

Supplemental Information

Systematics of H₂ and H₂O evolved from chlorites during oxidative dehydrogenation

Małgorzata Lempart (1) *, Arkadiusz Derkowski (1) *, Tomasz Strączek (2), Czesław Kapusta (2)

(1) Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Krakow, Senacka St. No. 1, PL-31002 Krakow, Poland (2) AGH University of Science and Technology, Faculty of Physics and Applied Computer Sciences, Al. Mickiewicza St. No. 30, PL-30059, Krakow, Poland

* Corresponding authors. Email: ndlempar@cyf-kr.edu.pl (M. Lempart);
ndderkow@cyf-kr.edu.pl (A. Derkowski)

Methods

X-ray diffraction

The products of heating chlorites and biotite to 1000 °C were analyzed using ex-situ X-ray powder diffraction (XRD) in order to identify the mineral composition of recrystallization products. Approximately 15 mg of the sample recovered after TG-MS analysis was gently ground and dispersed on a silicon low-background holder that did not allow performing quantitative analysis. XRD patterns were recorded over a $5 - 65^{\circ}2\theta$ range with $\text{CuK}\alpha$ radiation for 3s/0.02 2θ step on the ARL X'tra Thermo diffractometer. The diffractometer was equipped with two Soller 2° slits with 0.9 mm divergent slit, 0.3 mm receiving slit and 1.6 mm divergent scatter slit (a fixed divergence of 0.6940°). To identify newly formed phases the Crystallography Open Database (COD) was used.

Results and Discussion

Recoil-free fraction

As the Fe(II)/ Fe(III) ratio determined by Mössbauer spectroscopy is strongly influenced by the recoil-free fraction (f), this separate section is dedicated to discussing this issue. In the previous works related to Mössbauer measurements of heated phyllosilicates, f fraction of Fe(II) and Fe(III) was not determined or its ratio was only assumed be approximately equal 1.00 (works of Rancourt D.G. and MacKenzie K.J.D. e.g. Rancourt et al. 1993, 2001; MacKenzie and Berezowski 1984; MacKenzie et al. 1986). However, more recent studies revealed the importance of the evaluation of f , when using Mössbauer spectroscopy for determination of Fe(III)/Fe(II) ratio (Eeckhout and De Grave 2003; Dyar et al. 2006). As the determination of f for chlorites and biotite analyzed in the present study would require a new investigation based on Mössbauer

spectroscopy measurements in various temperature ranges (Dyar et al. 2006), hence the Fe(III)/Fe(II) ratios determined only at room temperature measurements was corrected using various published values of f (C_f values in Tab. 4). In the samples heated under air gas atmosphere all the Fe(II) was oxidized, hence the f fraction did not need to be determined. As the aim was to achieve as close to true Fe(II) and Fe(III) contents, we had to separately consider three structurally varied group of minerals: the natural chlorites, biotite and oxybiotite, and the recrystallization products of chlorites.

Dyar et al. (2008) studied the effect of f on Fe(III)/Fe(II) ratios across selected clay minerals, but f for natural chlorites has not yet been determined. Kodama et al. (1982) and Aja and Dyar (2002) assumed that f fraction for Fe(II) is equal to Fe(III) in Fe-rich clinocllore and Mg-rich chamosite. Gailhanou et al. (2009) and De Grave et al. (1987) showed an agreement between Fe(III)/Fe(II) ratio obtained at 300K and 77K for chlorites. This observation can serve as evidence that f fractions of Fe(III) and Fe(II) can be similar (cf. Dyar et al. 2006). As the f fraction is dependent on the geometry of sites and bond strength (Dyar et al. 2006, 2008) and our tested chlorites contained Fe(II) and Fe(III) occupying the same octahedral positions (without Fe(III) in the tetrahedral position), the f^{3+}/f^{2+} ratio should not be strongly affected by the difference in the cation environment. Therefore, we assumed that the f fraction for tested natural chlorites was equal for Fe(II) and Fe(III) (within the absolute errors), and is independent of their crystallographic site.

