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AN OCCURRENCE OF AUTHIGENIC NACRITE

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Abstract—Euhedral, pseudohexagonal nacrite was discovered as a thin layer coating a carbonaceous shale in the Sherwood Tunnel in Durban, Republic of South Africa. The nacrite apparently formed authigenically within a few weeks at ambient temperature by precipitation from pore solutions, probably as a result of evaporation. This observation suggests that nacrite can no longer be considered to indicate a high-temperature genetic environment. Precipitation from saturated pore solution may have been the mechanism of formation for this kaolin-mineral polymorph.

Key Words—Authigenesis, Kaolin-group mineral, Nacrite, Pore solution, Shale.

INTRODUCTION

Minerals of the kaolinite subgroup (Bailey, 1980) are common products of weathering, diagenesis, and hydrothermal activity. The mechanism by which they form, however, and the factors controlling the crystallization of the various species are far from understood.

Clay minerals are known to form in and from solutions. The required concentration of the initial solution, however, is still a source of disagreement. Garrels and Christ (1965) suggested that kaolin-group minerals could form only from extremely dilute solutions. Low-temperature synthesis of kaolinite and halloysite has indeed only been achieved from highly dilute silica and alumina solutions (see summary in Van Oosterwyck-Gastuche and La Iglesia, 1978). Lippmann (1982), on the other hand, regarded fine grain size as an indicator of abundant nucleation, which suggests the formation of clay minerals from highly supersaturated solutions. In this respect, it is interesting to note that, at least to the author's knowledge, nacrite is one of the few clay minerals that has not yet been synthesized.

Nacrite is the rarest polymorph of the kaolin-group minerals. It has been observed and reported only from definitely high-temperature environments (Ross and Kerr, 1931; Firman, 1953; Hanson *et al.*, 1981). Lippmann (1982) therefore regarded nacrite as the typical high-temperature polymorph, and Hanson *et al.* (1981) proposed nacrite to be a valid kaolin-group mineral indicator of high-temperature.

The purpose of the present paper is to report the occurrence of authigenic nacrite, formed within a few weeks at ambient temperature by precipitation from evaporatory pore solutions on the surface of a recently exposed, unweathered Permian carbonaceous shale.

GEOLOGICAL SETTING

The Natal Province of the Republic of South Africa (RSA) is part of the Great Karoo basin, which accumulated sediments from early Permian to probably early Jurassic time. The extensive Permo-Carboniferous glaciation on the Gondwana supercontinent is reflected in the RSA by the deposition of a massive diamictite (Dwyka diamictite, formerly called Dwyka tillite), which in Natal grades into diamictitic sandstone, diamictitic shale, and finally into a fissile shale in which scattered dropstones give evidence of a progressive deglaciation (von Brunn and Gravenor, 1984). The Dwyka sediments are conformably overlain by a sequence of carbonaceous argillites of the Pietermaritzburg Formation (Ecca Group).

During excavation for the construction of a water supply tunnel (Sherwood Tunnel) in Durban in 1982–1983, sedimentary strata from the diamictite to the Pietermaritzburg Formation were exposed, permitting easy access to each unit. A white coating which covered the tunnel wall was observed on some horizons within the black fissile shale over a horizontal distance of several tens of meters. The coating, which measured a few tenths of a millimeter in thickness, clearly formed by precipitation from pore solutions. Huge fans provided air circulation in the tunnel which led to the evaporation of moisture from the walls. The tunnel construction was inspected and a piece of black shale containing the white coating was sampled about one month after excavation. Shortly afterwards, and before this investigation of the white material commenced, the tunnel walls were sprayed with concrete, preventing further sampling, as well as extraction of pore solutions from the shale which the author assumes to be the source of the constituents of the white precipitate.

METHODS

The white coating was scraped off the piece of fissile shale that was sampled in the Sherwood Tunnel and investigated by means of X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The small quantity of white material did not permit further studies. The shale was also examined by XRD.

