

HEXAHYDRITE ($MgSO_4 \cdot 6H_2O$) AS AN EFFLORESCENCE OF SOME OHIO DOLOMITES

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The water-soluble salts which are present in many limestones and dolomites are believed to have some effect on the industrial behavior of these rocks, particularly when used in lime-burning and in building stone (Kessler and Sligh, 1927; Lamar and Shrode, 1953). Such salts often appear as a natural efflorescence on exposed but protected surfaces of these carbonate deposits. Several years ago a mineralogical study of the efflorescence of the dolomites of Ohio was undertaken by the authors. In all instances where efflorescence occurred, the only major mineral constituent found to be present was hexahydrate ($MgSO_4 \cdot 6H_2O$). This purportedly rare mineral has never before been reported in Ohio. Because of both the mineralogical and economic implications of these studies it was thought that a description of the occurrences and a discussion of their origin might be of interest. This is a portion of a broader investigation of the mineralogy of Ohio, one paper on which has already been published (Brant and Foster, 1959).

DISTRIBUTION OF HEXAHYDRITE OCCURRENCES

Since its discovery in British Columbia, Canada, about fifty years ago (Johnston, 1910), hexahydrate has received scant attention at the hands of mineralogists. It has been described as very rare (Winchell, 1931), and as occurring sparingly as a dehydration product of epsomite, and rarely as a direct deposit in salt lakes (Palache, Berman, and Frondel, 1957). Its discovery as a hydration product of kieserite (Leonhardt and Berdesinski, 1951), itself an uncommon mineral, is also suggestive of rarity. It has been noted as a laboratory efflorescence (Brownell, 1959), but this could scarcely qualify as a natural occurrence. Certainly, the mineralogical literature suggests a scarcity for this mineral which is hardly substantiated by the numerous occurrences noted in Ohio, and reported below.

TABLE 1
Known Ohio Hexahydrate Localities

County	Locality	Age	Formation
Adams	Monro Twp.	Silurian	Brassfield
Adams	Bratton Twp.	Silurian	Peebles
Hancock	Findlay	Silurian	Greenfield
Highland	Brush Creek Twp.	Silurian	Bisher
Sandusky	Gibsonburg	Silurian	Guelph
Wood	West Milgrove	Silurian	Greenfield
Wood	Milton Twp.	Devonian	Dundee
Wyandot	Carey	Silurian	Greenfield
Wyandot	Carey	Silurian	Guelph
Wyandot	Crane Twp.	Silurian	Tymochtee

The known Ohio occurrences of hexahydrate are located in the four northern counties of Wood, Sandusky, Hancock, and Wyandot, and the two southern counties of Highland and Adams (fig. 1). The known stratigraphic, or geological, distribution of the deposits ranges from the "Belfast beds" of the Brassfield limestone, Silurian in age, to the Dundee Limestone of Devonian age. Between these limits, the following Silurian formations, in order of decreasing age, were found to contain hexahydrate deposits: Bisher, Guelph, Peebles, Greenfield, and

Tymochtee. These occurrences are listed by county and locality in table 1. To date, no such efflorescence has been found on Ohio carbonate rocks older than Silurian nor younger than Devonian age. Further search, however, may reveal this phenomenon to be even more widespread, both geographically and geologically.

The best sites for the observation and collection of the hexahydrite deposits have been near-vertical or somewhat overhanging quarry-faces that have not been worked for some time. Freshly-worked quarry-faces are unlikely to display such deposits, because of insufficient time for their formation. Generally, the initial hexahydrite coating on a quarry face is first noted in the shattered area in the vicinity of a blast hole, or in unshattered rock that is porous in texture. From such growth-centers the deposit may continue to spread outward to more massive and less porous rock. Fresh deposits are white, fluffy, and fine-grained, and the thin layers may be brushed off without difficulty. Older deposits, believed in some cases to have weathered the rigors of one or more winters, are somewhat grayish in color, quite coarsely recrystallized, and much more strongly adherent to the dolomite host-rock.



FIGURE 1. Map of Ohio showing counties and localities (indicated by stars) where hexahydrite has been found.

