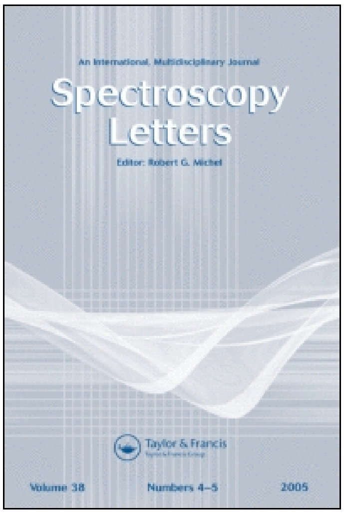

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A MÖSSBAUER STUDY OF EVOLUTION OF GLAUCONITE FROM CHINESE SEAS

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ABSTRACT

The formation of glauconite from the Chinese Yellow Sea and the Chinese Eastern Sea was studied by the use of Mössbauer spectroscopy. The process of glauconite formation appears to differ between the respective seas, due to different initial substances of the formation. The results show the valence states and the crystallographic sites of the iron cations, and suggest that there may be a correlation between the formation process of glauconite and Mössbauer parameters.

Key Words: Authigenic minerals; Glauconite; Mossbauer spectroscopy

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INTRODUCTION

Glauconite, an iron-rich mica, is the most common sediment iron silicate and exists as an authigenic mineral of marine sediments that forms on the sea floor in some areas where clastic sedimentation is slight or not taking place; it occurs in seawater at low temperature and in an environment which is neither strongly oxidizing nor reducing[1]. Typical glauconite belongs to monoclinic crystal structure with $C2/m$ space group.

Mössbauer spectroscopy has contributed considerably to the understanding of the crystal chemistry of iron in silicates, and to the identification of iron-bearing phases in unknown mixtures involving silicates, such as sediments, soil and coal deposits. As the formation and evolution of glauconite is of interest in both oceanography and mineralogy, Mössbauer studies of glauconite were carried out by a number of authors, for instance see[2–5]. Nevertheless, we have performed Mössbauer spectroscopy to study the glauconite of the Chinese Yellow Sea and the Chinese Eastern Sea in order to obtain more structural information about the glauconite of that area, and also to investigate whether there is a correlation between glauconite formation and the Fe^{57} Mössbauer parameters.

The probe samples of this study were collected from pale to dark green sand-sized grains of deposited layers in the continental shelves located at about 100 meters deep. The chemical composition of typical glauconite granules were shown to be in the following ranges[6]: 47.2–52.9% SiO_2, 5.5–23.6% Al_2O_3, 6.1–27.9% Fe_2O_3, 0.8–8.6% FeO, 4.0–9.5% K_2O, 0.0–3.0% Na_2O and 4.9–13.5% H_2O.

EXPERIMENTAL

Samples

Particles with grain size 0.25–0.5 mm were collected by sieving and then concentrated by the magnetic method and microscope-guided hand-sorting. Sorting was based on color and morphology. Four samples, out of seven, were collected from the Chinese Yellow Sea while the other three were sampled from the Chinese Eastern Sea (see Table 1).

The Chinese Yellow Sea samples (YDS series) consist of irregular clusters of mineral grains. The range of colors is from yellow to dark green and forms an integrated series of evolution. X-ray diffraction (XRD) and microscopic observations show that both YDS-1 and YDS-2 possess only a few glauconite characteristics. This is because they are precursors of mineral glauconite with quartz, montmorillonite and kaolinite. Both theYDS-3

Table 1. Appearance of Various Glauconite Samples

YDS-1 Sample	Yellow Clay-like cluster
YDS-2 Sample	Greenish-green sand with pockmarked surface
YDS-3 Sample	Greenish-yellow irregular particle without cracks
YDS-4 Sample	Glaucous particle with cracks
DDC-1 Sample	Green mica-like sheet with clear {0 0 1} cleavage
DDC-3 Sample	Dark-green sheet-like particles with smooth surface
DDC-4 Sample	Dark-green particles with cracks

and YDS-4 samples belong to the mid-period of glauconitization, but only YDS-4 sample is relatively matured.

The Chinese Eastern Sea samples (DDS series) matrices are sheet mica. They develop gradually into sheet-like sediment, and then undergo structural dewatering and evolving into black glauconite with cracks.

The X-ray fluorescence analysis of the chemical compositions of the samples compared to Cambrian, Eocene samples, and the samples 29D and 21 of Buckley et al.[7] is listed in Table 2.

Mössbauer Measurements

Mössbauer spectra of powdered sample were recorded in the transmission geometry. A 2×10^9 Bq $^{57}Co/Pd$ Mössbauer source provided the gamma rays. Isomer shifts were given relative to $\alpha - \mathrm{Fe}$. Typical room temperature Mössbauer spectra of the glauconite samples are illustrated in Fig. 1. The analysis of the spectra was performed by conventional least-square fitting method using MOSFUN program[8]. Mössbauer parameters are given in Table 3.

