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Fe SPECIATION IN WEATHERED PYROCHLORE-GROUP MINERALS FROM THE LUESHE AND ARAXÁ (BARREIRO) CARBONATITES BY ^{57}Fe MÖSSBAUER SPECTROSCOPY

MOHAMED NASRAOUI[§] AND JOÃO C. WAERENBORGH

Instituto Tecnológico e Nuclear, Estrada Nac 10, 2686-953 Sacavém, Portugal

ABSTRACT

The minerals of the pyrochlore group exhibit a large range of chemical composition. The general structural formula can be written as $A_{2-m}B_2X_{6-w}Y_{1-n}\bullet pH_2O$. The occupancy of the eight-fold-coordinated *A* site can reflect the degree of alteration of the pyrochlore. In unaltered pyrochlore-group minerals, this site is completely filled by Na and Ca, whereas in the altered equivalents, the *A* site is only partly filled by cations as K, Ba, Sr and Ce. In the literature, the structural formula is systematically calculated assuming an ideal stoichiometry, *i.e.*, a total of two six-fold-coordinated *B*-site cations per formula unit, dominantly Nb, with subordinate Ti and Ta in certain rock-types, *e.g.*, carbonatites. Fe is systematically considered as Fe^{3+} and assigned to the *B* site. The present ^{57}Fe Mössbauer study focuses on altered pyrochlore-group minerals from two Nb ore deposits in laterite: Lueshe in the Democratic Republic of Congo, and Araxá in Brazil. In contrast to the common assumption that all Fe is present as Fe^{3+}, 47 ± 2% of the total Fe is in the Fe^{2+} oxidation state in the kalipyrochlore sample from Lueshe. Spectra of both samples are consistent with the presence of all the Fe^{3+} at the *B* site, but with two different coordination spheres. Fe^{3+} coordinated by 6 O^{2-} is observed in both cases. In the Lueshe sample, it is also coordinated by 5 O^{2-} and 1 OH^-, whereas in bariopyrochlore from Araxá, the unusually large value of the quadrupole splitting, 3 mm/s, affecting ~19 ± 2% of the Fe^{3+}, suggests that this Fe^{3+} is coordinated by only 5 O^{2-} owing to the presence of anion vacancies at the *X* site.

Keywords: pyrochlore-group minerals, kalipyrochlore, bariopyrochlore, weathering, Fe speciation, ^{57}Fe Mössbauer spectroscopy.

SOMMAIRE

Les minéraux du groupe du pyrochlore présentent une large gamme de compositions chimiques. La formule structurale générale peut s'écrire $A_{2-m}B_2X_{6-w}Y_{1-n}\bullet pH_2O$. On peut établir une corrélation entre le taux de remplissage du site *A* octacoordonné et le degré d'altération du pyrochlore. Dans les membres non altérés du groupe du pyrochlore, ce site est complètement occupé par Na et Ca, alors que dans les membres altérés, le site *A* n'est que partiellement rempli par des cations tels que K, Ba, Sr et Ce. Dans la littérature, la formule structurale unitaire d'un pyrochlore est calculée systématiquement en supposant que la somme des cations dans le site *B* est égale à 2. Le site *B* hexacoordonné est occupé majoritairement par le Nb et, accessoirement, par le Ti, voire le Ta dans certains types de roches telles que les carbonatites. Le Fe est systématiquement considéré comme étant du Fe^{3+} et affecté au site *B*. D'après la présente étude par spectroscopie Mössbauer du ^{57}Fe réalisée sur des membres altérés de la famille du pyroclore provenant de deux gisements latéritiques à Nb, celui de Lueshe en République Démocratique du Congo et celui d'Araxá au Brésil, l'idée généralement admise que tout le fer est présent sous la forme Fe^{3+} est sujette à caution. En effet, dans l'échantillon de kalipyrochlore de Lueshe, 47 ± 2% du Fe total est présent sous forme de Fe^{2+}. Les spectres des deux types de pyrochlore altérés indiquent que tout le Fe^{3+} est présent dans les sites *B* mais avec deux coordinences différentes. Le Fe^{3+} coordonné par 6 O^{2-} est observé dans les deux cas. Dans le kalipyrochlore de Lueshe, une partie du Fe^{3+} est coordonné par 5 O^{2-} et 1 OH^-, tandis que dans le bariopyrochlore d'Araxá, la valeur anormalement élevée du dédoublement quadrupolaire, 3 mm/s, impliquant environ 19 ± 2% de Fe^{3+}, fait penser que ce Fe^{3+} n'est coordonné que par 5 O^{2-}, ce qui serait dû à la présence de lacunes anioniques dans le site *X*.

