

TRANSFORMATION OF IRON-BEARING KAOLINITE TO IRON-FREE KAOLINITE, GOETHITE, AND HEMATITE

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Abstract—Ferruginous clay partings in limestones of the marine, largely evaporitic, Upper Triassic Mohila Formation (Makhtesh Ramon, Israel) contain hexagonal plates and cube-like bodies up to one millimeter across. Analyses by electron microscopy, infrared and Mössbauer spectroscopy, and X-ray powder diffraction indicate that the matrix contains Fe-rich anhedral kaolinite, up to 100 μm in size; the hexagonal plates are composed of euhedral, Fe-free kaolinite covered with well-developed acicular goethite and platy hematite (0.5 to 2 μm in size), and the cubes consist of fine-grained goethite with minor amounts of kaolinite. The anhedral kaolinite appears to be detrital, the hexagonal plates to be authigenic, and the cubes to be pseudomorphs after pyrite. Oxidation appears to have altered Fe-rich kaolinite and pyrite to Fe-free kaolinite, goethite, and hematite and was accompanied by recrystallization and pseudomorphic replacement. The alteration process was slow and was probably induced by a small increase in pH and in the Al/Fe ratio, resulting from oxidation of reduced components (pyrite, ferrous carbonate, organic matter) in a semiclosed, sediment-mud system. Overlying kaolinitic flint clay deposits may be the final product of a similar process.

Key Words—Goethite, Hematite, Iron, Kaolinite, Mössbauer spectroscopy, Oxidation, Pseudomorphism.

INTRODUCTION

Kaolinite is a common product of the weathering and degradation of feldspars and other aluminosilicates, occasionally proceeding to aluminum oxides and hydroxides (see, e.g., Grim, 1968). The process involves removal of different cations and concomitant enrichment of the product in Al. Fe may be leached from the kaolinite and precipitated as an oxide or oxyhydroxide. The laminated limestones of the Late Triassic Mohila Formation (Makhtesh Ramon, Israel) are interbedded with dolomite, gypsum, and some illite, kaolinite (mostly Fe-rich), and mixed-layer clay. They contain rare aggregates, up to a few centimeters across, of cubes of iron oxide, pseudomorphous after pyrite. This formation shows a lateral and vertical diversity of lithologies marking a transition between inner marine lagoons to salt marshes that were occasionally under alternating reducing and oxidizing conditions (Zak, 1981). It is overlain, and in places merges and interfingers laterally with lateritic and bauxitic clays and flint clays of the uppermost Mohila, Mish'hor, and Ardon Formations, which contain kaolinite and boehmite and some goethite, hematite, diaspore, anatase, and rutile (Slatkine and Heller, 1961; Rozenson *et al.*, 1980). Goldberg and Friedman (1974) and Goldbery (1979) suggested that the Mish'hor flint clays were formed during a period of emergence, through weathering in the vadose zone, and that in part they were transported and redeposited as continuous beds.

The present study intends to clarify by Mössbauer spectroscopy and scanning electron microscopy the characteristics and the genetic relationship between Fe-rich kaolinite, Fe-free kaolinite and iron oxides and oxyhydroxides present in the limestones of the Mohila

Formation, a relation that is important for understanding the formation of the flint clay deposits in the area.

EXPERIMENTAL

Samples of the Mohila laminated limestones containing about 98% calcite, were dissolved in 2 M HCl at room temperature. After rinsing with double distilled water, the residue was dried. This process was repeated until no trace of calcite was detected by X-ray powder diffraction (XRD) nor by the infrared (IR) absorption at 1430 cm^{-1} . The residue (see Results) was found to consist of a matrix of Fe-rich anhedral kaolinite, with embedded hexagonal plates and cubes, which were hand picked under the binocular microscope.

An IR examination between 4000 and 600 cm^{-1} was performed with a Perkin Elmer 237 spectrophotometer using KBr disks dried at 110°C for 24 hr. To estimate the relative amount of goethite and kaolinite, a calibration curve was constructed from spectra of mixtures of goethite (Hebrew University; HU-736) and kaolinite (from Georgia; Ward's Natural Science Establishment, Rochester, New York), in ratios ranging from 1:1 to 50:1. IR bands used for quantitative determinations were 1000 cm^{-1} for kaolinite and 810 cm^{-1} for goethite. XRD analysis was performed on the clay fraction (preferred orientation). The separated fractions (hexagonal plates and cubes) were analyzed by scanning electron microscopy (SEM) using a Cambridge S4 instrument coupled with a Link nondispersive X-ray analyzer.

