Supplementary Material for:

A record of magmatic differentiation in plutonic xenoliths from Santorini (Greece)

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Whitley et al. (2024) should be cited if this material is used independently of the article.

A1 ANALYTICAL METHODS

A1.1 Electron microprobe

Major element concentrations in minerals, and major element, chlorine and sulphur concentrations in interstitial glasses and melt inclusions were determined with a JXA 8900 electron microprobe at the University of Kiel, Germany. Silicate and oxide minerals were analysed with a 2 µm beam diameter, 15 kV accelerating voltage and 15 nA beam current. Glasses were measured with a 5 µm defocused beam at 15 kV accelerating voltage and a 12 nA beam current. Na was measured first to minimise Na-loss. Measurement times were 15 s peak and 7 s background, excluding S, Cl, and P, which were measured for 60 s peak and 30 s background. Natural mineral standards (topaz, rutile, baryte, tugtupite, fayalite, forsterite, mica, anorthite, wollastonite, apatite, tephroite) were used for calibration and Smithsonian basaltic glass A-99, forsterite 83 (USNM 2566), plagioclase (USNM 115900), garnet RV2 (USNM 87375), and obsidian ASTIMEX Block SPGLASS7 were used as secondary within-run standards to assess accuracy and precision (see Table S1 in Supplementary Material 2). Relative accuracy and precision are better than 5 % for major elements and 10 % for minor elements. A CITZAF matrix correction was applied. All Mg# values were calculated assuming all Fe as Fe^{2+} using $Mg\# = Mg/(Mg + Fe_{total})$. Fe^{3+} was estimated for clinopyroxene from stoichiometry using formulations by Droop [1987].

A1.2 Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS)

Trace elements in minerals and glasses were analysed at the GEOMAR Helmholtz Centre for Ocean Research Kiel using a Nu Instruments AttoM HR-ICP-MS connected to a Coherent GeoLasPro 193 nm Excimer laser ablation system. Spot analyses on samples were done by 30 s ablation at a laser repetition rate of 10 Hz and a fluence of 5 J/cm^2 using 44 µm spot diameter for silicate minerals and 24 µm for glasses. 50 s gas background were collected prior to each ablation. Measurements were made on the same polished sections used for EMPA to provide a robust internal standard using the sum of ^{29}Si and ^{43}Ca for internal standardization. The NIST 610 standard reference material (SRM) was used for mass calibration. Repeated measurements of the USGS basaltic glasses BCR-2G and BHVO-2G as secondary SRMs were made throughout each analytical session to check accuracy and precision (see Table S2 in Supplementary Material 2). Measurements were made in blocks of 8 samples and 8 SRMs to minimise the effects of instrumental drift. Data evaluation has been performed applying the linear regression slope method [Fietzke et al. 2008]. Full details of the analytical setup are provided in Fietzke and Frische [2016].

A1.3 Whole-rock geochemistry

Samples were powdered at Keele University after washing and removal of surface altered material, using a jaw crusher followed by an agate mill. Whole-rock analyses were carried out for 8 samples by Bureau Veritas (AcmeLabs), Canada, by X-ray fluorescence (XRF). Samples were fused with a lithium tetraborate flux in a crucible before analysis of major and selected trace elements. For oxides >1 wt%, two internal standards reproduced expected values to better than 3 %. Due to sample size constraints, whole-rock compositions for an additional 7 samples were determined by point counting (1000–2000 points; [Whitley et al. 2020]). Averaged mineral and glass compositions were used with the phase volumes counted, corrected for varying mineral and glass densities using mineral

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densities from Deer et al. [1997]. The bulk compositions were obtained using the Rock-Maker spreadsheet [Büttner 2012], which generates bulk whole rock compositions from phase volumes and densities.