MINERALOGY

Hexahydrate bears a strong resemblance in physical and chemical properties to epsomite, a mineral with which it is said often to be associated. The similarity in properties is apparent from table 2. Chemically the two minerals are too nearly identical to be distinguished by other than quantitative analysis for water content. The crystal systems are different, but the natural material is generally too poorly crystallized and fine-grained to allow distinction on this basis. Indeed, such efflorescences, be they epsomite or hexahydrate, seldom exhibit the fibrous habit implied in this table. Specific gravity differences, though measurable, would require pure material and the use of a fluid other than water to prevent dissolution

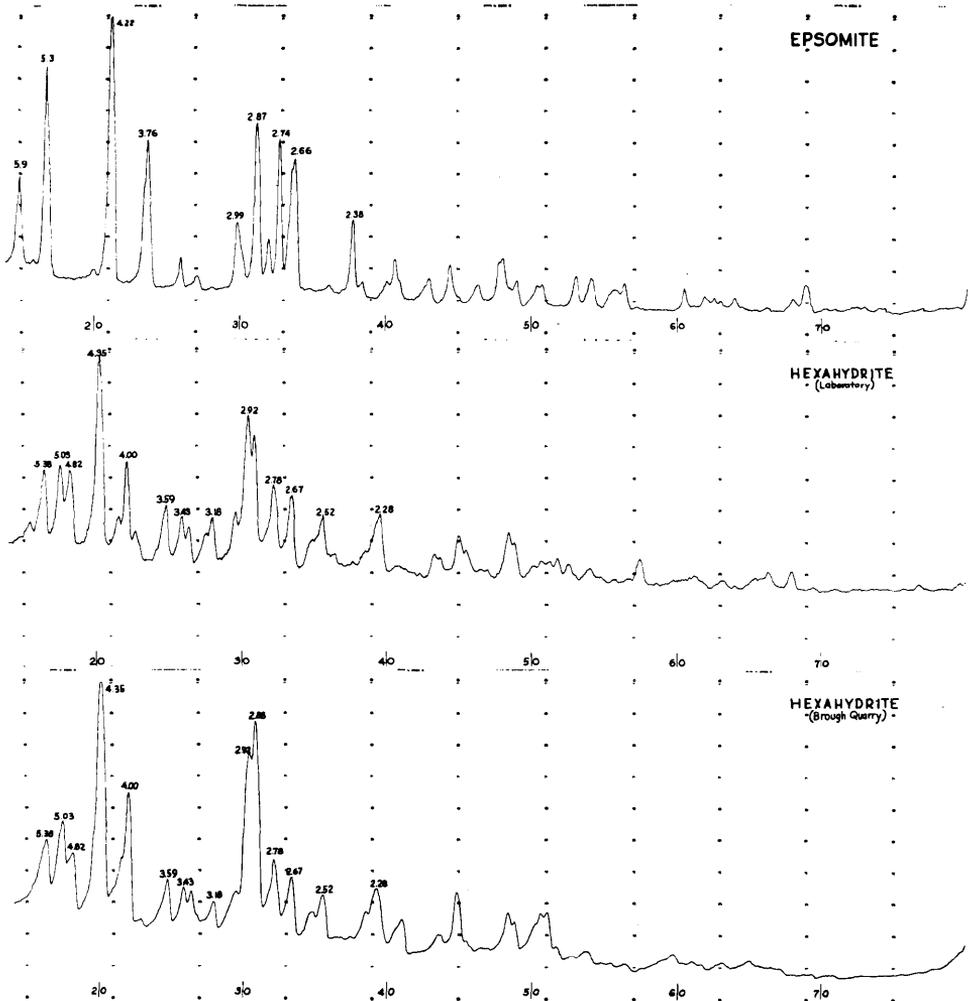


FIGURE 2. X-ray diffractometer patterns: (Copper $K\alpha$ radiation)
 Units at base of patterns: 2θ (Bragg angle)
 Principal peaks indexed in angstrom units
 Top Pattern: Epsomite (synthetic)
 Middle Pattern: Hexahydrate (synthetic)
 Bottom Pattern: Hexahydrate (natural)

of the sample during the determination. A diagnostic method described by the senior author should be applicable (Foster, 1947). Refractive indices are the most frequently used data for the optical identification of non-opaque minerals. Because of the poorly crystallized nature of efflorescences, the near-identity of the indices of these two minerals could easily lead to erroneous identification. It seems highly probable that optical methods might often have led to mis-identification of hexahydrate as epsomite.

