

Mössbauer spectra of iron in 1:1 phyllosilicates

ISRAEL ROZENSON

*Department of Geology, The Hebrew University
Jerusalem, Israel*

ERIKA R. BAUMINGER

*Racah Institute of Physics, The Hebrew University
Jerusalem, Israel*

AND LISA HELLER-KALLAI

*Department of Geology, The Hebrew University
Jerusalem, Israel*

Abstract

One sample of chamosite and a number of kaolinites, dickites, and serpentines were examined by the Mössbauer effect technique at room temperature. Some of the spectra were also recorded at 77° and 4°K. Only one type of octahedral site was found in the dioctahedral minerals and in antigorites. Two different sites were distinguished in chamosite, lizardites, and chrysotiles. Fe²⁺ occupies octahedral sites randomly in chamosite, but different site preference was found in various lizardites. Fe³⁺ occurs in one or two octahedral sites, and in at least two samples also in tetrahedral coordination.

The temperature-dependence of the quadrupole splittings of both Fe²⁺ doublets shows that the *M*1 doublet, with the smaller quadrupole splitting, is associated with the less distorted sites.

Fe³⁺/Fe²⁺ ratios determined by Mössbauer spectroscopy differ from those previously established by chemical methods, casting some doubt on the validity of proposed correlations between these ratios and the structure of serpentines.

Introduction

This study was undertaken to establish the correlation between the Mössbauer spectra of iron in serpentines and their structure. The spectra of chamosites, kaolinites, and dickites were examined for comparison.

Little is known about the structure of chamosites, beyond the fact that they are 1:1 trioctahedral phyllosilicates, the iron-rich analogues of serpentines. Serpentine minerals have a fairly narrow range of chemical composition, and their iron content does not exceed a few percent. The dioctahedral 1:1 phyllosilicates kaolinite and dickite do not depart appreciably from the ideal composition, and their iron content is very low.

The structures of kaolinite and dickite have been established, but detailed structure determination of

serpentines presents some difficulties, because of the poor crystallinity of the samples. Serpentine minerals are divided into three main groups—antigorites, chrysotiles, and lizardites—according to the adjustment of the misfit between the tetrahedral and octahedral sheets: corrugation of the layers in antigorites, formation of cylindrical layers and buckling of the octahedral sheets of chrysotiles, and flat layers with more strongly buckled octahedral sheets in lizardites. Wicks and Whittaker (1975) reviewed the information available from X-ray diffraction measurements, and the correlation between structural features and IR spectra of serpentines was investigated by Yariv and Heller-Kallai (1973). In the present study a correlation between the different structures and the Mössbauer spectra of iron is attempted. It should be stressed that due to the low iron content of serpentines, the information derived from the

spectra is strictly confined to iron and does not necessarily apply to other ions occupying crystallographically equivalent sites in the structure.

Experimental

Materials

The following minerals were studied: chamosite B1, labelled "bertierine, Dielette, Mancho," from the collection of S. Caillere; dickite samples No. 14 (D14), from Ouray, Colorado and D16 from St. George, Utah, supplied by Wards Natural Science Establishment; eight different samples of kaolinites including one from Oneal Pit, Macon, Georgia (O.P.) supplied by Wards, and sample IZ2 from Mizpe Ramon, Israel. Most of the serpentine samples were described in previous papers (Yariv and Heller-Kallai, 1973; Heller-Kallai *et al.*, 1975). Specimens with the prefix F are from the collection of Faust and Fahey (1962). Two additional analyzed samples of chrysotiles, Nos. 12176 and 12180, from the Takaka Igneous Complex, N. W. Nelson, New Zealand, were provided by B. F. Kohn.

Method

All the samples were examined in their natural form. Some kaolinites and serpentines were also investigated after 2 hours treatment with hot 1:6 HCl solution to remove iron-containing surface coatings. Two ground samples of serpentines (HU176 and HU11759) were treated for 48 hours with 20 percent H₂O₂ solution. The samples which served as absorbers were ground to a thin powder. About 20–40 mg of powder, which contained about 2 mg iron, were placed into a lucite holder of about 2 cm diameter. The source consisted of 50 mCi ⁵⁷Co in Rh at room temperature. The Mössbauer spectra were obtained with a conventional constant acceleration drive (Cohen *et al.*, 1963) coupled to a Harwell proportional counter and a 200 or 256 multi-channel analyzer working in the multiscaler mode. The absorption spectra were automatically folded in the multichannel analyzer (Nadav and Palmai, 1967). The velocity scale was calibrated using a 20 mg/cm² (25 μm) thick Fe-metal foil as absorber. The widths of the individual absorption lines in the calibration spectra were about 0.25 mm/sec.

The experimental spectra were analyzed by least-squares computer fits to two, three, or four doublets. The individual lines of each doublet were assumed to have the same height and width. The good fits obtained indicate that there were no preferred orienta-

tion effects. χ^2 obtained in the computer fits ranged from 200 to 270.

