

NOTES

MÖSSBAUER SPECTRA OF GLAUCONITES REEXAMINED

(Received 29 September 1977)

Key Words—Glauconite, Mössbauer, Nontronite, Phyllosilicate.

Glauconites are an interesting group of minerals which have been extensively investigated. Several Mössbauer studies have been published, but some of the interpretations are open to question. Rolf et al. (1977) presented spectra of nine glauconites which they resolved into four doublets, corresponding to Fe²⁺ and Fe³⁺ in both M1 (*trans*) and M2 (*cis*) sites. In assigning these doublets they considered that "the splitting should be larger for Fe³⁺ which occupy the distorted M2 sites." For Fe³⁺ in dioctahedral phyllosilicates, however, it can be shown theoretically that M1 doublets have the greater splitting, as discussed by Rozenson and Heller-Kallai (1977). This assignment, in fact, was used for glauconites by Annersten (1975).

Cimbáľníková et al. (1973) published spectra, which they resolved into three doublets, two Fe³⁺ and one Fe²⁺. These authors assigned the more intense Fe³⁺ doublet to octahedral sites and were unable to characterize the other. Inspection of their data suggests that the strong doublet corresponds to Fe³⁺ in M2 and the unassigned one to Fe³⁺ in M1 positions.

Table 1 shows the Mössbauer parameters of glauconites taken from the literature, with amended assignments, together with those of a sample from Verona, Italy, studied in our laboratory. Following Annersten (1975) the Fe²⁺ doublet with larger splitting was assigned to iron in M2 positions. Cimbáľníková et al. assigned Fe²⁺ to one octahedral site only. In Table 1 we assigned their Fe²⁺ doublets to M1 or M2 sites, by comparison of the quadrupole splittings with those of other glauconites. The considerable width of some of the Fe²⁺ doublets (up to 1.37 mm/sec!) shows that they are composite and should be resolved

into two. The assignment therefore is meaningful only for the narrower doublets.

With the corrected assignments, the Fe³⁺ Mössbauer parameters of glauconites conform to the various relationships previously developed for smectites (Rozenson and Heller-Kallai, 1977). Thus Figure 2 in the paper by Rozenson and Heller-Kallai (1977) shows the relationship between the quadrupole splitting of Fe³⁺ in M2 versus that in M1 sites for various smectites, and the theoretical line corresponding to a 1:2 ratio. Most of the glauconites, like most smectites, fall below this theoretical line, indicating that the quadrupole splitting of M1 is larger than twice that of M2, i.e., that M1 sites are more readily distorted.

Figures 1a and 1b show the relationship between the *b* cell dimension of the glauconite samples, where available, and the quadrupole splitting of Fe³⁺ in M2 and M1 sites respectively. It is evident that this is inverse and approximately linear, as was previously found for smectites.

In general a higher concentration of Fe³⁺ in the octahedral sheets of dioctahedral phyllosilicates leads to an increase in *b* and decreases the misfit between the octahedral and tetrahedral sheets, thus decreasing the distortions of the octahedral sites. It is to be expected, therefore, that specimens poor in iron show greater quadrupole splitting than iron-rich ones, as was observed by Rolf et al. (1977). Since the iron content is not linearly related to *b*, neither is it to the quadrupole splitting, but the general trend can be observed.

Most of the iron in glauconites is in the Fe³⁺ form. This is concentrated entirely in the M2 sites in the two samples studied by Annersten (1975) and in the sample from Verona. Cimbáľníková et al. (1973)

Table 1. Mössbauer parameters and *b* dimensions of glauconites.

