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READILY HCl-SOLUBLE IRON IN THE FINE FRACTIONS OF SOME CZECH BENTONITES

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Abstract: The rate of acid dissolution in HCl is a common method for differentiating various phases of Fe in clay samples. A readily soluble Fe phase, denoted herein as the RS phase, is often observed in bentonite, but its identity has yet to be established. Seven Czech bentonites were studied by acid dissolution in 6 M HCl and by Mössbauer spectroscopy. A highly-soluble Fe phase was found in the <2-μm fractions of all seven Czech bentonites, ranging from 15 % to 67 % of total Fe. In all seven samples, Mössbauer spectroscopy revealed a goethite phase; in six, the goethite phase correlated well with the amount of RS Fe. In the seventh sample, Hroznětín, Fe(II) identified by both chemical analysis (phenanthroline method) and Mössbauer spectroscopy was the main source of RS Fe.

Key words: bentonite, smectite, goethite, acid dissolution, Mössbauer spectroscopy, hydrochloric acid.

Introduction

Previous investigations of the dissolution of smectites in HCl revealed the presence of a highly soluble Fe phase that apparently is separate from Fe(III) in the clay crystal structure (Osthaus 1954, 1956; Gastuche & Fripiat 1962; Čίčel et al. 1990, 1992; Luca & MacLachlan 1992). This phase has yet to be identified definitively, although it was proposed as due to an Fe-oxide admixture or coating.

A highly soluble form of Fe could arise from at least three different sources. First, Fe in octahedral sites near the edges of smectite particles may be more susceptible to acid attack than ions in less accessible sites located away from crystal edges, giving the appearance of Fe in a separate phase from the smectite. Second, a phase containing Fe(II) may be more soluble than Fe(III) in the smectite structure. And third, Fe oxides commonly are admixed with or coat smectite particles (Murad 1987; Goodman et al. 1988; Lear et al. 1988), and their solubility changes with crystallinity and Al substitution (Schwertmann 1984, 1988). Schwertmann (1984) observed a decreasing dissolution rate in 6 M HCl at 297 K as the Al content of synthetic goethite increased from 0 to 10 mole %. So the highly soluble phase found in smectites may be an Fe oxide with low Al content. Of the Fe oxides in soils, sediments, and clays, goethite is the most prevalent (Vandenberghe et al. 1990), but hematite and maghemite are also common.

Mössbauer spectroscopy has been widely used to identify Fe oxides in clays and soils (Murad 1988; Vandenberghe et al. 1990). Substitution of Fe by Al in natural hematite and goethite is common, and produces a lower Néel (magnetic ordering) temperature and a lower magnetic hyperfine field. The result of the change in magnetic ordering temperature is that the six-line pattern representing magnetically ordered goethite is absent from the room-temperature Mössbauer spectrum, but usually appears when the temperature is lowered to that of liquid N_2 (77 K). But in some Al-substituted goethites the Néel temperature may be well below

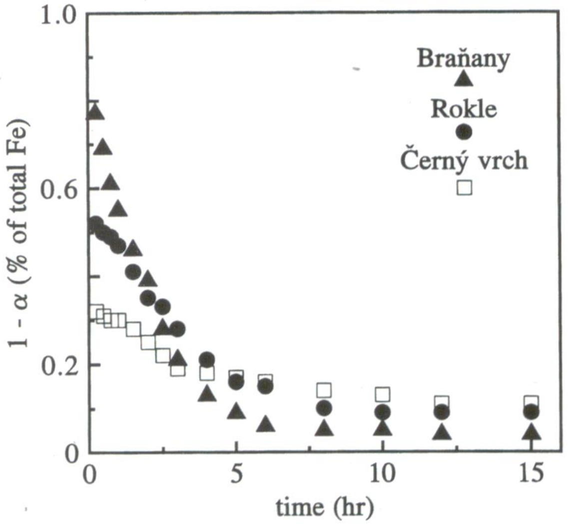

Fig. 1. Dissolution of Brańany 2, Rokle , and Černý vrch samples in 6 M HCl at 368 K.

