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Hydrogen Incorporation in Plagioclase

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Abstract

We conducted experiments at high pressure (P) and temperature (T) to measure hydrogen solubility in plagioclase (Pl) with a range of compositions (An₁₅ to An₉₄). Experiments were run at 700–850 °C, 0.5 GPa, and f_{O_2} close to either the Ni–NiO (NNO) or iron–wüstite (IW) oxygen buffers. Experiments at 700 °C on An₁₅ (containing 0.03 wt% FeO) reveal no dependence of H solubility on f_{O_2} between IW and NNO, but experiments at 800–850 °C on other compositions (with 0.3–0.5 wt% FeO) demonstrate that H solubility is enhanced by a factor of ~2 to 3 at IW compared to NNO, consistent with previous experiments by Yang (2012a) on An₅₈. By analogy with synthetic hydrogen feldspar (HAlSi₃O₈), we infer that the predominant mechanism for H incorporation in Pl is through bonding to O atoms adjacent to M-site vacancies, and we propose likely O sites for H incorporation based on M–O bond lengths in anhydrous Pl structures. Increased uptake of structurally bound H at low f_{O_2} is explained by the formation of defect associates resulting from the reduction of Fe³⁺ in tetrahedral sites to Fe²⁺, allowing additional H to be incorporated in adjacent M-site vacancies. This mechanism counteracts the expected effect of water fugacity on H solubility. We also speculate on possible substitutions of H on tetrahedral vacancies, as well as coupled H–F substitution. Enhanced incorporation of H in Pl at low f_{O_2} may have implications for estimating the water content of the lunar magma ocean. However, mechanisms unrelated to low f_{O_2} are needed to explain high H contents in terrestrial Pl xenocrysts, such as those found in basalts from the Basin and Range.

1. INTRODUCTION

Plagioclase (Pl) feldspar is the most abundant mineral in the crusts of the Earth and the Moon. Like most other nominally anhydrous minerals (NAMs), Pl can incorporate trace amounts of hydrogen into its structure (Wilkins and Sabine, 1973; Hofmeister and Rossman, 1985; Johnson and Rossman, 2003), which implies that it could be an important host for water in the shallow interiors of these planetary bodies. The hydrous component in Pl has a strong influence on transport properties such as viscosity (Griggs, 1967; Tullis and Yund, 1980; Rybacki and Dresen, 2004), diffusion (Yund and Anderson, 1978; Elphick et al., 1988; Farver and Yund, 1990; Liu and Yund, 1992), and electrical conductivity (Yang, 2012b; Yang et al., 2012). Furthermore, there is growing interest in using measurements of H in Pl

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as a magmatic hygrometer for both the Earth (Johnson, 2005; Hamada et al., 2011, 2013; Caseres et al., 2018; Mosenfelder et al., 2018) and the Moon (Hui et al., 2013; Caseres et al., 2017; Lin et al., 2019). This technique could complement more widely used hygrometers based on measurements of volatile contents in melt inclusions hosted in phenocrysts (e.g., Métrich and Wallace 2008), experimental phase equilibria (e.g., Grove et al., 2012), and H₂O-sensitive mineral-melt exchange equilibria (e.g., Lange et al., 2009).

Based on infrared (IR) spectroscopic studies, H in Pl is incorporated in the form of structurally bound OH groups (Johnson and Rossman, 2003, 2004), with concentrations of up to 900 µg/g H₂O reported for Pl from lower crustal granulite xenoliths (Xia et al., 2006; Yang et al., 2008). Such high concentrations are likely to be overestimated, owing to revision of the IR molar absorption coefficient by a factor of ~2 (Mosenfelder et al., 2015), the possibility that some IR spectra in the O-H stretching region include absorption from molecular H₂O or hydrous phases, and perhaps uncertainties introduced by the use of unpolarized IR spectroscopy (Withers, 2013). Nevertheless, it is clear from these studies as well as the extensive survey of Johnson and Rossman (2004) that H is a common trace component in Pl at levels rivaling those of other NAMs in the pressure range within which they are mutually stable.

In order to model geophysical and geochemical processes affected by H in NAMs, experimental data are needed on H solubility in these minerals (at sub-solidus conditions) and H storage capacity and partitioning with other minerals and melts above the solidus. Note that for the sake of simplicity we refer to sub-solidus, water-saturated experiments as “solubility experiments”, even though this term is ill-defined when the activity of water is not unity and/or other thermodynamic variables are insufficiently constrained (Hirschmann et al., 2009). Although a considerable amount of effort has been expended to acquire such data for olivine, pyroxenes, and other phases relevant to the mantle (e.g., Hirschmann et al., 2009), much less work has been done on feldspars. Relevant solubility and mineral-melt partitioning studies were conducted by Yang (2012a) and Hamada et al. (2013), respectively. Yang (2012a) measured H in labradorite, albite, and anorthoclase (Na-rich alkali feldspar) under a range of P - T - f_{O_2} conditions, in the absence of melt. Here we build on that work by exploring additional compositions, including anorthitic Pl directly relevant to the Moon. We demonstrate a strong dependence of H solubility on f_{O_2} for a variety of compositions, as first seen in labradorite (Yang, 2012a), and propose a model for structural H incorporation consistent with this observation.

2. METHODS

2.1. Starting materials

We used natural Pl starting materials (Table 1) with compositions ranging from Ab₈₁An₁₅Or₄ to Ab₆An₉₄ for annealing experiments at high pressure and temperature (Table 2). Hereafter we refer to these materials by their anorthite end-member mole fractions (An₁₅, An₄₇, An₅₉, An₇₁, and An₉₄) and/or their localities. For each composition from An₄₇ to An₇₁, we crushed and sieved a single gem-quality crystal (1 cm or more in original dimensions) with no optically visible inclusions to produce size fractions less than 125 µm, 125 to 250 µm, and 250 to 295 µm in size. As a result of the tabular/elongate habit of the

cleaved and crushed fragments, crystal lengths (parallel to the *c* axis) were sometimes greater than the nominal sieve size. An₁₅ (consisting of smaller crystals from Mantena, Brazil that presumably came from a plutonic environment, possibly a pegmatite) and An₉₄ (extracted from a gabbroic xenolith from Great Sitkin Island, Alaska) were similarly derived by crushing and sieving multiple crystals that we handpicked for clarity and lack of attached or included minerals (chiefly olivine and amphibole in the case of Great Sitkin anorthite).

The starting materials were characterized by electron probe microanalysis (EPMA, Section 2.3), Fourier transform infrared spectroscopy (FTIR, Section 2.4), and secondary ion mass spectrometry (SIMS, Section 2.5). Major and minor element compositions are generally homogeneous (Table 1), but variation from An₉₁ to An₉₅ has been reported for Great Sitkin anorthite (Larsen, 2005). Some variability in trace H and F concentrations is evident from SIMS measurements (Table 1), particularly for Great Sitkin anorthite (An₉₄), Mantena oligoclase (An₁₅), and Chihuahua labradorite (An₅₉).

Chips from three separate An₉₄ crystals were measured by SIMS (Table 1). FTIR spectra were also acquired for one of the crystals (“crystal 3”). The H₂O concentration estimated by FTIR (63 µg/g H₂O) is within the range of concentrations measured by SIMS (62–73 µg/g H₂O). The H₂O concentrations measured by SIMS are positively correlated with F contents (ranging from 0.3 to 0.6 µg/g). We interpret this correlation to reflect H and F loss by diffusion during transport of the xenolith to the Earth’s surface. Zonation of H and/or F is also implied by the SIMS results for An₁₅, An₄₇, and An₅₉, although we have limited data for these compositions with only 3 to 6 total measurements (on 2 or 3 different chips) per sample. H₂O measured in an An₁₅ crystal by FTIR (18 µg/g) is similar to the concentration measured by SIMS on two of three chips of this material (24–25 µg/g) but lower than the amount measured on the third chip (33–44 µg/g), indicating some heterogeneity in this material that was insufficiently probed. Unfortunately, the original state of this sample – for instance, whether the crystals were derived from crushing of a larger crystal – is unknown.

2.2. Experimental methods

The starting materials were contained in one of two different capsule designs in order to explore the effect of f_{O_2} on H solubility in Pl at conditions close to either the Ni-NiO (NNO) or iron-wüstite (IW) oxygen buffers. For NNO experiments we employed the compound capsule technique of Ayers et al. (1992), using an outer, thick-walled nickel sleeve (O.D. 6.3 mm, I.D. 4.0 mm, length 9–10 mm) and an inner, thin Au capsule that was arc welded (using a PUKTM welder) on the bottom end; a seal was formed by cold pressurization (to about 80% of the final pressure, maintained for a minimum of one hour before heating) of an Au lid to the open end of the Au capsule. The use of this technique mitigates crushing of Pl crystals during pressurization and improves chances of retaining excess H₂O. For these experiments, we ensured oxygen buffering by pre-oxidizing the nickel capsule (at 1000 °C in air for ~15 hours) and loading 9–12 mg of a 50:50 mix of Ni and NiO in the bottom of the capsule.

Experiments at IW were conducted using Fe capsules (with similar dimensions to the Ni capsules) sealed by arc welding. We sought to maintain the oxygen buffer in these

experiments by adding 7-21 mg of FeO to the capsule, but the final buffer phase assemblage was complicated as a result of reactions among all the starting materials (Section 3.1).

Each experiment also contained 30-60 μL of deionized water, 11-32 mg of 250-295 μm size-fraction Pl, and 7-60 mg of < 250 μm size-fraction Pl. The finer grained Pl (with larger surface area per volume) was added with the intention of mitigating dissolution of the larger crystals. In the IW experiments, we also loaded 4-7 mg of silicic acid ($\text{SiO}_2 \cdot \text{XH}_2\text{O}$) to increase the chance of retaining excess water after the experiment, after we conducted several runs (not reported here) that failed in this respect.

Experiments at a nominal pressure of 0.5 GPa, temperatures between 700 and 850 $^{\circ}\text{C}$, and durations between 68 and 308 hours were performed using an end-loaded piston cylinder device. We used 19.1 mm pressure cells consisting of a CaF_2 outer sleeve, a tapered graphite furnace, and internal parts made of crushable MgO , with the exception of a pressed disk of CaF_2 inserted below the sample capsule. Temperature was measured using type B thermocouples, uncorrected for the effect of pressure on electromotive force. Estimated pressure and temperature uncertainties in these experiments are ± 0.1 GPa and ± 30 $^{\circ}\text{C}$.

Experiments were quenched to less than 200 $^{\circ}\text{C}$ within 20 s by switching off power to the heater. Recovered capsules were punctured to confirm the presence of excess water and run products were extracted with a needle. Pl crystals were then embedded in ethyl-2-cyanoacrylate (“Super Glue”) and polished individually, either on one face only (for SIMS and/or EPMA) or on two parallel faces (for FTIR, and/or SIMS and EPMA). Garnets, amphiboles, and other phases pulled from the capsules were similarly prepared for analysis by EPMA. Some Pl crystals with exposed, parallel cleavage faces were measured as is by FTIR without any preparation, in order to mitigate the pervasive signature of C-H organic contamination (presumably residue from adhesive and/or solvents) that can interfere with O-H absorbance spectroscopy.

2.3. EPMA

Electron microprobe analyses were obtained with the JEOL JXA-8530FPlus at the University of Minnesota, using an accelerating voltage of 15 kV, beam current of 20 nA, and spot size of 1 μm . We used the mean atomic number (MAN) background correction method (Donovan and Tingle, 1996) and processed our data with Probe for EPMA (PfePMA) software (Probesoftware, Inc.), using the CITZAF matrix correction algorithm (Armstrong, 1988) and mass absorption coefficients from Chantler et al. (2005). Peak counting times were 15 seconds for Mg and Na and 10 seconds for all other elements. Na and K were measured first on their respective spectrometers to minimize the effects of alkali migration. In addition, time dependent intensity (TDI) data were collected for Na, Si, and K. We used the TDI data to correct for counting loss or gain using a self-calibrated, logarithmic correction for all Pl (Na only) and hydrous glass analyses (Na, Si, and K).

Reference materials used for calibration of peak intensities included natural anorthite (NMNH 137041; for Ca and Al), albite (Amelia; for Na and Si), chromite (NMNH 117075; for Cr), ilmenite (NMNH96189; for Fe), orthoclase (for K), and rutile (for Ti), as well as synthetic end-member olivines (forsterite for Mg; Mn_2SiO_4 for Mn; and Ni_2SiO_4 for Ni).

Additional reference materials used for the calibration of MAN backgrounds included synthetic corundum and periclase, Fe metal, Si metal, Kakanui hornblende (NMNH 143965), Frank Smith Mine pyrope (Royal Ontario Museum M36875), Brazilian spessartine (Verma, 1960), and K-411 glass (NIST SRM470).

For garnet and amphibole, we calculated cation assignments using the Excel spreadsheets devised by Locock (2008) and Locock (2014), respectively. Cation assignments for other phases were made using PfEPMA, except in the case of spinel for which we recalculated Fe^{3+} , Fe^{2+} , and other cations using the method of Droop (1987). We make no claims of accuracy for determinations of Fe^{3+} and Fe^{2+} using any of these methods.

2.4. FTIR

Infrared spectra of starting materials and Pl crystals recovered from the experiments were acquired with a Bruker Tensor 37 FTIR spectrometer attached to a Hyperion 2000 microscope. Spectra were taken using a KBr beamsplitter, a CaF_2 wire-grid polarizer, between 128 and 512 scans, and 2 cm^{-1} or 4 cm^{-1} resolution. Analysis areas were selected using a knife-edge aperture closed to a square area between 40 and $100\text{ }\mu\text{m}$ in diameter. Spectra used to quantify total absorbance were corrected with spline-fit baselines with concave-up curvature (accounting for the tail of absorption from T-O-T overtone modes). Sample thicknesses were measured using a Mitutoyo digital micrometer and the molar integral absorption coefficient for Pl from Mosenfelder et al. (2015) was applied to determine H_2O concentrations from total absorbance using the Beer-Lambert law.

For two starting materials (An_{15} and An_{94}) with substantial H_2O contents we measured three polarized spectra in mutually orthogonal directions. In the case of An_{15} , the three spectra were fortuitously close to the principal optical indicatrices (within $\sim 5^\circ$, as judged by examination of centered Bxa and Bxo interference figures), because they are approximately parallel and perpendicular to cleavage for this composition. In contrast, spectra for An_{94} were collected on a randomly oriented cuboid. For most experiments, no attempt was made to obtain three polarized spectra in orthogonal directions on individual crystals, because of their small size (cf. Yang, 2012a). In theory, the method of Asimow et al. (2006) could be employed for quantifying H from polarized spectra of populations of randomly oriented grain sections. However, this approach requires determination of grain orientations, either by a direct method (e.g., electron backscatter diffraction) or via calibration of the orientation dependence of the T-O-T overtone bands. Owing to the continuous variation in structure and Si/Al contents across the solid solution, the variation in overtone bands is especially complicated for Pl compared to other silicates such as olivine and orthopyroxene. Furthermore, accurate application of the technique proposed by Kovács et al. (2008) using averaging of unpolarized spectra requires a large number of grains to be analyzed, particularly when the bands are strongly polarized as in Pl or olivine (Withers 2013). Therefore, although spectra were acquired for multiple crystals from each experiment, no attempt was made to quantify H concentrations from these data. Instead, we used SIMS for this purpose.

