SHABYNIN, L. I. (1955) Ascharite and other borates in magnetite ores of contact-metasomatic deposits. *Doklady Akad. Nauk SSSR*, **101,** 937–940 (in Russian).

——— (1961) The so-called magnioborite. *Zapiski Vses. Mineralog. Obshch.* **90,** 754–755 (in Russian).

TAKÉUCHI, Y. (1952) The crystal structure of magnesium pyroborate. *Acta Cryst.* **5,** 574–581.

TOROPOV, N. A. AND P. F. KONOVALOV (1940) The binary system magnesium oxide-boric anhydride. *Zhur. Fiz. Khim.* **14,** 1103–1109 (in Russian).

WATANABE, TAKEO (1953) Suanite, a new magnesium borate from Hol Kol, Suan, North Korea. *Mineral. Jour. (Japan)*, **1,** 54–62; (abs.) *Am. Mineral.* **40,** 941 (1955).

THE AMERICAN MINERALOGIST, VOL. 48, JULY-AUGUST, 1963

SOME UNUSUAL MINERALS FROM THE "MOTTLED ZONE" COMPLEX, ISRAEL

Y. K. BENTOR, *Geological Survey of Israel and Hebrew University, Jerusalem* AND S. GROSS AND L. HELLER, *Geological Survey of Israel.*

In most parts of Israel a chalky-shaly rock sequence, the Ghareb and Takiye formations is found overlying flint beds of Campanian age. In subsurface sections this sedimentary rock sequence is generally highly bituminous and may contain 25 per cent or more organic matter. In a number of widely separate areas, however, such as the Hatrurim region and the Beersheba Valley in the northern Negev, near Ramleh in the coastal plain and at Maaleh Adumim in the Jordanian part of the Judean Desert, a peculiar rock complex, the so-called "Mottled Zone," appears instead of this normal sequence. The "Mottled Zone," which reaches a maximum thickness of 220 m, comprises a large number of rock types such as limestone, chalk, marl, shale as well as gypseous, ferruginous and phosphatic rocks, all distinguished by a pronounced but highly irregular coloration. These various rock types occur without any apparent regularity and pass into each other without distinct boundaries. No bedding can be observed, but a schist-like structure is fairly common. This rock sequence contains an abundance of trace elements, among which Ag, V, Ni and Cr are prominent. Chromium, in the form of green chromium silicates in particular is found in many veins up to 1 m thick and may make up 6 per cent of the vein material.

One of the most widespread rock types of the "Mottled Zone" is a very hard, dense, splintery, brown, violet or black rock. Microscopic examination shows it to be composed mainly of calcite and spurrite,[1] approxi-

---

[1] Spurrite has also been found in these rocks by E. Sass and tobermorite by C. Milton (private communication).

mately in the ratio 2:1. Calcite appears as xenomorphic grains, some twinned and up to 0.6 mm in size. The spurrite crystals, which reach up to 0.3 mm, are idiomorphic to hypidiomorphic with pseudohexagonal or prismatic outlines. They show high relief, medium birefringence and are biaxial negative, with small 2V, weak dispersion ($r>v$), $x=b$, $y\wedge c=-33°$, $z\wedge a \sim 0°$. The crystals exhibit two sets of cleavages, one distinct, the other poor, at an angle of 79°. Two types of twinning, one simple, the other polysynthetic, are characteristic; the angle between the two planes is 57°. The crystals appear granulated due to intense cracking and generally contain round or elliptical, drop-like inclusions of calcite up to 0.02 mm across. Minor constituents of the rock are chlorite and an as yet unidentified iron sulfide. This composition, derived by microscopic examination, is compatible with the results of chemical analyses, which in addition indicate the presence of some tenths per cent of organic material.

The rock is traversed by a criss-cross system of small veinlets, rarely exceeding 1 mm in width. In these veinlets a number of uncommon minerals have been identified, which include vaterite, portlandite, bayerite, minerals of the tobermorite group,[1] an as yet unknown calcium silicate hydrate related to tobermorite, thaumasite and, very much more abundantly, ettringite. With the exception of portlandite, thaumasite and ettringite these minerals occur in a very fine state of subdivision and frequently show a fibrous habit.

