

MÖSSBAUER CHARACTERISTICS OF CAMBRIAN GLAUCONITE, CENTRAL U.S.A.

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Abstract—Mössbauer characteristics of ^{57}Fe nuclei in 8 samples of mineral glauconite of Cambrian age and one sample of Cretaceous age (slightly disordered) were obtained at temperatures between 50 and 295 K to evaluate the site occupation of iron in the octahedral sheet and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. It was found that the resolution of Mössbauer spectra of glauconite is increased at low temperature.

The octahedral sheet in mineral glauconite is believed to contain two types of cationic environments with slight symmetry differences because of the position of oxygen and hydroxyl ions around the cation sites. One environment consists of two equivalent sites (M_2), whereas the other is a single site (M_1).

The Mössbauer spectra were fitted to a four-doublet model, two Fe^{3+} sites (M_2 and M_1) and two Fe^{2+} sites, and a three-doublet model, two Fe^{3+} sites (M_2 and M_1) and an average Fe^{2+} site. The former (four-doublet) model yielded lower χ^2 and, also, line widths in close agreement with previous studies. However, since the Fe^{2+} concentration in the samples is low, the error in intensity of the Fe^{2+} occupation of the M_1 and M_2 sites leads us to conclude that $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios are more accurate for the three-doublet model.

Calculation of area ratios for the two Fe^{3+} doublets indicates that trivalent iron is strongly concentrated in the M_2 site, which is smaller than the M_1 site. Site preference of divalent iron could not be determined. The ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ obtained from the Mössbauer spectra were usually within 8% of those obtained from chemical analyses.

INTRODUCTION

The Mössbauer effect is especially useful for studying the iron content and the nature of the environment of iron atoms in iron-bearing minerals (Bancroft, 1973). Moreover, Mössbauer studies appear to be comparable to chemical means for the determination of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (Annersten, 1974; Bancroft, 1973).

A Mössbauer study of ^{57}Fe nuclei was made on 8 glauconite samples from the Cambrian of the central U.S. and one sample from the Cretaceous of New Jersey at temperatures between 50 and 295 K. The Mössbauer shifts and quadrupole splittings were used to determine the charge states of the Fe atoms. The area of absorption is proportional to the product of the number of iron atoms in a given environment and the Mössbauer fraction. At low temperature, where the Debye–Waller factors tend to be close to each other, the area ratios for thin absorbers are a reasonably good measure of the relative number of Fe^{3+} and Fe^{2+} ions. Relative concentrations of Fe^{3+} and Fe^{2+} ions were also obtained by means of chemical analyses.

This study was undertaken to ascertain if Mössbauer characteristics might give useful information on

cation site occupation in the octahedral sheet. Cambrian glauconite was chosen for study because it is “mineral glauconite”; that is, it has a consistently well-crystallized 1M structure, yet is chemically variable. For comparison, a less well-crystallized glauconite sample from New Jersey was also studied. The mineralogical and chemical nature of the Cambrian glauconite has been summarized by Odom (1976). The mineralogy of the New Jersey sample was described by Tapper and Fanning (1968), and its chemistry is reported herein.

In mineral glauconite, the octahedral sheet contains significant amounts of trivalent Al and Fe and divalent Fe and Mg with trivalent Fe usually being the most abundant. Even with this diverse composition, most mineral glauconite is dioctahedral; i.e. octahedral cation abundance indicates that only two-thirds of the possible cation sites in the octahedral sheet are filled.

Most dioctahedral layer silicates have *b*-axis dimensions of $\sim 9 \text{ \AA}$, whereas trioctahedral species have *b*-dimensions of $\sim 9.2 \text{ \AA}$. The *b* parameter of mineral glauconite (~ 9.1) is, however, intermediate between these values. It has been suggested (Bradley and Grim, 1961) that this relation can be explained on the basis of cation size. In fact, for most of the Cam-

brian samples studied, an excellent correlation has been found between the size of the *b*-cell dimension and ionic content of the octahedral sheet (Odom, 1976). Ionic size may not, however, be the only factor that determines the *b*-dimension of mineral glauconite. The experiments of Lindqvist (1962) indicate that cation ordering may also influence the *b*-parameter of micas. He found that heating of a dioctahedral mica caused disordering of the octahedral cations with the result that the *b*-dimension was increased to such a degree that the mica was no longer recognizable as dioctahedral. An additional objective of this study was to explore whether the *b*-axis dimension of mineral glauconite might also be related to octahedral cation order.

