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**A magnetite–clinopyroxene vanadium oxybarometer for  
reconstructing magmatic redox conditions in plutonic rocks**

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## 36 Abstract

37       Reliable reconstruction of primary magmatic oxygen fugacity ( $fO_2$ ) in plutonic systems  
38 remains challenging because most existing oxybarometers either require equilibrium melts or  
39 are restricted to specific mineral assemblages. Here we develop the first melt-independent  
40 vanadium-based magnetite–clinopyroxene (Mt–Cpx) oxybarometer by transferring  
41 experimentally calibrated V partitioning from clinopyroxene–melt and magnetite–melt systems  
42 into an experimentally constrained mineral-pair framework using machine learning. The  
43 framework also yields complementary V-in-Cpx and V-in-Mt oxybarometers for systems in  
44 which equilibrium melts are available or can be independently reconstructed. The calibrated  
45 models accurately reproduce experimental V partitioning and  $fO_2$  over a wide range of  
46 temperatures,  $fO_2$ , and compositions. Model interpretation indicates that V partitioning provides  
47 the primary control on predicted  $fO_2$ , whereas temperature and mineral–melt chemistry mainly  
48 account for equilibrium-related corrections. Independent experimental tests and comparisons  
49 with established mineral-based oxybarometers support the reliability of the models within the  
50 investigated calibration and compositional ranges. Application of the melt-independent V-in-  
51 Mt–Cpx oxybarometer to the Panzhihua intrusion and the Upper Zone of the Bushveld Complex  
52 reveals contrasting redox evolution during magma differentiation. Panzhihua preserves  
53 persistently oxidized conditions ( $\Delta FMQ = +1.29$  to  $+1.99$ ), consistent with redox buffering by  
54 repeated recharge of relatively oxidized magma or carbonate wall rocks assimilation, whereas  
55 the Bushveld Upper Zone records progressive reduction ( $\Delta FMQ = +0.06$  to  $+1.31$ ) associated  
56 with differentiation in a predominantly closed magmatic system. These results establish V  
57 partitioning between magnetite and clinopyroxene as a practical melt-independent proxy for

reconstructing magmatic  $f\text{O}_2$  during magnetite saturation. The method is particularly valuable for oxide-bearing mafic–ultramafic intrusions and hydrous, oxidized arc magmas in which magnetite crystallization is favored. By directly linking magnetite crystallization with magmatic redox evolution, the method offers new opportunities to investigate the coupled evolution of oxygen fugacity, magma differentiation, and open-system processes across diverse magmatic environments.

**Keywords:** mafic-ultramafic intrusions; magma evolution; machine learning; oxygen fugacity; V-in-magnetite–clinopyroxene oxybarometer

## 1. Introduction

Oxygen fugacity ( $f\text{O}_2$ ) is a key thermodynamic parameter that controls the redox state of magmatic systems. It plays a fundamental role in regulating element valence and partitioning, mineral crystallization, sulfide saturation, and metal enrichment (Hirschmann et al. 2012, Namur et al. 2016, Armstrong et al. 2019, Gennaro et al. 2020, Alex and Zajacz 2022, Ge et al. 2023). Layered mafic–ultramafic intrusions, such as the Bushveld Complex and the Panxi intrusions, host major Fe–Ti–V oxide and Cu–Ni–PGE sulfide deposits (Naldrett, 2004, 2011; Zhou et al., 2005; Cawthorn, 2010; Bai et al., 2012). Accurately constraining magmatic  $f\text{O}_2$  and its evolution during crystallization is therefore critical for understanding magma differentiation and associated ore-forming processes (Frost, 1991; Carmichael, 1991; Kress and Carmichael, 1991; Ghiorso and Evans, 2008; Bai et al., 2012). However, the magmatic redox conditions and their evolution in mafic–ultramafic intrusions remain poorly constrained because of methodological limitations.

79 Recently developed Fe-, Ti-, and V-based magnetite–melt oxybarometers require  
80 magnetite to have equilibrated with a melt of known composition ([Arató and Audétat 2017a, b](#),  
81 [Shepherd et al. 2022a](#)). Because equilibrium melts are rarely preserved and are difficult to  
82 reconstruct in plutonic rocks ([Charlier et al. 2015](#)), the application of these oxybarometers to  
83 plutonic rocks remains limited. Magnetite–ilmenite oxybarometer avoids the need for melt  
84 compositions, but typically records the temperature and  $f\text{O}_2$  of the final equilibration between  
85 the two oxides rather than primary magmatic conditions ([Andersen et al. 1993](#), [Ghiorso and](#)  
86 [Evans 2008](#)). The recently developed Eu-in-clinopyroxene–plagioclase oxybarometer offers  
87 another melt-independent approach for redox constraints ([Dygert et al. 2025](#)). Its application,  
88 however, is restricted to rocks that preserve this mineral assemblage and may, for example, be  
89 limited in hydrous and oxidized magmatic systems where plagioclase crystallization is delayed  
90 ([Almeev et al. 2012](#)). Additional mineral-pair oxybarometers based on different redox-sensitive  
91 elements and mineral assemblages are therefore needed to provide complementary constraints  
92 for reconstructing magmatic redox evolution across diverse intrusive systems.

93 Magnetite-clinopyroxene pairs are particularly promising because they commonly coexist  
94 over a broad interval of crystallization in plutonic rocks following oxide saturation. Magnetite  
95 is one of the principal hosts of vanadium and ferric iron in mafic magmas, and its crystallization  
96 not only records but also influences magmatic redox evolution ([Ai et al. 2025](#)). Clinopyroxene  
97 incorporates appreciable amounts of vanadium and is one of the most abundant rock-forming  
98 minerals in plutonic systems. Therefore, the Mt–Cpx pair is a potentially powerful recorder of  
99 magmatic redox evolution. Vanadium provides an attractive basis for developing such an  
100 oxybarometer because its valence state and mineral–melt partitioning behavior vary  
101 systematically with  $f\text{O}_2$  ([Toplis and Corgne 2002](#), [Mallmann and O'Neill 2009, 2013](#), [Davis et](#)

al. 2013, Wang et al. 2019, Leuthold et al. 2023). V partitioning may be less susceptible to subsolidus re-equilibration than Fe–Ti exchange between coexisting oxide pairs and may therefore preserve primary magmatic redox information more effectively (Mallmann and O’Neill 2013, Arató and Audétat 2017a, Sievwright et al. 2020). Unlike the Eu-in-clinopyroxene–plagioclase oxybarometer, which relies on Eu partitioning between silicate minerals, the Mt–Cpx oxybarometer directly utilizes the redox-sensitive behavior of vanadium in magnetite, providing complementary constraints for oxide-bearing mafic magmatic systems.

However, V partitioning between magnetite and clinopyroxene is jointly governed by oxygen fugacity, temperature, melt composition, and mineral chemistry, producing nonlinear relationships that are difficult to capture using conventional empirical calibrations. Machine-learning methods provide an effective framework for resolving these coupled controls and establishing a robust Mt–Cpx oxybarometer from heterogeneous experimental datasets (Zou et al. 2024; Wang et al. 2025).

Here, we develop a machine-learning V-partitioning framework to establish a melt-independent Mt–Cpx oxybarometer. Given the scarcity of paired Mt–Cpx experiments, we first calibrate V partitioning in the Cpx–melt and Mt–melt systems using compiled experimental datasets, and then transfer these relationships to the directly measurable Mt–Cpx pair to construct a melt-independent V-in-Mt–Cpx oxybarometer. The same datasets are also used to derive complementary V-in-Cpx and V-in-Mt oxybarometers for systems with preserved or independently constrained equilibrium melts. Model performance is evaluated against measured mineral–melt partition coefficients, independent experimental  $fO_2$  constraints, and natural samples benchmarked against established V-in-olivine and Eu-in-Cpx–Pl oxybarometers. We further assess the effects of ilmenite exsolution from magnetite and apply

the new calibration to the Panzhihua intrusion and the Upper Zone of the Bushveld Complex to compare redox evolution in Fe–Ti–V-bearing plutonic systems.

## 2. Methods

### 2.1 Theoretical basis and calibration framework of the V-in-Mt–Cpx oxybarometer

Under relatively reducing conditions, V occurs predominantly in lower valence states, particularly  $V^{3+}$ , whereas increasing  $fO_2$  progressively shifts its speciation in silicate melts toward  $V^{4+}$  and  $V^{5+}$ . Because these species differ in their crystal-chemical affinities for minerals and melts, both  $D_V^{Cpx/melt}$  and  $D_V^{Mt/melt}$  decrease systematically with increasing  $fO_2$  (Toplis and Corgne 2002; Sossi et al. 2018; Shepherd et al. 2022a). In clinopyroxene, V is incorporated primarily into the octahedrally coordinated M1 site (McCanta et al. 2004, Mallmann et al. 2009, Wang et al. 2019, Salazar-Naranjo and Vlach 2025), whereas in magnetite it is preferentially accommodated within the octahedral sublattice of the inverse-spinel structure (Arató and Audétat 2017a, Sievwright et al. 2020). Differences in site geometry and charge-balancing mechanisms impart distinct redox sensitivities to V partitioning in the two minerals. Within the compositional and redox ranges represented by the calibration datasets,  $D_V^{Mt/melt}$  decreases more steeply with increasing  $fO_2$  than  $D_V^{Cpx/melt}$  (Toplis and Corgne 2002, Shepherd et al. 2022a), as illustrated by the contrasting regression slopes in Fig. 1a. Consequently, the ratio  $D_V^{Cpx/Mt}$  increases systematically with increasing  $fO_2$  over the common calibration range (Fig. 1b). This differential response provides the crystal-chemical basis for applying Cpx–Mt V partitioning to oxybarometry. Temperature and mineral–melt composition further modulate the absolute partition coefficients and must therefore be incorporated into quantitative calibrations.