A1.4   Mineral Oxygen Isotope Analysis

Minerals were picked from sieved grain size fractions (125 and 63 microns) of powered rocks at Keele University, using magnetic separation to remove minerals with magnetite inclusions. Minerals were then washed in diluted HCl. Oxygen isotope analyses were carried out in the Stable Isotope Laboratory of the University of Lausanne using a CO_2-laser fluorination line linked to a Finnigan MAT 253 gas-source mass spectrometer. The methodology is based on Sharp [1990] and described in detail in Lacroix and Vennemann [2015]. Between 1.4 and 2.4 mg of sample material was used for the analyses. Oxygen isotope compositions are presented in the standard δ-notation relative to Vienna Standard Mean Ocean Water (VSMOW) in per mil (‰). The in-house quartz standard LS-1 with an accepted value of 18.1 ‰ [Seitz et al. 2016]) was measured to evaluate analytical uncertainty. During the course of this study, measurements of LS-1 quartz gave 18.10 ± 0.11 ‰ (1 standard deviation, $n = 5$).

A2   Melt inclusion post-entrapment crystallisation (PEC)

Melt inclusion compositions can be modified by post entrapment processes such as diffusive equilibration and crystallisation on the melt-crystal interface [e.g. Danyushevsky et al. 2000; Kent 2008; Nielsen 2011]. Therefore, care is required in establishing whether the melt inclusions represent typical melt compositions of the host magmatic system. As is common in plutonic material, many samples contain melt inclusions that show clear textural evidence for post-entrapment modification, such as dusting (devitrification) and crystallisation within the inclusion, which varies with host phase and sample. Only melt inclusions with a clear glassy appearance were selected for analysis. Melt inclusion major element data have been corrected for post entrapment crystallisation using methodologies summarised for individual minerals below and described in detail in Whitley et al. [2020]. The compositions of melt inclusions are assessed relative to the liquid line of descent and corrections are applied to melt inclusions that appear to have been modified. These corrections assume the trapped melt was originally in equilibrium with the host mineral, and plot within the liquid line of descent for Santorini magmas.

A2.1   Olivine-hosted inclusions

Olivine-hosted melt inclusions fall outside the liquid line of descent and show a strong elevation in CaO/Al_2O_3 and depletion in Fe (Fe loss: Danyushevsky *et al.*, 2000), coupled with $K_D{}_{Fe-Mg}^{olivine-melt}$ values below the equilibrium range of 0.3 ± 0.03 [Toplis 2005; Putirka 2008]. These melt inclusions were corrected for post entrapment modification using Petrolog [Danyushevsky and Plechov 2011]. The original melt FeO* is estimated based on the amount of FeO* required to bring

the inclusions back to the liquid line of descent, and comparison with clinopyroxene and plagioclase hosted melt inclusion compositions. Ford et al. [1983] was used as the olivine-melt model and fugacity was set at QFM [Gertisser et al. 2009]. PEC corrections required 0.5 to 17.9 % olivine addition.

A2.2   Clinopyroxene- and orthopyroxene-hosted inclusions

We follow the methodology of Bali et al. [2018] by adding host clinopyroxene to the melt inclusion until $K_D{}_{Fe-Mg}^{cpx-melt}$ = 0.28 is reached. This approach requires plausible correction percentages (<20 %) and yields Al_2O_3 concentrations that overlap the literature volcanic rock data and interstitial glasses analysed in this study (Whitley, 2020). Melt inclusions in orthopyroxene were corrected by adding the host orthopyroxene back to the inclusion until $K_D{}_{Fe-Mg}^{opx-melt}$ = 0.29 ± 0.06 [Putirka 2008] is approached, which produced plausible melt compositions that follow the liquid line of descent and overlapping interstitial glass analyses, requiring less than 8 % orthopyroxene addition.

A2.3   Plagioclase-hosted inclusions

PEC of plagioclase-hosted melt inclusions is evidenced by a fine micron-scale rim of lower An plagioclase around melt inclusion rims, and elements strongly compatible in plagioclase such as Al_2O_3 diverging from the liquid line of descent along a plagioclase crystallisation vector [Whitley et al. 2020]. These inclusions were corrected following the approach of Neave and Putirka [2017] and Bali et al. [2018], where the original melt inclusion composition is assumed to lie on the liquid line of descent. Host plagioclase composition is added back to the inclusion until the Al_2O_3 vs MgO concentration in the melt inclusion approximates that predicted by a linear regression through the literature volcanic whole rock and glass dataset. This results in 9 to 19 % plagioclase addition.