2.5. SIMS

Individually polished crystals were pressed into indium together with reference materials and sputter coated with 30 nm of gold. SIMS analyses were then obtained on the Cameca 7f-GEO at Caltech, using a Cs^+ primary beam and previously outlined methods (Mosenfelder et al., 2011, 2015). Data were acquired over the course of three different multi-day sessions, in 2015, 2016 and 2018. Hydrogen and F concentrations were determined from blank corrected $^{16}\text{O}^1\text{H}/^{18}\text{O}$ and $^{19}\text{F}/^{18}\text{O}$ ratios, respectively. Analyses were screened for organic contamination using $^{12}\text{C}/^{18}\text{O}$ and either rejected or reprocessed if possible (by eliminating one or more of 20 cycles taken through the mass sequence) in order to meet criteria for uncontaminated analyses (Mosenfelder et al., 2011). Background levels of ^{16}OH and ^{19}F were periodically assessed by measuring previously characterized “blank” reference materials GRR1017 forsterite (for ^{16}OH and ^{19}F), GRR145-HT (for ^{16}OH and ^{19}F), and GRR145 feldspar (for ^{16}OH), which were used to blank correct the data. We also corrected some and ^{19}F data for An_{94} experiments using GS-HT, a crystal of the starting material that was dehydrated in a 1-atm gas-mixing furnace at 1200 °C. Detection limits ranged from 0.7 to 2 $\mu\text{g/g}$ for H_2O and 0.1 to 0.2 $\mu\text{g/g}$ for F. ^{35}Cl was collected for a limited number of analyses in the 2018 session, but Cl was under the detection limit in all cases (0.05 $\mu\text{g/g}$, as determined from $^{35}\text{Cl}/^{18}\text{O}$ in GRR1017, presumed to be Cl-free).

York (1966) regressions were applied to data collected on reference materials in order to establish working curves for H and F. For H in Pl (Fig. 1) we used two different working curves based on reference materials characterized by Mosenfelder et al. (2015). For compositions between An_{15} and An_{71} , we used GRR145, GRR145-HT, GRR1604, GRR1679, GRR580, GRR25, GRR1280, and/or GRR1389. For anorthite (An_{94}), we used GRR1968 (also Ca-rich, An_{96}), which lies significantly off the line established for the other feldspars. The offset has been attributed to a matrix effect (Mosenfelder et al., 2015), which is further supported in this study. SIMS data (Fig. 1) for “crystal 3” of the An_{94} starting material lie significantly closer to the calibration based on GRR1968 than the working curve determined for the other Pl compositions, if we assume the concentration determined by FTIR (63 $\mu\text{g/g}$). If the FTIR data are ignored (as assumed in Fig. 1), application of the general feldspar and anorthite calibrations instead would give values of 45 or 70 $\mu\text{g/g}$, respectively.

Fluorine contents were calibrated using two MPI-DING glasses (ML3B-G and KL2-G), two USGS glasses (BHVO-2G and BCR-2G), and/or a synthetic, F-doped glass (Fba-1) from the study of Guggino et al. (2011). We revised our reference values for F in these glasses (cf. Mosenfelder and Rossman, 2013) by comparing new SIMS and EPMA data for five glasses (Fba-1, 2, 3, 4, and 5) from Guggino et al. (2011) with SIMS data for the MPI-DING and USGS glasses. Details of this analysis are provided in the supplementary material.

3. RESULTS

3.1. Phase assemblages and constraints on oxygen fugacity

Experiments that contained excess water and clear Pl crystals with no optically visible inclusions were considered successful runs (Table 2). Failed runs with no excess water

and/or turbid crystals (resulting from exsolution into two Pl compositions) are not reported here. Experiments in Ni-Au capsules yielded Pl and both phases of the Ni-NiO buffer, providing a firm constraint on f_{O_2} at NNO. Runs in Fe capsules contained clear Pl crystals together with complex phase assemblages as a result of reactions among the Fe capsule and added components (Pl, powdered FeO, and silicic acid). The Fe capsules were intact after the experiment and trace to minor amounts of wüstite (Fig. 2a) were identified by EPMA, suggesting that f_{O_2} was buffered at IW. However, we cannot exclude the possibility of f_{O_2} gradients within these capsules (Faul et al., 2018). Although a detailed analysis of phase equilibria in these experiments is beyond the scope of this study, we describe the phases in the following paragraphs and provide representative compositions in Tables 3 and 4.

Each individual Pl crystal measured by SIMS was also measured by EPMA, and no statistically meaningful changes in composition compared to the respective starting material were found with one important exception: as discussed in Section 3.3, we obtained SIMS analyses on a single grain from A1291 with a very different composition, assumed to be a contaminant in the starting material. However, some Pl in contact with newly grown silicates in the “buffer assemblage” (e.g., Pl intergrown with amphibole in A1305) contains higher amounts of Fe (up to 1.1 wt% FeO) compared to the respective starting material (up to 0.5 wt% FeO). These unusually high measured FeO contents for Pl could be an artifact of secondary fluorescence (e.g., Longhi et al., 1976).

Fayalite, present in all Fe capsule experiments (Fig. 2a and 2b), contains only trace amounts of Mg but significant amounts of Ca. CaO contents vary considerably, even in a single experiment, but generally correlate with the An content of the Pl as follows: 0.2 to 0.3 wt% (A1330, An₁₅), 0.4 wt% (A1321, An₄₇), 0.3 to 0.6 wt% (A1319, An₅₉), 0.2 to 2.1 wt% (A1305, An₉₄), and 3.8 to 4 wt% (A1332, An₉₄). The formation of fayalite at the expense of silica and iron is consistent with an oxygen fugacity higher than the quartz-iron-fayalite (QIF) buffer, which is ~1 log unit below IW at 800 and 850 °C and 0.5 GPa (Frost, 1991).

All experiments in Fe capsules also contained Fe-rich, calcic amphiboles (Table 4) with similar compositions (all classified as ferro-sadanagaite, keeping in mind that we have poor constraints on Fe^{3+}/Fe_{tot}). For some experiments (A1305, and A1330, and A1332), we were able to pick out single crystals of amphibole, with lengths up to ~700 μm (Fig. 2c). In other cases, the amphiboles were finer-grained and intimately intergrown with other phases (Fig. 2b). Minor amounts of pyroxene (likely metastable) were found in A1305 and A1332, in contact with and/or intergrown with amphibole. Measured compositions correspond to hedenbergite (A1305) and highly aluminian hedenbergite (A1332).

The highest temperature experiment (A1332, at 850 °C) yielded red garnets (Fig. 2d) with a hopper growth habit (containing obvious voids, as picked out of the charge) that were easily handpicked and individually polished for analysis. EPMA revealed no evidence of major element zoning in the crystals. The representative analysis in Table 3 corresponds to Gr₆₇Alm₂₃And₁₀. These garnets contain hercynite-rich spinels (Fig. 2d) on the hercynite-magnetite join ($Fe^{2+}(Fe^{3+}_{0.3}Al_{1.7})O_4$), which were also found adjacent to other phases elsewhere in the recovered run products. Coexistence of garnet and hercynite at the conditions of this experiment (0.5 GPa and 850 °C, $f_{O_2} \sim IW$) is roughly consistent with

experiments in the system FeO-Al₂O₃-SiO₂ (Bohlen et al., 1986), although our system is obviously more complicated owing to the presence of significant CaO, H₂O, and (to a lesser extent) Na₂O.

Hercynite-rich spinel with a marginally different composition (more magnetite component compared to the hercynite in A1332; Table 3) was present in the experiment at lower temperature (800 °C) on the same Pl composition (A1305, An₉₄). Small (1-3 µm in diameter) hercynite-rich spinels were also found in A1321 (Fig. 2b, dark arrow), but we were unable to obtain precise, acceptable analyses owing to secondary fluorescence from adjacent glass, amphibole, and fayalite.

A1305 also contained nearly pure magnetite (Fe²⁺(Fe³⁺_{1.9}Al_{0.1})O₄) in apparent equilibrium with fayalite and wüstite (Fig. 2a). The presence of magnetite contradicts our assumption of f_{O_2} buffered at IW, because the wüstite-magnetite buffer is located at an f_{O_2} about 1.5 log units above IW at 800 °C and 0.5 GPa (Frost et al., 1991). The hercynitic component only slightly extends magnetite stability to lower f_{O_2} (Sack and Ghiorso, 1991). Therefore, we suggest that the domain in which the phase was found was out of equilibrium with other parts of the experiment. Owing to the loose nature of the water-saturated run products in our experiments, we made no attempt to characterize any spatial relationships with regards to phase distribution.

Glass (Table 3) was found in IW experiments on the two most Na-rich Pl compositions (An₁₅ at 700 °C, A1330; An₄₇ at 800 °C, A1321). The glasses were identified on the basis of texture, presence of vapor bubbles, low wt% totals suggesting large concentrations of H₂O, high Na contents, and TDI data indicating Na and K loss coupled to Si gain. Partial melting severely limits the temperature at which H solubility experiments can be conducted on Na-rich compositions (Bohlen et al., 1982). However, both A1321 and A1330 evolved excess water after the experiment, consistent with limited partial melting.

3.2. FTIR spectra

Mid-IR spectra of starting materials and Pl recovered from the experiments are compared in Fig. 3. All crystals show evidence of structurally-bound type IIa OH (Johnson and Rossman, 2004), characterized by a combination of one or more polarized, broad absorption bands centered at ~3200, ~3400, and ~3600 cm⁻¹. There is no indication in any sample for liquid H₂O (in fluid inclusions), structurally bound H₂O, or dissolved H₂ (Yang et al., 2016). Although the three type IIa OH bands are centered at different frequencies for different compositions, for the sake of simplicity we refer hereafter to these general peak positions. We were only able to easily obtain spectra in principal optical orientations for An₁₅ (Fig. 3a); polarized spectra for other compositions are in off-axis orientations generally corresponding to the two extinction directions in a given polished or unpolished section, typically perpendicular to one of the two cleavage planes.

Spectra of the An₁₅ starting material (Fig. 3a) are similar to previously published spectra from a sample of similar composition (An₁₆), GRR580 (Johnson and Rossman, 2003), but with lower absorbance for the 3200 cm⁻¹ band. Spectra taken on multiple crystals from the two experiments on An₁₅ (Fig. 3a) conducted at 700 °C (A1288 and A1330, at NNO and IW

respectively) are almost identical in X and Y (the Z spectrum for A1330 was not obtained). Spectra of PI from both experiments show a significant increase in absorbance in the O-H region compared to spectra from the starting material, with an increase in peak heights at 3400 and 3600 cm^{-1} relative to 3200 cm^{-1} .

Fig. 3b compares the X spectrum of GRR2651 from Mosenfelder et al. (2015) to off-axis, polarized spectra of PI from A1321 and a polarized spectrum of “H-feldspar” (HAlSi_3O_8) synthesized by Behrens and Müller (1995). Comparison between the PI and H-feldspar spectra will be discussed in Section 4.2 in the context of mechanisms for H incorporation. GRR2651, an An_{47} PI estimated to have 0.7 $\mu\text{g/g}$ H_2O (Mosenfelder et al., 2015), comes from the same locality as GRR3031a, the An_{47} starting material for the experiment. Spectra taken on crushed chips of GRR3031a have a high signal to noise ratio but look similar to spectra of GRR2651, suggesting a similarly low H concentration (under the detection limit of SIMS at the time data were acquired on this sample). Spectra of PI from A1321 clearly indicate an increase in absorbance relative to GRR2651, consistent with enhanced hydrogen incorporation at high P and T . The comparison also suggests a change in relative peak heights, with higher absorbance at 3600 cm^{-1} in the annealed sample. However, this inference hinges on limited data, with polarized spectra in only two orientations.

The two experiments on labradorite compositions (A1319 on An_{59} , at IW; and A1301 on An_{71} , at NNO) show similar spectra (Fig. 3c), with the exception of a sharp band at 3655 cm^{-1} in the crystal recovered from A1319. This band is at a significantly higher frequency than the “3600 cm^{-1} ” band in An_{15} or An_{47} and to our knowledge has not been identified previously in spectra of natural labradorites (Johnson and Rossman, 2004). It may reflect the presence of a hydrous phase included in the crystal (presumably amphibole, identified elsewhere in the charge), or it may reflect coupled H-F substitution, (Section 4.4). Otherwise, these spectra are similar to those measured by Yang (2012a) for An_{58} annealed under a large range of f_{O_2} conditions.

Fig. 3d compares polarized spectra of PI from two of the three experiments on An_{94} with spectra of the starting material taken in three orthogonal (off-axis) directions. Spectra from A1305 (at 800 $^{\circ}\text{C}$, IW) are not plotted but are similar to those in A1332 (850 $^{\circ}\text{C}$, NNO), with both samples displaying more absorbance than in A1291 (800 $^{\circ}\text{C}$, NNO) or in the starting material. All spectra are dominated by a single, broad band at 3200 cm^{-1} , similar to spectra of anorthites GRR1597 and GRR1968 from Johnson and Rossman (2003, 2004). PI from A1291 also exhibits a weak band at $\sim 3650 \text{ cm}^{-1}$, which is broader than the band described above that is seen in PI from A1319.

3.3. SIMS

SIMS data are summarized in Table 2, where we list average H (as H_2O) and F concentrations for each experiment. In the supplementary material, we provide a second summary table containing these values for each individual analysis.

Multiple analyses were acquired for many individual crystals, and no systematic zoning patterns were found in H or F concentrations. Internal precision of $^{16}\text{OH}/^{18}\text{O}$ ranged from 0.5 to 5.3% relative (calculated from $2s_{\bar{x}}$, standard error of the mean for 20 cycles through

the mass sequence) in all experiments with one exception, A1332. Seven of 19 analyses (on eight crystals) from this run yielded similarly good precision, but the remaining 12 were characterized by erratic cycle profiles (Fig. 4) and correspondingly high values of $S_{\bar{x}}/\hat{S}_{\bar{x}}$ (where $\hat{S}_{\bar{x}}$ is the precision predicted by Poisson statistics; Fitzsimons et al., 1999). This behavior cannot be caused by organic (surface) contamination, because none of these analyses had ^{12}C counts above background levels. Similar phenomena have been documented for natural olivines (Mosenfelder et al., 2011) and orthopyroxenes (Mosenfelder and Rossman, 2013), and linked to the presence of sub-micron to micron-sized hydrous phases that do not reflect the inherent, structurally bound OH in the mineral itself. Possible culprits include amphibole (identified elsewhere in the run product) or incipient partial melt, neither of which was directly identified in the respective grains during post-SIMS examination with EPMA. We chose to process five of these “bad analyses” by subjectively eliminating cycles, as illustrated by the example in Fig. 4, but the end result is exactly the same if only the seven good analyses are averaged (the average H_2O content is 248 $\mu\text{g/g}$ in both cases).