Mössbauer spectra were measured at room temperature in the velocity range -10 to $+10$ mm/sec, and detailed analysis was carried out also in the velocity range -4 to $+4$ mm/sec. Spectra of the hexagonal plates were also recorded at liquid air temperature (90°K). The

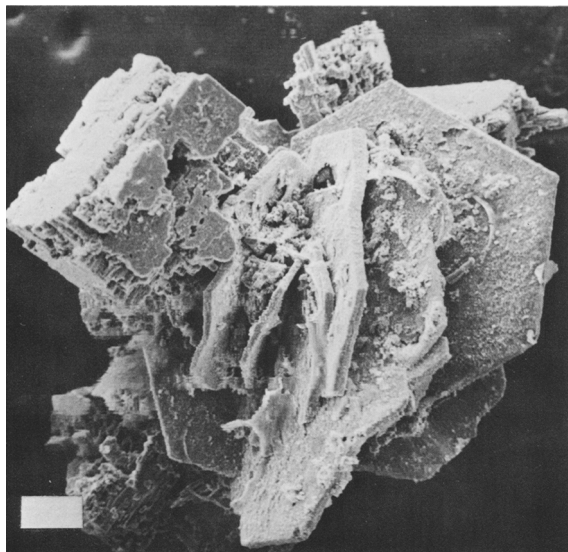


Figure 1. Scanning electron micrograph of hexagonal plates of kaolinite covered with goethite and hematite, and cubes of goethite clusters, pseudomorphous after pyrite. Scale bar = 200 μm .

analytical procedure was described by Rozenon *et al.* (1979). The spectra of samples containing magnetic fractions at room temperature (hexagonal plates and cubes) were assigned by fitting to a central doublet and a split 6-line spectrum. The fitting was satisfactory for the cubes (giving $\chi^2 = 250$ for 200 channels). The spectra of the hexagonal plates corresponded well with a central doublet and two split 6-line sub spectra ($\chi^2 =$

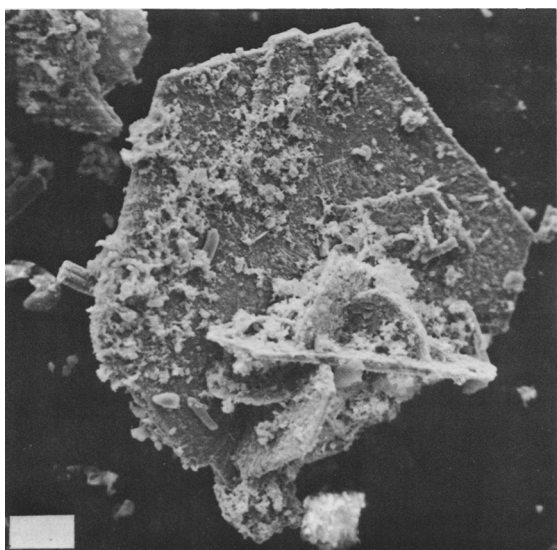


Figure 2. Scanning electron micrograph of kaolinite pseudohexagons covered with goethite and hematite (higher magnifications in Figures 3 to 5). Scale bar = 50 μm .

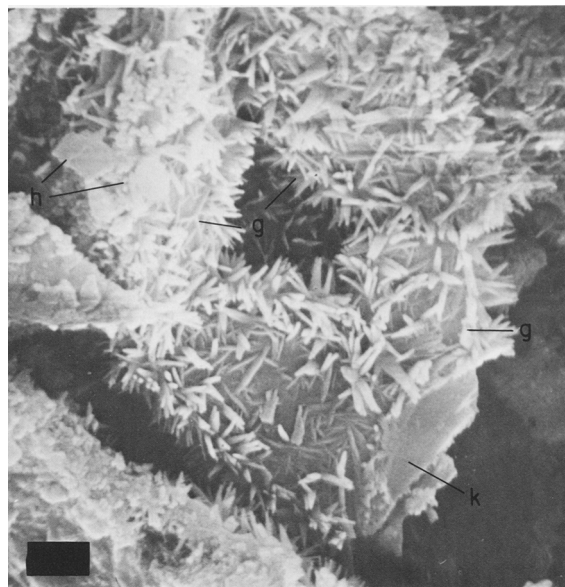


Figure 3. Scanning electron micrograph of acicular and blade-like goethite (g) and platelets of hematite (h) covering euhedral kaolinite (k). Scale bar = 2 μm .

236). The anhedral clay fraction was fitted to a single doublet ($\chi^2 = 225$), and although the line width was comparatively large, the addition of a doublet did not improve the fitting or the χ^2 value.

