An extended calibration of the olivine–spinel aluminum exchange thermometer: Application to the melting conditions and mantle lithologies of large igneous provinces

Yishen Zhang\textsuperscript{1,2}, Olivier Namur\textsuperscript{1}, Weiran Li\textsuperscript{2,3}, Oliver Shorttle\textsuperscript{2}, Esteban Gazel\textsuperscript{4}, Eleanor Jennings\textsuperscript{5}, Peter Thy\textsuperscript{6}, Timothy L. Grove\textsuperscript{7}, Bernard Charlier\textsuperscript{8}

\textsuperscript{1} Department of Earth and Environmental Sciences, KU Leuven, 3000 Leuven, Belgium
\textsuperscript{2} Department of Earth Sciences, University of Cambridge, Cambridge, UK
\textsuperscript{3} Department of Earth Sciences, University of Hong Kong, Hong Kong, China
\textsuperscript{4} Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY, USA
\textsuperscript{5} Department of Earth and Planetary Sciences, Birkbeck, University of London, Malet Street, London WC1E 7HX, United Kingdom
\textsuperscript{6} Department of Earth and Planetary Sciences, University of California, Davis, CA 95616, USA
\textsuperscript{7} Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, 02139 Massachusetts, USA
\textsuperscript{8} Department of Geology, University of Liège, 4000 Sart Tilman, Belgium

* Corresponding author. E-mail address: yishen.zhang@kuleuven.be

© The Author(s) 2023. Published by Oxford University Press. All rights reserved. For Permissions, please email: journals.permissions@oup.com
ABSTRACT

The application of the olivine–spinel aluminum exchange thermometer to natural samples is limited by the restricted experimental dataset on which it was calibrated. Here, we present a new dataset of 46 high-temperature crystallization experiments and 21 reanalyzed published experiments, which we used to extend the calibration to higher and lower temperatures. The final calibration dataset spans a range of conditions relevant to crustal and upper mantle processes: 1174–1606 °C, 0.1–1350 MPa, QFM–2.5 to QFM+7.2 (oxygen fugacity, $f_{O_2}$ reported in log units relative to the quartz–fayalite–magnetite buffer, QFM), and 0–7.4 wt.% $H_2O_{melt}$. We propose three new models. The first is thermodynamically self-consistent, based on spinel Fe, Mg, Al, and Cr compositions and Al exchange between olivine and spinel. The second and third are empirical models that consider fewer elemental exchanges: the second uses only Al exchange and spinel compositions, whereas the third considers olivine–spinel Al and Cr exchange. All models include the modest effect of pressure on olivine-spinel equilibrium chemistry, whereas $f_{O_2}$ and water content have negligible effects.

In general, as fewer elements are considered in the olivine–spinel exchange, the fit to experimental data worsens. Conversely, the associated decrease in model complexity improves their robustness against systematic errors when applied to natural crystal pairs: the thermodynamic model may underestimate crystallization temperatures in natural samples due to spinel subsolidus re-equilibration, whereas the empirical models (independent of Fe and Mg in spinel) are less sensitive to re-equilibration but yield temperatures with larger uncertainties. We applied a statistical test to select the most appropriate model for application to natural samples. When applied to lavas from mid-ocean ridges, Iceland, Skye, Emeishan, Etendeka, and Tortugal, our new temperature estimates are 30–100 °C lower than previously proposed. The lower temperature estimates cause a lower mantle melting temperature and significant impacts on the mantle lithology constraints.

Keywords: Cr-spinel; Large igneous province; Mantle melting; Olivine; Thermometry
DATA AVAILABILITY

Additional data is available as supplementary electronic files. All calculations of each model, the protocol to choose the results are written in a python script and Excel spreadsheet (https://github.com/eazzzon/olspthermo).

ACKNOWLEDGEMENT

We thank T. D. van Gerve for sharing olivine for the use of the models, T. Bechon for sharing samples used in this study, and S. Matthews for discussion of our usage of pyMelt. R. Dennen is thanked for his help in editing the manuscript. We thank Adam Kent for the editorial handling. Maxim Gavrilenko, Eric Brown, and an anonymous reviewer for their constructive comments that significantly improved this work. This work was supported by an ERC Runner-up FWO grant to ON. BC is a Research Associate of the Belgian Fund for Scientific Research-FNRS. OS and WL acknowledge NERC grant NE/T012633/1 for support.
INTRODUCTION

In the mantle, convection and upwelling plumes generate substantial magma volumes in mid-ocean ridge (MOR) systems and can produce oceanic or continental large igneous provinces (LIPs; e.g., Morgan, 1971; White & McKenzie, 1989; Campbell & Griffiths, 1990). Buoyantly ascending plume materials melt at relatively shallow depths (Sleep, 1992, 1996), eventually producing large volumes of magma through decompression melting of the plume head. Mantle plumes are sustained by temperature-induced density differences (e.g., Rayleigh-Taylor instability) compared to the ambient mantle (White & McKenzie, 1995), and large thermal anomalies (ca. 100–200 °C; White & McKenzie, 1989) are generally considered requisite for LIP activity. This thermal anomaly is commonly expressed as the excess temperature ($T_{ex}$), which is the difference between the mantle potential temperature ($T_p$, the mantle temperature extrapolated along the adiabat at 1 bar without melting; McKenzie & Bickle, 1988) at hotspots and of the ambient mantle (i.e., average MORs, $T_p \approx 1330$ °C; e.g., Green & Falloon, 2005; Falloon et al., 2007), where melts are generated by near-adiabatic upwelling of the upper mantle (McKenzie & Bickle, 1988).

The temperatures of LIP mantle sources have often been estimated by applying olivine-liquid geothermometers (Beattie, 1993; Putirka, 2005, 2008) to picritic basalts containing forsteritic olivine (forsterite content expressed as Fo = 100 × molar Mg/[Mg + Fe]) to calculate the olivine-melt equilibrium temperature and then $T_p$ (Putirka et al., 2007).

Other approaches involve modeling mantle melting as a function of pressure and temperature and comparing the modeled primary magmas with those determined from natural (near-) primary melts (Ghiorso & Sack, 1995; Ghiorso et al., 2002; Herzberg & Asimow, 2015; Brown Krein et al., 2021). However, these models require assumptions of primary melt compositions, even though near-primary melts rarely erupt (O’Hara, 1968; Neave et al., 2019; Neave & Namur, 2022). Therefore, primary melt compositions are usually estimated by adding or subtracting an olivine component iteratively based on olivine-melt Fe-Mg exchange until equilibrium with a mantle Fo target is attained, often
leading to large uncertainties in the FeO and MgO contents of the calculated primary melt (e.g., Herzberg et al., 2007).

The olivine-spinel aluminum exchange thermometer (hereafter OSAT; Wan et al., 2008; Coogan et al., 2014) is based on the exchange of Al between olivine and spinel, written as $K_{D_{\text{Al}}} = [\text{Al}_2\text{O}_3]_{\text{Ol}}/[\text{Al}_2\text{O}_3]_{\text{Spl}}$ (Al$_2$O$_3$ concentrations in wt.%). This thermometer obviates the need to assume a melt composition because it determines the crystallization temperature directly from the equilibrium compositions of olivine and coexisting spinel.

However, the OSAT was only calibrated at low pressure (0.1 MPa) and a restricted range of dry melt compositions (SiO$_2$: 40.5–45.9 wt.%, MgO: 17.5–23.5 wt.%, FeO: 10.6–12.2 wt.%, Al$_2$O$_3$: 9.0–15.4 wt.%), olivine compositions (Fo$_{86-100}$), spinel compositions (Cr# = 0–0.69, where Cr# = molar Cr/[Cr + Al]), and oxygen fugacities ($f_{O_2} = \text{QFM}–1.5$ to QFM+0.5, with 70% of the experiments performed at QFM–1.5; QFM indicates the quartz–fayalite–magnetite equilibrium). Therefore, its applicability in diverse geological settings, particularly those with Cr-rich spinel in equilibrium with Fo-rich olivine, is questionable; it is unknown how intensive parameters such as pressure, $f_{O_2}$, and volatile contents affect the OSAT calibration.

In this study, we performed and analyzed new experiments, reanalyzed prior experiments, and combined our results with the high-quality measurements of Wan et al. (2008) and Coogan et al. (2014) to extend the OSAT calibration. Our final experimental database spans 0.1–1350 MPa, 1174–1606 °C, and QFM–2.5 to QFM+7.2 (i.e., air), and includes three hydrous experiments containing 3.7–7.4 wt.% H$_2$O$_\text{melt}$.

We also developed a thermodynamic formalism to better understand olivine–spinel Al exchange. Our model suggests that, besides $K_{D_{\text{Al}}}$ and spinel Cr#, other components involving Fe and Mg in spinel have a significant impact on the calculated olivine–spinel equilibrium temperature and therefore on the previous OSAT calibration. This model is expected to be the most accurate parameterization for olivine and spinel compositions that quenched rapidly, inhibiting Mg–Fe exchange during cooling. However, this comprehensive
thermodynamic model may retrieve systematically low temperature estimates when applied
to natural rocks due to subsolidus olivine–spinel Fe–Mg re-equilibration. Therefore, we also
report two empirical expressions that may be less prone to underestimating olivine–spinel
equilibration temperatures in variably re-equilibrated natural samples, but are less precise
and accurate than the thermodynamic model. The first empirical model follows a similar
formalism as Coogan et al. (2014), only involving $K_{\text{DA1}}$ and spinel Cr#. The second
incorporates the exchange of Cr between olivine and spinel ($K_{\text{DCr}} = \frac{[\text{Cr}_2\text{O}_3]_{\text{Ol}}}{[\text{Cr}_2\text{O}_3]_{\text{Spl}}}$,
Cr$_2$O$_3$ concentrations in wt.%) which improves the accuracy of this model. We find that
pressure has a moderate impact on the temperature calculations in all models, whereas $f_\text{O}_2$
and water have negligible effects.

We applied our new models to re-constrain the crystallization temperature for
published olivine-spinel pairs in natural rocks. A multi-component mantle melting model
(Phipps Morgan, 2001; Shorttle et al., 2014) is then applied to match crystallization
temperature with geochemical constraints to estimate mantle temperatures and mantle
lithology components (Matthews et al., 2016; 2021). Our results suggest that previous
studies using the model of Coogan et al. (2014) may have overestimated the crystallization
temperature of olivine by as much as ~30–100 °C for intra-plate LIPs, significantly
overestimating $T_p$ and impacting constraints on the mantle lithology. Based on our results,
we provide new constraints on mantle melting conditions and mantle lithologies for MORs,
Iceland, Skye, and intra-plate LIPs including Emeishan, Etendeka, and Tortugal.

**The olivine-spinel aluminum exchange thermometer (OSAT)**

The OSAT (Wan et al., 2008; Coogan et al., 2014) determines the equilibrium temperature
of olivine-spinel pairs, which corresponds to the minimum saturation temperature of these
two phases near the liquidus of their primitive parental melts (e.g., Jennings et al., 2019).
The crystallization temperature is calculated based on the concentration (in wt.%) of Al$_2$O$_3$
in olivine and those of Al$_2$O$_3$ and Cr$_2$O$_3$ in spinel as:
\[ T (K) = \frac{10,000}{0.575(0.162) + 0.884(0.043) \text{ Cr#} - 0.897(0.025) \ln(K_{PD})} \]  

(1)

with the standard errors on the determined coefficients reported in parentheses. The slow diffusion rate of Al$_2$O$_3$ in olivine minimizes the effect of re-equilibration at low temperatures (Spandler & O’Neil, 2010). The OSAT has been widely used to investigate the temperature of formation of terrestrial and extraterrestrial magmas (Gavrilenko et al., 2016; Prissel et al., 2017; Trela et al., 2017; Goltz et al., 2020; Jennings et al., 2020; Matthews et al., 2021; Ramsey et al., 2021; ), including those of LIPs. However, the model has faced criticism for the limited experimental database used for its calibration, which has limited its application. The main issues with the previous calibration are: (1) the range of experimental spinel compositions is quite narrow compared to those observed in natural rocks (see next subsection); (2) the highest experimental temperature in the database (1450 °C) is significantly lower than magmatic temperatures calculated in many natural settings (>1500 °C; e.g., komatiite, Trela et al., 2017; LIPs, Matthews et al., 2021; Martian shergottites, Ramsey et al., 2021), implying that the currently available expression must be extrapolated beyond its calibration range; and (3) high-pressure and hydrous experiments are absent in the calibration database.

Comparison of the original calibration experiments with natural rocks

To demonstrate the limitations of the existing olivine–spinel aluminum exchange calibration, we compare the olivine and spinel compositions used in the calibration experiments to those most common in LIPs.

To compare spinel compositions, we used the ternary projection of the spinel prism, Al–Cr–Fe$^{3+}$ (Fig. 1a). Spinel Fe$^{3+}$ contents were calculated by charge balance on a four-oxygen basis (Droop, 1987). Both experimental and natural spinel compositions show a dominant trend from the Cr apex towards the Al apex. However, spinel in primitive basalts commonly have compositions plotting far beyond the calibration range (Cr# = 0.23–0.85 in natural spinel vs. 0–0.69 in the calibration experiments; Fig. 1b). Natural spinel also has higher Fe$^{3+}$
contents and occasionally higher TiO$_2$ contents (>5 wt.%; Fig. 1c) compared to the calibration dataset. Therefore, the experimental spinel compositions are only directly comparable to MORB compositions and partially overlap those from Iceland. The chemical composition of igneous spinel is known to be a complex function of intensive parameters (pressure, temperature, fO$_2$) and melt composition (Katsura & Ito, 1989; Ballhaus et al., 1991; Ariskin & Nikolaev, 1996; Kamenetseky et al., 2001). The chemical differences between experimental spinel compositions in the calibration dataset and natural spinel may be due to the narrow fO$_2$ range and/or restricted melt compositions used in the experiments; many of the experiments were performed in the Cr-free simplified CaO–MgO–Al$_2$O$_3$–SiO$_2$ (CMAS) system, with pure spinel in equilibrium with forsterite. However, the observed differences could also be partly related to subsolidus Fe–Mg re-equilibration between olivine and spinel in natural rocks.

Figure 2 compares olivine Al$_2$O$_3$ and Cr$_2$O$_3$ concentrations as a function of Fo content. The restricted experimental conditions also limited the range of experimental olivine compositions to Fo$_{86-100}$ (Fo$_{100}$ crystallized in CMAS experiments), compared to the much wider range observed in natural olivine (Fo$_{68-94}$, Fig. 2). The Al$_2$O$_3$ (190–1,519 µg/g) and Cr$_2$O$_3$ (165–3,420 µg/g) contents of natural olivine crystals also commonly fall outside the calibration interval (Al$_2$O$_3$, 450–1,686 µg/g; Cr$_2$O$_3$, 45–2,990 µg/g).

**EXPERIMENTAL STRATEGY AND ANALYTICAL METHODS**

**Selection and preparation of starting materials**

To co-saturate olivine and spinel at different temperatures from a wide range of melt compositions, we used a variety of natural and synthetic starting compositions with 10.1–34.9 wt.% MgO, 38.0–50.2 wt.% SiO$_2$, 3.8–16.3 wt.% Al$_2$O$_3$, 0.2–6.0 wt.% total alkalis (Na$_2$O + K$_2$O) and 0.1–2.0 wt.% Cr$_2$O$_3$. Details of the different starting compositions are reported in Table 1 and summarized here.