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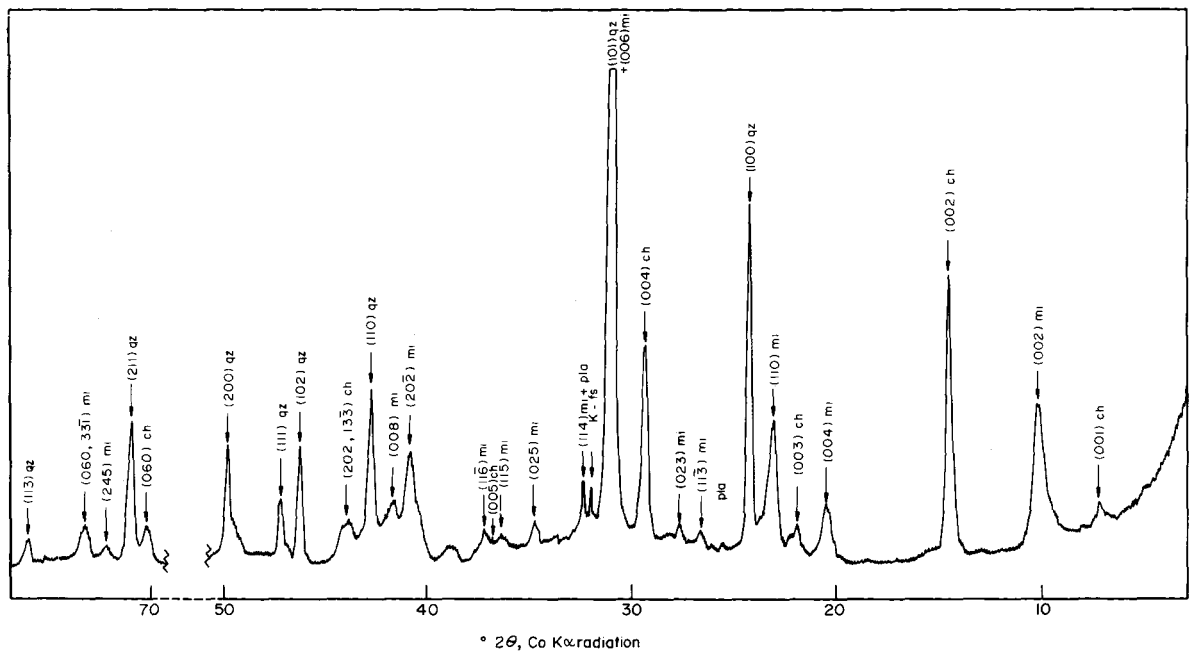


Figure 1. X-ray powder diffraction pattern of fissile shale from the Sherwood Tunnel, Durban, Republic of South Africa (ch = chlorite, mi = mica, qz = quartz, pla = plagioclase, K-fs = potassium feldspar).

Transmission electron microscopy

TEM investigation of the white material revealed the presence of euhedral platelets, which closely resemble pseudohexagonal crystallites, commonly reported for certain phyllosilicates, especially kaolinitic clays (Figures 3a and 3b). The morphology of the material, the crystal size of ≤ 1 μm, and the high degree of crystallinity, are typical of a clay mineral of authigenic origin (Keller, 1976).