Direct calibration of  $D_V^{\text{Cpx/Mt}}$  is limited by the scarcity of experiments reporting reliable V concentrations for both coexisting minerals. By contrast, V partitioning in the Cpx–melt and Mt–melt systems is constrained by substantially larger experimental datasets. We therefore first calibrated forward models for the two mineral–melt systems:

$$\log_{10} D_V^{i/\text{melt}} = F_i(T, \Delta\text{FMQ}, X_i, X_{\text{melt}}), \quad (1)$$

where  $i$  denotes clinopyroxene or magnetite,  $T$  is temperature,  $\Delta\text{FMQ}$  is  $f\text{O}_2$  relative to the fayalite–magnetite–quartz buffer, and  $X_i$  and  $X_{\text{melt}}$  denote the compositions of the mineral and coexisting melt, respectively. The functions  $F_{\text{Cpx}}$  and  $F_{\text{Mt}}$  thus describe the redox dependence of V partitioning while accounting for the associated thermal and compositional controls.

The same datasets were also used to derive inverse mineral–melt oxybarometers:

$$\Delta\text{FMQ} = G_i(T, X_i, X_{\text{melt}}, \log_{10} D_V^{i/\text{melt}}), \quad (2)$$

where  $G_{\text{Cpx}}$  and  $G_{\text{Mt}}$  represent the V-in-Cpx and V-in-Mt oxybarometers, respectively. These inverse calibrations provide complementary estimates of  $f\text{O}_2$  for systems in which the equilibrium melt composition is preserved or can be independently reconstructed, but they are ancillary to the mineral-pair transfer procedure described below.

For clinopyroxene and magnetite that equilibrated with the same silicate melt, the common melt term can be eliminated, such that

$$D_V^{\text{Cpx/Mt}} = \frac{D_V^{\text{Cpx/melt}}}{D_V^{\text{Mt/melt}}}, \quad (3)$$

and, in logarithmic form,

$$\log_{10} D_V^{\text{Cpx/Mt}} = \log_{10} D_V^{\text{Cpx/melt}} - \log_{10} D_V^{\text{Mt/melt}}. \quad (4)$$

Equation (4) allows the two mineral–melt partitioning models to be combined without retaining melt V concentration as an explicit variable. For each experimental Mt–Cpx assemblage,  $F_{\text{Cpx}}$  and  $F_{\text{Mt}}$  were evaluated using the same temperature, imposed  $\Delta\text{FMQ}$ , and melt composition, together with the measured composition of the corresponding mineral. The difference between the two model outputs defines the transferred mineral-pair partition coefficient:

$$\log_{10} \widehat{D_V^{\text{Cpx/Mt}}} = F_{\text{Cpx}}(T, \Delta, \text{FMQ}, X_{\text{Cpx}} X_{\text{melt}}) - F_{\text{Mt}}(T, \Delta, \text{FMQ}, X_{\text{Mt}} X_{\text{melt}}), \quad (5)$$

where the hat denotes a value transferred from the two mineral–melt models rather than calculated from direct V analyses of a coexisting Mt–Cpx pair.

These transferred values were used to calibrate the mineral-pair inverse model:

$$\Delta\text{FMQ} = H(T, X_{\text{Cpx}}, X_{\text{Mt}}, \log_{10} \widehat{D_V^{\text{Cpx/Mt}}}). \quad (6)$$

Because  $\Delta\text{FMQ}$  is an input to the forward models used to generate Eq. (5), the fit of Eq. (6) to the transferred dataset evaluates the internal fidelity of the transfer-and-inversion procedure, rather than providing an independent test of the oxybarometer. This dependence arises from the scarcity of experiments with reliable V measurements in both coexisting minerals. The accuracy of the mineral-pair calibration was therefore evaluated separately using directly measured experimental Mt–Cpx partition coefficients and external comparisons with natural samples, as described in Section 2.4.

Throughout this study, the mineral assemblage is referred to as Mt–Cpx, whereas the partition coefficient is defined in the Cpx/Mt direction because it increases with increasing  $f\text{O}_2$  over the calibration range. During calibration, the partition coefficient supplied to Eq. (6) was

the transferred value from Eq. (5). For experimental validation and application to natural samples, it was calculated directly from measured V concentrations:

$$\log_{10} D_V^{\text{Cpx/Mt}} = \log_{10} \left( \frac{C_V^{\text{Cpx}}}{C_V^{\text{Mt}}} \right). \quad (7)$$

Application of the V-in-Mt–Cpx oxybarometer therefore requires an independent temperature estimate, the major-element compositions of coexisting clinopyroxene and magnetite, and their measured V concentrations. Reconstruction of the equilibrium melt composition is not required. The method assumes that the selected minerals equilibrated with a common melt and subsequently retained their primary inter-mineral V distribution.

## 2.2 Calibrating and validation datasets for V partitioning models

With the aim of constructing a V-in-Mt–Cpx oxybarometer from experimentally constrained V partitioning relationships, we compiled three experimental datasets: a Cpx–melt dataset, a Mt–melt dataset, and a coexisting Mt–Cpx dataset. The Cpx–melt and Mt–melt datasets were used to calibrate forward mineral–melt V partitioning models, whereas the Mt–Cpx dataset was used to construct the transferred mineral-pair oxybarometer. A subset of experiments in which V was measured in both magnetite and clinopyroxene was reserved for independent validation of both the transferred  $D_V^{\text{Cpx/Mt}}$  values and the final V-in-Mt–Cpx oxybarometer. Only experiments with well-constrained temperature,  $f\text{O}_2$ , phase compositions, V concentrations or V partition coefficients, and complete model input variables were retained. The full datasets and original references are provided in [Supplementary Data S1–S3](#).

The Cpx–melt dataset comprises 227 experiments and was used to calibrate the Cpx–melt V partitioning model. It covers temperatures from 835 to 1900 °C and  $f\text{O}_2$  from  $\Delta\text{FMQ} = -4.84$

to +7.19, with melt SiO<sub>2</sub> contents ranging from 41.56 to 73.50 wt.%. The Mt–melt dataset comprises 87 experiments and was used to calibrate the Mt–melt V partitioning model. It covers temperatures from 1068 to 1325 °C and  $f_{O_2}$  from  $\Delta FMQ = -3.83$  to +4.89 with melt SiO<sub>2</sub> contents of 30.84 to 76.80 wt.% and Na<sub>2</sub>O + K<sub>2</sub>O contents of 0 to 8.01 wt.%.

The Mt–Cpx dataset comprises 190 coexisting magnetite–clinopyroxene pairs and was used to construct the transferred V-in-Mt–Cpx oxybarometer. This dataset includes experimental temperatures,  $f_{O_2}$ , clinopyroxene and magnetite major-element compositions, and melt compositional information. Because paired reliable V analyses in both magnetite and clinopyroxene are limited,  $D_V^{Cpx/Mt}$  values for most experiments were derived from the Cpx–melt and Mt–melt forward models using the transfer procedure described below. The Mt–Cpx dataset spans 800–1160 °C and  $\Delta FMQ = -2.47$  to +4.32 with melt SiO<sub>2</sub> contents of 46.64–73.59 wt.% and Na<sub>2</sub>O + K<sub>2</sub>O contents of 2.64–11.91 wt.%.

A subset of eight experiments with measured V concentrations in both magnetite and clinopyroxene was withheld from model training and used for independent validation. These experiments were used in two ways: first, to compare measured and predicted  $\log_{10} D_V^{Cpx/Mt}$ ; and second, to test whether the final V-in-Mt–Cpx oxybarometer can reproduce independently constrained experimental  $f_{O_2}$  ( $\Delta FMQ$ ).

The compositional coverage of the datasets was evaluated using melt total alkali–silica diagrams, magnetite FeO–Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> ternary diagrams, and clinopyroxene Wo–En–Fs diagrams (Fig. 2). These diagrams define the calibration range of the models and provide a basis for assessing extrapolation when the oxybarometers are applied to natural samples.

### 2.3. Machine-learning workflow and model interpretation

All forward partitioning models and inverse  $f\text{O}_2$  models were calibrated using a consistent machine-learning workflow. Seven algorithms were tested: CatBoost, Random Forest, Support Vector Regression (SVR),  $k$ -nearest neighbors (KNN), Decision Tree, multilayer perceptron (MLP), and Elastic Net (Cortes and Vapnik 1995, Breiman 2001, Breiman et al. 2017, Prokhorenkova et al. 2019). For each modeling task, each algorithm was evaluated in 100 repeated runs using independent random 80:20 training–test splits. Random splitting was adopted because the models are intended primarily for interpolation within the pooled temperature, compositional, and redox ranges of the calibration datasets, whereas splitting by experimental study or series may remove entire data domains and therefore primarily test extrapolation. In each run, the training subset was used for model fitting, cross-validation, and grid-search hyperparameter optimization, whereas the test subset was reserved for performance evaluation. Depending on dataset size, either 10-fold or 3-fold cross-validation was applied (Hastie et al. 2009). Model performance was assessed using  $R^2$  and root-mean-square error (Okoye and Hosseini 2024). The best-performing algorithm for each task was selected from its overall performance and stability across the 100 runs and was subsequently used with the optimized hyperparameters to construct the final model.

For scale-sensitive algorithms, such as support vector regression, input variables were standardized using parameters fitted only on the training subset, and the same transformation was then applied to the test subset. Tree-based algorithms, including decision trees, random forests, and CatBoost, were trained using unscaled input variables (Cortes and Vapnik 1995, Breiman 2001, Hastie et al. 2009, Breiman et al. 2017, Prokhorenkova et al. 2019). All preprocessing steps were fitted only on the training data to avoid information leakage.

Because experimental petrology datasets are commonly small, model performance was also tested using different random splits. Final models were selected by jointly considering cross-validation performance, independent test-set performance, stability across random splits, and geochemical interpretability. When several algorithms produced similar statistical performance, preference was given to the model that yielded stable predictions and feature responses consistent with known controls on V partitioning.

Feature-importance and SHAP analyses were used to evaluate the relative influence of input variables on model predictions (Lundberg et al. 2020). SHAP is an interpretability method that shows how each feature contributes to model predictions (Lundberg and Lee 2017). These analyses were used to assess whether the models were mainly controlled by geochemically meaningful variables, especially V partition coefficients, temperature, and phase compositions, rather than by incidental correlations in the datasets. All models were implemented in Python using scikit-learn and CatBoost. The datasets, optimized parameters, and scripts used for model training and prediction are provided in the Supplementary Materials.

