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MINERALOGICAL NOTES

RECENT ANHYDRITE FROM CLAYTON PLAYA, NEVADA

R. J. MOIOLA AND E. D. GLOVER, *Socony Mobil Oil Company, Inc., Field Research Laboratory, Dallas, Texas.*

OCCURRENCE

Clayton Playa (Fig. 1) is a saline playa entirely devoid of vegetation and occupies an area of approximately 32 sq mi. It is covered with a thin crust of halite, 0.1 to 4.0 mm thick, which overlies a thick sequence of Pleistocene and Recent clays, silts, and sands with interbeds of halite (Dole, 1913). The water table in the playa is close to the surface and the sediments underlying the halite crust are usually saturated with saline water (pH. 7.0), the solids of which consist almost entirely of NaCl (Dole, 1913). The climate of the area is arid, with an average rainfall of approximately 5 inches. Summer daytime temperatures commonly exceed 95° F., but nighttime temperatures are considerably lower; the mean annual temperature of the area is approximately 60° F.

Gypsum crystals formed upon the natural drying of NaCl-saturated sediment which was removed from a 25 foot deep pit dug in the playa. Examination of the sediment, predominantly blue-gray, silty clay, immediately after its removal from the pit revealed the presence of only a very few small (less than 0.2 inches in diameter) crystals of gypsum. When the area was revisited 11 months later and the dried sediment examined it was found to contain abundant crystals of gypsum, 0.25 to 3.0 inches in diameter, many of which were coated with a more or less adherent white material. The coating was best developed on the faces of the crystals which were exposed to the atmosphere and not directly in contact with the sediment. Subsequent *x*-ray and thin-section analysis of the white material reveals that it is hemihydrate and anhydrite.[1]

DESCRIPTION OF THE GYPSUM CRYSTALS

Some of the crystals are blade-like or lath-like with more or less rounded ends and their elongate prism faces are the (110) and $(1\bar{1}0)$ planes (The unit cell of gypsum suggested by Bragg (1937) having $a=5.68$, $b=15.18$, $c=6.52$ Å and $\beta=118°\ 23'$ (Atoji and Rundle, 1958)

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[1] In this paper the intermediate form between gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) with one-half or less molecules of water per $CaSO_4$ is called calcium sulfate hemihydrate or, simply, hemihydrate. No attempt has been made at this point to determine the water content or to decide, on the basis of *x*-ray diffraction, whether the material described is closer to $CaSO_4 \cdot \frac{1}{2}H_2O$ or to "soluble anhydrite" as discussed by Posnjak (1938). This material occurring naturally has been called bassanite (Zambonini, 1910).

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Description of the Gypsum Crystals

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and the unit cell of anhydrite of Dickson and Binks (1926) having $a=6.238$, $b=6.991$ and $c=6.996$ Å (Swanson *et al.*, 1955) are used in this paper.) Examples of these crystals may be seen in Fig. 2, Nos. 4, 5 and 6. They are often twinned as in No. 4. The main cleavage is parallel to the length of the blades. Other crystals vary from those described above, to irregular, discoid crystals with their surfaces perpendicular to the cleavage plane (010) as illustrated in Fig. 2, Nos. 1, 2 and 3. The two types are similar in that they are extended in a plane perpendicular to the cleavage plane. Cavities and dark patches of sediment are present in most crystals.

Neither anhydrite nor hemihydrate was identified in thin sections of the crystals which showed no obvious alteration (Fig. 2, Nos. 2, 3, 4, 5). X-ray diffraction patterns, however, show the presence of a small amount of hemihydrate in the bulk crystal. Thin sections made parallel to the cleavage surface of the altered crystals (Fig. 2, Nos. 1, 6) exhibit a core of gypsum surrounded by a somewhat irregular layer, averaging .062 mm

