

## THE CRYSTALLINITY OF MINERALS—A NEW VARIABLE IN PEDOGENETIC PROCESSES: A STUDY OF GOETHITE AND ASSOCIATED SILICATES IN LATERITES

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**Abstract**—The crystallinity of minerals in terms of crystallite size distribution and lattice perfection is quantified by means of statistical measures derived from X-ray line profiles ( $2\sigma$  values). A low degree of crystallinity facilitates the non-stoichiometric incorporation of foreign elements in the crystal lattice. Crystallinity is affected by a number of factors and in natural profiles it may vary laterally as well as vertically.

For instance, goethite in laterite deposits shows decreasing crystallinity with increasing depth. Serpentine type minerals, on the other hand, show the lowest crystallinity at the surface where the degree of weathering is the most advanced. The presence of silica in migrating solutions prevents crystal growth and results in a low degree of crystallinity of minerals such as goethite. This has been observed in natural profiles and has been confirmed by laboratory experiments on the synthesis of goethite and sodium-birnessite. The crystallinity of minerals affects their response to extractive procedures. It could also be an important parameter in soil science.

### INTRODUCTION

In dealing with laterites from a geochemical and a technological point of view, some variability in thermal properties of goethites of different horizons within the lateritic alteration profiles has been observed. This information could be of interest to soil science and it could also find application in soils other than lateritic. In a recently published paper (Kühnel, van Hilten and Roorda, 1974), it was attempted to quantify crystallinity on the basis of statistical measures derived from the analysis of X-ray line profiles. Crystallinity is, despite frequent usage of the term, not always uniformly interpreted. It is often confused with particle size distribution. The latter, however, is often strongly affected by aggregation, and can therefore not be used as a measure of crystallinity.

### BRIEF CHARACTERISTICS OF THE DEVELOPMENT OF CRYSTALLINITY

The alteration of basic rocks into iron-rich laterites is a complicated process which is accompanied by drastic alterations of the physical, chemical mineralogical, structural and textural properties which in turn determine the properties of the final product. Laterites are important raw materials not only as a source of iron ore but also of nickel, cobalt and chromium.

All natural processes tend to approach equilibrium. The soil represents a multicomponent open system. Under continuously changing physical and chemical conditions, many minerals become unstable and are replaced by more stable ones. The process of alteration proceeds at different rates and at different times

as far as particular mineral components are concerned. Since the multicomponent system is open, migration provides supply and removal of some components. This results in the natural redistribution and, to some extent, in a segregation and concentration of elements. As a result, a new mineral assemblage results which corresponds to the new condition. However, in open system complete equilibrium is never reached. There are numerous reactions and processes which take place during weathering, including dissolution, nucleation, crystal growth, recrystallization, hydration, oxidation and reduction. All of these tend to establish steady state conditions, or at least a *partial equilibrium* between phases in mutual contact.

During this alteration, the crystallinity of particular mineral phases develops. It begins with the nucleation and crystalline growth as controlled by many internal (structural) and external (environmental) conditions. Crystallinity changes may also result from recrystallization, which can be either spontaneous or induced by external conditions. Frequently, the developments of the crystallinities of co-existing phases proceed at different rates and in different directions. Crystallinity therefore becomes a *new variable* in the development of a soil because the same mineral may show different degrees of crystallinity in vertical and lateral profiles.

### THE QUANTIFICATION OF CRYSTALLINITY

Particle size distribution is frequently used as an important diagnostic value of a soil. Another important parameter is the fraction of amorphous constituents. However, these cannot fully characterize crystallinity because the aggregation of fine particles

modifies the true size distribution especially in the sub-sieve ranges (below 50 microns). Crystallinity should be understood in terms of *crystal size distribution and of structural perfection*. This interpretation of crystallinity is in accordance with the original crystallochemical and structural crystallographic concepts (see Bragg, 1933; Jones, 1937; and Kochendorfer, 1944). Recently, it appears that a new term should be taken into the consideration, namely the shape (habit) of the crystallites since this greatly influences the orientation of crystallites in natural and artificial mixtures. The key problem is the quantification of crystallinity. A method has been published recently (*loc. cit*) which proposes the standard deviation (actually  $2\sigma$  value) in  $2\theta^\circ$  obtained from the statistical evaluation of the X-ray line profile, taken as frequency curve of relative intensities, as a measure of crystallinity. For goethite, the main line  $d_{110} = 4.18$  Å is used and the line profile is either recorded on an expanded scale or step-scanned. The most important conclusion is that the *value  $2\sigma$  remains constant* at different degrees of dilution. In other words it is a measure that is independent on the amount of the mineral in the mixture. A simple comparison of data processed by a computer program can quantify the broadening of line profiles normally used for particle

