SYNTHESES OF VALLERIITE

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Abstract

Syntheses in the range 400-700°C at 1000 bars indicate a range of composition of valleriite from $2.0[Mg_{0.68}Al_{0.32}(OH)_2] \cdot [CuFeS_2]$ to $2.3[Mg_{0.68}Al_{0.32}(OH)_2] \cdot [CuFeS_2]$, with an upper stability temperature between 600 and 650°C. The composition determined by synthesis does not agree with that based on the crystal structure of Evans, or with the electronprobe analyses of natural material by Springer.

According to Evans *et al.* (1968), the structure of valleriite as a whole requires a large superlattice, but can be defined in terms of two separate sublattices: one rhombohedral with hexagonal axes $a = 3.792 \pm 0.005$ Å and $c = 34.10 \pm 0.05$ Å, corresponding to the sulfide layers; and the other hexagonal with $a = 3.070 \pm 0.006$ Å and $c = 11.37 \pm 0.02$ Å, corresponding to the hydroxide layers. The length ratio of the *a*-axes of these two subcells is in the ratio of 21:17, hence the chemical composioton of valleriite is $1.526[Mg_{0.68}Al_{0.32}(OH)_2] \cdot [Cu_{0.93}Fe_{1.07}S_2]$. Springer (1968) made quantitative electronprobe analyses of valleriites from Kaveltrop, Sweden, and Bushveld and Palabora, South Africa, and suggested that the chemical ratio of hydroxide layer to sulfide layer is greater than 1.526 (*i.e.* 1.57~1.70), and that Fe^{3+} also enters the hydroxide layer by replacing Al^{3+}.

Experiments were carried out in sealed Ag or Au capsules, which were enclosed in a conventional cold-seal pressure vessel (Tuttle, 1949). The starting materials for the syntheses were natural chalcopyrite from Ashio Mine, Japan, or special grade reagent of iron, copper and sulfur for the sulfide layers, and MgO for magnesium, γ-Al_2O_3 for aluminum, and $Cr(OH)_2$ for chromium in the hydroxide layers. The temperature range was from 400°C to 700°C, and the water vapour pressure was always 1000 bars.

The experimental data on the syntheses of valleriites are shown in Table 1. The X-ray powder patterns and the cell dimensions of these synthesized and natural valleriites are shown in Tables 2 and 3. The relationships of the phases obtained to the compositions of starting materials and the temperatures are summarized as follows:

TABLE 1. EXPERIMENTAL DATA FOR VALLERIITE SYNTHESES

Run No.	Compositions of Starting Materials	Temp. (°C)	Time (days)	Condensed Phases[a] Obtained
V-1	$1.526[0.68MgO+0.32(\frac{1}{2}Al_2O_3)]\cdot[CuFeS_2]^b$	400	7	cp > vl
		500	10	vl, cp
		600	8	vl, cp, ?
		700	5	spinel, po?, cov?, ?
V-2	$2.0[0.68MgO+0.32(\frac{1}{2}Al_2O_3)]\cdot[CuFeS_2]^b$	400	7	vl, cp
		500	5	vl > cp
		600	5	vl > cp
		700	5	spinel, po?, cov?, ?
V-3	$2.3[0.68MgO+0.32(\frac{1}{2}Al_2O_3)]\cdot[CuFeS_2]^b$	400	7	vl≫cp
		500	5	vl≫cp
		600	5	vl≫cp
		650	5	bru, po?, cov?, ?
		700	5	spinel, po?, cov?, ?
V-4	$2.5[0.68MgO+0.32(\frac{1}{2}Al_2O_3)]\cdot[CuFeS_2]^b$	400	7	vl≫bru > cp
		500	5	vl≫bru > cp
		600	5	vl≫bru > cp
		700	5	spinel, po?, cov?, ?
V-5	$3.0[0.68MgO+0.32(\frac{1}{2}Al_2O_3)]\cdot[CuFeS_2]^b$	400	7	vl≫bru > cp
		500	5	vl≫bru > cp
		600	5	vl≫bru > cp
		700	5	spinel, po?, cov?, ?
V-6	$1.526[0.68MgO+0.32(\frac{1}{2}Al_2O_3)]\cdot[Cu_{0.93}Fe_{1.07}S_2]^c$	400	10	cp > vl
		500	20	vl, cp
V-7	$2.3[0.68MgO+0.32(\frac{1}{2}Al_2O_3)]\cdot[Cu_{0.93}Fe_{1.07}S_2]^c$	400	10	vl > cp
		500	15	vl≫cp
V-8	$2.3[MgO]\cdot[CuFeS_2]^b$	500	5	cp, bru
V-9	$2.3[0.9MgO+0.1(\frac{1}{2}Al_2O_3]\cdot[CuFeS_2]^b$	500	5	vl > cp, bru
V-10	$2.3[0.5MgO+0.5(\frac{1}{2}Al_2O_3)]\cdot[CuFeS_2]^b$	500	5	vl > cp > boeh
V-11	$2.3[0.68MgO+0.32(\frac{1}{2}Cr_2O_3)]\cdot[CuFeS_2]^b$	500	5	vl > cp

[a] cp = chalcopyrite, vl = valleriite, po = pyrrhotite, cov = covellite, bru-brucite, boeh = boehmite.