An unerring technique for distinguishing hexahydrate from epsomite is that of X-ray powder diffraction. It is possible thereby to "fingerprint" a mineral and to distinguish it from all others, even those which are chemically and optically almost identical, and even those which are too fine-grained for successful microscopic identification. Figure 2 presents X-ray diffractometer patterns for a sample of epsomite (reagent grade $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), a sample of hexahydrate (formed by partial dehydration of epsomite), and a sample of natural efflorescence from an

TABLE 2
Comparison of Properties of Hexahydrate and Epsomite

Property	Hexahydrate	Epsomite
Chemical Formula	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Crystal System	monoclinic	orthorhombic
Habit	fibrous, columnar	fibrous, reniform
Specific Gravity	1.757	1.677
Refractive Indices		
alpha	1.426	1.432
beta	1.453	1.456
gamma	1.456	1.461
Optic Sign	negative	negative
Optic Angle	38°	52°

Ohio dolomite (Greenfield dolomite from the Brough quarry at West Milgrove, Wood County, Ohio). The first two patterns match the X-ray diffraction data recorded by the American Society for Testing Materials for known samples of epsomite (A.S.T.M. Card No. I-0399) and hexahydrate (A.S.T.M. Card No. I-0354), respectively. Comparison of the third to the other two patterns leaves little doubt that the efflorescence corresponds with $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (hexahydrate) rather than $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite). Samples from all ten of the localities listed in table 1 likewise gave hexahydrate diffraction patterns.

ORIGIN OF HEXAHYDRITE

The origin of hexahydrate can be conveniently discussed with the aid of the phase diagram for the system $\text{MgSO}_4\text{-H}_2\text{O}$ (fig. 3). The data used in its construction have been calculated from published solubility data (Bronsted, 1928). This diagram shows the equilibrium relationships of hexahydrate to such other hydrated magnesium sulfates as $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (kieserite), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite), and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$. In several respects the diagram is recognized to be incomplete. It does not depict the stability relations of several other known or alleged hydrates of magnesium sulfate, including $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ (sanderite), $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ (?), $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ (starkeyite), and $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ (pentahydrate). It does not differentiate between the orthorhombic and tetragonal polymorphs of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, nor between the orthorhombic and monoclinic polymorphs of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Nevertheless, the diagram does serve to suggest a number of the more probable modes of formation of hexahydrate.

Figure 3 indicates that stable equilibrium precipitation of hexahydrate from an evaporating aqueous solution of magnesium sulfate should occur only in the temperature range 48.2 to 68 C (arrow 1). Although evaporation of solutions above 68 C or below 48.2 C should deposit epsomite or kieserite, respectively, it is known that hexahydrate may be precipitated metastably (arrows 2 and 3). Hydration of kieserite may also form hexahydrate (arrow 4) as mentioned earlier (Leonhardt and Berdesinski, 1951). So also may the dehydration of epsomite (Palache, Berman and Frondel, 1957) as suggested by arrow 5. The well-known deterioration of Epsom salt crystals when left uncovered is due to this reaction. An additional possibility that has been suggested (Kuhn, 1952) is the solid state interaction of kieserite and epsomite (double arrow 6). Although not clearly indicated by the diagram the hydration of sanderite, starkeyite, or pentahydrate should also produce hexahydrate.

Instances of most, if not all, of the above methods of hexahydrate formation have been noted, either in nature or in the laboratory, or both. However, sufficient is known regarding the depositional environment of the Ohio occurrences to rule out all but a few of these possible mechanisms. Since the deposits are obviously forming by evaporation of solution, the hydration of any preexisting crystalline lower hydrate is eliminated from consideration. The solid state interaction of several hydrates is likewise excluded. There remain only the methods depicted by arrows 1, 2, 3, and 4. The temperature required for the mechanism suggested by arrow 2 is never attained in these deposits. Temperatures required for the direct stable precipitation of hexahydrate (arrow 1) would be attained rarely, and only in the most intense heat of the hottest of summer days. The only remaining alternatives appear to be, then, the metastable precipitation of hexahydrate in the stability range of epsomite (arrow 3), or the stable precipitation of epsomite followed by its partial dehydration to yield hexahydrate (arrow 4).