Mots-clés: minéraux du groupe du pyrochlore, kalipyrochlore, bariopyrochlore, altération supergène, spéciation du Fe, spectroscopie Mössbauer du ^{57}Fe.

[§] *E-mail address*: nasraoui@itn.pt

INTRODUCTION

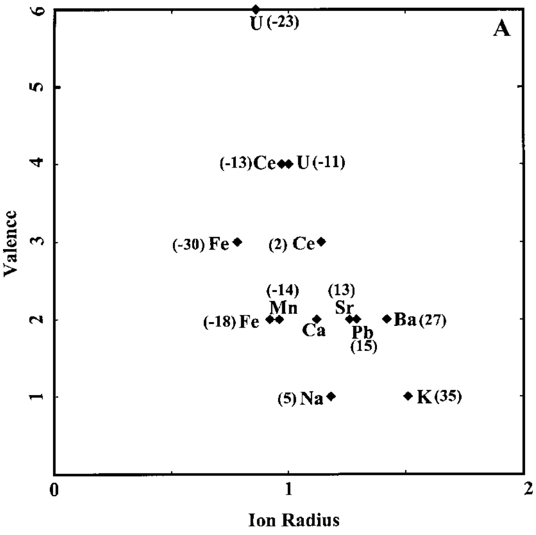
The structure of pyrochlore-group minerals can be described in terms of a cubic face-centered unit-cell and space group $Fd\bar{3}m$ (Chakoumakos 1984). Considering the generalized formula $A_{2-m}B_2X_{6-w}Y_{1-n}{\cdot}p\mathrm{H_2O}$ (Hogarth 1977, Lumpkin *et al.* 1986, Lumpkin 1989) and the origin of the unit cell at the center of symmetry, the larger *A* cations, in eight-fold coordination, occupy the 16*c* sites (0, 0, 0), the smaller *B* cations, in octahedral coordination, occupy the 16*d* sites (½, ½, ½), the *X* anions are on the 48*f* sites (*x*, ⅛, ⅛), and the *Y* anions are on the 8*a* sites (⅛, ⅛, ⅛). The *A* cation may be Ca, Na, Sr, Ba, K, *REE*, U, Th, Mg, Mn and Sn, and the *B* cations include Nb, Ti, Ta and subordinate Si, Zr (Hogarth 1989). The *X* site contains O and, in some cases, OH (Ercit *et al.* 1994). The ideal formula for unaltered pyrochlore can be written as $\mathrm{(Ca,Na)_2Nb_2O_6(OH,F)}$, but altered pyrochlore-group phases commonly are strongly hydrated and reveal a large deficiency of *A* cations. Molecules of H_2O are located on the 96*g* sites (*x*, *x*, *y*), most of them close to the vacant *A* sites, and the remaining ones are close to the vacant *Y* sites (Subramanian *et al.* 1983, Smith & Lumpkin 1993). The structural formulas of pyrochlore-group minerals are systematically calculated to produce an ideal stoichiometry for the *B* site (a total of 2 atoms per formula unit). There is some ambiguity concerning the correct assignment of Fe.

In this paper, we therefore consider the oxidation state and the location of Fe in the structure of pyrochlore, particularly in the weathered pyrochlore from the Lueshe carbonatite, in the Democratic Republic of Congo, and the Barreiro carbonatitic complex at Araxá, in Brazil, using ^{57}Fe Mössbauer spectroscopy. Although Fe constitutes only a small fraction of the total atoms in the pyrochlore structure, it can provide information on geochemical environment and redox conditions.

BACKGROUND INFORMATION

Comparing the radii (Shannon 1976) of six-fold and eight-fold coordinated Fe^{3+} and Fe^{2+} in oxides with those of other cations usually present, respectively, at the *B* and *A* sites of the pyrochlore-group minerals (Figs. 1A, B), one may conclude that the presence of Fe^{2+} at the *A* site and of Fe^{3+} at the *B* site is plausible, whereas Fe^{2+} at the *B* site and Fe^{3+} at the *A* site are highly improbable. However, oxidation of Fe^{2+} may result in unexpected distributions.

Weathered pyrochlore with high concentrations of Fe, say a few percent, is generally considered as being contaminated with Fe-oxide, but where the concentrations are low, Fe is systematically considered as Fe^{3+} and assigned to the *B* site (even though it is assumed that the *B* site remains intact during weathering) because (1) its atomic size is relatively small, (2) the primary magmatic variations in the concentrations of *B*-site elements such as Nb, Ti and Ta are much larger than the variations in Fe concentrations, commonly by many orders of magnitude, and consequently the Fe content does not affect dramatically the nomenclature of a pyrochlore-group mineral, (3) in supergene geochemical systems, the simplifying assumption that all the Fe is present as Fe^{3+} seems to be justified by the oxidizing conditions, and (4) the secondary incorporation of Fe in