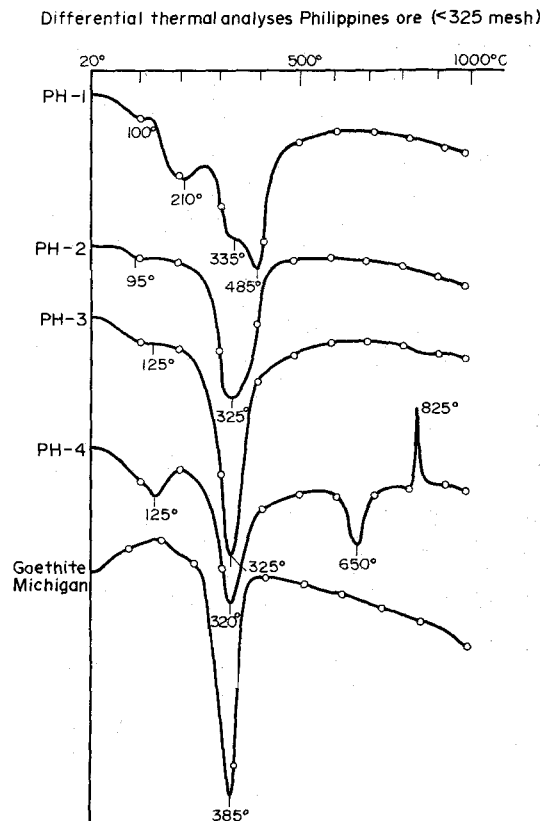


Fig. 1. DTA curves of four laterite zones show the characteristic thermal phenomena of goethite, serpentine and gibbsite. The dehydroxylation of goethite culminates at 320–330°C, compared with 385°C for the well-crystallized goethite standard from Michigan. P.E. Queneau (1971).

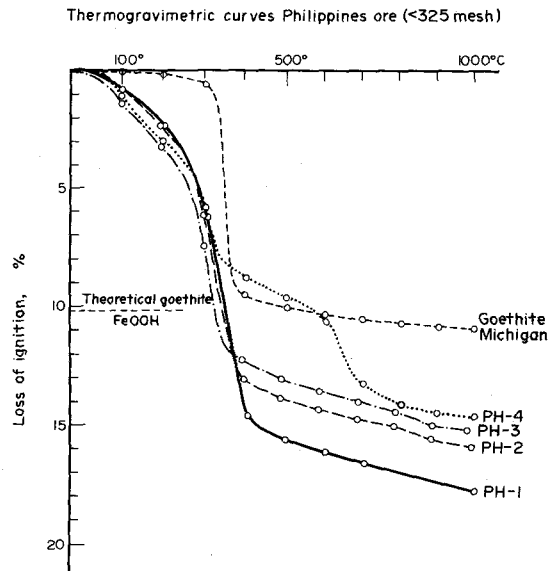


Fig. 2. TG curves of four laterite zones show that the poorly crystalline goethite contains generally more water than the theoretical goethite. However, the curves are influenced by the presence of other minerals (e.g. serpentine mineral in PH-4). P.E. Queneau (1971).

size distribution. No special “index of crystallinity” is introduced. These data are compared with a well-crystalline standard mineral. The best crystallinity has been observed on goethite from Michigan. Any synthetic goethite exhibits lower crystallinity. The chemical composition of Michigan goethite is very close to the theoretical. The crystallinity of goethite affects its thermal properties as well as its composition. Figures 1 and 2 compare thermal properties of poorly crystalline natural goethite from a laterite with perfectly crystalline goethite from Michigan (Mineralogical and Geological Museum, Delft, no. 12558). The problem of the crystallinity of minerals has not yet been solved completely and it is being further investigated by means of instrumental techniques, including Scanning and Transmission Electron Microscopy, Electronprobe Microanalysis, Differential Thermal Analysis, Thermogravimetric Analysis and Infrared Absorption Spectroscopy. The last mentioned was used by Landa and Gast (1973) to evaluate the crystallinity of hydrated ferric oxides.

