IDENTIFICATION OF OXIDE IMPURITY PHASES AND DISTRIBUTION OF STRUCTURAL IRON IN SOME DIAGENETIC ILLITIC CLAYS AS DETERMINED BY MÖSSBAUER SPECTROSCOPY

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ABSTRACT: Seven diagenetic illitic clays have been investigated by Mössbauer spectroscopy to characterize the forms of iron. Four specimens had measurable amounts of iron oxide impurity phases, accounting for up to ~95% of the total Fe. Goethite, microcrystalline and probably aluminous, was identified as the oxide phase in three of these samples, the other containing hematite. This latter sample was also the only one which had tetrahedral Fe(III). Five of the samples contained measurable amounts of Fe(II), but the aluminosilicate Fe was present largely as 6-coordinated Fe(III) which had two distinctly different sets of parameters. These results are discussed in terms of the structural properties of illites.

Diagenetic illitic clays have been the subject of a recent detailed investigation of their chemical nature using X-ray fluorescence (XRF), X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Nadeau & Bain, 1986). Some of these materials, which had significant Fe contents (>1%) have been studied by Mössbauer spectroscopy in order to provide a comprehensive characterization of the nature of the Fe contained in them.

Recent papers on the use of Mössbauer spectroscopy in investigations of mineralogical samples have demonstrated that information can be produced that is not available from other techniques. For example, small amounts of oxide or hydroxide impurity phases can be detected at levels well below the limits of detection by more conventional methods, such as XRD or infrared spectroscopy (IR) (e.g. Goodman, 1981). Distinction between the Fe(III) and Fe(II) oxidation states is readily made and the coordination number can be identified, but with greater difficulty (e.g. Bancroft, 1973; Goodman, 1980). Many workers also claim to be able to distinguish the spectra from the different crystallographic sites with octahedral coordination in layer-silicates (e.g. Bancroft, 1973; Rozenson & Heller-Kallai, 1977; Darby Dyar & Burns, 1986), but these assignments are not uncontroversial and there has been criticism of this approach (e.g. Goodman, 1976b, 1978; Mineeva, 1978).

The present work falls into two categories, (i) identification of oxide impurity phases and assessment of their contributions to the total Fe contents of the minerals, and (ii) resolution of the various components arising from Fe in the aluminosilicate structure.

MATERIALS AND METHODS

Samples of diagenetic illitic clays from North American Cretaceous bentonites (C2B, N1B, ORB, TGB) and North Sea Sandstones (ROT, RAN1, RAN2) (Table 1) were Na-saturated

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TABLE 1. Sample details.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Size Fraction</th>
<th>X-ray Diffraction Mineralogy</th>
<th>Total Fe(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2B</td>
<td>Cerrillos, New Mexico</td>
<td>&lt;0.5 µm</td>
<td>I-S, 73% illite layers</td>
<td>1.04</td>
</tr>
<tr>
<td>N1B</td>
<td>New Castle, Colorado</td>
<td>&lt;0.5 µm</td>
<td>I-S, 73% illite layers</td>
<td>2.92</td>
</tr>
<tr>
<td>ORB</td>
<td>Ophir, Colorado</td>
<td>&lt;0.5 µm</td>
<td>I-S, 77% illite layers</td>
<td>4.85</td>
</tr>
<tr>
<td>TGB</td>
<td>Tioga Fm., New York</td>
<td>&lt;0.5 µm</td>
<td>I-S, 90% illite layers</td>
<td>0.92</td>
</tr>
<tr>
<td>RAN1</td>
<td>Rannock Fm., North Sea</td>
<td>&lt;2 µm</td>
<td>I-S, 88% illite layers</td>
<td>1.81</td>
</tr>
<tr>
<td>RAN2</td>
<td>Rannock Fm.,</td>
<td>&lt;2 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROT</td>
<td>Rotliegend Fm., North Sea</td>
<td>&lt;2 µm</td>
<td>Illite</td>
<td>2.64</td>
</tr>
</tbody>
</table>

and size fractionated. The mineralogy of these materials was previously established by XRD and IR, and total Fe contents determined by XRF (Nadeau & Bain, 1986).