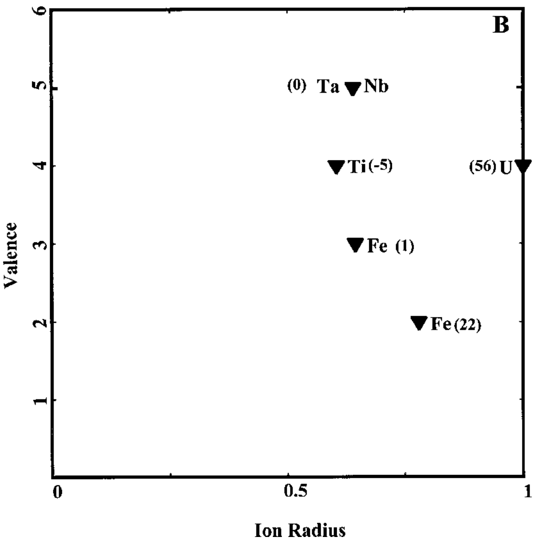


FIG. 1. Ion radii and valence of the chemical elements that can be present in the *A* and *B* sites (Shannon 1976). The label indicates the comparison (in percent) with the principal element substituted, Ca in the *A* site and Nb in the *B* site.

the deficient *A* site is limited, compared to other cations such as K, Ba, Sr, which together can account for 90% or more of the atoms present.

However, estimates of the ratio Fe^{3+}/Fe^{2+}, based on electron-microprobe results and *a priori* assumptions about stoichiometry and oxidation state, may give incorrect results. This is the case for altered oxide spinels, where the ideal stoichiometry of a spinel is commonly assumed, but ^{57}Fe Mössbauer spectroscopy studies have shown that the degree of oxidation of Fe may be greater than expected, and cation vacancies are present (Figueiras & Waerenborgh 1997). Numerous studies of spinel-group and silicate minerals have shown that the precision and accuracy of the $Fe^{3+}:Fe^{2+}$ ratios obtained by ^{57}Fe Mössbauer spectroscopy are comparable to those in wet-chemical determinations (Dyar *et al.* 1989, Wood & Virgo 1989).

MATERIAL AND METHODS

Altered grains of kalipyrochlore with K_2O up to 4.6% (Nasraoui & Bilal 2000), from the Lueshe laterite were separated magnetically and with heavy liquids. A pure fraction was obtained by hand-picking. A concentrate of bariopyrochlore with BaO up to 19% (Mariano *et al.* 1997) from Araxá was used for the present investigation.

All samples were powdered in an agate mortar in order to prepare the Mössbauer absorbers. To detect contamination of these pyrochlore samples by other phases, a thin uniform layer of a fraction of these powder samples was spread on a glass plate. X-ray-diffraction (XRD) patterns of these preparations were obtained with a Philips PW1710 powder diffractometer using Cu$K\alpha$ radiation, a curved graphite crystal monochromator and a PW1820 Bragg–Brentano goniometer.

The dithionite–citrate–bicarbonate iron-removal method (Mehra & Jackson 1960) was used for the removal of possible iron oxides from the pyrochlore samples. This method uses sodium dithionite ($Na_2S_2O_4$) for the reduction, sodium citrate $Na_3C_6H_5O_7{\bullet}2H_2O$ as a chelating or complexing agent for ferrous and ferric iron, and sodium bicarbonate ($NaHCO_3$) as a buffer. The buffer maintains a neutral pH, at which the oxidation potential of the system is high.

A fraction of all the pyrochlore powders (iron-oxide-free and untreated) were pressed in perspex holders in order to prepare absorbers for ^{57}Fe Mössbauer spectroscopy. The absorber thickness was calculated on the basis of the corresponding electronic mass-absorption coefficients for the 14.4 keV radiation, according to Long *et al.* (1983). Owing to the very low Fe content of the samples, each spectrum had to be collected for a long time (2–3 weeks). Spectra were obtained between 297 K and 5 K and collected in transmission mode using a conventional constant-acceleration spectrometer and a 25 m Ci ^{57}Co source in Rh matrix. The velocity scale was calibrated using an α-Fe foil at room temperature. Low-temperature measurements were performed using a liquid nitrogen – liquid helium flow cryostat. The spectra were fitted to Lorentzian peaks using a modified version of the non-linear least-squares computer method of Stone (1967). The widths and relative areas of both peaks in each quadrupole doublet and of peaks 1–6, 2–5 and 3–4 in each magnetic sextet were constrained to remain equal.

