MINERAL PHASES AND PROCESSES WITHIN GREEN PELOIDS FROM TWO RECENT DEPOSITS NEAR THE CONGO RIVER MOUTH

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ABSTRACT: In the recent sediments of the Congo River estuary, the green Fe-bearing peloids containing 7 Å phases are nearer to the river mouth than the 10 Å phyllosilicates. Measurements of $d_{100}$ for 7 Å minerals in various density fractions indicated a progressive transformation of kaolinite into trioctahedral 1:1 phyllosilicates in the zone with a high sedimentation rate. Projection of the chemical composition from the approximate crystallochemical formula onto a classification field confirmed the transformation of kaolinite into a 7 Å Fe-rich phase via substitution of Fe$^{3+}$ and Mg for Al in the octahedral sheet, with insignificant changes in the tetrahedral sheet. The resultant transition phase has a composition closer to greenalite than berthierine. The possible advancement of the evolution process was stopped by massive formation of goethite. The 10 Å minerals formed in the grains deposited in the off-shore sediments have a homogenous composition and occur in association with goethite and quartz. These peloids show an enrichment in Al although no kaolinite is present.

The occurrence of green peloids containing Fe-silicates in Recent marine deposits has been reported in numerous papers (e.g. Porrenga, 1967; Giresse & Odin, 1973; Hein et al., 1974; Odin & Matter, 1981; Van Houten & Purucker, 1984; Giresse et al., 1987). Formation of these peloids is related to the content and mobility of Fe in the sediments. The peloids are found on a large scale on the West African intertropical shelf, near rivers flowing over regions with sandy subsoils e.g. the Congo river, which carries considerable amounts of particulate Fe and suspended matter (Figuères et al., 1978).

In the zone of high sedimentation rate near the mouth of the Congo, we have observed massive formation of Fe-bearing 7 Å phyllosilicates. This process proceeds in organic-rich mud in an acid environment, and involves the introduction of Fe inside the grains over a period of $\sim 10^2$–$10^3$ years (Giresse, 1985). In off-shore conditions, farther from the river mouth, sedimentation is slower and grains remain for longer at the sediment-water interface transition zone; consequently, kaolinite is dissolved and micaceous layers are neoformed in a slow process which involves fixation of K from sea water. This process is estimated to take $10^4$ years (Giresse, 1985).

The aim of this paper is to give further information on mineral and chemical compositions of phases within the green peloids, and to continue the discussion of the two distinctly different mineral processes that take place in the superficial layer of the bottom sediments. The samples studied were collected $\sim 45$ km NW (sample 191) and $\sim 110$ km N (sample 210) of the Congo estuary. In these regions of the ocean, the bottom sediments vary in Fe$_2$O$_3$ and
C<sub>org</sub> contents. Sample 191 is derived from an area of 7 Å minerals containing 20–30% Fe<sub>2</sub>O<sub>3</sub> and 2–3% C<sub>org</sub>, and sample 210 is derived from a glauconite area with 10–20% Fe<sub>2</sub>O<sub>3</sub> and 3–4% C<sub>org</sub> (Gresse et al., 1987).

MORPHOLOGY OF THE PELOIDs

The magnetically-enriched Fe-bearing fractions were separated into density fractions using bromoform and methyl alcohol.

Sample 191 was divided into 5 density fractions. The most dense peloids (2.78 g/cm<sup>3</sup>—sample 2G) are ovoidal and brown, with shiny and smooth surfaces. The peloids from the next two fractions (2.70–2.78 g/cm<sup>3</sup>—4G, and 2.64–2.70 g/cm<sup>3</sup>—5G) are characterized by the occurrence of deep and irregular fissures, and brown, dull surfaces. The grains with density 2.53–2.64 g/cm<sup>3</sup> (6G) and with density < 2.53 g/cm<sup>3</sup> (7G) are ovoidal, black and dark with smooth surfaces. Among the grains of the latter fractions (7G) are also grains with the same morphology but with a pale gray colour (8G).

Sample 210 was divided into 4 density fractions. The heaviest fraction, > 2.78 g/cm<sup>3</sup> (9G) contains ovoidal peloids with shiny surfaces cut by a polygonal net of fine fissures infilled with green and white minerals. The grains from the 2.70–2.78 g/cm<sup>3</sup> density fractions (11G) are also ovoidal but deeply fissured. The 2.64–2.70 and 2.53–2.64 g/cm<sup>3</sup> density fractions (12G and 13G, respectively) contain typical botryoidal grains, with exactly the same morphology as those described by Boyer et al. (1977).

