Low-TP, 810-910 °C and 2.9-3.5 GPa) and high- temperature and pressure eclogites (High-TP, > 1050 °C and 4.4-6.9 GPa). b: The classification is from Huang et al. 2016. c: CaO content is from Gréau et al. 2011. d: Whole rock $\delta^{44/40}\text{Ca}$ (‰) is calculated based on mineral separate data in this study and mineral modal abundance from Huang et al. 2016. e: The analytical uncertainty of $\Delta^{44/40}\text{Ca}$ and $\Delta^{26}\text{Mg}$ is calculated by propagating the analytical errors on both garnet and clinopyroxene.

f: Bulk rock $\Delta^{26}\text{Mg}$ values are from Huang et al. 2016. g: For the calculation method for bond lengths of the garnets and clinopyroxenes at 0 GPa and their equilibrated pressures (P GPa), see the main text.

Note: Grt-garnet, Cpx-clinopyroxene, Replicate-replicate digestion of the same sample powder.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Journal Pre-proofs

Figure 1

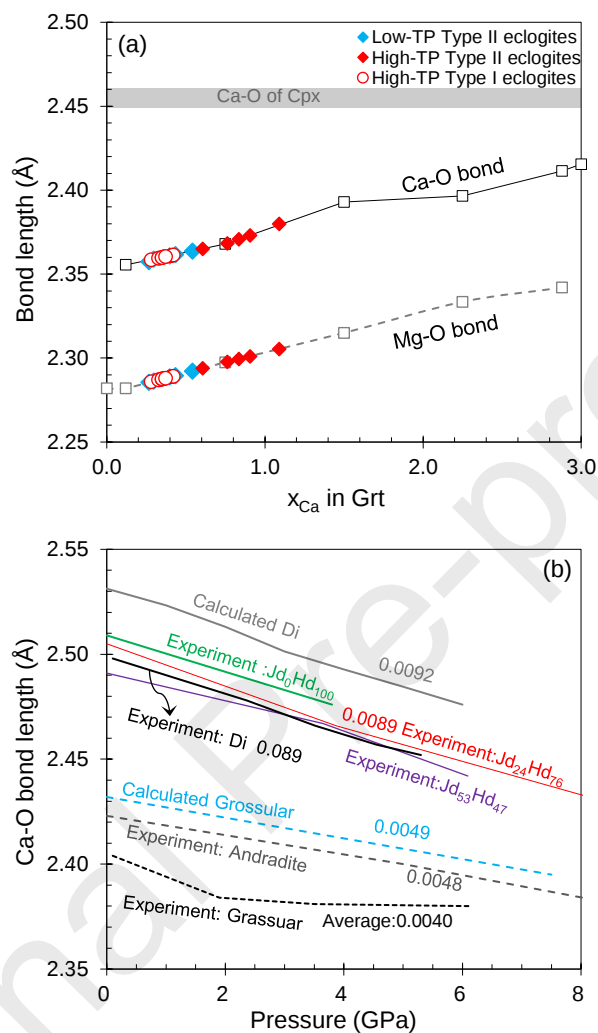


Figure 2

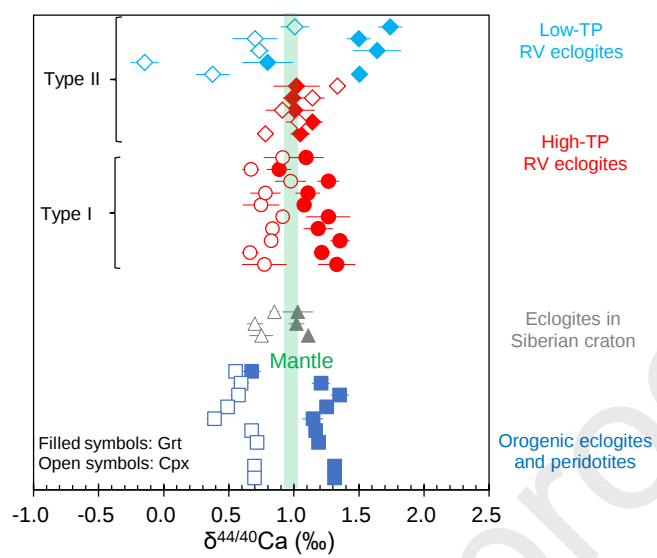


