

Caratiite, a new sulphate-chloride of copper and potassium, from the lavas of the 1869 Vesuvius eruption

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ABSTRACT. Caratiite is a sulphate-chloride of potassium and copper with ideal formula $K_4Cu_4O_2(SO_4)_4MeCl$ (where $Me = Na$ and/or Cu); it formed as fine green acicular crystals in lava of the 1869 eruption of Mt. Vesuvius, Naples, Italy. Caratiite is tetragonal, space group $I4$; a 13.60(2), c 4.98(1) Å, $Z = 2$. The strongest lines of the powder pattern are [d Å, l , hkl]: 9.61 100 (110); 6.80 80 (200); 4.296 60 (310); 3.015 100b (420,321); 2.747 70 (411); 2.673 60 (510); 2.478 60 (002); 2.388 70 (431,501); 2.281 60 (600). The mineral is uniaxial positive, ω 1.598, ε 1.711; it does not fluoresce under either short- or long-wavelength ultra-violet light. The specific gravity is 3.0 (meas.) and 3.22 (calc.).

A NUMBER of rare chlorides and sulphates of copper occurred in the lavas of the 1869 eruption of Mount Vesuvius. Eugenio Scacchi (1854-1929), writing in 1884, mentioned five minerals—euchlorine, melanothallite, hydrocyanite, eriochalcite, and dolerophanite—all found originally by his father, Arcangelo Scacchi (1810-1893); to these E. Scacchi (1884) adds (our translation) ‘. . . another species . . . [which] occurs as green acicular crystals with a greasy-vitreous lustre, and is so scarce that the Director of the Mineralogical Museum did not want to part with any, even for a chemical analysis’. Recently a small quantity of this material has been made available to us and has been found to be a new mineral with chemical affinities to those species mentioned above.

This specimen (BM 1983,74) consists of a tube of fine green needles up to about 1 cm in length; about 10 mg now remains. The mineral, a sulphate-chloride of copper and potassium, has been named caratiite for Mariano Carati (b. 1951) of Naples, collector of Vesuvius minerals and author of ‘Guida alla mineralogia vesuviana’, who supplied us with the sample for this study. The mineralogical data and name have been approved prior to publication by the IMA Commission on New Minerals and Mineral Names.

Physical and optical properties. The needles of

caratiite are green with green streak and have a greasy to vitreous lustre. The mineral is translucent and, in transmitted light, many fragments show alteration to fine-grained paratacamite along edges parallel to [001]. Caratiite is brittle but shortage of material prevented determination of the hardness. Nor was it possible, with such fine needles, to observe cleavage and fracture. The specific gravity, obtained with a Berman balance on 1.7 mg of material, was 3.0; the calculated value was 3.22.

Optically, caratiite is uniaxial positive with strong birefringence and distinct dichroism; $\omega = 1.598$ (pale yellowish green), $\varepsilon = 1.711$ (yellowish green). It did not fluoresce under either long- or short-wavelength ultra-violet light.

Chemical analysis. Electron probe analyses of caratiite were obtained using a Cambridge Geoscan fitted with a Link Systems energy-dispersive detector and a Cambridge Microscan 9 wavelength-dispersive instrument. The latter instrument was used for the sodium determination as this element could not be detected in the energy-dispersive system. The energy-dispersive system was generally preferred because it involved a shorter exposure time of the specimen to the electron beam, arising from its somewhat unstable behaviour under electron bombardment. In addition, a slightly defocused electron beam was used.

The energy-dispersive spectra were measured relative to that from a pure cobalt standard which had been previously calibrated against pure copper, sylvine (for K and Cl) and analysed pyrite (for S); the sodium standard was analysed jadeite. The mean of four determinations is given in Table I, column 1. Column 2 gives the ideal composition of caratiite, $[K_4Cu_4O_2(SO_4)_4MeCl]$, where Me may be Na and/or Cu. This formula represents the cell content of caratiite given by Zemmann and Effenberger (1984) in their structure determination, carried out on a portion of this specimen.

TABLE I. *Electron probe analysis of caratiite*

	1	2
CuO	41.45	38.00
K ₂ O	17.38	21.18
Na ₂ O	2.89	1.74
SO ₃	35.88	36.00
Cl	3.91	3.98
Less O=Cl	0.88	0.90
Total	100.63	100.00

1. Average of four determinations. Cu, K, S, and Cl by energy-dispersive techniques; Na by wavelength-dispersive method.

2. Theory for K₄Cu₄O₂(SO₄)₄MeCl with Me calculated with Na:Cu = 1:1.

The most significant departures from stoichiometry in the analyses are a rather low potassium figure and a slightly high value for Cu. There are two possible reasons for this, and both may well

contribute to the figures obtained. First, potassium is a notoriously unstable element under an electron beam and some loss is to be expected. Secondly, since caratiite shows evidence of alteration to paratacamite, Cu₂(OH)₃Cl, particularly on the surface of the needles, electron probe analysis of a microscopic intergrowth would tend to give higher Cu and lower overall K figures.

