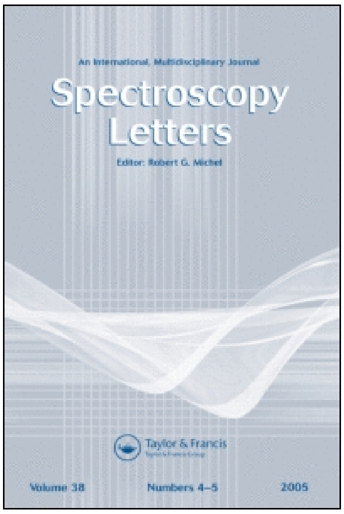

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Mössbauer Study of the Geological Samples from Permian Period

Zhi Yu[a]; Xiaodi Du[b]; Shaoming Pan[c]; Haoguo Zhu[a]; Zhicheng Huang[b]; Yuanfu Hsia[d]; Xiaozeng You[a]
[a] Coordination Chemistry Institute. State Key Laboratory of Coordination Chemistry, Nanjing, P.R.China [b] Department of Earth Science, Nanjing, P.R.China [c] State Pilot Laboratory of Coast and Island Exploitation, Nanjing, P.R.China [d] Department of Physics, Nanjing University, Nanjing, P.R.China

To cite this Article Yu, Zhi , Du, Xiaodi , Pan, Shaoming , Zhu, Haoguo , Huang, Zhicheng , Hsia, Yuanfu and You, Xiaozeng(1997) 'A Mössbauer Study of the Geological Samples from Permian Period', Spectroscopy Letters, 30: 8, 1733 — 1738

To link to this Article: DOI: 10.1080/00387019708006755

URL: http://dx.doi.org/10.1080/00387019708006755

SPECTROSCOPY LETTERS, 30(8), 1733-1738 (1997)

A Mössbauer Study of the Geological Samples from Permian Period

Zhi Yu[1*], Xiaodi Du[2], Shaoming Pan[3], Haoguo Zhu[1]
Zhicheng Huang[2], Yuanfu Hsia[4], Xiaozeng You[1]

[1] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry,*
[2] *Department of Earth Science,*
[3] *State Pilot Laboratory of Coast and Island Exploitation,*
[4] *Department of Physics,*
Nanjing University, Nanjing, 210093, P.R.China

Abstract: *The samples from Permian period in east China were investigated by Mössbauer spectroscopy, X-ray powder diffraction and TGA-DTA methods. According to the different valence states of the iron in samples, the divisions of the Permian may also be separated by such methods at first report. The result shows a new approach for the studies in Permian.*

1. Introduction

A good deal of Mössbauer work on minerals has been devoted to determining the iron valence state and coordination number from the isomer shift, and identifying subspectra with specific sites in the minerals. Especially, the spectra can be used to determine iron sites in populations in a pure mineral which may be important, for example, in geothermometry. The ability to detect amorphous or poorly crystallized minerals, ferric hydroxides in particular, is an advantage of Mössbauer technique than that of other conventional analysis methods such as X-ray diffraction. The application of Mössbauer effect on mineral science has been reviewed in some article.[1-2]

Permian period is a geologic time scale in the range of 250Ma and 283Ma years ago. The Permian in east China is divided into six groups (see Table 1) in general and each group represents a relative stable period.

Table 1. Selected samples location in the section and its relative Permian stratigraphic sequence and geological time

Name		Group	*Time*	*Selected Sample*
Low Triassic		Yinkeng Fm.		Ach12
			250Ma	
Permian	*Upper Permian*	Dalong Fm.		Ach10, Ach11
			255Ma	
		LongTai Fm.		Ach9
			260Ma	
	Lower Permian	Yingpin Fm.		Ach8
		Gufeng Fm.		Ach4, Ach5, Ach6, Ach7
			270Ma	
		Qixia Fm.		Ach2, Ach3
		Laingshan member		Ach1
			283Ma	
Upper Carboniferous		Chuanshan Fm.		

From Geological observation, between Liangshan member and Qixia Fm. it seems to be a continuous sedimentation, the sea level was gradual rising since glacial ablation of Gondwana land. There are sedimentation hiatuses between the Qixia Fm. and Gufeng Fm. as well as between Gufeng Fm. and Yingpin Fm., strong volcanic explosions were happened frequently during the periods. The event surface of the Longtai Fm. and the lower Permian period was formed due to a strong volcanic explosion and tectonic reforming. The Upper Permian is also a continuous sedimentation. The weather in Longtai Fm. was wet and good for the plant generations, and this time was a main period for the coal building. Because of strong extensions, rapid sea-level rising and strong volcanic explosions were occured during Dalong Fm., the water depth was much more than 200m in that time. The event surface between the Yinkeng Fm in the Low Triassic Period and Dalong Fm. indicates that strong volcanic explosions and meteorite were very common events and the living things died out during the time.

In this paper, Mössbauer effect, x-ray diffraction and other tools were performed to study some samples of minerals from east China in the Permian. The iron ions with different valence states and in different positions in minerals are expected to be a probe to reflect the environmental changing or happened events in that ages.