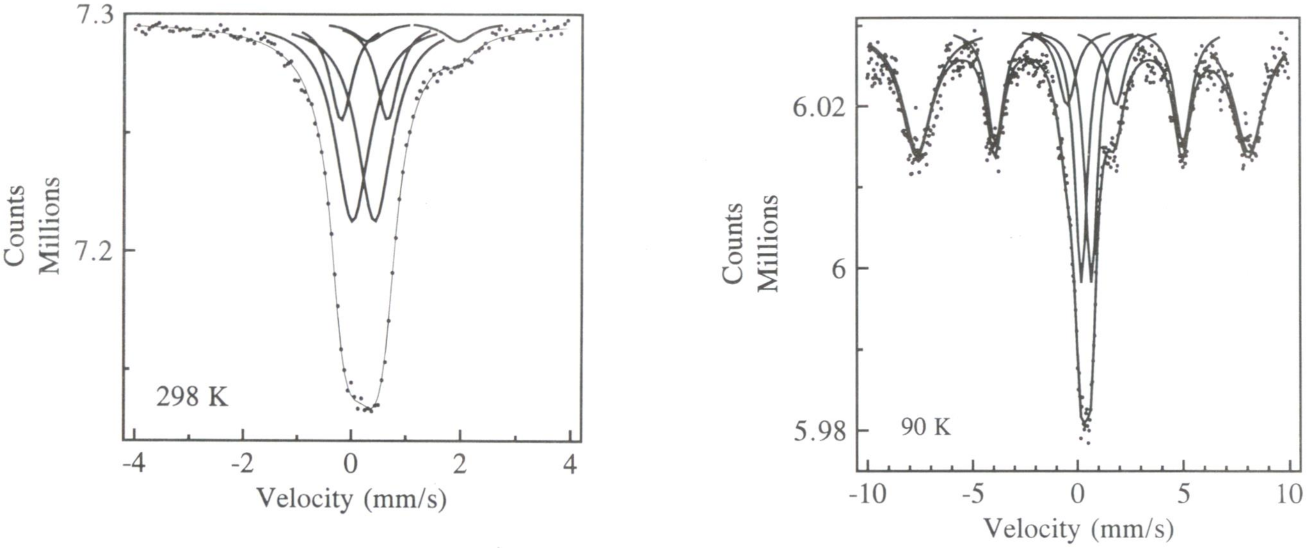

Fig. 2. Mössbauer spectra of sample Střimice at: **a** - room temperature (left); and **b** - 90 K (right).

77 K, causing them to be incompletely ordered at liquid N_2 temperature. In this case, the relative areas of the Mössbauer spectral components will underestimate the goethite content (Golden et al. 1979).

Low crystallinity in the Fe oxide also decreases the magnetic hyperfine field (Murad 1988). The effect of small particles and poor crystallinity could be minimized by taking the Mössbauer spectra at liquid He temperature and with an external magnetic field applied (Pollard et al. 1992).

The purpose of this study was to identify the source of Fe that is readily soluble in HCl in the <2-μm fractions of some Czech bentonites.

Materials and methods

Seven samples from six Czech bentonite deposits (Tab. 1) were Ca^{2+} saturated, fractionated to <2-μm, washed free of excess salts, dried at 60 °C, and ground to pass a 0.2 mm sieve. X-ray powder diffraction (XRD) and infrared spectroscopy (IR) (Číčel et al. 1992; Madejová et al. 1992) revealed smectite as the primary mineral, but the smectite was admixed with anatase (all samples) and kaolinite (all except Rokle). A 500-mg portion of each sample was mixed with 100 ml of 6 M HCl at 368 K (via a water-bath thermostat) in a 250-ml Pyrex flask with reflux. The mixture was reacted, with occasional stirring, for a specified time (ranging from 0.25 to 15 h), then filtered and washed with water. The filtrate and wash supernatant solutions were combined and analyzed for total Fe by absorption photometry of the rhodanide complex (Malát 1973) giving the amount of Fe dissolved (w_t) from the clay. Dissolution curves (Fig. 1) were constructed by plotting the undissolved portion of Fe (1 - α) as a function of time - t. The value of α was calculated from the relation

$$\alpha = \frac{w_t}{w_o}$$

where w_o is the total Fe content of the undissolved sample.