A3   Thermobarometry

Several mineral-only and mineral-melt thermobarometers were applied to the xenoliths to place constraints on the temperature and pressure of xenolith formation. As the interstitial liquids found within the xenoliths are often too felsic to be in equilibrium with the coexisting minerals, and some xenoliths may not be cogenetic with the eruptive layers they are found in, several mineral-melt equilibria models were used to determine a range of plausible equilibrium liquids from known Santorini liquid compositions. An extensive database of Santorini whole rock, melt inclusion and groundmass glass analyses from the literature (n=1226) and this study (n=118) were paired with each mineral phase and plausible pairs were filtered via equilibrium tests [Putirka 1999; Putirka 2008; Mollo et al. 2013; Neave et al. 2013; Neave and Putirka 2017]. A detailed assessment of the equilibrium tests, effects of iterative calculations and applicability of the thermobarometers to Santorini compositions is given in Whitley et al. [2020] and key aspects are summarised in the following.

Clinopyroxene, orthopyroxene and plagioclase were paired with plausible liquids using this method and thermobarometers were solved iteratively; barometers were paired to ther-

mometers. As most thermobarometric equations are H_2O sensitive but most potential liquids in the database used for mineral melt thermobarometry lack water measurements, published water content measurements were used to develop a linear model to estimate water contents in the melt as a function of SiO_2 (Whitley, 2020). A new plagioclase liquid equilibrium test is derived from a large experimental dataset including Santorini experiments [Blundy and Wood 1994; Cadoux et al. 2014; Andújar et al. 2015; 2016] based on X^{Si}_{liquid} and is used instead of the two-temperature bracketed test of Putirka [2008]:

$$\ln(KD^{Ab-An}_{Plagioclase-Liquid}) \pm 0.4541 = 1.26954 - 5.38702 X^{Si}_{liquid}.$$
(1)

Olivine-melt thermometry was based on using both equations 21 and 22 of Putirka [2008] on post-entrapment crystallisation-corrected (PETROLOG [Danyushevsky and Plechov 2011]) melt inclusion compositions and paired with equilibrium melts. For clinopyroxene, the most accurate thermometer and barometer combination is using equation 33 of Putirka [2008] (temperature) paired with equation 32b (pressure). Orthopyroxene thermobarometers (equations 28, 29a, 29b in Putirka [2008]) perform well for experiments with relevant compositions, but overestimate pressures in the < 5 kbar pressure range applicable to Santorini, so that a 2 kbar pressure correction is applied to these results. For plagioclase-melt equilibria, the results from plagioclase thermometry and hygrometry are paired with a constant value of 2 kbar, which is the average of results of barometry from clinopyroxene and orthopyroxene-melt calculations.

A4 TRACE ELEMENT PARTITION COEFFICIENTS

Partition coefficients for mineral-melt exchange were calculated for three minerals based on the sources indicated: plagioclase [Bédard 2006], clinopyroxene [Bédard 2014], and orthopyroxene [Bédard 2007]. These models use regressions through extensive experimental databases and observed natural partitioning values to calculate partition coefficients based on mineral and/or melt variables. These were chosen over the lattice strain model [Blundy and Wood 1994]) and recent models built upon this [e.g. Hill et al. 2011; Sun and Liang 2012; Sun et al. 2017] as the Bédard models are calibrated over a wider range of mineral compositions, melt compositions and temperature, applicable for the large variations seen within the xenoliths. For clinopyroxene rare earth element partition coefficients, nearest neighbour parameterisations were used based on an initial calculation of LnD Sm, as recommended by Bédard [2014]. Each neighbour element is predicted with an $R^2 > 0.95$ from this initial partition coefficient. Calculated plagioclase partition coefficients take the form $RTlnD$, therefore temperature is estimated using plagioclase molar An content [Druitt et al. 2012; Fabbro et al. 2018], consistent with our temperatures calculated from plagioclase-melt thermobarometry using the equation from [Druitt et al. 2012]:

