SPECTROSCOPIC INVESTIGATIONS OF IRON DISTRIBUTION IN SOME BENTONITES FROM SARDINIA

Iron is present in phyllosilicates in both tetrahedral and octahedral lattice sites; the two octahedral sites being distinguished on the basis of *cis* or *trans* arrangements of hydroxyl groups in the coordination sphere. Iron may also be present in clay assemblages in the form of finely divided accessory minerals, including iron oxides and hydroxides, admixed with or coating clay surfaces. In the latter form, they are extremely difficult to characterize by standard mineralogical techniques. Moreover, iron-bearing impurities are commonly present in such materials below the detection limit of infrared spectroscopy or X-ray powder diffractometry. Mössbauer spectroscopy has been shown to be a valuable technique for obtaining information about iron compounds, if their particle size is not too small (Gangas *et al.*, 1973).

The present study was carried out to detect and characterize the iron present in five samples of bentonite from Sardinia. In addition to standard infrared spectroscopic, X-ray powder diffraction, and elemental analytical techniques, each sample was examined by Mössbauer, electron spin resonance (ESR), and diffuse reflectance spectroscopy.

EXPERIMENTAL

Materials

Representative samples of bentonite were collected from quarries at Uri and Costa Paradiso (C.P.), Sardinia. The latter samples differ in color from red to grey to white. The main non-ferrous impurities identified by X-ray powder diffraction were cristobalite and other forms of silica, K-feldspar, and plagioclase. Illite was detected in the Uri sample (see also Pietracaprina *et al.*, 1972), and kaolinite was found in the green bentonite from Costa Paradiso (Green C.P.).

Methods

Spectroscopic examinations were made of: (1) raw bentonite samples which had not undergone purification of size fractionation, (2) clay-size fractions ($<2~\mu$m) after they had been saturated with H^+ by HCl treatment (Harward and Coleman, 1954), and (3) clay-size fractions after they had been treated with Na-dithionite according to the dithionite-citrate-bicarbonate (DCB) method of Mehra and Jackson (1960).

Mössbauer spectra were recorded on powders using an Elscint AME-40 spectrometer with constant acceleration relative to a $Co^{57}(Rh)$ source with a 100 mCi activity. Velocity calibration was made using a high-grade metallic iron lamina. Data points were fitted with Lorentzian components by a least-squares program. X-band ESR spectra were obtained on powdered samples with a Varian E-9 spectrometer using diphenylpicrylhydrazyl (DPPH) as a standard. Diffuse reflectance spectra were recorded using a Beckman Acta M IV spectrophotometer equipped with a reflectance sphere and using $BaSO_4$ as a reference. Powder X-ray diffraction (XRD) data were obtained with a Philips PW 1049/50 diffractometer using Ni-filtered $CuK\alpha$ radiation. Infrared (IR) spectra were recorded on a Beckman 4250 spectrophotometer using the KBr-pellet technique. Free iron oxides were determined by sequential extractions with sodium dithionate-citrate-bicarbonate (DCB). The extracts were analyzed for iron using a Perkin-Elmer Model 372 atomic absorption spectrophotometer. Total iron was analyzed by spectral technique with an arc-spectrograph Hilger E 478, applying standard methods (Harvey, 1950). An iron content of less than 2–3% was found for all samples.

