MINERALOGICAL MAGAZINE, SEPTEMBER 1977, VOL. 41, PP. 371–4

The metavoltine problem: metavoltine from Madeni Zakh and Chuquicamata, and a related artificial compound

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SUMMARY. Bandy (1938) described as metavoltine? a mineral coming from Chuquicamata (Chile) with chemical composition $K_2Na_6Fe^{3+}(SO_4)_{12}(OH)_2 \cdot 20H_2O$. Owing to some differences between this mineral and that first described by Blaas (1883), doubts persist on the identity of these two compounds. X-ray analyses were performed to clarify the relation between them. An artificial product, closely related to metavoltine as regards lattice and chemical composition, was also studied, and affords a better understanding of the Na and K diadochy already observed in metavoltine.

THERE has been a good deal of confusion between several sulphates of the alkali metals and ferric iron—the minerals metavoltine (Blaas, 1883) and metavoltine (?) (Bandy, 1938) and the artificial products β-metavoltine (Scharizer, 1927) and Maus's salt (Maus, 1827; Haidinger, 1853, used the name mausite); Scharizer's α-metavoltine, also an artificial product, has been shown to be Maus's salt.

Scordari, Vurro, and Menchetti (1975) compared Maus's salt with metavoltine from Sierra Gorda, Chile, and showed that they are similar but distinct. Giacovazzo, Scordari, and Menchetti (1975) and Giacovazzo, Scordari, Todisco, and Menchetti (1976) have determined the crystal structures of Maus's salt and of the Sierra Gorda metavoltine respectively.

Three problems remain: Is the Sierra Gorda material the same species as the metavoltine described by Blaas? Is the metavoltine (?) of Bandy a distinct species? And what are the relations of Scharizer's β-metavoltine to the other compounds?

A sample of metavoltine from the type locality, Madeni Zakh, Iran, was kindly supplied by Professor Zemann (Inst. Mineral. Kristallogr., Vienna), who states that although not directly documented the specimen is probably part of the original material of Blaas; it gives an X-ray powder pattern identical with that of the Sierra Gorda material (Table I), which is therefore correctly designated metavoltine. A second, rather better crystallized specimen of metavoltine from Madeni Zakh was kindly supplied by Dr. G. Niedermayr of the Naturhistorisches Museum, Vienna, labelled C5878/XXII1883; it also gave an identical powder pattern.

Crystals from the holotype specimen of Bandy's metavoltine (?) from Chuquicamata, Chile, were kindly supplied by the U.S. National Museum (U.S.N.M. 115162). They gave an X-ray powder pattern identical with that of Sierra Gorda and Madeni Zakh material, and are therefore also metavoltine. Bandy doubted the identity because of chemical differences: the K:Na ratio of the Chuquicamata material is much smaller than that of Blaas's metavoltine, and the latter contains nearly 3 % FeO, which Bandy did not detect. However, Scordari, Vurro, and Menchetti (1975) have shown that the K:Na ratio in metavoltine varies considerably, and a test with α:α'-dipyridyl showed that the Chuquicamata material contains appreciable FeO.

In an attempt to prepare the β-metavoltine of Scharizer, artificial crystals were obtained by evaporation at about 70 °C of a solution of ferric, potassium, and sodium sulphates (Van Tassel, 1961), and by slow evaporation at room temperature of solutions of metavoltine from San Bernardino County, California, and from Sierra Gorda.

These two artificial preparations were shown to be identical by Weissenberg pictures. Further attempts to obtain artificial crystals, following Van Tassel's recipe, produced two

