Cuspidine from dolomite contact skarns, Broadford, Skye.

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CUSPIDINE was first described by Scacchi (1876) in the ejected blocks of metamorphosed linestone at Vesuvius, but a detailed and systematic morphological description of well-terminated crystals was given first by vom Rath (1883) from material at Cozzolino in Resina, Vesuvius. The monoclinic character of the spear-shaped crystals was then established with $a;b:c = 0.7243:1:1.9342, \beta - 89^{\circ} 22'$, and twins on (100) giving $c:c = 1^{\circ}$ 16'. Scacchi (in Arzruni, 1877) had earlier indicated the possibility that cuspidine he had described as orthorhombic was monoclinic and twinned when he recognized a re-entrant angle of 178° 42' on the cleavage truncating the acute ends of the crystals.

Groth's optical data (in vom Rath, 1883) supported the monoclinic character with the optic axial plane (010) and $\gamma:c = 5^{\circ} 30'$ in the acute angle β . Inclined dispersion.

Both Scacchi and vom Rath had recognized the essential composition of cuspidine as a calcium fluosilicate, but a more complete analysis was given much later by Zambonini (1910). Meantime C. H. Warren had analysed in 1899 a mineral from Franklin Furnace, New Jersey, the analysis of which was discussed by Palache (1910, 1935). He recognized it as that of a cuspidine to which he assigned in the first place a formula $Ca_2Si(O,F_2)_4$ already suggested by Dana (1892). Zambonini's analysis yielded him the formula $Ca_4Si_2O_7F_2$ which was later accepted by Palache (1935) for the Franklin Furnace mineral. This formula is that at present recognized in the literature. In none of the existing analyses to date is there any record of a determination of water. Warren's material was associated with nasonite; the mineral had a density between 2.965 and 2.989, but no material was left after analysis for the determination of other physical or optical properties. It is clear, however, that there is room for little water in either Warren's or Zambonini's analyses. Larsen (1921) first reported on the refractive indices of the Vesuvian material with the data α 1.590, β 1.595, γ 1.602, 2V, 62°, $\mathbf{r} > \mathbf{v}$.

The mineral custerite was first described by Umpleby, Schaller, and Larsen (1913) from a limestone contact (inclusion in granite-porphyry) in Custer Co., Idaho. Their analysis gave the results $Ca_4Si_2O_7(F,OH)_2.H_2O$ thus identical with that of cuspidine except for the additional H_2O . These authors recognized a repeated twinning on (001) and a comparison of the optical properties of custerite and cuspidine was given as follows:

with the optic axial plane in cuspidine (010), $\beta = b$, $\gamma:c = 5^{\circ}$, cleavage (001); and for custerite $\alpha = b$, $\beta: a = 6\frac{1}{2}^{\circ}$, cleavage (001) and prismatic.

Since this time custerite has been described from a number of limestone contact-zones including Crestmore, California (Tilley, 1928), and Carlingford, Ireland (Osborne, 1932), while cuspidine has been reported from the Alban Hills, Rome (Stella Starrabba, 1913), and much more recently from the Lower Tunguska river in Siberia associated with spurrite and merwinite (Sobolev, 1935). The striking resemblance in the optical properties of cuspidine and custerite has been commented on by more than one writer and has led to the suspicion that the two minerals might indeed be identical.

In a recent investigation of the skarn zones in the Durness limestone at its contact with the Beinn an Dubhaich granite near Broadford, Skye, Professor W. Q. Kennedy and the writer have recognized a custeritelike mineral forming an important constituent in a large number of the skarn zones. The description of the metasomatic phenomena associated with the dolomite contact-zones of the Broadford area will be given later by Kennedy and myself: here I shall present data identifying the mineral, leaving the details of its paragenesis to the forthcoming contribution.

Examination of the properties of the mineral shows that it must be designated as cuspidine. It occurs associated in the skarns with magnetite, diopside, wollastonite, calcite, and other minerals, and is developed as lanccolate crystals like the Vesuvian mineral (fig. 1). On the other hand, polysynthetic twinning, as seen between crossed nicols, is its most striking character, in that resembling the descriptions of custerite. The mineral behaves as a monoclinic crystal, cross-sections of the spears

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showing the emergence of the acute bisectrix γ . In sections parallel to the optic axial plane the polysynthetic lamellae (taken as parallel to (001)) give symmetrical extinction α :(001) = 6°. Twinning on (100) is also present in some sections. These data are summarized with other optical determinations as follows: α 1.591, β 1.595, γ 1.603, $2V_{\gamma}$ 60°, α :(001) = 6°, $\beta = b$, dispersion $\mathbf{r} > \mathbf{v}$. These properties are clearly those of the Vesuvian cuspidine.