## 2.4 Experimental and natural sample validation

The model framework was evaluated through a sequence of partitioning, experimental, and natural-sample tests. First, the transfer from mineral–melt to mineral-pair partitioning was assessed using the eight independent Mt–Cpx experiments in which V was measured in both magnetite and clinopyroxene (Shepherd et al. 2022a). For these experiments, measured  $\log_{10} D_V^{Cpx/Mt}$  values were calculated using Eq. (5) and compared with values predicted by combining the Cpx–melt and Mt–melt forward models using Eq. (3).

The same experiments were then used to test the final V-in-Mt–Cpx oxybarometer. For each experiment,  $\log_{10} D_V^{Cpx/Mt}$  was calculated directly from the measured V concentrations in magnetite and clinopyroxene, and  $fO_2$  was calculated using Eq. (4). The calculated values were compared with the independently constrained experimental  $fO_2$ . This validation provides a direct test of whether the transferred mineral-pair model can reproduce experimental  $fO_2$ , rather than only mineral-pair V partitioning.

For natural samples, crystallization temperatures were estimated using a previously calibrated clinopyroxene thermometer ([Chicchi et al. 2023](#)). These temperatures were used as input parameters for all V-based oxybarometers. For mineral–melt calculations, reconstructed equilibrium melt compositions were used together with clinopyroxene compositions in the temperature calculation, whereas the V-in-Mt–Cpx oxybarometer required only the clinopyroxene-based temperature estimate and measured mineral compositions. Samples yielding temperatures outside the calibration range of the V-partitioning models were excluded from subsequent  $fO_2$  calculations.

Natural sample validation was carried out using independent mineral-based redox constraints. For picrite samples from the Emeishan Large Igneous Province,  $fO_2$  values calculated using the V-in-Cpx oxybarometer were compared with those obtained from a V-in-olivine oxybarometer ([Wang et al. 2025](#)). For mid-ocean-ridge gabbro,  $fO_2$  values calculated using the V-in-Mt–Cpx oxybarometer were compared with estimates from the Eu-in-Cpx–Pl oxybarometer ([Dygert et al. 2025](#)). Published data from the Panzhihua layered intrusion were also used to compare results from the V-in-Cpx, V-in-Mt, and V-in-Mt–Cpx oxybarometers. All natural samples were analyzed following the procedures described in the [Supplementary Methods](#), with the full dataset presented in [Supplementary Data S4](#).

For applications of the mineral–melt inverse models to natural samples, equilibrium melt compositions were constrained before calculating  $fO_2$ . Where quenched melts were unavailable, melt compositions were reconstructed from whole-rock compositions by adding or subtracting olivine components until Fe–Mg exchange equilibrium was reached between the reconstructed melt and the analyzed minerals. For clinopyroxene-based calculations, the reconstructed melt was adjusted to satisfy  $K_D^{Fe-Mg} (Cpx-melt) = 0.27$  (Villiger et al. 2006) whereas for olivine-based reference calculations it was adjusted to satisfy  $K_D^{Fe-Mg} (Ol-melt) = 0.33$  (Toplis 2005). This procedure provides an internally consistent estimate of the melt composition in equilibrium with the analyzed mineral, rather than assuming that the measured whole-rock composition directly represents the equilibrium liquid.

## 2.5 Exsolution sensitivity and application to layered intrusions

The effect of ilmenite exsolution from magnetite on calculated  $fO_2$  was evaluated by mass-balance correction of magnetite compositions. For each oxide or trace element component  $j$ , the pre-exsolution magnetite composition was estimated as:

$$C_0^j = X_{Mt}C_{Mt}^j + X_{Ilm}C_{Ilm}^j \quad (8)$$

where  $C_0^j$  is the reconstructed pre-exsolution composition,  $C_{Mt}^j$  and  $C_{Ilm}^j$  are the compositions of residual magnetite and exsolved ilmenite, and  $X_{Mt}$  and  $X_{Ilm}$  are their modal fractions, with  $X_{Mt} + X_{Ilm} = 1$ . Ilmenite compositions were taken from measured lamellae where available, or from representative published analyses of ilmenite exsolution lamellae in comparable layered mafic intrusions. The range of  $X_{Ilm}$  was chosen to cover observed or petrographically reasonable exsolution proportions.

For each corrected magnetite composition,  $fO_2$  was recalculated using the V-in-Mt–Cpx oxybarometer while keeping clinopyroxene composition and temperature fixed. This procedure isolates the effect of magnetite modification on the recovered  $fO_2$ .

The V-in-Mt–Cpx oxybarometer was then applied to coexisting magnetite and clinopyroxene from the Panzhihua and Bushveld layered intrusions. For each mineral pair,  $\log_{10} D_V^{Mt/Cpx}$  was calculated directly from measured V concentrations, and  $fO_2$  was calculated using measured mineral compositions and clinopyroxene-based temperature estimates. Only texturally associated Mt–Cpx pairs with compositions within, or close to, the experimental calibration range were retained. Analyses showing alteration, secondary replacement, strong exsolution-related disturbance, or anomalous trace-element behavior were excluded. Calculated  $fO_2$  values were grouped by sample and stratigraphic position for comparison between intrusions.

### 3. Results

#### 3.1 Mineral–melt V partitioning models and associated inverse oxybarometers

Among the algorithms calibrated for Cpx–melt V partitioning, CatBoost gives the lowest prediction error (Fig. S1). The selected model closely reproduces experimental  $\log_{10} D_V^{Cpx/melt}$ , with an  $R^2$  of 0.982 and an RMSE of 0.086 log units on the test dataset (Fig. 3a). Predicted values are distributed around the 1:1 line across the calibration range, and residuals remain centered near zero without systematic variation with  $fO_2$  ( $\Delta FMQ$ ) temperature, melt composition, or clinopyroxene composition. Feature importance and SHAP analyses rank  $\Delta FMQ$ , melt  $SiO_2$ , melt  $CaO$ , and clinopyroxene  $Mg\#$  among the principal controls on

$D_V^{\text{Cpx/melt}}$  (Fig. S2a). The SHAP dependence of  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) is negative, showing that more oxidizing conditions generally reduce V partitioning into clinopyroxene. Temperature and compositional variables contribute smaller but systematic effects, consistent with the dependence of Cpx–melt V partitioning on both V valence state and crystal–melt chemistry.

When the Cpx–melt dataset is calibrated in inverse form, CatBoost also yields the most accurate V-in-Cpx oxybarometer (Fig. S1). The model predicts experimental  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) with an  $R^2$  of 0.971 and an RMSE of 0.480  $\Delta\text{FMQ}$  units on the test dataset (Fig. 3b). Most predictions lie close to the 1:1 line, although the largest residuals occur near the reduced and oxidized limits of the calibration range. In the SHAP analysis,  $\log_{10} D_V^{\text{Cpx/melt}}$  is the dominant predictor, followed by temperature and selected melt and clinopyroxene compositional variables (Fig. S2b). The inverse model therefore uses the V partition coefficient as the main redox-sensitive variable: higher  $\log_{10} D_V^{\text{Cpx/melt}}$  corresponds to lower calculated  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ), whereas compositional terms account for variations in clinopyroxene–melt equilibrium. For the collected experimental petrological data, the new V-in-Cpx oxybarometer is likewise based on empirical formulae (Fig. S3).

The Mt–melt forward calibration is best represented by CatBoost (Fig. S1). This model reproduces experimental  $\log_{10} D_V^{\text{Mt/melt}}$  with an  $R^2$  of 0.988 and an RMSE of 0.077 log units on the test dataset (Fig. 4a). It accounts for the large range of magnetite–melt V partition coefficients, including both reduced and oxidized experiments, and residuals show no clear dependence on  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ), melt composition, or magnetite composition. SHAP results identify  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ), magnetite  $\text{TiO}_2$ , Fe components, and melt composition as the main variables controlling  $D_V^{\text{Mt/melt}}$  (Fig. S4a). As in the Cpx–melt model, increasing  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) generally lowers predicted  $D_V^{\text{Mt/melt}}$ , reflecting the lower compatibility of oxidized V species.

The additional influence of Ti and Fe components indicates that spinel solid solution and site occupancy also affect V incorporation into magnetite.

The inverse Mt–melt calibration defines the V-in-Mt oxybarometer, for which CatBoost gives the lowest prediction error (Fig. S1). The model predicts experimental  $fO_2$  with an  $R^2$  of 0.990 and an RMSE of 0.163  $\Delta FMQ$  on the test dataset (Fig. 4b), with slightly less scatter than the V-in-Cpx oxybarometer. Comparative analysis reveals that the V-in-Cpx oxybarometer outperforms the empirical oxybarometers (Fig. S5). SHAP values show that  $\log_{10} D_V^{Mt/melt}$  dominates the prediction, whereas temperature and magnetite compositional variables provide secondary corrections (Fig. S4b). The negative dependence of calculated  $fO_2$  ( $\Delta FMQ$ ) on  $\log_{10} D_V^{Mt/melt}$  is consistent with redox-controlled V partitioning into magnetite. Together, the two forward mineral–melt models provide the quantitative inputs needed to calculate transferred  $\log_{10} D_V^{Cpx/Mt}$ , whereas the V-in-Cpx and V-in-Mt oxybarometers serve as associated mineral–melt reference models for samples with constrained equilibrium melt compositions.

### 3.2 Calibration and feature controls of the transferred V-in-Mt–Cpx oxybarometer

The calibrated Cpx–melt and Mt–melt forward models were coupled to calculate transferred  $\log_{10} D_V^{Cpx/Mt}$  values for the Mt–Cpx experimental dataset. For each experiment, predicted  $\log_{10} D_V^{Mt/melt}$  and  $\log_{10} D_V^{Cpx/melt}$  were combined according to Eq. (3). The resulting transferred partition coefficients span a broad range and vary systematically with experimental  $fO_2$  ( $\Delta FMQ$ ), indicating that the redox dependence captured by the two mineral–melt models is retained after conversion to the mineral-pair form. The transferred Mt–Cpx dataset was then used to calibrate the final V-in-Mt–Cpx oxybarometer. CatBoost gives the best

performance for this model (Fig. S1), predicting experimental  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) with an  $R^2$  of 0.979 and an RMSE of 0.225  $\Delta\text{FMQ}$  units on the test dataset (Fig. 5). Predicted values closely follow the experimental values from reduced to oxidized conditions, and residuals are centered near zero.