Solubility curves were calculated and drawn according to the procedure of La Iglesia and Van Oosterwyck-Gastuche (1978) for the species $\text{Al}(\text{OH})_3^0$, $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$, and Al^{3+} for Al-kaolinite and the species $\text{Fe}(\text{OH})_4^-$, $\text{Fe}(\text{OH})_3^0$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_2^{2+}$, and Fe^{3+} for Fe^{3+} -kaolinite. The free energy of the hypothetical species $\text{Si}_4\text{Fe}_3\text{O}_{10}(\text{OH})_4$ was calculated according to the method of Tardy and Garrels (1974), because no experimental free energy data for Fe^{3+} -kaolinite were available.

RESULTS

The constituents of the clay partings, determined by the various methods and described in the following, include: anhedral, Fe-rich kaolinite, which constitutes the matrix fraction; hexagonal plates, consisting of Fe-free kaolinite with acicular goethite and platelets of hematite; and cubes composed of closely packed mass of very fine goethite.

Texture and morphology

The matrix fraction consists of anhedral clay grains, a few tens to about 100 μm across, showing abraded surfaces. The hexagonal plates and cubes are from a few hundred micrometers to somewhat more than one thousand micrometers across (Figures 1 and 2). They occur in about equal amount and constitute 10–25% of

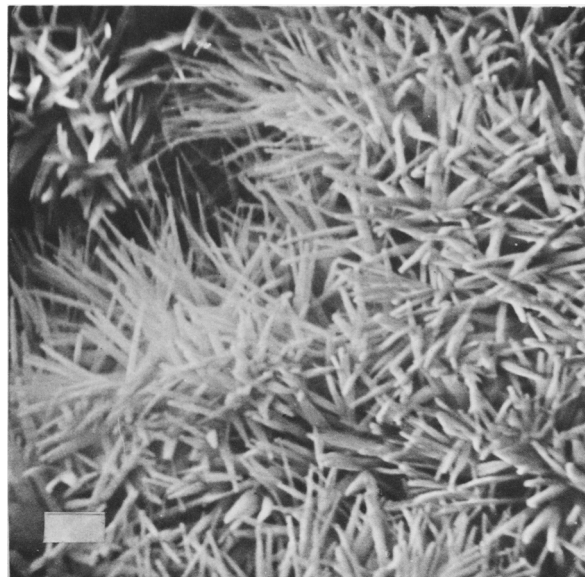


Figure 4. Scanning electron micrograph of acicular goethite crystals. Scale bar = 1 μm .

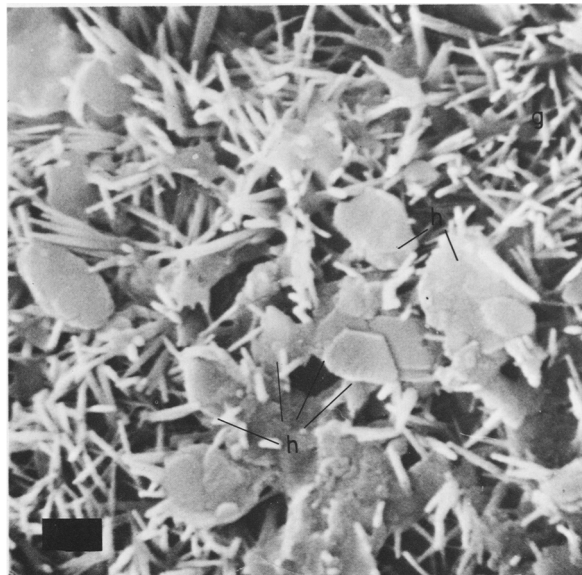


Figure 5. Scanning electron micrograph of platelets of hematite (h) and acicular goethite (g). Scale bar = 1 μm .

the partings, by weight. Under high magnification the hexagonal plates appear to consist of smaller plates, in a closely packed arrangement. The plates are lined with clusters of needle- or blade-like crystals, 1–2 μm long and 0.1 μm broad (Figures 3–5). These acicular crystals locally occur together with small platelets, 0.5–2.0 μm in size (Figures 3 and 5), similar to those that make up the large hexagonal plates but considerably smaller. The acicular crystals resemble artificially precipitated goethite, whereas the small platelets resemble hematite (Atkinson *et al.*, 1977). Neither was observed on the anhedral clay grains. The cubes have etched surfaces and consist of very fine crystals (goethite) packed in massive bands (Figure 6), probably following the rectangular etch pattern of the pyrite that they replaced.