Mössbauer spectra were obtained at room temperature and 90 K using a Ranger Scientific MS-900 spectrometer (equipped with ^{57}Co source in 10 % Rh matrix and a Technology Systems cryostat) and deconvoluted with a least-squares computer program assuming Lorentzian line shapes. Parameters were calculated relative to Fe foil. The areas and widths of the two members of each doublet and of the respective pairs in each sextet, i.e., peaks 1 and 6, 2 and 5, and 3 and 4, were constrained to be equal. No constraind was applied to require a 3 : 2 : 1 ratio of the sextet pairs. The isomer shift (IS), quadrupole splitting (QS), quadrupole shift ($\in$), and magnetic hyperfine field (B_{hf}) of the sextet patterns were calculated from the peak positions using the methods described by Lear et al. (1988) and Pollard at al. (1992). The value of $\in$ was calculated using the relation

$$\in = \frac{(L_1-L_2) - (L_5-L_6)}{4}$$

where L is the position of the respective line or peak in the sextet (mm/s).

Iron(II) was measured quantitatively by the 1,10-phenanthroline method described by Komadel & Stucki (1988). X-ray diffraction patterns were obtained on a Scintag PAD V two-theta diffractometer.

Results and discussion

The Fe dissolution curves from the <2-μm fractions of Braňany 2, Rokle, and Černý vrch bentonites are presented in Fig. 1, and are representative of the types

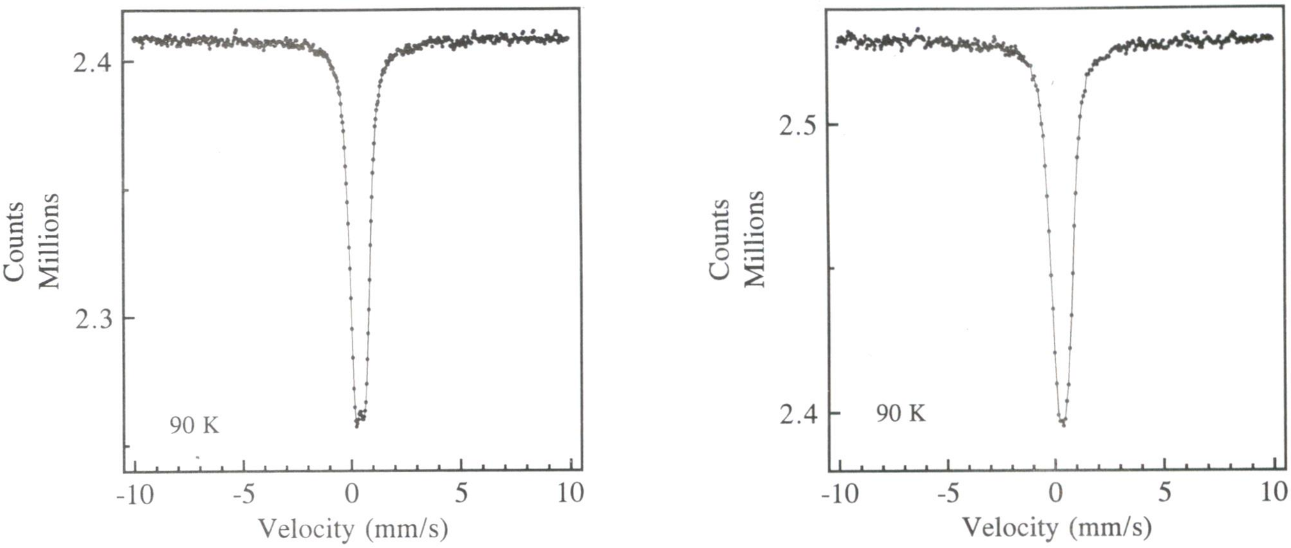

Fig. 3. Mössbauer spectra at 90 K of samples; **a** - Rokle and (left), **b** - Černý vrch(right) treated 15 min. in 6 M HCl at 368 K.