Figure 3

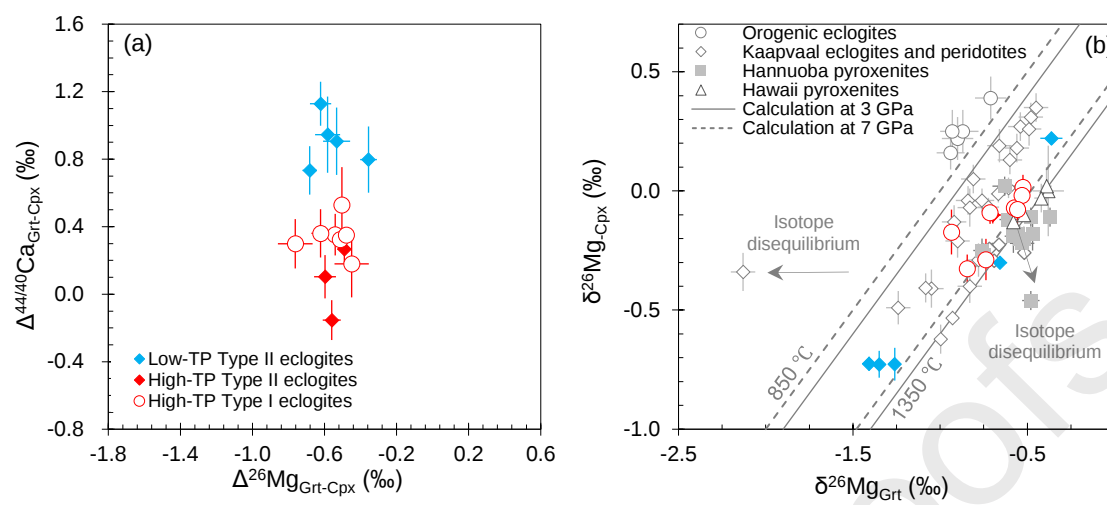


Figure 4

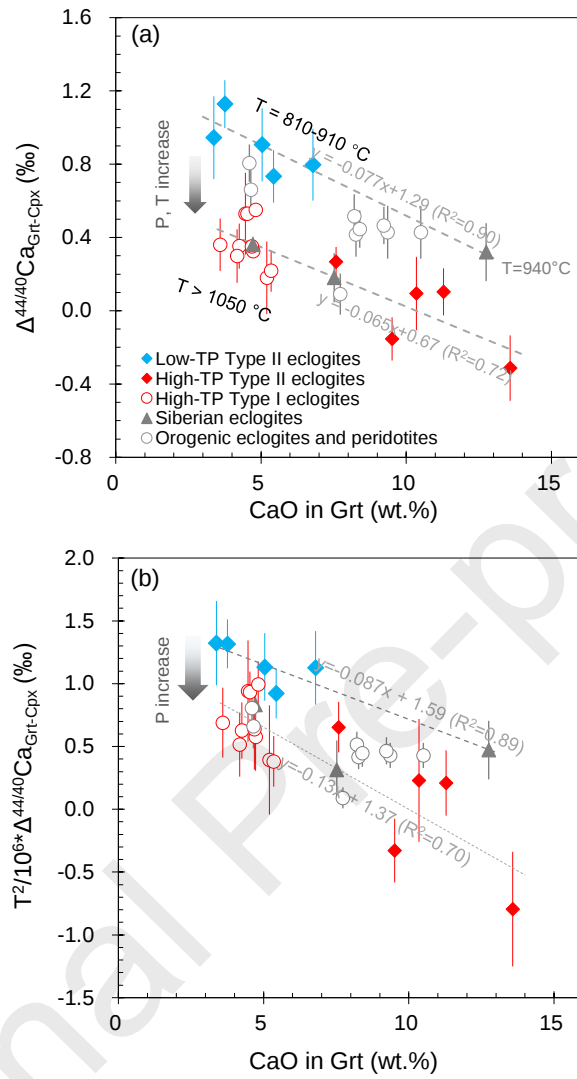


Figure 5

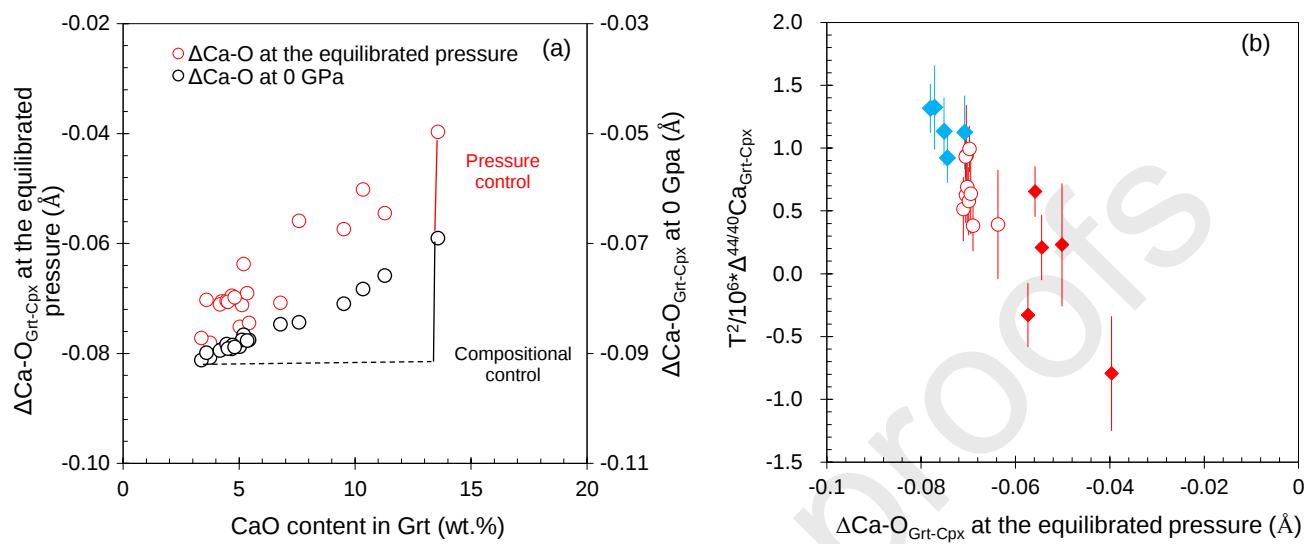


Figure 6

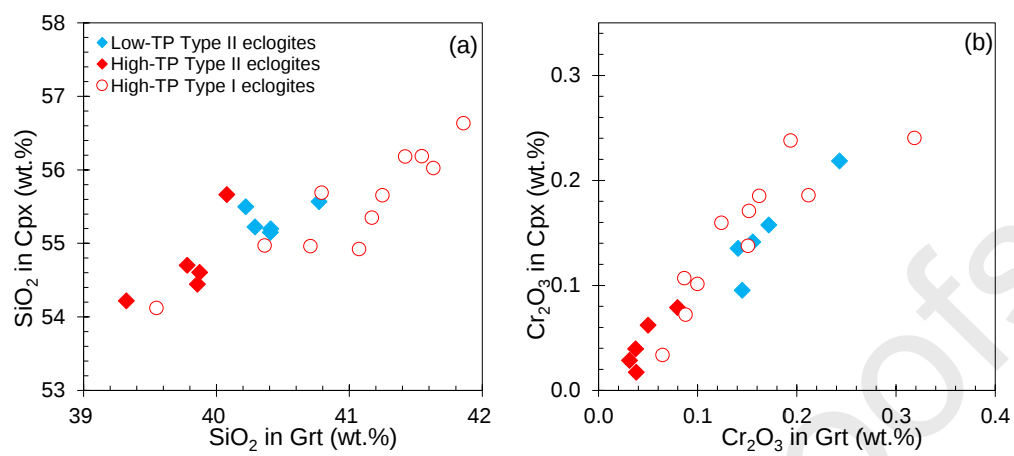


Figure 7

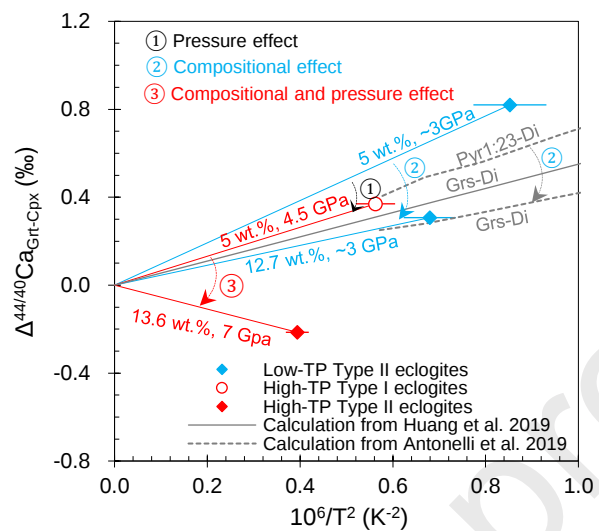


Figure 8

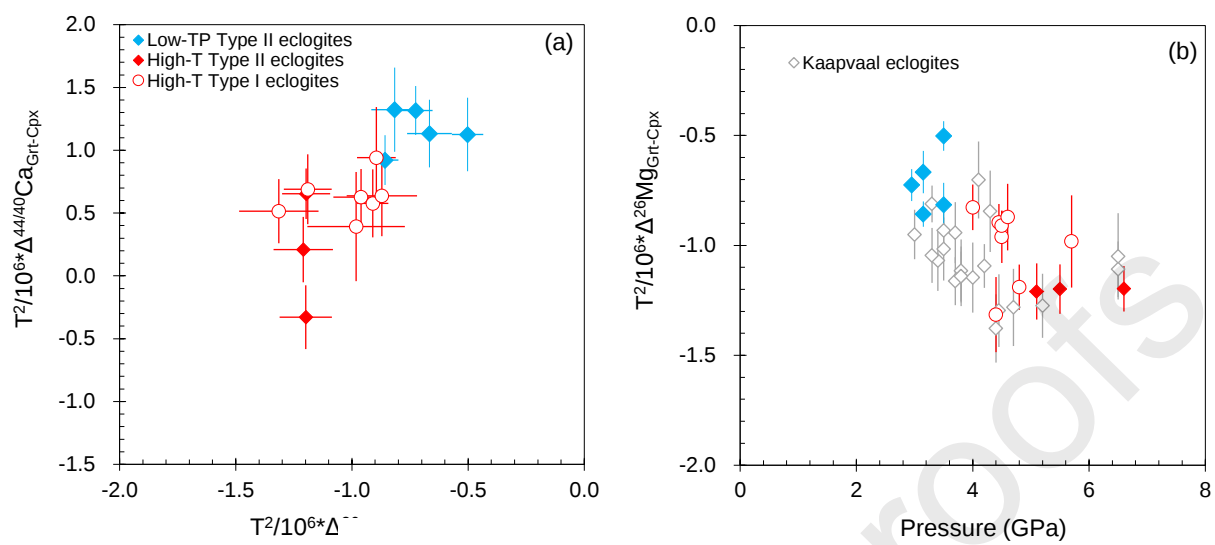


Figure 9

