American Mineralogist, Volume 63, pages 326–329, 1978

Diaspore recrystallized at low temperature

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Abstract

Diaspore from clay deposits in Missouri is shown in scan electron micrographs to have recrystallized into relatively coarse crystals in a weathering environment and at surface temperatures. Recrystallization at such low temperatures is unexpected, in view of synthesis temperatures in the range of 200–300°C. Aluminum hydroxide thus is not intractably "insoluble" under certain soil-water conditions.

Introduction

For two and a half decades the apparent crystallization and stability of diaspore at earth-surface ("room") temperature has been an intriguing problem. The geologic home of diaspore traditionally has appeared to be in an environment of metamorphism or in a genetic environment above 200°C (laboratory synthesis). In contradistinction to genesis at high temperature and high pressure, however, diaspore also occurs abundantly in association with sedimentary deposits of flint clay and bauxite. Despite an apparent low-T,P origin for these deposits, geologists usually have diligently searched for a possible part-time existence for them at higher temperature in an effort to reconcile field observations and laboratory data.

In this paper, however, scan electron micrographs, SEM, will show diaspore that has recrystallized in "surface boulder" diaspore exposed only to the surface weathering environment (necessarily a low temperature and pressure) in central Missouri since the Tertiary.

Scan electron micrographs

Scan electron micrographs were taken of representative specimens from a typical sequence of flint clay—burley—diaspore in a clay pit in the central Missouri clay region (McQueen, 1943; Allen, 1935, 1952; Keller *et al.*, 1954). Although reserves of diaspore in Missouri are essentially depleted (Keller, 1977a), a typical deposit has been temporarily, or accidentally, spared from mining; this is the Schaefferkoetter pit, about 11 km NW of Owensville (Keller, 1977b). Missouri diaspore has originated by desilication of parent kaolinitic flint clay, according to all writers cited above. The kaolin and/or illite parent to the flint clay was derived as a residual weathering product from adjacent Paleozoic limestones (Robbins and Keller, 1952). The transition from flint clay to diaspore usually took place laterally or vertically within a range of a few cms to a meter or more, as in the Schaefferkoetter pit.

Figure 1 is an SEM of representative flint clay from the Schaefferkoetter deposit (3000×). This specimen, which is typical of Missouri flint clay, is fine-grained, has low porosity, and is very compact due to the interlocking of tiny crystals and small books of kaolinite. The micrographed surface is a freshly fractured surface—no grinding, etching, or other processing which might introduce an artifact was done. Other types of flint clay are shown in detail elsewhere (Keller, 1976, II; 1977c). A few cms inward on the outcrop, toward the diaspore core of the pit, the clay becomes a "burley" in character. Some oolites, or "burls" (a miner's term for oolites, from which the name "burley clay" originated) of diaspore are present, while the matrix also includes plates or blades of diaspore, Figure 2 (3000×). The estimated Al_2O_3 content of this specimen is 55 to 60 percent, whereas that of the flint clay of Figure 1 is about 45 percent Al_2O_3.

First-grade diaspore, 68 percent Al_2O_3 and higher, and the interior of "burls" contain dominantly blades, scales, or flakes, some of them with irregular or "lacey" edges, as seen in Figure 3 (3000×). A local, richest small lens of diaspore, 1 m long and 0.25 m thick, shows incipient recrystallization of diaspore within the massive body of the deposit, Figure 4

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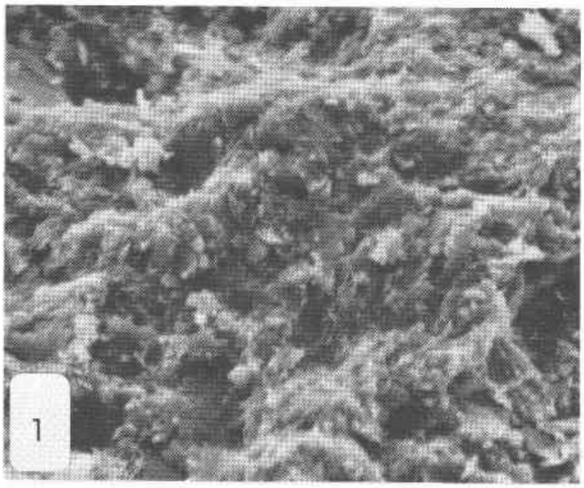