X-ray powder diffraction, infrared spectra and nondispersive X-ray analyses

The matrix fraction insoluble in dilute HCl gave rise to IR spectra of well-ordered kaolinite (as defined by Parker, 1969). The IR spectra of separated, hand-picked grains of hexagonal plates and cubes showed absorption of well-ordered kaolinite and bands at 890 cm^{-1} and 790 cm^{-1} , characteristic of Al-free goethite (Mendelovici *et al.*, 1979). The goethite to kaolinite ratio in the hexagonal plates and cubes (estimated from IR spectra of artificial mixtures) is 10:1 and 50:1, respectively. Kaolinite seems thus to be the second major constituent of the hexagonal plates; in the cubes it is present as an impurity. XRD patterns of the plates and cubes showed well-crystallized kaolinite (though with less intense peaks for the cubes), but the patterns of iron oxides were poor probably due to low crystallinity

(Mendelovici *et al.*, 1979). Quantitative estimation of the phases is therefore based on IR spectra alone. By means of nondispersive X-ray analysis, the anhedral kaolinite was found to consist of Fe, Si, and Al in approximately constant ratio. The same constituents, but with variable Fe, were recorded for the hexagonal plates. Only Fe was found in the acicular (goethite) crystals and the small (hematite) platelets.

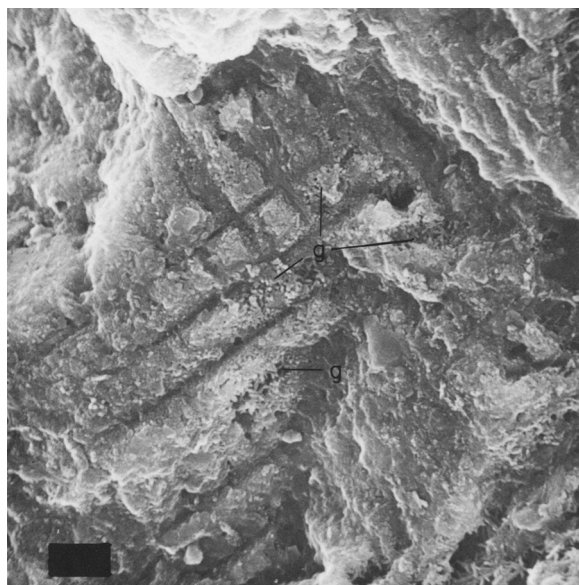


Figure 6. Scanning electron micrograph of acicular goethite (g) densely packed in rectangular, etched bands, in a cube pseudomorphous after pyrite. Scale bar = 1 μm .

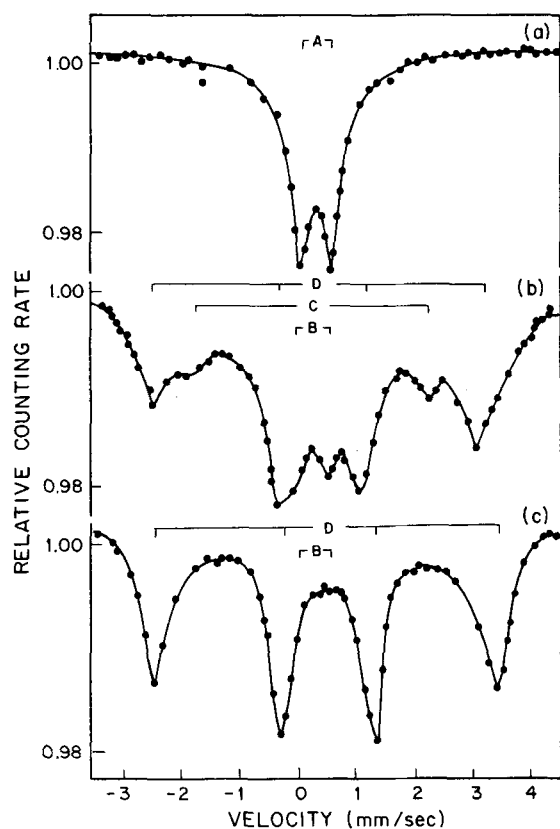


Figure 7. Mössbauer spectra taken at room temperature in the velocity range -4.0 to $+4.0$ mm/sec. (a) anhedral kaolinite; (b) hexagonal plates; (c) cubes. A and B = central doublets of Fe^{3+} in kaolinite and in fine-grained superparamagnetic phase, respectively; C and D = central lines of 6-line spectra of Fe^{3+} in hematite and in goethite, respectively.

Mössbauer spectra

Mössbauer spectra of the anhedral clay fraction and separated hexagonal plates and cubes revealed phases containing Fe^{3+} and no high-spin Fe^{2+} (Table 1 and Figure 7). In these fractions Fe^{3+} may occur in: (1) octahedral sites of kaolinite, (2) crystalline oxides and oxyhydroxides, and (3) very fine-grained iron oxides or oxyhydroxides which show superparamagnetic behavior. These phases have characteristic Mössbauer parameters which permit their identification and the estimation of their relative abundance, assuming similar free recoil fractions for all phases. To establish the parameters of the central doublet, spectra were measured between -10 and $+10$ mm/sec, and also between -4 and $+4$ mm/sec.