Results

Some typical Mössbauer spectra are shown in Figure 1, and the parameters obtained from the least-squares computer fits are summarized in Tables 1 and 2. Isomer shifts are given relative to Fe metal. Some of the samples were also examined at 77° and 4°K, and the parameters obtained are included in Tables 1 and 2. There was no change in the line width at lower temperatures and the isomer shifts changed by 0.10±0.02 mm/sec, compatible with the change caused by the second-order Doppler shift.

Chamosite

A single sample of chamosite (B1) was available for this study. The experimental spectrum was resolved into three doublets, two corresponding to Fe²⁺ and one to Fe³⁺ in high-spin octahedral coordination. This is in agreement with the results reported by Yershova *et al.* (1975).

Antigorites

All the antigorites examined except one (F1) give rise to spectra consisting of two doublets, compatible with Fe²⁺ and Fe³⁺ in high-spin octahedral coordination (Fig. 1a and Table 1). The parameters obtained for all the Fe²⁺ doublets are very similar [Q.S. (298°K) = 2.73±0.03 mm/sec and I.S. (298°K) = 1.13±0.01 mm/sec] and the line widths are relatively narrow (~0.36±0.01 mm/sec), indicating that the environment of the Fe²⁺ ions in all the samples is similar. The quadrupole splittings are strongly temperature-dependent. The parameters of the Fe³⁺ doublets are less uniform, the line widths are greater, and the temperature-dependence of the quadrupole splittings is small, as expected.

The Mössbauer spectrum of sample F1 (Fig. 1b) shows no indication of the presence of Fe²⁺. It can be fitted by two doublets, corresponding to tetrahedrally and octahedrally coordinated Fe³⁺.

Chrysotiles and lizardites

The Mössbauer spectra of these minerals are more complex than those of the antigorites. They were generally resolved into three doublets, as shown in Figures 1c and d. The parameters obtained are given in Table 1. Resolution into only two doublets gives rise to large line widths of either the Fe³⁺ or the Fe²⁺ doublets. Fe³⁺ doublets are frequently broad, but the line widths of about 0.6 mm/sec are greater than

those usually observed for phyllosilicates, including antigorites. In two spectra, resolution of the Fe^{2+} lines into two doublets leads to reasonable Fe^{2+} line widths, accompanied by a significant reduction in χ^2 . The Fe^{3+} doublets remain broad even when the Fe^{3+} lines are resolved into two subspectra, but such resolution is justified for some spectra, because it leads to considerably lower values of χ^2 . Resolution into four doublets does not reduce χ^2 further. The spectra were therefore resolved into a maximum of three doublets, though the presence of an additional site cannot be excluded.

Only two specimens, chrysotile HU3261 and a lizardite from New Zealand (not included in the table), gave rise to the characteristic magnetic spectrum of $\alpha\text{-Fe}_2\text{O}_3$. The iron in these serpentines was present entirely in the trivalent form.

Treatment with HCl or H_2O_2 solutions

HCl treatment of some of the samples (kaolinites and serpentines) did not affect their Mössbauer spectra, which shows that the effects observed were not due to surface coatings.

H_2O_2 treatment of two samples of serpentines did not lead to oxidation of Fe^{2+} , indicating that it is most unlikely that any changes in composition of the specimens had occurred due to prolonged storage in the laboratory.

Kaolinites and dickites

The spectra of all the kaolinites but one (IZ2) and of the two samples of dickite showed a single doublet, corresponding to Fe^{3+} in octahedral coordination, which, although relatively broad, could not be meaningfully resolved. All the kaolinite spectra except that of IZ2 were similar and resemble those reported in the literature (Jefferson *et al.*, 1975). The data for a single representative sample are presented in Table 2. The spectra of the two samples of dickite closely resemble those of kaolinites. Kaolinite sample IZ2 showed a second doublet, corresponding to Fe^{2+} , which is also relatively broad (Fig. 1e).

Discussion

The ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$

This ratio was derived from the Mössbauer spectra on the assumption that the recoil-free fraction is equal in all sites and that the ratio is therefore given by that of the areas under the corresponding doublets. This assumption is supported by the fact that

