OXIDATION STATE OF IRON IN GLAUCONITE FROM OXIDIZED AND REDUCED ZONES OF SOIL-GEOLGICAL COLUMNS

D. S. FANNING AND M. C. RABENHORST
Department of Agronomy, University of Maryland
College Park, Maryland 20742

LEOPOLD MAY
Department of Chemistry, The Catholic University of America
Washington, D.C. 20064

D. P. WAGNER
Geo-Sci Consultants, Inc., College Park, Maryland 20740

Abstract—Glaucnite from the oxidized and reduced zones of soil-geologic columns at two Coastal Plain sites, one in Maryland and one in New Jersey, was examined by Mössbauer spectroscopy. The data indicate that glauconite in the reduced zones had a higher proportion of its structural iron in the ferrous, as opposed to the ferric state. The Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio ranged from 0 to 0.2 for the glauconite from the oxidized zone and was about 0.35 for the glauconite in the reduced zones. Despite the presence of pyrite in the reduced zone, which might be expected to make ferric iron unstable because of the presence of sulfide S, about 75% of the Fe in the glauconite in the reduced zone was in the ferric state. Thin section analysis showed some glauconite in the reduced zones to be intimately associated with pyrite and some aggregates of fine pyrite crystals were locally present in cracks in glauconite pellets. In the oxidized zones, pyrite was absent and the glauconite was more yellow under plane-polarized light, as opposed to more green for the glauconite in the reduced zones. These data indicate that reports of studies of glauconite should stipulate whether samples are from the oxidized or reduced zone of soil-geologic columns.

Key Words—Glaucnite, Iron, Mössbauer spectroscopy, Oxidized zone, Pyrite, Reduced zone, Soil.

INTRODUCTION

Acid-sulfate weathering studies indicate that ferric iron is unstable in the presence of sulfide sulfur (Nords trom, 1982). Based on this line of reasoning, Fe in glauconite should be mainly in the ferrous form in the reduced zone of geologic columns, in which sulfur is present mainly as pyrite. Similarly, Fe in glauconite should be mainly in the ferric form in the oxidized parts of the same columns, in which sulfur, if present, occurs as jarosite or gypsum (Wagner, 1982; Wagner et al., 1982; Carson et al., 1982). Most chemical analyses of glauconite in the literature show the structural Fe to be mainly Fe\textsuperscript{3+} (e.g., see analyses presented by Fanning and Keramidas, 1977; Odom, 1984). Typically 10–15% of the Fe in analyses in the literature is reported as Fe\textsuperscript{2+}, suggesting that most analyzed samples of glauconite were from the oxidized zone. Most papers, however, fail to indicate whether the glauconite came from the oxidized or the reduced zone.

This paper reports the oxidation state of Fe in glauconite from the oxidized and reduced zones at two sites, one in Maryland and one in New Jersey, as determined by Mössbauer spectroscopy. Thin sections were also examined with a petrographic microscope to identify the association between the pyrite and glauconite in the reduced zone and the color of the glauconite in both zones.

MATERIALS AND METHODS

Materials

The Maryland samples were obtained at a cliff face exposure on the Potomac River near Bel Alton, Charles County, Maryland, at a site studied by Wagner (1982). At this site the Nanjemoy Formation of Eocene age is covered by a thin mantle of Holocene silt. The soil at this site is a Typic Albaquult, fine, mixed, mesic (Wagner, 1982). The sample from the oxidized zone was obtained from a depth of about 2.25 m (Figure 1) in a zone that contained jarosite and iron oxide mottles on the faces of a weak, coarse, platy structure in a Cj horizon (j indicating the presence of jarosite). The material for Mössbauer spectral analysis was taken from the interior of plates of the soil-sediment structure in which no iron oxides or jarosite were visible. The overall material at this depth had a slurry pH of 4.0, and
the color of the soil matrix was brown (10YR 5/3) when moist. The reduced-zone sample at this site was obtained with a hand operated bucket auger at a depth of about 7 m, about 1 m below sea level at the base of the cliff (Figure 1). It was very similar in color, texture, and other field observable properties to the Cg3 horizon at a depth of 5–6 m described by Wagner (1982) at this site, which contained a few calcareous shells, had a pH in water of 7.1, and was very dark gray (5Y 3/1) when moist. The glauconite in both samples from the Maryland site occurred as sand-size pellets, generally similar to those described by Tapper and Fanning (1968) from another site in the Nanjemoy Formation. Oriented “undisturbed” samples from other depths of the oxidized and reduced zones were obtained for thin section studies.