RESULTS AND DISCUSSION

From Table 2, we see that the ferric component of YDS series increases and both SiO_2 and Al_2O_3 decrease during the evolution of glauconite. For DDS series, the contents of Fe and Mg decrease while SiO_2 and Al_2O_3 increase during the evolution of glauconite. This is because they retain some chemical features of biotite, such as higher contents of iron and magnesium and lower content of silicon. These changes indicate that the formation of glauconite in the two seas undergo different processes depending on the different initial substances of glauconitization. See Table 4 for the iron distribution in different crystallographic sites.

Table 2. Chemical Composition of Glauconite

	Chemical Composition													
Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	MgO	CaO	K_2O	Na_2O	MnO	P_2O_5	CO_2	H_2O^+	H_2O^-
YDS-1	46.28	13.28	11.96	1.20	0.72	3.47	5.91	3.25	1.17	0.34	0.33	5.12	6.80	–
YDS-2	56.00	8.44	11.40	0.90	0.65	1.50	6.31	3.05	1.67	0.24	0.23	3.90	5.20	–
YDS-3	48.24	7.47	21.66	0.84	0.53	3.24	2.02	3.45	1.13	0.15	0.25	2.41	7.60	–
YDS-4	48.00	6.69	23.58	1.10	0.26	3.24	2.00	2.34	0.27	0.14	0.21	–	6.27	4.49
DDS-1	32.38	8.65	25.07	6.39	1.05	7.10	0.96	7.10	0.60	0.42	–	1.47	10.50	1.96
DDS-3	43.50	5.05	23.46	1.50	0.33	6.88	1.38	3.30	0.26	–	0.13	–	–	–
DDS-4	44.65	4.95	23.82	1.44	0.29	4.87	1.62	4.48	0.44	–	0.15	0.62	7.00	6.07
DGBP*	50.12	2.41	20.33	2.07	0.02	6.35	0.16	8.19	0.02	–	–	–	–	–
OGP**	49.11	9.41	21.0	2.71	0.04	3.06	0.35	8.68	0.03					
Eocene	42.11	6.00	15.06	0.67	–	4.42	8.60	6.79	0.37	–	4.86	0.6	5.40	3.68
Cambrian	51.40	12.81	15.20	1.09	0.19	2.51	0.44	6.61	0.57	0.03	1.26	–	5.16	3.10

*Dark Green Botryoidal Pellets (sample 29D of Buckley et al. 1978).

**Olive Green Pellets (sample 21 of Buckley et al.).

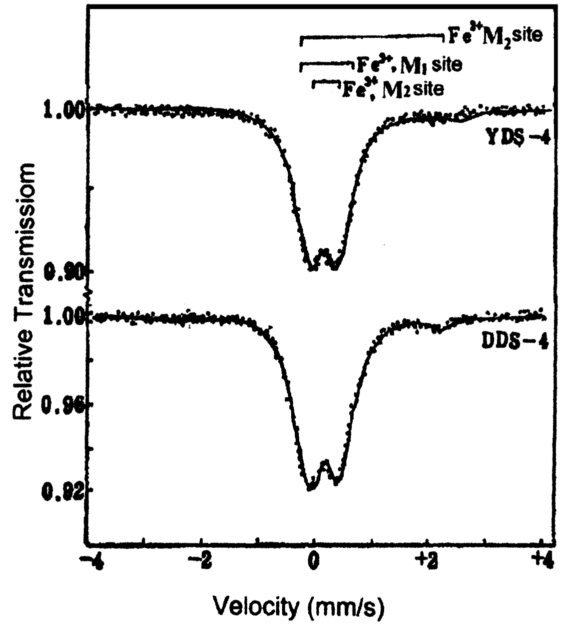

Figure 1. Room temperature Mössbauer spectra of typical glauconite samples from Chinese Eastern Sea.

For the 2:1 layered silicates, there are two different kinds of crystallographic sites in the octahedral sheet: trans-configuration (*M*1 site) and cis-configuration (*M*2 site)[4,6] as shown in Fig. 2. The ratio of possible cis-configuration to trans-configuration sites is 2:1. Fe^{2+} is recognized by its high value of isomer shift and large quadrupole splitting. On the other hand, Fe^{3+} has a lower isomer shift and smaller quadrupole splitting value. Due to deformation, the ferric cation in the *M*1 or *M*2 site has different values of quadrupole splitting. The ferrous cation preferentially occupies *M*2 sites and there are few, if any, ferrous cations in the *M*1 site[9].

As the glauconitization proceeds (according to layer lattice theory) there is an increase in lattice charge and decrease in the proportion of expandable layers. Accordingly, the various glauconite types reflect differences in both the extents of layer collapse and of the mineral maturity[10]. During this process, the changing trend of ^{57}Fe Mössbauer parameters is as follows:

(1) The relative absorption areas of Fe^{2+} decrease gradually, which implying that the maturation process is accompanied by iron oxidation.