GEOGRAPHICAL AND GEOLOGICAL SETTING

The Barreiro carbonatitic complex of Araxá

The Barreiro carbonatitic complex of Araxá (19°38' S, 46°56 W) belongs to the alkaline rock – carbonatite Alto Paranaíba province. It is situated about 6 km south of the city of Araxá in the state of Minas Gerais in Brazil. The Barreiro complex is geographically related to six other carbonatite bodies emplaced along northwesterly trending deep-seated faults related to a cratonic arch (100 km wide and 300 km long). This carbonatite complex, dated at 91 Ma (Issa Filho *et al*. 1984), is approximately circular in shape, 4.5 km in diameter, and composed of carbonatite, glimmerite and phoscorite intruding quartzite and mica schist country-rocks. The effects of the alkali metasomatism are observable in the country rocks as a fenitization aureole up to 2.5 km wide. In addition to the metasomatic minerals (*e.g.*, arfvedsonite, sodic pyroxene), hematite, goethite, anatase, rare-earth phosphate, titanite and pyrochlore also occur in the wallrocks.

The Barreiro complex consists mainly of a central core (about 2 km in diameter) of medium- to coarse-grained dolomite carbonatite. Dolomite is the major mineral, with subordinate calcite and ankerite. Barite, apatite, magnetite, perovskite, quartz, pyrite, phlogopite, Na-amphibole, isokite and strontianite may also be present. Bariopyrochlore is a common accessory mineral. In the central part of the complex, thick masses of phoscorite are associated with the dolomite carbonatite. The fine- to coarse-grained phoscorite consists mainly of magnetite, apatite, phlogopite and carbonates. Of all rock types of the complex, the phoscorite shows the highest concentration of pyrochlore, which occurs as individual grains of bariopyrochlore or associated with magnetite in veins. Glimmerite is found as an aureole between the dolomite carbonatite core and the fenitized quartzite ring. The glimmerite is fine to coarse grained and consists mainly of phlogopite, with subordinate dolomite and accessory magnetite and apatite. A circular lateritic cover 1800 m in diameter and up to 230 m thick occurs in the central part of the domal structure of the complex. Residual bariopyrochlore has become concentrated (Mariano *et al.* 1997), giving rise to the largest known niobium reserves in the world. The laterite mineralogy is composed of limonite, goethite, barite and magnetite as major phases, with subordinate bariopyrochlore, gorceixite, monazite, ilmenite and quartz (Issa Filho *et al*. 1984).

The carbonatite complex of Lueshe

The Lueshe syenite–carbonatite complex (29°7' E, 0°59' S) is located in the northestern part of the Democratic Republic of Congo, in the Rwindi Mountains, about 40 km southwest of Lake Edward (Idi Amin) and 70 km north of Lake Kivu. This carbonatite complex is related to the anorogenic plutonic and subvolcanic alkaline complexes located along the western branch of the East African Rift System. This complex is an alkaline plutonic massif intruding metamorphic series of mica schists, quartzites and amphibolites of Burundian age (1100 Ma). The K/Ar dating on biotite from the calcite carbonatite (sövite) yields an age of 516 ± 26 Ma (Bellon & Pouclet 1980). The subelliptical Lueshe complex consists in a central core of cancrinite syenite and syenite 800 m in diameter, bordered by a horseshoe-shaped sövite unit 200–600 m wide that opens to the north. The outcrop area of dolomite carbonatite is limited to the southeastern part of the complex (Maravic *et al.* 1989). Sodic and potassic fenitization of variable intensities may be observed at some contacts between carbonatite and the host rocks. After an episode of hydrothermal alteration (Nasraoui 1996, Nasraoui *et al.* 2000), a long period of ferralitic weathering produced an important laterite cover from 30 to 150 m thick in the southern half of the complex. It is mined for Nb, which is hosted by pyrochlore. Weathering of the fresh rocks led to (1) loss of carbonate, correlated with a high reduction in volume and relative enrichment of the content of resistant primary minerals such as apatite, feldspar, pyrochlore and zircon, (2) the dissolution of apatite and significant increase in the amount of secondary minerals, such as aluminum phosphate of the crandallite group, clay minerals of the kaolinite–serpentine group, and Fe hydroxides.

The weathering of the primary pyrochlore (with composition near the ideal stoichiometry) at Lueshe resulted in a large apparent deficiency in *A* cations. As a first approximation, the *B* site remains stable (Nasraoui 1996, Wall *et al.* 1996). Since the correct position of Fe and its valence state in the structure of weathered pyrochlore are generally unknown, all the Fe determined by chemical analysis was assumed to be in the Fe^{3+} oxidation state and to be located at the *B* site. The speciation of the Fe in pyrochlore was determined by Mössbauer spectroscopy in the present work.