An important question is whether our experiments at 700 °C attained equilibrium. On the one hand, the measured H concentrations in these two runs (A1288 with 36 $\mu\text{g/g}$ H_2O and A1330 with 37 $\mu\text{g/g}$ H_2O) have poor external precision (i.e., higher relative standard deviation) compared to the higher- T runs and are within the range of values (24–44 $\mu\text{g/g}$ H_2O) measured on the starting material (but significantly higher than the value of 18 $\mu\text{g/g}$ H_2O estimated by FTIR). On the other hand, longer durations were chosen for these low- T experiments (Table 2), taking into account H diffusion data from Johnson and Rossman (2013). An approach to equilibrium is also suggested by the fact that experiments by Yang (2012a) at 700 °C on larger-diameter An_{58} (cuboid dimensions of $\sim 1 \times 1 \times 1.5$ mm, as opposed to the 250–295 μm grain size fraction we used) resulted in an increase in H concentration by a factor of ~ 2 . Finally, FTIR spectra (Fig. 3a) suggest that additional H was dissolved in the crystals compared to the starting material.

In Figs. 5–7, our results on H solubility in Pl are plotted as a function of composition, temperature, and oxygen fugacity. We discuss these trends in comparison to previously published solubility data (Yang, 2012a) and data on natural samples (Johnson and Rossman, 2004) in Sections 4.1 and 4.5, respectively. Note that we include a data point for An_{15} at 800 °C that was derived from three analyses of a single contaminant grain recovered from A1291 (on An_{94}). The composition of the grain was confirmed by EPMA. The fact that it contains twice as much H_2O as An_{15} in experiments at 700 °C (A1288 and A1330) indicates that it did not come from cross contamination from those sample charges but from A1291.

Fluorine concentrations in Pl were below detection limit in four experiments and ranged from 0.5 to 33 $\mu\text{g/g}$ in the other four, with high reproducibility (Table 2). These concentrations cannot be considered as solubilities because none of the experiments were purposely doped with excess F. Moreover, F partitions into other phases (particularly in the experiments carried out at IW). Possible sources of F include inherent concentrations in the starting Pl (Table 1), impurities in silicic acid or the oxygen buffer powders, and contamination from the mortar and pestle used for grinding the oxygen buffer mixtures.

Previous experiments conducted in our laboratory (Crépeau et al., 2014; Rosenthal et al. 2015) and other laboratories (Hauri et al., 2006) produced NAMs with trace amounts of F that came from unintentional contamination, which is probably a common but seldom-recognized phenomenon in experimental petrology. Our data suggest significant mobility of F at 800 °C, based on differences between F contents of the starting Pl and run products. In particular, An₇₁ from A1301 contains 33 µg/g F (no F was detected in the starting material) and An₄₇ from A1321 contains 1.3 µg/g F (the starting material contained 32 to 41 µg/g F, which is consistent with another crystal measured from this locality by Mosenfelder et al., 2015).

Mobility of F during the experiments is also evident from a SIMS analysis of amphibole from A1305 that gave a F content of ~0.2 wt% and H₂O content of 3.8 wt%, using the F calibration on glasses and the H calibration used for An₉₄. This H concentration is too high for an amphibole by a factor of ~2, and the value for F is probably similarly overestimated, owing to matrix effects. Matrix effects are known to be particularly non-trivial in the case of Fe-rich amphiboles, which give higher ¹H ion yields than Fe-poor amphiboles (Koga et al., 2003).

4. DISCUSSION

4.1. H solubility in Pl as a function of *P*, *T*, composition, and *f*_{O₂}

To supplement our dataset on H solubility in Pl as a function of *P*, *T*, composition, and *f*_{O₂} we include solubilities for An₅₈ published by Yang (2012a). In order to compare all data on the same scale, we adjust H concentrations from the previous study using the IR absorption coefficient determined by Mosenfelder et al. (2015). We neglect Yang's data on nearly pure albite for two reasons. First, the IR spectra of albite have a strong signature of type I OH (Johnson and Rossman, 2004), indicating a different incorporation mechanism compared to other Pl compositions with type IIa OH patterns. Second, it is not straightforward to compare the H concentrations in albite to those in other compositions because the IR absorption coefficient is probably frequency dependent (Mosenfelder et al., 2015). However, concentrations measured by Yang on the alkali feldspar anorthoclase (Ab₇₀An₅Or₂₅), which has type IIa OH bands with a mean frequency similar to Pl, should be directly comparable to data on Pl.

The effects of *T* (at 0.5 GPa) and composition on H solubility for experiments at the NNO and IW oxygen buffers are summarized in Fig. 5a. Solubilities measured in our two experiments (at NNO and IW) on An₁₅ at 700 °C are indistinguishable (Fig. 6), demonstrating no apparent effect of *f*_{O₂} for this composition under these conditions. The results at 800 °C, however, are quite different. Hydrogen concentrations measured on An₁₅ (69 µg/g H₂O), An₇₁ (76 µg/g H₂O), and An₉₄ (77 µg/g H₂O) retrieved from our experiments at 0.5 GPa, 800 °C and NNO suggest that there is no statistically meaningful effect of composition on solubility at these conditions. This inference is consistent with the solubility (71 µg/g H₂O) measured by Yang (2012a) on An₅₈ at 800 °C, 0.6 GPa at NNO. However, solubilities at 800 °C and IW are significantly higher and depend on composition, ranging from 103 µg/g H₂O (An₄₇) to 202 µg/g H₂O (An₉₄). Solubility in An₉₄ at 850 °C and IW is even higher (248 µg/g H₂O). The drastic increase in solubility associated with the

reduction in f_{O_2} from NNO to IW in our study confirms the results of Yang (2012a) on labradorite at 0.2 GPa, extending this observation to other compositions (Fig. 6).

Despite the mutual uncertainties (in P , T , and H concentrations) involved in comparing the two datasets, our results are also consistent with the effects of P and T demonstrated by Yang (2012a), with solubility in An₅₈ at fixed f_{O_2} (NNO) increasing linearly with increasing P from 0.2 to 1 GPa at constant T (800 °C) and non-linearly at 0.2 GPa with increasing T from 700 to 850 °C. As seen in Fig. 6, the solubilities measured at 0.2 GPa at either IW or NNO are consistently lower than solubilities respectively measured at 0.5 GPa in An₅₉ (IW) and An₇₁ (NNO). Our value for An₇₁ (NNO) is also identical within error with Yang's value on An₅₈ at 0.6 GPa, and lower than that at 1 GPa. The effect of T was not explored extensively in our study, but the increase in solubility of ~ 50 µg/g H₂O for An₉₄ between 800 and 850 °C is similar to the increase of ~ 60 µg/g for An₅₈ between these temperatures seen by Yang. These effects can mostly be attributed to the increase in water fugacity caused by increasing P and T (Yang, 2012a).

The lack of a compositional effect along the binary between An₁₅ and An₉₄ at NNO is difficult to reconcile with data on anorthoclase (Ab₇₀An₅Or₂₅) provided by Yang (2012a). Both natural anorthoclase (e.g., Johnson and Rossman, 2004) and the annealed samples from high P exhibit FTIR spectra with band structures very similar to Pl, but the solubility measured for anorthoclase at 800 °C is ~2.5 times that in An₅₈ at the same conditions (the discrepancy illustrated in Fig. 5a is lower because the anorthoclase data at 0.2 GPa are compared to our Pl data obtained at higher P). This result may explain why natural anorthoclase crystals can contain relatively high H contents compared to Pl (Johnson and Rossman, 2004; Fig. 5b), but the mechanism for enhanced solubility is unclear. Yang (2012a) suggested that the large K⁺ cation site plays a role in incorporation of OH defects, as it apparently does in the incorporation of structurally bound H₂O in other alkali feldspars (e.g., Johnson and Rossman, 2003). However, it is not obvious why the large size of the cation site (compared to Na⁺ and Ca²⁺ sites) should matter for incorporation of the small OH⁻ ion, compared to larger H₂O molecules. The enhanced solubility might instead reflect a higher proportion of equilibrium cation vacancies in K-rich feldspars compared to Pl. We discuss vacancy mechanisms for H incorporation in greater detail in Section 4.2.

Based on the combined dataset, it is clear that oxygen fugacity is a critical variable influencing incorporation of H in Pl. The trends in Fig. 6 are difficult to rationalize by the effect of f_{O_2} on f_{H_2O} because f_{H_2O} (assuming a pure fluid phase) increases going from IW to NNO, yet solubility (which increases with f_{H_2O}) goes down in this interval. Therefore, the most straightforward explanation for an effect of f_{O_2} entails coupled substitution of H and a redox-sensitive, minor or trace element for one of the major elements in the structure, with the most obvious candidate being Fe. Yang (2012a) dismissed any effect of Fe, Ti or Mn, based on the chemistry of his three different starting materials (labradorite, albite, and anorthoclase). In our study, however, we have used additional Pl starting materials with different FeO contents. Indeed, a plot of FeO content against H solubility at 800 °C (Fig. 7) shows a positive correlation ($r^2 = 0.85$) at the IW buffer and no correlation (within uncertainties) at the NNO buffer, suggesting that total Fe content has an effect on solubility at low f_{O_2} . The lack of an f_{O_2} effect at 700 °C for our An₁₅ experiments can be attributed to

the fact that this Pl contains an order of magnitude less Fe (0.03 wt% FeO) than all other starting materials (0.3 to 0.5 wt% FeO), including the Ansg employed by Yang (2012a). Such a low Fe content is not surprising in light of the tendency for total Fe in Pl to increase with increasing An content (Ribbe and Smith, 1966).

The above analysis based on total FeO is overly simplistic because it does not take into account the oxidation state and site occupancies for Fe in Pl, which is a longstanding, controversial topic (e.g., Ribbe and Smith, 1966; Bell and Mao, 1972; Longhi et al., 1976; Hofmeister and Rossman, 1984; Behrens et al., 1990; Wilke et al., 2001; Lundgaard and Tegner, 2004). Furthermore, if Fe redox is responsible for the f_{O_2} dependence, a different mechanism would be needed to explain the unexpected result from Yang (2012a) that H solubility decreases (from ~150 $\mu\text{g/g}$ to ~50 $\mu\text{g/g}$ H₂O) with an *increase* in f_{O_2} from IW to NNO but then increases (from ~50 $\mu\text{g/g}$ to ~70 $\mu\text{g/g}$ H₂O) with a further *increase* in f_{O_2} from NNO to the Re-ReO (RRO) and hematite-magnetite (HM) buffers (Fig. 6). After developing a general model for H incorporation in Pl in Section 4.2, we take these issues into consideration in Section 4.3.

4.2. Mechanisms of H incorporation in Pl

The first detailed crystallographic model for H incorporation in Pl (Fig. 8a) was proposed by Beran (1987), who used the measured anisotropy of O-H vibrations in An₅₉ and bond valence calculations to deduce that H is attached to O at the O_{Cm} position, with the O-H dipole pointing towards a non-adjacent O_{Bm} atom (i.e., not the O_{Bm} within the same T_{1m} tetrahedron). Beran's model implicitly assumes full cation and anion occupancy, with local charge balance (in the sense of fulfilling Pauling's second rule; Pauling, 1929) provided by Na⁺ in the adjacent M-cation site (also commonly referred to as the A-cation site) and Al³⁺ in one of the T-cation sites adjacent to O_{Cm}. There are at least three problems with this model, which was also adopted by Mrosko et al. (2010) to explain their IR data on natural An₈₆ and synthetic An₁₀₀. First, global charge balance in the structure is unaccounted for, because point defects (vacancies, interstitials, or substitutions) are not considered, although the model could be modified to explicitly consider such defects. Second, in situ FTIR studies using heating/cooling stages (Mrosko et al., 2010; Yang et al., 2015) demonstrate that the most prominent type IIa OH band in natural Pl (and anorthoclase), at 3200 cm⁻¹, splits into at least three sharper bands upon cooling to -150 °C. The sharpening indicates increased proton ordering at low *T*. Moreover, the emergence of multiple bands suggests that there is more than one site for H incorporation. Finally, the distance between O_{Cm} and O_{Bm} in labradorite (3.168 Å) is inconsistent with the distance of 2.71 Å predicted by the correlation between frequency and O...O distances established by Libowitzky (1999) for hydrogen bonding (O-H...O, where the second O is the proton acceptor). Below we elaborate on problems with using this correlation.

Further insight comes from characterization of H-feldspars, with the ideal formula HAlSi₃O₈, where the M-cation is nearly fully exchanged with H. These metastable feldspars were synthesized in a two-stage process involving exchange of Na for K in sanidine (or adularia) by immersion in molten NaCl at ~800 °C, followed by exchange of H for Na by immersion in H₂SO₄ at 310 °C (Müller, 1988). After this treatment, almost all of the Na and

K was removed but minor amounts of Ba as well as the original Al and Si concentrations remained unchanged. The resulting single crystals were amenable to study by single-crystal X-ray crystallography (Paulus and Müller, 1988; Fig. 8b) and polarized IR spectroscopy (Behrens and Müller, 1995; Fig. 3b). After initial synthesis, the IR spectra were characterized by broad absorbance bands with maxima at $\sim 3000\text{ cm}^{-1}$ and 2485 cm^{-1} . Further steam treating (at $500\text{ }^{\circ}\text{C}$) resulted in a shift of the larger 3000 cm^{-1} band to higher frequency (with a peak at 3275 cm^{-1} and multiple shoulders). D/H exchange experiments and near-IR spectra clearly demonstrate that these bands reflect the presence of OH groups, with no molecular H_2O present. After adjusting for scale, the steam-treated IR spectra from Behrens and Müller (1995) bear a broad resemblance to IR spectra of Pl with trace amounts of H (Fig. 3b). Furthermore, the polarization of the bands is similar, with maximum absorbance closest to [100] in both H-feldspar and most natural Pl compositions.

These similarities led Johnson and Rossman (2003, 2013) to suggest that H-feldspar may be a useful analogue for determining the location of H in the structure of feldspars. Accordingly, we base our model on the assumption that the majority of H atoms in Pl are bonded to O atoms adjacent to vacant M-sites, as in the H-feldspar structure (Fig. 8b). Using Kröger-Vink (1956) notation, these charge-balanced defect associates can be written as follows,

for OH^- adjacent to Ca, Na, and K vacancies, respectively. The superscripts $\times$, $\cdot$, and $'$ represent null, positive, and negative charges relative to the perfect lattice, respectively.

Hereafter for simplicity we use shorthand notation such as $(2\text{H})_{\text{Ca}}^{\times}$ or $\text{H}_{\text{Na}}^{\times}$ to represent these defects, while recognizing that the H does not actually reside “in” the former location of the now-vacant site. We also ignore K because all defect reactions involving Na can be rewritten simply with a substitution of K for Na.