SAMPLES AND EXPERIMENTAL METHODS

Eight glauconite samples of Cambrian age from the Mississippi Valley and one sample of Cretaceous age from New Jersey were investigated. The chemistry and mineralogy of seven of the Cambrian samples was previously described (Odom, 1976). The compositions of the additional samples are given in Table 1. Sample 8 is also of Cambrian age, but it was not included in the previous study (Odom, 1976) because its high Al_2O_3 and K_2O contents, compared to other Cambrian samples, suggests that it probably contained a small amount of $<2\ \mu\text{m}$ potassium feldspar. Small-size K-feldspar is abundant in Cambrian sandstones and the glauconite occurred in a very fine-grained, argillaceous bed, so that the possibility of this contamination is likely.

Glauconite pellets were purified by magnetic separation, and sample purity was evaluated by microscopic examination. The Mössbauer samples were a split of the samples submitted for chemical analysis. The glauconite was placed in suspension and then spray-dried by means of an apparatus similar to that described by Hughes and Bohor (1970). Spray-drying was employed to achieve a random orientation of the

crystals. A more detailed description of the sample preparation is given by Odom (1976).

The Mössbauer sample ranged from 25 to 50 mg/cm². Measurements were made at 50, 77.3 and 295 K. The data were least-squares fitted to sets of quadrupole doublets with Lorentzian line shapes; the number in a given set was model dependent as described below. A 25 mCi ⁵⁷Co in Cu source was used, but all shift measurements are reported with respect to Fe in iron at 295 K. The shift correction is $\pm 0.225 \pm 0.002$ mm/sec (Stevens and Stevens, 1973). The line width (FWHM) for the inner lines (3, 4) of the iron spectrum for a 0.5 mil foil of natural iron at 295 K is 0.242 ± 0.004 mm/sec.

DISCUSSION AND RESULTS

Typical Mössbauer spectra of the glauconite samples studied are shown in Figures 1 and 2. These spectra illustrate that resolution is markedly temperature dependent. Each spectrum is characterized by at least two quadrupole doublets with an isomer shift in the range from 0.12 to 0.18 mm/sec and from 0.9 to 1.3 mm/sec, respectively. The quadrupole splitting

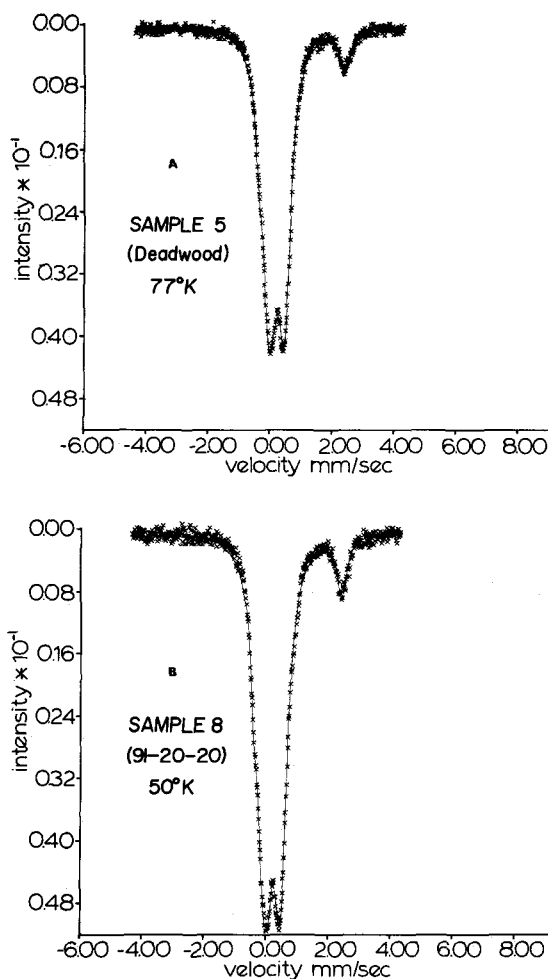


Figure 1. Typical Mössbauer spectra at 50 K.