Sample	Fe ³⁺						Fe ²⁺						Fe ³⁺ AM(1) AM(2)	Fe ²⁺ AM(1) AM(2)	Fe ²⁺ Fe ³⁺	<i>b</i>	
	M2 (<i>cis</i>)			M1 (<i>trans</i>)			M2 (<i>cis</i>)			M1 (<i>trans</i>)							
	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ					
1. Verona, Italy (1)	0.16	0.32	0.42	—	—	—	—	—	—	—	—	—	—	0.00	—	0.00	9.09 (1)
2. H1 (2)	0.36	0.44	—	—	—	—	1.16	2.66	—	1.02	1.72	—	—	0.00	0.60	0.16	9.07 (2)
3. H3 (2)	0.35	0.47	—	—	—	—	1.17	2.57	—	1.11	1.65	—	—	0.00	0.60	0.21	9.07 (2)
4. 72 (3)	0.64	0.38	0.42	0.72	0.97	0.40	*	2.24	0.20	—	—	—	—	0.31	—	—	0.097
5. 41 (3)	0.61	0.40	0.43	0.65	1.10	0.41	1.32	2.70	1.37	—	—	—	—	0.40	—	—	0.162
6. 74 (3)	0.64	0.45	0.36	0.67	0.87	0.42	1.26	2.37	0.50	—	—	—	—	0.22	—	—	0.136
7. 14 (3)	0.62	0.42	0.45	0.67	1.04	0.40	1.41	2.69	0.20	—	—	—	—	0.38	—	—	0.05
8. 38 (3)	0.63	0.35	0.37	0.65	0.94	0.52	—	—	—	1.32	2.05	0.73	0.40	—	—	—	0.172
9. 62 (3)	0.64	0.34	0.35	0.65	0.95	0.53	—	—	—	1.24	2.05	0.33	0.56	—	—	—	0.08
10. R-90-54-20 (4)	0.136	0.460	0.42	0.202	1.18	0.42	0.97	2.88	0.30	0.93	1.92	0.30	0.74	—	—	0.10	9.05 (5)
11. C-90-45-20 (4)	0.142	0.425	0.42	0.176	1.17	0.42	0.99	2.56	0.30	0.75	2.07	0.30	0.16	—	—	0.12	9.07 (5)
12. 91-20-27 (4)	0.123	0.299	0.42	0.129	0.678	0.42	0.65	2.13	0.30	1.54	1.47	0.30	0.12	—	—	0.11	9.08 (5)
13. 91-3-10 (4)	0.120	0.423	0.42	0.127	0.935	0.42	1.22	2.28	0.30	0.95	1.74	0.30	0.11	—	—	0.11	9.096(5)
14. Dead Wood (4)	0.127	0.294	0.50	0.126	0.673	0.50	—	—	—	0.92	1.91	0.50	0.21	—	—	0.12	9.106(5)
15. Vermilion Franconia (4)	0.130	0.259	0.42	0.135	0.641	0.42	0.96	2.66	0.30	0.88	1.86	0.30	0.20	—	—	0.19	9.108(5)
16. Vermilion Eau Claire (4)	0.125	0.248	0.42	0.131	0.640	0.42	0.94	2.69	0.30	0.89	1.82	0.30	0.23	—	—	0.21	9.126(5)
17. 91-20-20 (4)	0.124	0.369	0.42	0.122	0.791	0.42	1.18	2.24	0.30	0.89	1.76	0.30	0.12	—	—	—	0.13
18. New Jersey (4)	0.130	0.346	0.50	0.125	0.767	0.50	1.02	2.09	0.50	—	—	—	0.2	—	—	—	0.13

(1) This study; (2) Annersten (1974); (3) Cimbáľníková et al. (1973) amended, see text; (4) Rolf et al. (1977) amended, see text; (5) Odom (1976).

* Assignment doubtful, see text.

I.S. = isomer shift relative to Cu in (1) and (4), Pd in (2) and (3); Q.S. = quadrupole splitting; Γ = peak width, all in mm/sec; and AM(1)/AM(2) = ions in site M1/ions in site M2.