of curves obtained from all seven samples. A constant rate of dissolution indicated that the Fe was being dissolved from a homogeneous Fe phase or environment; a rate change signified a different Fe environment. All curves disclosed an initial, readily-soluble Fe phase (denoted hereafter as the RS phase), as indicated by extrapolating the linear segment in the time interval $0.25 < t < 1$ h to $t = 0$, and a second phase that dissolved at a much slower rate. The latter was attributed by Číčel et al. (1992) to structural Fe(III) in the octahedral sheets of the clay crystals, and the former is assigned as discussed below. For the more soluble phase, these extrapolations yielded values of $(1 - \alpha)$ ranging from 0.33 to 0.85, which corresponded to Fe contents from 67% to 15% of total Fe, respectively (Tab. 2, column RS).

XRD analyses of the seven bentonites revealed that the only Fe-bearing mineral except smectite was goethite, which was identified only in Rokle and Černý vrch. However, because of possible Al-substitution and poor crystallinity of the Fe oxides, the lack of definitive Fe oxide peaks in the XRD patterns of other samples was not considered to be conclusive evidence of their absence from those samples. Further evidence was acquired from Mössbauer analysis.

The Mössbauer spectra of samples Střimice, Rokle, Blšany 1 and 2, Braňany 2, and Černý vrch at room temperature and 90 K (representative spectra shown in Fig. 2) revealed Fe(III) in two environments: **1** - the octahedral sheet of the smectite (main central doublet); and **2** - a superparamagnetic phase that was mostly relaxed into a doublet at room temperature, but displayed a magnetically ordered sextet at 90 K. A small doublet for Fe(II) was also observed in the spectrum of the Střimice sample at room temperature (Fig. 2a). In the 90 K spectrum (Fig. 2b), the Fe (II) doublet could not be differentiated from the components of the magnetically ordered spectrum due to its broad peak width and relatively low intesity. After treatment for 15 min with 6 M HCl, in every case the sextet disappeared completely from the 90 K spectrum (representative spectra given in Fig. 3).

Mössbauer parameters (Tab. 1) IS, ϵ, and B_{hf} calculated from the sextet patterns are characteristic of natural goethite in all samples where a sextet pattern appeared. The magnetic hyperfine field ranged from 45.6 to 48.8 T at 90 K (Tab. 1), and is typical of goethite having relatively high and somewhat variable substitution of Al for Fe and/or low crystallinity (Murad 1988; Vandenberghe 1990). The value of B_{hf} for ideal goethite is about 50.0 T at 80 K.

The superparamagnetic behavior exhibited by these samples at room temperature, which disappeared at 90 K with the development of a sextet pattern, is also a well-known indicator of natural goethite. The fraction of total absorption attributable to this phase ranged from 8 % in sample Hroznětín to 72 % in Černý vrch (Tab. 1).

With the exception of bentonite Hroznětín, the amount of Fe in the RS phase correlated well with the amount of goethite observed in the 90 K Mössbauer spectrum (Fig. 4). In all samples containing goethite, some discrepancies existed between the amount of goethite determined by Mössbauer spectroscopy and the amount of RS Fe found by acid dissolution. Small differences probably are due simply to the lack of a quantitative relationship between Mössbauer peak area and chemical composition. But other possible factors include: **a** - Fe bound at the edges of the clay particles, although no independent evidence exists to confirm this assignment; **b** - ferrihydrite or other Fe oxide phases that are readily soluble but undifferentiated by Mössbauer spectroscopy at 90 K from structural Fe(III) in the smectite; or **c** - incompletely ordered goethite at 90 K (Golden et al. 1979; Murad 1988).

Table 1: Mössbauer parameters for Fe in Czech bentonites at 90 K.

