NOTES

NACRITE, DICKITE, AND KAOLINITE IN ONE DEPOSIT IN NAYARIT, MEXICO

Key Words-Dickite, Genesis, Hydrothermal, Kaolinite, Nacrite.

A hydrothermal deposit of kaolin in which nacrite, dickite, and kaolinite are intergrown occurs in the foot hills of the Sierra Madre Occidental in the state of Nayarit, Mexico. This paper records data on the identification of the nacrite, and briefly describes the geology of the deposit insofar as scanty outcrops and exploratory prospect tunneling have exposed it.

GENERAL GEOLOGY

As shown on the 1968 (International Geological Congress) Geologic Map of Mexico, Cenozoic volcanic rocks of andesitic to rhyolitic compositions extend more than 100 km eastward from Santiago Ixquintla, Nayarit, Mexico. Hydrothermal activity has altered these volcanic rocks in a few, small, localized areas. The most visible geologic evidence of loci of hydrothermal action are surficial, silica (quartz) pinnacles, ridges, or caps, deposited from the rising waters, that cover (crest) or drape over, topographic highs. The silica caps, usually scantily vegetated, resist erosion-hence they form relatively barren, high prominences over former hydrothermal sites. Appropriately, these crest-type features have been described in Mexico by the Spanish word crestónes (crestón, singular). Beneath a few of the crestónes, the desilication of the country rock has progressed far enough to generate commercial deposits of kaolin, and rarely, pyrophyllite.

Approximately 20 km east of Santiago Ixquintla, such a deposit of kaolin, known as the Chon property, is exposed beneath a crestón in a few small outcrops and prospect tunnels. Dickite and kaolinite are the dominant clay minerals in the deposit, but nacrite is also present in minor quantity, commonly intergrown with dickite. All three occur in homogeneous massive form and are best recognized by X-ray powder diffraction.

EXPERIMENTAL RESULTS

X-ray powder diffraction studies were carried out using monochromatized CuK α radiation. The goniometer was calibrated against quartz, and the range of the strip chart recorder was set so as to yield peaks high enough to be meaningfully measured for the prismatic and pyramidal reflections necessary to differentiate nacrite from dickite and kaolinite. Such a setting produced basal spacing peaks that were greater than 100 intensity, the maximum on the recorder chart, but basal spacings are not diagnostic between the kaolin minerals. Xray powder diffractograms of the three kaolin minerals from the Chon deposit are shown in Figure 1. Another diffractogram of the same sample of nacrite run at a goniometer speed of $0.5^{\circ}2\theta/min$ yielded reflections (Table 1) that compare favorably with those observed for nacrite by Bailey (1963).

A differential thermogram, Figure 2, resembles thermograms typical of dickite (Mackenzie, 1970) and of Keokuk kaolinite (Keller *et al.*, 1966). Infrared spectra of the nacrite, Figure 3, show absorptions at approximately 3710, 3655, and 3635 cm^{-1} that compare favorably with those reported by Van der Marel and Beutelspacher (1976) for nacrite.

Under cathode luminescence, as in a "Luminoscope" operated at 10 kV and $0.5 \mu a$, the dickite from the Chon deposit luminesces to a bright, light-blue color. Nacrite and kaolinite from the Chon deposit show a subdued blue background speckled with micrometer size flecks of higher brightness that might be dickite.

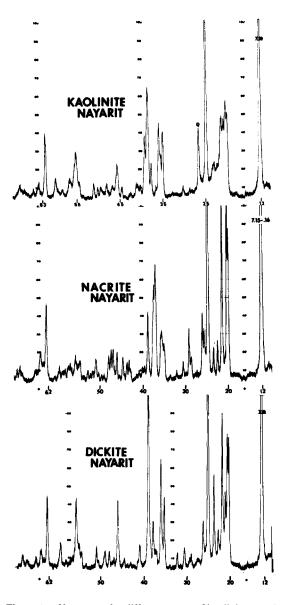


Figure 1. X-ray powder diffractograms of kaolinite, nacrite, and dickite from Nayarit, Mexico. CuK α radiation.

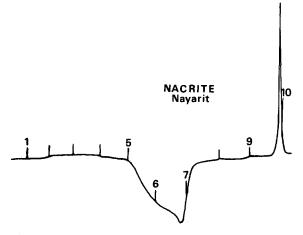


Figure 2. Differential thermogram of nacrite, heating rate approximately 12°/min. Temperatures in hundreds of degrees C are indicated.

