MÖSSBAUER SPECTRA OF PRIDERITE
AND SYNTHETIC IRON-BEARING HOLLANDITE

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ABSTRACT

Mössbauer spectra for synthetic iron-bearing hollandites with nominal compositions of $K_2Fe_2Ti_6O_{16}$ and $BaFe_2Ti_6O_{16}$ and one natural sample of priderite were recorded at room temperature. All iron in the phases was found to occur as octahedral Fe^{3+} with no evidence for Fe^{2+}. Quadrupole splitting values show a trend consistent with increasing bond-length deviation of the octahedral sites.

Keywords: priderite, hollandite, Mössbauer spectrometry.

SOMMAIRE

Nous présentons des spectres de Mössbauer pour deux phases synthétiques du groupe de la hollandite ayant une composition nominale de $K_2Fe_2Ti_6O_{16}$ et $BaFe_2Ti_6O_{16}$, ainsi que pour un échantillon naturel de priderite. Ces spectres, enregistrés à température ambiante, montrent que tout le fer est présent sous forme ferrique et en coordinence octaédrique. Les valeurs d'écartement quadrupolaire montrent une dépendance conforme à une augmentation de la déviation des longueurs de liaison dans les sites octaédriques.

(Traduit par la Rédaction)

Mots-clés: priderite, hollandite, spectrométrie de Mössbauer.

INTRODUCTION

Priderite, nominally $(K,Ba)(Ti,Fe^{3+})_8O_{16}$ (Norrish 1951), a member of the hollandite structural group of compounds, is a common accessory mineral in lamproites (Mitchell & Bergman 1991). Following the original gravimetric analysis by Norrish (1951), in which only Fe_2O_3 was reported, the total Fe present in this mineral is commonly expressed as Fe_2O_3, as all subsequent compositional data for priderite have been obtained by electron-microprobe analysis. Given that Fe is commonly present as Fe^{2+} and Fe^{3+} in other Fe-bearing titanates, it is important to establish the oxidation state of Fe in priderite. This cannot be reliably estimated from the composition by standard methods of recalculation based on stoichiometry methods (*e.g.*, Droop 1987), as all naturally occurring hollandite-group titanates and many synthetic examples are known to be

nonstoichiometric (Mitchell & Bergman 1991, Myrha *et al.* 1988, Kesson & White 1986). The nonstoichiometry is expressed as a deficiency of cations in the tunnel (*A*) site and in the *B*-site octahedral polyhedra; the composition of priderite is best expressed as $[(K,Ba)_{2-x}Fe_{2-y}Ti_{8-z}O_{16}]$, where x and y range from 0 to 1, and z from 1 to 2.

To the authors' knowledge, there have been no gravimetric determinations of the FeO content of priderite. Spectroscopic studies useful in determining the valence state of iron in hollandite-group compounds and priderite are limited to the single Mössbauer study of Pring & Jefferson (1983). In that study, the authors did not give any details of the experimental method, nor did they present spectra to substantiate their claim that only Fe^{3+} is present in priderite. These data are discussed below in conjunction with new Mössbauer data for priderite and two synthetic Fe-bearing hollandite-group phases.

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SAMPLES AND EXPERIMENTAL METHODS

Samples

The sample of priderite used in this investigation originates from a pegmatitic lamproite occurring in the Walgidee Hills intrusion, West Kimberley, Australia (Mitchell & Bergman 1991). The material occurs as large orange-brown crystals overgrown by opaque jeppeite in association with wadeite, perovskite, shcherbakovite, K–Ti-bearing richterite and alteration products after potassium feldspar. Priderite was separated from the associated phases by conventional heavy liquid and magnetic methods. The final concentrate used for the Mössbauer study was hand-picked and considered to be near-monomineralic. An X-ray powder pattern of the separated priderite, in addition to the expected peaks, exhibited a very small peak corresponding to the most intense peak of jeppeite, with an intensity of about 2% of that of the strongest peak of priderite. Determination of the priderite composition by ARL–EMX electron microprobe with wavelength-dispersion methods gave an average composition (wt.%) of 72.6% TiO_2, 12.3% Fe_2O_3, 7.4% BaO, 7.4% K_2O and 1.3% MgO, total 101.0 wt.%, corresponding to $(K_{1.14}Ba_{0.35})_{\Sigma1.49}$ $(Ti_{6.58}Fe_{1.12})_{\Sigma7.70}O_{16}$.