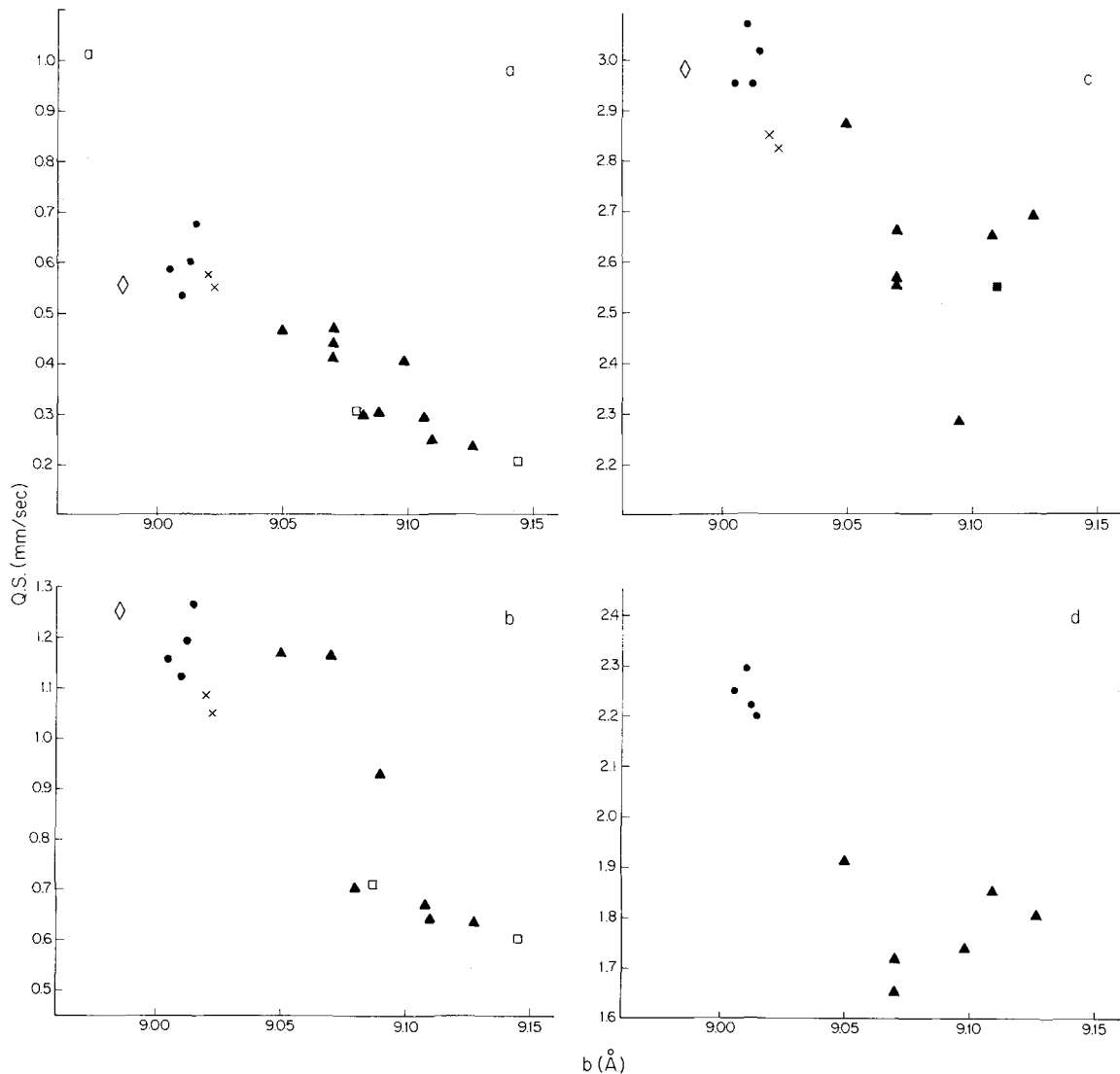


Fig. 1. Relationship between b and quadrupole splitting of: a) Fe^{3+} in M 2; b) Fe^{3+} in M 1; c) Fe^{2+} in M 2; d) Fe^{2+} in M 1 sites. \blacktriangle glauconite, \diamond montmorillonite, and \square nontronite (Rozenon and Heller-Kallai, 1977); \blacksquare nontronite reduced with hydrazine (Rozenon and Heller-Kallai, 1976); \times illite and \bullet muscovite (unpublished).

showed that Fe^{3+} preferentially occupied the sites with smaller quadrupole splitting, i.e., M2 sites. Rolf et al. (1977) also concluded that Fe^{3+} "is concentrated strongly in the M2 site, which is smaller than the M1 site," but their reasoning is puzzling. Figure 3 of their paper does, indeed, show M2 to be the stronger doublet, but this, according to the text and to Table 3, has a larger quadrupole splitting than M1, whereas in the figure the opposite applies. Moreover, according to the table there is a difference in isomer shift of only 0.001 mm/sec between the two Fe^{3+} doublets of sample 4, yet in the figure it is of the order of 0.3 mm/sec.