Hexagonal plates. The spectrum obtained from the hexagonal plates (Figure 7b shows its central lines) may be resolved into three subspectra: (1) a six-line spectrum of Al-free goethite (D in Figure 7b) characterized

by H_{eff} of 370 kOe and 500 kOe at room temperature and 90°K , respectively (Hogg *et al.*, 1975; Kodama *et al.*, 1977); (2) a six-line spectrum of hematite (central lines, C in Figure 7b) having an H_{eff} of 520 kOe and of 555 kOe at room temperature and 90°K , respectively; and (3) a central doublet (B in Figure 7b) which shows a QS of 0.51 mm/sec at room temperature. This central doublet may be identified with three possible phases: Fe^{3+} in kaolinite; Fe^{3+} in paramagnetic crystalline oxides and oxyhydroxides (such as lepidocrocite and ferrihydrite); and with fine-grained superparamagnetic phases of Fe^{3+} oxides and hydroxides. An indication for a very fine-grained superparamagnetic phase is the disappearance of the central doublet in a room temperature spectrum after treating the sample with a 2 M HCl solution (cf. Spiro and Rozenson, 1980). This central doublet almost completely disappears at 90°K (indicating the absence of paramagnetic crystalline oxides and oxyhydroxides; Kodama *et al.*, 1977), whereas the intensity of the 6-line spectrum of goethite increases, an indication of a crystal size of about 100 Å (Kündig *et al.*, 1966). These data also show that no Fe^{3+} is contained in the kaolinite. It is therefore concluded that the hexagonal platy kaolinite does not contain structural iron and that the superparamagnetic behavior of finely crystalline goethite gave rise to a doublet at room temperature.

Cubes. The dominant component of the Mössbauer spectrum of the cubes is a 6-line spectrum of goethite (the four central lines are shown in D, Figure 7c) with an H_{eff} of 370 kOe at room temperature. A small central doublet (B in Figure 7c) indicates the presence of associated fine-grained oxides (kaolinite is only a minor constituent, as indicated by the IR spectra, and thus Fe^{3+} in kaolinite may at most make a minor contribution to the Mössbauer spectrum of this fraction).

Anhedral, Fe-rich kaolinite. A central doublet with parameters characteristic of structural Fe^{3+} in kaolinite (Rozenson *et al.*, 1979) is the main feature of the spectrum of anhedral, Fe-rich kaolinite (Table 1 and A in Figure 7a). The total area of the spectrum (Spiro and Rozenson, 1980) indicates a content of about 10% Fe_2O_3 . To estimate the amount of surficial fine-grained iron oxide which may contribute to this doublet, the kaolinite was treated with 2 M HCl at room temperature for 24 hr, a treatment which should have removed any adsorbed, finely crystalline, noncrystalline iron oxides and oxyhydroxides (Spiro and Rozenson, 1980). No decrease in the total area was recorded following this treatment, indicating that no finely crystalline iron oxides (such as that in the hexagonal plates and cubes) is associated with the anhedral kaolinite, and that the Fe^{3+} is structural. This conclusion agrees with the finding that no significant variations of the Fe:Si:Al ratios were recorded by the nondispersive X-ray analyzer from

Table 1. Mössbauer parameters of the anhedral kaolinite, hexagonal plates, and cubes.

Sample	Temp. °K	Fe ³⁺ in goethite				Fe ³⁺ in hematite				Fe ³⁺ central doublet			
		IS	QS	H _{eff}	Fe ³⁺ (%)	IS	QS	H _{eff}	Fe ³⁺ (%)	IS	QS	Γ	Fe ³⁺ (%)
Hexagonal plates	298	0.65	-0.40	320	60	0.65	0.51	520	20	0.48	0.50	0.55	20
Hexagonal plates	90	0.75	-0.30	500	80	0.50	-0.60	555	20	—	—	—	—
Cubes	298	0.63	-0.45	365	70	—	—	—	—	0.47	0.49	0.60	30
Anhedral kaolinite	298	—	—	—	—	—	—	—	—	0.33	0.62	0.43	100
Anhedral kaolinite (2 M HCl)	298	—	—	—	—	—	—	—	—	0.33	0.62	0.43	100

IS = isomer shift relative to Fe metal at room temperature; QS = quadrupole splitting; Γ = line width; all in mm/sec. H_{eff} = effective magnetic field (kOe); Fe³⁺ (%) = weight percent of total Fe³⁺. Errors for IS, QS, and Γ are ± 0.03 mm/sec; error for H_{eff} is ± 2 kOe, and for Fe³⁺ (%) is $\pm 4\%$.

grain surfaces and cleavage planes of several anhedral kaolinite particles in treated and untreated samples. The line widths given by the magnetic phases are somewhat large (0.50–0.55 mm/sec) which may be due to structural imperfections (Murad, 1979).