1) We used two komatiitic compositions from the Tortugal lava suite, Costa Rica: TO-080514-1 and TO-080514-2 (Trela et al., 2017), here abbreviated as TO1 and TO2,
respectively. These lavas have >33 wt.% MgO, different TiO$_2$ contents (TO1: 0.79 wt.%; TO2: 0.89 wt.%) and preserve olivine with high-Cr# spinel inclusions (Cr# >0.85).

2) Five basaltic compositions cover a range of melt SiO$_2$ (38.0–50.2 wt.%) and Al$_2$O$_3$ contents (3.8–16.3 wt.%), which may affect the exchange of Al between the liquid, olivine, and spinel (Evans et al., 2008; Hanson & Jones, 1998). These five compositions include: primitive basalts from Pico, Azores (PI052, van Gerve et al., 2021) and Osorno volcano, Chile (OS082; Bechon et al., 2022); two alkali-rich (>5 wt.%), SiO$_2$-undersaturated basalts from Nyiragongo volcano, DR Congo (Ny17-135 and Ny17-161, Molendijk et al., 2023a); and a porphyritic basalt from the Nyamuragira volcano, DR Congo (NYA2012-09-018, here abbreviated as NYAM).

3) We prepared three synthetic compositions as analogues to TO1, TO2, and Ny17-135 (Table 1). The objective here was to test the potential effect of relict olivine and spinel grains in natural materials with liquidus temperatures too high to completely melt in a standard muffle furnace prior to experimental runs in the vertical gas mixing furnace (see Experimental methods, below).

4) Finally, we synthesized the starting composition of Wan et al. (2008; here named 2Cr'+1Cr) to check interlaboratory experimental reproducibility and test analytical uncertainties under different analytical settings.

Natural samples were crushed to finer than 1 μm in a ball mill and melted three times at >1500 °C in a Pt crucible in a muffle furnace: the first melting batch was used to saturate the Pt crucible and was not kept; the two additional batches were used to ensure the compositional homogeneity of the glass. The synthetic compositions were prepared from mixtures of high-purity oxides and silicates (SiO$_2$, TiO$_2$, Al$_2$O$_3$, MnO, MgO, Fe$_2$O$_3$, CaSiO$_3$, AlPO$_4$, Na$_2$SiO$_3$, K$_2$Si$_2$O$_3$, Cr$_2$O$_3$, NiO) in appropriate proportions. The silicates (CaSiO$_3$, Na$_2$SiO$_3$, and K$_2$Si$_2$O$_3$) were prepared following Zhang et al. (2023).

Due to the dramatic increase of Cr$_2$O$_3$ solubility in the melt (>1 wt.%) at high temperatures (>1450 °C; Borisova et al., 2020) and the potential increase of the Cr$_2$O$_3$...
evaporation rate with increasing temperature (Sossi et al., 2019) in the gas mixing furnace, most natural and all synthetic compositions were doped with 1–2 wt.% Cr$_2$O$_3$ (compositions with ‘Cr1’ suffixes for 1 wt.% and ‘Cr2’ for 2 wt.% dopant, respectively; Table 1). In some experiments, chromite and forsterite powders were added to change the liquidus of olivine and spinel (Table 1). All starting powders were mixed and ground in ethanol for one hour then dried at 120 °C before use in experiments.

**Experimental methods**

Experiments were conducted in a Nabertherm HTRV 50/150/17 vertical tube furnace at KU Leuven, Belgium, or a GERO HTRV 70-250/18 vertical tube furnace at the University of Liège, Belgium. Approximately 50 mg of starting material was suspended on a 0.2-mm-diameter Pt loop. To avoid potential Fe loss, the Pt loops were pre-saturated with the experimental material for ~24 h at the same temperature and fO$_2$ to be used in the experiment, then cleaned with HF. Prior to experiments, all sample pellets were briefly heated in a muffle furnace at 1550 °C to ensure sintering. Experimental samples were then suspended for 7–120 h in the hot spot of the vertical furnace (~5 cm in height, where temperature is stable to within ±3 and ±1 °C in the Nabertherm HTRV 50/150/17 and GERO HTRV 70-250/18 furnaces, respectively). Temperature was measured using a S-type (Pt–Pt$_{90}$Rh$_{10}$) thermocouple calibrated against the melting points of Ag and Au. Oxygen fugacity was controlled using mixtures of high-purity CO and CO$_2$ flushed upward from the bottom of the alumina ceramic furnace tube. Bronkhorst gas-flow controllers were used to set the flow rate at 0.12 cm/s. The accuracy on the fO$_2$ was checked with a zirconia oxygen sensor. Because it is challenging to produce large spinel and olivine crystals above 1500 °C, in experiments at such high temperatures, the temperature was first oscillated by ±10 °C for ~1–2 h to increase the sizes of olivine and spinel crystals before holding the experiments isothermally for the remainder of the experiment. All experiments were drop-quenched in water. Experimental run conditions are detailed in Table 2.
Selection of previous experiments

To expand the experimental database and test the effects of pressure and water content on the Al exchange between olivine and spinel, we also selected and reanalyzed 21 published experiments, including crystallization experiments on Munro komatiite, Canada (Thy, 1995), lunar magma ocean (Charlier et al., 2018), harzburgite melting experiments (Parman & Grove, 2004), hydrous melting experiments on komatiite from Commondale Ultramafic Suite, South Africa (Barr et al., 2009), and melting experiments on fertile mantle component (Mitchell & Grove, 2015). These experiments span a range of temperature between 1215 and 1350 °C, pressure between 0.1 and 1350 MPa, \( f_O^2 \) from QFM \(-2.5\) to QFM, and between 0 and 7.4 wt. % \( H_2O_{melt} \).

Analytical methods

Analyses were performed using a JEOL JXA-8530F Wavelength Dispersive Spectrometer (WDS) Field Emission Gun Electron probe micro-analyzer (EPMA) at the Department of Material Engineering, KU Leuven, Belgium, and a Cameca SX-100 Electron Microprobe at the Department of Earth Sciences, University of Cambridge. Major and trace elements were measured with different calibrations and analytical setups detailed in the Supplementary data and summarized here. Major element concentrations in olivine and spinel were generally within 98% accuracy of the reference values.

Experimental products were mounted in high-purity epoxy and polished for analysis. Electron probe micro-analyzer measurements of trace elements in olivine, especially Cr and Al, are known to suffer from secondary fluorescence from surrounding spinel or melt (Llovet et al., 2012, Gavrilenko et al., 2023; Llovet et al., 2023). We used FANAL (Llovet et al., 2012) and PENEPMA (Llovet & Salvat, 2017), Monte Carlo simulation tools to model coupled electron-photon transportation, and simulated analyses of San Carlos olivine and VG-2 glass standards. The results show that measuring olivine compositions at least 5 \( \mu m \) (based on FANAL) and 15 \( \mu m \) (based on PENEPMA) inward from the phase margin dramatically reduces the influence of secondary fluorescence (Fig. S1). This analytical
strategy was applied to sufficiently large olivine (> 10 µm) crystals in the experimental
charges. Analytical results for experiments with smaller olivine (~ 10 µm) were manually
filtered by removing anomalous outliers (see more details below).

At KU Leuven, Al, P, Cr, and Ca in olivine were measured with a focused beam operating at
20 kV and 300 nA and calibrated with a MongOl sh11-2 olivine (Batanova et al., 2019).
Detection limits were 6 µg/g for Al₂O₃, 9 µg/g for P₂O₅, and 4 µg/g for Cr₂O₃. High-
precision wavelength scanning at 20 kV and 300 nA was performed prior to each session to
accurately determine the Al, Cr, and P peak positions (Fig. S2). Background positions were
chosen near (~0.5 mm) the base of the peak to minimize the subtraction of background
counts (Batanova et al., 2015). Because it is difficult to properly analyze major elements by
WDS at high beam currents due to the high counting rates and the possibility of
oversaturating the detectors, Si, Mg, and Fe in olivine and all elements in spinel were
measured afterwards with a focused beam at 15 kV and 20 nA and calibrated with natural
and synthetic primary standards (see Supplementary data). To ensure reproducibility
between sessions, secondary standards (San Carlos olivine NMNH 111312-44 for olivine,
chromite NMNH 117075 for spinel) were analyzed at regular intervals to correct for any
instrumental drift. In the San Carlos olivine, we measured 338 ± 14 µg/g Al₂O₃ (1σ, n = 72),
43 ± 22 µg/g P₂O₅ (1σ), and 135 ± 9 µg/g Cr₂O₃ (1σ), which are comparable with the results
of Batanova et al. (2015; 330 ± 10 µg/g Al₂O₃, 50 ± 10 µg/g P₂O₅, 152 ± 8 µg/g Cr₂O₃,
uncertainties in 2σ). Glasses were analyzed at KU Leuven using a beam defocused to 10–30
µm diameter and operating at 15 kV and 10 nA. Quench textures were observed in the
highest temperature experiments (>1500 °C), which causes MgO depletion in the interstitial
melt. For those experiments, melt compositions were measured on mixtures of melt and
quenched crystals, increasing the 1σ standard deviations for melt MgO and FeO contents to
1.0–4.7 wt.% and 0.4–1.3 wt.%, respectively. Glass secondary standards NMNH 111312-44,
VG2, and GOR 132-G (Jochum et al., 2006) were analyzed at regular intervals, and the
results were again within 98% accuracy of the reference values (see supplementary dataset).
X-ray compositional maps were acquired following the procedure of Shea et al. (2019), but using a 20 kV and 300 nA electron beam.

At the University of Cambridge, we followed a similar procedure using a focused beam operating at 15 kV and 100 nA beam to measure Al, Cr, and P in olivine. Detection limits were 28 µg/g for Al$_2$O$_3$, 117 µg/g for P$_2$O$_5$, and 87 µg/g for Cr$_2$O$_3$. We used the MongOl sh11-2 olivine ($n$ = 8) as a secondary standard and obtained $487 \pm 10$ µg/g Al$_2$O$_3$, $228 \pm 40$ µg/g P$_2$O$_5$ ($1\sigma$), and $209 \pm 20$ µg/g Cr$_2$O$_3$ ($1\sigma$), again consistent with the reference values ($463 \pm 18$ µg/g Al$_2$O$_3$, $152 \pm 8$ µg/g P$_2$O$_5$, $182 \pm 6$ µg/g Cr$_2$O$_3$, uncertainties in $2\sigma$; Batanova et al., 2019).

**Interlaboratory experimental and analytical uncertainties**

To calibrate our extended OSAT with as many relevant experiments as possible, we chose to include the experimental results of Wan et al. (2008) and Coogan et al. (2014), which we could not reanalyze for this study. It is therefore important to critically assess whether we can reproduce their phase equilibria observations and reproduce their chemical measurements, including minor elements such as Al in olivine. Therefore, we reproduced two experiments from Wan et al. (2008): w83 (~QFM−1.6, 1250°C), reproduced here in experiment NAB89U, and w71 (~QFM−1.6, 1300°C), reproduced here in experiment NAB90U. We chose these two relatively low-temperature experiments because it is more challenging to attain equilibrium under those conditions.

Experiments NAB89U and NAB90U produced phase equilibria (liquid, olivine, and spinel) and compositions similar to those reported by Wan et al. (2008). Importantly, $\ln(K_{D_{Al}})$ values were almost identical: $-6.16 \pm 0.04$ ($1\sigma$, uncertainty calculated from error propagation with a Monte Carlo algorithm) in NAB89U vs. $-6.14 \pm 0.05$ ($1\sigma$) in w83, and $-5.80 \pm 0.03$ ($1\sigma$) in NAB90U vs. $-5.90 \pm 0.05$ ($1\sigma$) in w71. Spinel compositions were also identical: Fe$^{3+}$/Fe$^{2+}$ in spinel was 0.16 ± 0.05 ($1\sigma$) in NAB89-U vs. 0.17 ± 0.09 ($1\sigma$) in w83, and 0.21 ± 0.03 ($1\sigma$) in NAB90-U vs. 0.21 ± 0.07 ($1\sigma$) in w71. This suggests that
interlaboratory analytical and experimental uncertainties are minor, and further that we can include the published experimental results from Wan et al. (2008) and Coogan et al. (2014) in our new OSAT calibration database. This also suggests that our experiments attained equilibrium (see next subsection).

Attainment of equilibrium

The attainment of equilibrium between melt, olivine, and spinel, especially for slowly diffusing minor elements, is critical to our study. The considerably long durations of our experimental runs (7–120 h), most much longer than in high-temperature experiments in the previous calibration (Wan et al., 2008) or other high-temperature experimental studies (e.g., Tuff et al., 2005; Matzen et al., 2011; Krasheninnikov et al., 2017; Koshlyakova et al., 2022), were chosen to ensure that equilibrium was attained. We note that a few high-temperature experiments (>1500 °C, Table 2) lasted only a few hours (≥7 h), but that the fast elemental diffusion at such high temperatures and the low crystallinity of those experiments suggest that equilibrium was attained even in those shorter runs.

We also evaluated the attainment of equilibrium based on compositional and textural characteristics. Olivine and spinel were generally euhedral, suggesting they formed at equilibrium. The experimental charges also show homogeneous backscattered electron intensities for melts and minerals (Fig. 3). Fe-Mg partition coefficients between olivine and melt ($K_{\text{Ol-melt}}^{\text{Fe-Mg}}$) range from 0.26 to 0.34 (see in the Supplementary data), consistent with previous experiments (e.g., Roeder & Emslie, 1970; Toplis & Carroll, 1995) and thermodynamic models (e.g., Toplis, 2005; Blundy et al., 2020). In general, $K_{\text{Ol-melt}}^{\text{Fe-Mg}}$ is positively correlated with the melt SiO$_2$ content, which supports the impact of melt silica activity on Fe-Mg exchange between olivine and melt (Gee & Sack, 1988; Toplis, 2005; Koshlyakova et al., 2022). In particular, experiments using silica-undersaturated and alkali-rich compositions have $K_{\text{Ol-melt}}^{\text{Fe-Mg}} < 0.27$ (0.22–0.26), consistent with experimental results on similar compositions (Gee & Sack, 1988; Molendijk et al., 2023b). In contrast, high-
temperature experiments with quench textures occasionally have $K_{\text{Fe-Mg}}^{\text{OL-melt}} = 0.34–0.35,$ beyond the range $0.30 \pm 0.03$; such high values may have resulted from analytical heterogeneity due to the glass analyses involving mixtures of quench crystals and interstitial melt (Mitchell & Grove, 2015).

Trace element (Al, P, Cr) partitioning in olivine may be affected due to the formation of a boundary layer enrichment during initially rapid crystal growth (e.g., Shea et al., 2019; Lang et al., 2022). This means that the above indicators of equilibrium (Fe-Mg exchange and textural constraints) may not reflect trace element equilibration. Therefore, we measured rim-to-core profiles comprising 6–7 spot analyses (ca. 5–6 µm spacing) per profile in one olivine crystal from each experiment to check the homogeneity of their trace element distributions. The profiles generally show very small deviations (~50 µg/g, 1σ) for Al$_2$O$_3$ and even less variability for other trace elements (see Supplementary material, Section 2). We also acquired EPMA X-ray compositional maps of experiments treated with thermal oscillation and experiments that were run at more than 200 °C below their liquidus. Chemical maps do not show any apparent P, Al, or Cr zoning (see Supplementary material, Section 2). Relict phases were occasionally observed in the cores of olivine crystals in experiments performed on compositions with high liquidus temperatures. The uniform compositions of the crystal rims, however, suggest that the early disequilibrium did not preclude the attainment of equilibrium between the outer part of the crystals and the adjacent melt. Experiments conducted at more than 300 °C below the liquidus typically produced small olivine crystals (~10 µm in length) with dendritic P and Al zoning patterns. These experiments also produce olivine populations with distinct high and low Al$_2$O$_3$ concentrations; we used the low-concentration population in this study because it may represent relaxation and equilibration during equilibrium crystal growth (Shea et al., 2019).