The Eh was measured in the field at 25 cm above and 25 cm below the boundary between the oxidized and reduced zones and at the base of the cliff at about 6 m depth using a LDC digital multimeter and Pt electrodes and a calomel reference electrode. The readings were corrected by adding 244 mV to the readings with the calomel electrode to give Eh values.

The New Jersey samples were collected at a site in Medford Township, Burlington County, New Jersey, at which samples of the Marlton soil (Typic Hapludult, clayey, glauconitic, mesic) were taken for earlier studies in 1975. The site represents the Paleocene Horners-town Formation. The oxidized-zone sample for Mössbauer analysis was taken from samples of Btl (B21t, by older nomenclature) horizon material collected in 1975. Johnson and Chu (1983) examined the mineralogy of the <2-μm clay fraction (sample contained 70% clay) and found it to be highly micaceous (7.72% K2O). Our X-ray powder diffraction (XRD) analysis showed this material to be essentially all glauconite. Cation-exchange capacities (both CaEC and KEC were about 20 cmole/kg (20 meq/100 g) showing no K fixation and thus no vermiculite by methods of Coffman and Fanning, 1974; similar values were reported for the clay fraction by Johnson and Chu, 1983) and XRD patterns suggested some interstratified smectitic layers. The soil in the field has strong shrink-swell characteristics, as shown by many slickensides in the Bt horizon. A deep, oxidized-zone Cj horizon containing yellow (2.5Y 7-8/6) jarosite mottles and a slurry pH of about 4 was found to extend from about 130 cm to a depth of 575 cm, where the reduced zone was encountered (examination and sampling below a depth of about 150 cm was with a bucket auger in 1984). The black (10YR
2.5/1) reduced zone had a slurry pH of about 5 at a depth of about 6 m. Samples were also collected for thin section analysis.

Methods

Thin section preparation and examination. Undisturbed, oriented clods were collected from the oxidized and reduced zones of the Maryland site and from the oxidized zone of the New Jersey site. The sample from the reduced zone in New Jersey was taken with a bucket auger, and thus the field fabric was somewhat altered. This sample was, however, still useful for evaluation of pyrite-glaucionite relationships. Clods were impregnated under vacuum using Scotchcast #3 epoxy resin, which had been heated to 95°C to reduce the viscosity. Thin sections were cut and polished to about 30-μm thickness and examined using plane and cross-polarized transmitted and reflected light.

Mössbauer spectral studies. The <2-mm material from the New Jersey oxidized-zone sample collected in 1975 was examined by Mössbauer spectroscopy. The glauconite pellets in all the other samples were concentrated by washing the materials on a 300-mesh sieve and, after air-drying, manually removing some of the non-glaucionite sand grains (mainly quartz by visual examination) prior to Mössbauer examination. All samples were powdered and mounted in plastic holders.

The Mössbauer spectra were obtained at 80 K with a Ranger model MS-900 Mössbauer spectrometer, equipped with a liquid nitrogen cryostat, and operated in the acceleration mode with moving source geometry. A 12-mc 57Co in Pd source was kept at room temperature, and the velocity range was calibrated with sodium nitroprusside. The resultant spectra were analyzed by a least-squares fit to Lorentzian-shaped lines constrained to three or more doublets with the following approximate parameters (quadrupole split, isomer shift, both in mm/s): glauconite Fe3+ (two lines), 1.0, 0.35 and 0.42, 0.40; Fe2+ (two lines), 2.0, 1.5 and 2.6, 1.5; and pyrite Fe, 0.6, 0.3.

