THE AMERICAN MINERALOGIST, VOL. 53, MARCH-APRIL, 1968

MINERALOGICAL NOTES

ZINCIAN DAUBREELITE FROM THE *KOTA-KOTA* AND *ST. MARK'S* ENSTATITE CHONDRITES

KLAUS KEIL, *Space Sciences Division, Ames Research Center, NASA, Moffett Field, California 94035.*

Daubreelite ($FeCr_2S_4$) was discovered by Smith (1878) in the *Coahuila* iron meteorite, and has since been identified in several hexahedrites and octahedrites (*e.g.* Heide *et al.*, 1932; Perry, 1944; El Goresy, 1965, Marshall and Keil, 1965). In stone meteorites it has been observed only in the highly-reduced enstatite achondrites (*e.g.* Keil and Fredriksson, 1963), and enstatite chondrites (*e.g.* Ramdohr, 1963; Mason, 1966; Keil, 1968a).

Because of complex intergrowth of the mineral with other phases, notably troilite, and difficulties involved in clean separation for wet chemical analysis, few reliable analyses of daubreelite have been reported. With the recent development of the electron microprobe X-ray analyzer, which allows analysis of small mineral grains *in situ* in polished sections, this difficulty has been overcome. The first electron microprobe analysis of daubreelite was reported by Keil and Fredriksson (1963), who studied the phase in the *Norton County* enstatite achondrite. They found it to contain about 1 percent manganese besides the elements specified in the formula. Later, Keil and Andersen (1965) reported an analysis of daubreelite containing 2.4 percent manganese and 0.05 percent titanium from the *Jajh deh Kot Lalu* enstatite chondrite.

In the present note an unusual variety of daubreelite, containing up to 5.5 percent zinc, is described. This mineral occurs in the Type I enstatite chondrite *Kota-Kota* and in the Intermediate Type enstatite chondrite *St. Mark's* (classification after Keil, 1968a), and because of its high zinc content, it is referred to as zincian daubreelite. Daubreelite in other enstatite chondrites (*Indarch, Daniel's Kuil, Hvittis, Atlanta, Blithfield, Jajh deh Kot Lalu, Khairpur, Pillistfer*, and *Ufana*) is of the manganoan variety and contains $\sim$0.04–0.3 percent zinc (the mineral was not detected in the sections studied of the *Adhi-Kot, Abee*, and *Saint Sauveur* enstatite chondrites). Zincian daubreelite was recently also described from nodules of the *Odessa* iron meteorite; there it contains between 0.6 to 11 percent zinc (El Goresy, 1967).

Zincian daubreelite is similar in its optical appearance in reflected light to ordinary manganoan daubreelite and occurs closely associated and intergrown with troilite (Fig. 1). The chemical compositions of the mineral from *Kota-Kota* and *St. Mark's* are given in Table 1 and compared to the average composition of manganoan daubreelite from the