Table 1. Chemical composition of samples 8 and 9

	Sample 8 91-20-20	Sample 9* New Jersey
SiO ₂	48.39	48.36
Al ₂ O ₃	11.28	5.84
TiO ₂	0.18	0.10
Fe ₂ O ₃	17.28	21.49
FeO	2.13	2.92
MnO	0.05	0.01
MgO	2.67	3.45
CaO	0.82	0.51
Na ₂ O	0.03	0.16
K ₂ O	8.19	6.91
P ₂ O ₅	0.40	0.08
H ₂ O ⁺	5.18	5.89
H ₂ O ⁻	2.94	4.29
C	0.14	nd

* Chemical formula for sample 9— $\text{K}_{0.66}\text{Na}_{0.02}\text{Ca}_{0.02}(\text{Al}_{0.19}\text{Fe}_{1.23}^{3+}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.39})(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$.

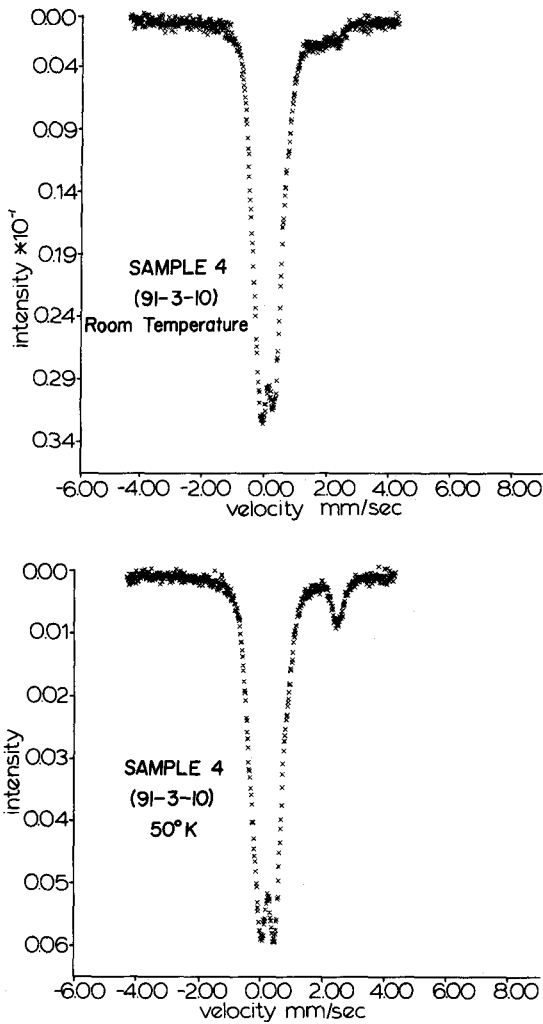


Figure 2. Mössbauer spectra of sample 4 (91-3-10) showing the influence of temperature on resolution.

E_Q for the major peaks ranges from 0.25 to 1.2 mm/sec; these values are typical of those associated with Fe^{3+} ions. The spectra also contain minor components with E_Q in the range from 0.75 to 2.7 mm/sec; these peaks reflect the presence of Fe^{2+} ions.

The Mössbauer parameters reported here are in the same range (within experimental error) as given in previous studies of other glauconites. Bowen *et al.* (1969) reported shifts for Fe^{2+} and Fe^{3+} ions of 1.2 mm/sec and 0.36 mm/sec (relative to iron), respectively. Hofmann *et al.* (1967) give shift ranges for Fe^{2+} and Fe^{3+} of 1.0–1.3 mm/sec and 0.24–0.49 mm/sec, respectively. The range of quadrupolar splitting reported in previous studies of Cambrian glauconite (Taylor *et al.*, 1968; Arnott, 1968) is also close to those found in this study, but the resolution of the two charge states of Fe in our spectra is much clearer.