RESULTS AND DISCUSSION

Detection of structural iron by Mössbauer spectra

Mössbauer spectra of the Red C.P. (Figure 1), Grey C.P. (Figure 2), and White C.P. bentonites showed only one broad doublet with Fe^{3+} parameter values. This doublet can be resolved into two doublets having isomer shift (I.S.) and quadrupole splitting (Q.S.) values typical of Fe^{3+} in *trans* [M(1)] and *cis* [M(2)] octahedral sites. Mössbauer spectra of the Uri (Figure 3) and Green C.P. bentonites showed also the presence of octahedrally coordinated Fe^{2+}, as reported for Wyoming bentonite (Rozenson and Heller-Kallai, 1977). Treatment with HCl caused the oxidation of Fe^{2+} to Fe^{3+} and variations in the M(1)/M(2) ratios (see Table 1). The width of the band corresponding to Fe^{3+} doublets was generally >0.38 mm/sec, the value reported for Fe^{3+} in most of the other silicates (Bancroft, 1973). These data suggest that each doublet corresponds to several sites of slightly different symmetry with similar Mössbauer parameters. Calculation based on a point-charge model (Berrett and Fitzsimmons, 1967) shows that the ratio of the Q.S. values for M(1) and M(2) sites is 2.0. Experimental deviations from this value indicate distortion from octahedral symmetry (Rozenson and Heller-Kallai, 1977). Since larger Q.S. values correspond to greater distortions of octahedral geometry, it follows that the M(1) and M(2) Fe^{3+} sites in the C.P. and Uri bentonites are significantly less distorted than those in the Wyoming bentonite (Rozenson and Heller-Kallai, 1977). The variations of the Q.S. values of M(1) exceed those of M(2). Therefore, Fe^{3+} M(1) sites are more easily distorted, perhaps because of their larger dimensions (Rozenson and Heller-Kallai, 1977). The Fe^{2+} values of the Sardinian samples (Table 1) are much smaller than those of Wyoming bentonite (Rozenson and Heller-Kallai, 1977). The lower the Fe^{2+}
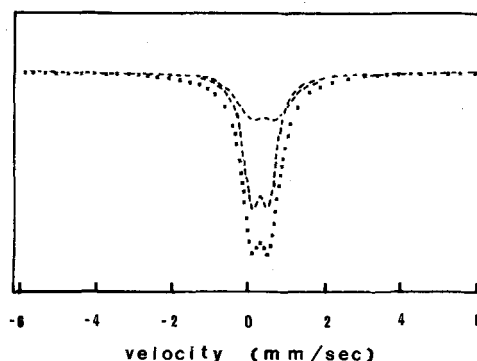

Figure 1. Mössbauer spectrum of red Costa Paradiso bentonite (Red C.P.) at room temperature.
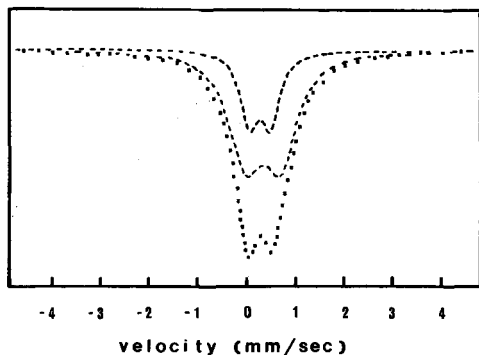
233

Figure 2. Mössbauer spectrum of grey Costa Paradiso bentonite (Grey C.P.) at 77°K.

Q.S. value, the greater is the distortion of the octahedra. Thus, the distortions of the Fe^{2+} sites of the Sardinian samples are more pronounced than those of the Wyoming bentonite.

Detection of extractable iron impurities

Iron oxides covering clay surfaces can be revealed by the Mössbauer spectroscopy in magnetic or paramagnetic form, the latter due to very small particles of oxides. Even at 77°K, the Mössbauer spectra of the Sardinian samples suggested no iron oxides. Based on the work of Gangas *et al.* (1973), oxide particles (if present) must have diameters <100 Å. The ESR spectrum of powdered Uri bentonite showed resonance values of g ~ 9.6 and g ~ 4.3 and a very broad resonance of g ~ 2 (see Figure 4). Similar spectra were obtained for the White C.P. and Grey C.P. bentonites. The resonances g ~ 9.6 and g ~ 4.3 are undoubtedly due to high-spin structural Fe^{3+} in octahedral sites (Meads and Malden, 1975). The very broad g ~ 2 resonance could be due to the coupling of Fe^{3+} in adjacent sites (Ried *et al.*, 1968). As the iron content of the mineral is low, the contribution to this resonance from ions randomly distributed in the bentonite structure must be negligible, suggesting that the samples contain phases in which the concentration of paramagnetic ions is high. The broad resonance weakened in materials treated with dithionite (see Figure 5), indicating that it was mainly due to the presence of extractable iron oxides.