Limited laboratory tests were conducted to determine which hydrate is precipitated from aqueous solution at temperatures normally prevailing in the depositional environment. A solution of magnesium sulfate in distilled water was prepared. Portions of the solution were heated in Pyrex beakers at selected temperatures in a drying oven. Heating was interrupted as soon as a layer of crystals had formed on the bottom of the beaker. Tests were conducted at 25, 40, 60 and 80 C. Epsomite was obtained in all cases, even in the stability ranges of hexahydrate and kieserite. In the latter instances the deposition of epsomite must be regarded as metastable. These controlled evaporation tests would seem to suggest that the formation of epsomite must precede the development of hexahydrate in the efflorescence on dolomites. However, the evaporation conditions are by no means the same in the laboratory and in the quarry. In the former case the crystals form under water and out of contact with air. In the latter, water seeps to the rock surface by capillarity, and evaporates as rapidly as it reaches the surface. Consequently, there is no continuous layer of water protecting the growing crystals, which develop, rather, in direct contact with air.

Numerous experimental efflorescence tests were made in order to simulate the conditions under which the natural efflorescence develops. Lumps of dolomite were placed in shallow pans partially filled with distilled water, so that the bottom portion only of the dolomite specimen was immersed in the water. In less than 24 hours efflorescence appeared on the exposed upper surfaces of the dolomite, and continued to accumulate slowly for days or even weeks. Water laden with soluble salts apparently was drawn up by capillarity through the rock pores, and evaporated and deposited the salts at the surface. Careful observation revealed no continuous film of water, and no sign of clear, vitreous crystals characteristic of freshly formed epsomite. In all cases the deposits were white, fluffy, poorly crystallized coatings closely resembling the natural hexahydrate efflorescence from the quarries. X-ray patterns confirmed the presence of hexahydrate. It is

therefore supposed that, in both natural and experimental efflorescences, hexahydrate forms directly from solution, without the prior deposition and subsequent dedhydration of epsomite.

Work already cited on water-soluble salts in representative Illinois limestones and dolomites (Lamar and Schrode, 1953) throws no direct light on the origin and nature of Ohio dolomite efflorescence. The cited authors found no hexahydrate, nor any other magnesium sulfate minerals, among the minerals identified in experimental efflorescences from six selected limestones and dolomites. However, five other carbonate rocks yielded "MgSO₄" in the leach solids obtained by evaporating water-soluble extracts to complete dryness. The authors speculated that an intergranular solid magnesium sulfate mineral (species not indicated), and possibly also intracrystalline fluid inclusions, were the source of these leach solids. We are inclined to accept such intergranular and intracrystalline sources for the

