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ENGLISHITE: NEW CHEMICAL DATA AND A SECOND OCCURRENCE, FROM THE TIP TOP PEGMATITE, CUSTER, SOUTH DAKOTA

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ABSTRACT

New determination of the chemical composition of englishite from near Fairfield, Utah, and from a second occurrence, the Tip Top pegmatite in South Dakota, require a revision of the chemical formula for this species. The new formula is $Na_2K_3Ca_{10}Al_{15}(PO_4)_{21}(OH)_7 \cdot 26H_2O$ which, with $Z = 4$, yields a calculated density of 2.69 g/cm^3, compared with the new observed value of 2.68 g/cm^3.

Keywords: englishite, chemical composition, pegmatite, South Dakota, Utah.

SOMMAIRE

Les résultats de nouvelles analyses chimiques d'englishite de Fairfield (Utah) ainsi que d'échantillons provenant d'un nouveau gîte dans la pegmatite de Tip Top (Dakota du Sud) requièrent la révision de la formule chimique de cette espèce. Pour $Z = 4$, la nouvelle formule, $Na_2K_3Ca_{10}Al_{15}(PO_4)_{21}(OH)_7 \cdot 26H_2O$, donne une densité calculée de 2.69, qui concorde avec la nouvelle valeur mesurée, 2.68.

(Traduit par la Rédaction)

Mots-clés: englishite, composition chimique, pegmatite, Dakota du Sud, Utah.

INTRODUCTION

Englishite was first reported from the variscite deposit near Fairfield, Utah, by Larsen & Shannon (1930), who described it as a new species, with the chemical formula $4CaO \cdot K_2O \cdot 4Al_2O_3 \cdot 4P_2O_5 \cdot 14H_2O$. Subsequent study by Larsen (1942) established the monoclinic symmetry of englishite and provided additional data concerning the paragenesis. Moore (1976) provided crystallographic data [*a* 38.43(2), *b* 11.86, *c* 20.67 Å, β 111°16′, space group *A2/a* or *Aa*] and proposed the formula $[K_2Na(H_2O)_4Ca_{4.5}(PO_3OH)_3][Al_3(OH)_6(PO_4)(PO_3OH)]_3$ ($Z = 8$), based in part on a suspected structural analogy with mitridatite. The recent discovery of a second occurrence of englishite in the Tip Top pegmatite in South Dakota (Dunn *et al.* 1983) prompted a re-analysis of the original englishite from Utah, which had not been chemically analyzed in the 53 years since the original description. The integrity of the type samples of englishite was probably inadvertently compromised by the accidental switching of vials, as described by Dunn (1978) in the discreditation of lewistonite and dehrnite, two other phosphates from this deposit, supposedly containing K and Na; these were shown to be carbonate-fluorapatite. However, englishite has a very characteristic appearance; its platy aggregates of lustrous, colorless crystals have a vitreous lustre and a very characteristic X-ray powder pattern (Moore 1976). The samples from Utah studied herein all conform to this description and yield powder data in good agreement with those published by Moore.

CHEMISTRY

The samples in this study were chemically analyzed using an ARL–SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA standardized on brass. The following standards were used: montgomeryite (Ca,Al,Mg,P) and hornblende (Na,K). The samples were analyzed using a large (50 μm) defocused beam-spot after first establishing chemical homogeneity with a smaller beam-spot. Water was determined by the Penfield method. The resultant compositions are presented in Table 1.

Calculation of unit-cell contents, using the crystallographic data of Moore (1976) and a newly determined density of 2.68 g/cm^3 (obtained using heavy-liquid techniques) yields, as an average of three analyses of englishite: $Na_{1.83}K_{3.01}(Ca_{9.79}Mg_{0.09})_{\Sigma 9.88}Al_{14.94}(PO_4)_{20.77}(OH)_{7.11} \cdot 26.14H_2O$ ($Z = 4$) or, ideally, $Na_2K_3Ca_{10}Al_{15}(PO_4)_{21}(OH)_7 \cdot 26H_2O$. This yields a calculated density of 2.69 g/cm^3, in excellent agreement with the measured value. The near-constancy of Na in the Utah material suggests that Na is essential in englishite. Results of the previous analysis, by Shannon (*cf.* Larsen & Shannon 1930), are presented in Table 1 for comparison, but are now considered highly suspect. The formula of Moore (1976) is likewise improbable inasmuch as the ratios of the non-alkali elements are now seen to be markedly different from those proposed by Moore. Gladstone–Dale calculations, using the optical data

TABLE 1. CHEMICAL COMPOSITION OF ENGLISHITE

	Fairfield, Utah					Tip Top	Theory***
	Original results	16676	R8314	R7834	Average of three		
Al_2O_3	24.7	21.0	21.3	22.1	21.5	21.8	21.50
FeO†	0.0	0.0	0.0	0.0	0.0	2.5	0.00
MgO	0.0	0.2	0.1	0.0	0.1	0.1	0.00
CaO	14.1	15.9	15.8	14.8	15.5	15.8	16.04
K_2O	5.4	4.0	4.1	4.0	4.0	3.6	3.97
Na_2O	1.6	1.6	1.5	1.8	1.6	0.9	1.74
P_2O_5	37.8	41.6	41.1	42.0	41.6	41.0	41.88
H_2O	16.5				15.1*	14.9**	14.87
Total	100.1††				99.4	100.6	100.00