**RESULTS**

**Experimental results**
All reported experiments contain melt, olivine, and spinel. Four experiments performed at more than 300 °C below the liquidus also contain clinopyroxene. Compositions of the phases are given in supplementary dataset (Table S1).

*Melt*

Melt compositions are plotted as functions of MgO (in wt.%) and temperature in Figs. 4 and S3, respectively. The experimental melts span a wide range of compositions, with 7.0–31.5 wt.% MgO, 38.9–54.6 wt.% SiO₂, 6.0–12.8 wt.% FeO, 3.9–17.3 wt.% Al₂O₃, 0.0–0.9 wt.% Cr₂O₃, and 0.1–4.6 wt.% Na₂O + K₂O. Melt Al₂O₃ contents are anticorrelated with melt MgO content, whereas melt Cr₂O₃ contents are positively correlated with melt MgO content and temperature, consistent with the higher solubility of Cr₂O₃ in the melt at higher temperature (Borisova et al., 2020).

*Olivine*

Olivine crystals are euhedral and ranged in size from ~10 µm to >100 µm (Fig. 3). Olivine Fo contents range from Fo₈₄ to Fo₉₆ (Fig. 2). Minor and trace elements span a wide compositional range: 0.1–1.3 wt.% CaO, 362–2118 µg/g Al₂O₃, 411–3706 µg/g Cr₂O₃, and below the detection limit to 511 µg/g P₂O₅. Al₂O₃ and Cr₂O₃ contents are weakly correlated with Fo content (Fig. 2). Olivine Cr₂O₃ content is positively correlated with melt Cr₂O₃ content (Fig. S4b). A broad positive correlation is also observed between olivine and melt CaO contents (Fig. S4c), and the highest olivine CaO contents occur in experiments on SiO₂-undersaturated compositions, consistent with previous findings (Gee & Sack, 1988; Molendijk et al., 2023b). No correlation is apparent between olivine and melt Al₂O₃ or P₂O₅ contents (Fig. S4a, d, respectively).

*Spinel*

Spinel crystals range in size from ~1 µm to ~40 µm (Fig. 3). Spinel compositions are shown in Figs. 1 and in Fig. S5 as functions of melt composition. Spinel Cr# ranges from 0.40 to
0.88, Mg# [= molar Mg/(Mg + Fe\textsuperscript{2+})] from 0.59 to 0.91, Fe\textsuperscript{3+}/Fe\textsuperscript{2+} from 0.08 to 2.48, the ratio of Fe\textsuperscript{3+} to the sum of trivalent cations, Fe\textsuperscript{3+}/(Fe\textsuperscript{3+} + Cr + Al), from 0.02 to 0.22, and TiO\textsubscript{2} content from 0.5 to 5.5 wt.%. Experiments NAB01-F and NAB02-F, performed on SiO\textsubscript{2}-undersaturated and alkali-rich compositions, show the highest spinel TiO\textsubscript{2} contents (>5 wt.%), which correspond to the highest melt TiO\textsubscript{2} contents (>3 wt.%; Fig. S5). Spinel FeO and Cr\textsubscript{2}O\textsubscript{3} contents are only weakly correlated with melt FeO and Cr\textsubscript{2}O\textsubscript{3} contents (Fig. S5).

A more significant correlation is observed between spinel and melt Al\textsubscript{2}O\textsubscript{3} contents (Fig. S5), consistent with previous observations (Borisova et al., 2020; Sack & Ghiorso, 1991b; Ariskin & Nikolaev, 1996; Poustovetov & Roeder, 2001).

**Summary of remeasured prior experiments**

Melt compositions in the reanalyzed published experiments and calibrations contain 8.4–25.0 wt.% MgO, 42.0–55.6 wt.% SiO\textsubscript{2}, 0–17.5 wt.% FeO, 8.3–21.6 wt.% Al\textsubscript{2}O\textsubscript{3}, and 0–0.54 wt.% Cr\textsubscript{2}O\textsubscript{3}. Olivine has Fo\textsubscript{95–100} and contain 0–1.4 wt.% CaO, 183–1,686 µg/g Al\textsubscript{2}O\textsubscript{3}, 0–2,990 µg/g Cr\textsubscript{2}O\textsubscript{3}, and 0–2,338 µg/g P\textsubscript{2}O\textsubscript{5}. Spinel has Cr# = 0–0.84, Mg# = 0.49–1, Fe\textsuperscript{3+}/Fe\textsuperscript{2+} = 0.08–0.71, Fe\textsuperscript{3+}/(Fe\textsuperscript{3+} + Cr + Al) = 0–0.17, and contains 0–1.38 wt.% TiO\textsubscript{2}.

**Evaluating the model of Coogan et al. (2014)**

We assessed the OSAT of Coogan et al. (2014), which incorporates the earlier experiments of Wan et al. (2008), by applying it to our updated experimental dataset (Fig. 5a). The results show that the model of Coogan et al. (2014) significantly overestimated temperatures, with a maximum deviation (ΔT [°C] = predicted temperature – measured temperature) of 197 °C, an average deviation of 44.7 ± 46.6 °C (1σ), and a root-mean-square error (RMSE) of ±64.3 °C. These errors further demonstrate the need for a new calibration covering a broader temperature range and accounting for additional factors affecting olivine–spinel Al exchange, including spinel composition, fO\textsubscript{2}, pressure, and melt H\textsubscript{2}O content.

**REGRESSION AND THERMODYNAMIC MODELS**
To improve the reliability of the OSAT for natural samples, we here develop a thermodynamic formalism for Al exchange between olivine and spinel and two empirical regression models. We applied a Monte Carlo cross-validation (MCCV; e.g., Xu & Liang, 2001) algorithm to estimate the uncertainties of regression models.

**Regression strategy and models**

In our regression models, we first split the experimental dataset into a training dataset (n = 95) used for regression and a test dataset including 21 experiments not included in the calibration to test the accuracy of the regression (details of training and test dataset are given in the supplementary dataset, Tables S2, 3). The standard error estimation (SEE) on the training dataset and RMSE on the test dataset were calculated accordingly. Then, to assess model uncertainties and eliminate sampling bias, we used a MCCV algorithm. In each calculation, we randomly divided the experimental dataset into a 5:1 ratio of training and test datasets, and then performed 10-fold cross-validation on the training dataset to estimate SEE_{MCCV} on the training dataset and then RMSE_{MCCV} on the test dataset, which is also the recommended error on the thermometric model. Detailed information on the training and test datasets, as well as the MCCV results, are given in the Supplementary data (Tables S2 and S3; Section 3).

**Thermodynamic formalism**

To better understand the Al exchange between olivine and spinel, we here follow a thermodynamic formalism. Coogan et al. (2014) argued that the most plausible mechanism for incorporating Al into olivine in a Cr-spinel-bearing system is:

\[
(MgAl_{TET})Al_{OCT}^{\text{spl}}O_4 = (MgAl_{TET})Al_{OCT}^{\text{ol}}O_4
\]

(2)

which we follow in our thermodynamic framework (see details in Appendix A). For simplicity, in the following we assume thermodynamic ideality in the incorporation of Al in olivine, i.e., the excess energy caused from site ordering of Al is negligible. This assumption is based on the following considerations: 1) trace element incorporation is usually...
considered as a dilution so the internal energy can be calculated as a simplified pure component (Ganguly, 2008); 2) to the best of the authors’ knowledge, there are currently no established models to accurately differentiate or calculate the coordination of different Al species in olivine and no calibration for the interaction parameters between sites. Al may also coordinate with a vacant site (Jollands et al., 2018; Shea et al., 2019; Lang et al., 2022); 3) established thermodynamic models for other trace elements in olivine (e.g., Ni) with similar assumption of ideality have shown a minimal influence on the internal energy (e.g., Matzen et al., 2013). We therefore believe our thermodynamic framework remains valid with this assumption. Al substitution in spinel is however more complicated due to its high Al abundance, site ordering, and the known non-ideal mixing behavior of spinel components.

We apply the thermodynamic framework of Sack (1982) and Sack & Ghiorso (1991a, 1991b), and express the internal energy of spinel by five independent compositional variables \( X \) (see details in Appendix A; Sack & Ghiorso, 1991b).

After organizing the thermodynamic framework, olivine–spinel Al exchange can be described as (see Appendix A):

\[
\ln \left( \frac{X_{Al_2O_3}}{X_{Mg^{2+}}^{\text{TET}} \cdot X_{Al^{3+}}^{\text{OCT}}} \right) + b = \frac{\varphi^{\text{Spl}}}{c_0 \times T}
\]  

(3)

which can be rearranged as:

\[
T = \frac{\varphi^{\text{Spl}}}{c_0 \times \left( \ln \left( \frac{X_{Al_2O_3}}{X_{Mg^{2+}}^{\text{TET}} \cdot X_{Al^{3+}}^{\text{OCT}}} \right) + b \right)}
\]  

(4)

where:
\[ \varphi_{\text{Spl}} = c_1X_2 + c_2X_2^2 + c_3X_2^3 \]
\[ + c_4(1 - X_2)(1 + X_4 - X_2) \]
\[ + c_5(1 - X_2)(X_3) + c_6(1 - X_2)(X_4) + c_7(1 - X_2)(X_5) \]
\[ + c_8X_3(X_3 + X_4 + X_5) \]
\[ + c_9X_4(X_3 + X_4 + X_5) \]
\[ + c_{10}X_5(X_3 + X_4 + X_5) \]
\[ - c_{11}(X_3)(X_4) - c_{12}(X_3)(X_5) - c_{13}(X_4)(X_5) + c_{14} \]

Here, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( X_{\text{Mg}^{2+}}^{\text{TET}} \) is the mole fraction of Mg in the spinel tetrahedral site, \( X_{\text{Al}^{3+}}^{\text{OCT}} \) is the mole fraction of Al in the spinel octahedral site, and \( T \) is temperature in Kelvin. In Eq. 4, \( X_i \) are independent compositional variables used to describe spinel composition (Si, Ti, Fe, Mg, Cr, Al, and Mn; Sack & Ghiorso, 1991b); they are listed in Table A1. Other parameters (\( b, c_0 - c_{14} \)) are regression coefficients fitted to the experimental dataset through a polynomial curve-fitting approach. In Eq. 3, because the term \( X_{\text{Mg}^{2+}}^{\text{TET}}X_{\text{Al}^{3+}}^{\text{OCT}} \) is proportional to spinel Al\(_2\)O\(_3\) content, we can simplify the equation by replacing the \( \ln \left( \frac{X_{\text{Al}^{3+}}^{\text{OCT}}}{X_{\text{Mg}^{2+}}^{\text{TET}}} \right) \) with \( \ln K_{\text{DAl}} \). The final regression on the training dataset is:

\[ T (K) = \frac{10,000 \times \varphi_{\text{Spl}}}{-0.168 \times (\ln K_{\text{DAl}} + 0.654)} \] (5)

where
\[ \varphi^{Spl} = 1.487X_2 - 0.593X_2^2 - 0.630X_2^3 \]
\[ + 0.390(1 - X_2)(1 + X_4 - X_2) \]
\[ + 0.009(1 - X_2)(X_3) - 2.492(1 - X_2)(X_4) + 0.065(1 - X_2)(X_3) \]
\[ - 0.031X_3(X_3 + X_4 + X_2) \]
\[ - 4.141X_4(X_3 + X_4 + X_2) \]
\[ - 0.428X_5(X_3 + X_4 + X_2) \]
\[ + 4.637(X_3)(X_4) + 0.054(X_3)(X_3) + 10.803(X_4)(X_3) + 2.744 \]

The regression result for Eq. 5 is shown in Fig. 5b and Table A2; the SEE and \( r^2 \) values for the training dataset are \( \pm 20.2 \) °C and 0.97, respectively, RMSE on the test dataset is 29.0 °C, and the \( p \)-value of the fit, where a no correlation alternative null hypothesis being tested against, is 1.11e−16. The MCCV result shows that the median \( \text{SEE}_{\text{MCCV}} \) and \( \text{r}^2_{\text{MCCV}} \) values for the training dataset are 20.2 °C and 0.97, respectively, and the median RMSE\( _{\text{MCCV}} \) value for the test dataset is ~23.9 °C.

**Empirical expressions**

By using our expanded experimental dataset, we first recalibrated an empirical model similar to the regression format of Coogan et al. (2014) but with unweighted multiple linear regression (see supplementary material for a comparison with a weighted regression method, Section 4):

\[ T (K) = \frac{10,000}{0.740(0.317) + 1.144(0.136)\text{Cr#} - 0.865(0.046)\ln\text{K}_{\text{DAI}}} \]

The regression result of this new thermometer is shown in Fig. 5c and Table A2; the SEE and \( r^2 \) values for the training dataset are \( \pm 44.8 \) °C and 0.83, respectively, RMSE on the test dataset is 34.4 °C, and the \( p \)-value of the fit is 2.88e−36. The MCCV result shows that the
median SEE_{MCCV} and r^2_{MCCV} values for the training dataset are 42.1 °C and 0.92, respectively, and the median RMSE_{MCCV} value for the test dataset is 43.3 °C.

Considering that Cr may have a coupled substitution with Al when entering olivine to form a (MgAl)CrO₂ structure (Hanson & Jones, 1998; Milman-Barris et al., 2008; Jollands et al., 2018), we explored whether the Cr exchange between olivine and spinel \((K_{D_{Cr}})\) would improve the empirical thermometric equation:

\[
T (K) = \frac{10,000}{0.049(0.241) - 0.657(0.040)\ln K_{D_{Al}} - 0.389(0.041)\ln K_{D_{Cr}} + 0.543(0.121)Cr# - 0.389(0.041)ln K_{D_{Cr}} + 0.543(0.121)Cr#}.
\]

Cr-free experiments were excluded during regression (Fig. 5d and Table A2). The SEE and \(r^2\) values for the training dataset are ±31.7 °C and 0.91, respectively, RMSE on the test dataset is 39.1 °C, and the \(p\)-value of the fit is 3.79e−47. The MCCV result shows that the SEE_{MCCV} and \(r^2_{MCCV}\) values for the training dataset are 35.8 °C and 0.94, respectively, and the median RMSE_{MCCV} value for the test dataset is 34.2 °C. We are aware that Eq. 8 includes all the regression variables from Eq. 7. To determine if the improved performance of Eq. 8 is due to more regression terms or statistical significance, we performed a F-test (see Appendix B for further details on the F-test model). The results of the F-test show an F score of 88.4 and a \(p\)-value of 5.4e−15, which is statistically significant \((p < 0.05)\) at 95% confidence. Therefore, the incorporation of Cr exchange as \(K_{D_{Cr}}\) into Eq. 8 produced a statistically superior fit compared to Eq. 7.