Synthetic hollandites corresponding to the nominal compositions $K_2Fe_2Ti_6O_{16}$ and $BaFe_2Ti_6O_{16}$ were prepared from stoichiometric proportions of anhydrous K_2CO_3, $BaCO_3$, TiO_2 and Fe_2O_3. Starting materials were heated in a Pt crucible in air at 900°C for 24 hours, reground and held in a vertical Pt-wound furnace at 1400°C for 24 hours. Reaction products were quenched in liquid nitrogen and examined by X-ray diffraction and X-ray energy-dispersion spectrometry. As was found in other low-pressure ceramic syntheses of hollandite-group compounds (Dubeau & Edgar 1985, Kesson & White 1986, Cheary 1986), reaction products consist of A-site-deficient hollandite plus other phases.

The bulk compositions $K_2Fe_2Ti_6O_{16}$ (sample R12) and $BaFe_2Ti_6O_{16}$ (sample R13) formed coarse crystals (70 μm to 0.3 mm) giving X-ray-diffraction patterns (see below) corresponding to those of other natural and synthetic titanate hollandite (e.g., Cheary 1986, Post et al. 1982). Back-scattered electron imagery revealed that each hollandite phase also contains minor (<5 vol.%) inclusions of other phases.

The $K_2Fe_2Ti_6O_{16}$ sample has an average composition (wt.%) of 11.5% K_2O, 19.5% Fe_2O_3 and 69.3% TiO_2, total 100.3%, corresponding to $K_{1.76}(Fe_{1.76}Ti_{6.24})_{\Sigma8}O_{16}$, and contains inclusions of titaniferous magnetite. The latter contains 8.9 wt.% TiO_2 and 84.3 wt.% FeO_T, corresponding to 38.8 wt.% FeO and 50.5 wt.% Fe_2O_3 if recalculated as a spinel on stoichiometric basis. This composition may be expressed as 25.2 mol.% Fe_2TiO_4 (ulvöspinel) and 74.8 mol.% Fe_3O_4 (magnetite). The formation of spinel during the synthesis of Fe-bearing hollandite has also been noted by Cheary

(1986). Preliminary Rietveld refinement of the X-ray powder pattern indicates that this hollandite is tetragonal (a 10.125, c 2.979 Å) and belongs to the space group I4/m.

The $BaFe_2Ti_6O_{16}$ sample has an average composition (wt.%) of 19.7% Fe_2O_3, 27.0% BaO and 53.3% TiO_2, total 100.0%, corresponding to $Ba_{1.50}(Fe_{2.10}Ti_{5.68})_{\Sigma7.78}O_{16}$. It contains inclusions identified by X-ray diffraction as rutile. The formation of rutile during the synthesis of Fe-bearing hollandite has been noted by Dubeau & Edgar (1985). Preliminary Rietveld refinement of the X-ray powder pattern indicates that this hollandite is either tetragonal (space group I4/m; a 10.097, c 2.969 Å) or monoclinic (space group I2/m; a 10.097, b 2.969, c 10.108 Å, β 89.96°). The latter data are in good agreement with those given by Cheary (1986) for synthetic monoclinic Ba–Fe-hollandite.

Mössbauer spectrometry

Samples were gently ground in an agate mortar with acetone. The resulting powders were mixed with benzophenone and loaded into plexiglass sample holders 12 mm in diameter. The effective thickness of the sample was 5 mg Fe/cm^2 for the synthetic K–Fe-hollandite and 3.5 mg Fe/cm^2 for priderite and the synthetic Ba–Fe-hollandite, these values being close to the ideal sample-thickness for these compositions (Long et al. 1983). Spectra were recorded at room temperature (293 K) in transmission mode on a constant-acceleration Mössbauer spectrometer with a nominal 50 mCi ^{57}Co source in a 6 μm Rh matrix. The velocity scale was calibrated relative to 25 μm α-Fe foil using the positions certified for National Institute of Standards reference material no. 1541; line widths of 0.28 mm/s for the outer lines of α-Fe were obtained at room temperature. The spectra were fitted using the commercially available program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany).

Data were fitted to Lorentzian doublets (components constrained to equal widths and areas) and if necessary, sextets (components constrained to equal widths, and areas constrained to the ratio 3:2:1:1:2:3), this approach being sufficient to account for all spectral absorption. Hyperfine parameters are given in Table 1, and spectra are illustrated in Figures 1 and 2.

TABLE 1. MÖSSBAUER PARAMETERS (293 K) FOR HOLLANDITE AND PRIDERITE

Sample	Site	δ mm/s	Δ mm/s	Γ mm/s
K-Fe-Hollandite (R12)	[6]Fe^{3+}	0.383(5)	0.50(1)	0.33(1)
Ba-Fe-Hollandite (R13)	[6]Fe^{3+}	0.376(5)	0.50(1)	0.32(1)
Priderite	[6]Fe^{3+}	0.385(5)	0.47(1)	0.35(1)

δ: centre shift (relative to α-Fe); Δ: quadrupole splitting; Γ: full width at half maximum.