SHAP analysis identifies  $\log_{10} D_V^{\text{Cpx/Mt}}$  as the dominant predictor in the final oxybarometer (Fig. 6), indicating that model predictions are governed primarily by the measured inter-mineral V partitioning signal rather than by major-element compositions alone. The next most influential variables are magnetite  $\text{TiO}_2$  and Fe components, followed by clinopyroxene compositional parameters such as CaO and  $\text{Al}_2\text{O}_3$ . These variables provide secondary corrections for crystal-chemical controls on V incorporation into the two minerals.

The dependence of  $f\text{O}_2$  on the Mt–Cpx partitioning term differs from that observed in the mineral–melt inverse oxybarometers. In the V-in-Cpx and V-in-Mt models, higher mineral–melt  $D_V$  values correspond to lower calculated  $f\text{O}_2$ . In contrast, the V-in-Mt–Cpx oxybarometer shows a positive dependence on  $\log_{10} D_V^{\text{Cpx/Mt}}$  (Fig. 6). This behavior reflects the ratio form of  $D_V^{\text{Cpx/Mt}}$ , which records the relative change in V compatibility between magnetite and clinopyroxene as redox conditions vary. To facilitate the practical application of the five models, an online platform has been made available at <https://kcct6hhpfn3h5yzfpzcmqh.streamlit.app/>.

### 3.3 Model validation using experimental and natural samples

The transfer from mineral–melt to mineral-pair partitioning was evaluated independently using eight experiments in which V concentrations were measured in both magnetite and clinopyroxene (Shepherd et al. 2022a). For these experiments, measured  $\log_{10} D_V^{\text{Cpx/Mt}}$  values were calculated directly from the mineral V concentrations and

compared with values predicted by combining the Cpx–melt and Mt–melt forward models. The predicted and measured values are closely matched, with a mean residual of 0.014 log units and no systematic offset across the validation dataset (Fig. 7a). Only 2 experiments show larger deviations, and these deviations remain small relative to the full range of  $\log_{10} D_V^{\text{Cpx/Mt}}$  represented by the calibration data.

The same experiments provide a direct test of the final V-in-Mt–Cpx oxybarometer. Using measured mineral V concentrations to calculate  $\log_{10} D_V^{\text{Cpx/Mt}}$ , the model reproduces independently constrained experimental  $\Delta\text{FMQ}$  values within  $\pm 0.5$  log units for six of the eight experiments (Fig. 7b). The experiment with larger discrepancies does not define a consistent positive or negative offset. Thus, the independent experimental tests support both the transfer of  $D_V^{\text{Cpx/Mt}}$  from mineral–melt partitioning models and the ability of the final mineral-pair oxybarometer to recover experimental redox conditions.

Natural sample comparisons provide an additional assessment of model applicability beyond the calibration experiments. For Emeishan picrite,  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) values calculated using the V-in-Cpx oxybarometer are broadly consistent with those obtained from the V-in-olivine oxybarometer, with an average difference of approximately 0.5  $\Delta\text{FMQ}$  units (Fig. 8a). For mid-ocean-ridge gabbro, the V-in-Mt–Cpx oxybarometer yields  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) values that agree with estimates from the Eu-in-Cpx–Pl oxybarometer within approximately 0.2 log units (Fig. 8b). Published samples from the Panzhihua intrusion also show comparable results among the V-in-Cpx, V-in-Mt, and V-in-Mt–Cpx oxybarometers (Fig. 8c). These comparisons indicate that the V-based models give redox estimates consistent with independent mineral-based oxybarometers in chemically diverse natural systems.

### 3.4 Uncertainty propagation and effect of ilmenite exsolution

Uncertainty associated with transferring the independently calibrated Cpx–melt and Mt–melt V-partitioning models was propagated through the V-in-Mt–Cpx oxybarometer. The corresponding  $1\sigma$  prediction uncertainties are 0.086 and 0.077  $\log_{10}D$  units, respectively (Fig. 3a, 4a). Because the inter-mineral partition coefficient is defined as

$$\log_{10} D_V^{\text{Cpx/Mt}} = \log_{10} D_V^{\text{Cpx/melt}} - \log_{10} D_V^{\text{Mt/melt}},$$

the uncertainty transferred to  $\log_{10} D_V^{\text{Cpx/Mt}}$ , assuming independent prediction errors in the two forward models, is

$$\sigma_{\log_{10} D_V^{\text{Cpx/Mt}}} = \sqrt{(0.077)^2 + (0.086)^2} = 0.115 \log_{10} D.$$

For each of the calibration experiments, the nominal  $\log_{10} D_V^{\text{Cpx/Mt}}$  was perturbed by  $\pm 0.115 \log$  units, and  $fO_2$  was recalculated while temperature and mineral compositions were held constant. The nonlinear response of the inverse model resulted in asymmetric shifts in calculated  $fO_2$  and in 25 experiments the nominal solution was not bracketed by the two perturbed calculations (Fig. S6a, b). The propagated uncertainty for experiment  $i$  was therefore represented by the mean absolute displacement of the perturbed solutions from the nominal result:

$$u_i = \frac{|\Delta FMQ_{i,-1\sigma} - \Delta FMQ_{i,0}| + |\Delta FMQ_{i,+1\sigma} - \Delta FMQ_{i,0}|}{2},$$

where  $\Delta FMQ_{i,0}$  denotes the nominal calculation, and  $\Delta FMQ_{i,-1\sigma}$  and  $\Delta FMQ_{i,+1\sigma}$  denote the results obtained using  $\log_{10} D - 1\sigma$  and  $\log_{10} D + 1\sigma$ , respectively.

The magnitude of  $u_i$  varies across the calibration range, demonstrating that the sensitivity of the oxybarometer to  $D_V^{\text{Cpx/Mt}}$  is not uniform (Fig. S6a). Most experiments yield

relatively small propagated uncertainties, whereas larger values occur locally at intermediate to relatively oxidizing conditions. The distribution is positively skewed, with a median of 0.132  $\Delta\text{FMQ}$  and a root-mean-square uncertainty of

$$u_{\text{RMS}} = \sqrt{\frac{1}{n} \sum_{i=1}^n u_i^2} = 0.227 \Delta\text{FMQ}.$$

Overall, 50% of the experiments have  $u_i < 0.132 \Delta\text{FMQ}$  and 90% have  $u_i < 0.391 \Delta\text{FMQ}$  (Fig. S6c). The RMSE value of approximately  $\pm 0.227 \Delta\text{FMQ}$  is therefore adopted as the representative uncertainty attributable specifically to transfer of the Cpx–melt and Mt–melt partitioning models. Using the nominal partition coefficients, the oxybarometer reproduces the experimental  $f\text{O}_2$  with a mean residual of  $-0.016 \Delta\text{FMQ}$  and a root-mean-square error of  $0.225 \Delta\text{FMQ}$ . If the calibration error and propagated transfer uncertainty are treated as independent, their quadrature combination is

$$\sigma_{\text{combined}} = \sqrt{(0.225)^2 + (0.227)^2} = 0.320 \Delta\text{FMQ}.$$

Accordingly,  $\pm 0.227 \Delta\text{FMQ}$  represents the transfer-specific uncertainty, whereas approximately  $\pm 0.320 \Delta\text{FMQ}$  provides an effective uncertainty for applications within the calibration range.

Mass-balance simulations were used to assess the influence of ilmenite exsolution from magnetite on  $f\text{O}_2$  estimates obtained using the V-in-Mt–Cpx oxybarometer. With increasing assumed exsolution, the mass-balance-corrected magnetite compositions show progressively higher FeO<sub>T</sub> and V contents and lower TiO<sub>2</sub> contents (Fig. S7a). The relative change in V concentration is substantially smaller than the pronounced depletion in TiO<sub>2</sub>, indicating that ilmenite exsolution affects Ti more strongly than V. Despite these pronounced compositional

changes, the calculated  $fO_2$  values remain broadly stable and exhibit no systematic dependence on the extent of exsolution (Fig. S7b). Across the modeled range, the total variation is less than approximately 0.3  $\Delta FMQ$ . These results indicate that ilmenite exsolution has only a limited influence on the redox estimates obtained with the V-in-Mt-Cpx oxybarometer under the simulated conditions. The effect of more extensive exsolution or substantially different ilmenite compositions remains to be evaluated.

### 3.5 Redox estimates for the Panzhihua intrusion and the Upper Zone of the Bushveld Complex

The V-in-Mt-Cpx oxybarometer was applied to coexisting magnetite and clinopyroxene from the Panzhihua intrusion and the Upper Zone of the Bushveld Complex to evaluate redox variations in Fe-Ti-V-bearing plutonic systems, based on published compositional data for Panzhihua (Song et al., 2013; Chen et al., 2017) and Bushveld (Ashwal et al., 2005). Panzhihua samples yield consistently oxidized values, with calculated  $fO_2$  ( $\Delta FMQ$ ) ranging from approximately +1.29 to +1.99 (Fig. 9a). The within-sample variation is generally limited, and calculated  $fO_2$  shows only a weak correlation with clinopyroxene Mg# ( $R^2 = 0.083$ ; Fig. 9c). These results indicate a relatively restricted range of redox conditions recorded by Mt-Cpx pairs in the analyzed Panzhihua samples.

Bushveld samples define a broader range of redox estimates. Calculated  $fO_2$  ( $\Delta FMQ$ ) values range from approximately +0.06 to +1.31 (Fig. 9d), extending to lower  $fO_2$  than the Panzhihua dataset. In contrast to Panzhihua, Bushveld samples show a clearer relationship between  $fO_2$  and clinopyroxene Mg#, with lower Mg# generally associated with lower calculated  $fO_2$  ( $R^2 = 0.773$ ; Fig. 9f). The calculated values also vary more strongly with

stratigraphic position, indicating greater redox heterogeneity within the sampled Bushveld section.