Paulus and Müller (1988) suggested $\text{O}_{\text{A}2}$ as the most likely atom for H to bond to in the H-feldspar structure, based on the fact that the $\text{M}-\text{O}_{\text{A}2}$ bond distance is substantially shorter than other M-O bonds. For the sanidine used for the exchange experiment, for instance, the original $\text{M}-\text{O}_{\text{A}2}$ bond length is $2.697\text{ \AA}$, compared to $2.899\text{--}3.125\text{ \AA}$ for other M-O bonds. After removal of the alkali cations the polyhedral volume surrounding the (now vacant) M-site contracts, but the refined $\text{M}-\text{O}_{\text{A}2}$ bond length ($2.396\text{ \AA}$) is still much shorter than the other M-O bonds (ranging from 2.716 to $3.139\text{ \AA}$). From the relatively short length of the $\text{M}-\text{O}_{\text{A}2}$ bond, it can be inferred that this O has the largest electron excess upon removal of the cation and thus will be most likely to bond to H^+ . This concept is central to our model for H incorporation. Another approach to determining likely O sites for H incorporation

entails calculating electrostatic potentials (Smyth, 1989), but simple examination of M-O bond distances has the advantage that a specific defect of interest is implicitly taken into account.

Although it is theoretically possible for charge balance in the ideal H-feldspar structure to be satisfied solely by $O_{A2}\text{-H}$, as illustrated schematically in Fig. 8b, both X-ray and IR data suggest that multiple sites are involved. Bonding of O_{A2} to H should result in an increase in T- O_{A2} bond length, but does not, leading Paulus and Müller (1988) to propose proton disorder caused by a statistical distribution of H attached not just to O_{A2} but to additional O sites (O_C and O_D) with relatively long T-O distances. Behrens and Müller (1995) also recognized that the complexity of the IR spectra implies that multiple OH sites are present.

Structural data for Pl compositions across the solid solution indicate that there are multiple M-O bonds with short lengths (less than ~ 2.4 Å) that are opportune for hydroxylation upon formation of an M-site vacancy, providing additional support for the idea that there are multiple, possible OH sites. Multiple sites are also inherently required if Ca^{2+} vacancies are involved in a defect associate, without any other charge balancing mechanism. In low albite (Downs et al., 1996), as in all Pl compositions, Na- O_{A2} (2.362 Å) is the shortest M-O bond, but the difference between this distance and the next longest bond (Na- O_{D0} , 2.414 Å) is much smaller than in sanidine. Similar M- O_{A2} and M- O_{D0} bond lengths are evident for oligoclase (An_{16} and An_{28} ; Phillips et al., 1971), andesine (An_{48} ; Fitz Gerald et al., 1986), labradorite (An_{62} - An_{66} ; Wenk et al., 1980), and anorthite (An_{100} ; Angel et al., 1990). Additionally, two other M-O bonds (M- O_{A1} and M- O_{B0}) can have lengths of ~ 2.4 Å, depending on composition. These possibilities are illustrated in Fig. 9, a perspective view of the split-atom M-site environment in An_{48} (modified after the view originally depicted by Fitz Gerald et al., 1986). In Fig. 10, this concept is applied to An_{100} , with OH replacing O_{A2} , O_{B0} , and O_{D0} atoms. The bonds between these positions and Ca have the three shortest lengths for each of the four uniquely refined Ca sites, ranging from 2.287 to 2.441 Å. However, two Ca- O_{A1} bonds also have comparably short lengths (Ca_{2i0}-Oa_{1zi} and Ca_{0i0}-Oa_{10i}, 2.445 and 2.453 Å, respectively). Those Ca sites are purposely not displayed in the limited perspective view of the structure in Fig. 10, for the sake of clarity.

Ultimately, the specific frequencies and polarization of the O-H bands need to be taken into account in any comprehensive model of H incorporation (Libowitzky and Beran, 2006). This task is particularly difficult for Pl owing to its low symmetry, the diversity of the IR spectra, and the broad width of the bands, suggesting a high degree of proton disorder.

Unfortunately, determination of the polarization of the bands as a function of experimental conditions is beyond the scope of the present study. Future work both with polarized spectroscopy on oriented crystals and first-principles calculations is needed to shed full light on this problem, but the following discussion highlights some of the important issues to consider in light of previous work on other NAMs.

The approach to determining the most likely locations for O-H bonds advocated by Libowitzky and Beran (2006) combines structural information and polarized IR data with correlations between IR frequencies and hydrogen bond ($\text{OH}\cdots\text{O}$) lengths, typically employing the frequency vs. $d(\text{O}\cdots\text{O})$ diagram for hydrous minerals determined by

Libowitzky (1999). Although this method has been used in a variety of studies (e.g., Koch-Müller et al., 2003; Bromiley et al., 2004), there are significant problems with its application to NAMs. Deviations from the correlations caused by bending and/or bifurcation of hydrogen bonds are well known (Libowitzky, 1999). Moreover, $\text{O}\cdots\text{O}$ distances determined by diffraction on a nominally dry structure change substantially when hydrous defects are introduced (Lager et al., 1989; Blanchard et al., 2009; Umemoto et al., 2011; Xue et al., 2017). For instance, $\text{O}\cdots\text{O}$ distances along tetrahedral edges increase by up to 19% for $(4\text{H})_{\text{Si}}^{\times}$ (“hydrogarnet”) substitution in grossular (by comparison to the end-member, Si-free katoite; Lager et al., 1989). In forsterite, as modeled by Umemoto et al. (2011), $(4\text{H})_{\text{Si}}^{\times}$ defects also increase the size of the tetrahedron (with attendant increases in tetrahedral edge $\text{O}\cdots\text{O}$ of 6 to 14%), whereas $(2\text{H})_{\text{Mg}}^{\times}$ defects in forsterite contract the octahedron (with a change of 6% in $\text{O}\cdots\text{O}$ along the relevant octahedral edge). Substitution of H into H-feldspar also results in a contraction of the large M-site (Paulus and Müller, 1988). Therefore, application of this method to NAMs should be used with caution as it may lead to erroneous site assignments.

For the $\text{O}_{\text{A}2}\text{-H}$ bonds in Fig. 8 and the various O-H bonds in Fig. 10, we have drawn each dipole schematically in an orientation close to an ideal electrostatic configuration if only the immediate coordination environment is considered, with the positively charged H^+ pointing away from the other positive charges (the tetrahedral atoms) bonded to the coordinating O^- . In fact, this configuration is probably rarely achieved in NAMs. H-H repulsion causes large deviations from this geometry for $(4\text{H})_{\text{Si}}^{\times}$ and $(2\text{H})_{\text{Mg}}^{\times}$ defects (cationic substitutions in adjacent polyhedra can also have an effect; e.g., Blanchard et al., 2017). For instance, the O-H dipoles in the hydrogarnet substitution, as determined by neutron diffraction, are aligned approximately along the O-O edges of the tetrahedron (Lager et al., 1989). In olivine, many configurations have been modeled for the $(4\text{H})_{\text{Si}}^{\times}$ defect but in all of them the O-H dipoles either lie close to the tetrahedral edges or outside the tetrahedron (e.g., Umemoto et al., 2011; Xue et al., 2017), while the O-H dipoles for $(2\text{H})_{\text{Mg}}^{\times}$ lie along the octahedral edge. In the case of a $\text{H}_{\text{Na}}^{\times}$ or $\text{H}_{\text{K}}^{\times}$ defect in Pl (or H-feldspar), H-H repulsion should not be a factor, but the orientation of the dipoles drawn in Fig. 8 for the $\text{O}_{\text{A}2}\text{-H}$ bond is still unlikely to be realistic. The IR spectra of H-feldspar (Behrens and Müller, 1995) indicate moderately strong H bonding, with most $\text{O}\cdots\text{O}$ distances predicted by the correlation of Libowitzky (1999) being 3 Å or less. This finding is inconsistent with an $\text{O}_{\text{A}2}\text{-H}$ dipole pointing directly to the location of the vacant cation, as assumed by Behrens and Müller and subsequent studies (Johnson and Rossman, 2003, 2013). An example of a more realistic dipole (also roughly consistent with the maximum polarization close to [100]) could be aligned near $\text{O}_{\text{A}2}\cdots\text{O}_{\text{C}}$ (2.651 Å, corresponding to $\sim 3000\text{ cm}^{-1}$), presumably with varying degrees of bending of the $\text{O-H}\cdots\text{O}$ bond (which increases the frequency). Similar logic could be applied to the O-H bonds drawn for anorthite in Fig. 10 (which indeed should be affected by H-H repulsion), but more quantitative information on the orientation of the dipoles (from polarized spectra on oriented crystals) is needed.

Heretofore our discussion has focused on an H incorporation mechanism of defect associates involving M-cation vacancies, based on the compelling analogy with H-feldspar. However,

we cannot rule out the possibility that tetrahedral cation vacancies also play a role. Indeed, it is tempting to attribute the narrow O-H bands in albite (Johnson and Rossman, 2003) that occur between ~ 3500 and 3600 cm^{-1} – resembling bands in quartz more than the broader bands seen in other PI compositions – to OH^- in tetrahedral vacancies, either $(4\text{H})_{\text{Si}}^{\times}$ or $(3\text{H})_{\text{Al}}^{\times}$. The relatively high frequencies of the bands in albite are typical for $(4\text{H})_{\text{Si}}^{\times}$ substitution in garnets (e.g., Lager et al., 1989) and proposed $(4\text{H})_{\text{Si}}^{\times}$ defects in olivine (e.g., Umemoto et al., 2011), enstatite (Balan et al., 2013), ringwoodite (Blanchard et al., 2009), coesite (Mosenfelder, 2000; Koch-Müller et al., 2003), and possibly quartz (Kronenberg, 1994). Furthermore, Downs et al. (1996) identified the O_{C0} position in low albite as significantly underbonded and thus a probable hydrophyllic site. By the logic expressed above, the long Na- O_{C0} distance ($2.967\text{ \AA}$) makes this an unlikely site for OH^- balanced by a Na vacancy, but rather more likely to be balanced by a tetrahedral site vacancy (the same logic could be applied to the O_{Dm} position, with a distance to Na of $2.958\text{ \AA}$).

It is unclear from our study if such a tetrahedral vacancy mechanism is feasible for intermediate PI compositions, which have broader O-H bands (type IIa OH) than the sharp bands (type I OH) in albite. Although we have identified a high-frequency absorption at $\sim 3650\text{ cm}^{-1}$ in two experiments – a relatively sharp band in A1319 (Fig. 3c) and a broader band in A1291 (Fig. 3d) – this absorbance may be related to an extrinsic source of O-H such as a hydrous phase in the beam path (Section 3.2), or perhaps to coupled H and F substitution (Section 4.4). The band at $\sim 3600\text{ cm}^{-1}$, present in several PI compositions (Fig. 3), might also be related to tetrahedral vacancies. It is worth noting that the frequency of this band does not shift significantly during in situ heating experiments, in contrast to the absorption at $\sim 3200\text{ cm}^{-1}$ that reversibly shifts to $\sim 3400\text{ cm}^{-1}$ upon heating to $500\text{--}600\text{ }^{\circ}\text{C}$ (Mrosko et al., 2010; Yang et al., 2015). This behavior could reflect stiffness of tetrahedral sites compared to M-sites (as expected from the relative strength of Si-O or Al-O bonds compared to M-O bonds) and thus be consistent with association of this absorption with tetrahedral vacancies. The greater width of the absorption band compared to the bands in albite or in olivine is not necessarily inconsistent with tetrahedral defects, as the absorption associated with $(4\text{H})_{\text{Si}}^{\times}$ is comparably broad in other structures such as garnet (Lager et al., 1989) and ringwoodite (Blanchard et al., 2009). In the case of PI, broadening of the band could also be related to the presence of both $(4\text{H})_{\text{Si}}^{\times}$ and $(3\text{H})_{\text{Al}}^{\times}$ defects, as well as Al-Si disorder, which could result in a range of O-H bond lengths.

4.3. Effect of Fe on H incorporation in PI

Models for the effect of Fe on H incorporation in PI require knowledge of where Fe^{3+} and Fe^{2+} can be housed in the structure. Based on optical and electron paramagnetic resonance spectra, Hofmeister and Rossman (1984) determined that terrestrial PI contains both Fe^{3+} and Fe^{2+} . They argued that all Fe^{3+} and Fe^{2+} are in tetrahedral or M-sites, respectively, in line with conventional assumptions of site occupancy (e.g., Ribbe and Smith, 1966). However, this interpretation of Fe^{2+} site occupancy clashes with other spectroscopic studies. For instance, an earlier optical spectroscopy study (Bell and Mao, 1972) concluded that most of the Fe^{2+} in Lake County labradorite (also studied by Hofmeister and Rossman) is in

tetrahedral sites. Mossbauer spectra of Fe-bearing lunar Pl (with very low Fe³⁺ content), characterized by two doublets, have been interpreted to represent Fe²⁺ at two distinct sites with different coordination, presumably tetrahedral and M-sites (Appleman et al., 1971; Hafner et al., 1971). XANES data (Wilke et al., 2001) on Chihuahua labradorite (the same locality as our An₅₉ starting material) also suggest that Fe²⁺ resides in both sites.

The site assignment for Fe²⁺ by Hofmeister and Rossman (1984) is also contradicted by petrological studies. EPMA data on Pl from lunar basalts (e.g., Crawford, 1973) show a significant excess of Si and deficiency of Al for a given Ca content. The stoichiometry is best reconciled with the coupled substitution

indicating that Fe²⁺ resides in tetrahedral sites. Longhi et al. (1976) concluded from chemographic projections that less than 10% of the Fe and Mg in lunar Pl resides in M-sites, and that this component could be neglected for the sake of analyzing their Pl-melt Fe partitioning data at low f_{O_2} . Subsequent studies have also used this assumption to successfully model Fe partitioning data for Pl with a wide range in An contents (e.g., Lundgaard and Tegner, 2004). Furthermore, Sclar and Kastelic (1979) successfully synthesized anorthite with major element levels of coupled substitution corresponding to equation 4, but failed to make anorthite with Fe²⁺ substituting for Ca.

If both Fe²⁺ and Fe³⁺ can be stably incorporated in tetrahedral sites, then the seemingly contradictory effects of f_{O_2} on H solubility in Pl (Fig. 6) can be partially explained by extending our model of H incorporated at M-sites. First, we address the marked decrease in H solubility between IW and NNO, followed by a discussion of the small increase in H solubility seen between NNO and HM. An important constraint is that there are differences in peak intensity but little difference in IR band shape among the starting material and crystals annealed at different f_{O_2} . This point can be appreciated for An₉₄ in Fig. 3d, and for An₅₈ in Fig. 4 of Yang (2012a). For this reason, we prefer models that result in hydration of M-site vacancies, as proposed in Section 4.2.