Factors affecting the performance of the models

Dependence of the models on spinel composition and olivine–spinel Cr exchange

Previous studies have noted limitations of the original thermometric calibration due to the restricted range of Cr# values used in the calibration (e.g., Heinonen et al., 2015; Xu & Liu, 2016; Trela et al., 2017). In Fig. 6, we compare spinel Cr# with the \(\Delta T\) calculated using our three new models and that of Coogan et al. (2014). There is no apparent
correlation between $\Delta T$ and spinel Cr# calculated using Eqs. 5, 7, and 8, whereas the model of Coogan et al. (2014) shows a moderate correlation ($r^2 = 0.41$). Spinel Fe$^{3+}$/Fe$^{2+}$ has a moderate impact on $\Delta T$ using the model of Coogan et al. ($r^2 = 0.47$), a limited impact using Eq. 7 ($r^2 = 0.24$), and negligible impacts on Eqs. 5 and 8 (Fig. S6). The effect of spinel TiO$_2$ content was negligible for all models (Fig. S7).

Spinel Mg# and Fe$^{3+}/($Fe$^{3+}$ + Cr + Al) affect the performance of Eq. 7 ($r^2 = 0.28$ and 0.66, respectively) and the model of Coogan et al. (2014; $r^2 = 0.13$ and 0.76, respectively), but have less effect on Eqs. 5 and 8 (Figs. 7, 8). Similarly, $K_{DCr}$ has a moderate effect on Eq. 7 and the model of Coogan et al. (2014), but not on Eqs. 5 and 8, suggesting that $K_{DCr}$ is indeed an important parameter for improving the accuracy of the empirical models (Fig. S8).

The thermodynamic model Eq. 5 including the spinel composition, may also mimic the effect of $K_{DCr}$. The correlation of $\Delta T$ with the spinel compositional parameters and $K_{DCr}$ indicates that using only spinel Cr# and $K_{DAi}$ is not sufficient to accurately predict temperature in all circumstances, particularly when spinel has a low Mg# or high Fe$^{3+}/($Fe$^{3+}$ + Cr + Al) as is often observed in natural LIP spinels (Fig. 1). In such cases, the model of Coogan et al. (2014) and Eq. 7 may have larger uncertainties and may strongly overestimate temperature.

**Dependence of the thermometers on $fO_2$, $H_2O$, and pressure**

$fO_2$ does not strongly affect the accuracy of the temperature calibrations of any of the models, but a weak negative correlation was observed for Eq. 8 (Fig. S9). We further tested the effect of melt water content and pressure with our reanalyzed experimental dataset (three hydrous experiments with 3.7–7.4 wt.% $H_2O$ in the experimental glass; seven dry high-pressure experiments at 500–1350 MPa). Although water is known to have a profound effect on the olivine liquidus (Médard & Grove, 2008), this appears to be of negligible consequence on the accuracy of any of the thermometric models (Fig. S10). A potential explanation of this is that the effect of water is compensated by changes to the olivine and
spinel compositions. Pressure, however, shows a moderate correlation in all models, although the results are within the uncertainty of each model (Fig. 9). It is unclear whether this correlation is due to sample bias related to the sparse high pressure experiments, or if pressure may affect on the molar volume of spinel and site occupancy (Hamecher et al., 2013). Nonetheless, D’Souza et al. (2020) proposed that pressure has no effect on the model of Coogan et al. (2014).

DISCUSSION

In this section, we discuss the limits of the thermometric models and their sensitivities to subsolidus re-equilibration. We then establish a protocol for selecting the appropriate model for applications to natural samples. Finally, we apply our models to constrain mantle melting conditions and lithological components in a range of geological settings and use thermodynamic calculations to assess potential re-equilibration in natural olivine-spinel pairs.

Concerns, limits, and sensitivities of the models

Our thermodynamic model (Eq. 5) is accurate but involves the exchange of Fe and Mg, which diffuse rapidly in spinel (Vogt et al., 2015). This means that temperature estimates in natural systems could be affected by low-temperature re-equilibration due to olivine-spinel subsolidus Fe-Mg exchange during cooling. We note that the system itself doesn’t have be subsolidus, i.e., the olivine-spinel pair could crystallize at high temperature but experienced a Fe-Mg reset after being carried along in an evolved melt, or set in a partially molten mush before re-entrainment and eruption. The empirical model Eq. 8 does not involve Fe and Mg but incorporates Cr exchange between olivine and spinel. Subsolidus Cr re-equilibration in olivine, potentially caused by Cr reset between the carrier liquid, could also result in Eq. 8 potentially yielding anomalously low temperature estimates, we however note that the diffusivity of Cr in olivine is poorly constrained and may vary with fO2 and Cr concentrations in olivine (Ito & Ganguly 2006; Jollands et al., 2018). In contrast, the
Empirical models of Eq. 7 and Coogan et al. (2014) only involve slow diffusive elements in spinel and olivine (Vogt et al., 2015; Spandler & O’Neill, 2010). Therefore they are not impacted by low-temperature re-equilibration, but tend to overestimate temperature when spinel has low Mg# or high Fe\(^{3+}/(Fe^{3+} + Al^{3+} + Cr^{3+})\) (Figs. 7 and 8).

To quantitively investigate the sensitivities of Eq. 5 to Fe-Mg re-equilibration and Eq. 8 to Cr re-equilibration in olivine, we performed two numerical simulations: 1) we modeled Fe-Mg re-equilibration in a stoichiometric Cr-spinel with the formula (Mg, Fe\(^{2+}\))(Al, Cr, Fe\(^{3+}\))\(_2\)O\(_4\), and 2) we progressively added Cr\(_2\)O\(_3\) to olivine to model Cr re-equilibration. In the Fe-Mg re-equilibration model, Al diffusivity in olivine is slow (Spandler & O’Neill, 2010), so we assumed that spinel exchanges only Fe\(^{2+}\) and Mg with olivine and, therefore, the spinel Cr# remains constant at a fixed \(f_{O_2}\), which is consistent with natural observations (Guo et al., 2009; Hu et al., 2022). Spinel Mg# were set to values vary from 0.3 to 1 with an increment of 0.01 at each spinel Cr#, which we varied from 0.4 to 0.9 with the same increment to cover the whole range observed in nature. We held spinel Fe\(^{3+}/Fe^{2+}\) constant at 0.5, corresponding to the median of natural spinel compositions, Olivine Al\(_2\)O\(_3\) content was set to 500 µg/g. Temperatures were then calculated using Eq. 5.

Because the mechanism of Cr re-equilibration in olivine has not been well determined (Milman-Barris et al., 2008; Shea et al., 2019; Lang et al., 2022), we modeled two scenarios. In the first scenario we assumed a decoupled substitution between Cr and Al, i.e., the Cr content changes but the Al content remains constant, consistent with our experimental observation. In the second scenario we assumed coupled substitution of Cr and Al with a molar ratio of 1, similar to the observations of Milman-Barris et al. (2008) in a fast growth regime. Both scenarios olivine Cr\(_2\)O\(_3\) start from 200 to 1500 µg/g. Olivine Al\(_2\)O\(_3\) content was set to 500 µg/g in the first scenario and range from 134 to 1006 µg/g in the second scenario, holding molar Cr/Al = 1. Temperatures were then calculated using Eq. 8.

Our model results are shown in Fig. 10. Decreasing spinel Mg# and decreasing olivine Cr\(_2\)O\(_3\) content (both decoupled and coupled substitutions) return lower temperatures when using Eqs. 5 and 8, respectively. For a given degree of Fe-Mg or Cr re-equilibration,
the decrease in apparent temperature after a given degree of re-equilibration is greater for spinel with higher Cr#, whereas Eq. 5 tends to underestimate temperature for spinel with lower Mg#.

Selecting the appropriate model for application to natural samples

The reliability of the empirical model in Eq. 7 is limited to a specific range of spinel compositions and has larger errors on the temperature estimation compared to the thermodynamic model Eq. 5 and the empirical model Eq. 8. In contrast, Eqs. 5 and 8 are more precise but may be affected by chemical re-equilibration, as discussed above. Given the greater uncertainties in the empirical expressions (Eqs. 7 and 8), for a fully equilibrated, primitive olivine-spinel pair, we expect them to return temperatures scattering above and below that returned by the thermodynamic expression (Eq. 5). In turn, we expect Eq. 5 to return lower temperatures than the Eqs. 7 and 8 if diffusive re-equilibration occurs.

Therefore, we consider that Eqs. 7 or 8 should be used when Eq. 5 has a more than 50% chance of underestimating the true temperature (i.e., when the mean temperatures estimated using Eq. 5 and either Eq. 7 or 8 differ sufficiently that a \( p \)-value test on the distributions having the same mean returns \( p < 0.5 \)). Model selection is then determined by the likelihood that Eq. 5 yields an underestimation. If the temperature estimated using Eq. 5 is higher than that estimated using Eq. 7 or 8, the result from the thermodynamic expression should be chosen. If not, a statistical \( Z \)-test is introduced to decide whether to choose the thermodynamic expression or empirical expression (e.g., Snedecor & Cochran, 1989):

\[
Z = \frac{|T_i - T_j|}{\sqrt{\sigma_{X_i}^2 + \sigma_{X_j}^2}}
\]

(9)

where \( \sigma_{X_i} \) and \( \sigma_{X_j} \) are the RMSEs of the two models being compared (Eqs. 5 vs. Eq. 7 and/or Eq. 8) and \( T_i \) and \( T_j \) are the respective temperature estimates. If \( Z > 1.35 \), there is a 50% chance that the two temperatures differ by a value larger than that attributed to their combined uncertainties, and that Eqs. 7 or 8 return a higher temperature which is closer to...
the true value. If both Eqs. 7 and 8 are compared with Eq. 5, the pair that yields with the higher Z score should be chosen to obtain a larger probability that the temperature estimates are different from each other. The Z value of 1.35 represents a width of 1.35 standard deviations, which is required for 50% of normal distributions with standard deviations given by each model to lie between the mean \(-\frac{1}{2}|T_i - T_j|\) and the mean \(+\frac{1}{2}|T_i - T_j|\) \((i \text{ and } j\) represent each thermometric model); i.e., when \(Z < 1.35\), 50% of the estimated temperatures should be more similar if they are measuring the same temperature. A python script and an Excel spreadsheet to perform all relevant calculations can be found at

https://github.com/eazzzon/olpthermo). Table 3 lists all scenarios for selecting the appropriate model.

To illustrate the use of the protocol outlined above, we provide two geological examples. In the first example, we take an ocean island basalt from Pico Island (Azores, Portugal) containing a Fo83 olivine crystal, which has two spinel inclusions (van Gerve et al., 2021). X-ray chemical maps show no Al, Cr, or P zoning in the olivine and stable Al concentration profiles were acquired from the olivine till approaching the spinel-olivine boundaries (see in the Supplementary material, Section 5). The spinel inclusions have Mg# \(\approx 0.51\) and \(\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al}) \approx 0.17\). The temperatures calculated using Eqs. 5, 7, and 8 are 1091 ± 23 °C, 1171 ± 43 °C, and 1184 ± 34 °C, respectively, with errors propagated from both analytical and thermometric uncertainties. Because the thermodynamic expression returns a lower temperature than the empirical expressions, we applied the Z-test model. The results show \(Z = 1.62\) between Eqs. 5, and 7 and \(Z = 0.76\) between Eqs. 5 and 8. Because of the larger Z-score, the result from Eq. 7 is statistically more robust, which is consistent with the temperature estimated from a melt inclusion within the same crystal using liquid thermometry (~1194 ± 46 °C; van Gerve et al., 2021) and previous experimental studies (e.g., Toplis & Carroll, 1995; Grove et al., 1992). According to these results, Eq. 5 significantly underestimates the temperature by ~80 °C.
For our second example, we take four published analyses of a MORB sample (A25-D20-8) from Coogan et al. (2014), which contains an Fo91 olivine and a spinel with Mg# = 0.81. Eqs. 5, 7, and 8 return temperatures of 1265 ± 23 °C, 1235 ± 43 °C, and 1198 ± 34 °C, respectively. Here, the thermodynamic expression is chosen because it returns a higher temperature than the empirical expressions, hence the recommended temperature is 1265 ± 23 °C.

Application of the extended OSAT to natural basalts

Here, we apply our new thermometers to basalts from various settings: the Siqueiros MOR, Iceland and Skye in the North Atlantic igneous province (NAIP), and the Emeishan, Etendeka, and Caribbean LIPs. The results of different models are shown in Table 4 and Fig. 11. In each case, and for each analysis, we chose results according to the Z-test protocol described above. For comparison, all temperature estimates from each model are shown in Fig. S11. Given the similarity of spinel compositions from MORB, Iceland and Skye with those from experiments used in the previous calibration of Coogan et al. (2014) and Wan et al. (2008), the new temperature estimates from our models are comparable or fall within mutual uncertainties. Intra-plate igneous provinces generally have higher Fe³⁺/(Fe³⁺ + Cr + Al) and lower Mg# (Fig. 1), therefore the model of Coogan et al. (2014) significantly overestimate the temperature by 30–100 °C (median) and 60–120 °C at the maximum.

MORB (Siqueiros)

MORB lavas erupted at Siqueiros are generated by near-adiabatic upwelling of the ambient upper mantle (e.g., Gregg et al., 2009). Siqueiros spinel has Cr# = 0.24–0.44, and potentially experienced less Fe-Mg subsolidus re-equilibration, with generally high Mg# values (0.70–0.81) and Fe³⁺/(Fe³⁺ + Cr + Al) values (0.03–0.07). Olivine contains 335–827 µg/g Al₂O₃ and 508–2,750 µg/g Cr₂O₃. Coogan et al. (2014) and Matthews et al. (2021) calculated the co-crystallization temperature of Siqueiros olivine and spinel to be 1230±59 °C (expressed
as median $+\frac{95^{th} \text{ percentile} - \text{median}}{\text{median} - 5^{th} \text{ percentile}}$, being consistent with the description of distribution used in Matthews et al. [2021]). Our new estimated temperatures are $1258^{+37}_{-76} \degree C$. These new estimates generally agree with the previous studies, which we attribute to the spinel composition in Siqueiros lavas being comparable to those used in the calibration experiments of Coogan et al. (2014) and Wan et al. (2008).

Our new estimated temperatures are $1258^{+76}_{-37} \degree C$. The new estimates generally agree with the previous studies, which we attribute to the spinel composition in Siqueiros lavas being comparable to those used in the calibration experiments of Coogan et al. (2014) and Wan et al. (2008).

NAIP (Iceland and Skye)

Iceland and Skye are within the NAIP, which is accepted as having a mantle-plume origin.

Spinel in Iceland has Cr# 0.24–0.60, Mg# 0.54–0.79 and $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al})$ 0.0–0.13.

Olivine ins Iceland contain $\text{Al}_2\text{O}_3$ 396–1,020 µg/g and $\text{Cr}_2\text{O}_3$ 345–2,686 µg/g. Spinel in Skye is slightly more primitive, containing Cr# 0.41–0.56, Mg# 0.70–0.77 and $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al})$ 0.0–0.06. Olivine in Skye has more $\text{Al}_2\text{O}_3$ (794–1,519 µg/g) and less $\text{Cr}_2\text{O}_3$ (1,030–1,890 µg/g). Previous crystallization temperature estimates (Spice et al., 2016; Matthews et al., 2016) using the model of Coogan et al. (2014) gave crystallization temperatures of $1283^{+84}_{-66} \degree C$ for Iceland and $1409^{+60}_{-65} \degree C$ for Skye. Our new results are $1275^{+52}_{-100} \degree C$ for Iceland and $1388^{+41}_{-53} \degree C$ for Skye, which are similar on the median values but ~ 40 °C lower for the high temperature populations (on the 95th).

