

# **$^{57}\text{Fe}$ Mössbauer investigations of manganese-containing spinels**

C.R. Bluncson, G.K. Thompson and B.J. Evans

*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA*

Cation distributions and related order–disorder phenomena in the naturally occurring Mn-spinels: iwakiite, galaxite and franklinite, have been investigated by means of  $^{57}\text{Fe}$  Mössbauer spectroscopy. Previous measurements on an iwakiite sample indicated the existence of Mn-rich and Mn-poor regions. This interpretation has been confirmed in this investigation by further measurements on annealed iwakiite samples. The  $^{57}\text{Fe}$  Mössbauer spectrum of galaxite from Bald Knob, NC, is a well-resolved quadrupole doublet and indicates the presence of a single crystallographic  $\text{Fe}^{3+}$  species. A “galaxite” sample from Thailand exhibited a complex spectrum of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  quadrupole doublets: This sample has been misidentified and should be regarded as a member of the  $(\text{Mg}, \text{Fe})(\text{Al}, \text{Fe})_2\text{O}_4$  series. The  $^{57}\text{Fe}$  hyperfine parameters of a rare franklinite from Långban, Sweden, are very close to those for synthetic zinc ferrite, confirming electron microprobe results of an unusually high zinc content.

## **1. Introduction**

Occasions to study manganese-containing spinels that have high degrees of thermal equilibration are rare opportunities to gain insights into order–disorder phenomena and crystal/chemical structures that are of fundamental importance in magnetic and electronic materials [1]. In this report, we present the results of our investigations of just such a suite of Mn-containing spinels. The minerals studied in this investigation are iwakiite (Gozaisho mine, Japan [1]), galaxite (Bald Knob, North Carolina [2], and Nakhon Pathom, Thailand), and franklinite (Långban, Sweden). Iwakiite samples from the Gozaisho mine are noteworthy inasmuch as manganese ferrites from this locality exhibit unusually high degrees of thermal equilibration and tetragonal distortions at Mn contents well below those observed for synthetic samples. The earlier suggestions of Mn clustering and consequent Mn-rich and Mn-poor regions have been investigated further by performing measurements on samples annealed at moderate temperatures, e.g. 1000 K, sufficient to induce ionic motion but well below the temperatures at which sintering occurs.

In this report, we present the first  $^{57}\text{Fe}$  Mössbauer data on galaxite and franklinite from Långban, Sweden [3]. The franklinite specimen is unique since it is one of the few authenticated occurrences of franklinite other than those at Franklin

and Sterling Hill, New Jersey, USA. Samples of galaxite are also rare and provide an opportunity to study order/disorder phenomena and crystal/chemical structures in spinels which, because of their high alumina contents, require very high synthesis temperatures. The high synthesis temperatures lead to considerable disorder in the structure and cation distribution.

## 2. Experimental

The chemical compositions of iwakiite and galaxite from Thailand were determined by means of electron microprobe analysis to be  $\text{MnFe}_{1.9}\text{O}_4$  and  $\text{Mg}_{0.7}\text{Al}_{1.7}\text{Fe}_{0.5}\text{O}_4$ , respectively. Phase analysis of all samples was performed using X-ray powder diffractometry.

Two iwakiite samples were annealed in evacuated quartz ampoules for 17 and 77 h., respectively, at 1000 K.

Using a <sup>57</sup>Co/Rh source held at 298 K, transmission <sup>57</sup>Fe Mössbauer spectra were obtained on polycrystalline samples maintained at 298 and in a vacuum cryostat at 85 K. The spectra were fitted using procedures described elsewhere [4, 5]. The filled circles are the experimental data and the solid lines are the results of the fitting procedure. Isomer shifts are reported relative to Fe metal at 298 K. The spectra of the three samples are shown in figs. 1 and 2. <sup>57</sup>Fe Mössbauer parameters for the iwakiite samples are listed in table 1.

## 3. Results and discussion

The spectrum for the unannealed iwakiite sample was fitted to one six-line pattern having  $H_{\text{eff}} = 388$  kOe. The samples annealed for 17 and 77 h at 1000 K were fitted to two six-line patterns: subpattern 1, with  $H_{\text{eff}} = 500$  kOe, as shown in fig. 1(b), is derived from the Fe-rich regions of the untreated iwakiite; subpattern 2, with  $H_{\text{eff}} = 318$  kOe, results from the phase separation of Mn-rich regions from the untreated iwakiite. Subpattern 2 of the spectrum in fig. 1(b) can be interpreted as being due to a poorly crystalline, Mn-rich spinel phase, as indicated by the large linewidths ( $\Gamma = 2.40$  mm s<sup>-1</sup>). Subpattern 1 corresponds to the Mn-poor region of the untreated iwakiite that has undergone phase separation into an Fe-rich, hematite-like phase, in accordance with both X-ray powder diffraction and the Mössbauer parameters. Upon heating further for 77 h, there is considerable recrystallization and growth of the Mn-rich spinel phase, as evidenced by the well-defined magnetic hyperfine pattern in fig. 1(c). The hematite-like phase, already highly crystalline after the 17 h anneal, exhibits no further changes in either overall appearance or in detailed parameter values.