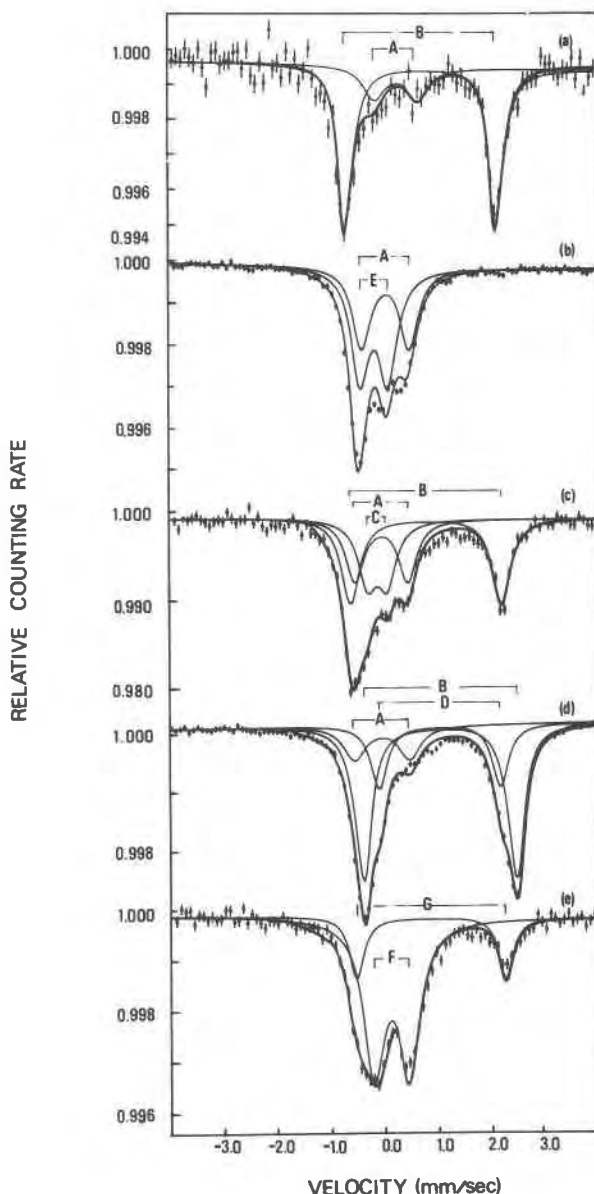


Fig. 1. Room-temperature Mössbauer spectra of serpentines. (a) antigorite (F14); (b) antigorite (F1); (c) chrysotile (12180); (d) lizardite (11759); (e) kaolinite (IZ2). A- Fe^{3+} in M(2), B- Fe^{2+} in M(2), C- Fe^{3+} in M(1), D- Fe^{2+} in M(1), E- Fe^{3+} in tetrahedral sites, F- Fe^{3+} and G- Fe^{2+} in single octahedral site.

for the samples measured at 77°K the ratio remained the same as at 298°K.

It appears that there are considerable discrepancies between the ratios determined by Mössbauer spectroscopy and by chemical analyses, despite the fact that most of these were carried out on aliquots of the same samples. The similarity between the chemical analyses of samples with prefix F performed by Faust