DISCUSSION

The Chon deposit exhibits geologic features that indubitably characterize hydrothermal types of deposits in Mexico. These include the silica crestón, sharply localized kaolinization, gradation of kaolin into partially altered volcanic country rock, highly irregular upper and lower surfaces of the clay body, and pronounced vertical and horizontal non-uniformity in clay mineralogy and content of fine-grained quartz within the clay. Its hydrothermal origin is not questioned by geologists familiar with clay deposits in Mexico.

Apart from the presence of minor nacrite, the most unusual feature of the Chon deposit, compared with other hydrothermal deposits in Mexico, is its high ratio of dickite to kaolinite. Although dickite and nacrite were cited 50 years ago by Ross and Kerr (1931) as high-temperature varieties of kaolin minerals, almost all of the hydrothermal kaolin commercially produced in Mexico has been kaolinite and halloysite (Keller and Hanson, 1969). Specific examples of such deposits include the Zaragosa mine (probably the largest known hydrothermal kaolin mine in Mexico) in San Luis Potosi (Keller and Hanson, 1968), the Sombrerete, Zacatecas, mine (Keller and Hanson, 1969), the mine at Etzatlan, Jalisco (Keller, 1963), and the hotspring occurrence at Los Azufres, Michoacan, where halloysite is currently being formed (Keller et al., 1971). Thus, a hydrothermal, or elevated-temperature, origin of kaolin minerals in addition to producing nacrite and dickite, does not

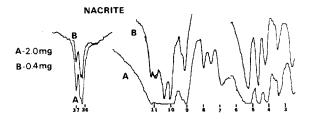


Figure 3. Infrared spectrogram of nacrite. Weights of clay used per 150 mg of KBr mounting material were 2.0 mg and 0.4 mg, respectively, for traces "A" and "B." Absorptions by the OH groups are at approximately 3710, 3655, and 3635 wave numbers cm^{-1} , as designated by numbers ×100 along base.

Table 1.	X-ray powder reflections of nacrite from Nayarit,
Mexico.	

d in (Å)	I (peak heights)	d in (Å)	I (peak heights)
7.16	>100		
4.42	80	2.035	14
4.36	>100	1.933	13
4.27	13	1.921	12
4.12	>100	1.914 ∫	
3.80	15	1.895	16
3.77	19	1.797	13
3.58	>100	1.784 ∫	
3.46	27	1.770	6
3.45 ∫		1.75	5
3.412	37	1.734	7
3.099	11	1.684B	10
3.048	27	1.647	13
2.912	17	1.618B	8
2.550	19	1.605B	8
2.52		1.589	7
2.49 }	24	1.555B	8
2.10	0	1.476	45
2.07	9	1.460	10

B refers to a broad reflection.

preclude the typical formation of dominant kaolinite and associated halloysite (probably originally 10Å, later collapsing to 7\AA).

What limiting role, if any, does temperature play in the genesis of kaolin minerals? Is any one of the kaolin minerals an indicator of the geochemical environment of its genesis? The sedimentary kaolin deposits, as at Jacal, Villa Victoria, Michoacan (Keller and Hanson, 1975) and the hydrothermal kaolin deposits along the volcanic arch of Mexico represent a field laboratory in which some problems of the geochemistry of diversified kaolin genesis may possibly be resolved. Currently, more questions than firm answers to this topic exist.

Geologically, nacrite has been observed and reported only from definitely high-temperature genetic environments. Apparently nacrite is a valid kaolin-mineral indicator of high temperature.

Dickite is known not only from high-temperature environments but also as an authigenic mineral in the pores of unmetamorphosed sandstone and in hollow chert nodules from a Pennsylvanian-age conglomerate derived from underlying Mississippian rocks in Missouri (Keller, 1976), neither of which represents a typical hydrothermal environment. Is an elevated temperature necessary for dickite to form, or may another geochemical factor critically promote its crystallization? Claim may be made that its authigenic (or diagenetic) growth in sandstones, and in the cited Pennsylvanian-age conglomerate, occurred during a time when the rocks were buried deeply enough to be heated geothermally above the minimum temperature of genesis and therefore qualify as "hydrothermal" in a chemical sense. From another viewpoint, most dickites are associated with nearby minerals of non-ferrous heavy metals, such as Hg, Pb, Zn, and Cu, for which numerous examples have been cited (Keller, 1976, p. 109). Sandstones, though not ore-bearing, commonly have had moving through them strongly saline brines that carried high concentrations of metal ions. In the Nayarit district, prospecting has been carried out for non-ferrous metals, but no large deposits have been reported. Conceivably, the crystallization of dickite might be catalyzed by either elevated temperature or the presence of trace amounts of metal ions (currently under investigation), or both.