MINERALOGICAL COMPOSITION

The mineralogy was determined by X-ray diffraction (XRD) methods using Cu radiation (Gresse et al., 1987) and a Sigma 2070 diffractometer (CGR, France) supplied with focussing quartz monochromators. To improve the quality of the X-ray patterns of highly ferruginous samples, Co radiation has also been used. Oriented samples were examined using reflection diffractometry, and non-oriented aggregates (obtained by gentle crushing) by transmission diffractometry. The detailed interpretation of the XRD patterns has been given by Gresse et al. (1987) and in this paper some of the data are used to evaluate the distribution of mineral phases between the density fractions in order to facilitate understanding of the chemical processes inside the grains.

The 2G density fraction of sample 191 is almost pure goethite (Figs. 1 & 2) containing ~9 mol% AlOOH as estimated from the position of the (111) reflection (Norrish & Taylor, 1961; Brown, 1980). With decreasing density of the particles, the basal reflections of the 7 Å minerals become stronger and better resolved. These minerals are characterized by variable chemical composition in the octahedral sheet as estimated from the (331, 060) peak position. The precise angular positions of the apparent (060) reflection found by transmission diffractometry give values of \( d_{060} \) from 1.55 Å for 5G, to 1.53 for 6G, and 1.52 for the 7G samples. The fractions with density < 2.53 g/cm<sup>3</sup> (8G) contain some kaolinite as indicated by a peak at 1.48 Å.

The heaviest density fraction (9G) of sample 210 is composed principally of goethite. For the other density fractions, a gradual decrease in the goethite content accompanied by an increase in the quartz content is observed (Fig. 3). With decreasing density, the basal reflections of the 10 Å mineral become stronger and are shifted toward lower angles (Fig. 4).
indicating that the $d_{001}$ spacing is “apparent”, due to small domain sizes estimated to be $\sim 100 \, \text{Å}$ (equal to 10 layers per domain) by comparison with the data of Ross (1968). SEM micrographs indicated dimensions of the order of 200–300 Å. The observed decrease in the intensity of the (001) reflection for the samples saturated with ethylene glycol may therefore be due to increased dispersion, most likely due to the presence of mixed-layered illite-smectite (> 30%) (Reynolds, 1980).

In the series of diffraction patterns of different density fractions related to both the 7 Å minerals and the glauconite-like phases, the quartz content is higher in the lighter fractions which are poorer in goethite. Because the quartz peaks are partly overlapped by those of goethite in the heaviest density fraction, sample 2G was treated with dilute HCl to remove iron oxyhydroxides (Fig. 2). The quartz content calculated from the bulk chemical composition is between 9-1 and 12.4 wt% (Table 1), which is the lowest value in all the samples. The highest quartz content is in the glauconitic sample (13G, Table 1).

**CHEMICAL COMPOSITION**

Elemental concentrations were determined using a Camebax microprobe using a wavelength dispersive system at 15 kV accelerating voltage and 2 nA current. These conditions allowed count integration for 30 s with minimum surface deterioration. Analyses were made on carbon-coated, polished thin sections, count rates were compared with standard materials, and data were corrected using the ZAF program. Measurements were made at points along profiles, each point being checked using a polarising microscope associated with the microprobe to ensure that quartz- or iron oxyhydroxide-rich grains were not analysed.

The elemental concentrations of most grains vary little along profiles, as illustrated in Figs. 5–7. On average, the goethite peloids contain 71.9% Fe$_2$O$_3$ (2G–191), and 59.1% (9G–210). The Fe$_2$O$_3$ content decreases to 42% for the peloids with Fe-rich 7 Å phases, and to 32% for those containing glauconite (Table 2). The average Al$_2$O$_3$ content approaches 12% for the peloids with Fe-rich 7 Å phases and 6% for glauconitic peloids, whereas the SiO$_2$ content is 37% and 49%, respectively.

The differentiation in the content of the main elements (Al, Fe, Mg) in the peloids is illustrated on the concentration triangle in Fig. 8. The peloids with 7 Å minerals and those with glauconite are clustered within two fields, parallel to the Fe-Al axis and slightly but
markedly separated with respect to the Mg content, which is lower in the 7 Å phases than in the glauconite. Another concentration triangle (Fig. 9) with Si, Al and (Mg + Fe) contents suggests processes towards 7 Å or 10 Å minerals from kaolinite, with goethite dissociated from these processes.