## Discussion

### 4.1 Clinopyroxene–melt V partitioning and the V-in-Cpx oxybarometer

The Cpx–melt calibration confirms that V partitioning into clinopyroxene provides a quantifiable redox signal, but also shows that this signal is modulated by temperature and crystal–melt chemistry. The decrease in  $D_V^{\text{Cpx/melt}}$  with increasing  $fO_2$  is consistent with the multivalent behavior of V in silicate melts (Toplis and Corgne 2002, Mallmann and O'Neill 2009, 2013, Davis et al. 2013, Wang et al. 2019, Leuthold et al. 2023). Under relatively reduced conditions, lower-valence V species, particularly  $V^{3+}$ , are more readily incorporated into the octahedrally coordinated M1 site of clinopyroxene. Oxidation increases the proportions of higher-valence V species that are less compatible with the clinopyroxene structure, thereby decreasing  $D_V^{\text{Cpx/melt}}$  (Toplis and Corgne 2002, Holycross and Cottrell 2022b, Shepherd et al. 2022a). This redox dependence provides the basis for a Cpx–melt V oxybarometer, but the SHAP results indicate that it cannot be treated as a simple one-variable relationship.

In the forward partitioning model,  $fO_2$  dominates the prediction, whereas clinopyroxene  $SiO_2$ ,  $CaO$ ,  $Al_2O_3$ ,  $TiO_2$ , and  $MgO$  and melt  $Al_2O_3$ ,  $SiO_2$ ,  $CaO$ , and  $MgO$  provide smaller compositional corrections (Fig.S2a). The clinopyroxene variables chiefly record variations in quadrilateral and Tschermak-type components that modify M1-site geometry and charge balance (Wang et al. 2019; Holycross and Cottrell 2022b; Shepherd et al. 2022b). In particular, coupled substitutions involving tetrahedral Al and octahedral  $Al^{3+}$  or  $Ti^{4+}$  regulate the

availability of sites suitable for multivalent V (Hill et al. 2000; Wang et al. 2019). Melt SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> control aluminosilicate-network structure and charge balance, whereas CaO and MgO modify melt depolymerization and the activities of clinopyroxene-forming components (Neuvill et al. 2006; Bédard 2010; Shepherd et al. 2022b). Together, these variables influence the activity and coordination of V in the melt and its energetic compatibility with the clinopyroxene lattice. The machine-learning approach captures these nonlinear and coupled effects without prescribing their functional form, unlike conventional regressions in which interactions among  $f\text{O}_2$  and compositional variables must be specified in advance (Higgins et al. 2022, Chicchi et al. 2023, Zou et al. 2024). The dominance of  $f\text{O}_2$  and the subordinate roles of crystal and melt composition are therefore consistent with established controls on Cpx–melt V partitioning and support the geochemical validity of the model.

The inverse V-in-Cpx oxybarometer recovers the redox information encoded in  $D_V^{\text{Cpx/melt}}$  when the equilibrium melt composition is known or independently constrained (Fig. 3b). The dominance of  $\log_{10} D_V^{\text{Cpx/melt}}$  confirms that  $f\text{O}_2$  is predicted primarily from redox-sensitive V partitioning, whereas the remaining variables provide additional constraints on melt structure and clinopyroxene Fe<sup>3+</sup>-bearing components (Fig. S2b). Although Al is not redox-active, its distribution between tetrahedral and octahedral sites (<sup>IV</sup>Al and <sup>VI</sup>Al) is stoichiometrically coupled to Fe<sup>3+</sup>. In structural formulae normalized to six oxygens, <sup>VI</sup>Al is constrained by the tetrahedral Si deficiency, <sup>VI</sup>Al by the remaining Al, and calculated Fe<sup>3+</sup> depends on the overall charge balance involving Si, Al, Na, Ti, Cr, Mg, and total Fe (Droop 1987, Neave et al. 2024). Increasing  $f\text{O}_2$  raises Fe<sup>3+</sup>/ΣFe in the melt and promotes incorporation of Fe<sup>3+</sup> into clinopyroxene, principally through essonite (CaFe<sup>3+</sup>AlSiO<sub>6</sub>) and, in Na-rich compositions, aegirine (NaFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub>) components (Luth and Canil 1993, McCanta et al. 2004,

[Neave et al. 2024](#)) The positive SHAP effects of melt  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  are therefore consistent with greater stabilization of  $\text{Fe}^{3+}$ -bearing clinopyroxene components and higher predicted  $f\text{O}_2$ , whereas the negative effect of clinopyroxene  $\text{SiO}_2$  reflects lower  $^{\text{VI}}\text{Al}$  and reduced capacity for essonite- and Tschermak-type substitutions. Because Na and Al may also enter redox-insensitive jadeite and Ca-Tschermak components, their effects are resolved jointly with  $\text{SiO}_2$  and CaO rather than interpreted independently. Melt  $\text{SiO}_2$ , CaO, and alkalis further correct for changes in melt polymerization and V activity, while temperature accounts for the temperature dependence of V redox and crystal–melt exchange equilibria ([Wang et al. 2019](#); [Shepherd et al. 2022b](#)). The weak clinopyroxene  $\text{K}_2\text{O}$  effect likely reflects covariance with alkali-rich melts rather than direct K–V substitution ([Salazar-Naranjo and Vlach 2025](#)).

The practical applicability of the V-in-Cpx oxybarometer is supported by its comparison with an independent V-in-olivine oxybarometer ([Wang et al. 2025a](#)) for Emeishan picrites ([Fig.8a](#)). The two approaches give broadly consistent  $f\text{O}_2$  estimates, indicating that the clinopyroxene-based model can recover redox conditions in natural mafic systems when the equilibrium melt composition can be reasonably constrained. This comparison is important because it tests the model outside the experimental calibration workflow and against an independent mineral-based redox proxy. The V-in-Cpx oxybarometer is therefore useful for volcanic rocks, melt-inclusion-bearing samples, and natural systems in which equilibrium melts can be estimated with confidence ([Toplis and Corgne 2002](#), [Li 2018](#), [Holycross and Cottrell 2022a](#), [Shepherd et al. 2022a](#)).

Its main limitation is the dependence on melt composition. In plutonic and cumulate rocks, whole-rock compositions may reflect crystal accumulation, trapped liquid, and post-cumulus modification rather than equilibrium liquids ([Holness et al. 2007](#), [Namur et al. 2013](#), [Leuthold](#)

et al. 2014, Charlier et al. 2015). Melt reconstruction can extend the applicability of the model, but it also introduces uncertainty that may be difficult to quantify. The V-in-Cpx oxybarometer is therefore best viewed as a robust mineral–melt reference model and as one experimentally calibrated component of the broader transfer framework, rather than as the primary solution for melt-absent plutonic rocks.

## 4.2 Magnetite–melt V partitioning and the V-in-Mt oxybarometer

Magnetite provides a more sensitive, but also more mineralogically complex, record of V partitioning. As a major host of V in mafic systems, magnetite incorporates V through substitutions in the spinel structure, and its V content responds to both  $fO_2$  and oxide solid solution (Toplis and Corgne 2002, Sossi et al. 2018, Shepherd et al. 2022a). The Mt–melt model captures the expected decrease in  $D_V^{Mt/melt}$  with increasing  $fO_2$  reflecting the lower compatibility of oxidized V species relative to reduced V in magnetite (Toplis and Carroll 1995, Andújar et al. 2016, Sossi et al. 2018, Sievwright et al. 2020).

The SHAP results identify  $fO_2$  and magnetite  $TiO_2$  as the two dominant controls on the forward partitioning model, accounting for 28.73% and 26.85% of the total feature importance, respectively (Fig. S4a).  $fO_2$  primarily controls  $D_V^{Mt/melt}$  by changing V speciation in the melt: reduced conditions increase the proportion of magnetite-compatible  $V^{3+}$ , whereas oxidation produces less compatible  $V^{4+}$  to  $V^{5+}$  species. Magnetite  $TiO_2$  provides an additional crystal-chemical control through solid solution toward ulvöspinel, represented by  $Ti^{4+} + Fe^{2+} \leftrightarrow 2Fe^{3+}$  (Buddington and Lindsley 1964, Backhaus-Ricoult and Dieckmann 1986, Van Orman and Crispin 2010). This substitution changes the  $Fe^{2+}/Fe^{3+}$  ratio, cation distribution, and octahedral-site environment governing V incorporation. Magnetite FeO, MgO, and MnO

further modify  $D_V^{\text{Mt/melt}}$  through substitutions involving  $\text{Fe}^{2+}$  and other divalent cations, thereby changing site dimensions and the activities of V-bearing spinel components (Buddington and Lindsley 1964; Backhaus-Ricoult and Dieckmann 1986; Papike et al. 2015; Sievwright et al. 2017).

Melt  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ , and  $\text{FeO}$  provide corresponding controls on the liquid side of the partitioning reaction (Fig. S4a). Melt  $\text{TiO}_2$  and  $\text{FeO}$  determine the activities of ulvöspinel- and magnetite-forming components and influence both the composition of crystallizing titanomagnetite and the chemical environment of V in the melt.  $\text{MgO}$  and  $\text{K}_2\text{O}$  modify melt polymerization, basicity, and the activity coefficients of V-bearing species. These variables therefore alter the baseline  $D_V^{\text{Mt/melt}}$  at a given  $f\text{O}_2$ , allowing the forward model to distinguish the primary effect of V valence from secondary controls imposed by oxide solid solution and melt composition (Toplis and Corgne, 2002; Arató and Audétat, 2017; Sievwright et al., 2017). Experimental calibrations similarly demonstrate that magnetite–melt V partitioning depends on  $f\text{O}_2$ , temperature, melt chemistry, and magnetite  $\text{TiO}_2$  content (Toplis and Corgne, 2002; Arató and Audétat, 2017).