Mössbauer spectra were obtained with a conventional spectrometer operating in transmission geometry and utilizing a constant acceleration saw-tooth waveform for the drive system, and an argon/methane proportional counter for γ-ray detection. Spectra were accumulated in 512 channels of an Ortec Model 6200 multichannel analyzer operating in the multiscalar mode. The source used was 57Co in Pd of nominal strength 25 mCi (0.93 GBq) and all shifts were calculated with respect to a thin Fe foil at ambient temperature, this foil also being used as a calibration standard for the spectrometer. Spectra were obtained at ambient temperature and 77 K, the latter being in a reservoir-type liquid nitrogen cryostat. All spectra were fitted by computer using an iterative method to a series of lines of Lorentzian shape. Components of doublets had their widths and areas constrained to being equal, and sextets from magnetic hyperfine splitting had their areas held to a 3:2:1:1:2:3 ratio.

Although workers with mineral systems generally assume that the areas of each of the components in a Mössbauer spectrum are proportional to the number of Fe atoms present in each phase, accurate quantitative Mössbauer spectroscopy is far more complicated (Collins, 1979; Bahgat, 1979; Fysh & Clark, 1984). The principal source of inaccuracy in a single measurement arises from the fact that different components may have different recoil-free fractions, \( f \), which are related to the mean-square displacement of nuclei along the γ-ray direction. Although \( f \)-factors may not differ greatly for ions held within the same crystal structure, they are influenced significantly by particle size effects and may be greatly different for the various phases in a geological specimen. Even component areas may sometimes be difficult to establish because of difficulties in the resolution of overlapping peaks. Furthermore, absorption areas are not linear with the effective thicknesses of components in absorbers (Hafmeister & Brooks Shera, 1966), thus creating further inaccuracies. In the present work, relative absorption areas for the components have been tabulated in the spectra and these should be considered as only semi-quantitative with regard to the actual amounts of the various component species.

RESULTS AND DISCUSSION

Of the seven specimens investigated, four gave Mössbauer spectra with sextet components at 77 K, whereas the other three produced only doublet components at this temperature. The complete spectra for the former group are shown in Fig. 1 where it can be seen that a number
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FIG. 1. Mössbauer spectra at 77 K of illitic clays (a) N1B; (b) C2B; (c) ORB; (d) ROT.
of different components are present in most samples. For convenience these can be divided into 3 categories:

(i) sextet components arising from magnetic hyperfine interactions;
(ii) doublets from Fe(III) with isomer shift, $\delta < 0.5$ mm/s;
(iii) doublets from Fe(II) with $\delta > 1.0$ mm/s.

The sextet components are not identical for all the samples and show large variations in their relative contributions to the spectra (Fig. 1, Table 2). Three samples (N1B, C2B, ORB) produced spectra at 77 K with asymmetric peak shapes and field maxima of ~47–49 T, which are typical of poorly crystalline or aluminous goethite (e.g. Janot & Gibert, 1970; Golden et al., 1979; Goodman & Lewis, 1981). Raising the temperature to ambient resulted in the complete collapse of the magnetic structure, which gives further support to its assignment to poorly-defined goethite. In contrast, the peaks of the sextet component from the ROT sample at 77 K are much sharper and have a significantly larger hyperfine field of 53-4 T. This is characteristic of hematite, an interpretation that is supported by the continued existence of the structure at ambient temperature (full spectrum not shown), where the hyperfine field is 51-0 T.