Emeishan large igneous province

The ~260 Ma Emeishan LIP in southwest China is considered to be of mantle-plume origin (Chung & Jahn, 1995; Xu et al., 2001; Xiao et al., 2004). Emeishan spinel compositions are much more varied compared to MORB, with Cr# = 0.42–0.72, Mg# = 0.48–0.72, and $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al})$ = 0.04–0.15. Olivine contains 340–990 µg/g $\text{Al}_2\text{O}_3$ and 165–1,420 µg/g $\text{Cr}_2\text{O}_3$. Previous temperature estimates give a crystallization temperature of $1271^{+108}_{-55} \degree C$ (Xu & Liu, 2016). Our new estimate is $1224^{+109}_{-54} \degree C$, with both the median and 95th value being ~ 47 °C cooler. Here, the compositional deviation of the natural olivine
and spinel from those used in the previous calibration results in the overestimated crystallization temperatures.

**Etendeka large igneous province**

The Etendeka LIP is the southern part of Paraná-Etendeka LIP, mainly outcropping in Namibia and southern Angola (Thompson et al., 2001; Gibson, 2002). The high crystallization temperatures and high \(^{3}\)He/\(^{4}\)He values (>26 \(R_A\); reported relative to that of the present-day atmosphere) of the lavas suggest a mantle plume origin (Strouk et al., 2017).

Etendeka spinel compositions are quite variable, with Cr\# = 0.40–0.70, Mg\# = 0.24–0.76, and Fe\(^{3+}\)/(Fe\(^{3+}\) + Al\(^{3+}\) + Cr\(^{3+}\)) = 0.04–0.31. Olivine contains 300–1,200 \(\mu g/g\) Al\(_2\)O\(_3\) and 200–2,200 \(\mu g/g\) Cr\(_2\)O\(_3\). Jennings et al. (2019) calculated the olivine crystallization temperature using the model of Coogan et al. (2014) to be 1323\(^\pm151\) °C. Our new results are 1307\(^\pm110\) °C, which are similar at the median value but 57 °C lower for the high temperature populations (on the 95\(^{th}\)).

**Caribbean large igneous province (Tortugal suite)**

The Tortugal suite in Costa Rica is considered to be the product of the initial melting of the Galapagos plume in the Caribbean large igneous province (Alvarado et al., 1997; Trela et al., 2017). Particularly, the Tortugal suite hosts high-Fo olivine (up to Fo\(_{94}\)) with compositions overlapping those of olivine in Archaean komatiites and containing 321–1,114 \(\mu g/g\) Al\(_2\)O\(_3\) and 807–2,195 \(\mu g/g\) Cr\(_2\)O\(_3\). Tortugal suite spinel span a wide range of compositions, with Cr\# = 0.66–0.85, Mg\# = 0.33–0.72, and Fe\(^{3+}\)/(Fe\(^{3+}\) + Cr + Al) = 0.0–0.14. Trela et al. (2017) used the model of Coogan et al. (2014) to estimate the crystallization temperature to be 1492\(^\pm173\) °C. Our new estimates, however, are much lower, at 1425\(^\pm149\) °C, which are 67 °C lower on the median and 79 °C lower for the high temperature populations (on the 95\(^{th}\)).
Implications for mantle melting, mantle lithologies, and subsolidus re-equilibration

Significant overestimation of temperature is often observed when the model of Coogan et al. (2014) is applied to specific geological settings (e.g., intra-plate igneous provinces). This model was however abundantly used to assess mantle melting conditions and lithologies in those cases (e.g., Matthews et al., 2016; 2021) which therefore necessitate a revision.

Olivine crystallization temperatures can be converted to mantle $T_p$ when a correction for the latent heat of melting is considered (Putirka et al., 2007), which is directly related to the total melt fraction. The total melt fraction can be constrained from melting of a homogeneous (e.g., Putirka et al., 2007) or a heterogenous mantle source (Matthews et al., 2016; 2021), and through geophysical observations of magmatic productivity, i.e., crustal thickness at spreading centers or magma flux at ocean islands (McKenzie & Bickle, 1988; Shorttle et al., 2014; Matthews et al., 2016; 2021).

To be self-consistent with previous $T_p$ and lithology estimates, we applied the protocol of Matthews et al. (2016; 2021) to estimate the mantle melting conditions and mantle thickness for the localities investigated in this study. In this melting model, crustal thickness at oceanic spreading centers and magma flux at ocean islands are used as observable proxies for magma productivity. A multi-lithology mantle melting model during adiabatic decompression following Phipps Morgan (2001) and Shorttle et al. (2014) is used to calculate melting behavior. The source lithologies are assumed to be in thermal equilibrium. A full description of the mathematical and computational formulation is available in Phipps Morgan (2001) and Shorttle et al. (2014). An extra constraint was added to prevent negatively buoyant solution in intra-plate magmatism, i.e., the multi-lithology mantle should be buoyant with respect to the ambient mantle during the plume-driven upwelling. We used the python interface forward model pyMelt (version 1.96; Matthews et al., 2022) to calculate the melting behavior of mantle compositions comprising multiple lithologies. The model considers three lithologies: lherzolite ($matthews.klb1$ lithology class in pyMelt) and silica-deficient pyroxenite ($matthews.kg1$ lithology class) from Matthews et
al. (2021), and non-melting harzburgite (shorttle.harzburgite lithology class) from Shorttle et al. (2014).

To convert an observation of primary crystallization temperatures ($T_{cry}$) to the value of $T_p$, the fractions of mantle lithologies ($\phi_{Hz}$, the harzburgite fraction; $\phi_{Px}$, the pyroxenite fraction; and $\phi_{Lz}$, the peridotite/lherzolite fraction), we used an inversion model of Matthews et al. (2021), a Bayesian Monte Carlo inference method (Feroz & Hobson, 2008; Feroz et al., 2009, 2013; Buchner et al., 2014) to find the set of solutions which can reproduce $T_{cry}$ and mantle lithologies with applicable constraints (e.g., crustal thickness, magma flux). The inversion model parameters (lithospheric thickness, crustal thickness, the fraction of pyroxenite derived melt, magma flux) were kept identical to Table 1 in Matthews et al. (2021), also given in supplementary dataset (Table S4), except for the $T_{cry}$, which we adapted to our new estimates above. We note that these parameters may not be the most appropriate for all our tested localities, but the focus here is on the influence of changing $T_{cry}$ on mantle $T_p$ and lithology estimates. The inversion model requires the selection of an appropriate olivine composition and crystallization temperature as the starting point of the calculation. Matthews et al. (2021) assumed Fo$_{91}$ olivine as the composition equilibrated with primitive mantle-derived melts based on the most primitive olivine observed in nature. However, both experimental and natural observations (e.g., the Tortugal suite) have shown olivine of higher Fo (>Fo$_{90}$), indicating that the source diversity controls primary olivine compositions at different localities (see further discussion below). Here, we chose the maximum of our calculated $T_{cry}$ estimates (the corresponding olivine Fo are close to or higher than 91) at each locality as the primary olivine temperature to simplify the constraints on the equilibrated olivine composition.

Our inversion results for $T_p$ and mantle lithological fractions are summarized in Table 5 and shown in Fig. 12, details are given in the supplementary dataset. Because different model parameters are used to constrain mantle $T_p$ in different methods (e.g., Putirka, 2005; 2016), we only compare our new $T_p$ values with those of Matthews et al. (2021) in Fig. 13 to be self-consistent.
Our new estimated $T_p$ and lithology fractions ($\phi_{M}$ and $\phi_{L}$) for MORB (1355$^{+24}_{-19}$ °C, 0.34$^{+0.25}_{-0.30}$ and 0.02$^{+0.02}_{-0.02}$, respectively), Iceland (1518$^{+21}_{-17}$ °C, 0.23$^{+0.18}_{-0.17}$, 0.08$^{+0.04}_{-0.04}$), Skye (1550$^{+80}_{-82}$ °C, 0.51$^{+0.32}_{-0.39}$, 0.12$^{+0.16}_{-0.10}$), and Etendeka (1577$^{+106}_{-90}$ °C, 0.53$^{+0.31}_{-0.38}$, 0.11$^{+0.19}_{-0.10}$) are comparable to those of Matthews et al. (2021). However, due to previous overestimation of crystallization temperatures for intra-plate LIPs, our newly estimated $T_p$ and lithological fractions differ significantly from Matthews et al. (2021). Our respective results for Emeishan (1481$^{+87}_{-78}$ °C, 0.53$^{+0.29}_{-0.36}$, 0.10$^{+0.14}_{-0.09}$) return a median $T_p$ that is 74 °C cooler than previous inversions (Table 4), and our results for the Tortugal suite (1648$^{+193}_{-91}$ °C, 0.50$^{+0.31}_{-0.38}$) return a median $T_p$ that is 165 °C cooler, which leads to a remarkable difference in the estimated lithological fractions (Table 4).

To verify the reliability of the mantle melting and lithological estimates, we performed forward thermodynamic modeling based on the estimated mantle $T_p$ and lithological fractions to calculate the equilibrated olivine composition in composition–temperature space. We used the Matlab/Julia Mineral Assemblages Gibbs Energy Minimization package (MAGEMin v1.3.0; Riel et al., 2022) to calculate the equilibrium melt composition of a given mantle lithology under mantle melting conditions calculated from inversion. For the modeling, we use the thermodynamic database of Holland et al. (2018). The KLB-1 peridotite (Wasylenki et al., 2003) and MIX1G pyroxenite (Hirschmann et al., 2003) were mixed with the median ratio of the estimated lithological fractions to generate an equilibrated melt with the mantle source for each locality. The equilibrated melt then crystallizes mineral phases within a given temperature interval at the base of the crust (same as the inversion model, see Table S3 in the supplementary dataset and Table 1 in Matthews et al. [2021]) at each locality. The model results are compared to our estimated crystallization temperatures at each locality in Fig. 11. The equilibrated olivine usually includes sub-populations containing higher-Fo (>Fo90) than those in the erupted lavas, but
are generally consistent with the crystallization temperatures calculated using our extended OSAT, whereas the results of Coogan et al. (2014) mostly overestimate the temperature.

CONCLUSIONS

We revised the formalism of the olivine-spinel aluminum exchange thermometer by performing new experiments and reanalyzing published experiments to extend the calibration $P$, $T$, $fO_2$, and $H_2O$ conditions. Three models were regressed on the extended dataset: a thermodynamic-based model (Eq. 5) and two empirical models (Eqs. 7 and 8).

The thermodynamic model of Eq. 5 shows the best performance with the lowest uncertainties. The exchange of Al and Cr between olivine and spinel significantly affects the results when using the empirical models, whereas $fO_2$, water, and pressure have little to moderate effects on all models. The empirical models may only be accurate within a restricted spinel composition, leading to temperature overestimations by ~30–100 °C in some intra-plate LIPs, but only minor differences in Iceland and MOR. These improved $T_{cry}$ estimates translate to a significant difference in the mantle $T_p$ and lithological fractions calculated for the investigated intra-plate LIPs.

APPENDIX A. THERMODYNAMIC MODEL OF OLIVINE–SPINEL AL PARTITIONING

Here, we develop our thermodynamic formalism to understand the Al exchange between olivine and spinel. The most plausible solution mechanism for the incorporation of Al into olivine and Cr-spinel is (Coogan et al., 2014):

$$ (MgAl^{TET})Al^{OCT}O_4^{Spl} = (MgAl^{TET})Al^{OCT}O_4^{Ol} \quad (A.1) $$

Thus, the equilibrium of the reaction is written as:

$$ \mu_{MgAl_2O_4^{Oli}} = \mu_{MgAl_2O_4^{Spl}} \quad (A.2) $$

where $\mu_{a}^{b}$ is the chemical potential of component $a$ in phase $b$. For a given phase:
\[ \mu_a^0 + RT \ln \alpha^a \]  

(A.3)

where \( \mu_a^0 \) is the chemical potential of component \( a \) at standard state, \( \alpha^a \) is the activity of component \( a \), \( R \) is the universal gas constant [8.314 J mol\(^{-1}\) K\(^{-1}\)], and \( T \) is the absolute temperature in Kelvin.

For olivine, we can write:

\[ a_{\text{MgAl}_2O_4}^\text{Ol} = \gamma \times X_{\text{MgAl}_2O_4}^\text{Ol} \]  

(A.4)

\[ X_{\text{MgAl}_2O_4}^\text{Ol} = \left( \frac{\text{Al}_2O_3 \text{ wt.} \%}{M_{\text{Al}_2O_3}} \right) \times M_{\text{MgAl}_2O_4} \]  

(A.5)

where \( \gamma \) is the activity coefficient and \( M \) the molar weight of the component, and \( X \) is the mole fraction. Combining Eqs. A.3–A.5, we obtain:

\[ \mu_{\text{MgAl}_2O_4} = \mu_{\text{MgAl}_2O_4}^0 + RT \ln \left[ \gamma \times \left( \frac{\text{Al}_2O_3 \text{ wt.} \%}{M_{\text{Al}_2O_3}} \right) \times M_{\text{MgAl}_2O_4} \right] \]  

(A.6)

We apply a thermodynamic model involving cation site ordering (Sack, 1982; Sack & Ghiorso, 1991a, 1991b) to describe the thermodynamic properties of the components in Cr-spinel. In this model, spinel is assumed to be stoichiometrically perfect (\( R_3O_4 \)), with \( Fd3m \) space group symmetry. Five 'fictive' independent compositional variables (\( X_i \)) and ordering parameters (\( s_i \)) are needed to describe the compositional change in Cr-spinel, which can be calculated from mole fractions of cations in the spinel.