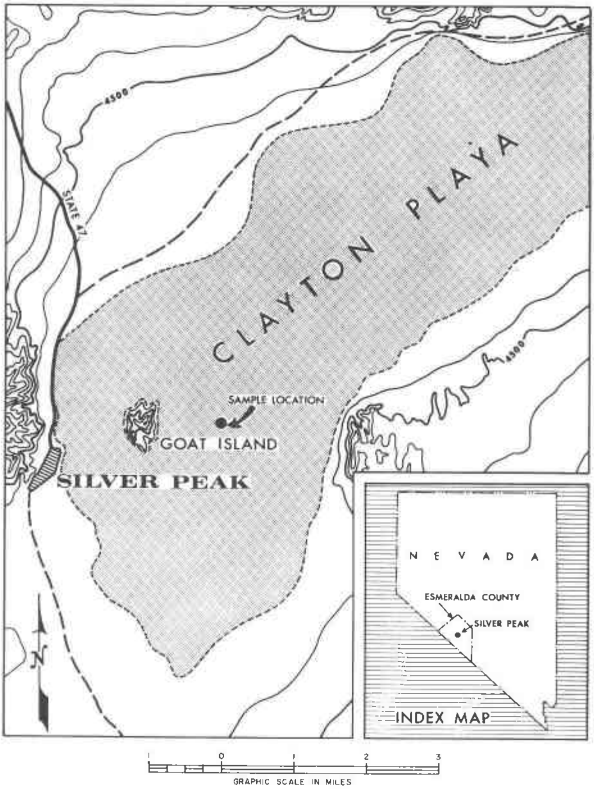

FIG. 1. Sample location map.

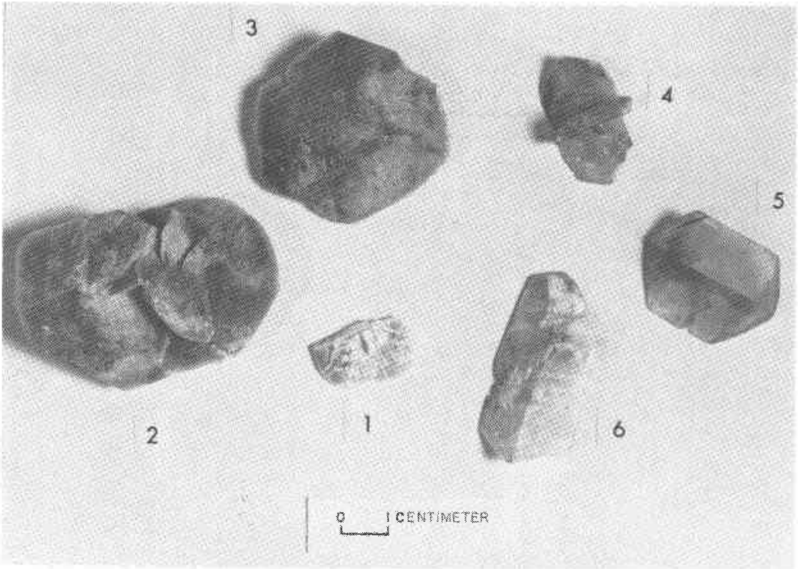

FIG. 2. Gypsum crystals from Clayton Playa, Nevada.

thick, of fibrous crystals of low birefringence, leading to an outer, microcrystalline layer, approximately 0.5 mm thick, of fibrous material of higher birefringence (Fig. 3). The refractive indices of the inner layer agree with those for hemihydrate which are 1.55 to 1.57, and the indices of the outer layer agree with those of anhydrite which are 1.57 to 1.61 (Palache *et al.*, 1944). One crystal examined showed only the inner layer. The *x*-ray patterns of material scraped from several spots on the surfaces of the crystals invariably showed a combination of the minerals, anhydrite, calcium sulfate hemihydrate and gypsum (Fig. 4). Commonly, either anhydrite or the hemihydrate was predominant. Thus, in crystal No. 6, Fig. 2, a sampling of three spots gave hemihydrate with gypsum each time (Fig. 4, No. 4). Crystal No. 1, Fig. 2, showed mainly anhydrite with a small amount of hemihydrate at three different spots sampled (Fig. 4, No. 3). At a fourth spot the *x*-ray pattern showed the presence of the three minerals (Fig. 4, No. 1).