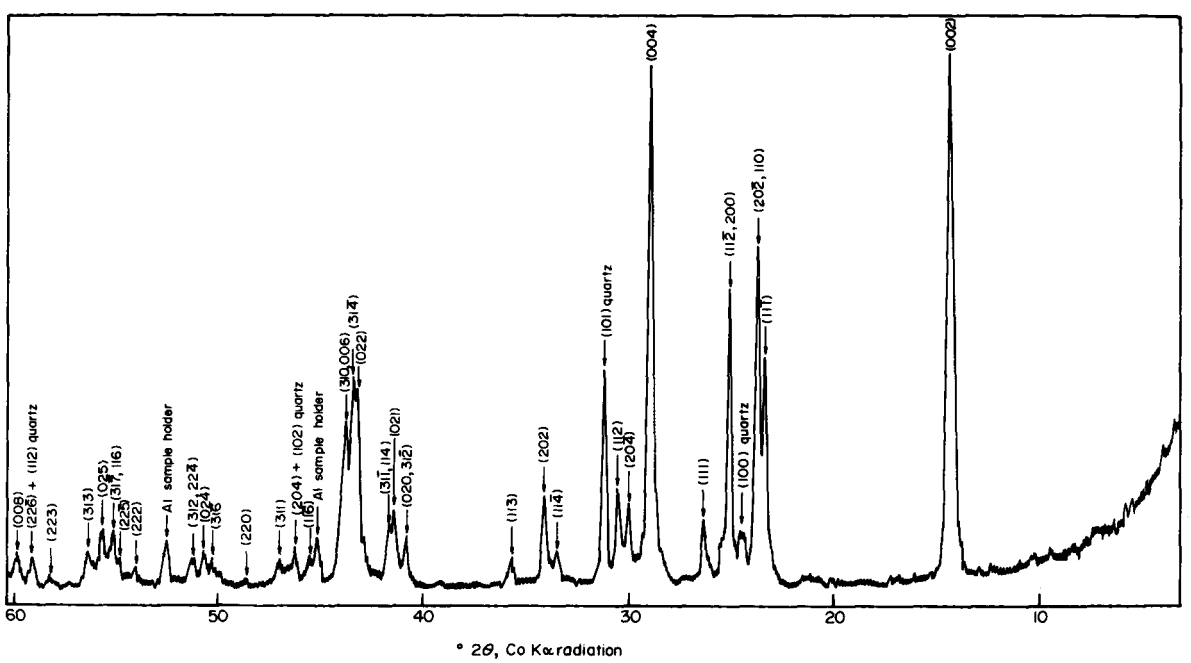


Figure 2. X-ray powder diffraction pattern of authigenic nacrite from the Sherwood Tunnel, Durban, Republic of South Africa.

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X-ray powder diffractometry

The sample for XRD studies was packed into a shallow cavity in an aluminum holder so as to minimize preferred orientation. XRD data were obtained using a Philips X-ray diffractometer and Fe-filtered CoKα radiation generated at 40 kV and 40 mA. The specimen was scanned at 1°2θ/min over the range 2°–60°2θ.

Transmission electron microscopy

A drop of the dispersed material was placed on a Formvar-coated Cu grid and air dried before viewing with a JEOL 100 CX transmission electron microscope.

RESULTS

X-ray powder diffraction

The dominant minerals in the fissile shale on which the white coating occurred, are, in order of decreasing amount, quartz, chlorite, mica, plagioclase, and potassium feldspar (Figure 1). Minerals of the kaolin-group are absent. The XRD pattern of the white precipitate is typical of that of a 7-Å phyllosilicate. Peak positions of the (00l) spacings are consistent with a polymorph of the kaolin group (Figure 2).

Nacrite is indicated by the (204, 112) doublet at 3.47 and 3.41 Å and strong reflections at 2.43 (022, 314), 2.40 (310, 006), and 2.93 Å (113) (Figure 2).

The weak quartz peaks in the XRD pattern of the white material are probably from quartz in the fissile shale.

Transmission electron microscopy

TEM investigation of the white material revealed the presence of euhedral platelets, which closely resemble pseudohexagonal crystallites, commonly reported for certain phyllosilicates, especially kaolinitic clays (Figures 3a and 3b). The morphology of the material, the crystal size of $\leq$1-μm-size fraction, and the high degree of crystallinity are typical of a clay mineral of authigenic origin (Keller, 1976).

