

Fe³⁺ distribution between garnet and pyroxenes in mantle wedge carbonate-bearing garnet peridotites (Sulu, China) and implications for their oxidation state

Nadia Malaspina ^{a,*}, Falko Langenhorst ^b, Patrizia Fumagalli ^c, Simone Tumiami ^c, Stefano Poli ^c

^a Dipartimento di Scienze Geologiche e Geotecnologie, Università degli Studi di Milano Bicocca, Piazza della Scienza 4, 20126 Milano, Italy

^b Institut für Geowissenschaften, Friedrich-Schiller Universität Jena, Carl-Zeiss Promenade 10, 00745 Jena, Germany

^c Dipartimento di Scienze della Terra, Università degli Studi di Milano, via Botticelli 23, 20133 Milano, Italy

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ABSTRACT

This study presents new measurements of Fe³⁺ in garnet, olivine, clinopyroxene and orthopyroxene of a mantle-derived garnet peridotite from Donghai County, the southeastern end of the Sulu ultrahigh pressure terrane. These rocks correspond to a slice of supra-subduction lithospheric mantle wedge, tectonically emplaced into the crust. They record a multistage metasomatism by an alkali-rich silicate melt at high temperature, and a subsequent influx of a slab-derived incompatible element and silicate-rich fluid during the Triassic UHP metamorphism. We employed two “unconventional” techniques to measure the Fe³⁺/ΣFe content of mineral phases with high spatial resolution: (i) the flank method electron microprobe analyses for garnet, performing for the first time quantitative Fe₂O₃ map analyses on zoned garnets at the Dipartimento di Scienze della Terra, University of Milano, and (ii) the electron energy loss spectroscopy (EELS) for garnet, olivine and pyroxenes, at the Bayerisches Geoinstitut, University of Bayreuth.

The results indicate that the pyrope-rich metasomatic garnets present a chemical zoning, with the complementary decrease in Al₂O₃ from ~23 to ~21 wt.%, relative to the increase of Fe₂O₃ from ~0.8 to ~2.5 wt.%. Such a trend is likely related to the Fe³⁺–Al substitution in the garnet octahedral site, which is sensitive to the garnet oxidation state. Clinopyroxenes are diopsidic in composition, whereas olivine and orthopyroxene have ~92 mol% of forsterite and enstatite, respectively. The EELS measurements show that clinopyroxene contains relatively high Fe³⁺/ΣFe ratios and Na contents, ranging from 0.48 to 0.51 and from 0.13 to 0.17 a.p.f.u., respectively. Interestingly, also orthopyroxene may contain Fe³⁺/ΣFe up to 0.10 (±0.05), a percentage comparable to that of garnet, with important consequences in the study of redox processes in mantle rocks and in the application of many geothermometers.

Garnet/clinopyroxene and orthopyroxene/clinopyroxene qualitative partitioning indicates a minimum redistribution of Fe³⁺ from clinopyroxene to garnet. The enrichment in Fe³⁺ of Ca-clinopyroxene requires the incorporation of a NaFe³⁺Si₂O₆ (aegerine) component, particularly in garnet peridotites where the Al content of clinopyroxene is buffered by its coexistence with garnet. The coupled Na–Fe³⁺ enrichment of our clinopyroxene likely suggests a corresponding enrichment in the whole rock. The Fe³⁺ substitution mechanism into clinopyroxene as aegerine component could be therefore favoured by the influx of Fe₂O₃-alkali-rich metasomatic fluid phases. This suggests that a possible net bulk oxidation and the redistribution of Fe³⁺ between garnet and pyroxenes could depend on additional variables besides temperature and pressure. Such mechanisms open new possibilities to unravel the redox processes occurring in the portion of mantle wedge interfacing the subducting slab, which is a key location where the mantle redox reactions likely occur.

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1. Introduction

Changes of oxygen concentration in the Earth's atmosphere can be closely related to the composition of volatiles released from magmatic activity, which in turn depends on the variations of the oxidation state and on the redox processes occurring in their source regions in

the deep mantle (Catling and Claire, 2005). Although much is known about the oxidation state of the upper mantle as described by oxygen fugacity (*f*O₂) as an intensive variable, the relationships between such *f*O₂ values and the oxygen extensity still remain largely unconstrained. The equilibria between Fe³⁺ and Fe²⁺ contents in mantle mineral assemblages (silicates and oxides) may buffer the oxygen fugacity and the speciation between C, H and S, the most important volatiles in the mantle. Conversely, equilibria between volatile species in an excess fluid may control the oxidation state of mantle phase assemblages by redox reactions (Canil et al., 1994; Catling

* Corresponding author.

