

Mössbauer study of some Argentinian chlorites

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Three chlorite samples obtained from mining areas in Mendoza, Argentina, have been studied by wet chemical analysis, X-ray diffraction and ^{57}Fe Mössbauer spectroscopy. The total Fe contents and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ atomic ratio are used to characterize the samples and are discussed in connection to the likely genesis of the minerals.

1. Introduction

Chlorite-group minerals are 2 : 1 : 1 sheet silicates in which a single sheet of cations octahedrally coordinated by hydroxyl groups is sandwiched between two 2 : 1 silicate layers. The general formula is $(\text{M}_{6-x}^{2+}\text{M}_x^{3+})(\text{Si}_{4-x}\text{M}_x^{3+})\text{O}_{10}(\text{OH})_8$, with $\text{M}^{2+} = \text{Mg}, \text{Fe}$ and $\text{M}^{3+} = \text{Al}, \text{Fe}, \text{Cr}$. Iron can replace both Mg and Al in the crystal structure in a fraction and site that depends on the thermal and chemical histories of the mineral.

X-ray diffraction of powder specimens cannot be used to determine the tetrahedral and octahedral cation populations. Although several papers have studied chlorites by means of Mössbauer spectroscopy, the interpretation of the results is not straightforward [1–6]. Furthermore, there is still divergence in the tetrahedral Fe^{3+} assignment of spectra of several minerals [7–9].

The present work intends to gain further information on the distribution of iron in the chlorite mineral structure and the relation between Mössbauer parameters and chemical composition.

2. Experimental

Three samples, in their natural forms were obtained from the talc deposits of

Cuchilla del Guarguaraz area in Mendoza, Argentina. They were analyzed by standard wet chemical procedures and X-ray diffractometry. The compositions were estimated as $\text{Mg}_{2.17}\text{Fe}_{1.03}^{2+}\text{Fe}_{0.64}^{3+}\text{Al}_{1.7}(\text{Si}_{3.12}\text{Al}_{0.87})$, $\text{Fe}/\text{Mg} = 0.766$ for sample No. 1, $\text{Mg}_{4.2}\text{Fe}_{0.5}^{2+}\text{Cr}_{0.39}\text{Fe}_{0.29}^{3+}\text{Al}_{0.5}(\text{Si}_{3.01}\text{Al}_{0.98})$, $\text{Fe}/\text{Mg} = 0.188$ for sample No. 2 and $\text{Mg}_{3.3}\text{Fe}_{0.7}^{2+}\text{Fe}_{0.12}^{3+}\text{Al}_{2.02}(\text{Si}_{2.76}\text{Al}_{1.23})$, $\text{Fe}/\text{Mg} = 0.248$ for sample No. 3. No other iron oxide phases were detected by these means. The room temperature Mössbauer spectra were taken in transmission geometry with a conventional spectrometer and fitted with a non-linear least-squares program with constraints to Lorentzian line shapes. Isomer shifts (δ) are referred to α -Fe at 300 K.

3. Results and discussion

Mössbauer spectra of the chlorites investigated are shown in fig. 1. They could be fitted with three doublets, except sample No. 3, where four quadrupolar interactions were needed. The hyperfine parameters are listed in table 1.

The results show that more than 80% of the total iron is in the ferrous state. Since for Fe^{2+} a lower quadrupole splitting (Δ) means more distortion around a site (the reverse of Fe^{3+}) the more intense ferrous iron doublet with Δ in the range 2.71 to 2.73 mm/s has been assigned to iron in cis-M2 sites and that of Δ in the range 2.46 to 2.48 mm/s to iron in trans-M1 sites.