RESULTS AND DISCUSSION

Powder X-ray diffraction (XRD)

Powder XRD of the samples used for Mössbauer spectroscopy shows the presence of only weathered pyrochlore. Although not detected by powder XRD, crandallite was observed covering some of the kalipyrochlore grains from Lueshe by scanning electron microscopy (Nasraoui *et al.* 1999). This crandallite does not contain Fe in higher concentration than the kalipyrochlore. Since the relative amount of this phase is very small, the contribution of Fe in the crandallite to the Mössbauer spectra is considered to be insignificant.

Mössbauer spectra of the untreated Lueshe sample

The Mössbauer spectrum of the Lueshe sample (Fig. 2) can only properly be fitted with three quadrupole doublets. Different ways of coupling the absorption peaks were tried, although it was assumed in every case that both peaks of each quadrupole doublet have the same width and relative area (*i.e.*, that the absorber has no significant texture effects). The best fit was obtained for the estimated parameters summarized in Table 1. One of the doublets has an isomer shift δ, relative to Fe metal at room temperature, equal to 0.95 mm/s, which is typical of high-spin Fe^{2+}. The pres-

TABLE 1. PARAMETERS ESTIMATED FROM THE MÖSSBAUER SPECTRA OF THE PYROCHLORE SAMPLES TAKEN AT DIFFERENT TEMPERATURES, BEFORE AND AFTER IRON-OXIDE-REMOVAL TREATMENTS

		δ (mm/s)	ε (mm/s) or Δ (mm/s	B_{hf}(T)	Γ (mm/s)	I (%)
		Lueshe				
297 K	Fe^{3+} (B)	0.40	0.56	-	0.26	26
	Fe^{3+} (B)	0.33	0.98	-	0.34	27
	Fe^{2+} (A)	0.95	1.00	-	0.37	47
		Lueshe: first iron-oxide-removal treatment				
297 K	Fe^{3+} (B)	0.38	0.55	-	0.34	54
	Fe^{3+} (B)	0.35	0.91	-	0.39	32
	Fe^{2+} (A)	0.92	1.09	-	0.37	14
		Araxá				
297 K	Fe^{3+} oxide	0.37	-0.17	50.8	0.52	18
	Fe^{3+} (B)	0.36	0.63	-	0.42	71
	Fe^{3+} (B)	0.30	3.00	-	0.32	10
15 K	Fe^{3+} oxide	0.54	0.05	52.7	0.58	22
	Fe^{3+} (B)	0.47	0.66	-	0.42	63
	Fe^{3+} (B)	0.42	3.00	-	0.41	15
		Araxá: first iron-oxide-removal treatment				
297 K	Fe^{3+} oxide	0.37	-0.17	50.7	0.40	7
	Fe^{3+} (B)	0.35	0.62	-	0.40	79
	Fe^{3+} (B)	0.29	3.00	-	0.35	14
		Araxá: second iron-oxide-removal treatment				
297 K	Fe^{3+} oxide	0.36	-0.19	50.6	0.34	9
	Fe^{3+} (B)	0.34	0.61	-	0.40	77
	Fe^{3+} (B)	0.28	2.92	-	0.34	14

δ isomer shift given relative to metallic Fe at room temperature (mm/s); Δ quadrupole splitting measured in the paramagnetic state (mm/s); $\varepsilon = (e^2 V_{ZZ} Q / 4)(3\cos^2\theta - 1)$ quadrupole shift calculated from $(\varphi_1 + \varphi_6 - \varphi_2 - \varphi_5)/2$, where φ_n is the shift of the *n*th line of the sextet due to quadrupole coupling; B_{hf}: magnetic hyperfine field. Γ: full width at half maximum (mm/s); I: relative areas. Estimated standard deviations are less than 2% for I, less than 0.2 T for B_{hf}, and less than 0.02 mm/s for the other parameters. (B) and (A) designate sites in the pyrochlore structure.

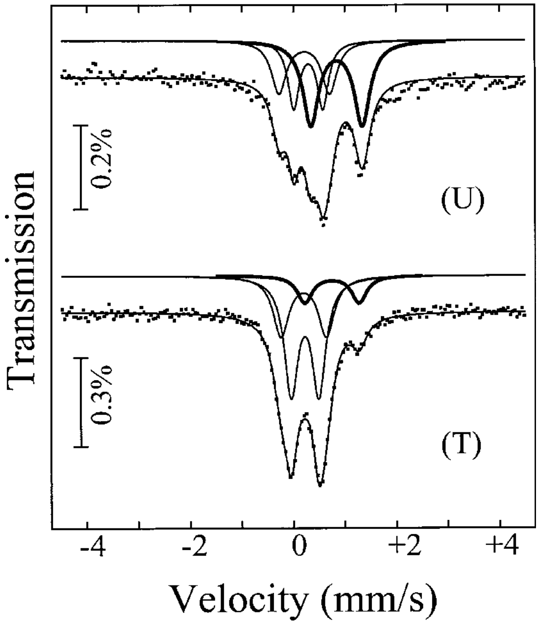


FIG. 2. Mössbauer spectra, taken at 297 K, of the untreated (U) and iron-oxide-depleted (T) samples of the Lueshe pyrochlore-group mineral. The lines over the experimental points are the fit of three doublets. The doublet with the largest isomer shift and quadrupole splitting, plotted in bold, corresponds to Fe^{2+}; the other doublets correspond to Fe^{3+} octahedrally coordinated by 6 O^{2-} (lower splitting) and by 5 O^{2-} and 1 OH^-.

