

Iron oxidation state in Greek Cr-ore minerals

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Although electron microprobe analysis (EMPA) is the most common analytical method for the study of mineral chemistry, it cannot recognize the multiple oxidation states of transitional metals and, as a sequence, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is calculated stoichiometric. In the case of spinels, this calculation method is applied assuming a proportion of 1 bivalent and 1 trivalent cation per 4 oxygens, thus ignoring the possibility of non-stoichiometry due to Fe^{3+} excess and cation vacancies in the lattice (Quintilani *et al.*, 2006).

For the determination of the actual Fe oxidation states in minerals, ^{57}Fe Mössbauer spectroscopy (MS) has been proven to be a very effective method (Wood and Virgo, 1989, McCammon *et al.*, 1998, Sobolev *et al.*, 1999, Quintilani *et al.*, 2006). The determination of the actual oxidation states of Fe and the attribution of Fe^{2+} and Fe^{3+} to the tetrahedrally and octahedrally coordinated T and M sites in spinels has been proven to be accurately calculated by the application of MS (e.g., Andreatti *et al.*, 2001, Hälenius *et al.*, 2002, Quintilani *et al.*, 2006). Furthermore, since Fe ratios of Cr-spinels are used for the estimation of $f\text{O}_2$ by the Ballhaus *et al.* (1990) oxygen geobarometer and for the estimation of equilibrium temperatures by the Ballhaus *et al.* (1991) geothermometer, the determination of the actual oxidation states of Fe and their use in these estimations is valuable for the accurate reconstruction of the thermo-oxidative history of Cr-spinel host rocks.

The aim of this study is to present new MS data of spinels (chromites) from Vourinos ophiolitic sequence chromitites and compare the actual Fe oxidation states calculated by MS with the stoichiometric calculations based on EMPA.

Four chromitite samples from three mining sites of Vourinos chromite mining district were used for this study: Xerolivado-Skoumtsa (2 samples), Aetoraches (1 sample) and Rizo (1 sample). All samples were examined in transmitted and reflected light optical microscopes. Mineral chemistry was determined with a JEOL 8200 electron microprobe equipped with a wavelength dispersive system (SEM-WDS). The system was operated using an accelerating voltage of 15 kV, a sample current on brass of 15 nA, a counting time of 20 s on the peaks and 10 s on the background. A series of natural minerals were used as standards. The approximate detection limit is 0.01 wt.% for each element. For each sample, 4-6 of unaltered Cr-spinel cores were analyzed and their compositions averaged to produce a statistical result. The samples were crushed, grained and, with the use of magnetic separator, chromite was separated from the other mineral phases present. These almost pure (>90 wt.%) chromite samples were analyzed by means of ^{57}Fe Mossbauer spectroscopy.

Fe^{2+} and Fe^{3+} cations based on four oxygen and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios calculated by different approaches are presented in Table 1, whereas MS spectra acquired for the four samples is presented in Figure 1.

Table 1. Calculations of Fe^{2+} and Fe^{3+} cations and $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for the studied samples.

Sample		XER5	XER10	RIZ3	AET4
Parameter	Method				
Fe^{2+} cations based on 4 (O)	EMPA	0.348	0.359	0.338	0.330
Fe^{3+} cations based on 4 (O)	EMPA	0.085	0.048	0.069	0.053
$\text{Fe}^{3+}/\text{Fe}^{2+}$	EMPA	0.246	0.135	0.205	0.161
$\text{Fe}^{3+}/\Sigma\text{Fe}$	EMPA	0.197	0.119	0.170	0.139
$\text{Fe}^{3+}/\text{Fe}^{2+}$	MS	0.250	0.140	0.330	0.200
$\text{Fe}^{3+}/\Sigma\text{Fe}$	MS	0.200	0.120	0.250	0.170

Comparison between spinel Fe^{3+} contents calculated by EMPA and measured by MS show significant differences: Fe^{3+} contents calculated by EMPA range between 11.9 to 19.7% of total Fe, whereas Fe^{3+} contents measured with MS range between 12 and 25%. In addition, the values of $\text{Fe}^{3+}_{\text{MS}}$ content is higher in all samples compared to the $\text{Fe}^{3+}_{\text{EMPA}}$ content. The differences observed in the Fe^{3+} contents by the different approaches are due to non-stoichiometry. MS can reveal

the Fe³⁺ excess of Cr-spinels while the EMPA approach cannot (Bosi *et al.*, 2004). Fe³⁺ excess is attributed the fact that during Cr-spinel oxidation, the only cations involved are Fe²⁺ and Fe³⁺. During this process, tetrahedrally coordinated Fe²⁺ oxidized to Fe³⁺ with the formation of a cation vacancy in the T site (Quintilani *et al.*, 2006).