Bentonite	Oxid. State	Peak Pattern	IS⁺ (mm/s)	QS† (mm/s)	ε‡ (mm/s)	B_{hf}§ (tesla)	Relative Peak Areas
Blšany1	3+	sextet	0.498		-0.148	45.8	0.39
	3+	doublet	0.430	0.469			0.61
Blšany2	3+	sextet	0.453		-0.101	45.6	0.36
	3+	doublet	0.457	0.367			0.64
Braňany2	3+	sextet	0.454		-0.143	46.7	0.14
	3+	doublet	0.404	0.339			0.86
Rokle	3+	sextet	0.456		-0.125	46.2	0.49
	3+	doublet	0.457	0.462			0.51
Střimice	3+	sextet	0.475		-0.156	48.8	0.69
	3+	doublet	0.387	0.473			0.31
Černý vrch	3+	sextet	0.485		-0.139	46.1	0.72
	3+	doublet	0.465	0.417			0.28
Hroznětín	3+	sextet	0.505		-0.088	47.0	0.08
	3+	doublet	0.461	0.556			0.61
	2+	doublet	1.397	1.990			0.31

+ Isomer Shift † Quadrupole splitting ‡ Quadrupole shift § Hyperfine magnetic field

The Mössbauer spectrum of sample Hroznětín revealed about 8 % of total Fe bound in a magnetically ordered sextet at 90 K (Fig. 5a), which is attributable to goethite. A doublet from structural Fe(II) was also observed (Fig. 5) in sample Hroznětín, which comprised about 31 % of the total absorption area in the ± 10 mm/s spectrum (Tab. 1) and about 34 % in the ± 4 mm/s spectrum (Fig. 5b). Chemical analysis of this sample, by the phenanthroline method, revealed the Fe(II) content to be 38.5 % (±0.80) of total Fe (Tab. 2). The difference between this value and that obtained from the Mössbauer spectra likely is due to the uncertainty in the relationship between Mössbauer peak areas and chemical composition (Rancourt 1989; de Grave & Van Alboom 1992; Stucki et al. 1993). Considering only the Mössbauer results, the combined Fe(II) and goethite fractions comprised about 39 - 42 % of the total Fe. Acid dissolution revealed the RS Fe fraction to be 45 % of the total Fe, which compares favorably with the sum of goethite and Fe(II) found by Mössbauer spectroscopy. The comparison is even better when the chemical determination for Fe(II) is used instead of the less accurate Mössbauer results. The fact that structural Fe(II) may be readily soluble in acid was noted by Gastuche & Fripiat (1962), who reported a high acid dissolution rate for structural Fe(II) from biotite in 2 M HCl at 304 K, in spite of the collapsed nature of the mineral. The reduced form of Fe apparently dissolves more rapidly than Fe(III) from a mixed-valent structure such as exists in the Hroznětín sample. Further evidence that structural Fe(II) is readily-soluble is that no Fe(II) was found in the Hroznětín sample after the HCl treatments. Hence, the composition of the RS fraction is principally goethite and structural Fe(II), with structural Fe(II) accounting for 85 % of the RS phase (Tab. 2).

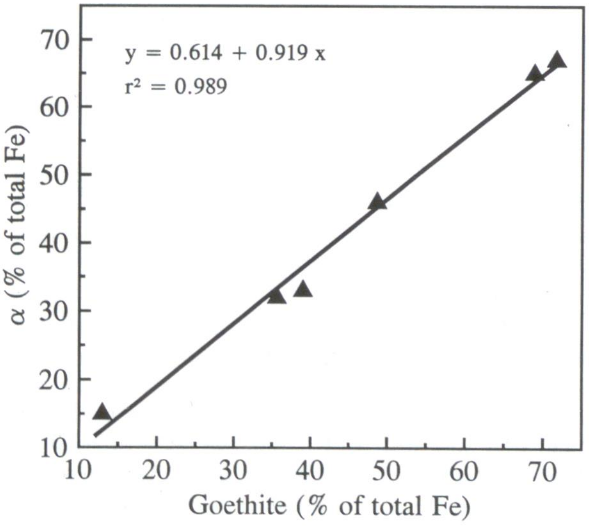

Fig. 4. Relation between goethite content as determined from Mössbauer sextet spectra and amount of readily-soluble (RS) Fe (from Tab. 2) in samples Blšany 1, Blšany 2, Braňany 2, Rokle, Střimice, and Černý vrch.