The inverse V-in-Mt oxybarometer benefits from the strong sensitivity of  $D_V^{\text{Mt/melt}}$  to  $f\text{O}_2$  (Toplis and Corgne 2002; Arató and Audétat 2017a; Sossi et al. 2018; Shepherd et al. 2022a). The dominance of  $\log_{10} D_V^{\text{Mt/melt}}$ , which accounts for 31.56% of the total feature importance, shows that high partition coefficients yield lower predicted  $f\text{O}_2$  because they require a larger proportion of compatible  $\text{V}^{3+}$  (Fig. S4b). The remaining variables determine how this primary partitioning signal is converted into  $f\text{O}_2$ . Their importance is consistent with phase relations in the  $\text{FeO}$ – $\text{Fe}_2\text{O}_3$ – $\text{TiO}_2$  system: at a given temperature, decreasing  $f\text{O}_2$  stabilizes ulvöspinel-rich, Ti-rich magnetite, whereas increasing  $f\text{O}_2$  favors more magnetite-rich, Ti-poor

compositions. This relationship arises from the coupled substitution  $\text{Ti}^{4+} + \text{Fe}^{2+} \leftrightarrow 2\text{Fe}^{3+}$ , through which increasing  $\text{TiO}_2$  lowers the ferric-iron proportion of titanomagnetite (Buddington and Lindsley 1964, Backhaus-Ricoult and Dieckmann 1986, Van Orman and Crispin 2010). Magnetite  $\text{TiO}_2$  therefore records both crystal-chemical and redox controls. Magnetite  $\text{FeO}$  shows the broadly opposite effect because higher total  $\text{FeO}$  generally characterizes more Ti-poor compositions along the magnetite–ulvöspinel solid solution (Buddington and Lindsley 1964). Magnetite  $\text{Cr}_2\text{O}_3$  and  $\text{MgO}$  produce smaller positive corrections:  $\text{Cr}^{3+}$  occupies the same octahedral sublattice as  $\text{V}^{3+}$ , whereas  $\text{Mg}^{2+}$  substitutes for  $\text{Fe}^{2+}$  and modifies cation inversion and charge balance. Their SHAP responses indicate that these substitutions increase the non-redox baseline of V compatibility within the calibration range, requiring a more oxidized prediction to reproduce a fixed  $D_V^{\text{Mt/melt}}$  (Papike et al. 2015). Thus, the inverse model uses magnetite and melt compositions to determine how much of the measured V-partitioning signal reflects redox conditions rather than phase composition alone.

The practical utility of the V-in-Mt oxybarometer is supported by its consistency with the V-in-Cpx and V-in-Mt–Cpx models in the Panzhihua dataset (Fig.8c). Although this comparison is not as independent as the experimental Mt–Cpx validation, it provides a useful natural sample check because the three oxybarometers use different input structures: Cpx–melt, Mt–melt, and Mt–Cpx. Their broadly comparable results suggest that the V-in-Mt model can yield realistic redox estimates in natural Fe–Ti–V-bearing systems when magnetite compositions are well preserved and equilibrium melt compositions are reasonably constrained.

For plutonic rocks, however, the same limitations that affect another mineral–melt oxybarometers remain. Equilibrium melts are rarely preserved, and reconstructed melt compositions may be uncertain in cumulate systems. Magnetite also requires additional caution

because it can be modified by ilmenite exsolution, oxidation, alteration, and subsolidus re-equilibration (Wei et al. 2020, Brzozowski et al. 2021, Hou et al. 2021, Wang et al. 2025b). Our exsolution calculations indicate that moderate ilmenite exsolution generally introduces deviations smaller than the propagated uncertainty of the V-in-Mt–Cpx oxybarometer, although petrographic screening remains essential. Magnetite grains showing extensive exsolution, alteration, or compositional heterogeneity should not be regarded as preserving primary magmatic compositions. In this study, the Mt–melt calibration therefore serves two roles: it provides a standalone mineral–melt oxybarometer for suitable samples, and more importantly, it supplies the magnetite-side partitioning term required to construct the melt-independent Mt–Cpx model.

#### 4.3 Transfer of V partitioning to a melt-independent Mt–Cpx oxybarometer

The V-in-Mt–Cpx oxybarometer transfers the experimentally calibrated V– $f\text{O}_2$  relationship from mineral–melt systems to a directly measurable mineral-pair framework. When Mt, Cpx, and melt are in equilibrium, the inter-mineral V partition coefficient can be expressed as:

$$D_V^{\text{Cpx/Mt}} = \frac{D_V^{\text{Cpx/melt}}}{D_V^{\text{Mt/melt}}}$$

This formulation eliminates the explicit melt term, allowing the redox information originally recorded by Mt/Cpx–melt partitioning to be inherited by the coexisting Mt–Cpx assemblage (Mallmann and O'Neill 2009, Papike et al. 2013, Holycross and Cottrell 2022b, Shepherd et al. 2022b, Dygert et al. 2025). The resulting oxybarometer therefore retains the experimental basis of V partitioning while avoiding the need to reconstruct equilibrium melt compositions in natural cumulates.

This framework differs from a purely empirical mineral-pair regression in several ways. First, the transferred variable is grounded in mineral–melt partitioning relationships that have explicit experimental redox dependence (Mallmann and O’Neill 2009, Shepherd et al. 2022b). Second, the machine-learning calibration allows the final oxybarometer to account for nonlinear effects of temperature and mineral chemistry, rather than forcing the data into a prescribed linear or polynomial form (Zou et al. 2024; Wang et al. 2025). Third, the final V-in-Mt–Cpx model removes the most problematic input for plutonic rocks: equilibrium melt composition. The model therefore retains the experimental basis of mineral–melt V partitioning while replacing melt-dependent inputs with directly measured mineral compositions and  $C_V^{Cpx}/C_V^{Mt}$ .

The SHAP feature hierarchy closely mirrors the established geochemical controls on V partitioning (Fig. 6). The dominant importance of  $\log_{10} D_V^{Mt/Cpx}$  reflects the fact that inter-mineral V partitioning carries the primary redox signal. Because V is multivalent, changes in  $fO_2$  systematically modify its valence state and thus its relative compatibility between magnetite and clinopyroxene (Toplis and Corgne, 2002; Mallmann and O’Neill, 2009; Leuthold et al., 2023). Consequently, the model derives most of its predictive power from the experimentally constrained response of  $D_V^{Mt/Cpx}$  to  $fO_2$  rather than empirical correlations among major elements. The remaining predictors mainly account for crystal-chemical effects on V partitioning. Magnetite FeO is the most influential compositional variable because it reflects  $Fe^{2+}$ – $Fe^{3+}$  systematics and spinel stoichiometry, both of which govern charge balance and V incorporation (Buddington and Lindsley 1964, Backhaus-Ricoult and Dieckmann 1986, Van Orman and Crispin 2010). Magnetite  $Al_2O_3$  and MgO, together with clinopyroxene  $Al_2O_3$ , MgO, and CaO, reflect variations in spinel solid solution, Tschermak substitution, and cation site

occupancy that modify V compatibility in the two minerals ([Papike 2005](#), [Shepherd et al. 2022a](#))  
Rather than directly recording  $f\text{O}_2$ , these variables constrain the crystal-chemical environment  
in which V partitioning occurs, allowing the model to isolate the redox signal carried by  
 $D_V^{\text{Cpx/Mt}}$ .

The generalizability of the V-in-Mt–Cpx oxybarometer is supported at three levels.  
Statistical generalization is indicated by cross-validation and repeated train–test splits, which  
show that model performance is not tied to a single partition of the experimental data.  
Experimental generalization is provided by paired Mt–Cpx experiments with measured V in  
both minerals. In these experiments, predicted and measured  $D_V^{\text{Mt/Cpx}}$  agree closely, and the  
final oxybarometer reproduces independently constrained  $\Delta\text{FMQ}$  for most experiments within  
uncertainty. Petrological generalization is indicated by natural-sample comparisons with  
independent mineral-based oxybarometers, including V-in-olivine and Eu-in-Cpx–Pl  
approaches. These tests are critical because high accuracy on a calibration dataset alone would  
not demonstrate that the model can be applied to natural intrusive rocks.

The natural-sample tests also clarify the practical niche of the Mt–Cpx oxybarometer. Its  
agreement with the Eu-in-Cpx–Pl oxybarometer ([Dygert et al. 2025](#)) in mid-ocean-ridge  
gabbro’s supports its use in melt-absent plutonic rocks where independent mineral-pair redox  
constraints are available. Its consistency with the V-in-Cpx and V-in-Mt models in Panzhihua  
further suggests that the transferred mineral-pair model can recover redox conditions  
comparable to those obtained from mineral–melt approaches, while avoiding the need to specify  
an equilibrium melt. This is the main practical advantage of the model: it converts  
experimentally calibrated mineral–melt V partitioning into a form that can be applied directly  
to coexisting minerals in cumulate rocks.

The model nevertheless has defined application limits. It should be applied to texturally associated magnetite–clinopyroxene pairs that plausibly crystallized from, or equilibrated with, the same melt domain (Papike et al. 2013). Reliable temperature estimates are required, and samples should lie within or near the experimental calibration range in terms of temperature and mineral composition. Accurate determination of V concentrations in both minerals is essential because  $D_V^{\text{Mt/Cpx}}$  is the dominant predictor of the V-in-Mt–Cpx oxybarometer (Fig. 6). Mineral pairs affected by extensive alteration, secondary oxidation of magnetite, or lacking petrographic evidence for equilibrium should be excluded. Finally, SHAP analyses are intended to aid geochemical interpretation of the calibrated models rather than establish causal relationships; they evaluate whether model responses are consistent with current geochemical understanding but should always be interpreted alongside petrographic observations and experimental constraints.

Within these boundaries, the V-in-Mt–Cpx oxybarometer provides a practical advantage over both conventional Fe–Ti oxide oxybarometry and mineral–melt V oxybarometers. Fe–Ti oxide equilibria may be reset during cooling and can record late subsolidus conditions rather than magmatic  $f\text{O}_2$  (Lattard et al. 2012, Loucks et al. 2018, Hou et al. 2021). Mineral–melt oxybarometers retain direct experimental meaning but require melt compositions that are often unavailable in plutonic rocks (Arató and Audétat 2017b, a, Shepherd et al. 2022b, Dygert et al. 2025). The Mt–Cpx V partitioning approach occupies the middle ground: it uses an experimentally transferred partitioning framework, but its final inputs are mineral-based. This makes it especially useful for layered intrusions and other cumulate systems in which magmatic redox information must be extracted from preserved minerals rather than from melts (Charlier et al. 2015, Dygert et al. 2025).

#### 4.4 Redox characteristics of the Panzhihua intrusion and the Upper Zone of the Bushveld Complex

Application of the V-in-Mt-Cpx oxybarometer to the Panzhihua layered intrusion and Bushveld complex reveals two contrasting redox evolution paths in deep seated mafic-ultramafic magmatic systems. The Panzhihua drill core spans the Lower, Middle, and Upper Zones and records the principal Fe-Ti oxide mineralization framework of the intrusion (Song et al. 2013, Chen et al. 2017), whereas the Bushveld Bellevue drill core covers key intervals of the Upper Zones with continuous lithological, stratigraphic, and mineral-chemical constraints (Ashwal et al. 2005).