DISCUSSION

Relations between mineral phases

The euhedral form of the kaolinite in the hexagonal plates, their large crystal size, their well-developed crystallinity (as inferred from SEM and IR spectra), and their Fe-free composition (as inferred from Mössbauer spectra) point to an authigenic origin. It seems unlikely that detrital kaolinite could preserve such large size and perfect morphology. These features are also characteristic of the kaolinite in the flint clay overlying the limestone of the Mohila Formation (Slatkine and Heller, 1961; Bendor, 1966; L. Heller-Kallai, Department of Geology, The Hebrew University, Jerusalem, Israel, unpublished data). The well-developed needles and blades of goethite associated with the Fe-free kaolinite in the hexagonal plates differ from goethite and other oxides and oxyhydroxides that commonly occur as poorly developed coatings on mineral grains (e.g., those in the overlying Ardon Formation; Rozenon *et al.*, 1980). They resemble, however, goethite crystals grown by ageing of noncrystalline iron oxides (Atkinson *et al.*, 1977). It is significant that the crystalline goethite and hematite occur exclusively on the authigenic, Fe-free kaolinite and not on the anhedral, Fe-rich kaolinite.

The morphology of the kaolinite and goethite and the chemical composition of the kaolinite suggest a process of recrystallization resulting on the one hand in euhedral, hexagonal, Fe-depleted kaolinite and the deposition of the Fe derived from the kaolinite as crystalline goethite and hematite on the other. The crystalline iron oxide associated with the euhedral kaolinite consists of three phases—superparamagnetic, fine-grained goethite, and well-developed goethite and hematite—as

defined by Mössbauer spectroscopy and by SEM. Although its relative stability is somewhat obscure, it seems that the surface of the Fe-free kaolinite acts as a substrate for the following stepwise or simultaneous reactions: fine grained iron oxides and hydroxides \rightarrow goethite \rightarrow hematite, as also suggested by the textural growth relationship shown in platelets of hematite hanging on needle- or blade-like goethite, which is rooted on kaolinite plates (Figures 3 and 5). It seems that much of the Fe associated with the hexagonal plates originated from the Fe-rich kaolinite. The occurrence of goethite pseudomorphous after pyrite is ubiquitous (see, e.g., Berry and Mason, 1959). In the present samples the cubic morphology preserved in the mass of tiny goethite crystals of the formation investigated may be related to pyrite cubes of similar dimensions found somewhat lower in the section, and to aggregates of cube pseudomorphs, a few centimeters across, found scattered in the section (Zak, 1981).

Mechanism

The morphology described above suggests a replacement mechanism, whereby Fe-rich kaolinite and pyrite are replaced by goethite and hematite, in a manner that resembles pseudomorphism. The kaolinite replacement is associated with recrystallization as revealed by its Fe-free chemical composition and its well-developed crystallinity and morphology. These processes are apparently sequential. The question arises as to why only one type of kaolinite recrystallized while the other in the immediate vicinity and exposed to the same conditions did not. The Fe content of the kaolinite may be a decisive factor. This suggestion is supported by probably analogous mineralogical features in the Ardon Formation, where similar mineral assemblages, also including Fe-rich kaolinite (approximately 0.4 Fe per formula unit, i.e., 11% Fe₂O₃) occur in a succession of progressive stages of decomposition (Rozenon *et al.*, 1980). Fe-rich kaolinite may react according to the following scheme: Fe³⁺-kaolinite \rightarrow Fe³⁺-oxides + Al-ka-

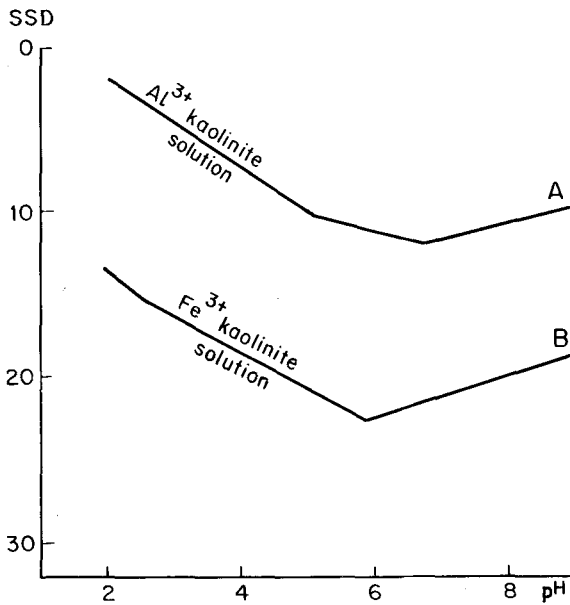


Figure 8. Stability diagram of Fe^{3+} -kaolinite and Al-kaolinite. SSD = degree of solubility, the activity product of soluble silicon species and aluminum or iron species (species are listed in the text). $\text{SSD} = -\log[\text{H}_4\text{SiO}_4] [\text{sp Al}; \text{sp Fe}]$.