Table 1. Mossbauer parameters of chamosite and serpentines

Temp °K	Fe ²⁺ M2			Fe ³⁺ M1			Fe ³⁺ M2			Fe ³⁺ /Fe ²⁺						
	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ	Moiss.	Chem.	A _{M1} /A _{M2}	Fe per formula unit
B1 (Ch)	298	1.13(1)	2.68(1)	0.40(1)	1.13(1)	2.28(1)	0.40(1)	0.42(2)	0.65(5)	0.60(2)	-	-	0.25(6)	-	0.48(5)	1.70
F1 (A)*1a)	298	-	-	-	-	-	-	0.37(1)	0.81(1)	0.43(2)	-	-	∞	0.00	-	0.08
F13 (A)	77	1.23(1)	2.96(1)	0.41(1)	-	-	-	0.47(3)	0.60(4)	0.85(3)	-	-	0.34(3)	0.10	-	0.24
F13 (A)	298	1.13(1)	2.73(1)	0.35(1)	-	-	-	0.38(4)	0.70(5)	0.84(3)	-	-	0.25(2)	-	-	-
F14(A)	298	1.12(1)	2.70(1)	0.35(1)	-	-	-	0.36(4)	0.70(5)	1.14(6)	-	-	0.47(17)	0.50	-	0.03
HU176 (A)	4	1.28(1)	3.02(1)	0.44(2)	-	-	-	0.55(4)	0.85(3)	0.70(3)	-	-	0.11(1)	-	-	0.41
HU176 (A)	77	1.25(1)	2.97(1)	0.40(1)	-	-	-	0.51(5)	0.80(5)	0.70(7)	-	-	0.18(2)	-	-	-
HU176 (A)	298	1.15(1)	2.75(1)	0.41(1)	-	-	-	0.42(3)	0.70(4)	0.55(7)	-	-	0.19(2)	-	-	-
F15 (A)	298	1.13(1)	2.70(1)	0.40(1)	-	-	-	0.43(4)	0.80(5)	0.80(4)	-	-	0.67(9)	0.40	-	0.45
F19 (A)**	298	1.14(1)	2.74(1)	0.31(1)	-	-	-	0.34(2)	0.76(1)	0.52(2)	-	-	0.25(5)	0.08	-	0.30
12176(C)1b)	298	1.14(1)	2.76(1)	0.30(1)	-	-	-	0.37(2)	0.82(4)	0.52(2)	-	-	1.87(20)	3.40	-	0.46
12180(C)	298	1.14(1)	2.74(2)	0.31(2)	-	-	-	0.38(3)	1.08(1)	0.60(2)	-	-	1.58(32)	4.50	-	0.22
6(2) (O)	77	-	-	-	1.18(1)	2.67(1)	0.36(1)	0.51(1)	0.97(2)	0.48(2)	0.44(4)	0.43(1)	0.45(2)	-	0.87(6)	0.18
6(2) (O)	298	-	-	-	1.07(1)	2.50(2)	0.35(2)	0.43(1)	0.92(2)	0.49(2)	0.32(2)	0.40(1)	0.32(2)	-	0.80(12)	-
HU(904) (C+L)	298	1.15(2)	2.74(1)	0.34(1)	-	-	-	0.45(1)	0.80(4)	0.52(2)	0.28(1)	0.34(3)	0.52(2)	2.30	-	0.20
HU11759(L)	4	1.28(1)	3.08(2)	0.38(2)	1.29(1)	2.64(2)	0.38(2)	0.55(4)	0.80(5)	0.95(6)	-	-	0.25(6)	-	0.48(4)	2.60
HU11759(L)	77	1.26(1)	3.09(1)	0.41(1)	1.27(1)	2.67(1)	0.41(1)	0.49(3)	0.65(2)	0.76(6)	-	-	0.21(3)	2.00	0.51(3)	-
HU11759(L)	298	1.15(2)	2.79(1)	0.40(1)	1.16(1)	2.21(2)	0.32(1)	0.37(3)	0.65(2)	0.82(4)	-	-	0.22(3)	-	0.58(4)	-
HU4050(L)	77	1.24(1)	3.08(1)	0.34(1)	1.18(1)	2.31(2)	0.34(2)	-	-	-	0.49(1)	0.52(2)	0.76(2)	2.80	0.15(7)	0.19
HU4050(L)	298	1.13(1)	2.70(2)	0.35(1)	1.07(1)	1.98(3)	0.41(2)	-	-	-	0.39(1)	0.53(1)	0.75(4)	-	0.18(4)	-
F47 (L)	298	1.13(2)	2.79(2)	0.41(2)	-	-	-	0.39(1)	0.75(1)	0.60(1)	-	-	0.31(6)	∞	-	0.27

Abbreviations: I.S. - isomer shift relative to Fe; Q.S. - quadrupole splitting;

Γ - peak width, all in mm/sec; A M(1)/A M(2) - ratio of amount of

Fe³⁺ or Fe²⁺ in sites M(1) to that in sites M(2).

* USNM 70160 ** USNM 80500

Ch - chamosite, A - antigorite, C - chrysotile, O - orthoserpentine,

L - lizardite

1) some Fe³⁺ present in tetrahedral sites with the following parameters (mm/sec)

a) I.S. = 0.21(2), Q.S. = 0.42(2), Γ = 0.43(2); b) I.S. = 0.21(2),

Q.S. = 0.40(4), Γ = 0.52(2)

Table 2. Mossbauer parameters of kaolinites and dickites

Sample	Temp. °K	Fe ³⁺			Fe ²⁺			Fe ²⁺ / Fe ³⁺	Fe per formula unit
		I.S.	Q.S.	Γ	I.S.	Q.S.	Γ		
O.P. (K)	298	0.40 (1)	0.65 (1)	0.58 (2)	-	-	-	-	0.17
I.Z.2 (K)	77	0.48 (1)	0.66 (4)	0.69 (4)	1.24 (1)	2.85 (5)	0.44 (2)	0.30 (6)	-
I.Z.2 (K)	298	0.39 (2)	0.66 (1)	0.60 (1)	1.13 (1)	2.68 (2)	0.41 (2)	0.31 (8)	-
D14 (D)	298	0.39 (1)	0.55 (2)	0.63 (1)	-	-	-	-	0.15
D16 (D)	298	0.39 (1)	0.61 (1)	0.55 (1)	-	-	-	-	0.09

Abbreviations as for Table 1 and K - kaolinite, D - dickite

and Fahey (1962) and in our laboratory was previously discussed (Yariv and Heller-Kallai, 1973).

Possible errors in the determination of Fe³⁺/Fe²⁺ ratios from Mössbauer analysis may be due to the presence of some magnetic phases or to paramagnetic relaxation effects, which may cause appreciable broadening of the lines in the Mössbauer spectra. The spectra were checked for these possibilities, and the inaccuracies in the Fe³⁺/Fe²⁺ ratios determined by Mössbauer analysis were estimated to be less than 5 percent.