The independent compositional and ordering variables as well as the definitions of site mole fractions are from Sack & Ghiorso (1991a, 1991b) and reported in Table. A1. The molar Gibbs energy \( \bar{G} \) is calculated from the vibrational Gibbs energy \( \bar{G}^* \) and the ideal molar configurational entropy \( S^{\text{IC}} \) as:

\[ \bar{G} = \bar{G}^* - T S^{\text{IC}} \]  

(A.7)

A second-degree Taylor expansion of the compositional and ordering variables is used to describe the molar vibrational Gibbs energy as (Thompson Jr, 1969):
\[ G^* = g_0 + \sum_i \left( g_i X_i + g_i^2 X_i^2 + \sum_{j < i} g_{ij} X_i X_j \right) \]
\[ + \sum_i \sum_k (g_{ik} X_i s_k) \]
\[ + \sum_k \left( g_{kk} s_k^2 + \sum_{l < k} g_{kl} s_k s_l \right) \]  
(A.8)

where \( g \) terms are Taylor coefficients from Table 3 in Sack and Ghiorso (1991b). The configurational entropy is calculated from compositional variables and site fractions as:
\[ S_{IC}^C = -R \sum_c \sum_r \bar{r} X_{c,r} \ln X_{c,r} \]  
(A.9)

where \( X_{c,r} \) is the fraction of cation \( c \) in site \( r \) in terms of \( X_i \) and \( s_i \), and \( \bar{r} \) is the number of \( r \) sites per formula unit. A Darken equation is then used to manipulate and express the chemical potential of the spinel endmembers (Darken & Gurry, 1953; Sack, 1982; Ghiorso, 1990; Sack & Ghiorso, 1991a):
\[ \mu_j = \bar{G} + \sum_{i} n_{ij} (1-X_i) \left( \frac{\partial G}{\partial X_i} \right) \frac{X_i}{X_i s_i} + \sum_{i} (q_{ij} s_i) \left( \frac{\partial G}{\partial s_i} \right) X_i s_i \]  
(A.10)

where \( n_{ij} \) and \( q_{ij} \) represent coefficients of \( X_i \) and \( s_i \), respectively, in 1 mol of spinel component \( j \). The chemical potential of component \( \text{MgAl}_2\text{O}_4 \) in a spinel solution can be written as:
\[ \mu_{\text{MgAl}_2\text{O}_4}^{\text{Spl}} = G_2^* + RT \ln [(X_2)/(1+X_4)(1-X_3-X_4-X_5)^2] + W_{\text{Fe-Mg}TET} (1 - X_2)(1 + X_4 - X_2) \]

\[ + \Delta G_{23}^0 (1 - X_2)(X_3) + \Delta G_{24}^0 (1 - X_2)(X_4) + \Delta G_{25}^0 (1 - X_2)(X_5) \]

\[ + W_{1'3'}X_3 (X_3 + X_4 + X_5) \]

\[ + W_{1'4'}X_4 (X_3 + X_4 + X_5) \]

\[ + W_{1'5'}X_5 (X_3 + X_4 + X_5) \]

\[ - W_{3'4'}(X_3)(X_4) - W_{3'5'}(X_3)(X_5) \]

\[ - W_{4'5'}(X_4)(X_5) \]

where \( G_2^* \) is the vibrational Gibbs energy of the \( \text{MgAl}_2\text{O}_4 \) endmember. The Gibbs energy along joins between vertices differing in composition (i.e., \( \Delta G_{23}^0, \Delta G_{24}^0, \) and \( \Delta G_{25}^0 \)) are standard state Gibbs free energies of the Mg-Fe exchange reactions between aluminate (\( G_2 \)), chromate (\( G_3 \)), titanate (\( G_4 \)), and ferrite spinel (\( G_5 \)). \( W_{\text{Fe-Mg}TET} \), \( W_{ij} \), and \( W_{ij}' \) are symmetric regular solution parameters describing deviations of the Gibbs energy from ideal mixing. To focus on Al partitioning between olivine and spinel, we combine Eqs. A.2, A.6, and A.10 with independent parameters \( X_i \) (Table A1) as:
\[
\mu_{\text{MgAl}_2\text{O}_4}^0 + R T \ln \left[ \gamma \times \frac{\text{Al}_2\text{O}_3^\text{OL} \text{ wt.\%}}{M_{\text{Al}_2\text{O}_3}} \times M_{\text{MgAl}_2\text{O}_4} \right] \\
= \bar{G}_2^* + R T \ln \left[ (X_2)/(1+X_4)(1-X_3-X_4-X_5)^2 \right] \\
+ W_{\text{Fe-Mg}}^\text{TET} (1 - X_2)(1 + X_4 - X_2) \\
+ \Delta G_{23}^0 (1-X_2)(X_3) + \Delta G_{24}^0 (1-X_2)(X_4) + \Delta G_{25}^0 (1-X_2)(X_5) \\
+ W_{1^\prime 3}(X_3)(X_3+X_4+X_5) \\
+ W_{1^\prime 4}(X_3+X_4+X_5) \\
+ W_{1^\prime 5}(X_3+X_4+X_5) \\
- W_{3^\prime 4}(X_4) \cdot W_{3^\prime 5}(X_3)(X_5) \\
- W_{4^\prime 5}(X_4)(X_5) \\
\]

(A.12)

After re-organizing terms:

\[
R T \ln \left[ \gamma \times \frac{\text{Al}_2\text{O}_3^\text{OL} \text{ wt.\%}}{M_{\text{Al}_2\text{O}_3}} \times \frac{(X_2)}{(1+X_4)(1-X_3-X_4-X_5)^2} \right] \\
= \bar{G}_2^* + \mu_{\text{MgAl}_2\text{O}_4}^0 \\
+ W_{\text{TET}}^\text{Fe-Mg} (1 - X_2)(1 + X_4 - X_2) \\
+ \Delta G_{23}^0 (1-X_2)(X_3) + \Delta G_{24}^0 (1-X_2)(X_4) + \Delta G_{25}^0 (1-X_2)(X_5) \\
+ W_{1^\prime 3}(X_3)(X_3+X_4+X_5) \\
+ W_{1^\prime 4}(X_3+X_4+X_5) \\
+ W_{1^\prime 5}(X_3+X_4+X_5) \\
- W_{3^\prime 4}(X_4) \cdot W_{3^\prime 5}(X_3)(X_5) \\
- W_{4^\prime 5}(X_4)(X_5) \\
\]

(A.13)
On the left side of Eq. A.13, \((X_2)/(1+X_4)(1-X_3-X_4-X_5)^2\) is equal to \(X_{Mg^{2+}}^{TET}X_{Al^{3+}}^{OCT}^2\); on the right side of Eq. A.13, all parameters are constants or barely change with temperature (see Sack & Ghiorso, 1991a), except \(\mu_{MgAl_2O_4}^0\), \(\bar{G}_2^\ast\) and the independent composition \(X_i\). \(\bar{G}_2^\ast\) can be rewritten as \(\left(c_1X_2+c_2X_2^2+c_3X_2^3\right)\) following Eq. A.8, where \(c_1\), \(c_2\) and \(c_3\) are constants derived from the Taylor expansion coefficients. However, given that the standard state of \(MgAl_2O_4\) (i.e., \(\mu_{MgAl_2O_4}^0\)) in olivine is not well constrained, \(\mu_{MgAl_2O_4}^0\), by definition, is relevant to temperature at any given pressure and composition. We thus simplified \(\mu_{MgAl_2O_4}^0\) to be a function of temperature and independent of olivine composition given the trace concentration of Al in olivine (Ganguly, 2008), and \(\gamma\) for \(Al_2O_3\) in olivine can be assumed to be 1. We thus encapsulate all parameters related to spinel as \(\phi^{Spl}\), and Eq. A.13 can be fitted with coefficients \((c_i)\) replacing the regular solution parameters, and related to the spinel composition as:

\[
\ln\left(\frac{X_{Al^{3+}}^{OCT}}{X_{Mg^{2+}}^{TET}X_{Al^{3+}}^{OCT}}\right) + b = \frac{\phi^{Spl}}{c_0} \times T \quad (A.14)
\]

where

\[
\phi^{Spl} = c_1X_2 + c_2X_2^2 + c_3X_2^3 + c_4(1 - X_2)(1 + X_4 - X_2)
\]

\[
+ c_5(1-X_3)(X_5) + c_6(1-X_2)(X_3) + c_7(1-X_2)(X_3)
\]

\[
+ c_8X_3(X_3+X_4+X_5)
\]

\[
+ c_9X_4(X_3+X_4+X_5)
\]

\[
+ c_{10}X_5(X_3+X_4+X_5)
\]

\[
- c_{11}(X_3)(X_4) - c_{12}(X_3)(X_5) - c_{13}(X_4)(X_5) + c_{14}
\]
The coefficients $b$, and $c_0-c_{12}$ can be then obtained by fitting the compositions of experimental olivine and spinel pairs.

**APPENDIX B. F-TEST MODEL**

An $F$-test is a statistical test with the null hypothesis that a distribution follows an $F$-distribution; $F$-tests have been used in solving geological problems involving regression (e.g., Abouchami et al., 2005). An $F$-test is commonly used to compare two models that give similar or identical results but use different numbers of parameters, with the aim of determining which model is statistically better or whether the model with fewer parameters is nested within the model with more parameters. In this case, the $F$-value can be calculated as:

$$F = \frac{(RSS_1 - RSS_2)/(p_1 - p_2)}{RSS_2/(n - p_2)}$$  \hspace{1cm} (B.1)

where $RSS_i$ represents the residual sum of squares of model $i$; $p_1$ and $p_2$ represent the number of parameters in models 1 ($m_1$) and 2 ($m_2$), and $p_1 < p_2$; and $n$ is the amount of data points used in the regressions. While comparing the two models, the null hypothesis is that $m_2$ is not better than $m_1$ (i.e., that $m_2$ is an overfitting of $m_1$). When comparing the $F$-value with the critical $F$-value, which can be calculated from the $F$-distribution with $(p_2 - p_1, n - p_2)$ degrees of freedom, if $F$ exceeds the critical value, the associated $p$-value is small ($<1 - \alpha$; e.g., $\alpha = 0.05$ for 95% confidence) and then null hypothesis is rejected, meaning that $m_2$ is indeed statistically better. If $F$ is below the critical value, the associated $p$-value is larger than $\alpha$ and $m_1$ is statistically better than $m_2$. 


REFERENCES


Thermobarometer Applied to 13,589 Mid-Ocean Ridge Basalt Glasses. 


Figure captions

**Fig. 1.** Spinel compositions in calibration experiments and natural rocks. (a) Ternary projection of spinel prism, Al-Cr-Fe³⁺. (b) Spinel Cr# as a function spinel Mg#. (c) Spinel TiO₂ (wt. %) as a function of spinel Fe³⁺/(Fe³⁺ + Cr + Al). (d) Spinel Fe³⁺/(Fe³⁺ + Cr + Al) as a function of spinel Fe³⁺/(Fe³⁺+Mg). Data from Barr et al. (2009), Mitchell and Grove (2015), Charlier et al. (2018), Parman and Grove (2004), and Thy (1995) are remeasured published experiments. Data from Matzen et al. (2011) and Hanson & Jones (1998) are used as part of the test dataset. See text for details on the calibration and test dataset. Natural samples are compiled from published studies: MORB (Coogan et al., 2014; Matthews et al., 2015), Iceland (Spice et al., 2016; Matthews et al., 2016), Skye (Spice et al., 2016), Emeishan (Xu & Liu, 2016; Zhang et al., 2021; Li et al., 2021; Wu et al., 2022), Etendeka (Jennings et al., 2019), Tortugal (Trela et al., 2017). † represents experiments used in the training dataset, * represents experiments used in the test dataset. Error bar represents 1σ standard deviation and is not observable if it is smaller than the symbol.

**Fig. 2.** (a) Al₂O₃, and (b) Cr₂O₃ concentrations in olivine (µg/g) as a function of Fo content (mol.%). Data sources are as in Fig. 1. Error bar represents 1σ standard deviation and is not observable if it is smaller than the symbol.

**Fig. 3.** Representative backscattered electron images of experimental products. Quench texture is observed in high temperature experiments (>1500 °C), euhedral olivine and spinel indicate the attainment of equilibrium in the experiments. Abbreviations: Gl, glass; Cr-Spl, Cr-spinel; Ol, olivine.

**Fig. 4.** Melt compositional variations as functions of melt MgO content (wt.%). Experimental data sources are as in Fig. 1. Error bar represents 1σ standard deviation and is not observable if it is smaller than the symbol.

**Fig. 5.** Comparison of crystallization temperatures calculated using (a) the model of Coogan et al. (2014) and (b–d) Eqs. 5, 7, and 8, respectively. The green line represents the results of a Monte Carlo simulation showing the robustness of the fit when 1σ standard errors on spinel and olivine compositions are considered. The r² values represent the robustness of the linear regressions between the measured temperatures and predicted temperatures. The brown and purple fields represent temperatures within ±50 °C and ±100 °C. Data sources as in Fig. 1.

**Fig. 6.** Effects of spinel Cr# on (a) the OSAT of Coogan et al. (2014) and (b–d) the extended OSAT using Eqs. 5, 7, and 8, respectively. Data sources as in Fig. 1.

**Fig. 7.** Effects of spinel Mg# on (a) the OSAT of Coogan et al. (2014) and (b–d) the extended OSAT using Eqs. 5, 7, and 8, respectively. Data sources as in Fig. 1.

**Fig. 8.** Effects of spinel Fe³⁺/(Fe³⁺ + Cr + Al) on (a) the OSAT of Coogan et al. (2014) and (b–d) the extended OSAT using Eqs. 5, 7, and 8, respectively. Data sources as in Fig. 1.

**Fig. 9.** Effects of pressure (MPa) on (a) the OSAT of Coogan et al. (2014) and (b–d) the extended OSAT using Eqs. 5, 7, and 8, respectively. Data sources as in Fig. 1.

**Fig. 10.** Modeled effects of (a) Fe-Mg re-equilibration in spinel on temperatures estimated using Eq. 5 and (b) Cr re-equilibration (decoupled substitution) in olivine on temperatures estimated using Eq. 8. (c) Cr re-equilibration (coupled substitution with Al) in olivine on temperatures estimated using Eq. 8.
Fig. 11. Estimated crystallization temperatures for natural samples. Gray symbols are results using the model of Coogan et al. (2014). Blue symbols are results using the extended OSAT of this study that passed the Z-test protocol described in the text. Red lines are the calculated equilibrated olivine compositions and temperatures from our forward thermodynamic modeling using MAGEMin. See text for more details. The histograms along the left axis show compare the distribution of results using our model to those using the model of Coogan et al. (2014). The histogram along the bottom axis shows the distribution of olivine Fo contents, which is the same in both datasets.

Fig. 12. Mantle lithologies and melting temperatures determined by our inversion analysis of natural samples using our extended OSAT, the contour lines represent density plot of the results.