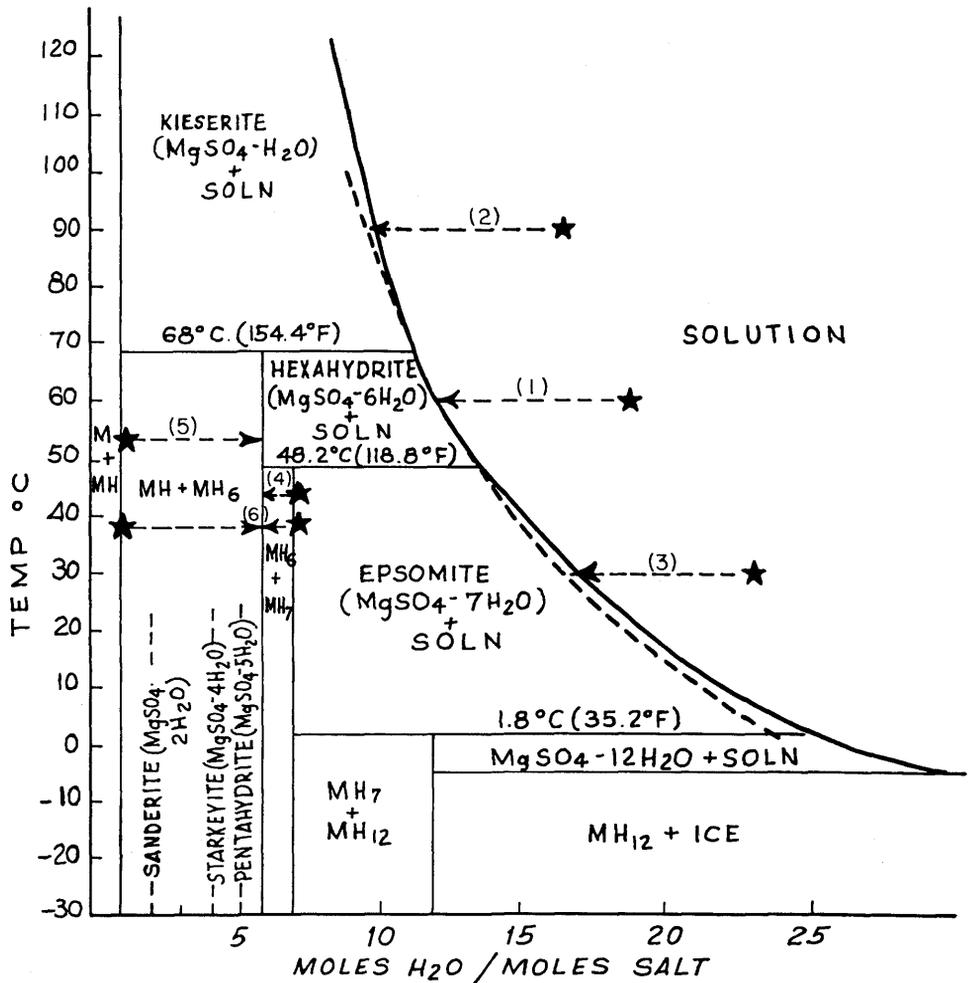


FIGURE 3. Phase diagram for the system MgSO₄-H₂O
 Arrows: possible modes of formation of hexahydrate
 Abbreviations: M=MgSO₄; H=H₂O; SOLN=Solution

magnesium sulfate which gives rise to the hexahydrate efflorescence observed on Ohio dolomites.

The genesis of the hexahydrate efflorescence occurring on the Ohio dolomites is believed to be somewhat as follows. Surface water percolates down through cracks, fissures and pores in the dolomite. As it descends, it dissolves magnesium sulfate in the form of intergranular solid soluble salts and intracrystalline fluid inclusions. Capillary action draws some of this salt solution to exposed surfaces, such as quarry faces, especially in the more porous and badly fractured strata. The solution is believed to evaporate as rapidly as it reaches these surfaces, precipitating hexahydrate directly without prior formation of epsomite. Hexahydrate is reported to alter to epsomite on exposure to moist air (Palache, Berman, and Frondel, 1957). Whether marked changes in humidity, to which the hexahydrate deposits are unquestionably exposed, result in repeated hydration to epsomite and dehydration to hexahydrate, is not clear. No evidence for such cyclic changes has been observed. On the contrary, the tendency for the deposits to become more dense, coarse, and tightly adherent with age would seem to suggest a unidirectional rather than a cyclic process. There appears, then, to be no need to postulate either an initial or an intermittent formation of epsomite to account for the hexahydrate efflorescence.

In summary, the occurrence of hexahydrate in widely scattered localities in Ohio strongly suggests that it is of common occurrence. This view is contrary to the suggestion in the various mineralogy textbooks that this mineral is uncommon. On the other hand, mineralogical manuals suggest that epsomite is of widespread occurrence under the conditions observed in this study for hexahydrate. In view of the close similarity in optical properties of the two minerals, and the failure to find epsomite in efflorescence on Ohio dolomites, it appears highly probable that many of the reported occurrences are in fact hexahydrate. It is believed that the ability of any given carbonate deposit to display such efflorescence depends ultimately on the presence in the rock of traces of readily soluble magnesium salts.

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