American Mineralogist, Volume 61, pages 326–328, 1976

On the crystal chemistry of picropharmacolite

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Abstract

A revision of available results for picropharmacolite points out strict crystallochemical similarities with guerinite, $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9H_2O$, and supports the formula $Ca_4MgH_2(AsO_4)_4.11H_2O$ with, possibly, a limited substitution involving H, Ca, and Mg.

Introduction

On the basis of IR spectra performed on natural and deuterated samples, Sumin de Portilla (1974) proposes for picropharmocolite the crystallochemical formula $Ca_2(MgOH)(HAsO_4)(AsO_4) \cdot 5H_2O$.[1] Such a formula, however, is at variance both with the five chemical analyses reported by Sumin de Portilla (1974), and with the following results which are not quoted by her.

Guérin *et al.* (1967) (GMBP, hereafter) obtained synthetic picropharmacolite (Table 1) to which they attributed the formula $4CaO.MgO.2As_2O_5.12H_2O$.

Abbona *et al.* (1969) (ACF, hereafter) showed that picropharmacolite is triclinic with

$$a = 13.549(8)\ b = 13.562(8)\ c = 6.737(9)\text{Å}$$

$$\alpha = 99°38'(11')\ \beta = 96°7'(11')\ \gamma = 91°31'(3')$$

and (on the basis of IR spectroscopy, a new chemical analysis, and GMBP work) suggested the crystallochemical formula $Ca_4MgH_2(AsO_4)_4.11H_2O$. This formula, for the above cell, implies $Z = 2$ and $D_{calc} = 2.576 gcm^{-3}$, in agreement with measured values of 2.55, 2.58, and $2.62 gcm^{-3}$ (*cf.* Abbona *et al.*, 1969); Sumin de Portilla's (1974) formula leads to $D_{calc} = 2.686 gcm^{-3}$ ($Z = 4$).

Pierrot and Schubnel (1972) showed that the new mineral irhtemite, $Ca_4MgH_2(AsO_4)_4.4H_2O$, has the same powder spectrum as the product which is obtained by heating picropharmacolite up to the loss of seven water molecules in the ACF formula. Further, they found crystallographic analogies between irhtemite and sainfeldite, $Ca_5(HAsO_4)_2(AsO_4)_2.4H_2O$, whose crystal structure has been solved by Ferraris and Abbona (1972).

Because of the variation in the chemical analyses, it is worthy to compare them critically.

Chemical analyses

Table 1 lists eighteen chemical analyses for picropharmacolite from several sources; nine of them (six are on synthetic material) come from the same laboratory (Guérin *et al.*, 1967). Genth's (1891) analyses have not been included because they were probably performed on poorly selected material.

The variation of CaO and MgO throughout Table 1 is undoubtedly beyond usual analytical errors but, clearly, does not support the hypothesis of a structural substitution limited to Ca and Mg (Fig. 1); a more complex substitution will be discussed later. On the other hand, the six analyses of synthetic material, with an X-ray powder spectrum identical to that of natural picropharmacolite (Guérin *et al.*, 1967), show CaO/As_2O_5 and MgO/As_2O_5 ratios which, especially for the calcium, are reasonably in agreement with the GMBP formula, $4CaO.MgO.2As_2O_5.12H_2O$; the average values of the two ratios are 2.00(3)[2] and 0.47(2), respectively. For the natural samples the same values are 2.16(15) and 0.48(6) or 2.10(7) and 0.46(5) with or, respectively, without analyses 10 and 11, which have been criticized by GMBP. In the light of the paragenesis of picropharmacolite, con-

[1] This formula, reported in the abstract of the quoted paper, is different from that in the text (p. 809–810) in which (probably for a typographic mistake) Ca/Mg = 1; the reference for chemical analyses 1 and 2 in the same paper is incorrect (*cf.* 7 and 8 in Table 1).

[2] The figures in parentheses represent the estimated standard deviations for a normal distribution of the experimental results.

TABLE 1. Chemical composition of picropharmacolite

	Synthetic						Natural											
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
CaO	23.9	23	24.1	24.2	24.05	23.84	24.65	25.77	24.1	26.7	27.9	24	24.3	23.9	24.49	24.65	24.48	28.2
MgO	3.92	3.84	4.07	3.83	4.32	4.16	3.22	3.73	3.2	4.26	4.45	4.32	3.88	3.98	4.43	3.17	4.40	4.4
As_2O_5	49.38	48.45	49.2	48.9	48.8	49.2	46.97	46.93	46.4	45.8	45.5	48.2	48.4	48.8	48.19	49.15	47.40	55.5
H_2O	22.8	23.3	22.63	23.07	22.83	22.70	23.98	24.01	23.3	22.1	21.36	23.4	22.7	23	22.42	23.65	23.02	11.5
Rem.							1.00		1.9	1.0	0.48				0.75			
Total	100.00	98.59	100.00	100.00	100.00	99.90	99.82	100.44	98.90	99.86	99.69	99.92	99.28	99.68	100.28	100.62	99.30	99.6
$\frac{CaO}{As_2O_5}$	1.98	1.95	2.01	2.03	2.02	1.99	2.15	2.25	2.13	2.39	2.51	2.04	2.06	2.01	2.08	2.06	2.12	2.08
$\frac{MgO}{As_2O_5}$	0.45	0.45	0.47	0.45	0.50	0.48	0.46[a]	0.45	0.40	0.53	0.56	0.51	0.46	0.46	0.52	0.37	0.53	0.45
$\frac{H_2O}{As_2O_5}$	5.89	6.13	5.87	5.99	5.97	5.85	6.51	6.53	6.41	6.15	5.99	6.19	5.98	6.01	5.93	6.14	6.19	-