Bayerite, $Al(OH)_3$, occurs as white fibers with parallel extinction, associated with calcite in one specimen and with calcite and gypsum in another. The mineral was identified by its distinctive *x*-ray powder pattern. Of the three polymorphic forms of $Al(OH)_3$ gibbsite is very common, nordstrandite has recently been reported from two localities, (Wall *et al.*, 1962; Hathaway and Schlanger, 1962), but this appears to be the first recorded natural occurrence of bayerite, although the material is readily prepared artificially.

Vaterite, the third polymorph of $CaCO_3$, has previously been reported from Ballycraighy (McConnell, 1960). In the present samples it was found intimately mixed with calcite and aragonite and in one specimen also with barite. The crystals are too small to be identified under the microscope; they were recognized by their *x*-ray powder pattern, which resembles that of the mineral from Ballycraighy.

Portlandite, $Ca(OH)_2$, forms tabular crystals which, together with fluorapatite and ettringite, line the walls of the very thin veins in the black spurritic-calcitic rocks. They are colorless, transparent, with pearly luster and high birefringence, uniaxial negative, $\omega=1.576\pm.001$. The *x*-ray pattern is identical with that of synthetic $Ca(OH)_2$, after correction for preferred orientation. Portlandite in nature is very rare; it has previously been found in Scawt Hill (Tilley, 1933), Vesuvius (Minguzzi, 1937; Carobbi, 1940) and Ettringen (Hentschel, 1961).

Minerals of the *tobermorite group*, predominantly 14 Å calcium silicate hydrate but less frequently also the 11 Å modification were identified in several samples scraped from veins in the reddish-brown rocks. The minerals occur as white fibers with silky luster and form mostly radial aggregates but locally also lenses up to 2 mm in size. Optical data: Negative elongation, biaxial positive, 2V very small, very low birefrigence, β approximately 1.552. *X*-ray data for the present samples of the 14 Å mineral very closely resemble those of the type mineral from Crestmore (Heller and Taylor, 1956). The 11 Å modification probably corresponds to a lower hydration state of the same material, since the hkO spacings are identical for all the 14 and 11 Å minerals examined.

In addition to 11 and 14 Å tobermorite another white fibrous material was found which, although it gives rise to a distinctive *x*-ray pattern, may be a member of the tobermorite group. The fibers show parallel extinction and mostly positive elongation. The strongest *x*-ray spacings are at 10.40, 2.92 and 1.806 Å; the repeat distance in the fiber direction is 7.2 Å, with pronounced pseudohalving. This value is slightly lower than the 7.3 Å spacing usually observed for fibrous hydrated calcium silicates, but pseudohalving of the fiber axis is a characteristic of the group.

The mineral usually occurs intergrown with some ettringite and tobermorite. Both the unknown material and ettringite exhibit strongly preferred orientation along the fiber axis, but complete randomness in the perpendicular directions. Ettringite is oriented with its hexagonal *c* as fiber axis. The associated tobermorite shows no preferred orientation.

Grinding the unknown mineral with water does not affect its *x*-ray pattern. On heating up to 850° C. the morphology of the fibers remains unchanged. Well oriented wollastonite and partially oriented larnite are obtained, with their *b* axes in the fiber direction. At lower temperatures various oriented but as yet unidentified products were formed; at about 400° C. the material is apparently amorphous to *x*-rays.

The thermal decomposition products of this mineral and the similarity of its *x*-ray pattern to those of fibrous hydrated calcium silicates suggest that the chemical composition is $xCaO$, SiO_2, yH_2O, where $1 < x < 2$. Unfortunately it has so far proved impracticable to isolate sufficient quantities of the pure material even for microchemical quantitative analysis.

The question whether this mineral represents a distinct species or merely a further modification of the tobermorite group must at present remain open.

Thaumasite, $CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 14.5H_2O$, has been identified in two specimens, apparently pure in one and mixed with aragonite, calcite and a modified form of ettringite in the other. It forms very thin prisms with parallel extinction, negative elongation and fairly high birefringence. The *x*-ray powder pattern is identical with that of thaumasite from County Down, Ireland (Knill, 1960), of which a specimen was kindly supplied by Dr. P. Sabine.