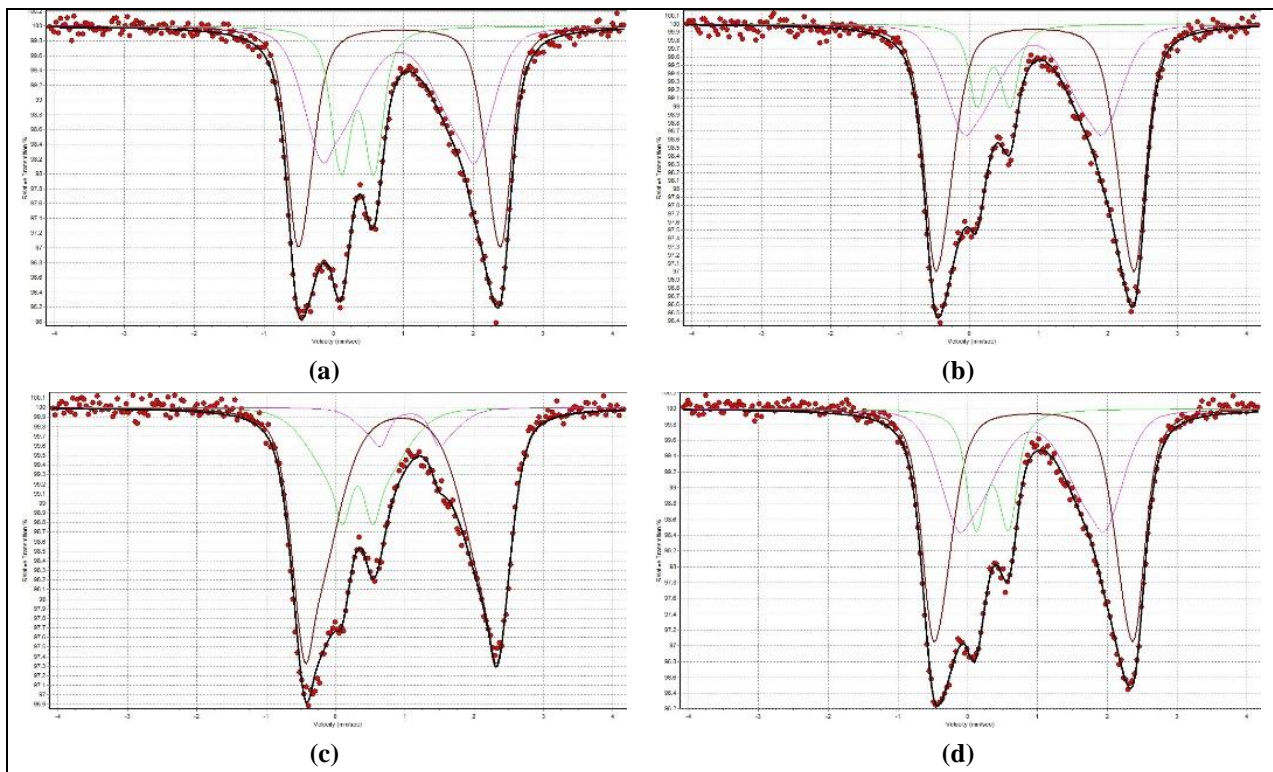


Figure 1. MS spectra of Vourinos Cr-spinel samples recorded at 77 K: (a) XER10, (b) XER5, (c) RIZ3 and (d) AET4.

The difference is slight in samples from Xerolivado-Skoumtsa (Southern Vourinos-samples XER5 and XER10) and significant in samples from Northern Vourinos (Rizo-sample RIZ3 and Aetoraches-sample AET4). This fact implies higher oxidation degrees (Bosi *et al.*, 2004) for Northern Vourinos Cr-spinels than of those from Southern Vourinos were oxidation seems to be insignificant, implying a relation between the degree of oxidation and provenance.

Ongoing research is targeting the further investigation of the latter remark and the estimation of the geothermo-barometric conditions via the accurate quantification of Fe³⁺ that has been revealed by MS measurements.

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