FIG. 1. Cuspidine in magnetite skarn, Kilchrist, Skye ($\times 27$ diams.). Typical lanceolate crystals of cuspidine set in magnetite which has intergrown bornite.

Examination of cuspidine from Vesuvian specimens has shown that, while simple twinning on (100) is dominant, a polysynthetic twinning is also present. This feature has previously been recognized by Cesaro (1928). Cuspidine with the optical characters given above has been isolated from a cuspidine-diopside skarn from Camas Malag, Loch Slapin, Skye, and analysed. At the same time cuspidine from an ejected block of skarn from Monte Somma, Vesuvius, has also been isolated and analysed, in order to be clear as to its water content. Both analyses have been carried out by Mr. H. C. G. Vincent and are set out in the following table, p. 93.

Examination of these results reveals the chemical identity of the two minerals and that the analyses conform to the formula $Ca_4Si_2O_7F_2$ in which there is little replacement of F by OH. If the small amount of

		I.	Mol. ratios.	Less CaCO ₃ .	Metals to 9(O,F,Cl).	II.	Mol. ratios.	Less CaCO3.	Metals to 9(O,F,Cl).
SiO ₂		31.31	5218	5218	2.01	31.79	5298	5298	2.01
R ₂ O ₃	• • •	1.64	—		_	1.53			_
CaO		59.05	10544	10371	3.99	59.16	10564	10424	3.96
MgO		0.11	—	·	—	nil			_
Alkalis		0.15			_	trace	—		_
F		9.80	5158 j	E100	1 00	10.05	5289	5289	2.01
Cl		0.10	28	5160	1.99	trace			_
CO2	•••	0.75	173	_		0.62	140		_
$H_{2}O +$		0.41	—		—	0.28	—		_
$H_2O -$		0.33		—	—	0.16	—		_
		103.65				103.59			
Less $O = F(Cl) - 4.13$						4.23			
		99.52				99.36			
Sp. gr.	•••	-2.95				-2.97			

 H_2O+ is taken into account in these two analyses the ratios become 1.99:3.95:2.14 and 2.00:3.94:2.12 respectively.

I. Cuspidine in cuspidine-diopside skarn, Camas Malag, Skye.

II. Cuspidine in skarn, ejected block, Monte Somma, Vesuvius.

Synthesis of cuspidine.-The accidental synthesis of cuspidine has been reported in an electric welding slag by Lapin (1941) who has detailed its properties. The slag consisted of cuspidine, fluorite, villiaumite, with perovskite and chrome-spinel and was formed as a thin crust on a welding seam at the expense of a fusion of the charge (42 % CaF2, 36 % chalk, 4 % ferromanganese, and 18 % soluble glass) placed on the metallic electrode. Cuspidine, the chief component, crystallized as elongated crystals or characteristic lanceolate (simple) twins (100), and polysynthetic on the third pinakoid. The mineral may indeed be readily synthesized by sintering together CaCO₃ and SiO₂ in the proportion 3:2 with excess CaF₂ at 1140° C. when a product is obtained consisting of rounded grains of fluorite with interstitial cuspidine (0.1 mm. diam.) appearing as irregular crystals flattened parallel to (001) or spear-shaped and showing simple and repeated twinning parallel (001). These synthetic cuspidine crystals enclose minute drop-like grains with optical properties that identify them as larnite.

Effect of heat on cuspidine.—Cuspidine heated to 1200° C. overnight is converted into fine polycrystalline aggregates of larnite showing the characteristic fine repeated twinning of that mineral. The same effect can be seen in rock sections carrying cuspidine similarly heated. Here the development of larnite begins on the edges of the larger grains and along fractures within the crystals. The identity of the product of heating has been confirmed by comparison of X-ray powder photographs with those of larnite of Scawt Hill, Co. Antrim (fig. 2).