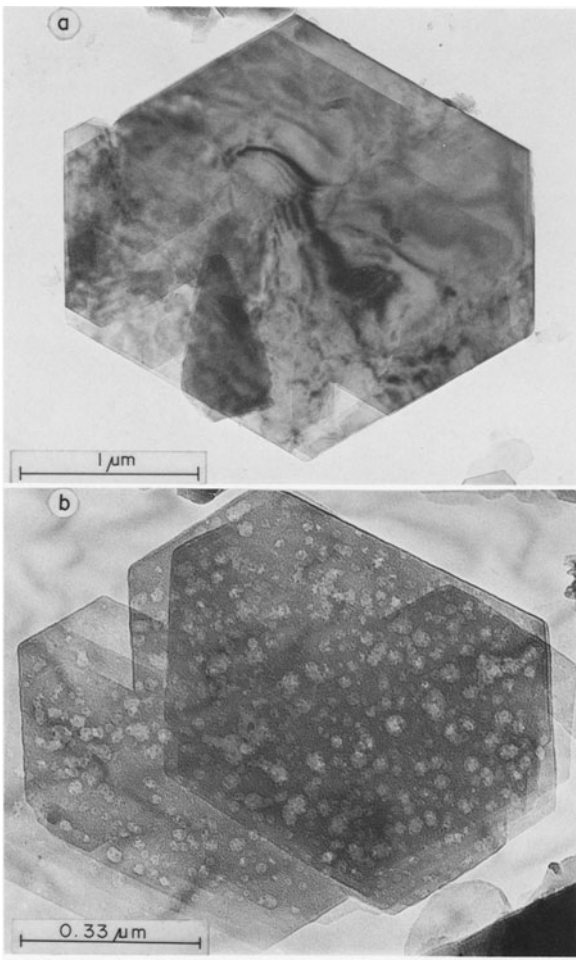


Figure 3. Transmission electron micrographs of authigenic nacrite from the Sherwood Tunnel, Durban, Republic of South Africa.

DISCUSSION AND CONCLUSION

Considering the near similarity of the "kaolin layers" in dickite and nacrite to those in kaolinite, the question arises as to the mechanism governing the crystallization of the various polymorphs. The formation of kaolinite and dickite is obviously not temperature-dependent, inasmuch as both polymorphs have been reported from high-temperature (hydrothermal, diagenetic) and low-temperature (weathering, sedimentary) geologic environments (Grim, 1968). Halloysite is regarded as a low-temperature species (Parham, 1969; Eberl and Hower, 1975). Only for nacrite has a high-temperature origin generally been accepted as the critical geochemical factor controlling genesis (Hanson *et al.*, 1981). The formation of nacrite as an authigenetic precipitate in the Sherwood Tunnel in Durban, however, demonstrates that the genesis of nacrite is equally temperature-independent and that other geochemical factors must promote its crystallization.

The most common origin of kaolin-group minerals, with the exception of nacrite, is the hydrolysis of most igneous, metamorphic and sedimentary rocks (Millot, 1970) in a strongly leached environment. Such weathering environments are characterized by pore solutions in which Si and Al contents are usually low at both high and low pH and by a broad spectrum of high pHs close to the parent rock, which decrease to $\leq$4 with increasing degree of weathering (Huang and Keller, 1973). The absence of nacrite from such weathering environments suggests that a mechanism involving a slow change in pH and dilute pore solutions does not favor nacrite formation. Attempts to synthesize kaolin-group minerals at room temperatures from dilute so-

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lutions have led to the crystallization of kaolinite and halloysite, but not nacrite (Van Oosterwyck-Gastuche and La Iglesia, 1978), suggesting, therefore, that solution concentration plays a decisive role. The absence of nacrite in the fissile shale itself demonstrates that nacrite did not precipitate in the pores of the carbonaceous shale. The crystallization of nacrite was probably triggered by chemical changes in the pore solution. The enhanced evaporation of these pore solutions in the tunnel probably increased the concentration of dissolved ions.

Near perfection in crystallinity and euhedral morphology support this assumption, inasmuch as La Iglesia and Van Oosterwyck-Gastuche (1978) reported that "good" crystals form only in supersaturated solutions in which a slow and regular rate of growth is ensured. Therefore, nacrite may be an indicator of concentrated pore solutions, and the sequence of formation of kaolin polymorphs is not dependent on pH and temperature, as suggested by Gorlich (1957), but rather on the concentration of the initial solution.

Although many unsolved problems still exist, two important observations can be offered in regard to the formation of nacrite: (1) the formation of nacrite does not appear to be temperature-dependent; (2) the genesis of nacrite may be related to concentrated pore solution conditions. The widespread occurrence of kaolinite, the most unstable kaolin-group polymorph (Newham, 1963; Giese, 1973), may perhaps only indicate the abundance of dilute pore solutions, which are decisive for the formation of that polymorph.

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