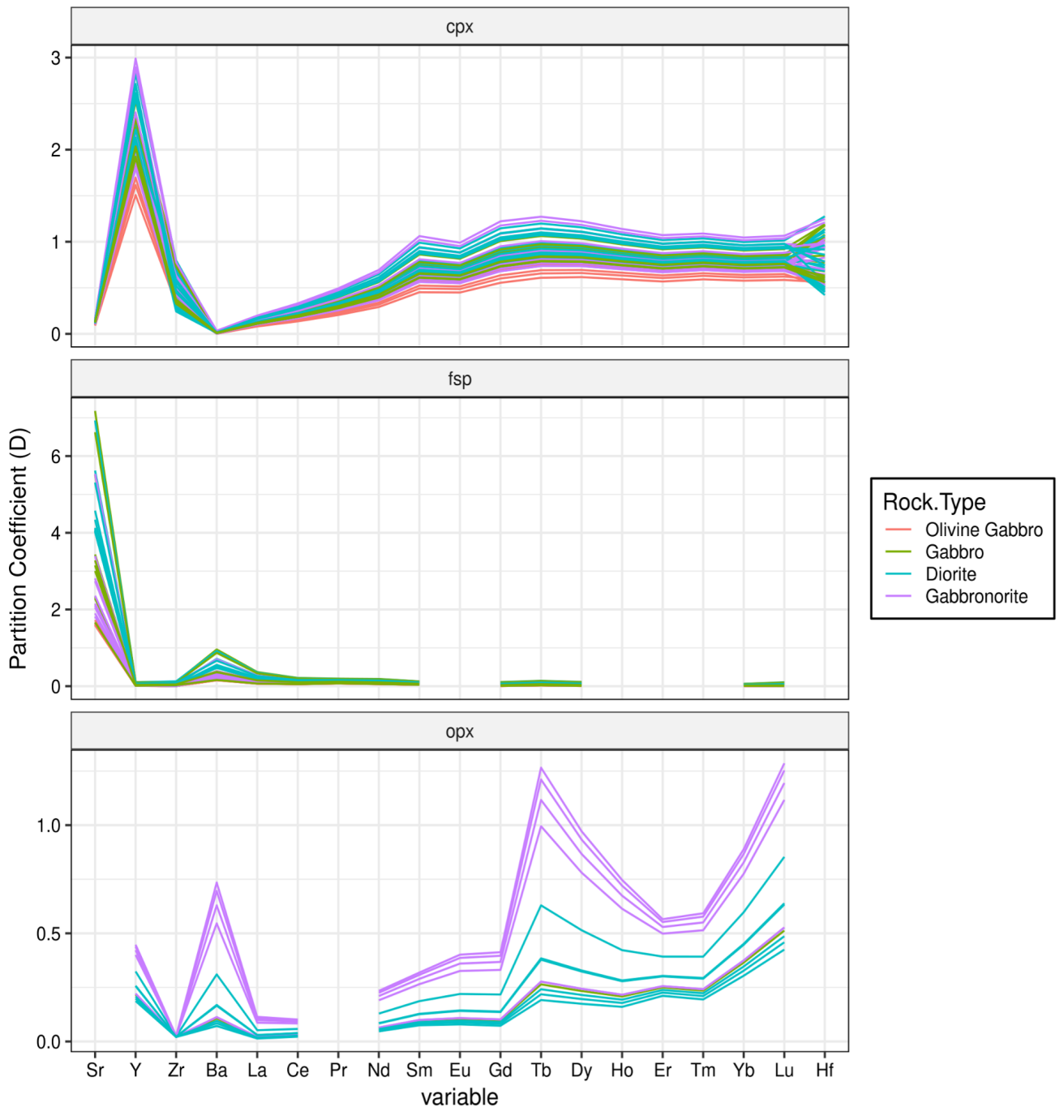$$T(K) = 1128 + 200\frac{X_{An} - 0.4}{0.4}.$$
(2)

Figure S1: Partition coefficients for clinopyroxene (cpx), feldspar (fsp) and orthopyroxene (opx) used in this study. Partition coefficients were calculated using the models described the text.

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