#### CRYSTALLINITY-COMPOSITION RELATIONSHIP

The importance of structural perfection in the evaluation of crystallinity has been indicated already. The degree of structural imperfection may be considered to be the second face of crystallinity. So-called “high defect materials” behave in a similar fashion to “poorly crystalline materials”. For the characterization of crystallinity the number of defects as well as their distribution are important. The basic task of geochemistry applied to mineral technology is the determination of *element distribution and partition in co-existing phases*. In laterites many minor elements

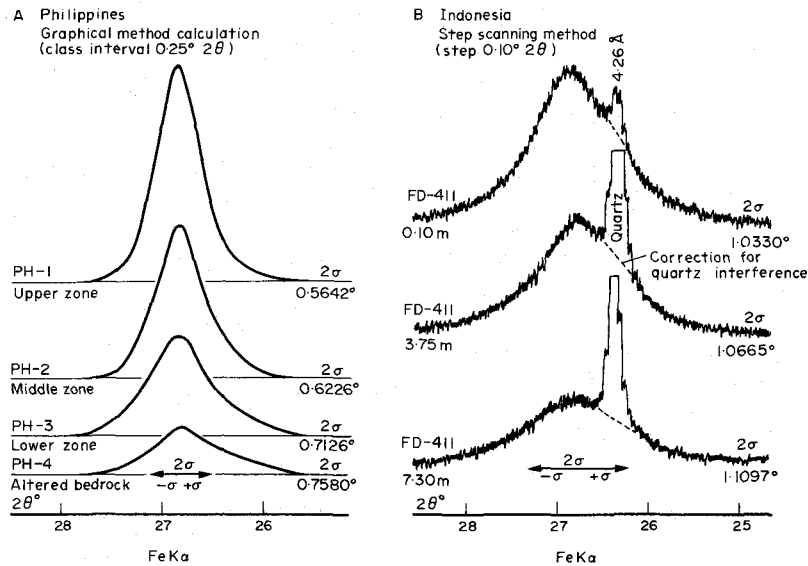


Fig. 3. Line profiles  $d_{110} = 4.18 \text{ \AA}$  of goethite from different depths of laterite profiles. The highest crystallinity is shown by the upper zone on the surface while lowest crystallinity is shown on goethite in altered bedrock. The value of  $2\sigma$  (standard deviation) is applied as measure of crystallinity.

of economic importance are present, such as nickel, cobalt, chromium, manganese, etc. (Roorda and Queneau, 1973). The "bonds" of these elements in the lateritic ores is of fundamental importance for the formulation of the optimum extractive process. Until now many of these minor elements were considered to be adsorbed on the large surfaces of fine-grained mineral constituents. Recent developments of chemical non-stoichiometry and the investigation of defect structures permits alternate interpretations. (see e.g. *Comprehensive Inorganic Chemistry* (Edited by Bailar, J. C. *et al.*) Vol. 4, pp. 453–540. Pergamon Press, Oxford). Poorly crystalline minerals usually exhibit highly defected (disordered) structures in which many "strange elements" can be incorporated readily such as the nickel, chromium and aluminum in goethite. The charge imbalance due to the defects in the structure must be compensated and non-stoichiometric incorporation of strange elements is one of the possibilities. Another characteristic feature of poorly crystalline materials is their higher water content because the charge imbalance of disordered structures with large surface areas is compensated by terminal  $-\text{OH}_2$  which compensates the broken edge by  $(0.5 +)$ . In laterites from many localities a large number of minor elements are associated with goethite and serpentine minerals. For instance Correns and van Engelhardt (1942) showed the influence of aluminum on the goethite structure. Further data on the system  $\text{FeOOH}-\text{AlOOH}$  were published by Correns and Thiel (1963). In this particular case the difference of ionic radii caused a shifting of the  $d_{hkl}$  values. Norrish and Taylor (1961) found in Australian soil goethite the replacement up to 25 molar %  $\text{AlOOH}$ . Roorda and Queneau (1973) reported the incorporation of nickel, cobalt and chromium in goethite as demonstrated by electron microprobe analysis. A similar

problem of substitution of iron by aluminum and incorporation of transition metals is the subject of experimental investigations by Janot *et al.* (1971) and Nalovic and Pinta (1972).