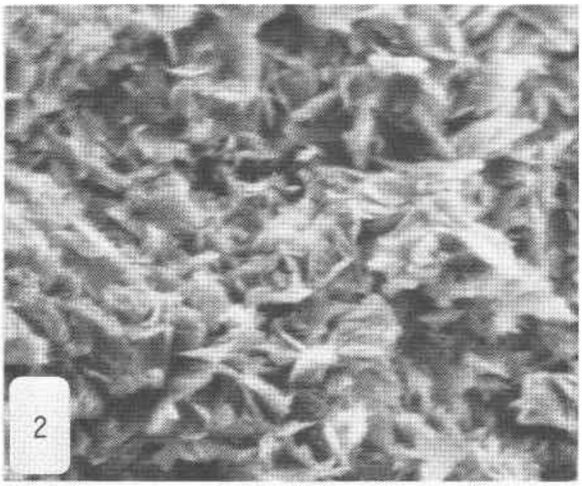

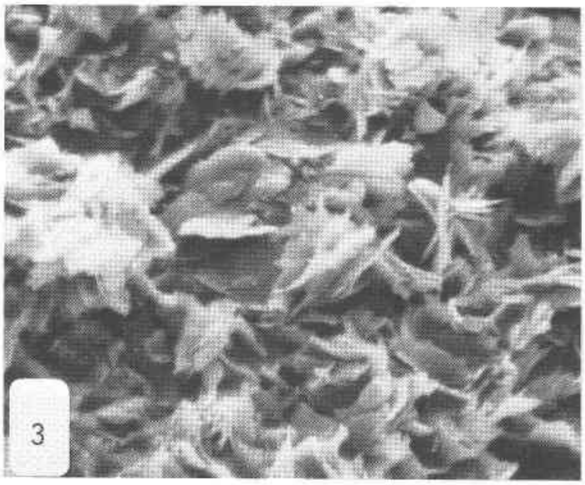

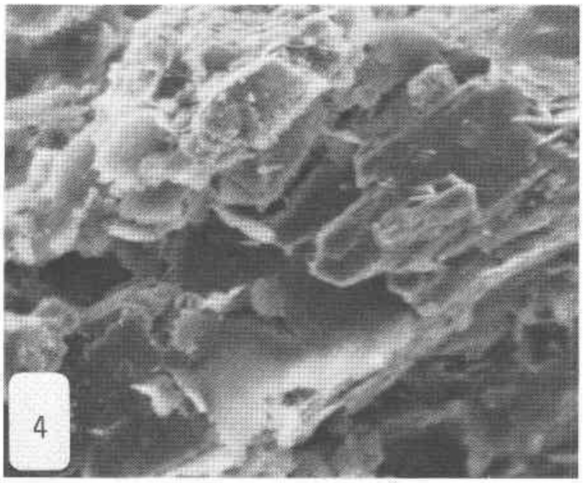

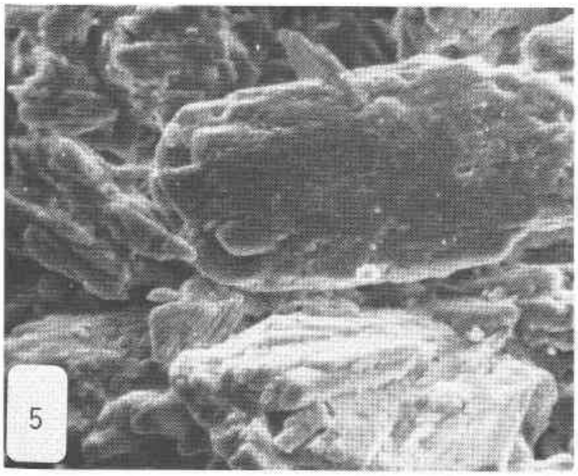

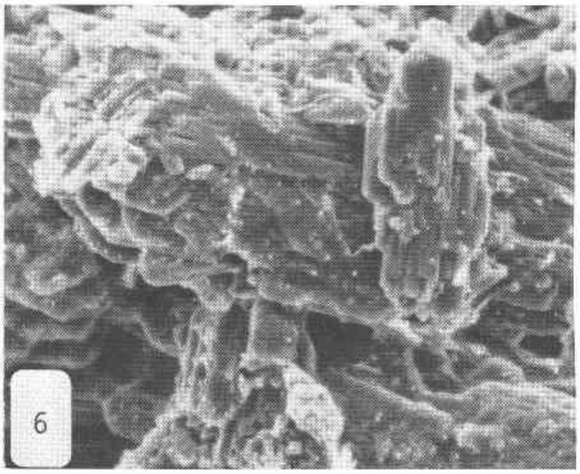

Fig. 1. Flint clay, Schaefferkoetter pit (3000×). Fig. 2. Matrix of burley clay derived from flint clay, a few cm. from location of Fig. 1 (3000×). Fig. 3. First-grade diaspore, estimated over 68% Al_2O_3. Approximately 1 m from location of Figure 1 (3000×). Fig. 4. Very rich diaspore from a small, local, relatively permeable lens in the diaspore core of Schaefferkoetter deposit (2000×), showing incipient recrystallization. Fig. 5. Recrystallized diaspore from "surface boulder," near Swiss, Missouri (2000×). Fig. 6. Recrystallized surface-boulder diaspore, Gaume pit, near Aud, Missouri (2000×).

(2000×). Figure 4 alone may not be convincing of incipient recrystallization. To best appreciate that effect, more striking views will be shown of "surface-boulder" diaspore.

"Surface-boulder" diaspore originated, as the term indicates, as residual boulders developed by weathering at the surface of diaspore deposits exposed by erosion. Probably this dates back to Pleistocene, but certainly the erosion surface is no older than the Eocene Wilcox formation (Bretz, 1965). A micrograph from a "surface boulder" from near Swiss, Missouri, is shown in Figure 5 (2000×). Another micrograph of surface-boulder diaspore from the now-depleted Gaume pit near Aud, Missouri, is shown in Figure 6 (2000×). The "surface-boulder" diaspore is present in well-formed, indeed euhedral, relatively large crystals, *e.g.*, 2 μm by 4 μm, in comparison to small, thin flakes, shown at 3000× magnification for the pit-generated diaspore. Reexamination of Figure 4 shows incipient recrystallization within a local lens in the massive deposit, whereas long exposure to weathering solutions developed matured, large and well-formed tabular crystals.

Small boulders of "surface diaspore" consist mainly of coarse crystals, whereas large boulders (a meter across) typically revert from coarser crystals on the outside to blades and scales, more like those in Figure 3, in the interior. This confirms that surface weathering of diaspore promotes its recrystallization. The SEM illustrations are convincing (at least to me) that recrystallization of diaspore does take place under an oxidizing, surface-weathering environment (temperature and pressure) as has existed in central Missouri since early Eocene.