MÖSSBAUER SPECTROMETRY RESULTS

The Mössbauer spectra of both synthetic Fe-bearing hollandites are illustrated in Figure 1, and show one dominant Lorentzian quadrupole doublet, which is assigned to Fe^{3+}. It is important to note that no peaks arising from Fe^{2+} can be observed in the spectrum of the rutile-bearing Ba–Fe-hollandite (R13). The center shift for this compound is 0.376 (Table 1), and thus is consistent with that of Fe^{3+} in octahedral coordination in a wide variety of oxides and silicates (Burns & Solberg 1990). The spectrum of the K–Fe-hollandite (R12), which contains inclusions of ulvöspinel–magnetite solid solution, not surprisingly shows the presence of a mag-

FIG. 2.   Room-temperature Mössbauer spectrum of priderite. The spectrum shows only the presence octahedrally coordinated Fe^{3+}.

FIG. 1.   Room-temperature Mössbauer spectrum of synthetic K–Fe-hollandite (R12) and of Ba–Fe-hollandite (R13). The bulk of each spectrum arises from octahedrally coordinated Fe^{3+} in hollandite. Spectrum R12 contains a small amount of inclusions of ulvöspinel–magnetite solid solution, a magnetic impurity.

netic phase (Fig. 1). The spectrum was recorded on a larger-velocity scale, where the following hyperfine parameters were obtained for the magnetic phase: δ (relative to α-Fe) = 0.39 mm/s; Δ = –0.21 mm/s; H = 50.9 T; Γ = 0.39 mm/s; relative area = 13%. These parameters are consistent with those found for synthetic ulvöspinel–magnetite (Tanaka & Kono 1987). Factors such as nonstoichiometry could account for the slight discrepancy between our values and those reported in the literature.

The Mössbauer spectrum of priderite (Fig. 2) shows one dominant quadrupole doublet consistent with Fe^{3+} in octahedral coordination. Pring & Jefferson (1983) also have reported hyperfine parameters for priderite from the Walgidee Hills locality; whereas the quadrupole splitting (Δ = 0.4552 mm/s) and line width (Γ = 0.333 mm/s) are consistent with our findings, the center shift (δ relative to α-Fe = 0.1777 mm/s) is not. Such a center shift value is too low for octahedrally coordinated Fe^{3+}, and would suggest a calibration error. Unfortunately, no details of the experimental method were given, such that it is difficult to evaluate the source of the disagreement. Pring & Jefferson (1983) observed no evidence for Fe^{2+}, and they assigned all Fe to Fe^{3+} in octahedral coordination.

The quadrupole splitting provides information on site distortion. Since Fe^{3+} has a $3d^5$ electronic configuration, the orbital moment is zero, and the electric field gradient at the nucleus (which is related to the quadrupole splitting) arises simply from the charges on the neighboring atoms. The quadrupole splitting is zero for cubic symmetry and should increase with increasing
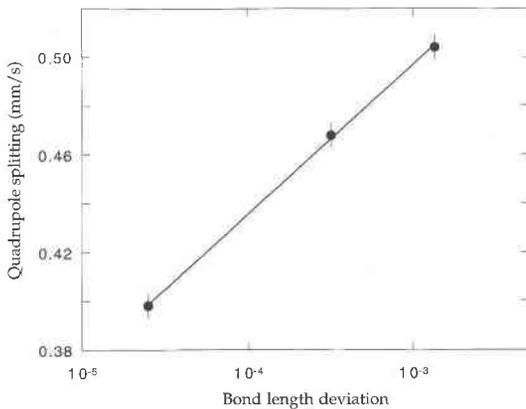
FIG. 3. Correlation between quadrupole splitting and bond-length parameter for hollandite structures. The bond length deviation is calculated as $1/N\Sigma[(R_i - R)/R]^2$, where R_i and R are individual and mean metal–oxygen distances for octahedral ($N = 6$) coordination sites (Fleet 1976). Structural data were taken from Cheary (1986) [K–Fe-hollandite], Sinclair & McLaughlin (1982) [priderite], and Mitchell *et al.* (1998) [latrappite].