TABLE I. *X-ray data for metavoltine and the stable artificial salt*

Metavoltine					Stable artificial salt				Metavoltine					Stable artificial salt			
	A	B	C							A	B	C					
hkil	$d_{obs.}$	$d_{obs.}$	$d_{obs.}$	*I*	*hkil*	$d_{calc.}$	$d_{obs.}$	*I*	*hkil*	$d_{obs.}$	$d_{obs.}$	$d_{obs.}$	*I*	*hkil*	$d_{obs.}$	$d_{obs.}$	*I*
0001	18.16Å	18.28Å	18.24Å	33	0002	17.967Å	18.00Å	30						$12\bar{3}3$	3.052	3.056	44
0002	9.08	9.12	9.11	100	0004	8.984	9.00	100						$02\bar{2}8$	–	–	–
$10\bar{1}0$	8.30	8.31	8.28	20	$10\bar{1}0$	8.350	8.35	30	$03\bar{3}6$	–	3.042	–	–				
					$10\bar{1}1$	8.133	8.13	18	0006	3.032	–	–	–				
$10\bar{1}1$	7.56	7.56	7.55	13					$12\bar{3}2$	2.965	2.964	2.962	13	$12\bar{3}4$	2.978	2.975	7
					$10\bar{1}3$	6.850	6.85	13	$11\bar{2}5$	2.897	2.899	2.901	30	$1.1.\bar{2}.10$	2.881	2.881	39
$10\bar{1}2$	6.13	6.14	6.12	13	$10\bar{1}4$	6.116	6.12	9	$12\bar{3}3$	2.788	2.785	2.784	17	$12\bar{3}6$	2.792	2.788	28
$10\bar{1}3$	4.89	4.90	4.90	10	$10\bar{1}6$	4.867	4.88	7	$20\bar{2}5$	2.727	2.731	2.730	10				
$11\bar{2}0$	4.79	4.79	4.79	10	$11\bar{2}0$	4.823	4.82	13	$30\bar{3}1$	–	–	–	–				
$11\bar{2}1$	4.63	4.64	4.63	7	$11\bar{2}2$	4.656	4.65	7						$03\bar{3}0$	2.713	–	–
0004	4.54	4.55	4.54	5										$30\bar{3}3$	2.711	2.714	9
					$10\bar{1}7$	4.373	4.37	7	0007	2.595	2.600	2.597	17	0.0.0.14	2.567	2.567	15
$11\bar{2}2$	4.24	–	–	–	$11\bar{2}4$	4.248	4.24	13	$12\bar{3}4$	–	–	–	–				
$20\bar{2}0$	4.15	4.15	4.15	10	$20\bar{2}0$	4.175	4.17	10	$30\bar{3}3$	2.516	–	2.514	13				
$20\bar{2}1$	4½.5	4.04	4.04	7					$22\bar{4}0$	2.394	–	–	–				
					$02\bar{2}3$	3.942	3.94	9	$22\bar{4}1$	2.378	2.375	2.374	23	$22\bar{4}2$	2.389	2.385	30
$11\bar{2}3$	3.76	3.76	3.75	17	$11\bar{2}6$	3.757	3.757	20	$21\bar{3}5$	–	–	–	–				
$20\bar{2}2$	–	–	–	–						2.228	2.224	2.225	10				
0005	3.635	3.635	3.635	10						2.203	2.203	2.204	7				
$20\bar{2}3$	3.422	3.424	3.415	8						–	2.183	–	–				
$10\bar{1}5$	3.325	3.330	–	–						2.018	2.002	2.020	37				
$11\bar{2}4$	3.294	3.300	3.299	37	$11\bar{2}8$	3.286	3.286	30						0.0.0.18	1.996	1.995	11
					$12\bar{3}1$	3.144	3.143	22						$2.2.\bar{4}.12$	1.878	1.880	5
$12\bar{3}0$	3.127	–	–	–										$14\bar{5}0$	1.822	1.816	11
$12\bar{3}1$	3.090	3.087	3.087	23	$12\bar{3}2$	3.108	3.105	30						$14\bar{5}1$	1.820		
$20\bar{2}4$	3.065	3.065	3.066	33										$0.3.\bar{3}.15$	1.816		
														$14\bar{5}2$	1.813		

Phillips powder diffractometer, Cu-$K\alpha$ radiation (Ni filter); NaF internal standard.
The calculated spacings for the stable artificial salt are based on *a* 9.642, *c* 35.93 Å.
Metavoltine data: A, Sierra Gorda; B, Madeni Zakh; C, Chuquicamata; intensity data are for C.

different crystallizations: Maus's salt, having a continuous K, Na diadochy over a definite range (Scordari *et al.*, 1975), and a mixture of Maus's salt with discontinuous diadochy and a new artificial salt.

The new artificial salt is stable in air, unlike Maus's salt, which effloresces (whatever its K:Na ratio), breaking down into whitish ferrinatrite and goldichite; this made it easy to separate crystals from the mixed crystallization. It is uniaxial negative, and pleochroic with ω green, ϵ reddish. X-ray powder data are included in Table I, and a chemical analysis in Table II. The powder pattern was indexed with the help of Weissenberg photographs, and the unit cell is compared with those of metavoltine and Maus's salt in Table III. A density determination by the flotation method gave 2·45; for 24 SO_4^{2-} in the unit cell of Table III the calculated density is 2·38.

The simple relation between their unit cells and the general similarity of their X-ray powder patterns suggest a close relation between the three compounds, and the analysis of the stable salt has therefore been recalculated in Table II on the same basis, 12 SO_4^{2-}, as metavoltine.