4.3.1. Low f_{O_2} —In the simplest terms, enhanced solubility at low f_{O_2} can be understood from the general reaction (with no site specification):

An equivalent reaction has been used to explain enhanced solubility of H in Cr-diopside at IW (Bromiley et al., 2004) and in Fe³⁺-rich pyroxenes heated in an H₂ atmosphere (Skogby and Rossman, 1989). The reverse (oxidation) reaction is also a primary mechanism for dehydration of NAMs during heating in air in the lab or ascent of xenoliths to the surface (e.g., Skogby and Rossman, 1989; Ingrin and Skogby, 2000). For Pl, we propose the following, more specific defect reactions:

These reactions represent hydration of an M-site vacancy adjacent to ferric iron substituting for Al^{3+} in a tetrahedral site, which is reduced to ferrous iron and locally charge balanced by an additional OH^- compared to equations 1 and 2. The resulting defect associate is illustrated for anorthite in Fig. 10. Importantly, the location of the additional H atom within the M-site vacancy is consistent with the similarity of FTIR spectra between samples annealed at different f_{O_2} .

For reactions 6 and 7 to take place, Ca and Na vacancies must diffuse out of the crystal on the timescale of the experiments. On the one hand, there is no direct information available on cation vacancy diffusion kinetics in Pl. On the other hand, vacancy diffusion must be faster than ionic diffusion as a result of the relationship $D_M = [V]_M \times D_{V_M}$ where $[V]_M$ is the concentrations of M-site vacancies (Schmalzried, 1974, p. 57). Furthermore, the rate of H diffusion in An_{30} (Johnson and Rossman, 2013) is comparable to the rate of Na tracer diffusion in An_{30} , as interpolated from data on other feldspar compositions (Behrens et al., 1990). These relationships suggest that H incorporation via the mechanism we have proposed is feasible at the conditions of our experiments.

Applying the law of mass action to reactions 6 and 7 yields the following expressions for the concentrations of the defect associates:

$$\left[\{(\text{3H})_{\text{Ca}} - \text{Fe}'_{\text{Al}}\}^{\times} \right] \propto f_{\text{O}_2}^{-1/4} f_{\text{H}_2\text{O}}^{3/2} a_{\text{CaO}}^{-1} a_{\text{Fe}_{\text{Al}}^{\times}}^1 \quad (8)$$

$$\left[\{(\text{2H})_{\text{Na}} - \text{Fe}'_{\text{Al}}\}^{\times} \right] \propto f_{\text{O}_2}^{-1/4} f_{\text{H}_2\text{O}}^1 a_{\text{Na}_2\text{O}}^{-1/2} a_{\text{Fe}_{\text{Al}}^{\times}}^1 \quad (9)$$

Both reactions thus predict the same dependence of H solubility on f_{O_2} ,

$$C_{\text{H}_2\text{O}} \propto f_{\text{O}_2}^m \quad (10)$$

where the exponent m is -0.25 . A plot of the solubility data for An_{58} and An_{94} as a function of f_{O_2} (Fig. 11) in log units demonstrates that the changes in solubility for these compositions between IW and NNO are compatible with this exponent. Straight lines drawn between the data at IW and NNO have slopes of ≈ -0.1 , but lines with a slope of -0.25 are also allowable and are consistent with the curved “apparent best fit” estimated by Yang (2012a) for An_{58} .

As demonstrated in Equations 8 and 9, hydrogen incorporation via the mechanism outlined above is also influenced by $a_{\text{Fe}_{\text{Al}}^{\times}}$. Barring diffusion of Fe into Pl, for which we have no

evidence in the present experiments, this term in Equations 8 and 9 is directly proportional to the concentration of Fe^{3+} in the PI starting material, which is unconstrained in our study but likely varies considerably among the different compositions (Hofmeister and Rossman, 1984). Water fugacity also changes significantly – by a factor of almost two – in the range of f_{O_2} constrained by the IW and NNO buffers (Eugster and Skippen, 1967). As seen in Equations 8 and 9, the $f_{\text{H}_2\text{O}}$ dependencies for concentrations of defect associates on Ca vacancies and Na vacancies are different, but we have no constraints on the relative concentrations of these associates. The rate of change in H solubility between IW and NNO for different compositions is also unconstrained since there are no experiments at intermediate f_{O_2} between these extremes. Finally, the mechanism we have proposed would be compromised if tetrahedral Fe^{3+} diffuses into octahedral sites during reduction, requiring a different charge balancing mechanism. For these reasons, a full thermodynamic treatment of the data is beyond the scope of this work. Future experiments employing a two-stage approach (Bai and Kohlstedt, 1993; Tollan et al., 2018) to control $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ by pre-annealing at fixed f_{O_2} prior to high-pressure annealing would go a long way towards addressing this shortcoming of the study.

4.3.2. High f_{O_2} —Yang (2012a) documented an increase in H solubility in PI with increasing f_{O_2} between the NNO and HM buffers and derived an m exponent (Eq. 10) of 0.026. After correcting the H_2O concentration data and recalculating f_{O_2} as we did for Fig. 6, we estimate essentially the same f_{O_2} dependence ($m = 0.027$). The mechanisms described by Equations 6 and 7 (with $m = -0.25$) obviously cannot explain the increase in H solubility in this f_{O_2} range. The very low m exponent is also difficult to reconcile with any other obvious point defect reaction that includes O_2 . Furthermore, the data cannot be explained as a consequence of increasing $f_{\text{H}_2\text{O}}$, which changes almost imperceptibly between NNO and HM (increasing by ≈ 0.001 GPa at 800 °C and 0.2 GPa confining pressure; Eugster and Skippen, 1967). The five data points from Yang (2012a) could be considered within mutual uncertainty of each other, given the cited, maximum 10% uncertainty (judged from uncertainties in baseline correction and the molar absorption coefficient). However, if consistent baseline corrections were applied to spectra from the different crystals then there is indeed a systematic increase in solubility in this f_{O_2} range.

Given the above issues, we presently have no satisfactory solution to explain the increase in H solubility between the NNO and HM buffers. We again emphasize that two-stage experiments are needed in order to elucidate the role of Fe in H incorporation in PI.

4.4. Fluorine incorporation in PI

Measurements of trace levels of F in natural PI crystals can in principle be used to infer the F content of the melt or fluid (Bernini et al., 2012) with which they were in equilibrium, in the same way that H in PI can be used as a hygrometer. It is well established that F^- , which has nearly the same ionic radius as an OH^- ion, can readily substitute for O^{2-} in NAM lattices, including PI (Mosenfelder et al., 2015). Therefore, in principle, F^- can be incorporated via the same vacancy-related mechanisms discussed above. Crépeisson et al. (2014) demonstrate that coupled H-F incorporation in olivine can have a pronounced effect on O-H stretching vibrations. For instance, $(3\text{F}, \text{H})_{\text{Si}}^{\times}$ defects in forsterite are characterized by an O-H vibration

at 3674 cm^{-1} (also seen in natural olivines and attributed to a coupled H-F defect by Mosenfelder et al., 2011), which is higher than the frequencies ($\sim 3612\text{ cm}^{-1}$) normally attributed to $(4\text{H})_{\text{Si}}^{\times}$ defects (e.g., Blanchard et al., 2017). $(\text{H}, \text{F})_{\text{Mg}}^{\times}$ defects are characterized by a similar frequency shift (compared to $(2\text{H})_{\text{Mg}}^{\times}$) from 3222 to 3291 cm^{-1} . By analogy, the band at 3650 cm^{-1} in PI could be related to a coupled H-F substitution, but this idea is quite speculative and not strongly supported by the low F concentrations (0.5 to $1.8\text{ }\mu\text{g/g}$) in crystals recovered from the respective experiments. At low F concentration, we would expect any effect of F on O-H stretching frequencies for coupled H-F defects in M-sites to be virtually impossible to distinguish, given the width of the bands we attribute to these defects. Deliberate doping with F is needed to probe the incorporation mechanism and determine whether coupled H-F substitution occurs in PI, as it does in olivine and likely in other NAMs.

4.5. H incorporation in natural PI

The experimentally determined solubilities from this study and from Yang (2012a) are most applicable to PI in rapidly exhumed metamorphic rocks, such as the granulite xenoliths from the China craton studied by Xia et al. (2006) and Yang et al. (2008). However, direct comparison to those two studies is not straightforward owing to differences in quantification methods (use of polarized vs. unpolarized spectra) and the diversity of the FTIR spectra. Whereas some PI from the Chinese granulites exhibit typical type IIa OH FTIR spectra dominated by a band at 3200 cm^{-1} , other samples have substantial absorption at higher frequencies that could reflect the presence of hydrous phases (such as mica or other alteration products) or perhaps structurally bound H_2O (previously seen only in alkali feldspars; Johnson and Rossman, 2003, 2004). Therefore, we discuss instead other data from Johnson and Rossman (2004) and Hamada et al. (2011, 2013) that were acquired using polarized FTIR and have been screened to exclude H from sources other than type IIa OH. These concentrations are plotted as a function of composition (X_{An}) in Fig. 5b, on the same scale as the experimental data in Fig. 5a.

Fig. 5b demonstrates that nearly all the volcanic feldspars measured by Johnson and Rossman (2004) are consistent with the experimental solubility limits set at $800\text{ }^{\circ}\text{C}$, 0.5 GPa , and NNO, but this result is not obvious because many of these samples must have equilibrated with hydrous melts at higher T and/or different P . Furthermore, H loss by diffusion may have affected even the most hydrous PI on this plot.

The three outliers circled in Fig. 5b are all derived from basalts in the Basin and Range province of the Western United States (GRR1276b and GRR1389 were collected from the Cima volcanic field in California; GRR1280 is from Black Rock Summit, near Lunar Crater in Nevada). These Na-rich ($\text{An}_{25}\text{-An}_{34}$) megacrysts are most likely xenocrysts plucked from veins, dikes, or pegmatites from the lower crust, rather than phenocrysts formed in equilibrium with the alkali basaltic magmas that transported them onto the surface (Colville and Novak, 1991; Richter and Carmichael, 1993; Mukasa and Wilshire, 1997). This interpretation contradicts Johnson and Rossman (2004), who implied that GRR1389 (the wettest PI in their study) was derived directly from the basaltic host. Richter and Carmichael (1993) estimated formation conditions for similar megacrysts from Lunar Crater of ~ 1000

°C, 0.5-1.5 GPa, and f_{O_2} close to NNO. The higher H concentrations in these megacrysts compared to the solubility data at 800 °C and 0.5 GPa could therefore largely be explained by the positive effects of P and T on f_{H_2O} (and thus H solubility, or storage capacity in the presence of a melt), rather than the effect of f_{O_2} below NNO. High H contents measured in other NAMs from the southern Basin and Range and the Colorado Plateau have been ascribed to hydration of the mantle from the shallowly subducting Farallon plate during the Cenozoic (Li et al., 2008), an explanation we also suggest to explain the high H contents in the Pl megacrysts (as well as anorthoclase GRR1276a, also collected from Cima, which has 181 µg/g H₂O). The hydration event therefore significantly predates the eruption of the host basalts (from a drier Pacific MORB source) through the slab window caused by the transition from convergent to transform tectonics (Farmer et al., 1995).

The utility of H contents in volcanic, plutonic, pegmatitic, or metamorphic Pl as a hygrometer and/or barometer relies on retention of H following emplacement and/or eruption and subsequent cooling. Although H diffusion in Pl is slower than in some other NAMs (Johnson and Rossman, 2013), available data show that this retention is a tenuous assumption in some cases. Pl phenocrysts from the 1986-1987 eruptions of Izu-Oshima volcano measured by Hamada et al. (2011) provide a useful illustration of this concept (Fig. 5b). Hamada et al. interpreted their data on Pl from scoria, bombs, and lava flows to represent tapping of distinct levels in the volcano with different magmatic water contents, with the highest measured H concentrations in each group representing the H₂O content of the magma chamber. An alternative interpretation is that the groupings in Fig. 5b simply reflect different rates of cooling, with the fastest cooled samples (scoria) retaining the highest record H contents, followed by bombs and then flows. Still lower H contents in Pl from MORB dredged from the Rodriguez triple junction in the Indian Ocean (Hamada et al., 2013; Fig. 5b) are consistent with the relatively low amounts of H₂O measured in their associated melt inclusions (up to 0.34 wt%).

Available estimates of H partition coefficients between Pl and melts ($D_H^{Pl-melt}$) under typical, terrestrial crustal conditions come from the experimental work of Hamada et al. (2013) in a basaltic system as well as comparison of H contents of phenocrysts and associated melt inclusions in rhyolitic to andesitic volcanic rocks in the Cascadian arc (Johnson, 2005; Caseres et al., 2018; Mosenfelder et al., 2018) and MORB (Hamada et al., 2013). The experimentally derived $D_H^{Pl-melt}$ ranges from 0.0025 to 0.005 (corrected according to Mosenfelder et al., 2015), with the lower value applicable to melts with greater than about 3 wt% total H₂O and the higher value reflecting apparently non-Henrian behavior at lower H₂O contents. The lower value is roughly consistent with $D_H^{Pl-melt} \approx 0.002$, derived by recalculation of the estimate of Johnson (2005) for data from Mt. St Helens as well as samples from Mt Hood (Caseres et al., 2018) and Mt. Mazama (Mosenfelder et al., 2018). Application of $D_H^{Pl-melt} = 0.0025$ to the highest measured value in scoria from Izu-Oshima yields a value of 6 wt% H₂O in the host magma. A similar exercise for the pegmatitic Pl from Johnson and Rossman (2004) (Fig. 5b) yields up to 6.6 wt% H₂O (using $D_H^{Pl-melt} = 0.002$).

The estimates of magmatic H₂O content above are very sensitive to the precise value of $D_H^{Pl-melt}$. It is currently unknown if the partition coefficient depends on Pl or melt composition, but recent experimental studies suggest it is dependent on other thermodynamic variables (Caseres et al., 2017; Lin et al., 2019). Preliminary data from our laboratory (Caseres et al., 2017) suggest that f_{O_2} exerts a strong effect, with $D_H^{Pl-melt} \approx 0.02$ near IW. This higher value of $D_H^{Pl-melt}$ (compared to the values discussed above) has important implications for the Moon, because most estimates of f_{O_2} in lunar rocks are near or below IW. For instance, a commonly assumed value for the lunar mantle is $IW = -1$ (e.g., Wadhwa, 2008). Lin et al. (2019) also measured high $D_H^{Pl-melt}$, up to 0.046, in experiments at low f_{O_2} relevant to the Moon. They attributed the high values to a strongly non-Henrian effect of H₂O content in the melt, rather than f_{O_2} , with $D_H^{Pl-melt}$ increasing as total H₂O content in the melt decreases. Another potential mechanism for increasing $D_H^{min-melt}$ at low f_{O_2} is incorporation of molecular hydrogen in NAMs (Yang et al., 2016). Although we have seen no evidence of H₂ in Pl recovered from experiments at 0.5 GPa, it is conceivable that H₂ plays a small role at higher P and/or at $f_{O_2} < IW$.