In the course of chemical analysis, some oxidation of the specimens may occur, thus increasing the chemically-measured Fe³⁺/Fe²⁺ ratio. The opposite effect, in which higher Mössbauer than chemical values are obtained for Fe³⁺/Fe²⁺, as observed most strikingly with sample F1 (Fig. 1b), is difficult to explain. In the Mössbauer spectrum of sample F1 no doublet corresponding to Fe²⁺ is seen. The limit obtained from the Mössbauer analysis shows that less than 3 percent of the total iron is divalent, in complete contradiction to Faust and Fahey, who found that the iron was present entirely in the divalent form. Oxidation of the serpentines during storage in the laboratory can be discounted, in view of the resistance of the ground specimens to oxidation on drastic H₂O₂ treatment. It should, however, be noted that the total concentration of iron is very low (0.35 percent FeO, according to Faust and Fahey), which may cause inaccuracies in the chemical analysis.

Whittaker and Wicks (1970) discussed the chemical differences between serpentines and concluded that antigorites have the highest FeO/(FeO + Fe₂O₃)

+ Al₂O₃) ratio and lizardites the lowest. Though this conclusion seems justified for most of the samples examined, there are some exceptions, like the antigorite sample F1 discussed above, which contains only Fe³⁺, and the lizardites F47 and HU11759, in which more than 70 percent of the iron ions are divalent. The Fe³⁺/Fe²⁺ ratios determined by Mössbauer analysis of these three samples, two of which were included in the selection of Whittaker and Wicks, suggest that the criterion they proposed for the classification of serpentine minerals should be treated with caution.

The Mössbauer parameters

All the parameters obtained for 1:1 phyllosilicates are compatible with those reported for 2:1 phyllosilicates. The line widths of the Fe²⁺ doublets are relatively narrow (0.32–0.40 mm/sec) and fall within the range given by Bancroft (1974) for silicates. The Fe³⁺ doublets have a much broader line width (0.40–0.75 mm/sec), even when Fe³⁺ ions are assigned to two different sites. This is a common feature of phyllosilicates (paper in preparation). No significant changes in the line widths were observed in spectra recorded at 77°K. The larger line widths of the Fe³⁺ doublets may be due to some inhomogeneity of the Fe³⁺ environment or to paramagnetic spin-spin relaxation effects, which are commonly observed for Fe³⁺ in samples with low iron content (Mørup, 1974). The crystal-field symmetry is usually sufficiently low to render the electronic ground state of Fe²⁺ a singlet, which cannot have a magnetic moment. Paramagnetic relaxation effects are thus not expected to

affect Fe^{2+} spectra (Lang and Marshall, 1966) and could, therefore, explain the observed differences in line width between the Fe^{3+} and Fe^{2+} doublets in phyllosilicates. Note that glauconites and nontronites, which are rich in Fe^{3+} , give rise to much narrower Fe^{3+} doublets than phyllosilicates with low Fe^{3+} content (Rozenson and Heller-Kallai, 1977). The changes in isomer shift from room temperature to 77°K are 0.11 ± 0.01 mm/sec, as anticipated from the second-order Doppler shift (Josephson, 1960).

Fe^{3+} in tetrahedral coordination. The presence of tetrahedral Fe^{3+} was inferred for two of the samples studied (12176 and F1) on the basis of the isomer shift, which resembles that of ferri-phlogopite (Annersten *et al.*, 1974). The spectra of samples 12180, 6(2) orthochrysotile, and HU904 show Fe^{3+} doublets with isomer shifts smaller than are generally found for octahedrally-coordinated Fe^{3+} in silicates, but larger than those generally associated with tetrahedrally-coordinated Fe^{3+} . The parameters fall in the range attributed to tetrahedrally-coordinated Fe^{3+} in nontronites by Goodman *et al.* (1976). It seems possible that these doublets in serpentines are due to both octahedral and tetrahedral Fe^{3+} , but that their quadrupole splittings are too similar to permit further resolution.

In calculating structural formulae from the experimentally-determined composition, it is customary to postulate Al-for-Si in preference to Fe^{3+} -for-Si substitution. While this is justified from similarity of ionic radii, the misfit between the octahedral and tetrahedral sheets of trioctahedral layer structures is more effectively relieved by Fe^{3+} -for-Si than by Al-for-Si substitution. Replacement by trivalent ions in both the tetrahedral and octahedral sheets of serpentines gives rise to characteristic IR absorption bands at about 3400 cm^{-1} , which persist after elimination of adsorbed water (Heller-Kallai *et al.*, 1975). Such absorptions appear in the IR spectra of samples 12176 and HU11759 but not in the spectrum of sample F1. According to the chemical and microprobe analyses, this sample contains no more than 0.08 Fe ions per formula unit. The amount of tetrahedral Fe^{3+} present is thus necessarily very small. Moreover, it is to be expected that Fe^{3+} -for- Si^{4+} substitution causes a smaller increase in the polarity of the layer than Al^{3+} -for- Si^{4+} substitution, and minor amounts of tetrahedral iron may not suffice for the formation of the interlayer H bonds which give rise to the band at about 3400 cm^{-1} .