The f fraction for biotite could be more affected than for chlorite, because Fe(III) can occupy both an octahedral and tetrahedral position. Based on the study of Dyar et al. (2008), Fe(III)/Fe(II) ratio for natural LP-6 biotite was corrected by $f^{3+}/f^{2+} = 1.28$, that was evaluated for 295 K Mössbauer spectroscopy measurements. Whereas Fe(III) calculated from direct area was

24 % (Fe(III)_I), the corrected value was 19.8 % (Fe(III)_{Cf}) and, accordingly 80.2% of Fe(II)_{Cf} (Tab. 4). Due to the incomplete dehydroxylation of LP-6 after heating to 1050 °C, the biotite structure did not undergo phase transformation and the product remained as oxybiotite (Vedder and Wilkins 1969), which has been confirmed by XRD measurements (Suppl. Fig. 2b). The XRD pattern also revealed a small amount of forsterite, it was not taken into account during calculations, because even if Fe(II) occurred in this forsterite, the f fraction of Fe(II) in forsterite and biotite is similar (cf. Sklute et al. 2005; Dyar et al. 2008). Therefore, the $\text{Fe(III)}/\text{Fe(II)}$ ratio was corrected using the same value as for the natural biotite, returning 74% of newly formed Fe(III) in the heated biotite ($\Delta\text{Fe(III)}_{Cf}$).

A recoil-free fraction correction for samples with a polymineral character has not been investigated yet, so the reaction products of chlorites should be investigated with a different approach than for biotite. After heating, all the tested chlorites recrystallized into an olivine belonging to the Mg-Fe solid solution series and spinel-like structures $\text{MgFeAl}_2\text{O}_3$; these phases are difficult to precisely identify and quantify by XRD (see Methods section). XRD patterns of the natural chlorites were shown by Luberdá-Durná et al. (2019). After heating, Mal, Sptb and CCa-2 revealed the presence of forsterite (COD 9013093) and spinel (COD 9002044), whereas Fe-rich clinochlores showed the presence of Fe-containing forsterite. In turn, for MtBl and SG7 heating products faylite (COD 9000540) and spinel close to hercynite (COD 9002793) were identified. Besides, the presence of some amorphous material cannot be excluded (Brindley and Youell 1952; Steudel et al. 2016). Such a complex composition of heating products did not allow precise identification of the Fe(III) position. It was expected, however, that Fe(III) resides in spinel-like minerals (Hålenius et al. 2002), whereas olivine is likely, exclusively, the Fe(II) -bearing phase. Therefore, no certain links to recoil-free fraction effects in clinopyroxenes and

olivines, and spinels (Sklute et al. 2005; Dyar et al. 2007; Sklute 2011) could be established. Therefore, because of the difficulties of f evaluation, a generalization that $f^{3+} > f^{2+}$ was made following the studies of De Grave and Van Alboom (1991) and Eeckhout and De Grave (2003) on a different set of minerals containing Fe(II) or Fe(III). The maximum reported overestimation of Fe(III) (~15%) evaluated from the relative spectral areas at 300K (De Grave and Van Alboom 1991) was taken into account to show the highest potential bias for Fe(II)/Fe(III) ratios. Fe(III) determined from direct area measurements (Fe(III)_I) for heated CCa-2, Sptb, and Mal returned: 34, 33, and 29 %, which, after f correction, returned: 29, 28, and 25 % (Fe(III)_{Cf}), hence taking into account Fe(III) occurring in the untreated samples, the newly formed Fe(III) equals: 21, 22, and 4% ($\Delta\text{Fe(III)}_{Cf}$), respectively. In turn, 7 and 8 % of $\Delta\text{Fe(III)}_{Cf}$ was found for chamosites: SG7 and MtBl, respectively, besides the phase Fe(II)-(III) represents a mixed-valence state of Fe of 21 and 29%. As a result of the mixed-valence doublet determined for chamosites, their Mössbauer spectroscopy results still have considerable uncertainty.

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