* - H_2O determined on a separate sample; ** - H_2O from theoretical value; *** - Ideal composition for $Na_2K_3Ca_{10}Al_{15}(PO_4)_{21}(OH)_7\cdot 26H_2O$; †† - From Larsen and Shannon (1930), after deduction of 7% variscite and 2% wardite impurities; † - Total Fe assumed as FeO: microchemical tests were inconclusive.

of Larsen & Shannon (1930) and the newly determined density, yield for the average of the three analyses of Utah englishite, a K_P of 0.213 and a K_C of 0.215, using the constants of Mandarino (1981). This calculation supports the accuracy of our analyses.

The englishite from the Tip Top pegmatite, near Custer, South Dakota (Dunn *et al.* 1983) is not amenable to a highly reliable analysis by microprobe inasmuch as it occurs in friable, puffy masses unsuitable for standard sample-preparation techniques. We prepared a pellet of this material and subjected it to microprobe analysis utilizing the same procedures used for the Utah englishite. We consider the resultant analytical data, given in Table 1, to be of markedly lower reliability than those of the Utah material. Even so, the data are in reasonably good agreement with those for the Utah englishite. Principal differences lie in the presence of some Fe in the Tip Top material and in a slightly different Ca:Na ratio. The presence of both Na and K in this material further supports the argument that K and Na are essential to the species.

It is of interest to compare the formula for the Utah englishite proposed above with that of Moore (1976). Recasting the two into comparable forms yields: $\{K_{1.5}Na(H_2O)_{1.5}Ca_5(PO_4)_{5.5}\}_2$ $\{Al_3[(OH)_{1.4}(H_2O)_{4.6}]_{\Sigma 6}(PO_4)_2\}_5$ (present study) and $\{K_2Na(H_2O)_4Ca_{4.5}(PO_3OH)_3\}_2\{Al_3(OH)_6[(PO_4)$ $(PO_3OH)]_{\Sigma 2}\}_6$ (Moore 1976). In each case the contents of the second pair of braces represent, according to Moore, alunite-like layers in the englishite structure, whereas the contents of the first pair of braces represent what is present between the layers. The chief differences between the two interpretations are the presence of 6 rather than 5 alunite-like layers in Moore's formula and the different amounts of molecular water and phosphate ions in the interlayer positions. In addition, Moore assumed the existence of monohydrogen phosphate as well as orthophosphate ions in englishite.

In the absence of a crystal-structure determination it is not possible to say which, if any, of the proposed formulas is correct. However, two points should be made. The first is that in his 1976 paper, Moore proposed a structural formula for mitridatite involving alunite layers and PO_3OH^{2-} ions, and then used that as the basis for his englishite formula. The proposed mitridatite formula was later abandoned by Moore & Araki (1977), who showed by crystal-structure analysis that mitridatite contains PO_4^{3-} as the only phosphate species and that, although related to alunite, this mineral contains no alunite-like layers. Secondly, Moore's provisional formula for englishite was derived from the analytical data of Larsen & Shannon (1930) for this mineral, whereas the new formula proposed here was obtained by modern microanalytical techniques using several specimens, all of which gave similar results that differ from the original data. In our opinion, therefore, our new empirical formula for englishite, in addition to having the virtue of relative simplicity, is more likely to accurately represent the composition of this complex and still enigmatic mineral.

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REFERENCES

DUNN, P.J. (1978): Dehrnite and lewistonite: discredited. *Mineral. Mag.* **42**, 282-284.

______, ROBERTS, W.L., CAMPBELL, T.J. & LEAVENS, P.B. (1983): Red montgomeryite and associated minerals from the Tip Top pegmatite, with notes on kingsmountite and calcioferrite. *Mineral. Rec.* **14**, 195-197.

LARSEN, E.S., 3rd (1942): The mineralogy and paragenesis of the variscite nodules from near Fairfield, Utah. *Amer. Mineral.* **27**, 281-300, 350-372, 441-451.

______ & SHANNON, E.V. (1930): The minerals of the phosphate nodules from near Fairfield, Utah. *Amer. Mineral.* **15**, 307-337.

MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

MOORE, P.B. (1976): Derivative structures based on the alunite octahedral sheet: mitridatite and englishite. *Mineral. Mag.* **40**, 863-866.

______ & ARAKI T. (1977): Mitridatite, $Ca_6(H_2O)_6[Fe^{III}_9O_6(PO_4)_9]\cdot 3H_2O$. A noteworthy octahedral sheet structure. *Inorg. Chem.* **16**, 1096-1106.

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