

SUPPLEMENTARY MATERIAL**Sample Descriptions and Selection**

Chromian spinel (hereafter spinel) is mainly present as inclusions in silicate minerals and less commonly it forms phenocrysts. For this study of spinel compositions we chose samples that satisfy the following requirements:

- 1) All rock samples have volcanic origin, i.e. they are relatively rapidly quenched submarine or subaerial lava flows and tuffs or thin dykes with chilled margins. The rocks are fresh to moderately fresh. The choice of samples eliminates, as far as possible, the effects of post-entrapment modification of spinel compositions due to re-equilibration or alteration.
- 2) The volcanic rocks are representative of the different magma types occurring in well constrained tectonic environments, namely, mid-ocean ridges (MORB), ocean islands (OIB) and a variety of island arc settings.
- 3) Within each magmatic series the most primitive compositions (the highest Mg# ($\text{Mg}/[\text{Mg}+\text{Fe}^{2+}]$) and Cr and Ni contents) have been studied to minimise effects of fractionation and degassing on the magma oxidation state.

A complete set of rock samples used in this study is listed in Table S1. The relevant petrological and geochemical information on the rock suites may be found in publications cited in this table. The abundance of olivine phenocrysts in these rocks is quite variable (from a few % to 40-50 vol. %), and hence the rocks' MgO contents vary proportionally from ~6 to ~40 wt%. The range in the composition of olivine cores (Table 1), sometimes very large (10-15 mol% Fo) even within a single sample, which suggests that none of the studied rocks represents a true melt composition. Therefore, we regard these porphyritic rocks as a mechanical mixture of olivine and other silicate phenocrysts when present (e.g. plagioclase and clinopyroxene in MORB, clinopyroxene in arc volcanics, and low-Ca pyroxene in boninites) and a residual melt (groundmass). The most Fe-rich olivines are usually in equilibrium with the groundmass composition, whereas more forsteritic olivines crystallised from more primitive melts at higher temperature, and were incorporated in the magma not long before the eruption. Forsteritic olivines may also be xenocrysts from the mantle, but inclusion relationships and crystal shape and size were used to exclude any such grains from this study. Olivine phenocrysts with their spinel and melt inclusions remain largely unequilibrated with the transporting melt, and thus offer snapshots of the preceding magmatic evolution.

Olivines

The ranges in olivine Fo content in the studied rocks (Table S1) extend to the highest values recorded for a given type of magmatism. The presence in our collection of olivine Fo92 (mid-ocean ridges), Fo90 (ocean islands), and Fo94.5 (island arcs) is good evidence for crystallisation from high-temperature mantle-derived melts. Information on the composition of melts parental to spinel in a number of samples was also obtained from the study of melt inclusions trapped in either spinel or olivine phenocrysts.

Spinel Inclusions in Olivine

Spinel inclusions are found in olivine phenocrysts from all magma types, but the abundance of spinel is highly variable. Some phenocrysts may contain numerous swarms of 5-6 to several tens of inclusions (typically in boninites), but more often they host either only occasional individual grains, or the majority of olivines are devoid of any inclusions.

Spinel inclusions are always octahedral varying in size from several μm (in boninites and arc tholeiites) to 0.5 mm (in MORB and OIB). The color of spinels in thin sections and brightness in reflected light depend on chemical composition, e.g. Fe-Ti-rich spinels are the brightest and almost opaque, Cr-rich spinels are translucent reddish- to yellow-brown, and Al-rich spinels are the least reflective, greenish-yellow to dull green in color.

Sample Preparation and Analysis

The samples were crushed and sieved, and 50-200 olivine phenocrysts (0.3-1 mm) from each sample were hand picked, mounted in epoxy mounts, exposed and polished. Spinel inclusions in olivine grains in these mounts were marked for analysis. Spinel inclusions and their olivine hosts were analysed by electron microprobe at the University of Tasmania and University of Paris VI (Cameca SX-50) and Vernadsky Institute of Geochemistry, Moscow (Camebax microbeam), using wavelength dispersive spectrometry at 15 kV. Mineral (San Carlos olivine USNM 111312/444 and Cr-spinel UV-126) secondary standards were analysed before and after each run, and 2-5 analytical points were used to calculate average composition. At least 25 grains of olivine and 5 spinels were studied in each sample. Host olivine was analysed not further than 20 μm from the spinel inclusions. The large number of analyses of individual olivine grains allowed determination of the entire range of olivine compositions, so that analyses of spinels were selectively performed on grains trapped in olivines over a wide range of Fo contents.

Spinel and olivine compositions were calculated on the assumption of stoichiometry. The electron microprobe was not specifically calibrated to obtain accurate Fe^{3+} contents, and previous workers (Wood and Virgo, 1989) noted inaccuracies in calculated $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios of spinel for microprobe measurements, which correlated with their $\text{Cr}/(\text{Cr}+\text{Al})$ ratio (Cr#). Although the arc data does show an overall trend of increasing $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ with decreasing Cr# (Fig. S1a), no such trend is visible in the data set as a whole, and the calculated differences in oxygen fugacities between MORB, OIB, boninite and arc are not related to their Cr# (Fig. S1b). Similar investigations were undertaken for relationships between other elements and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ but no significant relationship was found. The original oxy-barometer was calibrated for

orthopyroxene-bearing rocks and indeed it is likely that opx was present in the mantle source. However, an absence of opx is associated with uncertainties of less than half a log unit in the calculated oxygen fugacities (Ballhaus et al. 1991).