ESR spectra of the Red C.P. and Green C.P. bentonites were quite different (see Figure 4). The resonance in the ESR spectrum of the Red C.P. bentonite near g ~ 4.3 was partially concealed by a very broad resonance. In the Green C.P. ben-
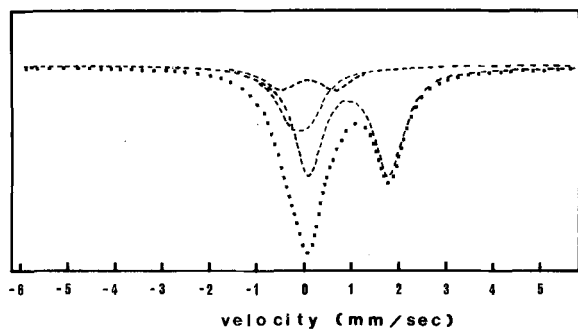

Figure 3. Mössbauer spectrum of Uri bentonite at room temperature.

Table 1. Mössbauer parameters of bentonites at 77°K.[1]

Sample[2]	Fe^{3+} M(1)			Fe^{3+} M(2)			Fe^{2+}			$\frac{Fe^{2+}}{Fe^{3+}}$	AM(1)/AM(2)
	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ	I.S.	Q.S.	Γ		
Uri	0.30 ± 0.02	0.58 ± 0.02	0.50 ± 0.02	0.22 ± 0.02	0.31 ± 0.02	0.51 ± 0.02	0.98 ± 0.03	1.86 ± 0.03	0.62 ± 0.04	1.60	1.16
H-Uri	0.06 ± 0.02	0.82 ± 0.03	0.62 ± 0.02	0.07 ± 0.02	0.41 ± 0.02	0.53 ± 0.02	—	—	—	—	1.05
White C.P.	0.27 ± 0.03	0.95 ± 0.03	0.45 ± 0.02	0.31 ± 0.03	0.38 ± 0.03	0.56 ± 0.02	—	—	—	—	0.36
H-White C.P.	0.26 ± 0.02	0.75 ± 0.02	0.55 ± 0.04	0.26 ± 0.01	0.41 ± 0.02	0.50 ± 0.03	—	—	—	—	0.68
Green C.P.	0.31 ± 0.02	0.79 ± 0.02	0.49 ± 0.02	0.32 ± 0.01	0.37 ± 0.02	0.54 ± 0.02	0.98 ± 0.03	1.61 ± 0.03	0.66 ± 0.04	0.10	0.71
H-Green C.P.	0.32 ± 0.01	0.76 ± 0.02	0.45 ± 0.02	0.33 ± 0.01	0.36 ± 0.02	0.53 ± 0.02	—	—	—	—	0.73
Red C.P.	0.23 ± 0.02	0.71 ± 0.02	0.55 ± 0.03	0.24 ± 0.02	0.37 ± 0.02	0.53 ± 0.04	—	—	—	—	1.20
H-Red C.P.	0.26 ± 0.02	0.70 ± 0.02	0.44 ± 0.02	0.25 ± 0.02	0.32 ± 0.02	0.58 ± 0.04	—	—	—	—	0.68
Grey C.P.	0.27 ± 0.01	1.00 ± 0.01	0.58 ± 0.02	0.23 ± 0.02	0.45 ± 0.03	0.62 ± 0.05	—	—	—	—	0.55