From these studies, it appears that the distribution and partition of elements in soil profiles are not only related to surface phenomena but also strongly influenced by structural phenomena. To some extent this explains the variable metallurgical recovery of minor elements from similar ore types but with different bonding energy.

The next steps in further research in the field of crystallinity studies should include:

- (1) the determination of possible incorporation ranges for particular elements and particular minerals;
- (2) the preference of incorporation of elements in defined mineral species (partition between co-existing phases);
- (3) mutual influences of elements during the incorporation on multicomponent systems;
- (4) quantification of structural disorder;
- (5) experimental studies of nucleation and crystal growth and
- (6) redistribution of elements during recrystallization.

#### CRYSTALLINITY OF GOETHITE IN LATERITIC PROFILES

Studies of several complete laterite profiles have shown a general tendency of *crystallinity decreasing with the depth*. Highest crystallinity is always observed at the surface, while the lowest crystallinity is observed in the transition zone between soil and bedrock where nucleation takes place. These characteristics seem to be diagnostic for laterite profiles formed *in situ*. The development of goethite crystallinity in

laterite profiles is shown in Fig. 3. The four laterite zones (thickness about 3–4 m) from the Philippines (Fig. 3a) show different shapes of the X-ray line profile of the main line  $d_{110}$  (4.18 Å). The upper zone has the most pronounced peak, while the altered bedrock exhibits only a broad band. In the second laterite profile, from Indonesia (Fig. 3b), there is a similar general tendency of the development of crystallinity. However, a more detailed study shows some irregularities of the crystallinity in different horizons probably caused by different hydrological regimes. Well-drained and poorly-drained areas exhibit different development of crystallinity. Moreover, the redeposition disturbs the normal sequence and some intercalations of allogenic materials frequently show strongly different crystallinity values. Another cause of variability can be dissolution, reprecipitation and recrystallization of goethite under conditions of Eh and pH values, mainly in poorly-drained areas. The laterite profile from Indonesia shows a notably lower crystallinity from that from the Philippines. Nevertheless, the highest crystallinity occurs in the upper zone in both profiles.

#### CRYSTALLINITY OF GOETHITE AND SILICIFICATION

Laterites are often silicified. This is a common phenomenon since serpentinization of the basic rock, preceding laterization, liberates large amounts of silica which is removed in migrating solutions. If the precipitation of silica coincides with goethite nucleation, the crystallinity of goethite is strongly affected. Silica precipitates initially as an amorphous gel which forms thin films around nuclei and so depresses further crystal growth of goethite. This concept was proved by the following experiment: From 0.01 M solution of  $\text{FeCl}_3$  amorphous  $\text{Fe}(\text{OH})_3$  was precipitated by slow addition of KOH at 20°C. The pH was controlled 9, 11 and 13. Similar tests were carried out with a KOH solution, containing 1% silica as sodium silicate. Remarkable differences of the precipitates were observed visually. Precipitates produced above pH 11 become yellow but remain reddish-brown in the presence of silica. The settling characteristics are also different. In the absence of silica, the precipitates settle quickly, while in the presence of silica, the precipitates remain gelatinous. These differences become more pronounced after 6 hr of aging under continuous shaking. The pure precipitate became powdery and khaki-yellow colored while the silica-contaminated precipitate remained reddish and gelatinous.

Transmission electron microscopy (see Fig. 4a, b, c) shows that after 24 hr aging at 20°C, including 6 hr shaking, needlelike goethite crystals (ca. 0.2  $\mu\text{m}$  long) grew from pure  $\text{Fe}(\text{OH})_3$ . From the precipitate contaminated with silica only minute spherical aggregates (diameter about 0.02  $\mu\text{m}$ ) had been formed. Both precipitates, however, were "X-ray amorphous" ( $\text{FeK}_\alpha$ ). Schwertmann and Taylor (1972a,b) have stud-

ied the transformation of lepidocrocite to goethite experimentally and they conclude that silica interferes mainly at the nucleation stage of the conversion. They also studied the influence of silica on this transformation. On their excellent photomicrographs the "blocking effect" is visible on the goethite crystals which become smaller, shorter and more imperfect. According to a personal communication from W. Schellmann (1974), he also observed different behaviour of iron oxides precipitated under different conditions (in presence of crushed glass). This explains why in strongly silicified, laterites goethite always shows extremely low crystallinity. This phenomenon was observed also on materials from the Solomon Islands, Venezuela, Brazil and other localities.