In the Upper Zone of the Bushveld Complex, calculated  $fO_2$  decreases systematically with declining Cpx Mg# and increasing stratigraphic height (Fig. 9f), indicating progressive reduction during magmatic differentiation. This pattern is consistent with prolonged fractional crystallization as the dominant control on Upper Zone evolution, locally modified by magma recharge and mixing, interstitial melt percolation, and cyclic magmatic processes. (Tegner et al. 2006; Namur et al. 2013; VanTongeren and Mathez 2012, Mangwegape et al. 2016). It also agrees in direction with previous Bushveld Upper Zone redox estimates based on Fe in plagioclase and Fe-Ti oxide constraints, which suggest  $fO_2$  near or below the FMQ buffer and, in some cases, progressive reduction during differentiation (Reynolds 1985, Tegner and Cawthorn 2010). In a relatively closed or weakly replenished system, continued Fe-Ti oxide crystallization may preferentially remove ferric iron from the melt, thereby lowering melt  $Fe^{3+}/\Sigma Fe$  and driving  $fO_2$  toward more reduced conditions during differentiation of the Bushveld Upper Zone (Brounce et al. 2014, Ai et al. 2025). The V-in-Mt-Cpx results therefore support

a differentiation-dominated redox trajectory for Bushveld, with intermittent open-system processes superimposed on a broadly evolving residual melt.

Panzhihua records a contrasting redox evolution. Calculated  $fO_2$  values remain consistently high, ranging from approximately +1.4 to +1.9  $\Delta FMQ$ , throughout the drill core despite extensive Fe–Ti oxide crystallization and accumulation (Fig. 9b). These oxidation states agree well with independent estimates for the parental high-Ti picritic magmas of the ELIP (Cao and Wang 2022, Bai et al. 2026), indicating that the calculated  $fO_2$  values are geologically realistic and preserve the primary redox state of the parental magma. If oxide fractionation alone governed magma redox evolution, sustained magnetite crystallization would progressively remove  $Fe^{3+}$  from the melt, decrease the melt  $Fe^{3+}/\Sigma Fe$  ratio, and drive  $fO_2$  toward lower values during differentiation. Instead, Panzhihua shows little systematic decrease in  $fO_2$  with decreasing Cpx Mg# or stratigraphic height (Fig. 9a, c), implying that differentiation-driven reduction was counteracted during oxide accumulation. The most consistent explanation is repeated recharge by relatively oxidized, Fe–Ti-rich magma. Reversals in augite Mg#, cyclic lithological variations, and the spatial association between cyclic units and massive Fe–Ti oxide layers have been interpreted as evidence for repeated replenishment and in situ Fe–Ti oxide crystallization (Song et al. 2013; Luan et al. 2014; Bai et al. 2021; Wang et al. 2023). Recharge of relatively oxidized primitive magma was therefore likely the important mechanism buffering the chamber against the redox decrease expected from progressive magnetite crystallization. Assimilation of the surrounding dolomitic carbonate wall rocks may have provided another oxidizing contribution. Carbonate breakdown introduces oxidized carbon species, principally  $CO_2$ , into the magma; reduction of this carbon to CO or graphite can be coupled with oxidation of  $Fe^{2+}$  to  $Fe^{3+}$ , thereby increasing the melt  $Fe^{3+}/\Sigma Fe$  ratio and buffering  $fO_2$  at relatively high

values (Ganino et al. 2008, 2013). These processes provide a plausible explanation for the persistently elevated  $fO_2$  recorded during magma differentiation.

Together, the Upper Zone of the Bushveld Complex and the Panzhihua intrusion show that redox evolution in layered intrusions reflects the balance between differentiation driven reduction and processes that sustain relatively oxidized conditions, rather than the effects of oxide crystallization alone. In the Bushveld Complex, the V-in-Mt–Cpx results are consistent with a comparatively closed system dominated by progressive magmatic differentiation. By contrast, the persistently high  $fO_2$  recorded at Panzhihua indicates that continued redox buffering accompanied oxide crystallization. This buffering may have been maintained by repeated replenishment with relatively oxidized magma, and/or assimilation of the surrounding carbonate wall rocks. The contrasting redox histories of the Bushveld Upper Zone and the Panzhihua intrusion demonstrate that  $fO_2$  evolution in layered intrusions reflects the combined effects of internal differentiation and external magma-system processes, such as repeated magma recharge, wall-rock assimilation, and other forms of open-system evolution. These observations emphasize that reconstructing magmatic redox evolution requires proxies capable of tracking  $fO_2$  throughout magma differentiation rather than simply recording isolated equilibrium conditions.

#### **4.5 Broader implications of Mt–Cpx oxybarometry for oxide-bearing magmatic systems**

The observations presented above underscore the need for redox proxies that can constrain  $fO_2$  across different stages of magma differentiation, rather than providing only a single snapshot of crystallization conditions. This is particularly important in oxide-bearing magmatic systems, where the onset and progressive crystallization of magnetite are closely associated

with the redistribution of multivalent elements and the evolving redox state of the residual melt. Resolving such changes is essential for reconstructing the broader redox trajectory of differentiating magmas.

A principal advantage of the Mt–Cpx oxybarometer lies in its use of the redox-sensitive partitioning of V between magnetite and clinopyroxene. Magnetite serves both as a recorder of magmatic redox conditions and as an active participant in their evolution. Its composition and element-partitioning relationships preserve information on crystallization conditions, while its growth redistributes  $\text{Fe}^{3+}$ , V, and other multivalent elements between crystals and melt. Magnetite crystallization therefore provides an important link among oxide saturation, element partitioning, and magmatic redox evolution. Where texturally constrained Mt–Cpx pairs from successive crystallization stages are preserved, the resulting ( $f\text{O}_2$ ) estimates may be placed within a broader petrogenetic sequence involving oxide saturation, crystal accumulation, and magma differentiation. This approach is especially valuable for magnetite-bearing intrusions, in which oxide crystallization commonly represents a major stage of magmatic evolution.

The Mt–Cpx oxybarometer also extends melt-independent mineral-pair oxybarometry to assemblages in which plagioclase is absent, delayed, or poorly preserved. It may therefore be particularly useful in hydrous and relatively oxidized basaltic systems, where high  $\text{H}_2\text{O}$  contents can postpone plagioclase saturation (Almeev et al. 2012), whereas oxidizing conditions favor magnetite stability. In such settings, Mt–Cpx pairs may preserve redox information that is difficult to recover using plagioclase-dependent oxybarometers. More broadly, the method complements existing mineral-pair redox proxies and, when integrated with textural, mineral-chemical, isotopic, and whole-rock geochemical evidence, can provide an independent redox

framework for evaluating the roles of magma differentiation, oxide saturation, magma recharge, and crustal assimilation in complex magmatic systems.

## Conclusions

A new melt-independent, V-based magnetite–clinopyroxene oxybarometer was developed by transferring experimentally calibrated V-partitioning relationships for clinopyroxene–melt and magnetite–melt equilibria to coexisting Mt–Cpx pairs. Validation against independent experimental datasets indicate that the V-in-Mt–Cpx oxybarometer provides reliable  $fO_2$  estimates across broad ranges of temperature, redox conditions, and mineral composition. By avoiding reconstruction of an equilibrium melt, the method extends V-based oxybarometry to plutonic systems where melts are rarely preserved. More importantly, because magnetite is both a sensitive recorder of and an active participant in magmatic redox evolution, the Mt–Cpx oxybarometer is particularly suited to tracing  $fO_2$  from magnetite saturation through subsequent oxide crystallization.

Application of the new oxybarometer to the Panzhihua layered intrusions and the Upper Zone of the Bushveld Complex reveals contrasting redox trajectories during magma differentiation. The Bushveld Upper Zone records progressive reduction during magma differentiation, whereas the Panzhihua intrusion remained relatively oxidized despite extensive Fe–Ti oxide crystallization. The persistently high  $fO_2$  values at Panzhihua are consistent with repeated recharge by relatively oxidized magma, assimilation of carbonate wall rocks, or a combination of these open-system processes. These contrasting redox histories indicate that redox evolution in layered intrusions reflects the interplay between magma differentiation and open-system processes.

The Mt-Cpx oxybarometer complements existing mineral-pair oxybarometers and is particularly valuable for oxide-bearing mafic–ultramafic intrusions and hydrous, oxidized arc magmas where suitable alternative mineral assemblages may be absent. More broadly, the new calibration provides a practical framework for investigating the coupled evolution of  $f\text{O}_2$ , magma differentiation, and open-system processes across diverse magmatic environments.

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## Data availability

The data supporting this study are provided in the online Supplementary Materials and have also been deposited in Mendeley Data (doi: [10.17632/yy4yj324xf.1](https://doi.org/10.17632/yy4yj324xf.1)). Supplementary Data S1–S3 contain the experimental datasets used for model calibration, whereas Supplementary Data S4 contains the natural-sample data used for validation and application, including new geochemical data generated in this study. The source code used for model training, validation, and prediction is archived in the same repository. The oxybarometers developed in this study are also available through an interactive web application at <https://kcct6hhpf3h5yzfpzcmqh.streamlit.app/>.

