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#### MÖSSBAUER SPECTROSCOPY OF IRON IN CLAY MINERALS

Iron forms a substantial constituent in most of the clay minerals. In the structure of sheet silicates both octahedrally and tetrahedrally coordinated iron may be present. Moreover, inequivalent sites of the same coordination can be distinguished. Different combinations of basic structural layers make possible wide variety of structure locations. In particular for octahedral iron. Due to origin in the weathering zone, clay minerals often contain both  $Fe^{3+}$  and  $Fe^{2+}$  at the same time. In addition, the case is complicated by mixed structures with variable proportions of different structure units. Poor crystallinity and small particle size are typical signs of natural clay minerals as well as often present impurities, predominantly the admixtures or coatings of iron oxides and oxyhydroxides. Complicated conditions of iron presence in clay minerals may lead to contradictory assumptions about its nature and location in structure.

This work studies selected pure clay minerals predominantly of Czechoslovakian provenience: Montmorillonite (Braňany-bentonite deposit), nontronite (Věchnov - weathering products on skarns), beidellite (Kamenskoe, Caucasus - clay deposit), glauconite (Písečná - cretaceous) sandstone), seladonite (Úhošťany - weathering products on basalts), illite (Vonšov - clay deposit), vermiculite (Dubina - weathering products on micaetta), saponite (Staré Ransko - hydrothermal alteration products), palygorskite (Křecví - cracks in gneiss), goethite (Nicaro, Cuba - laterite on serpentinites).

All samples were in powder form and their purity has been checked by x-ray diffraction and infrared spectroscopy. Mössbauer spectra has been measured by transmission method at the spectrometer of KFKI (Hungary) with count about  $10^6$  pulses per channel. Measurements were performed at room temperature with source  $Co^{57}$  in palladium matrix. Spectra have been fitted using least square method by computer MINSK-22 and plotted by calculator Hewlett - Packard. The values of isomer shift are related to sodium nitroprusside. The values of isomer shifts  $\delta$ , quadrupole splittings  $\Delta$  and line widths  $\Gamma$  were obtained with error  $\pm 0.03$  mm/s. From integral area Lorentzian curves the distribution of iron between subphases, which have been distinguished, can be calculated. The values of line intensities have been given with error  $\pm 0.02$  % giving for iron abundances in individual subphases the error  $\pm 2.0$  %.

In the spectra there have been resolved up to three quadrupole doublets, that is more, than has been reported by several groups of investigators [1,2,3]. These components of spectra for related minerals are similar. Parameters of measured Mössbauer spectra are given in table I.

For montmorillonite, nontronite and beidellite ferric ions in two inequivalent structure sites have been distinguished (spectrum of nontronite on figure 1a). There are observable changes of quadrupole splitting and isomer shifts, in the series montmorillonite-nontronite, generally depending on iron content (Table I).

In the spectra of glauconite and seladonite (figure 1b) the third component belonging to ferrous ion has been determined besides the two components resulting from contributions of ferric ions. Similarly as in montmorillonite minerals  $Fe^{3+}$  strongly prevails and occupies two inequivalent sites. Ferrous component can be interpreted as octahedral. The low content of  $Fe^{2+}$  does not permit to resolve two components presumably corresponding to two octahedrally coordinated sites. The detail measurements of series of glauconites with different content of 14 Å layers ranging from 5 to 25 % have shown no evidence of dependence on this most important characteristics of glauconite minerals.

Spectrum of vermiculite (fig. 1c) consists of two components corresponding to ferrous ions.

TABLE I

Parameters of Mössbauer spectra of clay minerals

Mineral	Comp.	$\delta$ [mm/s]	$\Delta/2$ [mm/s]	$\Gamma$ [mm/s]	c [%]
Montmorillonite	1	0.604	0.456	0.485	62.6
	2	0.698	1.076	0.528	37.4
Monttronite	1	0.676	0.396	0.414	59.2
	2	0.518	0.834	0.433	40.7
Beidellite	1	0.625	0.424	0.383	61.0
	2	0.620	0.884	0.518	39.0
Glaucosite	1	0.630	0.346	0.369	59.9
	2	0.650	0.942	0.518	24.4
	3	1.316	2.050	0.728	15.7
Seladonite	1	0.650	0.458	0.350	54.5
	2	0.821	1.140	0.406	27.5
	3	1.341	2.020	0.470	18.0
Illite	1	0.636	0.185	0.380	17.0
	2	0.635	0.505	0.530	83.0
Vermiculite	1	0.644	0.870	0.590	73.6
	2	1.201	2.180	0.350	12.0
	3	1.361	2.740	0.350	14.5
Saponite	1	1.460	2.401	0.401	33.7
	2	1.436	2.710	0.260	66.3
Palygorskite	1	0.596	0.430	0.350	62.0
	2	0.590	0.998	0.469	30.1
	3	0.576	1.015	0.290	7.9
Goethite	1	0.642	0.548	0.391	100.0

The third component belongs to ferric ion. The ferrous ions are present in two inequivalent structure sites with site occupancy ratio  $M_1/M_2 = 1.2$ . The spectrum is similar to those of biotites.