The variation in the chemical composition of glauconite peloids is frequently limited to the outer zones where the Fe distinctly decreases and Al increases (Fig. 7, see also Velde & Odin, 1975).

**TRANSFORMATION OF KAOLINITE INTO 7 Å FE-RICH PHASE**

The content of goethite calculated from the bulk chemical composition averages 46 wt% of sample 7G which has been shown by microprobe point analyses to contain Fe in the structure.
of the phyllosilicate. The presence of structural Fe appears to be correct as grains for microprobe analysis were carefully selected to avoid goethitic (or quartzitic) grains. Determination of the oxidation state of the Fe in the silicates was not possible by direct methods, but it appears that the Fe is mostly divalent as the (060) spacing is in the range 1.53–1.55 Å indicating that the Fe-bearing phases are trioctahedral.

Neglecting the possible presence of Fe$^{3+}$ in the structure of the mineral as indicated by Mössbauer measurements on bulk samples, and also the fact that the Fe$^{2+}$/Fe$^{3+}$ ratio in
berthierines is between 5 and 10 (Brindley, 1982), the approximate structural formula calculated from the data in Table 2 (average SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, MgO point data from Fig. 6a) is:

\[(\text{Fe}_{1.44}\text{Al}_{0.75}\text{Mg}_{0.25}\square_{0.36})\text{(Si}_{1.96}\text{Al}_{0.04})\text{O}_5\text{(OH)}_4\]

where \square = vacancies in the octahedral sheet.

Although this formula is not fully definitive, it may be used to indicate the direction of the transformation of kaolinite in the microenvironment of the fecal pellets deposited close to the mouth of the Congo.

Analyses can also be classified using the projection system in Fig. 10 (Wiewiora, 1987; Weiss et al., 1982). The point representing the calculated crystallochemical formula on Fig.

Table 2. Chemical composition (mean values and standard deviations) of goethite peloids (9G, 2G), peloids with 7 Å Fe-minerals (7G) and glauconite peloids (13G) obtained by microprobe point analysis.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Na\textsubscript{2}O</th>
<th>MgO</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>SiO\textsubscript{2}</th>
<th>K\textsubscript{2}O</th>
<th>CaO</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>9G</td>
<td>0.05 ± 0.02</td>
<td>4.68 ± 0.74</td>
<td>6.43 ± 1.02</td>
<td>25.29 ± 7.75</td>
<td>3.08 ± 1.29</td>
<td>0.35 ± 0.12</td>
<td>59.15 ± 10.76</td>
</tr>
<tr>
<td>2G</td>
<td>0.13 ± 0.03</td>
<td>3.36 ± 0.59</td>
<td>5.78 ± 1.32</td>
<td>15.95 ± 4.64</td>
<td>1.06 ± 0.37</td>
<td>0.29 ± 0.12</td>
<td>71.9 ± 5.72</td>
</tr>
<tr>
<td>7G</td>
<td>0.36 ± 0.05</td>
<td>3.24 ± 0.31</td>
<td>13.1 ± 1.02</td>
<td>38.36 ± 1.84</td>
<td>2.51 ± 0.11</td>
<td>0.34 ± 0.08</td>
<td>42.72 ± 0.92</td>
</tr>
<tr>
<td>7Gb</td>
<td>0.34 ± 0.06</td>
<td>3.88 ± 0.64</td>
<td>12.53 ± 1.79</td>
<td>35.54 ± 3.92</td>
<td>2.02 ± 0.21</td>
<td>0.37 ± 0.07</td>
<td>44.00 ± 1.61</td>
</tr>
<tr>
<td>13G</td>
<td>0.08 ± 0.03</td>
<td>4.62 ± 0.47</td>
<td>4.87 ± 0.93</td>
<td>43.37 ± 4.49</td>
<td>5.96 ± 1.98</td>
<td>0.3 ± 0.12</td>
<td>31.25 ± 4.55</td>
</tr>
<tr>
<td>13Gb</td>
<td>0.08 ± 0.01</td>
<td>4.45 ± 0.18</td>
<td>6.08 ± 2.92</td>
<td>47.88 ± 1.22</td>
<td>6.91 ± 0.68</td>
<td>0.31 ± 0.08</td>
<td>36.62 ± 3.4</td>
</tr>
</tbody>
</table>
Green peloids near the Congo River mouth