Elemental analyses. Elemental analyses for S and Fe of the same reduced-zone sample from the New Jersey site that was employed for the Mössbauer examination were obtained by X-ray spectroscopy by slight modifications of the methods described by Snow (1981).

RESULTS

Field relationships

In studies of glauconite-bearing soil-geologic columns in Maryland, the reduced zone has invariably been found to contain pyrite (Wagner, 1982; Wagner et al., 1982). In uplands in the Coastal Plain of southern Maryland (west of Chesapeake Bay), the oxidized zone is generally from 2 to 10 m thick. The oxidized zone is recognized in the field by the absence of the dark colors that are typical of the reduced zone and by the presence of iron oxides and/or jarosite. Jarosite is usually absent (or not visible) in the A and B horizons of the soils, but it is commonly visible as distinct or prominent mottles in the zone between the bottom of the Bt horizons and the top of the reduced zone (Figure 1). These horizons have been designated as Cj horizons in soil descriptions (Wagner, 1982). They have platy structure, originally interpreted as sedimentary in origin, that may, however, have formed as desiccation cracks after the exposure of the sediments at the land surface. If so, the horizons should possibly be designated as Bwj horizons to indicate that their genesis has been affected by “soil forming” processes. This designation would suggest a much deeper soil zone than has been recognized in these soils in the past.

The jarosite and iron oxides in the Cj, or Bwj, horizons typically occur on the faces of the structural partings, implying that as the sediments oxidized, these faces were more oxidizing than the materials away from these faces, in which, at least temporarily, lower Eh associated with pyrite may have prevented the formation of these Fe3+-bearing minerals. Advantage was taken of these mineral separations to obtain glauconite pellets showing no visible contamination by jarosite and iron oxides from the oxidized zone of the column examined in Maryland (see Materials section).

In the Maryland column examined in this study, the oxidized zone was only about 3 m thick (Figure 1). This column came from a bluff with active shore erosion on the east side of the tidal Potomac River. The bluff (cliff) is at the edge of a terrace in the Nanjemoy Formation that is considered to have been cut in Pleistocene time (Wagner, 1982). About 3 m of the reduced zone is exposed at this site above the tidal river at the base of the bluff (Figure 1), suggesting that the rate at which the oxidized zone has been deepened is slower than the rate of shore erosion. The overlying soil is poorly drained, and low places on the terrace are wet (standing or flowing water during a large part of most years). The reduced zone is very dense, which apparently has contributed to the slow rate of deepening of the oxidized zone. Active oxidation at the top of the reduced zone, however, at the face of the bluff, is evidenced by the occurrence of the lowest pH in the column in this zone (pH of about 3.0 at the bluff itself, where this zone is slightly deeper than in this active zone under the terrace away from the bluff where the pH ranges from about 3.7 to 4.3) as measured in water at a 1:1 soil to water ratio (Wagner, 1982). In the column above the active zone, which has previously been exposed to acid sulfate weathering as evidenced by the presence of jarosite mottles and the absence of pyrite, the pH ranges from 3.6 to 4.0 in the horizons containing jarosite (Wagner, 1982). In the underlying reduced zone, where calcareous shells are present, the slurry pH is about 7.1.
The Eh measurements at the Maryland site documented differences in redox conditions between the oxidized and reduced zones. The Eh values were 620, 470, and 220 mV for positions 25 cm above the boundary between the two zones, 25 cm below the boundary, and at a depth of 6 m (at base of cliff), respectively.