Spectrum of illite (figure 2a) has two components of  $Fe^{3+}$ . This result shows that it is impossible to distinguish, by means of Mössbauer spectroscopy, the components belonging to various types of layers in mixed structure minerals (e.g. 14 Å and 10 Å in glaucosites).

Saponite (figure 2b), the mineral related to montmorillonite group, yields spectra with only two components, which can be ascribed to two inequivalent sites of octahedral iron. Only very low content of  $Fe^{3+}$  is suspected.

The spectrum of palygorskite, the chain silicate, has been resolved into three components, two for  $Fe^{3+}$  and the third one represents a contribution of  $Fe^{2+}$ . The different character of spectrum is due to another type of structure (figure 2c).

For goethite - iron oxyhydroxide of the supergene origin, which is the most common admixture in natural clays, has the spectrum consisting of one quadrupole doublet. This proves its superparamagnetic nature, due to the small particle size.

The question of right interpretation of ferric components in spectra remains open. Measurements of tetrahedrally coordinated iron in feldspars provide possibilities of both octahedral and tetrahedral assignment of ferric iron in clay minerals. Some results obtained by Mössbauer spectroscopy of iron in clay minerals cannot be interpreted unambiguously.

In this contribution we have tried to bring another prove of usefulness of Mössbauer effect

in the study of clay minerals. Besides the reliable determination of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  by Mössbauer spectroscopy it is possible to distinguish iron in different inequivalent structure sites even in poor crystalline clay minerals.