**Fig. 5.** Microprobe point data for Fe$_2$O$_3$, SiO$_2$, Al$_2$O$_3$ and MgO along profiles in goethite grains.

**Fig. 6.** Microprobe point data for Fe$_2$O$_3$, SiO$_2$, Al$_2$O$_3$ and MgO along profiles in grains containing Fe-rich phases.
Green peloids near the Congo River mouth

10 is far away from kaolinite (dioctahedral species). It is in the field of trioctahedral species but fairly far from the end-member compositions of Fe-brindleyite, berthierine and greenalite. It is interesting to note that an arrow of transformation from kaolinite does not point to berthierine as the new phase. The process of transformation of kaolinite into 7 Å Fe-rich phases can hardly be called berthierinisation as suggested by Bhattacharyya (1983) for ironstones. In the observed initial stages of formation of the 7 Å Fe-rich phases in the environment inside the fecal pellets, the transformation seems to be limited to substitution of Fe$^{2+}$ and Mg for Al in the octahedral sheet with minor changes in the tetrahedral sheet. Therefore the transformation arrow points to greenalite rather than berthierine, but of course the process is far from being complete. The age of the sediments containing the minerals studied (always $<10^3$ years) may suggest that the phases studied are metastable during the "maturation" of the sediment, and may undergo changes not related to the process observed.

**DISCUSSION AND CONCLUSIONS**

Separation of the green peloids into different density fractions permitted their division into those containing predominantly phyllosilicates, and those composed mostly of goethite, thereby enabling the evaluation of the crystal chemistry of the individual phases with some precision.
Fig. 8. Differentiation of the main elements (Al, Fe, Mg) in Fe-bearing peloids.

Fig. 9. Differentiation of Si, Al and (Fe + Mg) in Fe-bearing peloids.
The most dense fractions are composed of goethite containing up to 9 wt% Al₂O₃. Other minerals are subordinate. With decreasing density, the content of quartz and phyllosilicate increases. As shown by microprobe analysis, the goethite peloids from the 7 Å and 10 Å mineral series contain 67% and 62% Fe₂O₃, respectively, and the Fe₂O₃ content decreases to 42% and 32% for peloids containing phyllosilicates in these series. The quartz content is higher in the lighter fractions and its distribution pattern in the different density fractions may be the result of the mechanical concentration of the siliclastics in certain very porous grains, and the result of relative accumulation during processes of transformation of phyllosilicates where the limit of stability of quartz may possibly be approached (Tardy & Gac, 1979).

As shown on the diagram for differentiation of the main elements (Al, Fe, Mg) the most aluminous peloids containing 7 Å minerals are clustered within two fields: one close to the Al corner representing peloids containing kaolinite, and the other peloids containing 7 Å Fe-rich phyllosilicates. Parallel to that cluster is the glauconite field, characterized by the highest Mg content in the 10 Å minerals studied. Within this field the triangles closer to the Al corner represent the border of the glauconite grains. With the exception of grain edges, the various glauconite grains have quite similar chemical compositions, and this homogeneity of glauconite grains may be explained by the quiescent off-shore conditions during low-rate
sedimentation. In these conditions the neoformation of glauconite proceeded according to characteristics provided by dissolution-precipitation theory (see e.g., Odin & Matter, 1981).

On the other hand, the formation of the 7 Å Fe-rich phyllosilicates takes place in the high-rate sedimentation zone, near the Congo River mouth, where the environment changes rapidly and where the dissolution and the transformation processes are never completed. In such conditions the transformation of kaolinite occurs initially in the octahedral sheet, where Fe can substitute for Al relatively easily due to an acid environment in which both cations are in a very mobile cationic form. With more massive introduction of Fe and with the increase in redox potential in the microenvironment of the fecal pellet due to bacterial activity, the transformation process is blocked. Then the transformation product has a composition intermediate between those of the end-members, kaolinite and greenalite, as shown in Fig. 9. This phase is metastable as indicated by its geological age (10²–10³ years) (Giresse, 1985). With changing sedimentation conditions and especially with diageneis this phase may undergo changes not necessarily related to those described above.

REFERENCES