#### CRYSTALLINITY OF MANGANESE OXIDES AND SILICIFICATION

Although not directly related to the subject of this article, data are presented on the influence of silica on the crystallinity of manganese oxides which sometimes occur in laterites. Using Wadsley's procedure McKenzie (1971) hydrated sodium manganese oxide ( $\text{Na}_4\text{Mn}_{14}\text{O}_{27} + 9\text{H}_2\text{O}$ —ASTM 23-1046) was made. This, in turn, was used for synthesis of todorokite and woodruffite. If only 1% silica was added to the sodium hydroxide, the resulting Na-birnessite ( $\text{Na}_4\text{Mn}_{14}\text{O}_{27} + 9\text{H}_2\text{O}$ —ASTM 23-1046) became extremely poorly crystalline as shown in Fig. 5. The main line at 7.12 Å became broad and the background increased. The expected higher reactivity of poorly crystalline material during the ionic exchange of sodium by other metals (nickel, cobalt and others) did not take place despite the higher specific surface

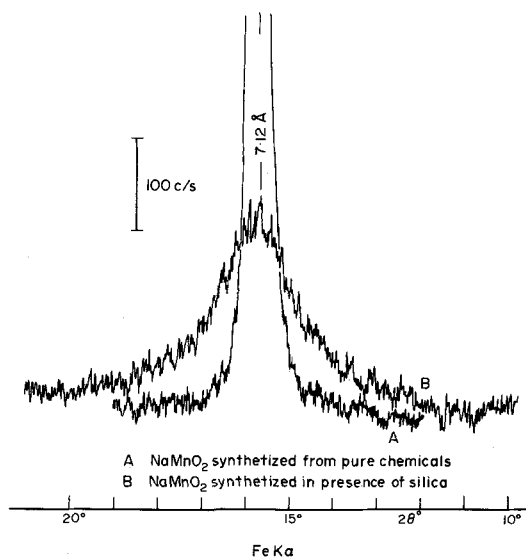


Fig. 5. Line profiles of the main line of Na-birnessite  $d_{002} = 7.12 \text{ \AA}$ . Curve A: Good-crystalline sodium manganese oxide synthesized at 5°C from pure chemicals. Curve B: The same compound synthesized in presence of about 1% silica under the same conditions. The crystallinity is poor as shown by the broadening of the peak.



area. The surface of the particles is covered with a thin film of amorphous silica and the reactivity does not change significantly. Generally speaking, it appears that the presence of silica has a similar influence on the nucleation and crystal growth of manganese oxides as it has on goethite.

#### CRYSTALLINITY OF OTHER MINERALS

*Serpentine* minerals are the second most frequent constituent in laterites. Line profiles of  $d_{001} = 7.3 \text{ \AA}$  show broadening which can be indicative for the crystallinity. In the case of serpentine minerals the decreasing crystallinity depends also on the degree of decomposition. The crystallinity of serpentine minerals is, in general, more complicated because of the different genetic types and the different polymorphs and changes during progressive weathering. Figure 6 presents one example of a weathered serpentine mineral. The green serpentine mineral (clino-chrysotile) is bleached along diaclasses due to the migrating solutions. A white crust (about 2 cm thick) is formed. At first sight the X-ray diffraction pattern of altered and unaltered serpentine does not show any remarkable difference. However, thermal gravimetric analyses showed a higher water content in the white altered serpentine. Crystallinities as established by step-scanning show distinct differences. In this particular case the crystallinity of altered serpentine decreases due to the interlayer hydration without proceeded dispersion (deformation of structural planes).

*Silica* is another frequent constituent in laterites. The recrystallization of amorphous silica was investigated by Carr and Fyfe (1958) under variable P-T conditions. They conclude that the path of crystallization is as follows:

Amorphous silica  $\rightarrow$  cristobalite  $\rightarrow$  keatite  $\rightarrow$  quartz.

In laterites, however, well-crystalline quartz is frequently observed. Figures 7(a) and (b) show the co-existence of perfect quartz crystals together with X-ray amorphous goethite (detected by thermal analysis). The presence in quartz complicates the determination of the crystallinity of goethite because of the coincidence of lines. (see Figure 3b). This should be corrected by subtraction of relative intensities.

*Clays* often show large variability of crystallinity. This is due to the frequent and abundant structural imperfections, including mixed layering and fine grain size. In general two tendencies are observed:

(1) decreasing crystallinity with progressive weathering and

(2) increasing crystallinity with progressive diagenesis and metamorphism.