Regardless of the cause of the high partition coefficients measured by Caseres et al. (2017) and Lin et al. (2019), application of H in lunar Pl as a magmatic hygrometer needs to be reconsidered. Hui et al. (2013) estimated an H₂O content for the magma in equilibrium with lunar ferroan anorthosites of ~1600 µg/g, based on their FTIR measurement of 6.4 µg/g H₂O in anorthite from a ferroan anorthosite sample and $D_H^{Pl-melt} = 0.004$ from Johnson (2005). They then applied a fractional crystallization calculation to estimate that the initial lunar magma ocean (LMO) contained ~320 µg/g H₂O. Recalculation using the revised IR calibration of Mosenfelder et al. (2015) and $D_H^{Pl-melt} = 0.02$ results in an order of magnitude less H₂O in the magma in equilibrium with lunar Pl (~165 µg/g H₂O) and consequently a lower value for the initial LMO (~50 µg/g H₂O). Similar conclusions were reached by Lin et al. (2019). They infer a H₂O content of ~5 µg/g for the initial LMO, subject to the proviso that large degrees of degassing may have occurred following the initial stage of LMO formation.

5. CONCLUSION

Plagioclase feldspar incorporates H in the form of OH defects, with no evidence from FTIR for structurally incorporated H₂O or H₂. Comparison with FTIR spectra of synthetic HAlSi₃O₈ suggests that H is predominantly incorporated through bonding to O atoms adjacent to M-site (Ca, Na, or K) vacancies. Whereas previous studies have used this analogy to propose the O_{A2} crystallographic site as a likely candidate for hydroxylation, consideration of M-O bond lengths in anhydrous structures across the Pl solid solution reveal multiple likely sites. A disordered distribution of H among these sites can explain the broad width of the O-H absorption bands. Additional, minor H incorporation mechanisms involving bonding to O atoms adjacent to tetrahedral vacancies and coupled H-F substitution are also possible but more speculative compared to the M-site vacancy mechanism.

Experiments at 800 °C at low pressure and f_{O_2} fixed at the NNO buffer reveal no statistically meaningful dependence of H solubility on major or minor element composition for Pl in the range between An₁₃ and An₉₄. At lower f_{O_2} (IW), however, solubilities go up – in contrast to the expectation based on the decrease in f_{H_2O} with decreasing f_{O_2} – and show an approximate dependence on total Fe content of the starting material. Increased H solubility at IW is not observed in An₁₃, most likely owing to the order of magnitude lower Fe content of this Pl compared to the other compositions. Enhanced solubility at IW can be reconciled with a model whereby Fe³⁺ in tetrahedral sites is reduced to Fe²⁺, allowing additional H to be incorporated in adjacent M-site vacancies to achieve charge balance. This mechanism need not result in significant changes in the shape of IR spectra, because the additional H is incorporated on similar crystallographic sites as at other conditions. The f_{O_2} dependence of this mechanism derived from considering point defect thermodynamics is consistent with the measured solubilities. On the one hand, increased H storage capacity in Pl at low f_{O_2} may have important implications for constraining the water content of the lunar magma ocean, which is estimated to have formed at $\sim IW = -1$. On the other hand, high H contents in terrestrial Pl xenocrysts such as those found in the Basin and Range are better explained as a result of the positive effects of P and T on f_{H_2O} , rather than the effect of f_{O_2} below NNO.

Supplementary Material

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REFERENCES

- Angel RJ, Carpenter MA and Finger LW (1990) Structural variation associated with compositional variation and order–disorder behaviour in anorthite-rich feldspars. *Am. Mineral* 75, 150–162.
- Appleman DE, Nissen H-U, Stewart DB, Clark JR, Dowty E and Huebner JS (1971) Studies of lunar plagioclase, tridymite, and cristobalite. *Proc. Lunar Sci. Conf.* 2nd 1, 117–133.
- Armstrong JT (1988) Quantitative analysis of silicate and oxide minerals, comparison of Monte Carlo, ZAF and $\phi(\rho z)$ procedures In *Microbeam Analysis* (ed. Newbury DE), pp. 239–246. San Francisco Press, San Francisco.
- Asimow PD, Stein LC, Mosenfelder JL and Rossman GR (2006) Quantitative polarized FTIR analysis of trace OH in populations of randomly oriented mineral grains. *Am. Mineral* 91, 278–294.
- Ayers JC, Brenan JB, Watson EB, Wark DA and Minarik WG (1992) A new capsule technique for hydrothermal experiments using the piston-cylinder apparatus. *Am. Mineral* 77, 1080–1086.
- Bai Q and Kohlstedt DL (1993) Effects of chemical environment on the solubility and incorporation mechanism for hydrogen in olivine. *Phys. Chem. Miner* 19, 460–471.
- Balan E, Blanchard M, Yi H, Ingrin J (2013) Theoretical study of OH-defects in pure enstatite. *Phys. Chem. Miner* 40, 41–50.
- Behrens H and Müller G (1995) An infrared spectroscopic study of hydrogen feldspar (HAlSi₃O₈). *Mineral. Mag* 59, 15–24.

- Behrens H, Johannes W and Schmalzried H (1990) On the mechanisms of cation diffusion in ternary feldspars. *Phys. Chem. Miner* 17, 62–78.
- Bell PM and Mao HK (1972) Measurements of the polarized crystal-field spectra of ferrous and ferric iron in seven terrestrial plagioclases. *Yearbook, CarnInst Wash* 72, 574–576.
- Beran A (1987) OH groups in nominally anhydrous framework structures: an infrared spectroscopic investigation of danburite and labradorite. *Phys. Chem. Miner* 14, 441–445.
- Bernini D, Wiedenbeck M, Dolejs D and Keppler H (2012) Partitioning of halogens between mantle minerals and aqueous fluids: implications for the fluid flow regime in subduction zones. *Contrib. Mineral. Petrol* 165, 117–128.
- Blanchard M, Balan E and Wright K (2009) Incorporation of water in iron-free ringwoodite: a first-principles study. *Am. Mineral* 94, 83–89.
- Blanchard M, Ingrin J, Balan E, Kovács I and Withers AC (2017) Effect of iron and trivalent cations on OH defects in olivine. *Am. Mineral* 102, 302–311.
- Bohlen SR, Boettcher AL and Wall VJ (1982) The system albite-H₂O-CO₂: a model for melting and activities of water at high pressure. *Am. Mineral* 67, 451–462.
- Bohlen SR, Dollase WA and Wall VJ (1986) Calibrations and applications of spinel equilibria in the system FeO-Al₂O₃-SiO₂. *J. Petrol* 27, 1143–1156.
- Bromiley GD, Keppler H, McCammon C, Bromiley FA and Jacobsen SD (2004) Hydrogen solubility and speciation in natural, gem-quality chromian diopside. *Am. Mineral* 89, 941–949.
- Caseres JR, Mosenfelder JL and Hirschmann MM (2017) Partitioning of hydrogen and fluorine between feldspar and melt under the conditions of lunar crust formation Lunar Planet. Sci. XXXXVIII. Lunar Planet. Inst., Houston #2303(abstr.).
- Caseres JR, Mosenfelder JL and Hirschmann MM (2018) H₂O and F contents in Mt. Hood magmas recorded by plagioclase phenocrysts Fall Meeting 2018 Amer. Geophys. Union, #V43I-0249(abstr.).
- Chantler CT, Olsen K, Dragoset RA, Kishore AR, Kotochigova SA and Zucker DS (2005) X-ray Form Factor, Attenuation, and Scattering Tables (ver. 2.1). National Institute of Standards and Technology, Gaithersburg, Maryland.
- Colville AA and Novak GA (1991) Kaersutite megacrysts and associated crystal inclusions from the Cima volcanic field, San Bernardino County, California. *Lithos* 27, 107–114.
- Crawford ML (1973) Crystallization of plagioclase in mare basalts. *Proc. Lunar Sci. Conf.* 4th, 705–717.
- Crépeau C, Blanchard M, Bureau H, Sanloup C, Withers AC, Khodja H, Surble S, Raepsaet C, Beneut K, Leroy C, Giura P and Balan E (2014) Clumped fluoride-hydroxyl defects in forsterite: implications for the upper-mantle. *Earth Planet. Sci. Lett* 390, 287–295.
- Donovan JJ and Tingle TN (1996) An improved mean atomic number correction for microanalysis. *J. Microscopy* 2, 1–7.
- Downs RT, Andelman A and Hudacsko M (1996) The coordination numbers of Na and K atoms in low albite and microcline as determined from a procrystal electron-density distribution. *Am. Mineral* 81, 1344–1349.
- Droop GTR (1986) A general equation for estimating Fe³⁺ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineral. Mag* 51, 431–435.
- Elphick SC, Graham CM and Dennis PF (1988) An ion microprobe study of anhydrous oxygen diffusion in anorthite: A comparison with hydrothermal data and some geological implications. *Contrib. Mineral. Petrol* 100, 490–495.
- Eugster HP and Skippen GB (1967) Igneous and metamorphic reactions involving gas equilibria In *Researches in Geochemistry* 2 (ed. Abelson PH). John Wiley & Sons, New York, pp. 492–520.
- Farmer GL, Glazner AF, Wilshire HG, Wooden JL, Pickthorn WJ and Katz M (1995) Origin of late Cenozoic basalts at the Cima volcanic field, Mojave Desert, California. *J. Geophys Res* 100, 8399–8415.
- Farver JR and Yund RA (1990) The effects of hydrogen, oxygen and water fugacity on oxygen diffusion in alkali feldspar. *Geochim. Cosmochim. Acta* 54, 2953–2964.

- Faul UH, Cline CJ, Berry A, Jackson I and Garapi G (2018) Constraints on oxygen fugacity within metal capsules. *Phys. Chem. Miner* 45, 497–509.
- Fitz Gerald JD, Parise JB and Mackinnon IDR (1986) Average structure of an An₄₈ plagioclase from the Hogarth Ranges. *Am. Mineral* 71, 1399–1408.
- Fitzsimons ICW, Harte B, Chinne IL, Gurney JJ and Taylor WR (1999) Extreme chemical variation in complex diamonds from George Creek, Colorado: a SIMS study of carbon isotope composition and nitrogen abundance. *Miner. Mag* 63, 857–878.
- Frost BR (1991) Introduction to oxygen fugacity and its petrologic importance. *Rev. Mineral. Geochem* 25, 1–9.
- Griggs D (1967) Hydrolytic weakening of quartz and other silicates. *Geophys. J. R. Astron. Soc* 14, 19–31.
- Grove TL, Till CB and Krawczynski MJ (2012) The Role of H₂O in Subduction Zone Magmatism. *Ann Rev Earth Planet Sci* 40, 413–439.
- Guggino SN and Hervig RL (2011) Synthesis and characterization of five new F-bearing basalt reference materials (Fba glasses): quantifying the fluorine content of the basaltic glass standards BCR-2G, BHVO-2G, GSA-1G, GSC-1G, GSD-1G, GSE-1G, ML3B-G, KL2-G, and ALV-519-4. Fall Meeting 2011 Amer. Geophys. Union, #V31C-2535 (abstr.).
- Hafner SS, Virgo D and Warburton D (1971) Oxidation state of iron in plagioclase from lunar basalts. *Earth Planet. Sci. Lett* 12, 159–166.
- Hamada M, Kawamoto T, Takahashi E and Fujii T (2011) Polybaric degassing of island arc low-K tholeiitic basalt magma recorded by OH concentrations in Ca-rich plagioclase. *Earth Planet. Sci. Lett* 308, 259–266.
- Hamada M, Ushioda M, Fujii T and Takahashi E (2013) Hydrogen concentration in plagioclase as a hygrometer of arc basaltic melts: Approaches from melt inclusion analyses and hydrous melting experiments. *Earth Planet. Sci. Lett* 365, 253–262.
- Hauri EH, Gaetani GA and Green TH (2006) Partitioning of water during melting of the Earth's upper mantle at H₂O-undersaturated conditions. *Earth Planet. Sci. Lett* 248, 715–734.
- Hirschmann MM, Tenner TJ, Aubaud C and Withers AC (2009) Dehydration melting of nominally anhydrous mantle: the primacy of partitioning. *Phys. Earth Planet. Int* 176, 54–68.
- Hofmeister AM and Rossman GR (1984) Determination of Fe³⁺ and Fe²⁺ concentrations in feldspar by optical absorption and EPR spectroscopy. *Phys. Chem. Miner* 11, 213–224.
- Hofmeister AM and Rossman GR (1985) A model for the irradiative coloration of smoky feldspar and the inhibiting influence of water. *Phys. Chem. Miner* 12, 324–332.
- Hui H, Peslier AH, Zhang Y and Neal CR (2013) Water in lunar anorthosites and evidence for a wet Moon. *Nat. Geosci* 6, 177–180.
- Ingrin J and Skogby H (2000) Hydrogen in nominally anhydrous upper-mantle minerals: concentration levels and implications. *Eur. J. Mineral* 12, 543–570.
- Johnson EA (2005) Magmatic water contents recorded by hydroxyl concentrations in plagioclase phenocrysts from Mount St. Helens, 1980–1981. *Geochim. Cosmochim. Acta* 69, A743.
- Johnson EA and Rossman GR (2003) The concentration and speciation of hydrogen in feldspars using FTIR and H-1 MAS NMR spectroscopy. *Am. Mineral* 88, 901–911.
- Johnson EA and Rossman GR (2004) A survey of hydrous species and concentrations in igneous feldspars. *Am. Mineral* 89, 586–600.
- Johnson EA and Rossman GR (2013) The diffusion behavior of hydrogen in plagioclase feldspar at 800–1000 °C: implications for re-equilibration of hydroxyl in volcanic phenocrysts. *Am. Mineral* 98, 1779–1787.
- Koch-Müller M, Dera P, Fei Y, Reno B, Sobolev N, Hauri E and Wysoczanski R (2003) OH in synthetic and natural coesite. *Am. Mineral* 88, 1436–1445.
- Koga K, Hauri E, Hirschmann MM and Bell D (2003) Hydrogen concentration analyses using SIMS and FTIR: comparison and calibration for nominally anhydrous minerals. *Geochim. Geophys. Geosys* 4, <https://doi.org/10.1029/2002GC000378>.

