

On the crystal chemistry of picroparmacolite

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Abstract

A revision of available results for picroparmacolite points out strict crystallochemical similarities with guérinite, $\text{Ca}_5(\text{HASO}_4)_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$, and supports the formula $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$ 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 picroparmacolite the crystallochemical formula $\text{Ca}_2(\text{MgOH})(\text{HASO}_4)(\text{AsO}_4) \cdot 5\text{H}_2\text{O}$.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 picroparmacolite (Table 1) to which they attributed the formula $4\text{CaO} \cdot \text{MgO} \cdot 2\text{As}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$.

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

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

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

and (on the basis of IR spectroscopy, a new chemical analysis, and GMBP work) suggested the crystallochemical formula $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$. This formula, for the above cell, implies $Z = 2$ and $D_{\text{calc}} = 2.576 \text{ gcm}^{-3}$, 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 $D_{\text{calc}} = 2.686 \text{ gcm}^{-3}$ ($Z = 4$).

Pierrot and Schubnel (1972) showed that the new mineral irhtemite, $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$, has the same powder spectrum as the product which is obtained by heating picroparmacolite up to the loss of

seven water molecules in the ACF formula. Further, they found crystallographic analogies between irhtemite and sainfeldite, $\text{Ca}_5(\text{HASO}_4)_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$, 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 picroparmacolite 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 picroparmacolite (Guérin *et al.*, 1967), show CaO/As₂O₅ and MgO/As₂O₅ ratios which, especially for the calcium, are reasonably in agreement with the GMBP formula, $4\text{CaO} \cdot \text{MgO} \cdot 2\text{As}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$; 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 picroparmacolite, 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 ₂ O 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 ₂ O	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
CaO	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
As ₂ O ₅																		
MgO	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
As ₂ O ₅																		
H ₂ O	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	-
As ₂ O ₅																		

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, Yehontova 1968, in Sumin de Portilla (1974); Rem. is insoluble. 17. Brosso, Abbona *et al.* (1969). 18. Synthetic ihtemite 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, $\text{Ca}_5(\text{H}_2\text{AsO}_4)_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$, 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 6.737 Å for *b* in guerinite and *c* in picropharmacolite, respectively). In guerinite pseudo-translations occur along [101] and $[\bar{1}01]$ both with a length $|a + c|/2 = 14.68 \text{ \AA}$ 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: 14.4 Å ($\bar{1}01$ or 101) and 13.59 Å (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 sup-

port 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, $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$. 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.

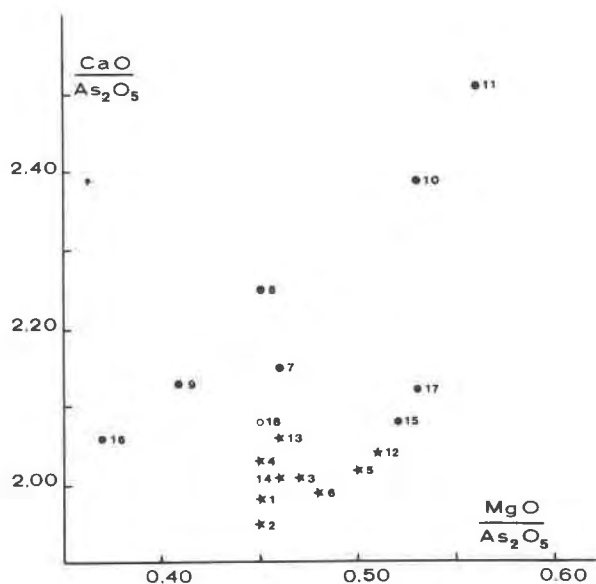


FIG. 1. CaO/As₂O₅ ratio vs. MgO/As₂O₅ for eighteen chemical analyses of picropharmacolite (Table 1). Guérin *et al.*'s (1967) and Pierrot's (1961) results are shown as stars and asterisks, respectively.

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