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## 1112 Figure captions

1113 **Fig. 1. Redox dependence of vanadium partitioning between clinopyroxene, magnetite,**  
1114 **and silicate melt. (a)** Experimental vanadium mineral–melt partition coefficients for  
1115 clinopyroxene–melt ( $D_V^{\text{Cpx/melt}}$ ) and magnetite–melt ( $D_V^{\text{Mt/melt}}$ ) plotted as a function of oxygen  
1116 fugacity relative to the fayalite–magnetite–quartz buffer,  $\Delta\text{FMQ}$ . Both partition coefficients  
1117 decrease with increasing  $f\text{O}_2$ , reflecting the progressive shift of V from lower-valence species,  
1118 particularly  $\text{V}^{3+}$ , toward  $\text{V}^{4+}$  and  $\text{V}^{5+}$  in silicate melts. The steeper decrease in  $D_V^{\text{Mt/melt}}$  relative  
1119 to  $D_V^{\text{Cpx/melt}}$  reflects differences in crystal-chemical incorporation and charge-balancing  
1120 mechanisms between the octahedral sites of clinopyroxene and magnetite. Solid lines show  
1121 linear regressions, and shaded envelopes denote 95% bootstrap confidence intervals. **(b)** Model-  
1122 derived clinopyroxene–magnetite partitioning, calculated as  $\log_{10} D_V^{\text{Cpx/Mt}} =$

1123  $\log_{10}D_V^{\text{Cpx/melt}} - \log_{10}D_V^{\text{Mt/melt}}$ , over the common  $f\text{O}_2$  range of the two calibration datasets.  
 1124 The increase in  $D_V^{\text{Cpx/Mt}}$  with increasing  $f\text{O}_2$  provides the crystal-chemical basis for applying  
 1125 Cpx–Mt V partitioning as an oxybarometer. The shaded envelope represents the propagated 95%  
 1126 bootstrap confidence interval. Cpx, clinopyroxene; Mt, magnetite; FMQ, fayalite–magnetite–  
 1127 quartz buffer.

1128 **Alt text:** Two-panel plots showing that vanadium partition coefficients for  
 1129 clinopyroxene–melt and magnetite–melt decrease with increasing oxygen fugacity ( $\Delta\text{FMQ}$ ),  
 1130 whereas the model-derived clinopyroxene–magnetite partition coefficient increases with  
 1131  $\Delta\text{FMQ}$ . Regression lines and confidence envelopes illustrate these opposing redox trends.

1132 **Fig. 2. Compositional distribution of the three experimental datasets in melt, magnetite,**  
 1133 **and clinopyroxene compositional spaces.** (a) Total alkali–silica (TAS) diagram for melt  
 1134 compositions, showing  $\text{SiO}_2$  versus  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ . (b)  $\text{FeO}$ – $\text{Fe}_2\text{O}_3$ – $\text{TiO}_2$  ternary diagram for  
 1135 magnetite compositions, with major oxide end-member fields indicated. (c) Wo–En–Fs ternary  
 1136 diagram for clinopyroxene compositions. Purple circles, coral squares, and cyan triangles  
 1137 represent the Cpx–Melt, Mt–Melt, and Cpx–Mt datasets, respectively.

1138 **Alt text:** Three compositional diagrams showing the coverage of the clinopyroxene–  
 1139 melt, magnetite–melt, and clinopyroxene–magnetite experimental datasets: a melt total alkali–  
 1140 silica diagram, a magnetite  $\text{FeO}$ – $\text{Fe}_2\text{O}_3$ – $\text{TiO}_2$  ternary diagram, and a clinopyroxene Wo–En–Fs  
 1141 ternary diagram.

1142 **Fig. 3. Predictive performance of the clinopyroxene and melt vanadium partitioning**  
 1143 **model and the V-in-clinopyroxene oxybarometer.** (a) Predicted versus observed  $\log D_V$   
 1144 values for the clinopyroxene and melt partitioning model. (b) Predicted versus observed  $f\text{O}_2$ ,  
 1145 expressed as  $\Delta\text{FMQ}$ , for the V in clinopyroxene oxybarometer. Blue and orange symbols

represent the training and test datasets, respectively. Red dashed lines indicate the 1:1 relationship, whereas black dashed lines show deviations of  $\pm 0.2$  log units in panel (a) and  $\pm 0.5$   $\Delta$ FMQ in panel (b). Model performance is summarized by the reported  $R^2$  and root mean square error values.

**Alt text:** Two predicted-versus-observed plots evaluating the clinopyroxene–melt vanadium partitioning model and the V-in-clinopyroxene oxybarometer. Training and test data cluster near the 1:1 line for both partition coefficients and calculated oxygen fugacity ( $\Delta$ FMQ).

**Fig. 4. Predictive performance of the magnetite and melt vanadium partitioning model and the V in magnetite oxybarometer.** (a) Comparison between predicted and observed  $\log D_V$  values for vanadium partitioning between magnetite and melt. (b) Comparison between predicted and observed  $fO_2$  ( $\Delta$ FMQ) values obtained using the V in magnetite oxybarometer. Blue and red symbols represent the training and test datasets, respectively. Red dashed lines indicate the 1:1 relationship, and black dashed lines delimit deviations of  $\pm 0.2$  log units in panel (a) and  $\pm 0.5$   $\Delta$ FMQ in panel (b). The corresponding  $R^2$  and root mean square error values are shown in each panel.

**Alt text:** Two predicted-versus-observed plots evaluating the magnetite–melt vanadium partitioning model and the V-in-magnetite oxybarometer. Training and test data lie close to the 1:1 line for both vanadium partitioning and calculated oxygen fugacity ( $\Delta$ FMQ).

**Fig. 5. Predictive performance of the V in clinopyroxene and magnetite oxybarometer.** Predicted  $\Delta$ FMQ values are plotted against the corresponding observed values for the training and test datasets. Purple and pink symbols represent training and test data, respectively. The red dashed line indicates the 1:1 relationship, whereas the black dashed lines define deviations of  $\pm 0.5$   $\Delta$ FMQ. The model yields  $R^2 = 0.979$  and a root mean square error of 0.225  $\Delta$ FMQ

**Alt text:** Predicted versus observed oxygen fugacity ( $\Delta\text{FMQ}$ ) for the V-in-clinopyroxene–magnetite oxybarometer. Training and test data closely follow the 1:1 relationship, with most predictions within  $\pm 0.5$   $\Delta\text{FMQ}$  and an overall RMSE of 0.225  $\Delta\text{FMQ}$ .

**Fig. 6. Feature importance and SHAP analysis of the top ten variables in the V in clinopyroxene and magnetite oxybarometer.** The bar plot shows the normalized importance of the ten most influential model variables, and the accompanying SHAP distributions show the direction and magnitude of their contributions to predicted  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ). Colors represent feature values from low in blue to high in pink. The vanadium partition coefficient provides the largest contribution to model predictions, followed by magnetite FeO and clinopyroxene  $\text{Al}_2\text{O}_3$  with additional contributions from the major element compositions of both minerals.

**Alt text:** Feature-importance bar chart and SHAP summary plot for the V-in-clinopyroxene–magnetite oxybarometer. The inter-mineral vanadium partition coefficient is the dominant predictor of  $\Delta\text{FMQ}$ , followed by magnetite FeO and clinopyroxene  $\text{Al}_2\text{O}_3$ , with other mineral major-element variables contributing smaller effects.

**Fig. 7. Evaluation of the V in clinopyroxene and magnetite oxybarometer using paired mineral data (Shepherd et al. 2022a).** (a) Comparison between observed and predicted magnetite to clinopyroxene vanadium partition coefficients. Open circles represent individual samples connected by dashed lines, whereas diamonds and error bars summarize the mean and standard deviation of the observed and predicted datasets. (b) Comparison between predicted and independently constrained  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) values. The dark dashed line indicates the 1:1 relationship, and the lighter lines represent deviations of  $\pm 0.5$   $\Delta\text{FMQ}$  error bars show the uncertainties associated with individual estimates.

**Alt text:** Two validation plots using independent paired magnetite–clinopyroxene data. Predicted inter-mineral vanadium partition coefficients closely match observed values, and oxybarometer-derived  $\Delta\text{FMQ}$  values generally agree with independently constrained experimental oxygen fugacities near the 1:1 relationship.

**Fig. 8. Validation of V partitioning oxybarometers using natural samples.** (a) Comparison of  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) values calculated using the V in clinopyroxene and V in olivine oxybarometers for samples from Dali and Lijiang. (b) Comparison of results from the Eu in clinopyroxene and plagioclase and V in clinopyroxene and magnetite oxybarometers for samples 206R 3 W and 238R 2 W. In panels (a) and (b), the dark dashed line represents the 1:1 relationship, lighter lines indicate deviations of  $\pm 0.5 \Delta\text{FMQ}$ , and error bars show the associated uncertainties. (c) Distributions of  $\Delta\text{FMQ}$  estimates for the Panzhihua intrusion calculated using three V-based oxybarometers, based on data from [Song et al. \(2013\)](#) and [Chen et al. \(2017\)](#). Violin envelopes show data density, individual symbols represent calculated values, and the internal boxes summarize the central distribution.

**Alt text:** Three-panel validation of vanadium-based oxybarometers using natural samples. Panels compare V-in-clinopyroxene with V-in-olivine estimates, V-in-clinopyroxene–magnetite with Eu-in-clinopyroxene–plagioclase estimates, and the distributions of three V-based oxybarometers for the Panzhihua intrusion.

**Fig. 9. Stratigraphic variations in  $f\text{O}_2$ , Fe and Ti oxide abundance, and clinopyroxene Mg number in the Panzhihua and Bushveld layered intrusions.** (a) Variation in  $f\text{O}_2$  ( $\Delta\text{FMQ}$ ) with height above the basal contact in the Panzhihua intrusion based on data from [Song et al. \(2013\)](#) and [Chen et al. \(2017\)](#). (b) Stratigraphic variation in the modal abundance of Fe and Ti oxides in Panzhihua. (c) Relationship between  $f\text{O}_2$  and clinopyroxene Mg number for the

1214 Panzhihua samples. (d) Variation in  $fO_2$  with borehole depth in the Bushveld Complex, based  
1215 on data from [Ashwal et al. \(2005\)](#). (e) Variation in Fe and Ti oxide abundance with borehole  
1216 depth in Bushveld. (f) Relationship between  $fO_2$  and clinopyroxene Mg number for the  
1217 Bushveld samples. Dashed lines in panels (c) and (f) show linear regressions, shaded regions  
1218 represent their confidence intervals, and the corresponding  $R^2$  values are reported in each  
1219 panel.

1220 **Alt text:** Six panels comparing redox evolution in the Panzhihua and Bushveld layered  
1221 intrusions. Oxygen fugacity and Fe–Ti oxide abundance are plotted against stratigraphic height  
1222 or borehole depth, and  $\Delta FMQ$  is compared with clinopyroxene Mg number; regression lines  
1223 summarize the redox–differentiation relationships in each intrusion

1224