1-6. Synthetic picropharmacolite, Guérin et al. (1967). 7. Riechelsdorf, Stromeyer 1819, in Pierrot (1961); a) includes Rem. which is CoO. 8. Freiberg, Frenzel 1873, in Pierrot (1961). 9. Riechelsdorf, Pierrot (1961); Rem. is 0.1 CoO and 1.8 insoluble. 10-11. Sainte-Marie-aux-Mines, Pierrot (1961); Rem. is insoluble. 12-14. Sainte-Marie-aux-Mines, Guérin et al. (1967). 15-16. Hovpu-Aksi, Yahontova 1968, in Sumin de Portilla (1974); Rem. is insoluble. 17. Brosso, Abbona et al. (1969). 18. Synthetic irhtemite from picropharmacolite of Salsigne, Pierrot and Schubnel (1972).

tamination by Ca arsenates and by other impurities like barite (Pierrot, 1961) makes the selection of the material very difficult and could largely justify an excess of CaO in comparison with the GMBP formula. Also the synthesis in the laboratory (Guérin *et al.*, 1967) is always preceded by crystallization of simpler Ca arsenates, and the equilibria are very slow.

In lack of a crystal structure determination, which could elucidate the interpretation of the chemical analyses, crystallochemical deductions can be inferred from analogies between picropharmacolite and guerinite, $Ca_5(H_2AsO_4)_2(AsO_4)_2.9H_2O$, whose structure is known (Catti and Ferraris, 1974).

Structural considerations

Both minerals are disordered-fibrous along a crystallographic direction with the same period (6.734 and 6.737Å for *b* in guerinite and *c* in picropharmacolite, respectively). In guerinite pseudo-translations occur along [101] and [$\bar{1}$01] both with a length $|a + c|/2 = 14.68$Å which is comparable to *a* and *b* of picropharmacolite; the same directions correspond to the scattering vectors of the strongest reflection in the powder spectra of each mineral: 14.4Å ($\bar{1}$01 or 101) and 13.59Å (100 or 010) for guerinite and picropharmacolite, respectively. It seems, therefore, plausible to suppose that the ($\bar{1}$01) layers formed by Ca coordination polyhedra and As tetrahedra in guerinite are present in picropharmacolite as well, with some slight modifications in order to include Mg.

In our opinion, the structural considerations support the GMBP hypothesis that picropharmacolite is a double salt which can be derived from guerinite by a one-to-one substitution of CaO with MgO as shown by the ACF crystallochemical formula, $Ca_4MgH_2(AsO_4)_4.11H_2O$. As a possible alternative, this formula can be considered only ideal in the sense that a limited substitution involving H, Ca, and Mg could occur as proposed by Genth (1891); partially occupied Ca positions and disordered acidic hydrogen atoms found in guerinite should be the structural bases for the proposed triple substitution.

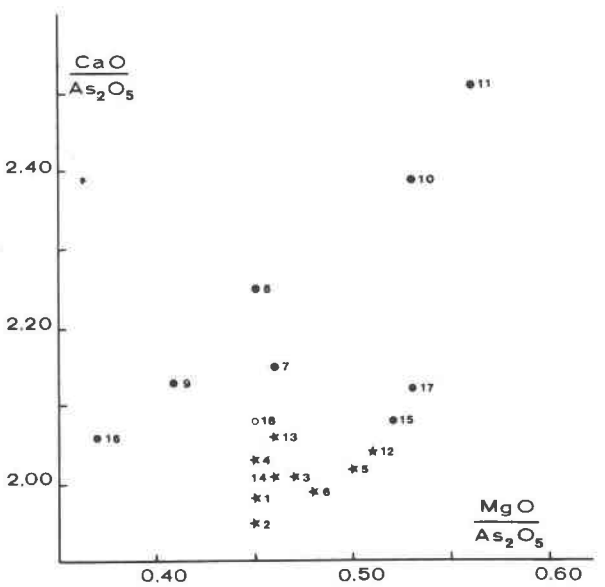

FIG. 1. CaO/As_2O_5 ratio *vs.* MgO/As_2O_5 for eighteen chemical analyses of picropharmacolite (Table 1). Guérin *et al.*'s (1967) and Pierrot's (1961) results are shown as stars and asterisks, respectively.

Acknowledgment

Research supported by the Consiglio Nazionale delle Ricerche, Roma.

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Manuscript received, July 1, 1975; accepted for publication, November 3, 1975.