Paratacamite contains over 12 wt. % H₂O but the structure determination for caratiite (Zemann and Effenberger, 1984) shows no water or (OH)⁻ groups to be present. Measurement of H in an elemental analyser (on 0.887 mg of material) gave a figure of over 4 wt. % H₂O. We assume this is due to the incorporation of some paratacamite in the determination and, possibly, a little organic contamination.

X-ray study. A relatively uncoated needle of caratiite was selected and mounted with its axis vertical. A *c*-axis rotation photograph and zero, first and second layer Weissenberg photographs showed the mineral to be tetragonal with a 13.60(2), *c* 4.98(1) Å and *Z* = 1, giving *c*:*a* 0.3662 and *V*

TABLE II. X-ray powder data for caratiite obtained using an 11.46cm diameter Philips Debye-Scherrer camera and Cu-Kα radiation

hkl	d _{calc.}	d _{obs.}	I _{obs.}	Impurity	hkl	d _{calc.}	d _{obs.}	I _{obs.}	hkl	d _{calc.}	d _{obs.}	I _{obs.}
110	9.617	9.61	100		701	1.810			941	1.331		
200	6.800	6.80	80		730	1.786	1.787	10	950	1.321		
		5.46	40	P or A	721	1.749	1.748	40	543	1.308		
		4.976	40	A	442	1.730			10.1.1	1.306		1.305
220	4.808				532	1.702	1.701	40	912	1.286		1.281
101	4.675	4.646			800	1.700			633	1.284		
310	4.301	4.296	60		602	1.676	1.674	10	10.4.0	1.263		
		4.091	20	P or A	820	1.649			703	1.262		1.259
211	3.853	3.846			103	1.648	1.645	20	10.3.1	1.260		
		3.674	10	n.i.	651	1.644			004	1.245		
		3.483	40	n.i.	622	1.627	1.625	10	932	1.242		
400	3.400				660	1.603			723	1.241		1.239
301	3.352	3.351	40		213	1.601			871	1.239		
330	3.206	3.217	60b		811	1.598	1.600	20	114	1.235		
420	3.041				741	1.598			11.1.0	1.231		
321	3.007				750	1.581			204	1.225		
		2.905	10	n.i.	303	1.559	1.557	10	961	1.219		1.222
		2.837	50b	A or NaCl	712	1.522			224	1.205		
411	2.750	2.747	70		552	1.522			772	1.203		
510	2.667	2.673	60		840	1.521	1.520	70	880	1.202		1.201
		2.555	40	n.i.	323	1.519			653	1.202		
002	2.490	2.478	60		831	1.516			11.0.1	1.200		
112	2.411				642	1.503	1.500	10			1.914	10b
440	2.404				910	1.502					1.183	20
501	2.387	2.388	70		413	1.483	1.475	20			1.167	10
431	2.387				732	1.451	1.451	20			1.149	10b
530	2.322	2.329	20		901	1.446					1.124	10
600	2.267	2.281	60		930	1.434					1.117	10
222	2.211	2.1917	10		433, 503	1.417	1.415	50b			1.103	10
312	2.155				921, 761	1.414					1.086	10
620	2.150	2.134	20		806	1.404					1.075	10
611	2.040	2.040	50		523	1.387					1.060	20
402	2.009	1.993	10		851	1.385					1.044	10b
332	1.966				822	1.375	1.376	40b			1.020	20b
541	1.954	1.959	50		770	1.374					0.9998	10
422	1.927				10.0.0,						0.9909	10
710	1.923				860	1.360	1.359	20			0.9813	40b
550	1.923	1.920	50		662	1.348					0.9624	20b
640	1.886				752	1.335					0.9337	10
631	1.878	1.881	20		10.2.0	1.334	1.332	50			0.9100	10
512	1.820	1.817	50		613	1.333					0.8938	10

P = paratacamite; A = atacamite; n.i. = unindexed

921.10 Å³. The indexed powder pattern is given in Table II. There are three possible body-centred space groups for the mineral, $I4$, $I\bar{4}$ and $I4/m$, and of these $I4$ led to the solution of the structure refined to R 0.055 (Zemann and Effenberger, 1984).

Discussion. The only other recorded sulphate-chloride of potassium and copper is chlorothionite, $K_2Cu(SO_4)Cl_2$. Although forming in a similar environment (chlorothionite was reported in the April 1872 Vesuvius eruption by A. Scacchi), the two minerals are quite distinct, with no chemical, physical, or optical properties in common.

We have not seen caratiite other than as detached needles, so its position in the crystallization sequence of copper minerals in the 1869 eruption is uncertain.

Type specimen. The type specimen of caratiite is preserved at the British Museum (Natural History) as specimen number BM 1983,74.

Acknowledgements. The authors are considerably indebted to Mr P. G. Embrey and Drs A. Kato and J. A. Mandarino and the late Dr M. H. Hey for their constructive comments during the study and initial description of caratiite.

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