of the year. Jambor and Traill conducted their investigations in Ottawa, Ontario, a mid-continental region of moderate humidity, in which rozenite is probably the stable phase for much of the year. Hence both sets of investigators reached correct conclusions for their particular localities.

The problem is to a great extent caused by the normal reluctance of melanterite to dehydrate under conditions of low humidity. This metastable persistence is probably due to large grain size and lack of appreciable air movement over the sample.

ACKNOWLEDGMENTS

The authors wish to thank the National Institute of Health for financial support of this project under grant WP-00340, as well as Michael Fleischer of the U. S. Geological Survey for information on the proper nomenclature of the minerals examined.

REFERENCES

BRANT, R. A. AND W. R. FOSTER (1959) Magnesium halotrichite from Vinton County, Ohio. *Ohio Jour. Sci.* **59**, 187–192.

ECKEL, EDWIN B. (1933) Stability relations of a Colorado pisanite (cuprian melanterite) *Am. Mineral.* **18**, 449–454.

JAMBOR, J. L. AND R. J. TRAILL (1963) On rozenite and siderotil. *Canad. Mineral.* **7**, 751–763.

MIDGLEY, H. G. (1962) On the occurrence of siderotil in Thames River gravel. *Am. Mineral.* **47**, 404–409.

THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

SULFATE MINERALS: THEIR ORIGIN IN THE CENTRAL KENTUCKY KARST[1]

E. R. POHL, *Cave Research Foundation, Yellow Springs, Ohio*

AND

WILLIAM B. WHITE, *Materials Research Laboratory and Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania.*

Sulfate minerals, especially gypsum, are present in large quantities in most of the extensive limestone caves of the Mississippian plateaus and outliers of Central Kentucky. Many descriptions of these deposits have been published (Locke, 1842; Weller, 1927; Huff, 1940); however, the origin of the deposits has remained obscure.

---

[1] Contribution No. 8 of the Cave Research Foundation and Contribution No. 63-78 of the College of Mineral Industries, The Pennsylvania State University.

Various sources have been suggested for the sulfates. These include sulfides occurring elsewhere in the stratigraphic column (Weller, 1927; Pohl and Born, 1935) and inwash materials from an arid soil presumed to exist in Pleistocene time (Davies and Chao, 1959). Other sources, such as ion exchange on the clays of the cave fills and oxidation products from sulfur-consuming bacteria have been discussed, although not formally published.

We shall argue that sulfides are the source of the sulfates, (i) by showing that an overlying source of sulfides exists, and (ii) by describing the processes of weathering, transportation and deposition that can reasonably be expected to have occurred in the given circumstances.

Because of their very rapid rate of weathering, sulfide minerals are not normally observable in outcrop. Fortunately, new road and facility construction in Mammoth Cave National Park and in the vicinity of the Nolin Reservoir have uncovered numerous unweathered exposures which have allowed us to make the observations described below.

Pyrite occurs disseminated in the upper 50 feet of the Girkin limestone. The contact at the base of the Big Clifty formation[2] is exposed in road cuts on Joppa Ridge, at Turnhole Bend, and on the Park Road to New Entrance of Mammoth Cave in Mammoth Cave National Park. On Joppa Ridge the basal Big Clifty is separated from the underlying Girkin limestone by six feet of black shale with sandstone lenses. The shale contains elemental sulfur in weathered section. At Turnhole Bend less than 1500 feet away, the black shale is missing but there is an extensive weathered layer with much loose powdery poorly crystallized silica and some organic material at the contact. At Cane Run, just north of the Park, the contact between the Big Clifty sandstone and the overlying Haney limestone is exposed. At the contact is two feet of black shale rich in plant remains and containing thin coals. Nodular pyrite occurs abundantly in this layer, making up approximately 5% of the total bulk. Some pyrite also occurs disseminated in the Haney limestone.