From the Mössbauer spectra, especially at low temperatures (50 K, 77.3 K) it is obvious that both Fe^{2+} and Fe^{3+} ions are present as indicated by the chemical analyses. A least squares fit for only two doublets

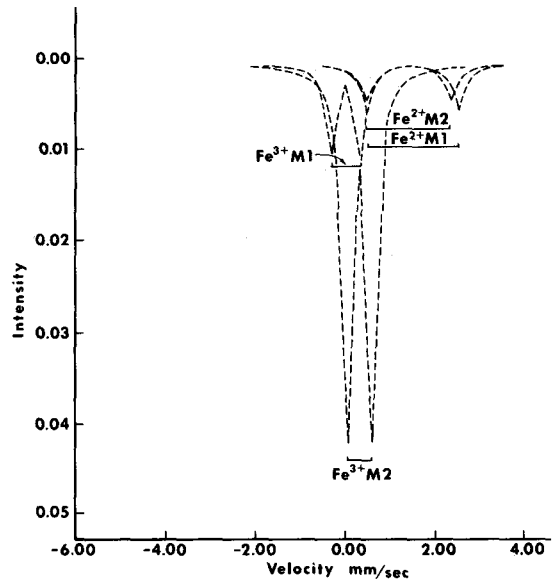


Figure 3. Interpretation of the Mössbauer subspectra in sample 4 at 50 K shown in Figure 2.

(one for Fe^{3+} and one for Fe^{2+}) is very poor, and it is apparent that three or more subspectra are necessary to fit the data (Figure 3).

Ideally, micas are either dioctahedral or trioctahedral. When dioctahedral, as previously pointed out, one out of three octahedrally coordinated cation sites is vacant. Monoclinic micas in space group $C2/m$ have two independent types of octahedrally coordinated cation sites herein called M_1 and M_2 (Figure 4). M_1 lies at a center of symmetry on the mirror plane. M_2 consists of a pair of equivalent sites related to each other by the above symmetry elements (Bailey, 1975, p. 178). The Mössbauer parameters for Fe^{3+} in the M_2 sites are identical which tends to corroborate our choice of $C2/m$ (rather than say $C2$) symmetry.

Of the two possible sites, the M_2 s are smaller in size with slight distortions from cubic symmetry. The

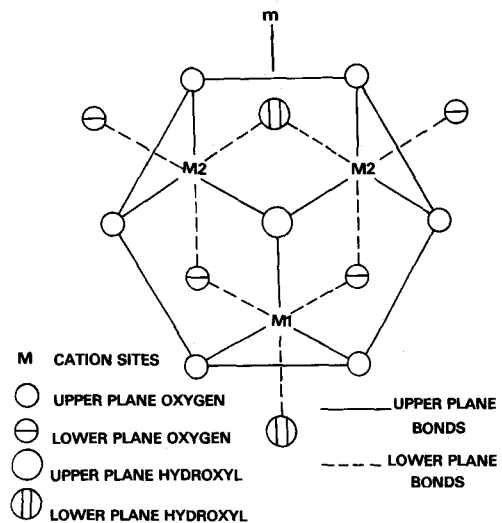


Figure 4. Cation sites in the octahedral sheet of a monoclinic mica in space group $C2/m$.

distortion arises because of the arrangement of oxygen and hydroxyl ions around these sites. Comparatively, the M_1 site is larger and much less distorted from cubic symmetry. Haggstrom (1969) suggests that these two types of sites can be identified in a Mössbauer spectrum by comparison of the quadrupole splitting for Fe^{3+} ions; i.e. the splitting should be largest for Fe^{3+} which occupy the distorted M_2 sites.

Substitution of Fe^{3+} for Si^{4+} is possible in some micas. Bailey (1975) and Tyler and Bailey (1961) report Fe^{3+} in the tetrahedral sheet of a glauconite associated with Precambrian iron-formation. Also, Thompson and Hower (1975) showed that glauconites with excess octahedral cations contain hydroxy-complexes of Fe, Mg and Al in interlayer sites. They conclude, however, that glauconites with octahedral occupancy within 0.05 of the ideal values of two per three octahedral sites probably do not contain significant interlayer hydroxy-complexes. For the glauconites studied (except sample 8—Table 1), the octahedral occupancy is within 0.05 of the ideal value of two.