[1] I.S. = Isomer shift relative to Co^{57}(Rh) source; Q.S. = Quadrupole splitting; Γ = Peak width, all in mm/sec; AM(1)/AM(2) = Ratio of amount of Fe^{3+} in sites M(1) to that in sites M(2).
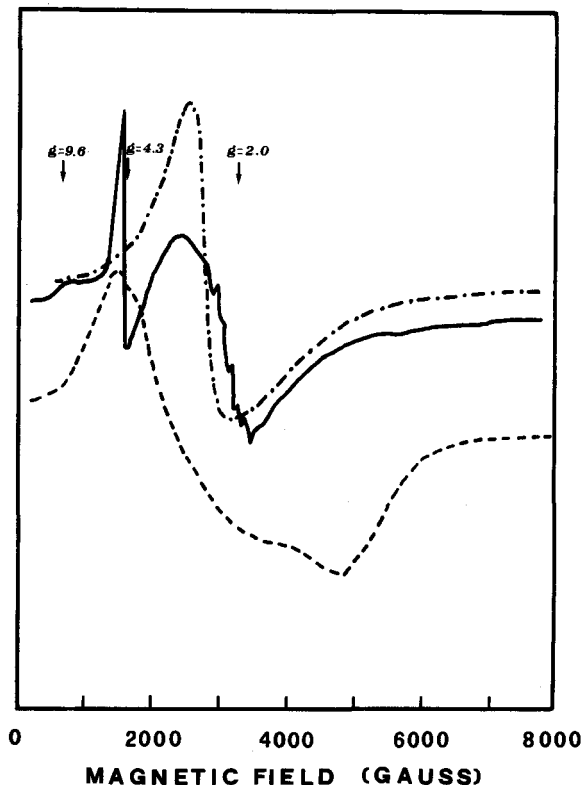[2] H-sample indicates H^+-saturated bentonite.

Figure 4. Electron spin resonance spectra of bentonites at room temperature: ——— Uri; ------ Red C.P.; ·-·-··-·· Green C.P.
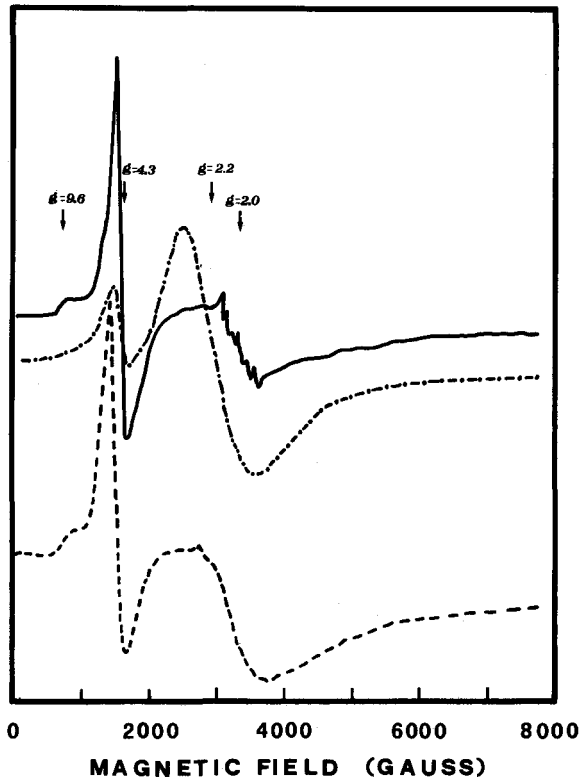

Figure 5. Electron spin resonance spectra at room temperature of bentonites washed with sodium dithionite: ——— Uri; ------ Red C.P.; ·-·-··-·· Green C.P.

tonite the band at 1550 G (g ~ 4.3) was masked by a strong signal centered approximately at 3000 G. The spectral resolution was notably higher after removal of iron oxides with sodium dithionite (see Figure 5). The amounts of free iron oxides removed by this treatment were 0.41% and 0.12% of the Red C.P. and Green C.P. samples, respectively. After extraction, the ESR spectrum of the Red C.P. bentonite was similar to that of the bentonites discussed above. However, a strong g ~ 2.2 resonance was still present in the spectrum of the Green C.P. bentonite after the removal of iron oxides.