Ettringite, ideal composition $6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 31\ H_2O$, is relatively widespread in veins and cavities in "Mottled Zone" rocks both in the Hatrurim and Ramleh areas. It is transparent and occurs in three morphologically different modifications: as lemon-yellow, hexagonal prisms, as colorless prisms and as very thin white fibers. The yellow crystals, which show vitreous luster, are only up to ½ mm across and have no terminal faces, but perfect $(10\bar{1}0)$ cleavage. Qualitative microchemical analysis indicates the presence of traces of Fe in addition to the major Ca, Al, SO_4 and H_2O, which may account for the coloration. The colorless prisms are exceptionally well developed, up to 3 mm across and terminated by rhombohedral faces (Fig. 1). They are coated with an opaque white powder, which may be a dehydration product. The fibers form radial aggregates or grow perpendicular to the vein walls.

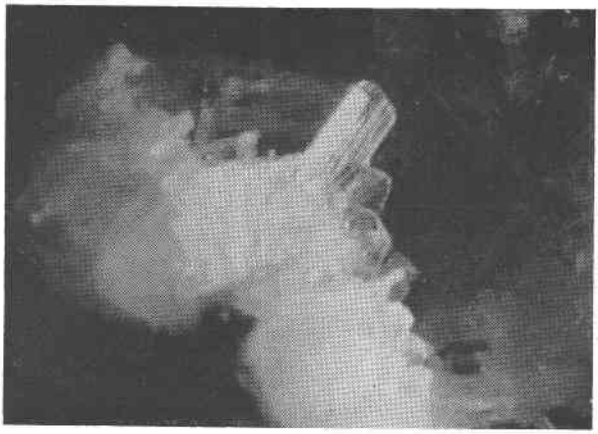

FIG. 1. Well-developed prisms of ettringite.

The optical data for the three modifications are as follows:

	Extinction	*Elongation*	ϵ	ω
yellow prisms	parallel	−	1.462 ± .001	1.468 ± .001
white prisms	parallel	−	1.458 ± .001	1.462 ± .001
white fibres	parallel	−	1.484 ± .001	

It is evident that ϵ of the fibrous modification is considerably higher than that of the other two. Microchemical analysis indicates the presence of some Si^{4+} and CO_3^{2-} in the fibrous, but not in the prismatic variety.

With one exception the x-ray powder photographs of all the samples examined, both fibrous and prismatic, closely resemble that of synthetic material. The data correspond to A.S.T.M. card No. 9-414. The notable exception is the specimen associated with thaumasite mentioned previously. The powder photograph of this sample can be satisfactorily indexed, if it is assumed that $a = 11.23$ Å (or 22.46 Å, *cf.* Hurlbut and Baum, 1960) as for synthetic ettringite, but $c = 21.19$ Å instead of 21.44 Å. The decrease in c axis spacing may perhaps be attributed to some Si^{4+} for Al^{3+} and/or CO_3^{2-} for SO_3^{2-} substitution. On the other hand no change in cell dimensions was observed for other fibrous specimens which are optically similar and also contain Si^{4+} and CO_3^{2-}.

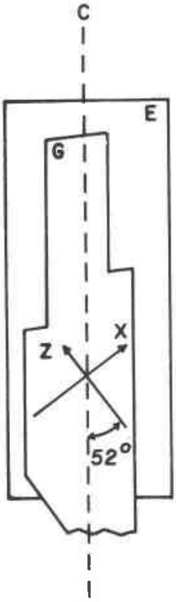

FIG. 2. Intergrowth of ettringite (E) with gypsum (G) (idealized).

An interesting phenomenon was observed when several colorless prisms, which at first sight appeared to be single crystals, were studied in greater detail. Under the microscope inclusions were revealed with considerably higher refractive index than the surrounding areas, positive elongation and optical orientation as indicated in Fig. 2. Single crystal oscillation and rotation photographs showed each individual to be composed of two well-defined crystals, gypsum and ettringite, in perfectly parallel orientation. With the crystal mounted along the direction of elongation, the layer lines are strictly parallel. The hexagonal *c* axis of the ettringite is parallel to the morphological *c* axis of the gypsum crystal (the [101] direction on Bragg's notation). The optical data are compatible.

It seems plausible to assume that, when a supply of Al^{3+}-containing solutions became available under highly specific physico-chemical conditions, ettringite grew directly upon existing gypsum crystals. A close structural relationship between gypsum and ettringite may, therefore, be inferred, but remains to be investigated.