The configuration of the octahedral sheets

Phyllosilicates in general have two octahedral sites, *M1* and *M2*, in the ratio 1:2. Structure determination showed that these sites differ in kaolinites (Zvyagin, 1967, p. 256) and dickites (Newnham, 1969). Kunze (1961) inferred that the two sites are indistinguishable in antigorites, and this was confirmed by their IR spectra (Yariv and Heller-Kallai, 1973). In chrysotiles and lizardites two distinct sites occur. Since the unit layers are buckled, in lizardites more than in chrysotiles (Wicks and Whittaker, 1975), different distortions of the two octahedral sites may be expected. No structure determination of chamosites seems to have been reported.

Chamosites. Yershova *et al.* (1975) found that Fe^{2+} ions occupy the two different octahedral sites of chamosite (sample 152) in the ratio 65:35, with the higher proportion of Fe^{2+} in the sites with higher quadrupole splitting. We derived a ratio of 100:48 for sample B1 (Table 1). These ratios, which are close to 2, suggest that Fe^{2+} in chamosites occupies sites *M2* and *M1* non-preferentially, as reported for biotites (*e.g.* Annersten, 1974). On this assumption it follows that the doublet with higher quadrupole splitting corresponds to Fe^{2+} in *M2* sites. This assignment receives some support from consideration of the structural formulae of the samples, provided that these are chemically pure. The FeO content of sample B1, inferred from the Mössbauer spectra, is 35 percent *i.e.* it is similar to that of sample 152, described by Yershova *et al.* (1975), for which a structural formula with 1.7 Fe^{2+} ions per formula unit was deduced. Since *M1* sites can accommodate a maximum of one cation per formula unit, and the population of the site with larger quadrupole splitting exceeds 1, this doublet must be assigned to *M2* sites.

Yershova *et al.* reported only a single Fe^{3+} doublet for all the natural samples studied. The ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ is 0.18 and 0.25 for samples 152 and B1 respectively, and accordingly the Fe^{3+} doublets are weak. Yershova *et al.* reported a narrow Fe^{3+} doublet with large Q.S. We observed a smaller Q.S. and broader line widths, as is usual for phyllosilicates with low Fe^{3+} content. Resolution of the Fe^{3+} doublet into two doublets did not decrease the value of χ^2 , but this does not prove that Fe^{3+} occupies only one type of site selectively. Yershova *et al.* found that spectra of samples of heated chamosite, in which the Fe^{2+} was partly or completely oxidized, could be resolved into four doublets, two Fe^{2+} and two Fe^{3+} . They inferred

that Fe^{3+} originally occupied one type of site only and that the other became populated by Fe^{2+} derived from oxidized Fe^{2+} . In interpreting the spectra, however, the problem of maintaining electrical neutrality of the sample on oxidation of Fe^{2+} seems to have been ignored. This could occur by partial deprotonation of the specimens, which may modify the corresponding sites.

Serpentines. The Mössbauer spectra of antigorites show that only one type of octahedral sites is occupied by Fe^{2+} or Fe^{3+} ions, in complete agreement with the conclusions reached by X-ray and IR studies. Most lizardites and chrysotiles contain Fe^{2+} or Fe^{3+} in two types of octahedral sites. Despite their different crystal structures, the Mössbauer spectra of antigorites, lizardites, and chrysotiles all show one Fe^{2+} doublet with similar parameters—quadrupole splittings at 298°K ranging from 2.70 to 2.79 mm/sec (2.70 to 2.76 mm/sec for nine of the eleven samples examined) and isomer shifts of 1.12 to 1.15 mm/sec. Only the Mössbauer spectrum of 6(2) orthochrysotile does not show this doublet, but the doublet observed has a relatively large Q.S. and its assignment is uncertain.

The second Fe^{2+} doublet seen in the Mössbauer spectra of chrysotiles and lizardites has a much wider range of parameters. The differences between the configuration of sites in the various samples probably depend on the type of serpentine and its chemical composition. Thus it is possible that the two Fe^{2+} doublets in sample HU11759 differ less from each other than those in HU4050, because the misfit between the octahedral and tetrahedral sheets is partly relieved by Al^{3+} -for- Si^{4+} substitution. This reduces the distortion of the octahedral sheets and renders *M1* sites more similar to *M2*. Further confirmation of this hypothesis is required, but no other suitable serpentine minerals were available for study.