The <sup>57</sup>Fe Mössbauer spectrum of the galaxite sample from Bald Knob, North Carolina, is a simple quadrupole doublet ( $\Delta E_Q = 0.940$  mm s<sup>-1</sup> and  $\delta = 0.356$  mm s<sup>-1</sup>) with narrow lines ( $\Gamma = 0.28$  mm s<sup>-1</sup>), indicating a limited number of local environments

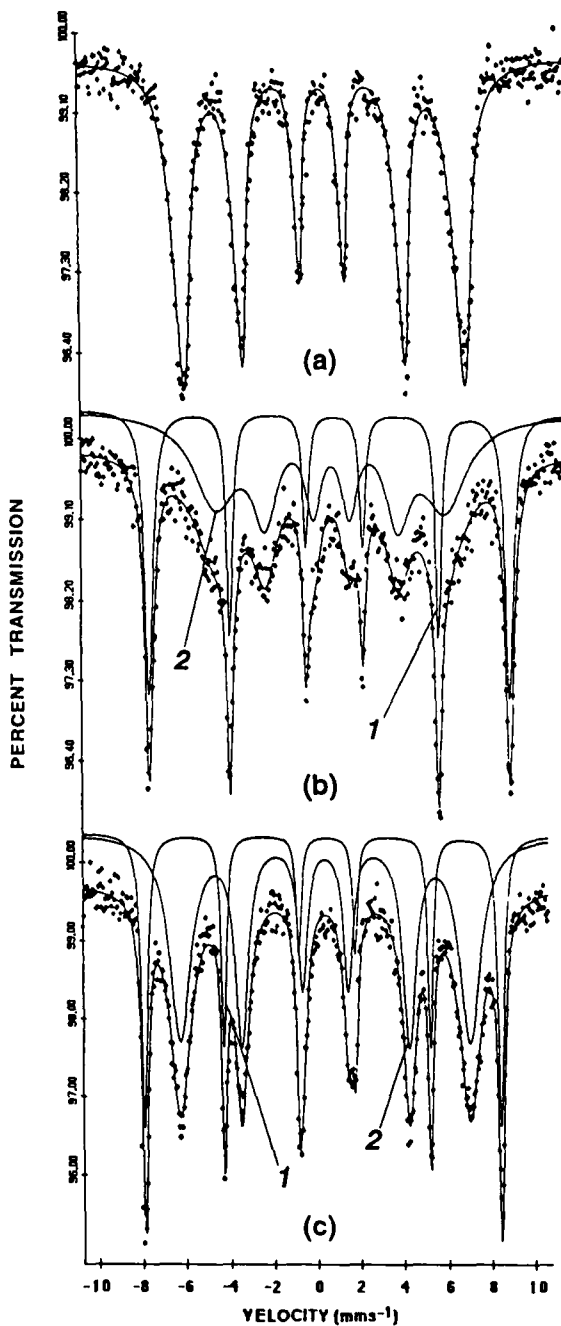


Fig. 1.  $^{57}\text{Fe}$  Mössbauer spectra (297 K) of (a) unannealed iwakiite, (b) iwakiite annealed for 17 h at 1000 K, and (c) iwakiite annealed for 77 h at 1000 K. Fe-rich and Mn-rich regions are represented by 1 and 2, respectively.

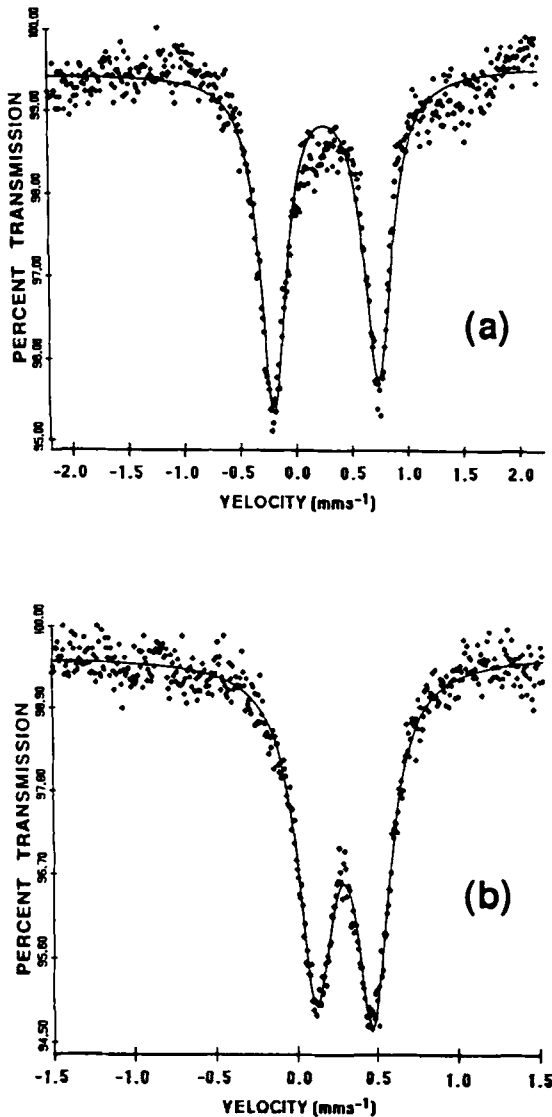


Fig. 2. (a)  $^{57}\text{Fe}$  Mössbauer spectrum (297 K) of galaxite from Bald Knob, North Carolina, USA. (b)  $^{57}\text{Fe}$  Mössbauer spectrum (297 K) of franklinite from Långban, Sweden.