There seems to be no question that the three phases seen in thin section and in the *x*-ray patterns are genetically related, the gypsum having altered successively to hemihydrate and anhydrite. The fiber axis of the hemihydrate appears to lie in the cleavage plane of the original gypsum and to make an angle of 55° with the length of the cleavage slices, that is, 55° with the [001] direction of gypsum. This same orientation is roughly preserved in the anhydrite portion. Atoji (1959) showed that on heating a gypsum single crystal, the [101] direction of gypsum became the fiber axis of fibrous anhydrite as well as the [100] direction of the anhydrite fibers, thus preserving the Ca-SO_4 chains. The angle we find of approximately 55° agrees satisfactorily with the angle of 52° 36′ between the gypsum [101] and [001] directions.

We find an extinction characteristic of fibrous aggregates in the hemihydrate and anhydrite layers of the thin sections. To further test if the relative orientation of the phases is similar to that of the heating experiments of Atoji (1959), we have compared the stage rotations necessary to go from the gypsum to the hemihydrate extinction position and from the gypsum to the anhydrite extinction position with those for a gypsum cleavage flake heated, first to 105° C. for twelve hours (hemihydrate), and, then, to 500° C. for twelve hours (anhydrite). We have found the relative extinction positions to be in agreement.

Thus, the available data conclusively demonstrate that:

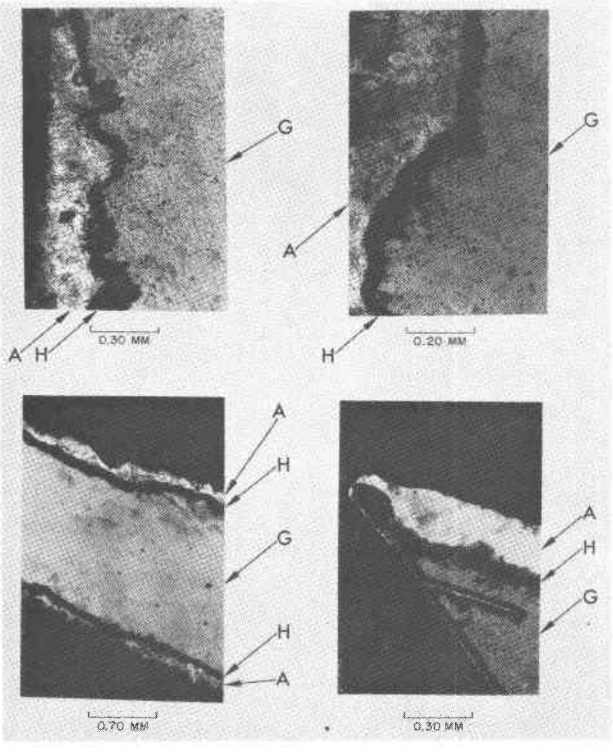

FIG. 3. Photomicrographs of altered gypsum crystals (all taken with crossed polars). G = gypsum, H = hemihydrate, A = anhydrite.

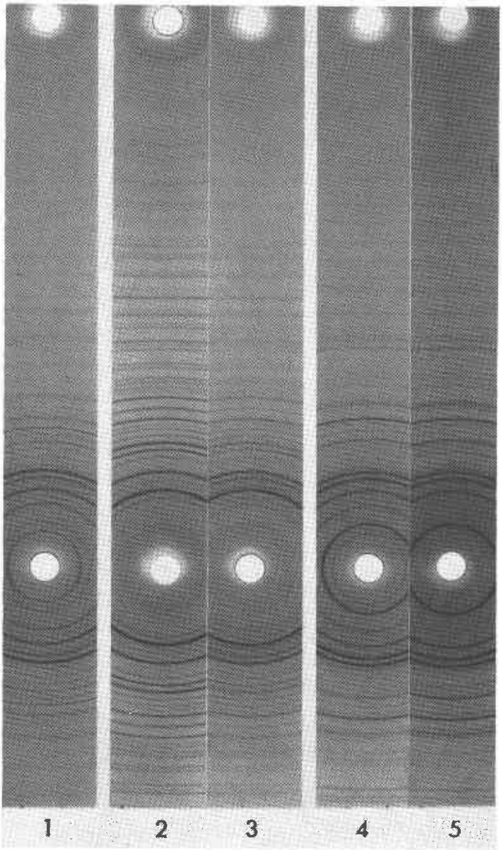

Fig. 4. *X*-ray diffractograms of altered material compared to standards.