E-mail address: nadia.malaspina@unimib.it (N. Malaspina).

Table 1

Representative major element compositions (wt.% and atoms per formula units) of garnets (cores) and coupled pyroxenes from the Sulu peridotite.

	Cpx ₁	Grt ₁	Cpx ₁	Grt ₁	Opx	Cpx ₂	Grt ₂	Opx	Cpx ₂	Grt ₂	Opx
SiO ₂	54.53	42.28	54.61	41.54	57.60	54.34	41.70	57.57	54.38	41.65	57.97
TiO ₂	0.16	0.02	0.03	0.03	bdl	0.03	bdl	0.01	0.01	0.02	bdl
Al ₂ O ₃	1.21	22.72	1.14	22.13	0.13	1.57	20.99	0.14	1.85	21.41	0.16
Cr ₂ O ₃	1.61	2.27	1.29	2.61	0.08	1.82	3.71	0.07	1.43	3.81	0.07
FeO	1.08	7.59	1.36	9.52	4.87	1.00	9.96	4.62	0.97	10.47	4.63
Fe ₂ O ₃	1.59	1.14	1.14	0.18	0.47	1.16	0.95	0.57	0.99	0.54	0.57
MgO	16.02	19.41	16.33	18.76	36.87	15.76	18.32	36.94	16.04	18.17	36.97
MnO	0.19	0.40	0.00	0.48	0.07	0.00	0.55	0.07	0.01	0.56	0.07
CaO	21.58	4.88	22.15	4.80	0.09	21.60	4.42	0.07	22.05	4.34	0.08
Na ₂ O	1.90	bdl	1.91	bdl	0.01	2.14	bdl	0.01	1.97	bdl	0.03
Total	99.87	100.71	99.97	100.04	100.20	99.42	100.59	100.07	99.71	100.98	100.55
Si	1.98	2.99	1.98	3.00	1.97	1.98	3.00	1.97	1.98	2.99	1.98
Ti	0.00	0.00	0.00	0.00	bdl	0.00	0.00	0.00	0.00	0.00	bdl
Al	0.05	1.90	0.05	1.88	0.01	0.07	1.78	0.01	0.08	1.80	0.01
Cr	0.05	0.13	0.04	0.15	0.00	0.05	0.21	0.00	0.04	0.22	0.00
Fe ²⁺	0.03	0.47	0.04	0.57	0.14	0.03	0.61	0.13	0.03	0.62	0.13
Fe ³⁺	0.04	0.04	0.03	0.02	0.01	0.03	0.04	0.01	0.03	0.05	0.01
Mg	0.87	2.05	0.88	1.96	1.88	0.86	1.96	1.89	0.87	1.94	1.88
Mn	0.01	0.02	0.00	0.03	0.00	0.00	0.03	0.00	0.00	0.03	0.00
Ca	0.84	0.37	0.86	0.37	0.00	0.84	0.34	0.00	0.86	0.33	0.00
Na	0.13	bdl	0.13	bdl	0.00	0.15	bdl	0.00	0.14	bdl	0.00
Total	4.01	7.97	4.02	7.99	4.02	4.02	7.98	4.02	4.02	7.99	4.01
Fe ³⁺ /ΣFe	0.57	0.08	0.43	0.03	0.08	0.51	0.06	0.10	0.48	0.07	0.10

and Claire, 2005; Luth, 1999). Such reactions therefore depend on the abundance of redox-sensitive elements, such as Fe, and on the moles of oxygen exchanged in the redox equilibria (Canil et al., 1994).