To see if other techniques can be used to detect iron oxides, the bentonites were subjected to reflectance spectroscopy. The spectra of the Green C.P. and Red C.P. bentonites, before and after dithionite treatment, are reported in Figure 6. In the visible region the spectra display the features of mixtures of iron oxides as reported by Kortüm (1969) with absorptions at approximately 450 and 530 nm. The intensities of the individual bands vary not only with chemical composition, but also with particle size and with the distribution of the oxides (Kortüm, 1969). The intensities of these bands decreased in the samples treated with sodium dithionite. The changes were more pronounced in the Red C.P. bentonite due to its iron oxide content.

Detection of unextractable iron impurities in the Green C.P. bentonite

The Green C.P. bentonite contains a kaolinite impurity as shown by the XRD peak at 7.12 Å and confirmed by the ν(OH) stretching vibrations at 3695, 3670, and 3650 cm^{-1} in the IR
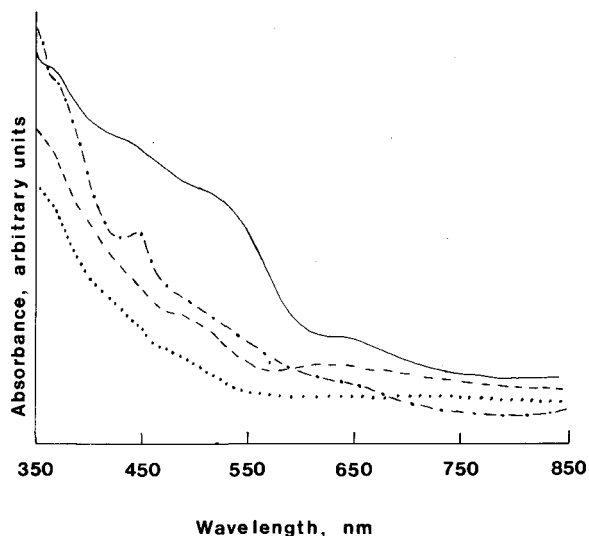

Figure 6. Diffuse reflectance spectra of bentonites: ——— Red C.P.; ------ Red C.P. washed with sodium dithionite; ·-·-··-·· Green C.P.; ···· Green C.P. washed with sodium dithionite.

spectrum (Van der Marel and Beutelspacher, 1976). The removal of the kaolinite impurity (by heating at 550°C and washing with DCB and NaOH solutions) did not modify the above mentioned ESR g ~ 2.2 signal. This resonance was removed only after the sample was reduced with hydrogen at 400°C followed by 1 N HCl or CDB washings. After this treatment, the sample gave a spectrum similar to that of an uncontaminated montmorillonite, in spite of the presence of the kaolinite impurity as shown by IR and XRD. On the basis of XRD and spectroscopic results, it was not possible to identify the species responsible for the broad g ~ 2.2 resonance in the spectrum of the Green C.P. bentonite. This impurity could be an iron-rich phase of interstratified mineral or a separate contaminant resistant to normal deferrification methods. However, since lattice Fe^{3+} ions in the bentonite were not modified by the removal of this impurity, as confirmed by the persistence of the ESR g ~ 4.3 resonance, it may be assumed that hydrogen-reducible iron was not present in the samples examined. Therefore, amorphous material rather than a layer-type mineral may be present on the surfaces of the Green C.P. bentonite. Such impurities have already been found in other montmorillonites (Goodman, 1978), although the methods of their removal were not sufficiently investigated.

CONCLUSIONS

This study has shown the advantages of using a combination of spectroscopic techniques in the investigation of iron-poor silicates. On the basis of the experimental results, the following conclusions can be drawn:

(1) The Mössbauer technique is the most valuable tool in detecting and characterizing lattice iron.
(2) ESR spectroscopy is effective in the detection of small amounts of iron-rich phases that are present as extractable or as more resistant surface contaminants.
(3) Reflectance spectroscopy is an efficient method of examining iron oxides, even if they are present in amounts of 0.1–0.5%.

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