Geology and discussion

Diaspore in Missouri was formed from desilication, as stated, of clay minerals deposited in karstic depressions within the Pennsylvanian Cheltenham formation. This was referred with slight reservation to the Atokan Series—but clearly the Cheltenham is below the Burgner formation which is post-Morrowan but pre-Desmoinesian (Searight and Howe, 1961, p. 79). The time or geologic date when genesis of diaspore was concluded remained undetermined until about 1950 when the Bueker diaspore pit, covered with Pennsylvanian-age rocks, was opened. At this pit, the upper surface of otherwise fresh flint clay was "rotten" and oxidized (weathered) but covered in sharp contact with overlying fresh, green, illitic, marine (?), thin Excello shale. This shale is coformably overlain by thick, indubitable Ft. Scott limestone (Marmaton-Des Moinesian, Searight and Howe, 1961). The field relationships and identifications were discussed in detail by Keller (1952, 1968; Keller *et al.*, 1954). Thus flint clay and diaspore were deposited and formed in the Paleozoic geologic time interval, Cheltenham to Ft. Scott! Whereas earlier hypotheses (including my own) of origin of the Missouri refractory clay had been primarily by downward leaching, evidence from later observations suggested prominent upward leaching and flushing away of metal ions (refractory fluxes) in fresh rain water by way of the Donnan effect (Keller, 1952, 1968; Keller *et al.*, 1954).

Early reference has been made to a high-temperature origin for diaspore. Ervin and Osborn (1951) studied phase equilibria in the system Al_2O_3–H_2O and reported that "the diagram shows pressure and temperature minima (2,000 lb/in^2, 275°C) for the stable existence of diaspore. . . ." They also, however, recognized problems of application of their work to the diaspore in the sedimentary refractory clays of Pennsylvania. Keller *et al.* (1954, p. 31–34) considered the work of Ervin and Osborn and the difficult possibility of geologic high temperature in the formation of Missouri diaspore, but decided in favor of a low-temperature origin.

Kennedy (1959) reexamined the phase relations in the system Al_2O_3–H_2O at high temperatures and pressures. He seeded alumina gel with a small trace of diaspore crystals, and reported (p. 569): "The lowest temperature at which the diaspore had appreciably increased in quantity and the crystals increased in size, in three months time, were the two runs at 220° at 1000 and 1500 bars H_2O pressure." He wrote further, however (p. 563): "The approximate slope of the boehmite–diaspore boundary, computed from thermodynamic data, indicates that diaspore in bauxite and clay deposits may have formed at atmospheric pressures and temperatures, a familiar conclusion from field observations."

The SEM figures in this paper are evidence that diaspore, as it occurs in Missouri, presumably dissolves and recrystallizes in a temperature, humid weathering environment. A variety of possible mineralogic transformations are thus available for the solution, deposition, and recrystallization of aluminum hydroxides in diverse clay and bauxite deposits. Restraint is called for in making an unreserved statement about blanket "insolubility" of alumina minerals in the zone of weathering. While it would be presumptous to speculate from SEM photographs the geochemistry of the surface solutions that mobilized the diaspore, the field occurrences of surface-boulder diaspore do not indicate any significantly unusual geochemical environment in which the recrystallization took place. Possibly complexing organic compounds, such as tannic, tartaric, or salicylic acids, which can mobilize Al (Huang and Keller, 1972), could have been contributed by macro-plants or bacteria, but any direct record of them, if they were present, was lost during oxidation of the surface boulders of diaspore. The geochemistry of mobile Al in the geologic environment of the earth's surface invites specialized study.

Note added in proof

After this paper was written, my attention was called by Professor Joe L. White to a report of crystallization of diaspore under 100°C. Wefers and Bell (1972) state in review that "Wefers (1967) synthesized diaspore hydrothermally below 100°C, using coprecipitated iron and aluminum hydroxide gels as a starting material. Goethite, α-FeOOH, which crystallizes spontaneously under mild hydrothermal conditions, provided the substrate for epitaxial growth of the isostructural aluminum oxide hydroxide thus reducing the nucleation energy for diaspore considerably." Because goethite is present in minor amounts in surface boulder diaspore, it may have served as a template or catalyst for the recrystallization of diaspore at ambient temperatures.

Acknowledgment

Research for this paper was supported by the Earth Sciences Section, National Science Foundation, NSF Grant EAR 76-18804.

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Manuscript received, July 11, 1977; accepted for publication, August 5, 1977.