olinite + silica and alumina residue. A strictly thermodynamic explanation is not straightforward, therefore the stability diagram of Fe^{3+} -kaolinite and Al-kaolinite (Figure 8) was calculated to determine the conditions under which these phases are stable (see above). It seems that a change in conditions may have caused the reaction, which affected only the Fe-rich kaolinite. The process may be described as an extraction of Fe from this mineral. Figure 8 shows that because Al-kaolinite is more soluble than Fe^{3+} -kaolinite, conversion of Fe^{3+} -kaolinite to Al-kaolinite implies a higher than critical Al/Fe ratio in the pore solution, at a limiting pH. The critical Al/Fe ratio is difficult to calculate because thermodynamic data are sparse. The data on Al/Fe ratios in seawater or formation water are not useful because Al and Fe may be present in metastable (colloidal) forms. Iron oxides are insoluble in this pH range and would precipitate. Thus, the reaction is not an equilibrium reaction, but, beyond a threshold, the removal of Fe from the solution caused the reaction to proceed. The well-developed euhedral crystals of kaolinite, goethite, and hematite point to a slow reaction. The change in pH is probably of subordinate importance, but may be related to the input of land-derived, Fe-rich kaolinite of soil or lateritic origin into marine carbonate environments, or to later stages of diagenesis. The Fe-poor kaolinite did not undergo this reaction.

The Fe/Al ratio in the hexagonal plates is not the same as that in the original kaolinite (see above). The recrystallization process probably took place in an

open system, and the excess solubilized Al could have been incorporated in goethite. However, the associated goethite contains no appreciable amounts of Al, which apparently was removed and may have precipitated elsewhere. This scheme may apply to sequences of Fe-rich kaolinite and Al-kaolinite associated with iron oxides and bauxites representing the result of extreme leaching. Such sequences are found in the laterally occurring and overlying iron clays and flint clays of the Mohila, Mish'hor, and Ardon Formations.

The occurrence of goethite (with no hematite) as pseudomorphs after pyrite in the upper part of the Mohila limestones does not seem to be directly related to the process affecting the Fe-rich kaolinite, but is regarded as indicating a change to oxidizing conditions. The occurrence of laterally developed pockets of flint clay within and overlying an irregularly dissolved surface in the upper Mohila limestones and dolomites points to a karst-like process. Similarly, the recurrence of clay partings within the limestone beds mark episodes of dissolution or hindered precipitation of carbonates. Slow reactions and recurring changes of pH and redox potential, however, seem to favor a dissolution process with little transfer of water. Such a process would require acids more concentrated than bicarbonate, which may be produced by oxidation of pyrite to goethite in these rocks, as well as by oxidation of organic matter and ferrous carbonate found in the vicinity, probably in an environment of stagnant, marine salt marshes.

CONCLUSIONS

Euhedral, pseudohexagonal, Fe-depleted kaolinite in clayey partings within the limestones of the upper part of the Mohila Formation were formed by the recrystallization of anhedronal, Fe-rich kaolinite, a process that also led to the deposition of the extracted Fe as well-developed acicular goethite and platy hematite and to the removal of alumina and silica residue. This reaction involves solutions having an Al/Fe ratio higher than a threshold ratio along with a slight increase in pH, as derived from stability diagrams of these phases. Associated cubes, consisting of fine-grained goethite pseudomorphous after pyrite, indicate a change from reducing to oxidizing conditions. The ratio of goethite and hematite to kaolinite in this assemblage is too high to be compatible with a closed system; the alumina removed was probably deposited in the laterally occurring and overlying flint clay pockets and beds. The recurrence of these clayey partings (and also beds, in the overlying section) indicates a transient physicochemical environment. A process of slow alteration is envisaged, induced by the oxidation of reduced components (pyrite, ferrous carbonate, organic matter) through lowering of the oxidation/reduction interface, in a semi-closed sediment-mud system, in accordance with a salt marsh environment.