site-distortion. Previous attempts to find correlations between site-distortion parameters and quadrupole splitting have met with varying degrees of success (Coey 1984, Steffen *et al.* 1984, Burns & Solberg 1990). Causes of the poor correlation have been discussed by Steffen *et al.* (1984); they include (1) structural data that do not reflect the geometry of the Fe^{3+} site where Fe^{3+} is a minor species, (2) an electric field gradient that is not adequately represented by purely geometrical parameters, and (3) a distortion for the polyhedra that is not adequately described by any of the distortion parameters (Fleet 1976). To provide further data on this question, we have plotted in Figure 3 the bond-length deviation (Fleet 1976) *versus* quadrupole splitting for the hollandite phases, combined with data for latrappite, a perovskite-group mineral (Mitchell *et al.* 1998). We find a linear correlation, although note that the slope and intercept parameters differ from those observed for other structures studied by previous investigators. It would be useful to extend this study to include X-ray and Mössbauer data on perovskite-type structures to investigate the degree to which composition and structure affect the correlation, particularly in terms of its general applicability to minerals.

CONCLUSIONS

We present the first data for Mössbauer hyperfine parameters for synthetic Fe-bearing hollandite-group phases, and provide new data for natural priderite. These data show conclusively that Fe occurs entirely as octahedrally coordinated Fe^{3+} in all samples studied.

REFERENCES

BURNS, R.G. & SOLBERG, T.C. (1990): ^{57}Fe-bearing oxide, silicate, and aluminosilicate minerals. *In* Spectroscopic Characterization of Minerals and their Surfaces (L.M. Coyne, S.W.S. McKeever & D.F. Blake, eds.). *Am. Chem. Soc.* **415**, 262-283.

CHEARY, R.W. (1986): An analysis of the structural characteristics of hollandite compounds. *Acta Crystallogr.* **B42**, 229-236.

COEY, J.M.D. (1984): Mössbauer spectroscopy of silicate minerals. *In* Chemical Applications of Mössbauer Spectroscopy **1** (G.L. Long, ed.). Plenum Press, New York, N.Y. (443-509).

DROOP, G.T.R. (1987): A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineral. Mag.* **51**, 431- 435.

DUBEAU, M.I. & EDGAR, A.D. (1985): Priderite stability in the system $K_2MgTi_7O_{16} - BaMgTi_7O_{16}$. *Mineral. Mag.* **49**, 603-606.

FLEET, M.E. (1976): Distortion parameters for coordination polyhedra. *Mineral. Mag.* **40**, 531-533.

KESSON, S.E. & WHITE, T.J. (1986): Comments on "Priderite stability in the system $K_2MgTi_7O_{16} - BaMgTi_7O_{16}$". *Mineral. Mag.* **50**, 537-538.

LONG, G.L., CRANSHAW, T.E. & LONGWORTH, G. (1983): The ideal Mössbauer effect absorber thickness. *Mössbauer Effect Ref. Data J.* **6**, 42-49.

MITCHELL, R.H. & BERGMAN, S.C. (1991): *Petrology of Lamproites.* Plenum Publ. Corp., New York, N.Y.

_____, CHOI, JIN-BEOM, HAWTHORNE, F.C., McCAMMON, C.A. & BURNS, P.C. (1998): Latrappite: a re-investigation. *Can. Mineral.* **36**, 107-116.

MYRHA, S., WHITE, T.J., KESSON, S.E. & RIVIERE, C.J. (1988): X-ray photoelectron spectroscopy for direct identification of Ti valence in $[Ba_xCs_y][(Ti,Al)^{3+}_{2x+y}Ti^{4+}_{8-2x-y}]$ hollandites. *Am. Mineral.* **73**, 161-167.

NORRISH, K. (1951): Priderite, a new mineral from the leucite-lamproites of the west Kimberley area, Western Australia. *Mineral. Mag.* **29**, 496-501.

POST, J.E., VON DREELE, R.B. & BUSECK, P.R. (1982): Symmetry and cation displacements in hollandites: structure refinements of hollandite, cryptomelane and priderite. *Acta Crystallogr.* **B38**, 1056-1065.

PRING, A. & JEFFERSON, D.A. (1983): Incommensurate superlattice ordering in priderite. *Mineral. Mag.* **47**, 65-68.

SINCLAIR, W. & McLAUGHLIN, G.M. (1982): Structure refinement of priderite. *Acta Crystallogr.* **B38**, 245-246.

STEFFEN, G., SEIFERT, F. & AMTHAUER, G. (1984): Ferric iron in sapphirine: a Mössbauer spectroscopic study. *Am. Mineral.* **69**, 339-348.

TANAKA, H. & KONO, M. (1987): Mössbauer spectra of titanomagnetite: a reappraisal. *J. Geomag. Geoelectr.* **39**, 463-475.