Redox Budget Calculations

The redox budget of a sample is defined as the number of moles of electrons that need to be added to the sample to reach the given reference state:

$$RB = \sum_i n_i v_i \quad [S1]$$

where RB is the redox budget, n_i is the number of moles of redox state i present in the sample of interest, and v_i is the number of electrons required to take one mole of redox state i to the reference redox state.

For example, the redox budget of two moles of FeO with respect to a reference state of Fe as Fe^{3+} and O as O^{2-} is -2, because 2 moles of electrons would need to be removed to oxidize the Fe^{2+} to Fe^{3+} . The term used for the redox budget of a unit mass or quantity is 'specific redox budget' (\underline{RB}); here \underline{RB} is used with the units of moles kg^{-1} .

The redox budget was plotted against the MgO content of the data analyses from the GeoRoc database to allow samples affected by fractional crystallisation to be recognised and removed from the datasets. Fractional crystallisation of olivine increases the redox budget of the residual liquid because ferric iron is incompatible in olivine and is retained in the melt. MgO minima of 8 – 9.5 % were used, depending on the arc. Obvious outliers with high Fe^{3+}/Fe_{tot} were assumed to have suffered post-eruption oxidation and were removed from the datasets. Additionally, arcs from which the number of data points was too small to define the fractionation trend, or where the fractionation trend could not be distinguished because of excessive scatter, were eliminated from the dataset.

For this work a reference state of Fe as Fe^{2+} , C as C^{+4} , S as S^{2-} , H as H^{+} , and O as O^{2-} was chosen to enable analyses to be compared to a mantle-like baseline. It was also assumed that carbon, hydrogen, oxygen and sulphur contents at oxidation states other than the reference states were negligible, so the specific redox budget of a sample is simply the total iron content in moles per kg, multiplied by the proportion of ferric iron.

The age of the basalts is not recorded in the GeoRoc database so it is not possible to state unambiguously that the basalts are young relative to the age of the subduction zone, an assumption which is implicit in the calculations. However, the sampling process favours the selection of the younger basalts, since these are more likely to be available at the surface for sampling. An additional implicit assumption is that the convergence rate has been constant over the life of the subduction zone. Clearly, this is a faulty assumption, because convergence rate increases as the arc ages, and it is for this reason that the product of convergence rate and subduction zone age is viewed as a proxy for total length of crust subducted rather than a realistic estimate. Effects of the assumption of constant convergence rate on the results are difficult to estimate because past convergence rates are not well constrained. However, the high

degree of significance of the observed relationship suggests that variations in subduction rate over the history of the subduction zone have not obscured the trends under investigation.