Oxygen fugacity in high pressure peridotites is traditionally determined from the Fe²⁺ and Fe³⁺ contents of garnet in equilibrium with olivine and orthopyroxene. However, the determination of the bulk oxidation state of most metasomatised garnet peridotites is a demanding task because several phases, besides garnet (or spinel), incorporate both ferric and ferrous iron (e.g. clinopyroxene, amphibole, phlogopite), and the Fe³⁺ distribution between peridotite minerals is often neglected. The partitioning systematics of Fe³⁺ between garnet and pyroxenes has important implications for the dynamics of the Earth's interior. On a global scale, redox processes not only govern volatiles speciation but also control melting processes via hydrous or carbonate redox melting (Foley, 2011). Furthermore, an accurate determination of ferric iron in peridotite mineral assemblages enables to obtain much more precise results in the use of thermometers such as the Fe²⁺–Mg exchange between garnet, olivine, orthopyroxene and clinopyroxene (Krogh-Ravna and Paquin, 2003; Nimis and Grütter, 2010). In natural garnet peridotites the Fe³⁺ content in garnet may increase significantly with increasing temperature and pressure. Previous studies by Canil and O'Neill (1996), Woodland and Peltonen (1999), Woodland and Koch (2003), Rohrbach et al. (2007, 2011) and Woodland (2009) demonstrated that the increase of Fe³⁺ in garnet with increasing temperature is not a simple relation with the whole rock Fe₂O₃, but is rather the consequence of the redistribution of Fe³⁺ from clinopyroxene into garnet. This implies that the Fe³⁺ content of all the mineral phases and their possible Fe³⁺ zonation must be considered to obtain reliable quantifications of the oxidation state of the whole rock.

Currently very little data are available on the Fe³⁺ content of mantle pyroxenes coexisting with garnet (Canil and O'Neill, 1996; Woodland, 2009; Woodland and Peltonen, 1999), in particular there is no data for supra-subduction mantle peridotites. This study presents new measurements of Fe³⁺ in garnet, clino- and orthopyroxene of a mantle-derived garnet peridotite from Donghai County, the southeastern margin of the Sulu ultrahigh pressure (UHP) terrane. These rocks correspond to a slice of supra-subduction lithospheric mantle wedge, tectonically emplaced into the crust (Yang, 2003; Yang and Jahn, 2000; Zhang et al., 1995, 2000). They record a multi-stage metasomatism by alkali-rich silicate melt at high temperature, and a subsequent influx of a slab-derived incompatible element and

silicate-rich fluid during the Triassic UHP metamorphism (Malaspina et al., 2009a). We employed two techniques to perform Fe³⁺/ΣFe measurements at very high spatial resolution: (1) flank method electron microprobe analyses for garnet, and (2) the electron energy loss spectroscopy (EELS) for garnet and pyroxenes, in order to quantify the Fe³⁺ distribution among the peridotite phases and estimate the bulk oxidation state of the peridotite.

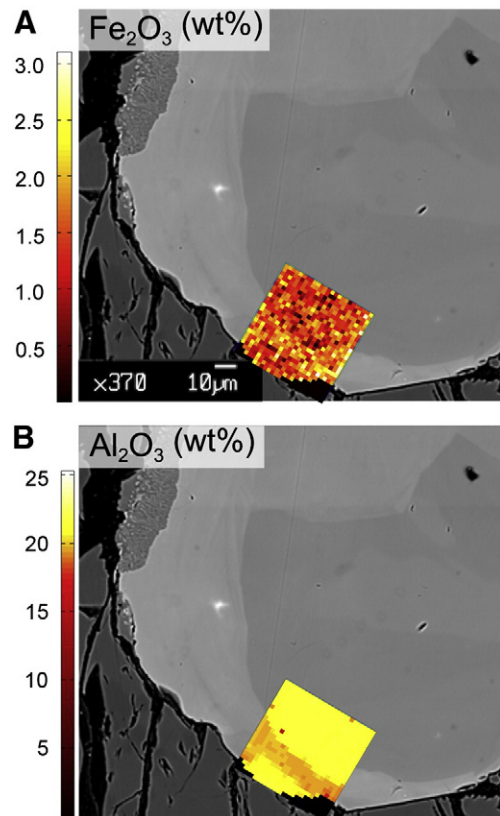


Fig. 1. Back scattered electron image of a zoned Grt₂ and quantitative map analyses of Fe₂O₃ (A) and Al₂O₃ (B) elaborated from a grid of 25 × 25 combined flank method and quantitative elemental analyses.

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