References

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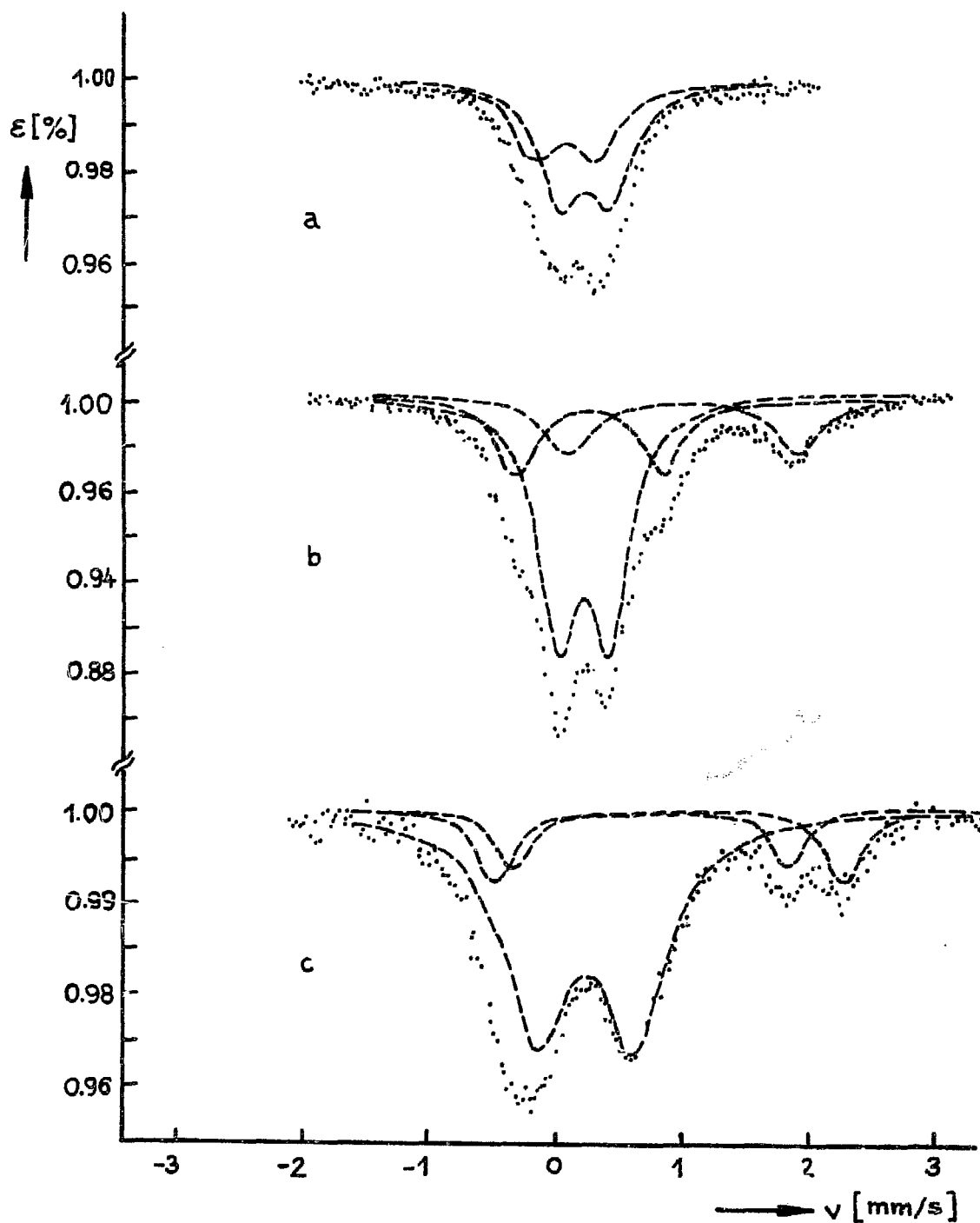
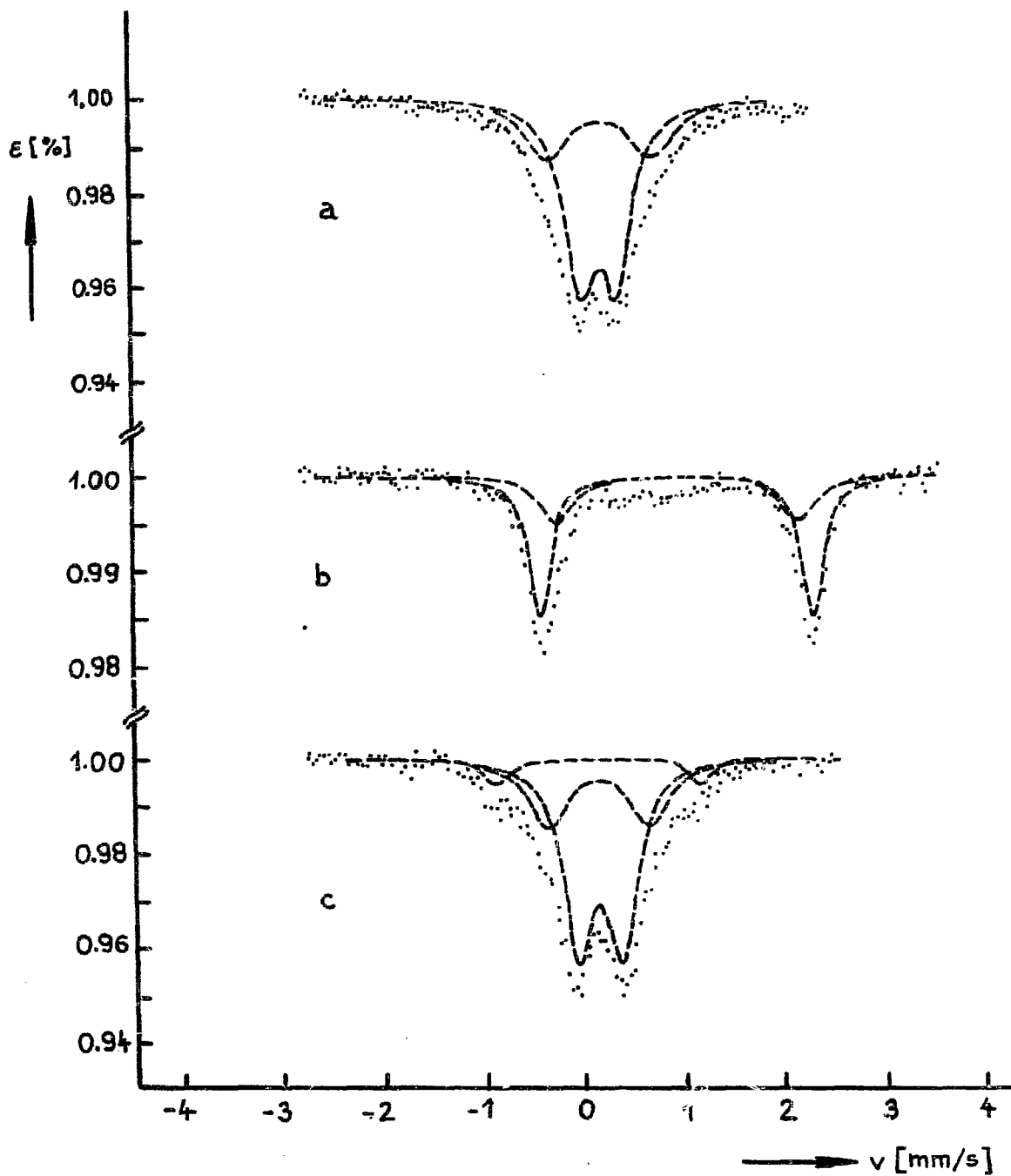


Fig.1. Mössbauer spectra of nontronite, seldanite and vermiculite



**Fig.2.** Mössbauer spectra of illite, saponite and palygorskite