The mechanisms responsible for the weathering and transport of the sulfur bearing species are complex; both inorganic and organic mechanisms may be at work. The inorganic chemistry of sulfide weathering has been well documented by Garrels (1960), Sato (1960) and Barnes and Kullerud (1961) and indicates that the sulfate ion is the stable species in solution under surface weathering conditions. If the pH of the solution falls near 2, sulfur may be precipitated and remain metastably, as the oxygen activity of the solution continues to rise. This may explain the

---

[2] We use for convenience the formation names adopted by the U. S. Geological Survey on their recent series of Kentucky Geological Quadrangle maps. The features described may be found on Mammoth Cave, Rhoda, and Cub Run $7\frac{1}{2}$ minute quadrangles.

sulfur which occurs in the black shale. If the pH is buffered near neutrality as it would be if the solution were in contact with carbonates, only the sulfate ion should appear.

Samples collected from the Cane Run occurrence were found to decompose, yielding an efflorescence of white salts within two months in either open or closed storage when temperatures and relative humidities were high. This extremely rapid decomposition of the pyrite is unusual and suggests that decomposition in the presence of atmospheric water may be bacteriogenic. Evidence of bacteriologic influence on the rate of sulfide weathering has, for example, been demonstrated in the case of acid mine waters by Lorenz and Tarpley (1963) and Barnes and Clark (1964).

Samples of pyrite from fresh exposures and seep waters from pyrite horizons were submitted to various bacteriological studies, including natural collections, crude and sub-cultures. In one series a modified Leathen medium (Leathen, *et al.*, 1951) at pH 3.0 was used in tubes and silica gel plates. In each case ferric iron was produced within one week at room temperature. Pure strains of highly motile autotrophic cells were produced, mostly occurring singly, less than one micron in largest diameter. Morphology was studied by phase contrast. These forms appear to by *Thiobacillus thiooxidans* and *T. ferrooxidans*. In another series one gram portions of crushed pyrite were isolated from nodule centers into sterile distilled water at pH 7.0. At 24 hours the pH had dropped to 3.5 from which point it continued to drop slowly and gradually in the succeeding three months to 2.0. A luxurious bacterial flora of wide variety culminated in a pure culture of single, motile ovoid cells, slightly less than one micron in diameter, sometimes arranged in tetrads and short streptococcus-like chains.

The transport of material from the weathered sulfide source in the over lying clastic rocks to the site of deposition in the cavern passages is not observable. We postulate that the source pyrite is weathered with the aid of bacterial action at the surface of the Big Clifty sandstone. The iron remains in the sediment as an isoluble iron oxide and hydroxide, or is transported only short distances to form the observed iron staining of the outcrops while the sulfate ion is carried in solution through breaks or absences of the basal shale into the limestone. Since the cavern passages are sparsely distributed, the sulfate bearing solutions reach passages on all levels in the limestone—not merely the highest level passages. The avenues of transport in the limestone are joints, fractures, bedding planes and clastic zones and may involve both vertical and horizontal motion of the solutions.

The earlier work of Weller (1927) and Huff (1940) and the recent report of Davies and Chao (1959) agree that the sulfate minerals occur both on walls and ceilings of passages as crusts and groups of curved acicular crystals, and in the clastic sediments of the cave floors. Davies and Chao claim that gypsum is uniformly dispersed in the cave fills. The wall and ceiling sulfates are not uniform in distribution; some passages are intensely mineralized, others very sparsely mineralized. Sulfates occur at all levels in the cave system except for the base level passages which are frequently flooded.

Sulfate minerals occur on the ceilings of certain caves of the Sinkhole Plain which carry perennial free-surface streams. The gypsum must have been deposited by downward moving solutions rather than by lateral movement with the stream sediments.

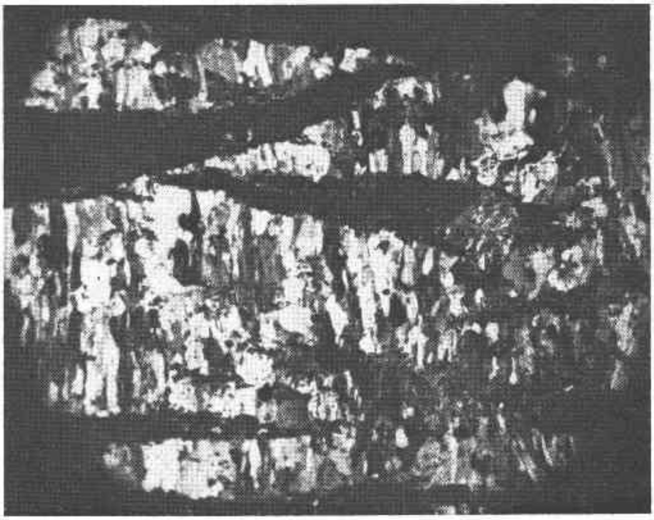

FIG. 1. Photomicrograph of limestone fragments now nearly replaced by gypsum. Crossed polars. ×12.