Our spectra do not show clear evidence of tetrahedrally coordinated Fe^{3+} and this agrees with Arnott's (1968) Mössbauer data on similar samples. We conclude that if there is substitution of Fe^{3+} for Si^{4+} in the samples studied, it is very minor. We further conclude that the value of the octahedral occupancy for our samples rules out any significant iron in the interlayer positions. Thus, the two ferric iron doublets shown in the Mössbauer spectra (Figure 3) are believed to be the result of Fe^{3+} ions located in slightly different cation sites in the octahedral sheet. Since it is highly unlikely that the Fe^{2+} substitutes for Si^{4+} in the tetrahedral sheet, it would seem that if two Fe^{2+} peaks also can be unfolded from the Mössbauer spectrum, they too must be due to site differences for divalent Fe in the octahedral sheet. Thus, three different quadrupole doublets (2 Fe^{3+} and 1 Fe^{2+}) or four quadrupole doublets (2 Fe^{3+} and 2 Fe^{2+}) are possible with line width variations due to a small quadrupole distribution because of local environmental differences (Figure 3). Local environmental differences are caused by the presence of Al and Mg.

In the case of the three site fit (see Table 2), the line widths of all peaks were 0.50 mm/sec. The value of χ^2 was, however, reduced considerably (5–19%) for a four-site model (2 Fe^{3+} and 2 Fe^{2+}); the line widths were 0.30 mm/sec for Fe^{2+} and 0.42 mm/sec for Fe^{3+} . Although these latter line widths are more consistent with the results of other studies, the large statistical fluctuation in the Mössbauer determination of Fe^{2+} occupation between sites leads us to conclude that the three-site model may be more reliable for determining the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio.

Values of isomer shift and quadrupole splitting with statistical error at room temperature for the three and four site models can be found in Tables 2 and 3. Parameters are separated into columns for both kinds of iron by the difference in values of quadrupole splitting and isomer shift. Statistical error values are high for Fe^{2+} parameters because of low intensity of absorption peaks and consequent uncertainty in their associated parameters. The consistency of data from one sample to another seems to indicate that Fe^{3+} atoms are located in two slightly different sites.

Shift and splitting results for Fe^{2+} are less consistent than for Fe^{3+} . If one assumes two Fe^{2+} doublets (Figure 2), the error values for shifts and splittings are significantly higher. Even though it may not be possible to distinguish accurately between the two sites for ferrous iron, several factors strongly suggest that Fe^{2+} atoms are located in two different sites. When looking only at the thinnest samples (<3.5% absorption), the four-site fit significantly reduces χ^2 and the line width values are more typical of those found by other investigators. For example, a fit to a single Fe^{2+} doublet for samples 4 and 7 at room temperature yielded a line width of ~ 0.75 mm/sec. When separated into two doublets, each doublet had more realistic widths (0.3–0.4 mm/sec); χ^2 was reduced in these cases by 9% and 12%, respectively. In Table 2 (three-site model) the parameters for sample 7 seem to deviate considerably from other samples; however, when fit with four quadrupoles (Table 3), sample 7 seems to be much more consistent with the Mössbauer parameters of the other samples.

Table 2. Shifts and splitting for three quadrupole doublets (all values at room temperature and in mm/sec)

Sample	δ	Fe^{2+}		Fe^{3+}			
		E_Q	δ M_1^{\ddagger}	E_Q M_1	δ M_2^{\ddagger}	E_Q M_2	
1. R-90-45-20	1.00 ± 0.11	2.29 ± 0.20	0.134 ± 0.007	0.465 ± 0.013	0.191 ± 0.009	1.23 ± 0.02	
2. C-90-45-20	0.866 ± 0.027	2.25 ± 0.06	0.134 ± 0.002	0.433 ± 0.005	0.183 ± 0.004	1.14 ± 0.01	
3. 91-20-27	0.940 ± 0.068	2.03 ± 0.13	0.129 ± 0.006	0.358 ± 0.033	0.127 ± 0.006	0.821 ± 0.067	
4. 91-3-10	1.04 ± 0.05	2.12 ± 0.09	0.123 ± 0.003	0.373 ± 0.003	0.124 ± 0.003	0.844 ± 0.038	
5. Deadwood	0.917 ± 0.060	1.91 ± 0.11	0.127 ± 0.005	0.294 ± 0.031	0.126 ± 0.003	0.673 ± 0.030	
6. Vermillion— Franconia	0.950 ± 0.040	2.06 ± 0.08	0.124 ± 0.005	0.298 ± 0.025	0.126 ± 0.003	0.691 ± 0.030	
7. Vermillion— Eau Claire	1.27 ± 0.03	1.53 ± 0.04	0.052 ± 0.002	0.156 ± 0.007	0.092 ± 0.002	0.601 ± 0.007	
8. 91-20-20	0.937 ± 0.053	1.98 ± 0.10	0.126 ± 0.004	0.339 ± 0.023	0.128 ± 0.003	0.765 ± 0.032	
9. New Jersey	1.02 ± 0.04	2.09 ± 0.07	0.130 ± 0.003	0.346 ± 0.020	0.124 ± 0.003	0.767 ± 0.038	

M_2 refers to distorted site. M_1 refers to undistorted site. δ refers to shift. E_Q refers to quadrupole splitting.