Fig. 13. Comparison of estimated mantle potential temperatures in this study (colored) with those of Matthews et al. (2021; gray). The temperature excess on the right axis is calculated here relative to the median $T_p$ of MORB (Siqueiros). The heights of the boxes show the interquartile range (25th–75th), and the upper and lower whisker bars show maximum and minimum values beyond which, data points represent outliers.
### Table 1. Starting compositions used in this study.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Ind ex</th>
<th>Si O₂</th>
<th>Ti O₂</th>
<th>Al₂ O₃</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Na₂</th>
<th>K₂</th>
<th>P₂</th>
<th>Cr₃</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>natural rocks</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ny17-135</td>
<td>A</td>
<td>40.</td>
<td>1.3</td>
<td>6.9</td>
<td>12.</td>
<td>0.1</td>
<td>28.</td>
<td>8.1</td>
<td>1.0</td>
<td>0.4</td>
<td>0.3</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>Ny17-135 Cr₂</td>
<td>B</td>
<td>53</td>
<td>3</td>
<td>1</td>
<td>21</td>
<td>8</td>
<td>14</td>
<td>8</td>
<td>3</td>
<td>70</td>
<td>4</td>
<td>5</td>
<td>00</td>
</tr>
<tr>
<td>Ny17-161 Cr</td>
<td>C</td>
<td>37.</td>
<td>1.2</td>
<td>6.4</td>
<td>11.</td>
<td>0.1</td>
<td>31.</td>
<td>7.6</td>
<td>0.9</td>
<td>0.4</td>
<td>1.9</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>Ny17-161 Cr₂</td>
<td>D</td>
<td>95</td>
<td>4</td>
<td>7</td>
<td>43</td>
<td>7</td>
<td>08</td>
<td>6</td>
<td>6</td>
<td>66</td>
<td>1</td>
<td>7</td>
<td>00</td>
</tr>
<tr>
<td>NYAM Cr₂</td>
<td>E</td>
<td>39.</td>
<td>3.1</td>
<td>10.</td>
<td>11.</td>
<td>0.2</td>
<td>10.</td>
<td>16.</td>
<td>3.0</td>
<td>2.4</td>
<td>0.0</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>Os82 Cr₂</td>
<td>F</td>
<td>67</td>
<td>9</td>
<td>61</td>
<td>50</td>
<td>2</td>
<td>99</td>
<td>30</td>
<td>1</td>
<td>97</td>
<td>8</td>
<td>6</td>
<td>00</td>
</tr>
<tr>
<td>PI-052 Cr₂*</td>
<td>G</td>
<td>39.</td>
<td>0.7</td>
<td>16.</td>
<td>9.3</td>
<td>0.1</td>
<td>10.</td>
<td>10.</td>
<td>2.1</td>
<td>0</td>
<td>0.0</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>TO1</td>
<td>H</td>
<td>42</td>
<td>6</td>
<td>5</td>
<td>9</td>
<td>2</td>
<td>93</td>
<td>68</td>
<td>0</td>
<td>11</td>
<td>6</td>
<td>8</td>
<td>00</td>
</tr>
<tr>
<td>TO1 Cr</td>
<td>I</td>
<td>44.</td>
<td>0.7</td>
<td>3.9</td>
<td>11.</td>
<td>0.1</td>
<td>32.</td>
<td>4.8</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>TO1 Cr₂</td>
<td>J</td>
<td>77</td>
<td>9</td>
<td>4</td>
<td>88</td>
<td>7</td>
<td>86</td>
<td>2</td>
<td>2</td>
<td>05</td>
<td>9</td>
<td>2</td>
<td>00</td>
</tr>
<tr>
<td>TO1 Cr₂</td>
<td>K</td>
<td>44.</td>
<td>0.7</td>
<td>3.8</td>
<td>11.</td>
<td>0.1</td>
<td>32.</td>
<td>4.7</td>
<td>0.1</td>
<td>0.1</td>
<td>1.9</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>TO2</td>
<td>L</td>
<td>45.</td>
<td>0.8</td>
<td>4.4</td>
<td>11.</td>
<td>0.1</td>
<td>31.</td>
<td>5.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>TO2 Cr</td>
<td>M</td>
<td>45.</td>
<td>0.8</td>
<td>4.4</td>
<td>11.</td>
<td>0.1</td>
<td>31.</td>
<td>5.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.7</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td>TO2 Cr₂</td>
<td>N</td>
<td>44.</td>
<td>0.8</td>
<td>4.4</td>
<td>11.</td>
<td>0.1</td>
<td>30.</td>
<td>5.1</td>
<td>0.1</td>
<td>0.2</td>
<td>1.9</td>
<td>100.</td>
<td></td>
</tr>
<tr>
<td><strong>synthetic material</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO1 syn Cr</td>
<td>O</td>
<td>45.</td>
<td>0.7</td>
<td>3.8</td>
<td>10.</td>
<td>0.2</td>
<td>31.</td>
<td>4.6</td>
<td>0.1</td>
<td>1.</td>
<td>0.1</td>
<td>1.0</td>
<td>100.</td>
</tr>
<tr>
<td>TO1 syn Cr₂</td>
<td>P</td>
<td>45.</td>
<td>0.7</td>
<td>3.8</td>
<td>10.</td>
<td>0.1</td>
<td>31.</td>
<td>4.6</td>
<td>0.1</td>
<td>1.</td>
<td>0.1</td>
<td>1.0</td>
<td>100.</td>
</tr>
<tr>
<td>TO2 syn Cr</td>
<td>Q</td>
<td>44.</td>
<td>3</td>
<td>0</td>
<td>12.</td>
<td>9</td>
<td>60</td>
<td>2</td>
<td>5</td>
<td>06</td>
<td>6</td>
<td>8</td>
<td>00</td>
</tr>
<tr>
<td>TO2 syn Cr₂</td>
<td>R</td>
<td>43.</td>
<td>2.2</td>
<td>4.8</td>
<td>11.</td>
<td>0.2</td>
<td>34.</td>
<td>0.5</td>
<td>0.2</td>
<td>0.</td>
<td>0.2</td>
<td>1.0</td>
<td>100.</td>
</tr>
<tr>
<td>Ny17 syn Cr</td>
<td>S</td>
<td>73</td>
<td>6</td>
<td>6</td>
<td>60</td>
<td>4</td>
<td>87</td>
<td>6</td>
<td>2</td>
<td>20</td>
<td>1</td>
<td>0</td>
<td>00</td>
</tr>
<tr>
<td>Ny17 syn Cr₂</td>
<td>T</td>
<td>30</td>
<td>3</td>
<td>1</td>
<td>49</td>
<td>4</td>
<td>52</td>
<td>6</td>
<td>2</td>
<td>20</td>
<td>1</td>
<td>0</td>
<td>00</td>
</tr>
</tbody>
</table>

* Indicates starting composition was doped with forsterite or MgO to increase liquidus.

* Indexes are used to indicate which starting composition was used during the experiments in Table 2.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Reference</th>
<th>T (°C)</th>
<th>Pressure (MPa)</th>
<th>logO₂</th>
<th>ΔQF</th>
<th>H₂O (wt%)</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAG03-K</td>
<td>This study</td>
<td>1606.0</td>
<td>0.10</td>
<td>-4.53</td>
<td>0.00</td>
<td>0.00</td>
<td>7.00</td>
</tr>
<tr>
<td>CAG03-N</td>
<td>This study</td>
<td>1606.0</td>
<td>0.10</td>
<td>-4.53</td>
<td>0.00</td>
<td>0.00</td>
<td>7.00</td>
</tr>
<tr>
<td>CAG03-H</td>
<td>This study</td>
<td>1606.0</td>
<td>0.10</td>
<td>-4.53</td>
<td>0.00</td>
<td>0.00</td>
<td>7.00</td>
</tr>
<tr>
<td>CAG04-N</td>
<td>This study</td>
<td>1568.0</td>
<td>0.10</td>
<td>-4.83</td>
<td>0.00</td>
<td>0.00</td>
<td>7.00</td>
</tr>
<tr>
<td>CAG04-E</td>
<td>This study</td>
<td>1568.0</td>
<td>0.10</td>
<td>-4.83</td>
<td>0.00</td>
<td>0.00</td>
<td>7.00</td>
</tr>
<tr>
<td>CAG05-R</td>
<td>This study</td>
<td>1571.0</td>
<td>0.10</td>
<td>-4.81</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>CAG05-S</td>
<td>This study</td>
<td>1571.0</td>
<td>0.10</td>
<td>-4.81</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>CAG06-P</td>
<td>This study</td>
<td>1571.0</td>
<td>0.10</td>
<td>-4.81</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>CAG06-R</td>
<td>This study</td>
<td>1571.0</td>
<td>0.10</td>
<td>-4.81</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>CAG06-T</td>
<td>This study</td>
<td>1571.0</td>
<td>0.10</td>
<td>-4.81</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>CAG07-T</td>
<td>This study</td>
<td>1600.0</td>
<td>0.10</td>
<td>-5.58</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB01-C</td>
<td>This study</td>
<td>1190.0</td>
<td>0.10</td>
<td>-8.53</td>
<td>0.00</td>
<td>0.00</td>
<td>72.00</td>
</tr>
<tr>
<td>NAB01-G</td>
<td>This study</td>
<td>1190.0</td>
<td>0.10</td>
<td>-8.53</td>
<td>0.00</td>
<td>0.00</td>
<td>72.00</td>
</tr>
<tr>
<td>NAB01-F</td>
<td>This study</td>
<td>1190.0</td>
<td>0.10</td>
<td>-8.53</td>
<td>0.00</td>
<td>0.00</td>
<td>72.00</td>
</tr>
<tr>
<td>NAB02-D</td>
<td>This study</td>
<td>1174.0</td>
<td>0.10</td>
<td>-8.72</td>
<td>0.00</td>
<td>0.00</td>
<td>94.00</td>
</tr>
<tr>
<td>NAB02-G</td>
<td>This study</td>
<td>1174.0</td>
<td>0.10</td>
<td>-8.72</td>
<td>0.00</td>
<td>0.00</td>
<td>94.00</td>
</tr>
<tr>
<td>NAB02-F</td>
<td>This study</td>
<td>1174.0</td>
<td>0.10</td>
<td>-8.72</td>
<td>0.00</td>
<td>0.00</td>
<td>94.00</td>
</tr>
<tr>
<td>NAB21-A</td>
<td>This study</td>
<td>1550.0</td>
<td>0.10</td>
<td>-5.84</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB24-I</td>
<td>This study</td>
<td>1401.0</td>
<td>0.10</td>
<td>-6.29</td>
<td>0.00</td>
<td>0.00</td>
<td>72.00</td>
</tr>
<tr>
<td>NAB31-L</td>
<td>This study</td>
<td>1401.0</td>
<td>0.10</td>
<td>-6.29</td>
<td>0.00</td>
<td>0.00</td>
<td>72.00</td>
</tr>
<tr>
<td>NAB31-A</td>
<td>This study</td>
<td>1401.0</td>
<td>0.10</td>
<td>-6.29</td>
<td>2.00</td>
<td>0.00</td>
<td>48.00</td>
</tr>
<tr>
<td>NAB41-J</td>
<td>This study</td>
<td>1469.0</td>
<td>0.10</td>
<td>-5.67</td>
<td>0.00</td>
<td>0.00</td>
<td>48.00</td>
</tr>
<tr>
<td>NAB41-M</td>
<td>This study</td>
<td>1469.0</td>
<td>0.10</td>
<td>-5.67</td>
<td>0.00</td>
<td>0.00</td>
<td>48.00</td>
</tr>
<tr>
<td>NAB45-K</td>
<td>This study</td>
<td>1529.0</td>
<td>0.10</td>
<td>-5.15</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB45-N</td>
<td>This study</td>
<td>1529.0</td>
<td>0.10</td>
<td>-5.15</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB45-B</td>
<td>This study</td>
<td>1529.0</td>
<td>0.10</td>
<td>-5.15</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB45-H</td>
<td>This study</td>
<td>1529.0</td>
<td>0.10</td>
<td>-5.15</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB49-Q</td>
<td>This study</td>
<td>1500.0</td>
<td>0.10</td>
<td>-5.40</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB49-R</td>
<td>This study</td>
<td>1500.0</td>
<td>0.10</td>
<td>-5.40</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB51-R</td>
<td>This study</td>
<td>1500.0</td>
<td>0.10</td>
<td>-5.40</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB51-S</td>
<td>This study</td>
<td>1500.0</td>
<td>0.10</td>
<td>-5.40</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB52-R</td>
<td>This study</td>
<td>1529.0</td>
<td>0.10</td>
<td>-5.15</td>
<td>0.00</td>
<td>0.00</td>
<td>24.00</td>
</tr>
<tr>
<td>NAB53-O</td>
<td>This study</td>
<td>1445.0</td>
<td>0.10</td>
<td>-5.89</td>
<td>0.00</td>
<td>0.00</td>
<td>72.00</td>
</tr>
<tr>
<td>NAB53-Q</td>
<td>This study</td>
<td>1445.0</td>
<td>0.10</td>
<td>-5.89</td>
<td>0.00</td>
<td>0.00</td>
<td>72.00</td>
</tr>
<tr>
<td>Sample</td>
<td>Re-analyzed experiment</td>
<td>Th/Yb</td>
<td>Tasma</td>
<td>Harker</td>
<td>Parman &amp; Grove (2004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------------------------</td>
<td>-------</td>
<td>-------</td>
<td>--------</td>
<td>-----------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAB53-R</td>
<td>This study</td>
<td>1445</td>
<td>-5.89</td>
<td>0.00</td>
<td>72.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAB53-S</td>
<td>This study</td>
<td>1445</td>
<td>-5.89</td>
<td>0.00</td>
<td>72.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAB57-R</td>
<td>This study</td>
<td>1530</td>
<td>-5.15</td>
<td>0.00</td>
<td>24.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAB57-T</td>
<td>This study</td>
<td>1530</td>
<td>-5.15</td>
<td>0.00</td>
<td>24.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAB58-R</td>
<td>This study</td>
<td>1397</td>
<td>-6.33</td>
<td>0.00</td>
<td>72.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*NAB88-R</td>
<td>This study</td>
<td>1350</td>
<td>-8.39</td>
<td>-1.60</td>
<td>118.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAB89-U</td>
<td>This study</td>
<td>1253</td>
<td>-9.41</td>
<td>-1.60</td>
<td>120.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*NAB89-R</td>
<td>This study</td>
<td>1253</td>
<td>-9.41</td>
<td>-1.60</td>
<td>120.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAB90-U</td>
<td>This study</td>
<td>1305</td>
<td>-8.85</td>
<td>-1.60</td>
<td>36.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*NAB91-Q</td>
<td>This study</td>
<td>1305</td>
<td>-8.85</td>
<td>-1.60</td>
<td>36.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*NAB91-R</td>
<td>This study</td>
<td>1305</td>
<td>-8.85</td>
<td>-1.60</td>
<td>36.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re-analyzed experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>com1-12</td>
<td>Barr et al. (2009)</td>
<td>1320</td>
<td>-7.09</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>com1-2</td>
<td>Barr et al. (2009)</td>
<td>1350</td>
<td>-6.79</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>com1-4</td>
<td>Barr et al. (2009)</td>
<td>1300</td>
<td>-7.30</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>213.00</td>
<td>Thy (1995)</td>
<td>1240</td>
<td>-7.95</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>214.00</td>
<td>Thy (1995)</td>
<td>1251</td>
<td>-7.83</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>215.00</td>
<td>Thy (1995)</td>
<td>1231</td>
<td>-8.05</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>216.00</td>
<td>Thy (1995)</td>
<td>1224</td>
<td>-8.17</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>218.00</td>
<td>Thy (1995)</td>
<td>1200</td>
<td>-8.41</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>224.00</td>
<td>Thy (1995)</td>
<td>1260</td>
<td>-7.73</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>228.00</td>
<td>Thy (1995)</td>
<td>1279</td>
<td>-7.52</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>230.00</td>
<td>Thy (1995)</td>
<td>1300</td>
<td>-7.30</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>233.00</td>
<td>Thy (1995)</td>
<td>1311</td>
<td>-7.18</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>234.00</td>
<td>Thy (1995)</td>
<td>1320</td>
<td>-7.09</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>235.00</td>
<td>Thy (1995)</td>
<td>1328</td>
<td>-7.01</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c553</td>
<td>Mitchell &amp; Grove (2015)</td>
<td>1215</td>
<td>-8.78</td>
<td>-0.54</td>
<td>6.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c559</td>
<td>Mitchell &amp; Grove (2015)</td>
<td>1250</td>
<td>-8.42</td>
<td>-0.59</td>
<td>3.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>on66-ha04</td>
<td>Charlier et al. (2018)</td>
<td>1230</td>
<td>500.0</td>
<td>-10.58</td>
<td>-2.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>twm-f0.6-b1255</td>
<td>Charlier et al. (2018)</td>
<td>1360</td>
<td>1350.0</td>
<td>-9.03</td>
<td>-2.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>twm71-b1295</td>
<td>Charlier et al. (2018)</td>
<td>1300</td>
<td>800.0</td>
<td>-9.72</td>
<td>-2.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>twm71-ha04</td>
<td>Charlier et al. (2018)</td>
<td>1230</td>
<td>500.0</td>
<td>-10.58</td>
<td>-2.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>w7</td>
<td>Parman &amp; Grove (2004)</td>
<td>1320</td>
<td>1200.0</td>
<td>-8.09</td>
<td>-1.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Literature data**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wan et al. (2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w39</td>
<td>1250.00</td>
</tr>
<tr>
<td>w83_1</td>
<td>1250.00</td>
</tr>
<tr>
<td>w83_2</td>
<td>1250.00</td>
</tr>
<tr>
<td>w83_3</td>
<td>1250.00</td>
</tr>
<tr>
<td>Experiment Code</td>
<td>Authors (Year)</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>matzen2011_8</td>
<td>Matzen et al. (2011)</td>
</tr>
<tr>
<td>matzen2011_46</td>
<td>Matzen et al. (2011)</td>
</tr>
<tr>
<td>H&amp;J_1998_FAD1b</td>
<td>Hanson &amp; Jones (1998)</td>
</tr>
<tr>
<td>H&amp;J_1998_FAD2</td>
<td>Hanson &amp; Jones (1998)</td>
</tr>
<tr>
<td>H&amp;J_1998_FAD3</td>
<td>Hanson &amp; Jones (1998)</td>
</tr>
<tr>
<td>H&amp;J_1998_FAS1</td>
<td>Hanson &amp; Jones (1998)</td>
</tr>
<tr>
<td>H&amp;J_1998_FAS1–1</td>
<td>Hanson &amp; Jones (1998)</td>
</tr>
</tbody>
</table>

* indicates 1–2 hour thermal oscillation (±10°C) was applied;
* Experiment number ends with the starting composition noted in Table 1;
* indicates chromite seeds were applied.
* indicates experiments contain clinopyroxene.
Table 3. Scenarios for selecting the appropriate model for OSAT.