Hematite undergoes a phase transition at ~260 K (Morin, 1950) as a result of a realignment of magnetic moments within the mineral structure. This Morin transition is suppressed if the mineral is poorly crystalline, or contains significant amounts of isomorphous substitutions within its structure. No Morin transition was observed for the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp.</th>
<th>$\Delta$</th>
<th>$\delta$</th>
<th>$\Gamma$</th>
<th>$%$</th>
<th>$\Delta$</th>
<th>$\delta$</th>
<th>$\Gamma$</th>
<th>$%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIB</td>
<td>77 K</td>
<td>1.21</td>
<td>0.48</td>
<td>0.50</td>
<td>59</td>
<td>2.78</td>
<td>1.31</td>
<td>0.24</td>
<td>6</td>
</tr>
<tr>
<td>C2B</td>
<td>77 K</td>
<td>1.07</td>
<td>0.47</td>
<td>0.63</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TGB</td>
<td>rt</td>
<td>0.56</td>
<td>0.37</td>
<td>0.26</td>
<td>84</td>
<td>2.93</td>
<td>1.10</td>
<td>0.38</td>
<td>16</td>
</tr>
<tr>
<td>ORB</td>
<td>rt</td>
<td>c</td>
<td></td>
<td></td>
<td>&lt;5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROT</td>
<td>rt</td>
<td>0.73</td>
<td>0.26</td>
<td>0.65</td>
<td>29</td>
<td>2.87</td>
<td>1.14</td>
<td>0.30</td>
<td>23</td>
</tr>
<tr>
<td>RAN1</td>
<td>rt</td>
<td>0.73</td>
<td>0.30</td>
<td>0.96</td>
<td>39</td>
<td>3.07</td>
<td>1.25</td>
<td>0.34</td>
<td>26</td>
</tr>
<tr>
<td>RAN2</td>
<td>rt</td>
<td>0.62</td>
<td>0.36</td>
<td>0.40</td>
<td>81</td>
<td>2.91</td>
<td>1.13</td>
<td>0.30</td>
<td>19</td>
</tr>
<tr>
<td>77 K</td>
<td></td>
<td>0.98</td>
<td>0.30</td>
<td>0.96</td>
<td>59</td>
<td>3.07</td>
<td>1.25</td>
<td>0.34</td>
<td>26</td>
</tr>
<tr>
<td>RAN1</td>
<td></td>
<td>0.62</td>
<td>0.31</td>
<td>0.31</td>
<td>26</td>
<td>2.91</td>
<td>1.14</td>
<td>0.34</td>
<td>26</td>
</tr>
<tr>
<td>RAN2</td>
<td></td>
<td>0.62</td>
<td>0.31</td>
<td>0.31</td>
<td>26</td>
<td>2.91</td>
<td>1.14</td>
<td>0.34</td>
<td>26</td>
</tr>
<tr>
<td>77 K</td>
<td></td>
<td>0.63</td>
<td>0.37</td>
<td>0.51</td>
<td>34</td>
<td>2.08</td>
<td>1.33</td>
<td>0.32</td>
<td>29</td>
</tr>
</tbody>
</table>

$\Delta$, $\delta$, and $\Gamma$ are in mm/s; $\delta$ is relative to iron foil, $\%$ represents contribution to total spectral area. Typical errors are ±0.02 for $\Delta$, ±0.01 for $\delta$, ±0.04 for $\Gamma$ and ±3 for $\%$.

$^a$ remaining spectral area is from goethite components (see Fig. 1 and text).

$^b$ spectral contribution is too weak for derivation of parameters (see Fig. 1c).

$^c$ remaining spectral area is from hematite components (see Fig. 1d and text).

$^d$ rt = ambient laboratory temperature (300 ± 4 K).
hematite phase in the ROT sample, suggesting that this phase is poorly crystalline and/or contains significant isomorphous substitutions. Since the sample originated in sandstone, it is possible that the hematite was co-extracted with the illitic clay, although no hematite was found in the RAN1 and RAN2 specimens which were developed on similar material.

The components from the iron oxide phases make a significant contribution to the total Fe, the most noticeable being in the ORB specimen in which ~95% of the spectral area is located in the impurity phase. Therefore, when allowance is made for the presence of such impurities, the structural compositions of the layer-silicate minerals become significantly different from those values obtained direct from chemical analysis data (see Nadeau & Bain, 1986).

Components originating from Fe(II) are seen in most of the spectra, but only become major in the ROT and RAN2 specimens. This latter specimen is the only one that shows two distinct Fe(II) components (Fig. 2d, e), that with the smaller quadrupole splitting being different from the Fe(II) components in any of the other specimens. However, species with similar values for \( \Delta \) have been reported for illites in the literature (Weaver et al., 1967; Heller-Kallai & Rozenson, 1981; Montano, 1981), so this should not be dismissed as an impurity phase. It is interesting that this component was not seen in the RAN1 sample which was extracted from the same crude material, and it would appear that a degree of fractionation of these illitic clays can be achieved by sequential separations.