Table 3. Shifts and splitting for four quadrupole doublets (all values at room temperature and in mm/sec)

Sample	Fe^{2+}				Fe^{3+}			
	δ M_1^*	E_Q M_1	δ M_2^*	E_Q M_2	δ M_1	E_Q M_1	δ M_2	E_Q M_2
1. R-90-45-20	0.97 ± 0.02	2.88 ± 0.03	0.93 ± 0.11	1.92 ± 0.25	0.136 ± 0.006	0.460 ± 0.012	0.202 ± 0.001	1.18 ± 0.02
2. C-90-45-20	0.99 ± 0.06	2.56 ± 0.12	0.75 ± 0.07	2.07 ± 0.13	0.142 ± 0.002	0.425 ± 0.005	0.176 ± 0.005	1.17 ± 0.02
3. 91-20-27	0.65 ± 0.02	2.13 ± 0.03	1.54 ± 0.02	1.47 ± 0.03	0.123 ± 0.002	0.299 ± 0.031	0.129 ± 0.004	0.678 ± 0.053
4. 91-3-10	1.22 ± 0.02	2.28 ± 0.05	0.95 ± 0.04	1.74 ± 0.09	0.120 ± 0.002	0.423 ± 0.014	0.127 ± 0.004	0.935 ± 0.003
5. Deadwood†								
6. Vermillion— Franconia	0.96 ± 0.01	2.66 ± 0.02	0.88 ± 0.07	1.86 ± 0.15	0.130 ± 0.010	0.259 ± 0.029	0.135 ± 0.004	0.641 ± 0.026
7. Vermillion— Eau Claire	0.94 ± 0.01	2.69 ± 0.02	0.89 ± 0.07	1.82 ± 0.14	0.125 ± 0.014	0.248 ± 0.040	0.131 ± 0.004	0.640 ± 0.026
8. 91-20-20	1.18 ± 0.05	2.24 ± 0.09	0.89 ± 0.11	1.76 ± 0.22	0.124 ± 0.009	0.369 ± 0.034	0.122 ± 0.002	0.791 ± 0.036
9. New Jersey†								

* M_2 refers to distorted site. M_1 refers to undistorted site. δ refers to shift. E_Q refers to quadrupole splitting.

† Parameters at room temperature not accessible because of large fitting errors.

Table 4. Relative concentration of Fe^{3+} in M_2 and M_1 sites and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios from Mössbauer spectra at 50 K and chemical analyses

Sample	Mössbauer spectrum		Chemical analysis $\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}$
	$\frac{\text{Fe}^{3+}(M_2)}{\text{Fe}^{3+}(M_1)}$	$\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}$	
1. R-90-45-20	7.2 ± 2.8	8.2 ± 1.8	9.9
2. C-90-45-20C	6.2 ± 0.5	8.3 ± 0.5	8.6
3. 91-20-27	8.3 ± 1.0	8.7 ± 0.7	7.2
4. 91-3-10	8.9 ± 0.8	8.9 ± 0.6	7.8
5. Deadwood	4.6 ± 0.4	8.0 ± 0.6	8.4
6. Vermillion— Franconia	5.0 ± 0.3	5.2 ± 0.3	5.2
7. Vermillion— Eau Claire	4.3 ± 0.3	4.6 ± 0.2	5.0
8. 91-20-20	8.2 ± 0.8	7.5 ± 0.5	8.1
9. New Jersey	5.0 ± 0.4	7.6 ± 0.6	7.9

Table 4 shows area ratios that compare the relative amounts of Fe^{2+} and Fe^{3+} atoms in each sample. Areas are an indication of site population since the area under the absorption curve is proportional to the product of f' , the recoil-free fraction for absorber, and ω , the number of absorbing nuclei in a given environment. In Table 4, the distribution of Fe^{3+} atoms between sites is also given. The occupation ratios that are most reliable are those for which the absorber is thin and where values of f' are approximately equal. These conditions are met for a number of our samples at low temperature. As seen in Table 4, ferric iron occupies two sites in all samples studied and strongly favors the M_2 over the M_1 site (Fig. 3). The large variation in the site occupation of Fe^{3+} probably results from the two possible Fe^{3+} locations. We estimate that in sample 4 (Table 4) approximately one M_1 site per 10 formula units is occupied by trivalent iron, but in sample 7 approximately one M_1 site per four formula units is occupied by Fe^{3+} . It appears that the higher the Fe^{3+} content the greater its occupation of the M_1 site.