2. Experimental details

12 samples (Ach1-Ach12) in different sections of the Permian and the lower Triassic were collected from Chaoxian of Anhui Province in P.R. China. The observation from a optic microscope shows all of them contain illite (>75%) as the dominant clay mineral, additionally one or several other clay minerals (kaolinite and mixed-layer sheet silicates), and often quartz or some volcanic products. The iron content of the samples were determined by ICP in the range of 4% to 14%.

The samples were milled into powder for X-ray diffraction analysis, Mössbauer effect and TGA-DTA (Thermgravimetric Analysis, Differential Thermal Analysis) measurements. The Mössbauer experiments were carried out using a ^{57}Co/Pd source and a constant acceleration spectrometer to collect the transmission spectra at room temperature. The spectrometer was calibrated using a standard α-Fe foil at room temperature. The isomer shifts are reported relative to the center of the α-Fe spectrum. The MOSFUN program was used to determine the Mössbauer parameters. The X-ray powder diffraction analysis was carried out by using Cu K_α radiation from a Shimadzu diffractometer. The TGA-DTA analysis were taken by Thermal 2100 Analyst TA instrument.

3. Results and discussion

The X-ray diffraction pattern of samples exhibited the characteristic peaks typical of illitic clays with distances d_{001}=10.1 Å, d_{003}=3.30 Å, d_{020}=4.43 Å and d_{006}=1.50 Å. This result agrees with the observations by an optical microscope. The TGA-TDA results for the samples have two main peaks at about 100 °C and 500-700 °C. The former peak is due to the loss of water from the minerals, and the latter peak reveals the dehydroxilation process in the clay minerals.

Characteristic Mössbauer spectra are plotted in fig. 1. According to those of illite,[3-4] the spectra indicate the presence of both Fe^{2+} and Fe^{3+} in the structure. Additionally the spectra of Ach1, Ach4 and Ach7 have a superparamagnetic relaxation pattern. The best fit for paramagnetic spectra has been obtained with three quadrupole doublets, two characteristic of octahedral ferric iron and one characteristic of octahedral ferrous iron. The Hyperfine parameters are listed in Table 2 and Table 3. The errors in the quadrupole splitting (Q.S.) and isomer shift (I.S.) values are in general better than 0.03mm/s and 0.02mm/s respectively, and the linewidth values are in the range of 0.25mm/s and 0.38mm/s. The first ferric doublet with Q.S. ~ 0.60 mm/s and I.S. ~ 0.45 mm/s appearing in all the spectra is from the Fe^{3+} in the M2

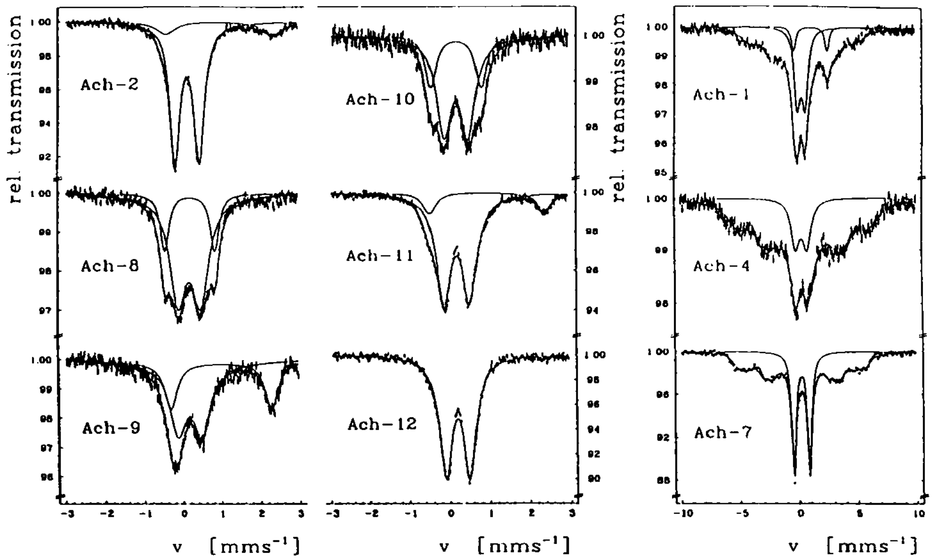

Figure 1. The Mössbauer spectra for some selected samples.

Table 2. The Mössbauer hyperfine parameters and its relative intensities for paramagnetic subspectra

	Fe^{3+} in M2 site			Fe^{3+} in M1 site			Fe^{2+} in M2 site		
Sample No.	Q.S. mm/s	I.S. mm/s	Fe^{3+} M2/ Tot. Fe	Q.S. mm/s	I.S. mm/s	Fe^{3+} M1/ Tot. Fe	Q.S. mm/s	I.S. mm/s	Fe^{2+} M2/ Tot. Fe
Ach1	0.58	0.46	41%				2.59	1.29	10%
Ach2	0.63	0.40	84%				2.76	1.22	16%
Ach3	0.62	0.39	76%				2.65	1.21	24%
Ach4	0.58	0.46	20%	1.35	0.52	7%			
Ach5	0.46	0.42	100%						
Ach6	0.44	0.44	100%						
Ach7				1.30	0.48	55%			
Ach8	0.58	0.44	74%	1.30	0.45	26%			
Ach9	0.61	0.44	63%				2.60	1.24	37%
Ach10	0.60	0.45	72%	1.25	0.45	28%			
Ach11	0.65	0.46	85%				2.84	1.24	15%
Ach12	0.61	0.46	100%						