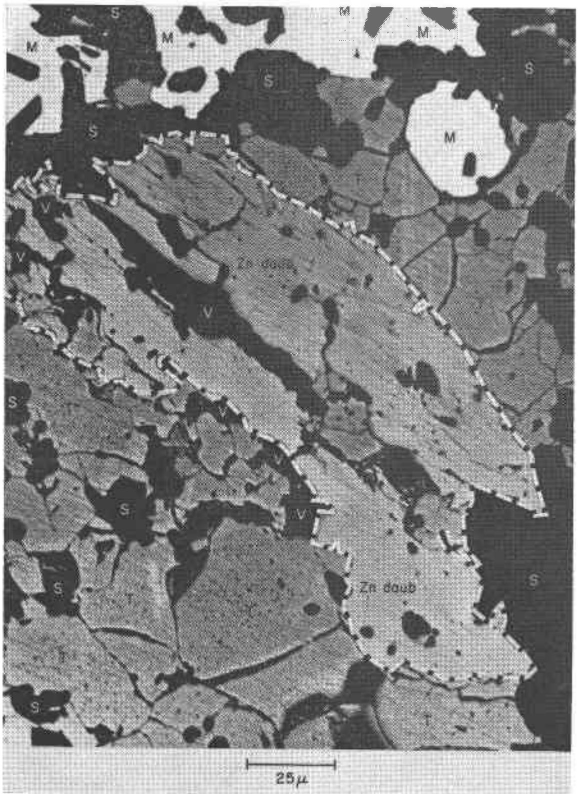

FIG. 1. Zincian daubreelite intergrown with titanium-bearing troilite (T) in close association with enstatite (S) and metallic nickel-iron (M). V are voids in the section. St. Mark's enstatite chondrite. Reflected, plane polarized light.

other enstatite chondrites. Also given in Table 1 are the average compositions of titanium-bearing troilite of *Kota-Kota* and *St. Mark's* from which zincian daubreelite appears to have exsolved, and of troilite of the other twelve enstatite chondrites studied. Zinc content of zincian daubreelite from *Kota-Kota* and *St. Mark's* varies from grain to grain, ranging from about 4.2 to 5.5 percent and 1 to 4.3 percent, respectively. This is in marked contrast to the compositional homogeneity of individual grains; no appreciable zoning occurs. Zincian daubreelite also differs in composition from ordinary manganoan daubreelite in elements other than zinc; it is lower in manganese and iron (*Kota-Kota* and *St. Mark's*) and slightly higher in titanium (*St. Mark's*). The titanium content of daubreelite, both of the zincian as well as of the manganoan variety, is remarkable in view of the fact that titanium is ordinarily lithophilic, associating itself

TABLE 1. COMPOSITION OF ZINCIAN AND MANGANOAN DAUBREELITE AND OF TITANIUM-BEARING TROILITE FROM ENSTATITE CHONDRITES, AS OBTAINED BY ELECTRON MICROPROBE TECHNIQUES (IN WEIGHT PERCENT)

Element	Zincian daubreelite		Manganoan daubreelite	Daubreelite	Troilite			
	Kota-Kota[a]	St. Mark's[b]	Average[c]	Theoretical	Kota-Kota	St. Mark's	Average[d]	Theoretical
Mg	<0.03	<0.03	<0.03	—	—	—	—	—
Ti	<0.02	0.12	0.07	—	0.27	0.38	0.57	—
Cr	34.1	35.2	35.5	36.10	0.60	0.70	1.52	—
Mn	1.04	0.73	2.53	—	0.05	0.09	0.12	—
Fe	14.7	14.9	16.7	19.38	62.3	61.7	60.7	63.53
Zn	5.2	4.26	0.12	—	0.12	0.11	0.09	—
S	43.0	43.9	44.5	44.52	37.4	36.4	37.0	36.45
Total	98.04	99.11	99.42	100.00	100.74	99.38	100.00	100.00
	Number of Ions on Basis of 4 Sulfur				Number of Ions on Basis of 1 Sulfur			
Ti	—	0.007	0.004	—	0.005	0.007	0.010	—
Cr	1.956	1.978	1.968	2.000	0.010	0.012	0.025	—
Mn	0.056	0.039	0.133	—	0.001	0.001	0.002	—
Fe	0.785	0.780	0.862	1.000	0.956	0.973	0.942	1.000
Zn	0.237	0.191	0.005	—	0.002	0.002	0.001	—
Metal to Sulfur Ratio	0.758	0.749	0.743	0.750	0.973	0.995	0.981	1.000