Figure 4. Scanning electron micrographs of representative nacrite, dickite, and kaolinite from the Nayarit deposit, Mexico. The length of each bar represents $5 \mu m$.

Kaolinite's genesis obviously is not critically temperature dependent between surface and ordinary hydrothermal temperatures. Even halloysite(10Å) has been found as a product of hydrothermal activity in Mexico (Keller, 1963; Keller *et al.*, 1971) and elsewhere, and this mineral can collapse to halloysite(7Å).

H. Lippman, University of Tübingen, Germany (personal communication), has offered a possible interpretation in terms of clay-mineral stabilities that may help explain the full spectrum of kaolin minerals in Mexico and elsewhere. He asserts, based on chemical data that the one stable kaolin mineral is dickite, and that all other kaolin minerals are metastable phases. Because differences in the free energies of formation of dickite and kaolinite are possibly as small as experimental errors in their measurements, kaolinite and its lower-ordered polymorphs persist over geologic intervals of time as metastable forms. Although dickite is apparently more widespread in occurrence than nacrite, would more precise identification by electron diffraction of many, tiny, euhedral authigenic crystals in sandstone pores reveal more nacrite than hitherto has been reported? If so, it might be asked whether nacrite is geologically "more stable" than "stable" dickite.

Looking forward, if thermodynamic properties are measured on the nacrite, dickite, and kaolinite, all collected from the single Chon deposit, geologic variables that otherwise might complicate data obtained from different genetic environments at separate deposits would be eliminated. If this deposit is found to be commercially useable and mineable so that three-dimensional exposure and mapping of the distribution of the three kaolin minerals is possible, light may be shed on the processes of their formation.

ACKNOWLEDGMENTS

We are indebted to Professor E. E. Pickett, Chemistry Department, University of Missouri-Columbia, for running the infrared spectrogram. The National Science Foundation Grant, EAR 76-18804, supported the scanning electron micrography.

Refractarios A. P. Green, S.A.	R. F. Hanson
Mexico, D.F., Mexico	R. Zamora
University of Missouri–Columbia Columbia, Missouri 65211	W. D. Keller

REFERENCES

- Bailey, S. W. (1963) Polymorphism of the kaolin minerals: Amer. Mineral. 48, 1196-1209.
- Keller, W. D. (1963) Hydrothermal kaolinization (endellitization) of volcanic glassy rock: in Clays and Clay Minerals, Proc. 10th Natl. Conf., Austin, Texas, 1961, Ada Swineford and P. C. Franks, eds., Pergamon Press, New York, 333– 343.
- Keller, W. D. (1976) Scan electron micrographs of kaolins collected from diverse environments of origin—1: Clays & Clay Minerals 24, 107–133.
- Keller, W. D. and Hanson, R. F. (1968) Hydrothermal alteration of a rhyolite flow breccia near San Luis Potosi, Mexico to refractory kaolin: *Clays & Clay Minerals* 16, 223–229.
- Keller, W. D. and Hanson, R. F. (1969) Hydrothermal argillation of volcanic pipes in limestone in Mexico: Clays & Clay Minerals 17, 9-12.
- Keller, W. D. and Hanson, R. F. (1975) Dissimilar fabrics by scan electron microscopy of sedimentary versus hydrothermal kaolins in Mexico: *Clays & Clay Minerals* 23, 201– 204.
- Keller, W. D., Hanson, R. F., Huang, W. H., and Cervantes, A. (1971) Sequential active alteration of rhyolitic volcanic rock to endellite and a precursor phase of it at a hot spring in Michoacan, Mexico: *Clays & Clay Minerals* 19, 121–127.
- Keller, W. D., Pickett, E. E., and Reesman, A. L. (1966) Elevated dehydroxylation temperature of the Keokuk kaolinite—a possible reference mineral: Proc. Int. Clay Conf., Jerusalem, 1966, 1, L. Heller and A. Weiss, eds., Israel Prog. Sci. Transl., Jerusalem, 75–85.
- Mackenzie, R. C. (1970) The Differential Thermal Investigation Of Clays: Academic Press, London, 775 pp.
- Ross, C. S. and Kerr, P. F. (1931) The kaolin minerals: U.S. Geol. Surv. Prof. Pap. 165E, 151-175.
- Van der Marel, H. W. and Beutelspacher, H. (1976) Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures: Elsevier, Amsterdam, 396 pp.
- (Received 5 October 1980; accepted 28 February 1981)