The New Jersey column (Figure 1) is much like the Maryland column except that the oxidized zone is deeper. It was not possible to get as deep into the reduced zone at this site because of the difficulty of obtaining samples with the hand-operated bucket auger. The reduced zone was extremely dense, as indicated by great difficulty in penetrating it with the auger. Despite attempts to obtain a reduced-zone sample not affected by sulfide oxidation, the sample obtained from the reduced zone in New Jersey had probably been somewhat affected by sulfuric acid produced by the oxidation of pyrite, because the pH was about 5, which is lower than the pH of about 7, which is typical for reduced-zone samples. The soil at the top of the column has been mapped as the Marlton soil series (Markley, 1971), which is classified as a Typic Hapludult. Because of mainly low chroma green colors in the B horizon, however, this soil is better classified as an Aeric Ochraquult, which, based on soil colors, is interpreted to be a somewhat wetter soil than a Typic Hapludult.

**Thin section examination**

Pyrite (Figure 2) (opaque in transmitted light, metallic luster and gold color in reflected light) was present in thin sections from the reduced zones of both sites. Pyrite was not present in samples from the oxidized zones. The pyrite occurred as 10–100-μm size aggregates of microcrystals (~1–5 μm in size) or as individual crystals. About half the pyrite occurred as aggregates within glauconite pellets (Figure 2). Although pyrite was common in glauconite pellets in the reduced zones examined, pyrite-free glauconite pellets were also present in these zones. The intimate association of pyrite and glauconite precluded the determination of the oxidation state of the glauconitic iron by standard wet chemical methods.

At both sites glauconite pellets in the reduced zone under plane transmitted light were blue-green (5GY-7.5GY 5/8-6/8), whereas those from the oxidized zone were more yellow green (Maryland sample = 5Y 6/8-7/8; New Jersey sample = 2.5GY 6/8-7/8). The Maryland oxidized-zone glauconite pellets appeared to have a slightly yellower hue than those from the New Jersey sites.
Table 1. Iron distribution based on analysis of Mössbauer spectra.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Glauconite % of total Fe as: Fe(^{2+}) / Fe(^{3+})</th>
<th>Ratio (Fe(^{2+})/Fe(^{3+})) for glauconite</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Jersey</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidized</td>
<td>16.5</td>
<td>83.5</td>
</tr>
<tr>
<td>Reduced(^1)</td>
<td>25.9</td>
<td>74.1</td>
</tr>
<tr>
<td>Maryland</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidized</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Reduced(^1)</td>
<td>26.2</td>
<td>73.8</td>
</tr>
</tbody>
</table>

\(^1\) Glauconitic Fe\(^{3+}\) reported for reduced-zone samples includes small quantities of pyrite Fe. Values for the ratio in parentheses are corrected for pyritic Fe based on S analyses. See text.

oxidized zone. This color difference is apparently related to the relative amount of Fe\(^{2+}\) and Fe\(^{3+}\) in the glauconite (Table 1). These findings generally coincide with findings of Stucki and Roth (1977) on the color of nontronite as related to Fe\(^{2+}\)/Fe\(^{3+}\) ratio.

Mössbauer spectroscopic data

The Mössbauer spectra of the glauconite examined in the present study (Figure 3) are generally similar to those of glauconites in the literature (e.g., McConchie et al., 1979). The lines attributed to the Fe\(^{3+}\) are imbedded in the major absorption region between 0 and +1.5 mm/s. Two doublets of glauconite Fe\(^{2+}\) were found, with the positive lines near +3 mm/s and the negative lines in the major absorption region. The absorption lines due to the pyrite are also within the major absorption region (see, e.g., Montano, 1981).

The primary interest in the studies reported here was in the relative amounts of ferrous and ferric iron in the glauconite of the oxidized and the reduced zones. The amount of Fe\(^{2+}\) was estimated by the intensities of the lines near +3 mm/s. Visual inspection of these lines in Figure 3 suggests that glauconite from the reduced zones of the two sites contains more Fe\(^{2+}\) than the glauconite from the oxidized zones. The relative amount of Fe\(^{2+}\) in the glauconite of a sample was taken to be twice the areas of the two lines in its spectrum located near +3 mm/s. The amount of Fe\(^{3+}\) was taken to be proportional to the area of the whole spectrum minus the area of the glauconite Fe\(^{2+}\) lines, assuming that the area of the spectrum due to the small amount of pyrite present is included in the area assigned to the Fe\(^{3+}\). These calculations gave the data in Table 1.