ence of Fe in this oxidation state is also confirmed by the fact that the quadrupole doublet with the lowest δ that may be obtained, by coupling the peaks that may be fitted at the highest (≈ 1.5 mm/s) and the lowest (≈ –0.165 mm/s) Doppler velocities, would have $\delta \approx 0.645$ mm/s. The fit obtained with this model is worse than the fit obtained with the values in Table 1. Furthermore a δ of 0.645 mm/s has only been found for an averaged valence state of Fe^{2+} and Fe^{3+}, which would imply a rapid exchange of electrons between continuous arrays of sites, as in magnetite, or within finite clusters of Fe^{2+} and Fe^{3+} cations. Electron-exchange frequencies higher than the Larmor frequency of the ^{57}Fe nuclei are only observed in materials where the concentration of Fe is much higher than in the case of the pyrochlore.

The present data are therefore consistent with the presence of Fe^{2+} in the sample. The presence of Fe^{2+} is more likely attributable to the kalipyrochlore structure than to the crandallite coating or to a hypothetical Fe oxide.

The other two doublets have a δ typical of Fe^{3+}. The quadrupole splittings, Δ, of the Fe^{3+} doublets in the Lueshe sample (Table 1) fall within the range of those reported by Filoti *et al.* (1998) for Fe^{3+} at the smaller *B* sites of synthetic oxides with the pyrochlore structure: Bi_2NbFeO_7, 0.41 up to 1.82 mm/s, and $Y_2W_{0.67}Fe_{1.33}O_7$, 0.87 up to 2.24 mm/s. It is very unlikely that Fe^{3+} is present at the larger *A* sites of a pyrochlore (Fig. 1). The presence of two doublets with different Δ for Fe^{3+} at the *B* sites may be due to different anion arrangements on the first coordination sphere or even to different arrangements of next-nearest neighbor cations, as explained below in detail.

Fe^{3+} at the *B* sites is coordinated by six anions at the *X* sites (Subramanian *et al.* 1983, Chakoumakos 1984). In Bi_2NbFeO_7 and $Y_2W_{0.67}Fe_{1.33}O_7$, according to Filoti *et al.* (1998), the sites with the highest Δ, 1.82 and 2.24 mm/s, are those with the larger number of Nb^{5+} and W^{6+} ions, respectively, as *B* next-nearest neighbors. Owing to the higher charge of these cations compared to Fe^{3+}, sites with the larger number of Nb^{5+} and W^{6+} next-nearest neighbors would also be those with the highest values of the electric field gradient (Filoti *et al.* 1998, Calage & Pannetier 1977). The rhombohedral distortion of $Y_2W_{0.67}Fe_{1.33}O_7$ ($\alpha = 92.68°$) and the presence of the high-valence W^{6+} would therefore explain the unusually large values of Δ in the W-bearing synthetic oxide (2.24 mm/s, larger than the highest Δ in the Nb-bearing oxide: 1.82 mm/s). In the case of our natural sample, the cation with the highest oxidation state present in significant amounts is Nb^{5+}, and no rhombohedral distortion was detected. On the other hand, whereas in the synthetic samples all the anions that constitute the first coordination sphere are O^{2-}, approximately 2% of the O^{2-} located at the *X* sites is replaced by OH^- in the altered Lueshe kalipyrochlore (Philippo 1995). The presence of structural OH^- was confirmed by infrared spectroscopy and thermal analysis (Nasraoui *et al.* 1999). Being closer to Fe^{3+}, the *X* anions have a more important effect on the electric field gradient than the other *B* cations. In the altered sample from Lueshe, the different Δ observed for Fe^{3+} should therefore be explained by the anion arrangements on the first coordination sphere rather than by the cation arrangements on the next-nearest-neighbor *B* sites. Assuming a random distribution of the O^{2-} and OH^- at the *X* sites, the probability of finding *m* OH^- in a shell of six nearest neighbor *X* sites is given by the binomial distribution function

$$P(m) = \frac{6!}{m!(6-m)!}\xi^m(1-\xi)^{6-m}$$

where ξ is the fraction of the *X* sites occupied by OH^-. Since $\xi \approx 0.02$, only two different coordination spheres should be observed; those consisting of six O^{2-} (≈ 88%) and those consisting of 5 O^{2-} and 1 OH^- (≈ 11%). Coordination spheres consisting of more than 1 OH^- are fewer than 1% in proportion. This inference agrees with the observation of only two doublets in the Mössbauer spectra. Owing to the different charge-densities of O^{2-} and OH^-, the Fe^{3+} coordinated by one OH^- should have a larger value of Δ.