Table 3. The Mössbauer hyperfine parameters and its relative intensities for superparamagnetic subspectra

Sample No.	B Kos	I.S. mm/s	Q.S. mm/s	Γ mm/s	Fe/ Tot. Fe
Ach1	310	0.53	0.20	0.83	49%
Ach4	342	0.49	0.62	0.95	73%
Ach7	325	0.47	0.80	0.58	45%

position, the other ferric doublet with Q.S. ~1.30 mm/s and I.S. ~ 0.52 mm/s found in some samples is assigned from the Fe^{3+} in the M1 position. In some spectra the ferric doublets are accompanied by a ferrous doublet (Q.S. ~2.70 mm/s and IS ~1.20 mm/s) which shows a relative low intensity. The lower ratios of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ in such samples than that in fresh illites may be explained in two ways. (1) The studies[5] of E. Murad et al indicates that the illites of the iron-rich group had noticeably lower $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios than those of iron-poor group. The mineral samples used here were determined more than 4% iron contents in the mixture minerals, and could belong to the rich-iron group for the illites in clays. (2) The samples from the Permian are very old illitic clays weathering in at least 250Ma. J. Blomquist et al[6] studied ratio of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ for biotite as a function of the weathering time. The result indicates that the longer weathering time, the lower ratio of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$. The lower ratio of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ for some biotitic samples in the Permian from Mendoza of Argentina was also observed.[7] The superparamagnetic positions in the spectra of sample ach1, ach4, ach7 were analysed in typical parameters of fine-particle goethite (α-FeOOH), very large broaden sextets (0.58 mm/s - 0.95 mm/s) and various hyperfine magnetic fields (310kOe - 342 kOe) of the superparamagnetic species are due to the relaxation of field, the distributions of particle size and hyperfine magnetic field.[8] Moreover, the existence of goethite in these samples is confirmed by the TGA-DTA analysis, the TGA-DTA data of these sample show a small peak in around 200 C° which is the conversion temperature for goethite changing into hematite (α-Fe_2O_3).

The outcome of Mössbauer spectra with various intensities Fe^{2+} in M2 and Fe^{3+} in M1, M2 positions reveals also the geological divisions of the Permian. (1) In Liangshan Fm. and Qixia Fm., selected three samples of Ach1 Ach2 and Ach3 having almost same parameters in Fe^{2+} and Fe^{3+} positions, and a slight intensity increasing of Fe^{2+} reveal that relative continuos sedimentation and the sea level were increasing slowly, respectively. (2) The appearance of Fe^{2+} is obvious to reflect the reduction condition[9] which may be caused by high sea level or wet weather. In particular, the Ach9 with highest ratio (37%) of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$, is in agreement with the coal building period in Longtai Fm. (3) The existence of α-FeOOH fine particles in the samples seems to be relate with the larger sedimentation hiatus, which was found in the sections between Chuanshan Fm. and Liangshan member, Qixia Fm., Gufeng Fm., and Yingpin Fm. Such gaps were often arisen by strong volcanic explosions.

4. Conclusion

The studies for the samples from the Permian indicate that ^{57}Fe Mössbauer spectroscopy is a useful tool to determine the valence states and occupied positions of iron in the mineral clays. Through the natural iron probe in the minerals, the division of the Permian in Geology may also be verified by the Mössbauer studies as a new approach.

Acknowledgments

This work was financially supported by the Foundation of Overseas Membership of Chinese Education Committee and Chinese Postdoctoral Fund.

References

1. P.G.L. Williams and G.M. Bancroft, M.G. Brown ad A.C. Turnock, *Nature Phys. Sci.*, 230.149 (1971).
2. J.M.D. Coey, "*Mossbauer Spectroscopy Applied to Inorganic Chemistry*", Volume I. P443.
3. H Pollak and J. G. Stevens, *Hyper. Intern.*, 29 (1986) 1153.
4. J.H. Johnston and C.M. Cardile, *Clay and Clay Minerals*, 35 (1987) 170.
5. E. Murad and U. Wagner, *Hyper. Intern.*, 91 (1994)685.
6. J. Bomquist, P. Kjall, M. Malmstrom and S. Banwart, Conference Proceedings Vol. 50, *ICAME-95* SIF, Bologna, 1996.
7. C. Saragovi, F. L.D. Kanter, L. Kleiman, R. Valentin and C. Puglisi, *Hyper. Intern.*, 57 (1990) 2285.
8. S. Bocquet, R.J. Pollard, and J.D. Cashion, *Phys. Rev.*, B.46 (1992) 11657.
9. S. Morup and H. Lindgreen, *Proc. Intern. Conf. on Appl. Moss. Effect* (jaipur), (1982), P290.

Date Received: February 17, 1997
Date Accepted: July 22, 1997