- Kovács I, Hermann J, O'Neill H.St.C., Gerald JF, Sambridge M. and Horvath G (2008) Quantitative absorbance spectroscopy with unpolarized light: Part II. Experimental evaluation and development of a protocol for quantitative analysis of mineral IR spectra. *Am. Mineral* 93, 765–778.
- Kröger F and Vink H (1956) Relations between the concentrations of imperfections in crystalline solids In *Solid state physics*, 3 (eds. Seitz F and Turnbull D). Elsevier, Amsterdam, pp. 307–435.
- Kronenberg AK (1994) Hydrogen speciation and chemical weakening of quartz. *Rev. Mineral. Geochem* 29, 123–176.
- Lager GA, Armbruster T, Rotella FJ and Rossman GR (1989) OH substitution in garnets: X-ray and neutron diffraction, infrared, and geometric-modeling studies. *Am. Mineral* 74, 840–851.
- Lange RA, Frey HM and Hector J (2009) A thermodynamic model for the plagioclase-liquid hygrometer/thermometer. *Am. Mineral* 94, 494–506.
- Larsen JF (2005) Experimental study of plagioclase rim growth around anorthite seed crystals in rhyodacite melt. *Am. Mineral* 90, 417–427.
- Li Z-XA, Lee C-TA, Peslier AH, Lenardic A and Mackwell SJ (2008) Water contents in mantle xenoliths from the Colorado Plateau and vicinity: implications for the mantle rheology and hydration-induced thinning of continental lithosphere. *J. Geophys Res* 113, B09210, doi: 10.1029/2007JB005540.
- Libowitzky E (1999) Correlation of O-H stretching frequencies and O-H...hydrogen bond lengths in minerals. *Mh. Chem* 130, 1047–1059.
- Libowitzky E and Beran A (2006) The structure of hydrous species in nominally anhydrous minerals: information from polarized IR spectroscopy. *Rev. Mineral. Geochem* 62, 193–230.
- Lin Y,H, Hui H, Li Y, Xu Y and van Westrenen W (2019) A lunar hygrometer based on plagioclase-melt partitioning of water. *Geochem. Persp. Let* 10, 14–19.
- Liu M and Yund RA (1992) NaSi-CaAl interdiffusion in plagioclase. *Am. Mineral* 77, 273–283.
- Locock AJ (2008) An excel spreadsheet to recast analyses of garnet into end-member components, and a synopsis of the crystal chemistry of natural silicate garnets. *Comp. & Geosci* 34, 1769–1780.
- Locock AJ (2014) An Excel spreadsheet to classify chemical analyses of amphiboles following the IMA 2012 recommendations. *Comp. & Geosci* 62, 1–11.
- Longhi J, Walker D and Hays JF (1976) Fe and Mg in plagioclase. *Proc. Lunar Sci. Conf.* 7th, 1281–1300.
- Lundgaard KL and Tegner C (2004) Partitioning of ferric and ferrous iron between plagioclase and silicate melt. *Contrib. Mineral. Petrol* 147, 470–483.
- Métrich N and Wallace PJ (2008) Volatile Abundances in Basaltic Magmas and Their Degassing Paths Tracked by Melt Inclusions. *Rev. Mineral. Geochem* 69, 363–402.
- Mosenfelder JL (2000) Pressure dependence of hydroxyl solubility in coesite. *Phys. Chem. Miner* 27, 610–617.
- Mosenfelder JL and Rossman GR (2013) Analysis of hydrogen and fluorine in pyroxenes: I. Orthopyroxene. *Am. Mineral* 98, 1026–1041.
- Mosenfelder JL, Le Voyer M, Rossman GR, Guan Y, Bell DR, Asimow PD and Eiler JM (2011) Analysis of hydrogen in olivine by SIMS: evaluation of standards and protocol. *Am. Mineral* 96, 1725–1741.
- Mosenfelder JL, Rossman GR and Johnson EA (2015) Hydrous species in feldspars: a reassessment based on FTIR and SIMS. *Am. Mineral* 100, 1209–1221.
- Mosenfelder JL, Caseres JR, Andrys J, Wright HM and Hirschmann MM (2018) Trace H and F concentrations in feldspar as monitors of volatile processes on the Earth and Moon. *Fall Meeting 2018 Amer. Geophys Union*, #MR23B-0085 (abstr.).
- Mrosko M, Koch-Müller M, Hartmann K, Wirth R and Dörsam G (2010) Location and quantification of hydrogen in Ca- and Sr-anorthite. *Eur. J. Mineral* 22, 103–112.
- Mukasa SB and Wilshire HG (1997) Isotopic and trace element compositions of upper mantle and lower crustal xenoliths, Cima volcanic field, California: implications for evolution of the subcontinental lithospheric mantle. *J. Geophys Res* 102, 20,133–20,148.
- Müller G (1988) Preparation of hydrogen and lithium feldspars by ion exchange. *Nature* 332, 435–6.

- Pauling L (1929) The principles determining the structure of complex ionic crystals. *J. Am. Chem. Soc* 51, 1010–1026.
- Paulus H and Müller G (1988) The crystal structure of a hydrogen feldspar. *Neues Jahrb. Mineral. Mh H.11*, 481–90.
- Phillips MW, Colville AA and Ribbe PH (1971) The crystal structures of two oligoclases: a comparison with low and high albite. *Z. Kristallogr* 133, 43–65.
- Pownceby MI and O'Neill HSC (1994) Thermodynamic data from redox reactions at high temperatures. IV. Calibration of the Re-ReO₂ oxygen buffer from EMF and NiO + Ni-Pd redox sensor measurements. *Contrib. Mineral. Petrol* 118, 130–137.
- Ribbe PH and Smith JV (1966) X-Ray-Emission Microanalysis of Rock-Forming Minerals IV. Plagioclase Feldspars. *J. Geol* 74, 217–233.
- Righter K and Carmichael ISE (1993) Mega-xenocrysts in alkali olivine basalts: fragments of disrupted mantle assemblages. *Am. Mineral* 78, 1230–1245.
- Rosenthal A, Hauri E and Hirschmann MM (2015) Experimental determination of C, F, and H partitioning between mantle minerals and carbonated basalt, CO₂/Ba and CO₂/Nb systematics of partial melting, and the CO₂ contents of basaltic source regions. *Earth Planet. Sci. Lett* 412, 77–87.
- Rybacki E and Dresen G (2004) Deformation mechanism maps for feldspar rocks. *Tectonophysics* 382, 173–187.
- Sack RO and Ghiorso MS (1991) Chromian spinels as petrogenetic indicators: thermodynamics and petrological applications. *Am. Mineral* 76, 827–847.
- Schmalzried H (1974) *Solid State Reactions*. Verlag Chemie, Weinheim, 214 pp.
- Sclar C and Kastelic R (1979). Iron in anorthite: An experimental study *Lunar Planet. Sci X., Lunar Planet. Inst., Houston*, pp. 1087–1089 (abstr).
- Skogby H and Rossman GR (1989) OH⁻ in pyroxene: an experimental study of incorporation mechanisms and stability. *Am. Mineral* 74, 1059–1069.
- Smyth J (1989) Electrostatic characterization of oxygen sites in minerals. *Geochim. Cosmochim. Acta* 53, 1101–1110.
- Tollan PME, O'Neill HSC and Hermann J (2018) The role of trace elements in controlling H incorporation in San Carlos. *Contrib. Mineral. Petrol* 173, 89.
- Tullis J and Yund RA (1980) Hydrolytic weakening of experimentally deformed Westerly granite and Hale albite rock. *J. Struct. Geol* 2, 439–451.
- Umemoto K, Wentzcovitch RM, Hirschmann MM, Kohlstedt DL, and Withers AC (2011) A first-principles investigation of hydrous defects and IR frequencies in forsterite: the case for Si vacancies. *Am. Mineral* 96, 1475–1479.
- Verma RK (1960) Elasticity of some high-density crystals. *J. Geophys Res* 65, 757–766.
- Wadhwa M (2008) Redox conditions on small bodies, the Moon and Mars. *Rev. Mineral. Geochem* 68, 493–510.
- Wenk H-R, Joswig W, Tagai T, Korekawa M and Smith BK (1980) The average structure of An₆₂–66 labradorite. *Am. Mineral* 65, 81–95.
- Whitney DL and Evans BW (2010) Abbreviations for names of rock-forming minerals. *Am. Mineral* 95, 185–187.
- Wilke M, Farges F, Petit P-E, Brown GE and Martin F (2001) Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *Am. Mineral* 86, 714–730.
- Wilkins RWT and Sabine W (1973) Water content of some nominally anhydrous silicates. *Am. Mineral* 58, 508–516.
- Withers AC (2013) On the use of unpolarized infrared spectroscopy for quantitative analysis of absorbing species in birefringent crystals. *Am. Mineral* 98, 689–697.
- Xia Q, Yang X, Deloule E, Sheng YM and Hao YT (2006) Water in the lower crustal granulite xenoliths from Nushan, eastern China. *J. Geophys. Res* 111 10.1029/2006JB004296.
- Xue X, Kanzaki M, Turner D and Lorocho D (2017) Hydrogen incorporation mechanisms in forsterite: New insights from ¹H and ²⁹Si NMR spectroscopy and first-principles calculation. *Am. Mineral* 102, 519–536.

- Yang X (2012a) An experimental study of H solubility in feldspars: Effect of composition, oxygen fugacity, temperature and pressure and implications for crustal processes. *Geochim. Cosmochim. Acta* 97, 46–57.
- Yang X (2012b) Orientation-related electrical conductivity of hydrous olivine, clinopyroxene and plagioclase and implications for the structure of the lower continental crust and uppermost mantle. *Earth Planet. Sci. Lett* 317–318, 241–250.
- Yang X, Deloule E, Xia Q, Fan Q and Feng M (2008) Water contrast between Precambrian and Phanerozoic continental lower crust in eastern China. *J. Geophys. Res* 113, B08207, doi: 08210.01029/02007JB005541.
- Yang X, Keppler H, McCammon C and Ni H (2012) Electrical conductivity of orthopyroxene and plagioclase in the lower crust. *Contrib. Mineral. Petrol* 163, 33–48.
- Yang X, Keppler H and Liu Y (2016) Molecular hydrogen in mantle minerals. *Geochem. Persp. Lett* 2, 160–168.
- Yang Y, Xia Q and Zhang P (2015) Evolution of OH groups in diopside and feldspars with temperature. *Eur. J. Mineral* 27, 185–192.
- York D (1966) Least-squares fitting of a straight line. *Canad. J. Phys* 44, 1079–1086.
- Yund RA and Anderson TF (1978) The effect of fluid pressure on oxygen isotope exchange between feldspar and water. *Geochim. Cosmochim. Acta* 42, 235–239.

Fig. 1.

Representative SIMS working curves (from 2015 session) for H₂O in Pl. For compositions between An₁₅ and An₇₁, we use a York (1966) fit to the data represented by circles (regression and 95% confidence intervals drawn as solid and dashed lines, respectively). For An₉₄ we use a fit to GRR145-HT (the blank) and GRR1968 (square data point, An₉₆). Each data point represents the average of two to three analyses. Reference H₂O values and uncertainties are from Mosenfelder et al. (2015); uncertainties (25) for ¹⁶OH/¹⁸O are within the symbol size. Also plotted (triangle) is the average value of four analyses (acquired immediately before these calibrations) on Great Sitkin crystal 3, with the H concentration determined by FTIR (63 µg/g).

Fig. 2.

Backscattered electron (a-b,d) and secondary electron (c) images of run products (besides PI) extracted from experiments conducted in iron capsules. **a.** Coexisting fayalite, magnetite, and wustite in A1305. **b.** Amphibole, fayalite, and hydrous glass in A1321. White arrow (lower left) points to an example of a vapor bubble in quenched glass; black arrow (upper right) points to a hercynite crystal (with BSE contrast intermediate between fayalite and glass). **c.** Amphibole clusters from A1330 (mounted on carbon tape). **d.** Garnet from A1332, embedded in adhesive (which appears black in BSE mode). Garnets contain hercynite

inclusions (brighter than the garnet in BSE mode), also found elsewhere in the charge in contact with other phases.

Fig. 3.

Representative mid-IR spectra of Pl starting materials and crystals recovered from experiments. All spectra are polarized, with the E-vector parallel – as labeled directly above each spectrum – either to an optical direction (*X*, *Y*, or *Z*), a crystallographic axis, or a random (off-axis) orientation (pol 1, pol 2, or pol 3). Unless otherwise specified, spectra are normalized to 1 cm, plotted without baseline correction, and arbitrarily offset from each other for clarity. **a.** An₁₅ starting material (Mantena oligoclase) juxtaposed with An₁₅ from A1288 (700 °C, NNO) and A1330 (700 °C, IW). Spectra from the two experiments are nearly identical (in identical corresponding orientations, *X* or *Y*) and show increased absorbance compared to the starting material. Relatively sharp bands in the region from 2800 to 3000 cm⁻¹ (most prominent in A1288) are C-H bands representing surface contamination, unlikely to significantly affect absorbance in the O-H region. **b.** An₄₇ from A1321 (800 °C, IW) juxtaposed with the A spectrum of GRR2651 (Mosenfelder et al., 2015), which came from the same locality as the starting material (GRR3031a) that was used for the experiment. Also plotted is the spectrum of H-feldspar scanned from Fig. 1b of Behrens and Müller (1995), normalized to 1mm from a nominal thickness of 50 µm. For

ease of comparison, spectra are normalized to significantly different path lengths, as labeled, **c.** Crystals recovered from A1301 (An₇₁, 800 °C, NNO) and A1319 (An₅₉, 800 °C, IW). **d.** An₉₄ starting material (three spectra from mutually orthogonal directions) compared to Ang₄ from A1291 (800 °C, NNO) and A1332 (850 °C, IW). Spectra from A1305 (800 °C, IW), not plotted here, are similar to those from A1332.

Fig. 4.

Three analyses of two separate Pl grains from A1332, demonstrating a “good” analysis (grain 2, rim, red circles) juxtaposed against imprecise analyses interpreted to be affected by ionization of an included hydrous phase. Each analysis consists of 20 cycles through the mass sequence following pre-sputtering and automated alignment; depth was not calibrated. Corresponding x_{XX}/x_{XX} values for $^{16}\text{OH}/^{18}\text{O}$ for the three analyses are 4.5 (grain 2, core), 1.2 (grain 2, rim), and 16.9 (grain 3, core). The grain 3 (core) analysis was reprocessed by eliminating cycles 1 to 7, resulting in $x_{XX}/x_{XX} = 1.2$ and a value for H_2O essential identical to the grain 2 (rim) analysis.

Fig. 5.

Experimental solubility data and comparison to concentrations measured in natural samples. Data in these plots from other studies were adjusted to take into account either the revised value for the IR molar absorption coefficient or otherwise re-estimated concentrations by Mosenfelder et al. (2015). **a.** Results from this study on H solubility as a function of composition (and oxygen fugacity, either at IW or NNO) at 700–850 °C, 0.5 GPa. Value for A1330 (An₁₅, 700 °C, IW) is not visible because it overlaps with value for A1288 (An₁₅, 700 °C, NNO). Also plotted are data from Yang (2012a) on anorthoclase (Ab₇₀An₅Or₂₅) at 800 °C, 0.2 GPa, NNO and labradorite (An₅₈) at 800 °C, 0.6 GPa, NNO. The dashed lines are only meant as guides to the eye. **b.** H concentrations of natural volcanic and pegmatitic Pl containing type IIa OH. Samples from Johnson and Rossman (2004) containing type I OH (i.e., low albite) or H from fluid inclusions or alteration are excluded. Dashed line is the same trend for 800 °C, NNO experiments as in **a**. Data sources for H in Pl from Izu-Oshima and MORB from the Rodriguez triple junction are from Hamada et al. (2011) and Hamada et al. (2013), respectively.

Fig. 6.

H solubility as a function of f_{O_2} . Results from this study at 0.5 GPa and 700–850 °C are compared to data on An_{58} at 800 °C and 0.2 GPa from Yang (2012a), corrected according to the IR calibration of Mosenfelder et al. (2015). Oxygen fugacities were calculated using equations from Frost (1991) and Pownceby and O'Neill (1994). Labels below the data points are abbreviations for the oxygen buffers used in the experiments. For the sake of clarity (owing to symbol overlap), this plot does not show additional data from Yang (2012a) at 0.2 GPa and temperatures other than 800 °C and at 0.6 to 1 GPa, 800 °C.