The first tendency has been observed by Arnold (1967) and others on the soils, the second tendency is the subject of several papers of Kübler (1968) and others. Structurally disordered clays behave specifically during the dissolution in organic acids as shown by Huang (1973). Clays consisting of illite and mixed

layered illite-montmorillonite exhibit a drastically altered line profile of the  $10 \text{ \AA}$  line after partial solution. The peak becomes distinct and sharp. In other words, the crystallinity of this clay increases after partial leaching because of the complete dissolution of defect mixed layers and the partial solution of the finest fraction. Therefore the existence of highly crystalline clays at the surface of the alteration profiles could possibly be explained as a result of differential dissolution by percolating solutions.

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#### REFERENCES

- Arnold, R. W. (1967) Application of clay crystallite-size in soil genesis studies: *Proc. Iowa Acad. Sci.* **74**, 122–129.
- Bragg, W. H. and Bragg, W. L. (1933) *The Crystalline State* Vol. I, pp. 188–192. G. Bell & Son Ltd., London.
- Carr, R. M. and Fyfe, W. S. (1958) Some observation on the crystallization of amorphous silica: *Am. Miner.* **43**, 908–916.
- Correns, C. W. and van Engelhardt, W. (1942) Reference cited in *Nachr. Akad. Wiss. Göttingen, Math. Phys. Kl.* (Correns, C. W. and Thiel, R. 1963) pp. 131–137.
- Correns, C. W. and Thiel, R. (1963) Zum System  $\alpha$ -Fe OOH- $\alpha$ Al OOH: *Naturwissenschaften* **50**, 16.
- Huang, W. H. (1973) The influence of organic acids on dissolution, transformation, and deposition of minerals: *Symposium The Chemistry of Sedimentary and Diagenetic Processes*. University of Sheffield (Synopsis.)
- Janot, Ch. *et al.* (1971) Etude des substitutions Al-Fe dans des roches latéritiques: *Bull. Soc. Fr. Min. Crist.* **94**, 367–389.
- Jones, F. W. (1937) The measurement of particle size by the X-ray method: *Proc. R. Soc. Lond.* **166A**, 16–43.
- Kochendörfer, A. (1944) The determination of particle size and lattice distortions in crystalline materials from the breadths of X-ray lines: *Z. Krist.* **105**, 393–480.
- Kübler, B. (1968) Evaluation quantitative dy métamorphisme par la cristallinité de l'illite: *Bull. Centre Rech. S.N.P.A., Pau* **2**, 385–397.
- Kühnel, R. A., van Hilten, D. and Roorda, H. J. The crystallinity of minerals in alteration profiles: an example on goethite in laterite profiles: *Delft Progr. Rep. Series E: Geosciences* **1**, 1–8.
- Landa, E. R. and Gast, R. G. (1973) Evaluation of crystallinity in hydrated ferric oxides: *Clays and Clay Minerals* **21**, 121–130.
- McKenzie, R. M. (1971) The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese: *Miner. Mag.* **38**, 493–502.
- Nalovic, L. and Pinta, M. Comportement de fer en présence des éléments de transition: *C.r. Acad. Sci., Paris* **275**, 153–156.
- Norrish, K. and Taylor, R. M. (1961) The isomorphous replacement of iron by aluminium in soil goethites: *J. Soil Sci.* **12**, 294–306.
- Queneau, P. E. (1971) *Cobalt and the Nickeliferous Limonites*. Dissertation Techn. University of Delft, The Netherlands.

- Roorda, H. J. and Queneau, P. E. (1973) Recovery of nickel and cobalt from limonites by aqueous chlorination in sea water: *Trans. Inst. Mining Met.* **C82**, 79–87.
- Schwertmann, U. and Taylor, R. M. (1972) The transformation of lepidocrocite to goethite: *Clays and Clay Minerals* **20**, 151–158.
- Schwertmann, U. and Taylor, R. M. (1972) The influence of silicate on the transformation of lepidocrocite to goethite: *Clays and Clay Minerals* **20**, 159–164.
- Schwertmann, U. (1966) Zur Göthit- und Hämatitbildung aus amorphem Eisen (III)-Hydroxid: *Z. Pflern. Bodenk.* **108**, 37–45.
- Schellmann, W., (1974) Personal communication.