Table 3. Mössbauer Parameters of the Glauconite Samples

	Fe^{2+} at *M*2 Site				Fe^{3+} at *M*2 Site				Fe^{3+} at *M*1 Site			
Sample No.	IS (mm/s)	QS (mm/s)	FWHM (mm/s)	Relative Area(%)	IS (mm/s)	QS (mm/s)	FWHM (mm/s)	Relative Area(%)	IS (mm/s)	QS (mm/s)	FWHM (mm/s)	Relative Area(%)
YDS-1	1.11	2.71	0.35	17.4	0.33	0.45	0.38	60.4	0.34	0.99	0.35	22.2
YDS-2	1.08	2.72	0.29	8.0	0.31	0.45	0.41	70.2	0.32	0.93	0.32	21.8
YDS-3	1.14	2.57	0.34	4.8	0.33	0.43	0.49	80.5	0.33	1.26	0.37	14.6
YDS-4	1.17	2.58	0.29	3.2	0.33	0.44	0.53	83.5	0.34	1.24	0.37	13.3
DDS-1	1.07	2.70	0.35	23.4	0.31	0.51	0.30	50.0	0.36	1.04	0.30	26.6
DDS-3	1.13	2.48	0.34	5.3	0.33	0.47	0.54	77.4	0.36	0.97	0.42	17.3
DDS-4	1.12	2.56	0.32	4.6	0.33	0.46	0.52	78.2	0.36	0.94	0.43	17.1

IS: Isomer Shift.
QS: Quadrupole Splitting.

Table 4. Iron Distribution in Different Crystallographic Sites

Ratio of Absorption Areas	$Fe^{3+}(M2)/Fe^{3+}(M1)$	$Fe(M2)/Fe(total)$	$Fe(M1)/Fe(total)$	Fe^{3+}/Fe^{2+}
YDS-1	2.72	77.8	22.2	4.75
YDS-2	3.22	78.2	21.8	11.50
YDS-3	5.51	85.3	14.6	19.83
YDS-4	6.28	86.7	13.3	30.25
DDS-1	1.88	73.4	26.6	3.27
DDS-3	4.47	82.8	17.1	17.87
DDS-4	4.57	82.7	17.3	20.73

(2) The relative absorption areas of Fe^{3+} at $M2$ sites increase gradually, while in contrast, those of Fe^{3+} at $M1$ sites decrease implying that the Fe^{3+} cation substitutes for Al in $M2$ sites.

Following the gradual glauconite maturation, the Fe^{3+}/Fe^{2+} ratio increases and also both $Fe^{3+}(M2)/Fe^{3+}(M1)$ and Fe(M2)/Fe(total) increase. These findings suggest that the process may occur in alternatively weak-reductive and weak-oxidative environments. Some iron cations realized the substitution of aluminum cations and then trend towards well-developed glauconite through dewatering shrinking and cracking.

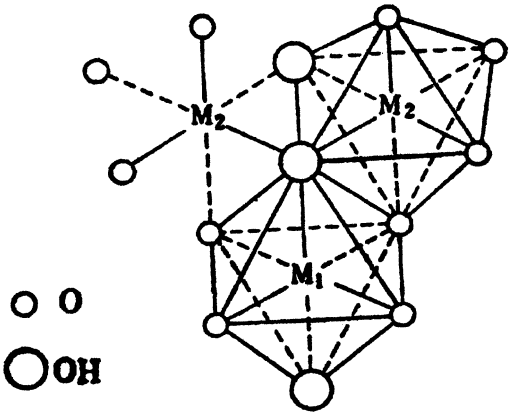

Figure 2. Two different kinds of crystallographic sites of octahedral layer: $M1$ and M2 sites.

This study compared glauconite maturity with Mössbauer results. A correlation seems to exist between glauconite maturity and Mössbauer parameters. The investigations, therefore, show that Mössbauer spectroscopy is a suitable tool for characterizing the glauconite.

REFERENCES

1. Berry, L.G.; Mason, B. *Mineralogy*; W. H. Freeman & Company: San Francisco, 1983; 436.
2. McConchie, D.M.; Ward, J.B. Clays and Clay Minerals. **1979**, *27*, 339–348.
3. Rolf, R.M.; Kimball, C.W. Clays and Clay Minerals. **1977**, *25*, 131–137.
4. Rosenson, I; Heller-Kallai, L. Clays and Clay Minerals. **1978**, *26*, 173–176.
5. Odom, J.E. Clays and Clay Minerals. **1977**, *24*, 231–238.
6. Li, Z.; Ying, Y.P. *Mössbauer Spectroscopy in Minerals* (in Chinese); Science Publishing Company: Beijing; 1996; 100–101.
7. Newman, A.C.D. *Chemistry of Clays and Clay Minerals*; John Wiley & Sons, Inc.,: New York; 1987; 74.
8. Gutlich, P.; *et al. MOSFUN SOFTWARE* (Description and user's guide); Mainz University: Germany; 1977.
9. Chen, R.Y. *Geological Science* (in Chinese); 1983; 3, 267–272.
10. Elderfield, H. *Chemical Oceanography*. Riley, J. P., Chester, R., Eds.; Academic Press Inc: London, 1976; 166.

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