Formula for Kota-Kota zincian daubreelite: $(Fe_{0.79}Zn_{0.21})(Cr_{1.96}Mn_{0.06}Zn_{0.03})S_4$.
Formula for St. Mark's zincian daubreelite: $(Fe_{0.78}Zn_{0.19}Mn_{0.03})(Cr_{1.98}Mn_{0.01}Ti_{0.01})S_4$.
Formula for average manganoan daubreelite: $(Fe_{0.86}Mn_{0.13}Zn_{0.005}Ti_{0.004})(Cr_{1.97})S_4$.
[a] Average composition of different grains with slightly variable zinc content.
[b] A total of six different grains were analyzed, showing variable Zn contents. This analysis is for the grain with the highest Zn content.
[c] This average is for the Type II enstatite chondrites Daniel's Kuil, Hvittis, Atlanta, Blithfield, Jajh deh Kot Lalu, Khairpur, Pillistfer and Ufana.
[d] This average is for the Type II enstatite chondrites listed under (*c*) plus the Type I enstatite chondrites Indarch, Adhi-Kot, and Abee, plus the Intermediate Type enstatite chondrite Saint Sauveur (for details compare Keil, 1968a).

with oxygen rather than sulfur. The presence of the element in daubreelite is, however, in accordance with its comparatively high concentration in troilite of these meteorites (about 0.2–0.8 percent; Keil, 1968b, also compare Table 1), and their highly reduced nature.

Distribution of zinc in enstatite chondrites is particularly noteworthy inasmuch as it occurs not only as a major constituent in zincian daubreelite of *Kota-Kota* and *St. Mark's*, but also in iron-rich sphalerite of *Kota-Kota*, *Adhi-Kot*, *Saint Sauveur*, *Hvittis*, *Atlanta*, *Khairpur*, and *Pillistfer* (Ramdohr, 1963; Keil, 1968a), and as a minor constituent in niningerite of *Abee* and in manganoan daubreelite and troilite of most other enstatite chondrites (compare Table 1). It should be noted that in case of *Abee*, niningerite is the major zinc carrier and not troilite, as was suggested by Nishimura and Sandell (1964). Niningerite contains 0.31 percent zinc

(Keil and Snetsinger, 1967), while troilite contains 0.17 percent of the element. On the basis of a bulk zinc content of 0.073 percent (Nishimura and Sandell, 1964) and average niningerite and troilite contents of 11.2 and 5.8 percent, respectively, it is calculated that approximately 50 percent of the total zinc of *Abee* is in niningerite, while only 14 percent is in troilite. These values are approximate: due to large variability in niningerite content of *Abee* (3–12 percent, Keil, 1968a), values for bulk zinc and average niningerite content may be affected by sampling errors.

From these findings, it appears that zinc is strongly chalcophilic in enstatite chondrites. This is in contrast to the behavior of the element in ordinary chondrites where it is predominantly lithophilic, occurring in the silicates (Nishimura and Sandell, 1964), and in chromite (Bunch, *et al.*, 1967). In polymineralic nodules of iron meteorites, zinc exhibits both chalcophilic and lithophilic tendencies, being a constituent of sphalerite and daubreelite (*e.g.* El Goresy, 1967), and of ferroan magnesiochromite (up to 1.1 percent in *Toluca*, Keil, unpublished; 1–2 percent in *Odessa* and *Campo del Cielo*, T. E. Bunch, personal communication), and magnesian chromite (2–2.6 percent in *Weekeroo Station*, T. E. Bunch, personal communication).

ACKNOWLEDGEMENT

I am indebted to Mr. J. Erlichman for assistance in the electron microprobe work and to Miss Sally Craig for the photomicrograph of zincian daubreelite.

REFERENCES

BUNCH, T. E., K. KEIL, AND K. G. SNETSINGER (1967) Chromite composition in relation to chemistry and texture of ordinary chondrites. *Geochim. Cosmochim. Acta.* **31,** 1569–1582.

EL GORESY, A. (1965) Mineralbestand und Strukturen der Graphit- und Sulfideinschlüsse in Eisenmeteoriten. *Geochim. Cosmochim. Acta.* **29**, 1131–1151.

——— (1967) Electron microprobe analyses of coexisting sphalerite and daubreelite in the Odessa iron meteorite (abstr.). *Trans. Amer. Geophys. Un.*, **48**, 159.