Mössbauer spectra of the untreated Araxá sample

The Mössbauer spectra of the untreated Araxá sample taken at room temperature and at 15 K (Fig. 3) show one magnetic sextet and two doublets, with estimated parameters as summarized in Table 1. The hyperfine parameters of the magnetic sextet may be attributed to an Fe^{3+} oxide, either hematite or maghemite. The estimated δ and magnetic hyperfine fields of this sextet (Table 1) are in good agreement with values published in the literature for an oxide impurity (*e.g.*, Bowen *et al.* 1993). The absence of the Morin transition (Fig. 3, Table 1) does not exclude the possibility of this oxide being hematite, since the suppression of this magnetic transition may be explained by impurity substitution, which is common in environmental samples. The incorporation of 10% Al in hematite or of a much smaller quantity of tetravalent cations, such as 0.3% Ti, is enough to suppress this magnetic transition (Murad & Johnston 1987).

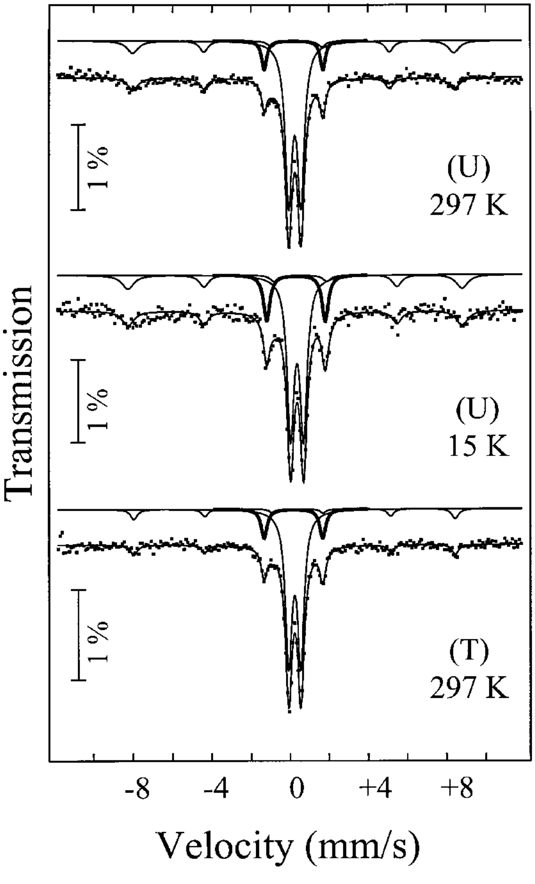


FIG. 3. Mössbauer spectra, taken at 297 K and 15 K, of the untreated (U) and iron-oxide-depleted (T) samples of the Araxá pyrochlore-group mineral. The lines over the experimental points are the fit of two doublets and one sextet. The doublets and the sextet are shown slightly shifted for clarity. The doublet plotted in bold, with the largest quadrupole splitting, corresponds to Fe^{3+} in 5-fold coordination; the other corresponds to Fe^{3+} in octahedral coordination; the sextet represents Fe^{3+} in an Fe oxide.

Owing to the low concentration of Fe in the bariopyrochlore (G.R. Lumpkin, unpubl. data), the estimated error of the relative areas of the sextet is large and, therefore, no significant changes of this parameter with temperature may be assessed (Table 1). A small increase in the relative area in the 15 K spectrum, however, would not be surprising and may reveal the presence of some small particles of an oxide which, at room temperature, is paramagnetic, *i.e.*, shows a rapid fluctuation of magnetization about its easy direction.

The doublet with Δ in the range 0.63–0.66 mm/s is similar to that observed in the Lueshe sample. It is attributed to Fe^{3+} at the *B* sites coordinated by 6 O^{2-}. The second doublet has a surprisingly high quadrupole splitting for Fe^{3+}, $\Delta \approx 3$ mm/s. The value of δ clearly shows that this doublet cannot be due to Fe^{2+}. On the other hand, both peaks of this doublet cannot be attributed to the inner peaks of a broad magnetic sextet caused by rapid relaxation of the direction of the Fe magnetic moments at room temperature. If this were the case, the difference between their Doppler velocities would increase as the temperature is lowered down to 15 K, and the other peaks of the sextet would become resolved.