No satisfactory explanation of the genesis of this unusual mineral assemblage can at present be given. The rock sequence in question is doubtlessly of sedimentary origin, as shown by the, admittedly very rare, occurrence of badly preserved fossils. It is most unlikely that the rocks of the "Mottled Zone" have been affected even by distant magmatic activity. There is no evidence of contemporaneous or later magmatic activity in or around any of the occurrences of this rock complex; more important, in all four localities mentioned the "Mottled Zone" rocks occupy the same stratigraphic position. In the Hatrurim area several hundred meters of the underlying strata, mainly limestones and dolomites of Middle to Upper Cretaceous age, are exposed, but no signs of contact metamorphism or hydrothermal alteration can be found in these underlying rocks.

It has been assumed (Bentor and Vroman, 1960) that the rocks of the "Mottled Zone" were originally similar in composition to the bituminous sediments of the Ghareb and Takiye Formations. At some time after burial of these strata by marine sediments of Eocene age, ground water rich in oxygen gained access to the sediments and caused oxidation of the sulphide minerals and of organic matter. Owing to low thermal conductivity of the overlying sediments the temperature of the ground water rose through the heat of oxidation and its geochemical activity was thereby enhanced. The result was a general redistribution of major and minor elements and the crystallization of new minerals. For processes of this kind the term *sedimentary hydrothermal activity* has been proposed. The minerals described in this paper probably developed in the final stages of this process through reactions between hot circulating groundwater and the rock. None of these minerals seems to have formed at a temperature higher than 100° C., but it is doubtful whether the abundant formation of spurrite, a mineral typical of high-temperature contact metamorphosed limestones, can be explained by this mechanism. The presence of minerals such as portlandite and ettringite indicates an extremely high alkalinity, in excess of pH = 11, which also remains unexplained. Water of such high alkalinity is most unusual, but has been observed, although not explained, in at least one case: the spring of Aqua de Ney, California. (Feth *et al.* 1961).

The data presented here are the result of a preliminary study of this interesting rock sequence. Further unusual mineral assemblages are under investigation.

ACKNOWLEDGMENT

We are grateful to Dr. M. Fleischer for drawing our attention to some of the references listed below.

REFERENCES

BENTOR, Y. K. AND A. VROMAN, (1960) The geological map of Israel. sheet 16: Mt. Sdom. *Geol. Survey Israel*, 58–61.

CAROBBI, G. (1940) *Bull. Volcan.* **7,** 25

FETH, J. H., S. M. ROGERS AND C. E. ROBERTSON, (1961) *Geochem. Cosmochim. Acta*, **22,** 75–86.

HATHAWAY, J. C. AND O. S. SCHLANGER, (1962) *Nature*, **196,** 265.

HELLER, L. AND H. F. W. TAYLOR, (1956) *Crystallographic Data for the Calcium Silicates.* H.M.S.O. London, 33.

HENTSCHEL, G. (1961) *Fortschr. Mineral.* **39,** 345.

HURLBUT, C. S. AND M. L. BAUM (1960) *Am. Mineral.* **45, 1137.**

KNILL, D. C. (1960) *Mineral. Mag.* **32,** 416.

MCCONNELL, M. D. C. (1960) *Mineral. Mag.* **32,** 535.

MINGUZZI, C. (1937) *Periodico Mineral.* **8,** 5.

TILLEY, C. E. (1933) *Mineral. Mag.* **23,** 419.

WALL, J. R. D., E. B. WOLFENDEN, E. H. BEARD AND T. DEANS (1962) *Nature*, **196,** 264.

THE AMERICAN MINERALOGIST, VOL. 48, JULY-AUGUST, 1963

THE PROBABLE CHEMICAL FORMULA OF AKSAITE, A NEW HYDRATED MAGNESIUM BORATE[1]

JOAN R. CLARK AND RICHARD C. ERD, *U. S. Geological Survey, Washington 25, D. C. and Menlo Park, California.*

Aksaite, a new hydrated magnesium borate, has recently been described by Blazko *et al.* (1962). Crystallographic, optical and chemical data were given, but these authors stated that the chemical composition of aksaite remains in doubt. The two chemical formulas suggested by them as most probable are: $2MgO \cdot 5B_2O_3 \cdot 8H_2O$ and $3MgO \cdot 7B_2O_3 \cdot 10H_2O$.

---

[1] Publication authorized by the Director, U. S. Gological Survey.