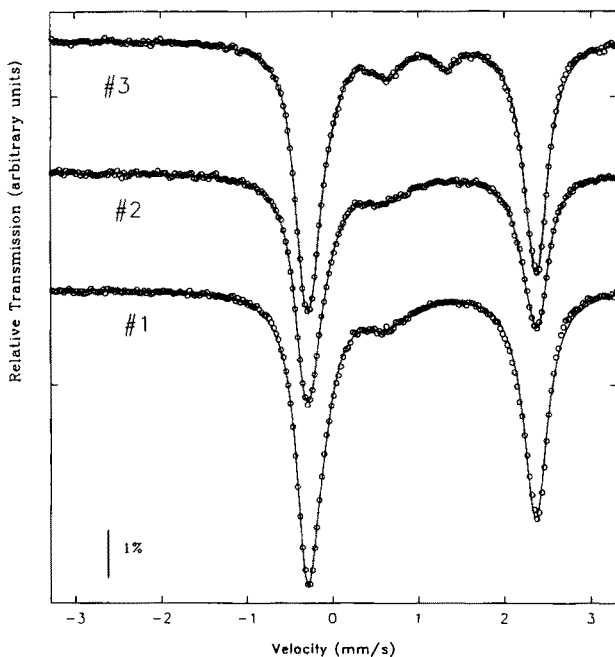


Fig. 1. Mössbauer spectra of chlorite samples Nos. 1–3 at room temperature.

Table 1

Mössbauer parameters. Isomers shifts (δ) relative to iron at 300 K. Γ is the linewidth and A is the relative area.

Sample No.	Δ (mm/s)	δ (mm/s)	Γ (mm/s)	A (%)
1	2.71 ± 0.01	1.13 ± 0.01	0.28 ± 0.01	48 ± 6
	2.46 ± 0.03	1.11 ± 0.02	0.35 ± 0.01	37 ± 5
	0.67 ± 0.05	0.42 ± 0.03	0.58 ± 0.03	15 ± 2
2	2.73 ± 0.01	1.12 ± 0.01	0.27 ± 0.01	40 ± 5
	2.51 ± 0.03	1.11 ± 0.02	0.34 ± 0.02	43 ± 6
	0.72 ± 0.04	0.37 ± 0.04	0.54 ± 0.04	17 ± 3
3	2.71 ± 0.01	1.16 ± 0.01	0.28 ± 0.01	57 ± 5
	2.48 ± 0.02	1.13 ± 0.01	0.31 ± 0.01	25 ± 4
	0.82 ± 0.05	0.44 ± 0.03	0.44 ± 0.05	12 ± 3
	0.76 ± 0.05	1.06 ± 0.03	0.29 ± 0.03	6 ± 3

The three samples display Fe^{2+} isomer shifts in the range 1.11–1.16 mm/s indicating that the bonding at these sites is similar in all samples. However, the increased Al substitution at tetrahedral sites (No. 1 = 0.87; No. 2 = 0.98; No. 3 = 1.23) that causes an augmented orbital overlap between the oxygen–iron bonds (increasing their covalence), may be the cause for the small changes in the isomer shifts of the predominantly ionic Fe–O bonds at the octahedral sites [10].

Fe^{3+} displays only one quadrupole doublet in all samples, in the range of values characteristic of octahedral coordination like those reported for biotite [10] or chlorite [2]. The broad line of the Fe^{3+} component is revealing the location of Fe^{3+} in the hydroxide sheet where the hydroxide layer contains a distribution of divalent (Mg) and trivalent ions (Fe^{3+} , Al^{3+}), close to Fe^{3+} ions, giving rise to slightly different quadrupole splittings at the Fe^{3+} sites.

The doublet with $\Delta = 0.76$ mm/s and $\delta = 1.06$ mm/s in sample No. 3 is likely originated in Fe^{2+} located in tetrahedral sites, that being only 6% of the total may not be detected by X-ray diffraction. Since sample No. 3 comes from a generalized alteration of ultra basic rocks originally constituted by olivine, Mg and Al spinels and pyroxenes, this signal may arise from an Al spinel formed during the cooling of the rock. Samples Nos. 1 and 2 have a different genesis instead. Coming from an hydrothermal vein that cross cuts different types of rock, by means of the fluid inclusions homogenization method we could determine that their depositional temperatures were in the range of 263–310°C.

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