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Резюме—В морских хемогенных известняках свиты Мохила (верхний триас р-на Махтеш Рамон, Израиль) встречаются тонкие обогащенные железом глинистые прослойки, содержащие гексагональные пластинки и кубики размером до 1 мм. Электронная микроскопия, инфракрасная и моссабауэровская спектроскопия и рентгеновская дифрактометрия позволили установить, что вмещающая порода состоит из ксеноморфных частиц железистого каолинита размером до 100 мкм. Гексагональные пластинки сложены идиоморфным безжелезистым каолинитом. Пластинки покрыты хорошо окристаллизованными игольчатыми агрегатами гетита и пластинчатого гематита размером 0,5 – 2,0 мкм. Кубики содержат тонкозернистый гетит со следами каолинита. Ксеноморфный каолинит по-видимому является обломочным, гексагональные пластинки—аутигенные. Кубики представляют собой псевдоморфозы по пириту. В результате окисления железистый каолинит и пирит были преобразованы в безжелезистый каолинит, гетит и гематит. Этот процесс сопровождался перекристаллизацией и псевдоморфизмом. Процесс замещения был медленным и вероятно был вызван небольшим увеличением рН и отношения Al/Fe как результат окисления пирита, железистых карбонатов и органического вещества в полузамкнутой системе рыхлого ила. Залегающие выше по разрезу слои каолиновых огнеупорных глин возможно являются конечным продуктом аналогичного процесса. [A. Cohen]

Resümee—Eisenhaltige Tonanteile in Kalken der marinen, hauptsächlich evaporitischen, obertriassischen Mohila Formation (Makhtesh Ramon, Israel) enthalten hexagonale Plättchen und würfelförmige Teilchen bis zu einem Millimeter Durchmesser. Untersuchungen mittels Elektronenmikroskop, Infrarot- und Mössbauerspektroskopie sowie Röntgenpulverdiffraktometrie deuten darauf hin, daß die Matrix Fe-reichen, xenomorphen, bis zu 100 μm großen Kaolinit enthält; die hexagonalen Plättchen sind idiomorphe Fe-freie Kaolinite, die mit gut kristallisiertem nadelförmigem Goethit, und plättchenförmigem Haematit (0,5 bis 2 μm groß) umgeben sind. Die Würfel bestehen aus feinkörnigem Goethit mit geringen Anteilen von Kaolinit. Die xenomorphen Kaolinite scheinen detritisch zu sein, die hexagonalen Kaolinite authigen und die Würfel dürften Pseudomorphosen nach Pyrit darstellen. Durch Oxidation scheint der Fe-reiche Kaolinit und der Pyrit in Fe-freien Kaolinit, Goethit, und Haematit umgewandelt worden zu sein, wobei es gleichzeitig zur Rekrystallisation und zur Bildung von Pseudomorphosen kam. Der Umwandlungsprozeß ging langsam vor sich und wurde wahrscheinlich durch eine kleine Erhöhung des pH-Wertes und des Al/Fe-Verhältnisses verursacht, was aus der Oxidation der reduzierten Komponenten (Pyrit, Fe-haltige Karbonate, organisches Material) in einem halbgeschlossenen Sediment-Schlamm-System resultierte. Die überlagernden kaolinitischen Flintclay-Lagerstätten könnten das Endprodukt eines ähnlichen Prozesses sein. [U.W.]

Résumé—Des lamines d'argiles ferrugineuses dans les calcaires de la formation Mohila, marine et en grande partie évaporitique du Triassique Supérieur (Makhtesh Ramon, Israël) contiennent des plaques hexagonales et des cubes mesurant jusqu'à un millimètre de large. Des analyses par microscopie électronique, par spectroscopie infrarouge et de Mossbauer, et par diffraction des rayons-X indiquent que la matrice contient de la kaolinite anhédrale riche en Fe mesurant jusqu'à 100 μm ; les plaques hexagonales sont composées de kaolinite euhédrale sans Fe couverte de goéthite aciculaire bien développée et d'hématite en plaquettes (mesurant de 0,5 à 2 μm), et les cubes consistent de goéthite à fins grains avec des quantités moindres de kaolinite. La kaolinite anhédrale semble être detritique, les plaques hexagonales authigéniques, et les cubes semblent être des pseudomorphes après la pyrite. L'oxydation semble avoir altéré la kaolinite riche en Fe et la pyrite en kaolinite sans Fe, goéthite et hématite, et avoir été accompagnée d'une recristallisation et d'un remplacement pseudomorphique. Le procédé d'altération était lent et a été probablement induit par une faible augmentation du pH et de la proportion Al/Fe résultant de l'oxydation de composants réduits (pyrite, carbonate ferreux, matière organique) dans un système sédiment-boue miconfiné. Des dépôts susjacentes de "flint-clay" kaolinitiques pourraient être les produits finaux d'un procédé semblable. [D.J.]