(1) Altered material showing gypsum, hemihydrate and anhydrite.
(2) Natural anhydrite heated to 500° C. for 18 hours.
(3) Altered material, predominantly anhydrite.
(4) Altered material, predominantly hemihydrate.
(5) Artificial hemihydrate made by heating gypsum (var. selenite) to 105° C. for 18 hours.

(1) the gypsum crystals formed predominantly after the sediment was removed from the playa and dried under natural conditions, (2) many of the gypsum crystals were subsequently altered successively to hemihydrate and anhydrite at surface temperatures and pressures in the absence of a liquid phase, (3) these processes took place within a period of 11 months, and (4) the hemihydrate and anhydrite are topotactically related to the gypsum.

Discussion

Gypsum-anhydrite-water equilibria under various conditions of pressure and temperature are still not well defined after many years of investigation. The gypsum-anhydrite transition temperature in pure water at one atmosphere pressure has been given as 40° C. (Kelley *et al.*, 1941) $42\pm1°$ C. (Posnjak, 1938), $57\pm2°$ C. (Hardie, 1964), and 63–66° C. (Van't Hoff, as cited in Posnjak, 1938); the gypsum-hemihydrate transition temperature in pure water at one atmosphere pressure is thought to be 97° C. (Kelley *et al.*, 1941). These transition temperatures are lowered with decreasing water activity (Kelley *et al.*, 1941).

It is known that the rate of formation of anhydrite in a water solution of calcium sulfate below 100° C. is slow. If a gypsum-water mixture is heated above the gypsum-hemihydrate transition temperature, hemihydrate is formed, followed by anhydrite, in a time interval of the order of a few days (Ostroff, 1964). Posnjak (1938), however, was unable to convert gypsum to anhydrite in 6 months when a gypsum-water mixture was heated at 75° C. (which is below the accepted gypsum-hemihydrate transition temperature of 97° C.) unless anhydrite seeds were present. Recent work by Hardie (1964) shows that the gypsum-anhydrite conversion time is of the order of several months in dilute sulfuric acid and sodium sulfate solutions near his transition temperature of 57° C. The samples described here demonstrate that gypsum crystals can be dried from salt solutions to form topotactically related hemihydrate and anhydrite in approximately a year at surface temperatures and pressures. No demonstration of the formation of anhydrite on the earth's surface has been made previous to the recent description of the Persian Gulf sediments by Kinsman (1964). He believes the anhydrite found there to be primary and not to form from gypsum. At any rate there is no evidence of a topotactic relationship in the Persian Gulf samples as there is in the Clayton Playa samples.

There has been some mention of the natural occurrence of hemihydrate in the literature. Popov and Vorob'ev (1947) discuss the presence of the hemihydrate in the salt soil deposits of central Asia where it is often described as anhydrite. Their investigation shows these materials to have the refractive indices of hemihydrate, not anhydrite. De la Hunty and Low (1958) describe a powdered gypsum called "kopi" in the arid areas of Western Australia. This material is said to come from the weathering of gypsum crystals although their analysis seems to indicate that the material is still gypsum. It seems possible that "kopi" is produced by successive alteration to hemihydrate and re-hydration to gypsum. In the zones of sulfate accumulation in Western Australia the rainfall is 10–15″/year, apparently higher than the 5″/year of Clayton Playa. Further investigation of natural occurrences of the topotactic alteration of gypsum to hemihydrate and anhydrite will be necessary before one can assess the geological significance of this phenomena.

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