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Model selection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compare 3 models (Eq. 5, Eq. 7 &amp; Eq. 8)</strong></td>
<td></td>
</tr>
<tr>
<td>S1: ( T_{\text{Eq5}} &gt; T_{\text{Eq7}}, T_{\text{Eq5}} &gt; T_{\text{Eq8}} )</td>
<td>Eq.5</td>
</tr>
<tr>
<td>If not S1, apply Z-test:</td>
<td></td>
</tr>
<tr>
<td>( Z_{(\text{Eq5}&amp;\text{Eq7})} &gt; Z_{(\text{Eq5}&amp;\text{Eq8})} &gt; 1.35 )</td>
<td>Eq.7</td>
</tr>
<tr>
<td>( Z_{(\text{Eq5}&amp;\text{Eq8})} &gt; Z_{(\text{Eq5}&amp;\text{Eq7})} &gt; 1.35 )</td>
<td>Eq.8</td>
</tr>
<tr>
<td>( Z_{(\text{Eq5}&amp;\text{Eq8})} &lt; 1.35, \ Z_{(\text{Eq5}&amp;\text{Eq7})} &lt; 1.35 )</td>
<td>Eq.5</td>
</tr>
<tr>
<td>( Z_{(\text{Eq5}&amp;\text{Eq7})} &gt; 1.35 &gt; Z_{(\text{Eq5}&amp;\text{Eq8})} )</td>
<td>Eq.7</td>
</tr>
<tr>
<td>( Z_{(\text{Eq5}&amp;\text{Eq8})} &gt; 1.35 &gt; Z_{(\text{Eq5}&amp;\text{Eq7})} )</td>
<td>Eq.8</td>
</tr>
<tr>
<td><strong>Compare 2 models (Eq. 5 &amp; Eq. 7)</strong></td>
<td></td>
</tr>
<tr>
<td>S2: ( T_{\text{Eq5}} &gt; T_{\text{Eq7}} )</td>
<td>Eq.5</td>
</tr>
<tr>
<td>If not S2, apply Z-test:</td>
<td></td>
</tr>
<tr>
<td>( Z_{(\text{Eq5}&amp;\text{Eq7})} &gt; 1.35 )</td>
<td>Eq.7</td>
</tr>
<tr>
<td>( Z_{(\text{Eq5}&amp;\text{Eq7})} &lt; 1.35 )</td>
<td>Eq.5</td>
</tr>
</tbody>
</table>
Table. 4. Comparison of the temperature estimates of models.

<table>
<thead>
<tr>
<th>Location</th>
<th>Observations</th>
<th>Eq. 5 Min-Max (°C)</th>
<th>Eq. 5 ( T_{\text{cry}} ) (°C)</th>
<th>Eq. 7 Min-Max (°C)</th>
<th>Eq. 7 ( T_{\text{cry}} ) (°C)</th>
<th>Eq. 8 Min-Max (°C)</th>
<th>Eq. 8 ( T_{\text{cry}} ) (°C)</th>
<th>Model of Coogan et al. (2014) Min-Max (°C)</th>
<th>Model of Coogan et al. (2014) ( T_{\text{cry}} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MORB (Siqueiros)</td>
<td>22</td>
<td>1167-1296</td>
<td>1250±7</td>
<td>1096-1260</td>
<td>1197±8</td>
<td>1115-1278</td>
<td>1218±8</td>
<td>1121-1292</td>
<td>1230±59</td>
</tr>
<tr>
<td>Iceland</td>
<td>85</td>
<td>1145-1362</td>
<td>1274±5</td>
<td>1112-1350</td>
<td>1247±8</td>
<td>1169-1345</td>
<td>1264±6</td>
<td>1183-1383</td>
<td>1283±88</td>
</tr>
<tr>
<td>Skye</td>
<td>35</td>
<td>1315-1436</td>
<td>1388±4</td>
<td>1290-1425</td>
<td>1348±4</td>
<td>1307-1436</td>
<td>1376±5</td>
<td>1337-1474</td>
<td>1409±38</td>
</tr>
<tr>
<td>Emeishan</td>
<td>48</td>
<td>1131-1391</td>
<td>1202±6</td>
<td>1061-1361</td>
<td>1145±6</td>
<td>1166-1397</td>
<td>1238±4</td>
<td>1188-1439</td>
<td>1271±35</td>
</tr>
<tr>
<td>Etendeka</td>
<td>62</td>
<td>926-1420</td>
<td>1178±5</td>
<td>1157-1447</td>
<td>1268±5</td>
<td>1178-1455</td>
<td>1295±4</td>
<td>1197-1588</td>
<td>1323±18</td>
</tr>
<tr>
<td>Tortugal</td>
<td>157</td>
<td>1109-1506</td>
<td>1405±5</td>
<td>1191-1471</td>
<td>1389±5</td>
<td>1217-1522</td>
<td>1426±7</td>
<td>1250-1601</td>
<td>1492±59</td>
</tr>
</tbody>
</table>

\( T_{\text{cry}} \) is reported as median value with 95th and 5th percentile quoted.
Table 5. Summary of the posterior distributions of the $T_p$, $\phi_{P_x}$, $\phi_{Hz}$ in the inversion model as a comparison with the results from Matthews et al. (2021).

<table>
<thead>
<tr>
<th>Location</th>
<th>$T_{cry}$ (°C)*</th>
<th>$T_p$ (°C)</th>
<th>$\phi_{P_x}$</th>
<th>$\phi_{Hz}$</th>
<th>$T_p$ (°C)</th>
<th>$\phi_{P_x}$</th>
<th>$\phi_{Hz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MORB</td>
<td>1266±22</td>
<td>1355±24</td>
<td>0.02±0.02</td>
<td>0.34±0.25</td>
<td>1364±22</td>
<td>0.02±0.02</td>
<td>0.40±0.16</td>
</tr>
<tr>
<td>Iceland</td>
<td>1363±24</td>
<td>1518±23</td>
<td>0.08±0.04</td>
<td>0.23±0.18</td>
<td>1525±21</td>
<td>0.08±0.05</td>
<td>0.27±0.16</td>
</tr>
<tr>
<td>Skye</td>
<td>1436±24</td>
<td>1550±80</td>
<td>0.12±0.16</td>
<td>0.51±0.32</td>
<td>1566±73</td>
<td>0.10±0.15</td>
<td>0.47±0.28</td>
</tr>
<tr>
<td>Emeishan</td>
<td>1391±24</td>
<td>1481±87</td>
<td>0.10±0.14</td>
<td>0.53±0.29</td>
<td>1555±100</td>
<td>0.13±0.14</td>
<td>0.55±0.31</td>
</tr>
<tr>
<td>Etendeka</td>
<td>1447±34</td>
<td>1577±106</td>
<td>0.11±0.19</td>
<td>0.53±0.31</td>
<td>1599±104</td>
<td>0.10±0.15</td>
<td>0.51±0.32</td>
</tr>
<tr>
<td>Tortugal</td>
<td>1506±24</td>
<td>1648±193</td>
<td>0.15±0.29</td>
<td>0.50±0.31</td>
<td>1813±157</td>
<td>0.29±0.18</td>
<td>0.45±0.32</td>
</tr>
</tbody>
</table>

* Crystallization temperature used in the inversion model.
Table. A1. Independent compositional, ordering variables and definitions of site mole fractions

\[
\begin{align*}
X_2 &= X_{\text{Mg}^{2+}}^{\text{tet}} + 2X_{\text{Mg}^{2+}}^{\text{oct}} \\
X_3 &= X_{\text{Cr}^{3+}}^{\text{tet}} + X_{\text{Cr}^{3+}}^{\text{oct}} \\
X_4 &= 2X_{\text{Ti}^{4+}}^{\text{oct}} \\
X_5 &= X_{\text{Fe}^{2+}}^{\text{tet}} + 2X_{\text{Fe}^{2+}}^{\text{oct}} \\
s_1 &= X_{\text{Mg}^{2+}}^{\text{tet}} - 2X_{\text{Mg}^{2+}}^{\text{oct}} \\
s_2 &= \frac{2X_{\text{Al}^{3+}}^{\text{oct}} - X_{\text{Al}^{3+}}^{\text{tet}}}{2} \\
s_3 &= \frac{2X_{\text{Cr}^{3+}}^{\text{oct}} - X_{\text{Cr}^{3+}}^{\text{tet}}}{2} \\
s_4 &= \frac{2X_{\text{Fe}^{2+}}^{\text{oct}} - X_{\text{Fe}^{2+}}^{\text{tet}}}{2} \\
X_{\text{Fe}^{2+}}^{\text{tet}} + X_{\text{Fe}^{2+}}^{\text{oct}} + X_{\text{Al}^{3+}}^{\text{tet}} + X_{\text{Cr}^{3+}}^{\text{tet}} + X_{\text{Fe}^{2+}}^{\text{tet}} + X_{\text{Ti}^{4+}}^{\text{oct}} &= 1 \\
X_{\text{Fe}^{2+}}^{\text{tet}} + X_{\text{Fe}^{2+}}^{\text{oct}} + X_{\text{Al}^{3+}}^{\text{tet}} + X_{\text{Cr}^{3+}}^{\text{tet}} + X_{\text{Fe}^{2+}}^{\text{tet}} + X_{\text{Fe}^{3+}}^{\text{oct}} &= 1 \\
X_{\text{Fe}^{2+}}^{\text{tet}} + X_{\text{Fe}^{2+}}^{\text{oct}} + X_{\text{Al}^{3+}}^{\text{tet}} + X_{\text{Cr}^{3+}}^{\text{tet}} + X_{\text{Fe}^{2+}}^{\text{tet}} + X_{\text{Fe}^{3+}}^{\text{oct}} + X_{\text{Ti}^{4+}}^{\text{oct}} &= 1
\end{align*}
\]

\[
\begin{align*}
X_{\text{Mg}^{2+}}^{\text{tet}} &= \frac{X_2 + s_1}{2} \\
X_{\text{Fe}^{2+}}^{\text{tet}} &= X_4 + s_2 + s_3 + s_4 - \frac{X_2 + s_1}{2} \\
X_{\text{Fe}^{2+}}^{\text{oct}} &= X_5 - s_4 \\
X_{\text{Al}^{3+}}^{\text{tet}} &= 1 - X_3 - X_4 - X_5 - s_2 \\
X_{\text{Cr}^{3+}}^{\text{tet}} &= X_3 - s_3 \\
X_{\text{Cr}^{3+}}^{\text{oct}} &= X_2 - s_1 \\
X_{\text{Fe}^{2+}}^{\text{oct}} &= \frac{1 - s_2 - s_3 - s_4}{2} - X_3 - s_1 \\
X_{\text{Fe}^{3+}}^{\text{tet}} &= \frac{X_5 + s_4}{2} \\
X_{\text{Fe}^{3+}}^{\text{oct}} &= \frac{1 - X_3 - X_4 - X_5 + s_2}{2} \\
X_{\text{Al}^{3+}}^{\text{oct}} &= 1 - X_3 - X_4 - X_5 + s_2 \\
X_{\text{Ti}^{4+}}^{\text{oct}} &= X_4 - \frac{s_2}{2}
\end{align*}
\]
Table A2. Coefficients and statistical parameters of regressions for OSAT.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Statistical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Eq. 5</strong></td>
<td></td>
</tr>
<tr>
<td>c0</td>
<td>-0.168</td>
</tr>
<tr>
<td>c1</td>
<td>1.487</td>
</tr>
<tr>
<td>c2</td>
<td>-0.593</td>
</tr>
<tr>
<td>c3</td>
<td>-0.630</td>
</tr>
<tr>
<td>c4</td>
<td>0.390</td>
</tr>
<tr>
<td>c5</td>
<td>0.009</td>
</tr>
<tr>
<td>c6</td>
<td>-2.492</td>
</tr>
<tr>
<td>c7</td>
<td>0.065</td>
</tr>
<tr>
<td>c8</td>
<td>-0.031</td>
</tr>
<tr>
<td>c9</td>
<td>-4.141</td>
</tr>
<tr>
<td>c10</td>
<td>-0.428</td>
</tr>
<tr>
<td>c11</td>
<td>-4.637</td>
</tr>
<tr>
<td>c12</td>
<td>-0.054</td>
</tr>
<tr>
<td>c13</td>
<td>-10.803</td>
</tr>
<tr>
<td>c14</td>
<td>2.714</td>
</tr>
<tr>
<td>b</td>
<td>0.654</td>
</tr>
</tbody>
</table>

| **Eq. 7**    |                        |
| Cr#          | 1.144(0.136)           | $r^2$ | 0.83 |
| ln$K_{DAI}$  | -0.865(0.046)          | SEE   | 44.80 |
| const        | 0.740(0.317)           | RMSE  | 34.40 |
|              |                        | $p$-value | 2.88E-36 |
|              |                        | $r^2_{\text{MCCV}}$ | 42.10 |
|              |                        | SEE_{\text{MCCV}} | 0.92 |
|              |                        | RMSE_{\text{MCCV}} | 43.30 |

| **Eq. 8**    |                        |
| Cr#          | 0.543(0.121)           | $r^2$ | 0.91 |
| ln$K_{DAI}$  | -0.657(0.040)          | SEE   | 31.70 |
| ln$K_{DCr}$  | -0.389(0.041)          | RMSE  | 39.10 |
| const        | 0.049(0.241)           | $p$-value | 3.79E-47 |
|              |                        | $r^2_{\text{MCCV}}$ | 0.94 |
|              |                        | SEE_{\text{MCCV}} | 35.80 |
|              |                        | RMSE_{\text{MCCV}} | 34.20 |

*a number in bracket indicates the 1σ error of coefficients for the linear regression.*