Except for the Δ value for the synthetic oxide $Y_2W_{0.67}Fe_{1.33}O_7$ referred to above, as far as we know, the highest values of Δ of Fe^{3+} were reported for phases where this cation is in 5-fold coordination: Fe_3PO_7, in which Δ = 1.3 mm/s (Modaressi *et al.* 1983, Waerenborgh & Figueiredo 1986), hexagonal ferrites, in which Δ may be as large as 2.3 mm/s (Rao *et al.* 1980, Gérardin *et al.* 1989). In altered pyrochlore-group phases, besides the replacement of O^{2-} by OH^-, anion vacancies may be found at the *X* sites. One anion vacancy located on the first coordination sphere of Fe^{3+} will give rise to a much larger distortion of the electrical charge distribution than the replacement of 1 O^{2-} by OH^-. The unusual $\Delta \approx 3$ mm/s found in the Araxá sample could therefore be attributed to 5-coordinated Fe^{3+} at the *B* sites of the pyrochlore. As δ invariably decreases with coordination number, the lower δ estimated for the doublet attributed to $^{V}Fe^{3+}$, when compared to that of the $^{VI}Fe^{3+}$ doublet, also supports this conclusion. These results therefore suggest that in contrast to the Lueshe sample, in which the *X* site are fully occupied by O^{2-} and OH^- (Philippo 1995), there are anion vacancies in the Araxá sample. Indeed, the presence of these anion vacancies is in agreement with the electron-microprobe data for the Araxá bariopyrochlore (Lumpkin, unpubl. data), which show vacancies at *X* in the range 0.31–0.59 per formula unit.

Mössbauer spectra of the samples obtained after oxide-dissolution treatment

The Araxá sample shows a significant decrease of the relative intensity of the magnetic splitting (Fig. 3, Table 1) after a first iron-oxide-removal treatment, confirming that this contribution to the spectra is due to an Fe oxide. The Fe in the bariopyrochlore structure seems to be more resistant to this treatment than the Fe in the binary oxides. However, after a second, longer treatment, all the contributions to the spectra seem to be affected, which suggests that eventually the bariopyrochlore structure also is attacked.

In the Lueshe sample, the doublet that is more affected by the treatment is the Fe^{2+} doublet. This is consistent with the Fe^{3+} being present in the kalipyrochlore, since the results obtained for the Araxá sample show that Fe in the Fe binary oxides would be more sensitive to the iron-oxide-removal treatment. These results further suggest that within the pyrochlore structure, Fe^{2+} is more easily removed than Fe^{3+}. This would not be surprising if Fe^{2+} is present at the *A* sites, where the cation-exchange reactions occur more easily.

CONCLUSIONS

^{57}Fe Mössbauer spectroscopy has shown that the common practice of assigning the 3+ oxidation state to Fe in pyrochlore-group minerals is not always correct. In the altered pyrochlore from Lueshe, a significant fraction of the total Fe is in the Fe^{2+} oxidation state (47 ± 2% if equal recoil-free fractions of Fe^{2+} and Fe^{3+} are assumed). Because of cation-radius considerations, this Fe^{2+} is most likely present at the *A* site. Fe^{3+} cations are located at the *B* sites, and it was possible to distinguish those that are coordinated by 6 O^{2-} from those that are coordinated by 5 O^{2-} and 1 OH^-. In addition to a high degree of leaching of *A*-site cations, together with partial uptake of new cations there, the principal effect of weathering in pyrochlore at Lueshe are: (1) a partial leaching of oxygen (up to 1 oxygen atom per formula unit) from the *X* site (Nasraoui & Bilal 2000), and (2) a hydration process marked in the infrared absorption spectrum by the presence of structural stretching OH band at 3413 cm^{-1}, and bending OH at 1630 cm^{-1} (Nasraoui *et al.* 1999).

Some of the Fe in the Araxá sample (~19%) is present in a coating of Fe^{3+} oxide. The remaining Fe, also Fe^{3+}, is located at the *B* sites of the structure. Besides Fe^{3+} coordinated by 6 O^{2-} as found in the Lueshe sample, Fe^{3+} with an unusually large Δ, ~3 mm/s, (~19% of the total Fe in the pyrochlore) was detected. This finding was attributed to coordination of the Fe^{3+} by only 5 anions due to the presence of anion vacancies on the *X* site, in contrast to the Lueshe sample where this site is fully occupied by O^{2-} and OH^- (Philippo 1995). Single-crystal XRD studies of the Araxá bariopyrochlore should be undertaken in order to test for the existence of anion vacancies, which are known to occur in bariopyrochlore in laterites from Bingo, Democratic Republic of Congo (Philippo 1995), and as is common in pyrochlore from all weathered carbonatites so far reported worldwide (Lumpkin & Ewing 1995).

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