The spectra of serpentines are reminiscent of those of biotite (Annersten, 1974), but the Q.S. of the outer Fe^{2+} doublets are about 0.1–0.2 mm/sec greater. This may be due to the different ligands: $\text{O}_2(\text{OH})_4$ in serpentines and $\text{O}_4(\text{OH})_2$ in biotites. Assignment of the doublets to the two octahedral sites, *M1* and *M2*, is difficult. The structure determinations reported in the literature are not sufficiently accurate to provide the exact configuration of the octahedra for correlation of distortion with the quadrupole splittings. Comparison of the Mössbauer data for serpentines and chamosites (Table 1) suggests that the doublet with

larger quadrupole splitting in the spectra of lizardites and chrysotiles should be assigned to Fe^{2+} in *M2* sites and that the single site in antigorites resembles *M2*.

In the mineralogical literature it has generally been assumed that larger quadrupole splittings of Fe^{2+} doublets indicate smaller distortion (*e.g.* Bancroft, 1974). As is well known, the quadrupole splitting is mainly due to an electric field gradient (EFG), caused by (a) the aspherical charge distribution of the 'valence' electrons of the Mössbauer atom and (b) the charges on ions surrounding the Mössbauer atom in the crystal. The first contribution to the EFG is usually denoted by q_{val} , the second by q_{lat} . For Fe^{3+} , an S state ion, $q_{\text{val}} = 0$ and the Q.S. is mainly due to q_{lat} . The theory for the Q.S. of Fe^{2+} was developed by Ingalls (1964). The Q.S. is expressed by $E(T) = \Delta E_0 F(T)$. The bare quadrupole coupling constant ΔE_0 is defined as

$$\Delta E_0 = \frac{2}{5} \langle r_{\text{eff}}^{-3} \rangle e^2 Q$$

where $\langle r_{\text{eff}}^{-3} \rangle$ is an effective value for the 3*d* electrons on the ferrous ion, including both covalency and anti-shielding effects, and *Q* is the quadrupole moment of $\text{Fe}^{57\text{m}}$. The reduction factor *F*(*T*) takes into account the thermal population of the crystal field levels of the Fe^{2+} ions, spin orbit coupling and q_{lat} . The values of ΔE_0 vary from compound to compound and are mainly influenced by effects of covalency (Ingalls, 1969). q_{lat} is temperature-independent. Its size is usually much smaller than that of q_{val} , and in most cases it has the opposite sign (Nozik and Kaplan, 1967). The temperature-dependence of *F*(*T*) is mainly dictated by the crystal field splittings Δ_1 and Δ_2 , and to a lesser extent by the spin orbit coupling Λ .

The conclusion that larger quadrupole splittings of Fe^{2+} doublets indicate smaller distortion (*e.g.* Annersten, 1974) was based on the assumption that Δ_3 is greater than approximately 800 cm^{-1} and any decrease observed from the maximum possible quadrupole splitting of Fe^{2+} doublets is due to a negative contribution of q_{lat} (Fig. 6–9, Bancroft, 1974). It did not take into account major changes in ΔE_0 and *F*(*T*). On the other hand the temperature-dependence of the quadrupole splittings measures in principle the crystal field splittings Δ_1 and Δ_2 and hence depends on the distortion—the smaller these splittings, the smaller the distortion, and the larger the temperature-dependence. In the present case the relative change of the quadrupole splitting with temperature

in the lizardites measured is larger for Fe^{2+} ascribed to the $M1$ than for Fe^{2+} ascribed to the $M2$ sites. This is clearly seen for sample 11759, where $\text{Q.S. (300}^\circ\text{K)}/\text{Q.S. (4}^\circ\text{K)} = 0.91$ and 0.83 for the $M2$ and $M1$ sites respectively, thus indicating that the $M2$ are more distorted than the $M1$ sites, though the quadrupole splitting of the $M2$ is larger than that of the $M1$ sites. Because of the similarity of the $M2$ parameters in all the serpentines measured, it is plausible to assume that in the other samples too the $M2$ site is more distorted than the $M1$ site.

With this assumption, the assignment of the Fe^{3+} doublets to the $M1$ and $M2$ sites may be based on that of the Fe^{2+} doublets. If $M1$ sites are less distorted than $M2$, *i.e.* the q_{lat} contribution is smaller, it follows that the quadrupole splitting of Fe^{3+} in such sites is expected to be smaller than that of Fe^{3+} in $M2$ sites. It seems, therefore, that Fe^{3+} doublets with the larger quadrupole splittings should be assigned to $M2$ sites. This assignment is supported by the spectra of antigorites, in which the quadrupole splittings of doublets corresponding to Fe^{3+} ions occupying the single site, like those of Fe^{2+} ions, resemble those of the corresponding ions assigned to $M2$ sites in the other serpentines.

It is impossible to decide whether the Fe^{3+} present in the chamosite and serpentines is primary or is due to oxidation of structural Fe^{2+} . The association with hematite in two samples in which iron is present entirely in the trivalent form (not included in Table 1) suggests that some oxidation may have occurred.