for the  $\text{Fe}^{3+}$  ions. There is no indication of the presence of  $\text{Fe}^{2+}$ , contrary to previous reports based on electron microprobe analyses of thin sections [2]. A comparison of the values of the hyperfine interaction parameters with those of other spinels suggests that  $\text{Fe}^{3+}$  occupies the octahedral site [6].

Table 1

Comparison of 298 K <sup>57</sup>Fe hyperfine parameters of iwakiite samples annealed at 1000 K.

Sample	Subpattern	$H_{\text{eff}}$ (kOe)	$\Delta E_Q$ (mm s <sup>-1</sup> )	$\delta^{\text{a}}$ (mm s <sup>-1</sup> )	$\Gamma$ (mm s <sup>-1</sup> )	Area (%)
iwakiite unannealed	–	388	–0.007	0.392	0.920	100
annealed 17 h	Fe-rich	500	–0.109	0.390	0.458	38
	Mn-rich	318	–0.020	0.347	2.400	62
annealed 77 h	Fe-rich	513	–0.104	0.373	0.343	30
	Mn-rich	417	–0.009	0.383	1.17	70

<sup>a</sup>) Isomer shifts are relative to Fe metal.

The spectrum of the galaxite sample from Nakhon Pathom, Thailand, is very similar to those previously reported for lherzolite spinels in mantle xenoliths [7], indicating the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> on the tetrahedral site. The necessity of fitting the 298 K spectrum to two Fe<sup>2+</sup> doublets with very similar isomer shifts ( $\delta_2 = 0.940$  mm s<sup>-1</sup> and  $\delta_3 = 0.900$  mm s<sup>-1</sup>) but different quadrupole splittings ( $\Delta E_{Q2} = 1.845$  mm s<sup>-1</sup> and  $\Delta E_{Q3} = 1.127$  mm s<sup>-1</sup>) suggests that the two spectral components are due to Fe<sup>2+</sup> ions on a single lattice site but with different local environments. One Fe<sup>2+</sup> and one Fe<sup>3+</sup> pattern provides an adequate fit to the 85 K spectrum. Based on the absence of manganese in this sample and the similarity of the spectrum to that of lherzolite spinels, it is concluded that this sample has been misidentified and should not be regarded as galaxite. It might be more appropriately assigned to the spinel series (Mg, Fe)(Al, Fe)<sub>2</sub>O<sub>4</sub>.

The <sup>57</sup>Fe Mössbauer spectrum of the Zn-rich franklinite is remarkably simple, suggesting the presence of only one crystallographic species of Fe, i.e. octahedral Fe<sup>3+</sup>. A comparison of the Mössbauer parameters of this sample ( $\Delta E_Q = 0.344$  mm s<sup>-1</sup> and  $\delta = 0.354$  mm s<sup>-1</sup>) with those of synthetic ZnFe<sub>2</sub>O<sub>4</sub> [6] ( $\Delta E_Q = 0.333$  mm s<sup>-1</sup> and  $\delta = 0.350$  mm s<sup>-1</sup>) provides clear support for this being a zinc-rich specimen. As in the case of the galaxite sample from Bald Knob, North Carolina, the <sup>57</sup>Fe Mössbauer data do not support the presence of Fe<sup>2+</sup>, as suggested by the formula (Zn<sub>0.9</sub>Fe<sub>0.1</sub>)(Fe<sub>1.9</sub>Al<sub>0.1</sub>)O<sub>4</sub> obtained from electron microprobe analysis [3]. Certainly, the Fe<sup>2+</sup> is not 6% of the total iron present.

## References

- [1] B.J. Evans, W.R. Dunham, C. Porter, S.M. Abernathy and C. Bluncson, *J. Appl. Phys.* 63(1988)4133.
- [2] E.J. Essene and D.R. Peacor, *Am. Min.* 68(1983)449.
- [3] E.A.J. Burke and C. Kieft, *Lithos* 5(1972)69.

- [4] B.J. Evans, R.G. Johnson, F.E. Senftle, C. Blaine Cecil and F. Dulong, *Geochim. Cosmochim. Acta* 46(1982)761.
- [5] Hang Nam Ok and B.J. Evans, *Phys. Rev.* B14(1976)2956.
- [6] B.J. Evans, S.S. Hafner and H.P. Weber, *J. Chem. Phys.* 55(1971)5282.
- [7] D. Canil, D. Virgo and C. Scarfe, *Contrib. Mineral. Petrol.* 104(1990)453.