[b] $[CuFeS_2]$: Chalcopyrite was used as the starting material.

[c] $[Cu_{0.93}Fe_{1.07}S_2]$: Special grade reagents of iron, copper and sulfur were used as the starting material.

Valleriite was found to exist with a large amount of chalcopyrite in Run V-1, but a small amount of chalcopyrite in Run V-2 (about 15%) and Run V-3 (about 5%). On the other hand, in addition to a small amount of chalcopyrite, a small amount of brucite was found to exist with a large amount of valleriite in Runs V-4 and V-5 (the amount of brucite in Run V-5 is greater than in Run V-4). From the results shown above it is probably certain that the chemical composition of valleriite

TABLE 2. X-RAY POWDER DIFFRACTION PATTERNS OF VALLERIITES

$hk \cdot l$	Valleriite[a] from Loolekop, South Africa		Valleriite synthesized in Run V-3 V-3 (500°C)		Valleriite synthesized in Run V-11 V-11 (500°C)	
	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I
$00 \cdot 3$	11.30	10	11.40	60	11.51	30
$00 \cdot 6$	5.71	10	5.72	100	5.71	100
$00 \cdot 9$	3.80	5	3.81	15	3.85	40
$10 \cdot 1$	3.27	6	3.27	20	3.28	20
$10 \cdot \bar{2}$	3.23	5	3.24	10	3.26	10
$10 \cdot \bar{11}$	2.259	2	2.265	5	—	—
$10 \cdot 13$	2.041	2	2.049	5	2.052	5
$00 \cdot 18$	1.885	5	1.893	10	1.908	5
$11 \cdot 3$	1.860	5	1.871	10	1.886	15

[a] Data from Evans *et al.* (1964).

will range from $2.0[\text{Mg}_{0.68}\text{Al}_{0.32}(\text{OH})_2] \cdot [\text{CuFeS}_2]$ to $2.3[\text{Mg}_{0.68}\text{Al}_{0.32}(\text{OH})_2] \cdot [\text{CuFeS}_2]$. The chemical composition obtained from our experiments of the syntheses is different from the composition which is determined on the basis of crystal structure by Evans *et al.* (1968), and from the composition of the natural valleriite determined through electronprobe analyses by Springer (1968). It is clear from the result of Runs V-6 and V-7 that valleriite can be also synthesized from mixtures of iron, copper and sulfur instead of chalcopyrite as the starting material. From Runs V-8, V-9, V-10 and V-11, it is certain that the trivalent ions in the hydroxide layer are indispensable to the formation of valleriite structure, but that the Al^{3+} can be replaced by other trivalent ions such as Cr^{3+}. The unit cell dimensions of the synthesized valleriites are almost the same for any composition of the starting material except for Runs V-9 and V-11. From this fact, it follows that the synthesized valleriites, except in Runs V-9 and V-11, are of almost the same chemical composition. In Run V-11, the c-axis was found to have lengthened on account of the effect of the replacement of Al^{3+} by Cr^{3+}. In the case of Run V-9, the c-axis was found

TABLE 3. CELL DIMENSIONS[a] OF NATURAL AND SYNTHESIZED[b] VALLERIITES

Run#	Loolekop[c]	V-1	V-2	V-3	V-4	V-5	V-6	V-7	V-9	V-10	V-11
$a(\text{Å})$	3.792	3.811	3.813	3.802	3.811	3.812	3.808	3.801	3.811	3.815	3.805
$c(\text{Å})$	34.10	34.29	34.21	34.18	34.29	34.18	34.18	34.21	34.44	34.21	34.35

[a] The deviation for a-axis is ± 0.005 Å and the deviation for c-axis is ± 0.05 Å.

[b] These specimens were synthesized at 500°C.

[c] Data from Evans *et al.* (1964)

to have lengthened because the ratio of $Mg^{2+}:Al^{3+}$ in the starting materials was greater than the ratio of $7:3$. Brucite was present in Run V-9 and boehmite was present in Run V-10; from this it seems that the range of the solid solution of Mg^{2+} and Al^{3+} in the hydroxide layer is limited. Valleriite was not produced at the temperature of 700°C in any of the runs, and valleriite was also not produced at the temperature of 650°C in Run V-3. From this fact, the upper stable temperature of this mineral appears to be between 600°C and 650°C.

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A "VALLERIITE-TYPE" MINERAL FROM NORIL'SK, WESTERN SIBERIA[1]

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ABSTRACT

Electron microprobe analysis of a "valleriite-type" mineral from Noril'sk, western Siberia, yields a formula $(Cu_{0.995}Fe_{1.005}S_2) \cdot 1.472$ $[Fe(OH)_2]$, which is the most iron-rich variant of this mineral reported to date.

INTRODUCTION

The structure of valleriite from Loolekop, South Africa, determined very recently by Evans and Allmann (1968), has been interpreted as layers of copper-iron sulphide alternating with layers of Mg-Al hydroxide. The formula for the Loolekop material is

$$(Fe_{1.07}Cu_{0.93}S_2) \cdot 1.526[Mg_{0.68}Al_{0.32}(OH)_2].$$

Springer (1968) re-examined valleriites from two localities: Kaveltorp, Sweden and Palabora, South Africa with the electron microprobe an-