Kaolinites and dickites. Structure determinations of kaolinite (Zvyagin, 1967) and dickite (Newham, 1961) showed that Al occupies two crystallographically-distinct sites in the octahedral sheets. Only single Fe^{3+} and Fe^{2+} doublets, however, were observed in the Mössbauer spectra. The interatomic distances and the distortion of the two types of sites are similar, as are the ligands and their spatial distribution. It therefore seems possible that the Mössbauer parameters of iron in the two sites are very similar. The presence of only one doublet for either Fe^{3+} or Fe^{2+} cannot therefore be attributed to selective occupancy of one type of site. The doublets are relatively broad. This may be attributed to relaxation effects for Fe^{3+} , but may also be due to inhomogeneity of the sites occupied by either Fe^{2+} or Fe^{3+} .

The similarity of the Mössbauer spectra of dickites and kaolinites shows that different methods of layer stacking do not appreciably affect the geometry of the octahedral sites.

The temperature-dependence of the Q.S. of Fe^{2+} doublets of kaolinites is smaller than that of serpentines, indicating that the corresponding sites are more distorted. This is in agreement with the data obtained for 2:1 layer silicates—the temperature-dependence of Fe^{2+} doublets of dioctahedral minerals, *e.g.* muscovite, is smaller than that of trioctahedral minerals, *e.g.* biotite (paper in preparation).

Comparison of Mössbauer parameters of Fe^{2+} in 1:1 and 1:2 phyllosilicates

Both 1:1 and 1:2 phyllosilicates contain two different octahedral sites, but the ligands differ—4(OH) groups in 1:1 and 4(O) and 2(OH) groups in 1:2 phyllosilicates. Moreover, while the distribution of the ligands in $M1$ and $M2$ sites in 1:1 phyllosilicates is similar, OH groups in 1:2 phyllosilicates occur in either *trans* ($M1$) or *cis* ($M2$) arrangements.

It would be desirable to compare the spectra of serpentines with those of talc, but all the samples of talc examined to date show only a single Fe^{2+} doublet assigned to $M2$ sites (Rozenson, unpublished). In biotites two Fe^{2+} doublets were distinguished, resembling those of serpentines, but the quadrupole splittings of the outer doublets are smaller by about 0.1–0.2 mm/sec, possibly due to the different ligands. The temperature-dependence of the quadrupole splitting of the two Fe^{2+} doublets in biotite is very similar (Annersten, 1974), whereas in lizardites the smaller quadrupole splitting, associated with $M1$ doublets, is much more temperature-dependent than the larger one. This is attributed to the greater distortion of $M2$ sites in serpentines. In contrast, the difference in the quadrupole splittings of the two Fe^{2+} doublets in 1:2 phyllosilicates is mainly due to the different q_{lat} contribution arising from the different distribution of the ligands, while the distortion of the sites, and hence the temperature-dependence of the quadrupole splittings, is similar.

Conclusions

Mössbauer spectra of some of the 1:1 phyllosilicates examined showed doublets corresponding to Fe^{2+} or Fe^{3+} ions in two different octahedral sites. Since the distribution of ligands in the $M1$ and $M2$ sites is similar in these minerals, in contrast with the *cis* and *trans* distribution in 2:1 phyllosilicates, the differences in Q.S. between doublets associated with the two types of sites reflect differences in distortion.

Although structure determinations of kaolinite and dickite show that Al occupies two different octahedral sites, only one type of site could be distinguished

by Mössbauer spectroscopy, probably due to the small difference between their Mössbauer parameters. In antigorites, also, only one type of site was found. In contrast, in chamosites and lizardites Fe^{2+} occurs in two clearly distinguishable sites, with well-defined ranges of quadrupole splittings, reflecting different distortions. In the chrysotiles examined it seems to be the Fe^{3+} and not the Fe^{2+} ions which occupy two different octahedral sites. Interpretation of the Fe^{3+} spectra is difficult, however, due to the large line width of the doublets and the possible presence of Fe^{3+} in tetrahedral coordination.

In general, the Mössbauer parameters of Fe^{2+} in $M2$ sites and their temperature-dependence are very similar for the sample of chamosites and all the serpentines studied. The corresponding parameters of the $M1$ sites differ appreciably and show a larger temperature-dependence of the Q.S. This indicates that these sites are less distorted than $M2$ sites, despite the smaller Q.S., in disagreement with the usual interpretation in the mineralogical literature, which correlates a smaller Q.S. of Fe^{2+} doublets with greater site distortion.

Fe^{2+} occupies octahedral sites randomly in chamosites and lizardite HU11759, while $M2$ sites are occupied preferentially in lizardite HU4050 and exclusively in F47. These distributions may reflect differences in energy associated with the site distortions and may throw some light on the history of the samples. Further study is required.

Acknowledgments

We are indebted to Dr. G. T. Faust, Dr. B. F. Kohn, Mlle. S. Caillere, Mr. C. D. Rushten, and the Smithsonian Institution for donation of specimens.

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Manuscript received, July 28, 1978;
accepted for publication October 27, 1978