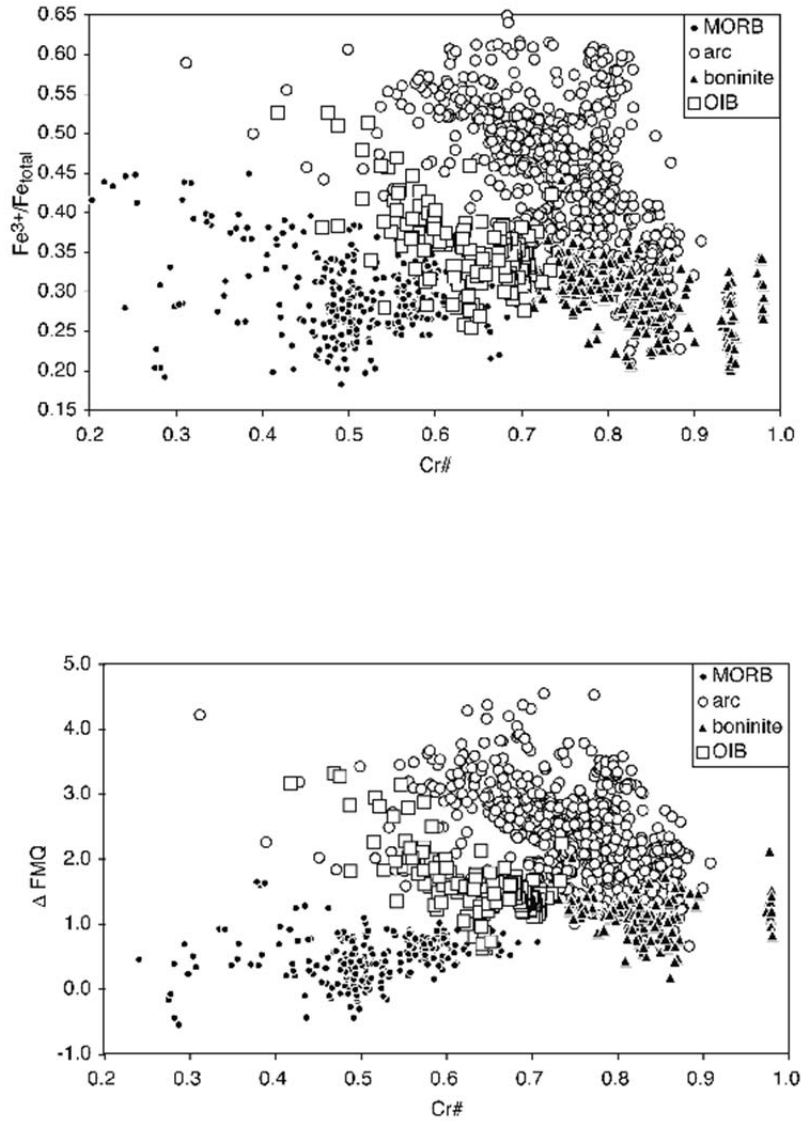


Figure DR1: a: Correlation between Fe^{3+}/Fe_{tot} (calculated from stoichiometry) and Cr# ($=Cr/(Cr+Al)$) of spinel. Although the arc data show a correlation, the differences in Fe^{3+}/Fe_{tot} between groups cannot be explained by variable Cr#. b: Correlation between calculated oxygen fugacity and Cr#, showing that differences between groups are again not correlated with Cr#.

Table DR1

Locality	Reference	Olivine, Fo	Spinel (compositional range)				
			Mg #	Cr#	TiO ₂	Fe ²⁺ /Fe ^{3+*}	
Mid-ocean ridges (MORB)							
15°20'N FZ, MAR	Dmitriev et al. (1991)	87.3-89.2	65-71	41-51	0.3-0.6	1.8-2.2	
FAMOUS area, MAR	Kamenetsky (1996), Langmuir et al. (1977)	88.3-92.0	68-79	28-56	0.1-0.4	2.2-4.4	
43°N, MAR	Kamenetsky and Crawford (1998), Kamenetsky et al. (1998), Shibata et al. (1979)	87.4-91.6	57-79	33-71	0.2-4.1	1.5-3.6	
Lamount seamounts, EPR	Allan et al. (1988)	88-91	66-84	20-54	0.2-0.9	1.2-1.9	
Macquarie Island, SW Pacific	Kamenetsky et al. (2000)	84.2-90.4	55-77	26-59	0.3-1.5	1.4-3.1	
Island arcs (tholeiitic, calc-alkaline, high-K)							
East Kamchatka (Valaginsky, Tumrok)	Kamenetsky et al. (1995)	84.7-94.3	33-74	67-87	0.2-1.0	0.6 – 1.0	
Aeolian arc (Vulcano, Lipari)	Gioncada et al. (1998), Kamenetsky and Clocchiatti (1996)	87.3-90.5	46-60	76-81	0.4-0.7	0.9-2.4	
Vanuatu (Ambae)	Eggins (1993)	81.9-93.4	34-72	43-81	0.3-1.7	0.8-1.9	
Vanuatu (Ambrym)	Picard et al. (1995)	85.1-93.8	34-71	83-91	0.2-0.5	1.4-3.7	
Solomon Islands (New Georgia)	Ramsay et al. (1984)	81.1-93.3	28-65	53-85	0.1-4.7	0.5-1.5	
Vanuatu (Tanna) tholeiite	Monzier et al. (1997)	82.1-92.3	40-64	82-87	0.2-0.3	1.9-3.8	
S. Vanuatu seamounts high-Mg andesites	Monzier et al. (1993)	80.9-94.5	34-79	50-81	0.2-1.4	0.6-2.2	
Hunter Ridge -Hunter FZ tholeiites	Sigurdsson et al. (1993)	80.5-94.3	38-77	39-87	0.1-0.5	1.0-2.8	
Island arc (boninitic)							
Howqua, Victoria (boninite)	Crawford (1980)	93.6-94.8	61-78	97-98	0-0.04	2.0-3.3	
Cape Vogel, PNG (boninite)	Walker and Cameron (1983)	92.0-94.1	65-79	89-95	0-0.2	2.1-4.0	
Hunter Ridge -Hunter FZ boninites	Sigurdsson et al. (1993)	85.2-92.2	47-69	72-90	0-0.4	1.3-4.1	
Troodos Upper Pillow Lavas (boninites)	Sobolev et al. (1993)	88.4-93.4	60-74	67-80	0.2-0.4	1.7-2.9	
New Caledonia boninites	Cameron (1989)	88.5-93.6	56-75	83-87	0.1-0.3	2.2-3.4	
Ocean islands (OIB)							
Hawaii (Kilauea, Mauna Loa, Mauna Kea)	Sobolev and Nikogosian (1994)	76.9-90.1	36-68	49-73	1.1-3.3	1.2-2.7	
Reunion	Sobolev and Nikogosian (1994)	79.8-88.9	40-62	57-65	1.5-7.5	1.6-2.9	
French Polynesia (Tubuai, Mangaia)	Maury et al. (1994), Woodhead (1996)	77.9-86.6	24-56	42-66	1.5-15	0.9-2.2	

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