Despite these discrepancies it appears that Fe^{3+} in glauconites is concentrated preferentially in M2 positions. In this respect glauconites resemble Al-rich smectites (Figure 5—Rozenon and Heller-Kallai, 1977), illites, and muscovites (paper in preparation), and differ from the iron-rich nontronites (Goodman et al., 1976). The isomer shifts of the two Fe^{3+} doublets in glauconites are either similar to each other, as for nontronites, or that of the M1 doublet exceeds that of M2, as for most Al-rich smectites.

Fe^{2+} occurs in both M1 and M2 sites in many of the glauconites studied, in contrast to smectites in which Fe^{2+} occupies a single site only. Even an iron-rich smectite, which was effectively reduced, gave rise to only one Fe^{2+} doublet (Rozenon and Heller-Kallai, 1976). Two Fe^{2+} doublets were observed for two muscovites studied by Hogg and Meads (1970) and for six samples investigated in our laboratory (unpublished). According to Annersten the Fe^{2+} in glauconites is disordered, in contrast to Fe^{3+} , which tends to be ordered.

Figures 1c and 1d show that there is no direct correlation between the quadrupole splitting of Fe^{2+} doublets and b , similar to that found for Fe^{3+} , despite the fact that this parameter is generally very sensitive to changes in site configuration. Moreover, there is a strong tendency for the quadrupole splittings to decrease with increasing b , i.e., for greater distortion of the sites with increasing cell dimension, in complete contrast to the relationships observed for Fe^{3+} . This problem is not confined to glauconites, but appears to be common to all dioctahedral phyllosilicates, as emerges from Figures 1c and 1d, in which the data for some representative minerals were included for comparison.

Whether the reduction in quadrupole splitting of Fe^{3+} , with increasing iron content and concomitant increase in b , is due to local adjustment of the sites, unrelated to the overall dimensions of the octahedral sheets, or whether it is caused by other factors, remains to be explained.

In summary, the Mössbauer spectra of glauconites resemble those of other dioctahedral phyllosilicates, but show some specific features which differentiate them from nontronites on the one hand and illites on the other. They support the contention that glauconites constitute a structurally distinct group of minerals.

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REFERENCES

- Annersten, H. (1975) A Mössbauer characteristic of ordered glauconite: *Neues Jahrb. Mineral. Monatsch.* **8**, 378–384.
- Cimbálníková, A., Raclavsky, K. and Lipka, J. (1973) Železo v glaukonitech a jeho Mössbauerova spektroskopie: *6th Conf. Clay Mineral. Petrol. Geologica, Praha*, pp. 57–65.
- Goodman, B. A., Russell, J. D., Fraser, A. R. and Woodhams, F. W. D. (1976) A Mössbauer and i.r. spectroscopic study of the structure of nontronite: *Clays & Clay Minerals* **24**, 53–59.
- Hogg, C. S. and Meads, R. E. (1970) The Mössbauer spectra of several micas and related minerals: *Mineral. Mag.* **37**, 606–614.
- Odom, I. E. (1976) Microstructure, mineralogy and chemistry of Cambrian glauconite pellets and glauconites, Central U.S.A.: *Clays & Clay Minerals* **24**, 232–238.
- Rozenson, I. and Heller-Kallai, L. (1976) Reduction and oxidation of Fe^{3+} in dioctahedral smectites. Part 1: Reduction with hydrazine and dithionite: *Clays & Clay Minerals* **24**, 271–282.
- Rozenson, I. and Heller-Kallai, L. (1977) Mössbauer spectra of dioctahedral smectites: *Clays & Clay Minerals* **25**, 94–101.
- Rolf, R. M., Kimball, C. W. and Odom, I. E. (1977) Mössbauer characteristics of Cambrian glauconite, Central U.S.A.: *Clays & Clay Minerals* **25**, 131–137.