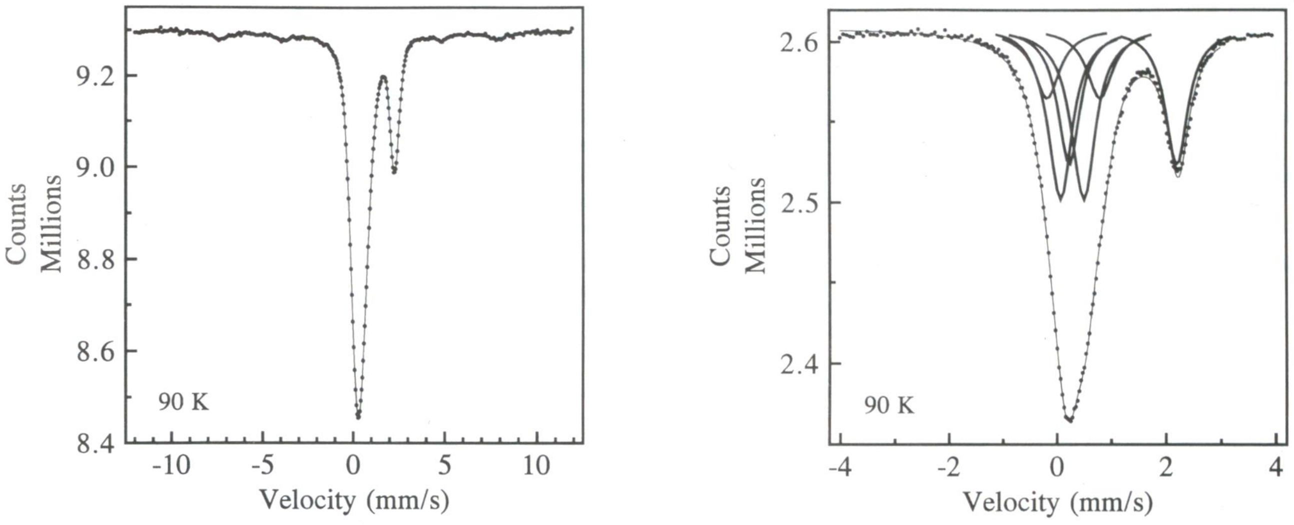

Fig. 5. Mössbauer spectra of sample Hroznětín at 90 K; **a** - ± 12 (left), and **b** - ± 4 mm/s(right).

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Table 2. Forms of Fe in the < 2-μm fraction of Czech bentonites.

Bentonite	Total Fe (mmole/g)	Fe(III)	Fe(II)†	RS#	G*
		% of Total Fe			
Blšany1	1.6790	99.69	0.31	33	37
Blšany2	1.7180	99.24	0.76	32	32
Braňany2	1.8012	99.57	0.43	15	14
Hroznětín	1.8051	61.12	38.50	45	8
Střimice	2.2170	96.89	3.11	65	67
Rokle	2.4561	99.68	0.32	46	52
Černý vrch	2.6640	99.71	0.29	67	70

† Determined by method of Komadel & Stucki (1988)
# Readily soluble in 6 M HCl at 368 K
* Bound in goethite

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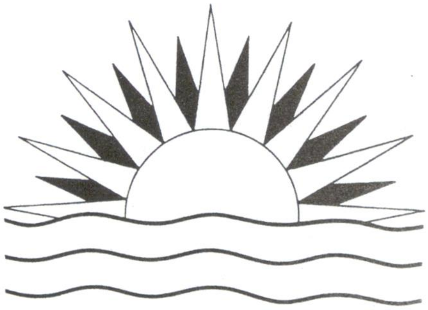

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