The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios determined from the Mössbauer spectra for more than one-half of the samples are in close agreement with those determined by chemical analysis (Table 4). The values differ by approximately 5% (3–8%), with the exception of samples 1, 3 and 4 which differ by approximately 17, 20 and 14%, respectively. Samples 6 and 7 have considerably smaller ratios than other samples, which the chemical analyses substantiate. We cannot explain the large deviation of samples 1, 3 and 4 from the chemically analyzed values.

In summary, it is clear that all samples of mineral glauconite, even of essentially the same age, are not exactly the same in terms of chemistry or in terms of the cationic site population of Fe. Large differences in Mössbauer parameters probably result from slight differences in iron content in the octahedral sheet, and individual glauconite samples show considerable variation in both total iron content and the ferric

to ferrous ratio. In this regard, it should be noted that two samples (1 and 2) give significantly different Mössbauer parameters than all others. Sample 1 is a form of glauconite that occurs as rims on glauconite pellets and also as isolated patches within pellets. It was removed from the pellets which constituted sample 2. This glauconite has a texture in which the crystals are oriented (Odom, 1976), whereas in the other samples most of the glauconite crystals are in a random orientation. Sample 2 is estimated to contain 20% of the oriented glauconite. Sample 1 showed a better degree of structural order than the glauconite from New Jersey (sample 9), but its structural order is less than that in other Cambrian samples. It is unclear at this time exactly why the iron in sample 1 gives larger shift and quadrupole splitting values for Fe^{3+} in both models, although it contains the least total iron and the highest $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio based on the chemical analysis. It is possible that the different parameters may be related to the presence of more Fe^{3+} relative to Fe^{2+} . Finally, it is also of interest that the Mössbauer parameters for the more structurally disordered New Jersey glauconite of Cretaceous age are similar to most of the Cambrian samples.

CONCLUSIONS

1. Mössbauer studies of ^{57}Fe nuclei between 50 and 295 K are useful for the determination of site occupation and the approximate ratio of trivalent to divalent iron in mineral glauconite. Resolution of the Mössbauer characteristics are markedly temperature dependent. The best resolution is obtained at low temperature (50 K).

2. Each spectrum of the samples studied is characterized by at least two quadrupole doublets with an isomer shift in the range of 0.12–0.18 mm/sec and 0.9–1.3 mm/sec; one for Fe^{3+} and one for Fe^{2+} . A least squares fit for only two doublets is very poor. Three or more subspectra are necessary to fit the data.

3. Analysis of the spectra indicates that two quadrupole doublets exist for Fe^{3+} and this is interpreted to mean that trivalent iron occupies two different octahedral environments. There is no evidence from these samples that Fe is in tetrahedral coordination or in interlayer positions. Values of χ^2 and line widths strongly suggest that Fe^{2+} also occupies two octahedral environments, but isomer shift and quadrupole splitting results for Fe^{2+} have larger errors because the Fe^{2+} intensities are low. Site ratios for Fe^{3+} in glauconite indicate that trivalent iron strongly prefers the M_2 site, thus the octahedral cations are partially ordered.

4. Ferric to ferrous ratios calculated from Mössbauer spectra are usually within 8% of the values obtained from chemical analyses. Because of the low concentration of Fe^{2+} in glauconite, the calculation of the approximate ferric to ferrous ratios from the

spectra is best done by assuming a three-site model (2Fe^{3+} and 1Fe^{2+}).

5. Intrasample variation in *b*-axis dimensions are believed to be largely due to the size of the octahedral cations and to the presence of chemically different forms of glauconite rather than to the degree of cation disorder.

6. Mineral glauconites even of the same age are not identical in chemistry or cation site population.

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