The actual amount of pyrite Fe in the reduced zones of the two sites was estimated from chemical analyses. The New Jersey reduced-zone material used for Mössbauer analysis contained 0.21% S (0.210 and 0.207% S in duplicate analyses) and about 6.6% Fe (6.0 and 7.2% Fe in duplicate analyses). The S values are equivalent to 0.18% pyrite Fe, which would only be about 3% of all the Fe in the material as pyrite, with the remaining 97% in the form of glauconite. Deduction of pyrite Fe from the Fe\(^{3+}\) in glauconite increases the Fe\(^{2+}\)/Fe\(^{3+}\) ratio slightly (Table 1).

Analyses of Fe and S for a sample from about 6-m depth from the reduced zone at the Maryland site by Wagner (1982) showed 6% of the total Fe to be pyrite, with the remainder (94%) attributable to glauconite. Here also, if this amount of pyrite Fe, which has a Mössbauer signature similar to that of the Fe\(^{3+}\) in glauconite, is deducted from the Fe\(^{3+}\) in glauconite, the Fe\(^{2+}\)/Fe\(^{3+}\) ratio for glauconite of the reduced zone from this site is slightly increased (Table 1).

Glauc. tone from the oxidized zone at the Maryland site contained essentially no Fe\(^{2+}\) (Table 1 and Figure 3). On the other hand, the glauconite from the oxidized zone from the New Jersey site had about 20% of its Fe as Fe\(^{2+}\), on the basis of Mössbauer spectra (Table 1).
DISCUSSION

The hypothesis that most of the Fe in the structure of glauconite from the reduced zone was Fe$^{2+}$ proved wrong. More of the structural Fe in glauconite of reduced-zone samples was in ferrous form than in the glauconite of the oxidized-zone samples, suggesting that oxidation state of the structural Fe does in part reflect the oxidation status of the material. At ambient temperatures the ferrous and ferric conditions in the silicate structures may not be as well defined as at 80 K (i.e., resonance may exist between the two forms), as McConchie et al. (1979) suggested to explain poorly defined peaks and broader shoulders between the ferrous and ferric peaks in Mössbauer spectra of glauconites at room temperature. Note that the Mössbauer patterns presented here were obtained at 80 K.

The oxidation state of Fe in phyllosilicate structures may be indicative of the Eh of soil and geologic materials. Stucki and Roth (1979), among others, showed that the oxidation state of Fe in nontronite may be changed in the laboratory by oxidizing and reducing agents and that this change is reflected in the color of the mineral. The present study shows that the relative amounts of Fe$^{2+}$ and Fe$^{3+}$ in glauconite under field conditions is related to the redox conditions under which it exists. This was also reflected in the color of the glauconite in thin sections.

Further studies of the glauconite in the reduced zones and its relationship to pyrite appear warranted. G. Odin (C.N.R.S., Laboratoire de Géologie des Bassins Sédimentaires, Université Paris VI, 75230 Paris Cedex 05, France, personal communication, 1984) has suggested that glauconite and pyrite should not form in the same environments. How then is the coexistence and intimate association of these minerals in the reduced zone of glauconite-bearing geologic columns to be explained? No answer to this question is currently available, but future investigations on glauconite should report from which part of the column the sample originates. The Mössbauer spectra and other differences noted here are clearly related to the zone of the column examined, reduced or oxidized.

ACKNOWLEDGMENTS

The computer time for this work was supported in full by of the Catholic University Computer Center. The analyses for total elemental S and Fe for the reduced-zone sample from New Jersey were made by Katie Haering and Mohammed El-Desoky, Department of Agronomy, University of Maryland.

REFERENCES


(Received 3 December 1987; accepted 1 July 1988; Ms. 1743)