The emplacement of gypsum in the caves results in much fragmenting and chemical attack on the wallrock. There are many rock fall zones containing up to 20% gypsum in which the collapse was apparently activated by crystal wedging. Thin sections of the rock fragments exhibit many veinlets of gypsum intruding into the limestone and evidence of attack and replacement of calcite by gypsum (Fig. 1). Other evidences of chemical attack are curved rock slabs in which replacement of limestone by gypsum is nearly complete and piles of calcite rock flour left as the final product of limestone degradation.

The emplacement mechanism involves the reaction of a sulfate-bearing solution with calcite wall rock and may be written as:

$$H^+ + SO_4^{2-} + CaCO_3 \rightleftharpoons CaSO_4 \cdot 2H_2O + HCO_3^-.$$

The equilibrium constant for this reaction can be calculated from Latimer's (1958) thermochemical data to yield:

$$\frac{[HCO_3^-]}{[H^+][SO_4^{2-}]} = 10^{6.6}.$$

Since the pH of solutions moving in limestone is expected to be near 7, the expected bicarbonate ion sulfate ion ratio would be near unity. Thus, the sulfate ion—bicarbonate ion concentrations are just balanced and any decrease in bicarbonate ion concentration will cause gypsum to be deposited. The necessity for releasing CO_2 gas in order for the reaction to proceed is a likely explanation for the observed fact that much of the gypsum is deposited in the cave wallrock rather than deeper in the limestone. Build-up of CO_2 pressure would halt the reaction until the percolation of the solution brings it near an open cave passage. Release of CO_2 into the cave atmosphere would cause the gypsum to be deposited by an *in situ.* reaction in the wallrock, thus causing the observed attack and replacement.

Additional transport of gypsum by solution could still take place and may be responsible for the gypsum which occurs in the clastic fills.

References

Barnes, H. L. and G. Kullerud (1961) Equilibria in sulfur-containing aqueous solutions, in the system Fe-S-O, and their correlation during one deposition. *Econ. Geol.* **56,** 648–688.

Barnes, I. and F. E. Clarke (1964) Geochemistry of groundwater in mine drainage problems. *U. S. Geol. Survey Prof. Pap.* **473-A,** 1–6.

Davies, W. E. and E. C. T. Chao (1959) Report on Sediments in Mammoth Cave, Kentucky. *Adm. Rpt. U. S. Geol. Survey to Natl. Park Serv.*

Garrels, R. M. (1960) *Mineral Equilibria.* Harper and Brothers, New York, p. 151.

Huff, L. C. (1940) Artificial helictites and gypsum flowers. *Jour. Geol.* **48,** 641–659.

Latimer, W. M. (1958) *Oxidation Potentials.* Prentice Hall, Englewood Cliffs, New Jersey.

Leathen, W. W., L. D. McIntyre and S. A. Braley (1951) A medium for the study of the bacterial oxidation of ferrous iron. *Science* **114,** 280.

Locke, John (1841) Alabaster in the Mammoth Cave of Kentucky. *Am. J. Sci.* **42,** 206–207.

Lorenz, W. C. and E. C. Tarpley (1963) Oxidation of coal mine pyrites. *U. S. Bur Mines Rpt. Invest.* **6247.**

Pohl, E. R. and K. M. Born (1935) Development of gypsum in limestone caves. *Proc. Geol. Soc. Am.* **96.**

Sato, M. (1960) Oxidation of sulfide ore bodies. *Econ. Geol.* **55,** 928–961, 1202–1231.

Weller, J. M. (1927) The geology of Edmonson County. *Kentucky Geol. Surv.* ser. vi., **28.**