DATA REPOSITORY ITEM

SUPPLEMENTARY MATERIAL

METHODS

Infrared Spectroscopy

Ideally the olivine crystals would be oriented allowing polarized spectra to be recorded from parallel sections orthogonal to the three crystallographic directions; this is necessary to allow accurate quantification of the water content. However, the small size of the crystals grown in the experiments (<< 1mm) made this impractical in most cases. The aim of this work is not to quantify the water content but to determine the factors controlling the number and energy of hydroxyl bands (spectral fingerprint). Unpolarised spectra were therefore recorded from unoriented single crystals since this optimizes the probability of light being absorbed by all the oriented OH dipoles in the sample. Spectra were recorded for a number of crystals (>10) of different orientations (inferred from the Si-O overtone bands, which also distinguish olivine from orthopyroxene). The differences between the spectra are relatively small and the results reported are representative of the average intensity distribution. Spectra were normalized to the maximum peak height allowing band energies but not intensities (water concentrations) to be compared between samples. In some cases a few crystals were large enough to be prepared as doubly polished plates, allowing the thickness to be accurately determined and the water content estimated using the calibration of Bell et al. (2003). Since not all the hydroxyl groups may be excited in these measurements, the calculated water contents represent a minimum value.

Ti Determination

The Ti content of the olivines was determined by wavelength dispersive spectrometry (WDS) using an SX100 electron microprobe operating at 25 kV with a beam current of 20 nA, and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) using a pulsed ArF (193 nm) EXCIMER laser and an Agilent 7500 ICP-MS. Laser sampling was performed in an Ar-He atmosphere using a spot size of 110μm, 5 Hz ablation rate, and a laser energy of 70 mJ. A Nist612 glass was used as external, and Si as internal, standard.

XANES Spectroscopy

Ti K-edge X-ray absorption near edge structure (XANES) spectra were recorded in fluorescence mode for Ti-bearing olivine (Hermann et al., 2005) and a number of natural and synthetic materials with known Ti coordination. A plot of normalized height against energy

of the 1s → 3d pre-edge feature for standard materials defines distinct domains for [4], [5], and [6] coordinated Ti (Farges et al., 1996). The pre-edge feature for Ti in olivine has a height of ~1.1 which is diagnostic of [4] coordination. Hydrated samples show a marked decrease in the pre-edge intensity suggesting [6] or mixtures of [4] and [6] coordination.

References

Bell, D.R., Rossman, G.R., Maldener, J., Endisch, D., and Rauch, F., 2003, Hydroxide in olivine: A quantitative determination of the absolute amount and calibration of the IR spectrum: Journal of Geophysical Research, v. 108, B2, 2105, doi:10.1029/2001JB000679.

Farges, F., Brown, G.E., Jr., and Rehr, J.J., 1996, Coordination chemistry of Ti(IV) in silicate glasses and melts: I. XAFS study of titanium coordination in oxide model compounds: Geochimica et Cosmochimica Acta, v. 60, p. 3023–3038, doi: 10.1016/0016-7037(96)00144-5.

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Table DR1. Experimental details for the synthesis of olivine crystals. All experiments were at 1.5 GPa and 1400 ˚C for 24 hours. Ti contents of olivine are given where measured.

Olivine	Buffer	Composition					Capsule	Comments	Fig. 1
		$(Mg,Fe)_2SiO_4$	$(Mg,Fe)SiO_3$	MgO	TiO_2	H_2O			
Fo_{100}	high $aSiO_2$	68.5	24.4	-	-	7.1	Pt	melt	B
Fo_{100}	low $aSiO_2$	83.6	-	9.7	-	6.7	Pt		D
Fo_{100}	high $aSiO_2$ + TiO_2	40.4	47.5	-	7.5	4.6	Pt	melt, 380 ppm Ti	E
Fo_{100}	low $aSiO_2$ + TiO_2	76.4	-	8.8	8.4	6.4	Pt		J
Fo_{90}	high $aSiO_2$	69.4	22.3	-	-	8.3	Pt	melt, Fe loss	C
Fo_{90}	high $aSiO_2$	79.0	20.0	-	-	1.0	olivine	melt	G
Fo_{90}	high $aSiO_2$ + TiO_2	71.1	18.0	-	10.0	0.9	olivine	melt, 690 ppm Ti	F