TABLE II. *Chemical analyses and atomic ratios of metavoltine and the stable artificial salt*

	1	2	3	4	5		1′	2′	3′	4′	5′
K_2O	9.87	4.69	4.36	4.45	7.98	K^+	4.29	2.11	1.98	2	3.50
Na_2O	4.65	8.15	8.75	8.78	6.88	Na^+	3.07	5.56	6.02	6	4.59
FeO	2.92	nil*	2.22†	3.40	–	H_3O^+	0.64	0.33	–	–	1.91
Fe_2O_3	21.20	23.31	22.45	22.64	23.15	R^{2+}	0.83	–	1.04	1	–
SO_3	46.90	45.42	45.02	45.41	46.46	Fe^{3+}	5.44	6.18	6.00	6	6.00
H_2O	14.58	17.83	15.30	15.32	15.78	SO_4^{2-}	12	12	12	12	12
Sum	100.12	99.56	99.51	100.00	100.25	O^{2-}	0.99	1.27	2.04	2	2.00
						H_2O	15.62	20.93	18.12	18	15.25

1. Metavoltine, Madeni Zakh (Blaas, 1883)
2. Metavoltine, Chuquimata (Bandy, 1938)
3. Metavoltine, Sierra Gorda (Scordari *et al.*, 1975)
4. Theory for $K_2Na_6Fe^{2+}Fe_6^{3+}(SO_4)_{12}O_2 \cdot 18H_2O$.
5. Stable artificial salt (F. Vurro, anal.).

1′ – 5′. Atomic ratios to 12 SO_4^{2-}. R^{2+} is Fe^{2+} in 1′, 0.66 Fe^{2+}, 0.32 Cu^{2+}, and 0.06 Zn^{2+} in 3′.

* Not found by Bandy, but detected qualitatively in holotype material.

† Also 1.18% CuO, 0.23% ZnO.

TABLE III. *A comparison of unit-cell dimensions*

	a	*c*	*c/a*	Space group
Metavoltine (Sierra Gorda)	9.575(5) Å	18.17(1) Å	1.898	*P*3
Maus' salt	9.71(1)	18.96(2)	1.953	$P6_3/m$
Stable artificial salt	9.642(3)	35.93(1)	3.726	$P\bar{6}2c$ or $P6_3mc$ or $P6_3/mmc$

It appears probable that in the stable artificial salt there are 'layers' like those found in metavoltine (Giacovazzo *et al.*, 1976) and in Maus's salt (Giacovazzo *et al.*, 1975) (see Scordari, this vol., p. 375).

K ⇌ Na diadochy in the new stable salt

Chemical analyses of the new stable salt, confined to determination of the K:Na ratio, reveal extensive diadochy between K and Na ions, Na:K ranging from 1·75:6·25 to 5·65:2·35. The broadening of the basal reflection 0004 confirms the chemical results; 2 θ ranges from 9·735 to 10·485° (Cu-$K\alpha$ radiation), corresponding to a difference of 0·65 Å in d_{0004}, very near to that calculated from the ionic radii for complete Na, K replacement between two 'layers', 0·68 Å. For $10\bar{1}0$ 2 θ ranges from 10·56 to 10·81°, corresponding to a range of 0·20 Å in $d_{10\bar{1}0}$, less than that observed for 0004; there is probably some readjustment of these 'layers' to ions of different radius.

A determination of the crystal structure of the new stable salt is in progress and will clarify these problems better. Attempts are also being carried out to prepare an artificial salt with only Na as alkali cation.

Chemical analyses of Maus's salt show that the range of Na:K ratio is smaller than for the new stable salt (Scordari, Vurro, and Menchetti, 1975), and in agreement with this the range in d_{0002} is only 0·32 Å, half that for the corresponding spacing of the stable salt.

The optical properties, symmetry, and unit-cell dimensions of the present stable artificial salt are quite different from those of the original β-metavoltine as described by Scharizer (1927) and from those of the product doubtfully assigned to β-metavoltine by Gossner (1936).

Acknowledgement. This paper was supported by the Italian C.N.R., contract no. 75.00034, 05.115,4593.

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[*Manuscript received 18 December 1975; revised 6 December 1976*]

Errata: Table I, col. 12, last line, *for* 2.002 *read* 2.022.
Table II, line 10, *for* Chuquimata *read* Chuquicamata.
Table III, last line, *for* $P62c$ *read* $P\bar{6}2c$.