The amounts of Fe(III) producing doublet components vary greatly from one sample to another and there is also a significant variation in the magnitudes of their parameters (Table 2). Thus the ROT sample has an Fe(III) component with an isomer shift much smaller than any of the other specimens. Its values of \( \sim 0.26 \text{ mm/s} \) at ambient temperature, and \( 0.30 \text{ mm/s} \) at 77 K are consistent with 4-coordination for Fe in an environment of oxygen atoms (see e.g. Goodman, 1980) and indicates that in this sample, the Fe(III) occurs preferentially in the tetrahedral sheet. Although similar isomer shifts are observed with some sulphide minerals (e.g. marcasite, Stevens et al., 1983), their presence can be discounted because of the low sulphur content (<0.01% SO\(_3\)) of this mineral (Nadeau & Bain, 1986). There are several instances of substantial amounts of tetrahedral Fe(III) being reported in aluminosilicate minerals, e.g. nontronites (Goodman et al., 1976), phlogopite (Sanz et al., 1978; Darby Dyar & Burns, 1986), ferriphlogopite and ferriannite (Darby Dyar & Burns, 1986), although, to the authors' knowledge, this is the first report of such a component in illite. It may be significant that the ROT sample is pink in colour. In work with a pink muscovite, Richardson (1975) suggested, on the basis of UV-visible absorption spectra, that the colour arose from transitions involving tetrahedral Fe(III), although Annersten & Halenius (1976), and Goodman (1976a) have shown that all the Fe(III) in a similar specimen had octahedral coordination. Annersten & Halenius proposed that the pink colour of their muscovite was in fact due to charge transfer transitions involving Mn. Nevertheless, it is possible that the pink colouration in sample ROT is due to transitions of the type suggested by Richardson, since EPR spectra showed no evidence for any tetrahedral Mn (B. A. Goodman, unpublished results), although the presence of hematite would also be expected to contribute to the colour. The isomer shift for Fe(III) in the other samples is consistent with 6-coordination in an environment of oxygen atoms and indicates that the Fe is present exclusively in the octahedral sheet. The quadrupole splittings, \( \Delta \), for the 6-coordinate Fe(III) differ from one sample to another (Table 2), with TGB and RAN1 having values <0.7 mm/sec and N1B, C2B and ROT having values >1.0 mm/sec. The RAN2 sample, with values of \( \sim 0.63 \) and 1.15 mm/sec, is the only specimen that required two different components with 6-coordinate Fe(III) in order to achieve a satisfactory computer fit to the data.
FIG. 2. Mössbauer spectra at ambient temperature of illitic clays (a) TGB; (b) ROT; (c) RAN1; (d) RAN2. (e) shows RAN2 at 77 K. Positions of component peaks from computer fits are indicated by bars, and the solid line represents the overall envelope from the fit.
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Several authors (e.g. Ericsson et al., 1977; Saporoschenko et al., 1980; Heller-Kallai & Rozenson, 1981) have assigned these Fe(III) components to the two crystallographically distinct sites in the illite structure, there being general agreement that the component with the smaller quadrupole splitting corresponds to Fe(III) in the M2 site (with cis hydroxyl groups) and that with the larger splitting to the M1 site (with trans hydroxyl groups). However, calculations of electric field gradient distributions in aluminosilicate structures (e.g. Goodman, 1976b; Mineeva, 1978) have shown that a range of values for $\Delta$ can exist at a single crystallographic site. Goodman (1978) has proposed that in nontronite the two Fe(III) doublets that correspond to octahedral coordination are derived from ions in M2 sites, whilst Cardile & Johnston (1986) have interpreted the spectra of montmorillonites in terms of both doublets corresponding to M1 site occupancy. It appears, therefore, that the validity of the conventional assignments is questionable and that further work is necessary in order to address these issues.

REFERENCES


B. A. Goodman and P. H. Nadeau