Fig. 7.

H solubility in Pl as a function of FeO content of the starting material, for experiments at 800 °C and at IW or NNO. Closed symbols = data from this study; open symbols = data from Yang (2012a), corrected according to the IR calibration of Mosenfelder et al. (2015). Each data point from Yang is an average from two repeat experiments. The data at IW are positively correlated ($r^2 = 0.85$), but the data at NNO are uncorrelated if uncertainties are taken into account.

Fig. 8.

a. Part of the structure of Lake County labradorite (Wenk et al., 1980) projected on (010), modified after view presented by Beran (1987). Two Ca/Na positions (M_1 and M_2) are shown, in accordance with the split-atom model of Wenk et al. O_{A2} (red), O_{Bm} (orange), and O_{Cm} (yellow) positions are drawn with spheres; other oxygen positions bridging Si/Al tetrahedra (dark blue) are not emphasized. Site occupancies of tetrahedra are not specified here. In the OH^- incorporation model of Beran (1987), O_{Cm} is replaced with an OH^- with the O-H dipole pointed approximately towards O_{Bm} in a non-adjacent tetrahedron (the $OH \cdots O$ bond is depicted with a dotted line). A contrasting model based on H-feldspar (Paulus and Müller, 1988; Behrens and Müller, 1995) is also illustrated in the upper part of the figure, with OH^- replacing O_{A2} ; the dipole is drawn pointing towards the split Ca/Na site, which is assumed to be vacant. The bond length between M_1 and O_{A2} is 2.319 Å, while the bond length between M_2 and O_{A2} is 2.342 Å. **b.** Structure of H-feldspar (Paulus and Müller, 1988) projected on (010). M-sites (grey spheres) are assumed to be vacant, although the refinement was on a single crystal with minor amounts of Ba, K, and Na present. The same mechanism of replacement of O_{A2} by OH^- illustrated in **a** is superimposed here on the known structure: all O_{A2} atoms are replaced by OH^- , with the O-H dipole pointed towards the vacant M-site and away from the T_2 atoms bridged by O_{A2} . As discussed in the text, this model is simplistic as other O atoms are likely involved in H incorporation.

Fig. 9.

Perspective view of the split-atom M-site environment in An_{48} (modified after Fitz Gerald et al., 1986) showing possible bonds between the M cation and various O atoms surrounding it. Projection is on (010). M_1 and M_2 correspond to M' and M'' , respectively, in the original site designation of Fitz Gerald et al. The [010] unit cell edge lies on a join between the two O_{A1} atoms. The thin grey lines between O atoms are not all meant to represent actual bonds but to help guide the eye with the perspective. The shortest M-O bonds are labeled with numbers in italics: 1 = $M_1\text{-O}_{A2}$ (2.336 Å); 2 = $M_2\text{-O}_{A2}$ (2.348 Å); 3 = $M_2\text{-O}_{A1}$ (2.402 Å); 4 = $M_1\text{-O}_{Do}$ (2.416 Å); 5 = $M_1\text{-O}_{A1}$ (2.425 Å).

Fig. 10.

Part of the structure of anorthite (Angel et al., 1990) projected on (010), showing some possible OH^- sites. For the sake of clarity, the y dimension (b-axis) of the projection is reduced such that only two of the four Ca positions (green) are visible ($\text{Ca}_z\text{o0}$ and $\text{Ca}_o\text{o0}$). O_A2 (red), O_B0 (orange), and O_D0 (yellow) positions are depicted as spheres; other oxygen positions bridging the alternating Si (dark blue) and Al (light blue) tetrahedra are not emphasized. On the middle left-hand side of the unit cell, a vacant (grey) M-site ($\text{Ca}_z\text{o0}$) is charge-balanced by two OH^- replacing O_A2zo and O_D0zo . On the lower right-hand side,

one $^{IV}\text{Al}^{3+}$ adjacent to a vacant (grey) M-site (Ca_{000}) has been replaced by $^{IV}\text{Fe}^{2+}$, requiring charge balance by three OH^- in total. The three OH^- are drawn replacing $\text{O}_{\text{A}200}$, $\text{O}_{\text{D}000}$, and $\text{O}_{\text{B}000}$. O-H bonds are drawn schematically with the dipole pointing approximately perpendicular to the respective T-O-T bridge and towards the vacant M-site; the realism of this assumption is discussed in the text. This example shows replacement of $\text{O}_{\text{A}2}$, $\text{O}_{\text{B}0}$, $\text{O}_{\text{D}0}$ with OH^- because the bonds between those positions and Ca have the three shortest lengths for each respective M-site (ranging from 2.287 to 2.441 Å), but other possibilities are discussed in the text.

Fig. 11.

H solubility as a function of f_{O_2} , displayed in log units on both axes. For simplicity, only data for An₉₄ (this study) and An₅₈ (Yang, 2012a) are plotted. H₂O concentrations and f_{O_2} were calculated as in Fig. 6. Labels below the data points are abbreviations for the oxygen buffers used in the experiments. A line with a slope (i.e., exponent m in Eq. 10) of -0.25 emanating from the data at IW indicates the expected f_{O_2} dependence of solubility between the IW and NNO buffers, based on our model of the associated defects $\{(3H)_{Ca} + Fe'_{Al}\}^{\times}$ (Eq. 7) and $\{(2H)_{Na} + Fe'_{Al}\}^{\times}$ (Eq. 8). This line is nearly coincident with the curved fit estimated by Yang for his data (the fit from his plot was scanned in and converted to the units plotted here). An upper limit of $m = -0.1$ is also displayed. Similar lines could be plotted between the two An₉₄ data points. The data on An₅₈ between the NNO and HM buffers are best fit with a line of 0.026, the significance of which is discussed in the text.

Table 1.

Compositional data for starting materials

Sample No.	00CNGS04x4	GRR3031a	GRR2058a	GRR2570a	JLM88
Locality	Great Sitkin Island, Alaska, USA	Mongolia	Ponderosa Mine, Oregon, USA	Chihuahua, Mexico	Mantena, Brazil
<i>n</i> (EPMA)	7	6	6	6	6
SiO ₂	42.91(32)	53.92(30)	48.81(22)	51.31(27)	62.66(43)
TiO ₂	<i>bdl</i>	0.06(1)	0.03(1)	0.07(1)	<i>bdl</i>
Al ₂ O ₃	35.85(25)	27.83(20)	31.53(15)	29.74(23)	22.66(23)
MgO	0.04(1)	0.08(1)	0.18(1)	0.11(1)	<i>bdl</i>
FeO	0.47(2)	0.33(1)	0.37(2)	0.36(2)	0.03(2)
Na ₂ O	0.63(9)	5.84(14)	3.30(11)	4.54(15)	9.99(35)
CaO	19.26(18)	9.97(6)	14.41(7)	12.17(9)	3.22(2)
K ₂ O	<i>bdl</i>	0.45(1)	0.05(1)	0.28(1)	0.76(1)
Total	99.15	98.50	98.68	98.58	99.32
<i>Ab</i>	5.6	50.1	29.2	39.7	81.4
<i>An</i>	94.4	47.3	70.5	58.8	14.5
<i>Or</i>	0	2.5	0.3	1.6	4.1
<i>n</i> (SIMS)	13	3	3	5	6
H ₂ O	62 – 73	<i>bdl</i>	<i>bdl</i>	<i>bdl</i> – 22	24–44
F	0.3 – 0.6	32 – 41	<i>bdl</i>	2 – 5	1–2
H ₂ O (FTIR)	63	0.7 [*]	0	0	18

n is number of analyses.Major element data expressed as oxide wt%, H₂O and F concentrations as µg/g.*bdl* indicates element below detection limit (Ni and Cr were also analyzed and below detection in all crystals).

Numbers in parentheses represent one standard deviation in terms of least units cited, for 6 to 7 EPMA analyses.

For SIMS analyses, ranges in H₂O and F are given.^{*} value for GRR2651 from same locality, from Mosenfelder et al. (2015).

Table 2.

Experimental conditions, run products, and SIMS data

Run no.	Temperature (°C)	Duration (h)	Pl composition (An content)	Capsule	log fO_2	Run products	SIMS data				
							Phase	No. grains analyzed	Total No. of analyses	H ₂ O (μg/g)	F (μg/g)
A1288	700	308	An ₁₅	Ni/Au	-16.03	An ₁₅ + H ₂ O	An ₁₅	12	28	36(8)	bdl
A1291	800	71	An ₉₄	Ni/Au	-13.66	An ₉₄ + H ₂ O	An ₉₄	10	15	77(4)	0.5(1)
							An ₁₅ (*)	1	3	69(3)	bdl
A1301	800	72	An ₇₁	Ni/Au	-13.66	An ₇₁ + H ₂ O	An ₇₁	4	10	76(5)	33(1)
A1305	800	68	An ₉₄	Fe	-18.66	An ₉₄ + Wus + Fa + Hc + Mag + Amp + Cpx + H ₂ O	An ₉₄	7	12	202(9)	0.9(2)
							Amp	1	1	37573(**)	1974(**)
A1319	800	72	An ₅₉	Fe	-18.66	An ₅₉ + Wus + Fa + Amp + H ₂ O	An ₅₉	5	8	158(1)	1.8(1)
A1321	800	72	An ₄₇	Fe	-18.66	An ₇ + Wus + Fa + Amp + Gl + H ₂ O	An ₄₇	8	15	103(7)	1.3(1)
A1330	700	264	An ₁₅	Fe	-21.27	An ₁₅ + Wus + Fa + Amp + Gl + H ₂ O	An ₁₅	5	15	37(14)	bdl
A1332	850	72	An ₉₄	Fe	-17.53	An _M + Wus + Fa + Hc + Grt + Cpx + Amp + H ₂ O	An ₉₄	8	12	248(15)	bdl

Notes:

All experiments conducted at a nominal pressure of 0.5 GPa.

Phase abbreviations follow Whitney and Evans (2010), except for Gl (glass).

Uncertainties in parentheses are 1 standard deviation. bdl = below detection limit.

* Contaminant grain, see text for explanation.

** Values based on A%4 and F-bearing glass calibrations, probably overestimated as discussed in text.

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Table 3.

Representative EPMA data for selected experimental run products

Phase	Fayalite	Clinopyroxene	Clinopyroxene	Garnet	Magnetite	Hercynite	Hercynite	Glass	Glass
Experiment No.	A1305	A1305	A1332	A1332	A1305	A1305	A1332	A1321	A1330
SiO ₂	29.89	47.53	40.14	38.19	0.25	0.14	0.09	50.92	50.17
TiO ₂	–	0.31	0.02	–	0.02	0.06	–	–	–
Al ₂ O ₃	–	1.55	14.07	19.80	1.41	46.00	47.74	25.36	25.87
MgO	0.10	2.73	0.05	0.03	–	0.01	0.02	–	0.01
FeO *	67.96	28.99	22.68	14.34	90.26	52.62	50.90	6.16	2.75
MnO	–	–	0.08	–	–	–	–	–	–
Na ₂ O	–	0.16	0.17	–	–	–	–	11.04	14.33
CaO	2.13	18.02	23.08	27.51	–	0.02	0.09	2.01	0.55
K ₂ O	–	–	0.02	–	–	–	–	1.01	0.89
Cr ₂ O ₃	–	0.05	–	–	–	–	–	–	–
Total	100.08	99.34	100.31	99.88	91.94	98.85	98.84	96.50	94.57
Recalculated Total **	100.08	99.34	100.31	100.33	98.52	100.31	100.11	96.50	94.57
Oxygen basis	4	6	6	12	4	4	4	–	–
Si	1.003	1.951	1.614	2.965	0.010	0.004	0.003	–	–
Ti	–	0.010	0.001	–	0.001	0.001	–	–	–
Al	–	0.075	0.667	1.811	0.065	1.652	1.704	–	–
Mg	0.005	0.167	0.003	0.004	–	0.001	0.001	–	–
Fe ³⁺	–	–	–	0.259	1.915	0.333	0.287	–	–
Fe ²⁺	1.908	0.996	0.763	0.673	1.010	1.008	1.002	–	–
Mn	–	–	0.003	–	–	–	–	–	–
Na	–	0.012	0.013	–	–	–	–	–	–
Ca	0.077	0.793	0.994	2.289	–	0.001	0.003	–	–
K	–	–	0.001	–	–	–	–	–	–
Cr	–	0.002	–	–	–	–	–	–	–
Cation total	2.993	4.006	4.059	8.001	3.000	3.000	3.000	–	–

* Total Fe calculated as FeO.

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**
Recalculated wt% total after cation calculations.

Dashed line indicates element below detection limit (Ni was also analyzed and below detection in all phases).

Table 4.

Representative EPMA data for amphiboles

Experiment No.	A1305	A1319	A1321	A1330	A1332
SiO ₂	34.04	34.72	34.38	35.44	32.97
TiO ₂	0.04	0.04	0.05	0.02	0.02
Al ₂ O ₃	18.50	19.55	20.10	17.14	20.48
MgO	0.26	0.06	0.07	0.07	0.13
FeO [*]	30.16	30.09	29.45	30.69	29.14
MnO	0.05	–	0.12	–	–
Na ₂ O	2.81	3.12	3.13	4.57	2.64
CaO	11.74	9.99	10.06	9.22	11.97
K ₂ O	0.06	0.25	0.45	0.26	0.05
Total	97.66	97.82	97.81	97.41	97.40
Recalculated Total ^{**}	100.18	100.30	100.28	100.10	100.01
<i>T site (8 apfu)</i>					
Si	5.427	5.491	5.434	5.64	5.233
Al	2.573	2.509	2.566	2.36	2.767
<i>C site (5 apfu)</i>					
Ti	0.004	0.005	0.006	0.003	0.003
Al	0.902	1.136	1.180	0.859	1.064
Fe ³⁺	0.783	0.697	0.693	0.956	0.876
Mn ²⁺	0.006	–	–	–	–
Fe ²⁺	3.239	3.147	3.104	3.129	2.992
Mg	0.062	0.014	0.017	0.016	0.030
<i>B site (2 apfu)</i>					
Mn ²⁺	–	–	0.017	–	–
Fe ²⁺	–	0.136	0.095	–	–
Ca	2.000	1.693	1.704	1.573	2.000
Na	–	0.171	0.184	0.427	–
<i>A site (0 to 1 apfu)</i>					
Ca	0.004	–	–	–	0.036
Na	0.868	0.785	0.774	0.983	0.811
K	0.013	0.051	0.09	0.053	0.011
Sum (T,C,B,A)	15.881	15.835	15.864	15.999	15.823

^{*} Fe calculated as FeO.^{**} Recalculated wt% total after cation calculations.

Dashed line indicates element below detection limit (Ni and Cr were also analyzed and below detection in all cases).

Cation assignments calculated using Locock (2014), on a 22O + 2(OH) basis.

OH, F, Cl not measured (see text for more information on F).