The foregoing data raise the question of the validity of custerite as a separate mineral. Through the kindness of Dr. F. A. Bannister of the Mineral Department of the Natural History Museum, South Kensington, I have been able to obtain a small fragment of the original custeritebearing rock from Idaho. In slice the mineral is associated with magnetite, diopside, and a little yellow garnet: there are associated areas



FIG. 2. X-ray powder photographs of: (1) Cuspidine (Skye), (2) Cuspidine (Vesuvius), (3) 'Custerite' — Cuspidine (Idaho), (4) Cuspidine (Skye), heated to 1200° C., (5) Larnite (Scawt Hill). Cu-K $_{\infty}$ filtered radiation; camera 9 cm. diameter ($\frac{5}{7}$ actual size).

rich in wollastonite which also occurs invested by the custerite. This custerite has beautifully developed polysynthetic twinning and shows in many of its sections the typical spear-shaped forms so characteristic of cuspidine. The mineral is, however, also developed flattened parallel to (001) and then shows negative elongation. A similar habit is found also in some of the Skye examples of cuspidine, and cuspidine occurs in that form in the synthetic product. The determination of the optical properties of the Idaho mineral shows that within the normal limits of error of the immersion method the refractive indices are identical with those of cuspidine, and further that the optic axial plane sections are those giving the symmetrical extinction α :(001) 6°. Obtuse bisectrix sections show parallel extinction. In its habit and paragenesis the Idaho mineral can be matched with the Skye examples of cuspidine. There can, I think, be little doubt that the Idaho 'custerite' is in fact cuspidine. This identity is further confirmed by X-ray photographs. Powder photographs of the analysed Vesuvian and Skye minerals, together with that of the Idaho 'custerite', are reproduced in fig. 2 for comparison.

The essential identity of the Idaho 'custerite' and a Vesuvian cuspidine on the basis of X-ray powder photographs had been indicated by Dr. F. A. Bannister to me when he had forwarded the specimen of the Idaho mineral now examined. In the same figure are also reproduced powder photographs of larnite obtained from heating the Skye cuspidine and the type larnite of Scawt Hill, Co. Antrim.

References.

- ARZRUNI (A.), Zeits. Kryst. Min., 1877, vol. 1, p. 398. (Abstract of Scacchi's 1876 paper with additional data supplied by the author.)
- CESÀRO (G.), Mem. (in 4°) Acad. Roy. Belg., 1928, ser. 2, vol. 9, no. 4, p. 90. [M.A. 4-190.]
- DANA (E. S.), System of mineralogy, 6th edit., 1892, p. 529.
- LAPIN (V. V.), Compt. Rend. Acad. Sci. URSS, 1941, vol. 31, pp. 694-696. [M.A. 9-11.]

LARSEN (E. S.), The microscopic determination of nonopaque minerals. Bull. U.S. Geol. Surv., 1921, no. 679, pp. 64, 215.

OSBORNE (G. D.), Geol. Mag., 1932, vol. 69, pp. 61 and 219. [M.A. 5 134.]

PALACHE (C.), Amer. Journ. Sci., 1910, ser. 4, vol. 29, p. 185.

- ---- Prof. Paper, U.S. Geol. Surv., 1935, no. 180, p. 101. [M.A. 6-261.]
- RATH (G. VOM), Zeits. Kryst. Min., 1883, vol. 8, pp. 38-46.
- SCACCHI (A.), Rend. R. Accad. Sci. fis. mat. Napoli, 1876, vol. 15, p. 208.
- SOBOLEV (V.), Mém. Soc. Russe Min., 1935, vol. 64, pp. 162-165. [M.A. 10-79.]
- STELLA STARRABBA (F.), Rend. R. Accad. Lincei, Cl. Sci. fis. mat., 1913, ser. 5, vol. 22, sem. 1, p. 871.
- TILLEY (C. E.), Geol. Mag., 1928, vol. 65, p. 371. [M.A. 4 84.]
- UMPLEBY (J. B.), SCHALLER (W. T.), and LARSEN (E. S.), Amer. Journ. Sci., 1913, ser. 4, vol. 36, p. 385; Zeits. Kryst. Min., 1914, vol. 53, p. 321.
- ZAMBONINI (F.), Mineralogia Vesuviana. Atti (Mem.) R. Accad. Sci. fis. mat. Napoli, 1910, ser. 2, vol. 14, no. 7, p. 273; 2nd edition by E. Quercigh, ibid., 1935, supplement to vol. 20, p. 253. [M.A. 6-504.]