HEIDE, F., E. HERSCHKOWITSCH, AND E. PREUSS (1932) Ein neuer Hexahedrit von Cerros del Buey Huerto, Chile. *Chem. Erde,* **7**, 483–502.

KEIL, K. (1968a) Mineralogical and chemical relationships among enstatite chondrites. *J. Geophys. Res.* (in press).

——— (1968b) Chalcophilic tendency of titanium in enstatite chondrites and achondrites. *Earth Planet. Sci. Lett.* (in press).

——— AND C. A. ANDERSEN (1965) Electron microprobe study of the Jajh deh Lot Lalu enstatite chondrite. *Geochim. Cosmochim. Acta,* **29**, 621–632.

——— AND K. FREDRIKSSON (1963) Electron microprobe analysis of some rare minerals in the Norton County achondrite. *Geochim. Cosmochim. Acta,* **27**, 939–947.

——— AND K. G. SNETSINGER (1967) Niningerite: A new meteoritic sulfide. *Science,* **155**, 451–453.

MARSHALL, R. R., AND K. KEIL (1965) Polymineralic inclusions in the Odessa iron meteorite. *Icarus,* **4**, 461–479.

MASON, B. (1966) The enstatite chondrites. *Geochim. Cosmochim. Acta*, **30**, 23–39.
NISHIMURA, M. AND E. B. SANDELL (1964) Zinc in meteorites. *Geochim. Cosmochim. Acta*, **28**, 1055–1079.
PERRY, S. H. 1944) The metallography of meteoric iron. *U. S. Nat. Mus. Bull.* **184**, 206 pp.
RAMDOHR, P. (1963) The opaque minerals in stony meteorites. *J. Geophys. Res.*, **68**, 2011–2036.
SMITH, J. L. (1878) On the composition of the new meteoric mineral daubreelite and its frequent, if not universal, occurrence in meteoric irons. *Amer. J. Sci.*, **16**, 270–272.

THE AMERICAN MINERALOGIST, VOL. 53, MARCH–APRIL, 1968

SECOND OCCURRENCE OF MAROKITE

P. R. DE VILLIERS, *Research Laboratories, South African Iron and Steel Corporation, Pretoria, South Africa*

AND

F. H. HERBSTEIN,[1] *Chemical Physics Group, Council for Scientific and Industrial Research, Pretoria, South Africa.*

The compound $CaMn_2O^4$ was first produced synthetically by Riboud and Muan (1963). Shortly thereafter a mineral with this ideal composition was identified by Gaudefroy, Jouravsky and Permingeat (1963) in ore from Tachgagalt, Morocco, and named marokite. Its crystal structure has been reported by Lepicard and Protas (1966).

We have recently identified marokite as a rare mineral in the ore from Black Rock Mine, N.W. Cape Province, Republic of South Africa. The geology of this area is briefly described by De Villiers and Herbstein (1967). Marokite was found in one sample only. The sample has a fibrous appearance owing to densely packed slender crystals. Marokite occurs as remnants in an unidentified alteration product(s) which is associated with pyrolusite in the form of possibly vug fillings and veins, cryptomelane as veins and opaline silica in vugs. A semi-quantitative spectrochemical analysis was carried out on 16 mg of material and the results conformed to the formula $CaMn_2O_4$. The Debye-Scherrer pattern (FeK_α) agreed well with that given by Gaudefroy *et al.* (loc. cit.). Incontrovertible evidence that our material is indeed marokite was given by single-crystal oscillation and Weissenberg photographs of a small fragment; we obtained cell dimensions and systematic absences identical with those reported by the other workers.

ACKNOWLEDGEMENTS

We are grateful to the South African Iron and Steel Corporation Ltd. for permission to publish this paper; to Dr. J. G. D. Steyn for drawing attention to the report on marokite.

[1] Present address: Department of Chemistry, Technion-Israel Institute of Technology, Haifa.