

Supplementary information to the paper

**New arsenate minerals from the Arsenatnaya fumarole,**

**Tolbachik volcano, Kamchatka, Russia. X. Edtollite,**

**$\text{K}_2\text{NaCu}_5\text{Fe}^{3+}\text{O}_2(\text{AsO}_4)_4$ , and alumoedtollite,**

**$\text{K}_2\text{NaCu}_5\text{AlO}_2(\text{AsO}_4)_4$**

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Table S1a. Bond valence calculations for edtollite.

	K	Na	As(1)	As(2)	Cu(1)	Cu(2)	Fe	$\Sigma$
O(1)	0.12			1.19	0.17		0.50	1.98
O(2)	0.10		1.15			0.40	0.18	1.83
O(3)		0.07 $\times 2 \downarrow$	1.15		0.42	0.05	0.28	1.97
O(4)	0.16 0.14			1.23	0.52			2.05
O(5)	0.09	0.27 $\times 2 \downarrow$	1.30		0.45			2.11
O(6)	0.07			1.19		0.15	0.52	1.93
O(7)						0.52 0.46	0.57 0.49	2.04
O(8)	0.14			1.38	0.44			1.96
O(9)	0.13	0.20 $\times 2 \downarrow$	1.24			0.45		2.02
$\Sigma$	0.95	1.08	4.84	4.99	2.00	2.03	2.54	

Table S1b. Bond valence calculations for alumoedtollite.

	K	Na	As(1)	As(2)	Cu(1)	Cu(2)	<i>M</i>	$\Sigma$
O(1)	0.13			1.19	0.17		0.51	2.00
O(2)	0.11		1.20			0.42	0.17	1.90
O(3)		0.07 $\times 2 \downarrow$	1.18		0.41	0.06	0.25	1.97
O(4)	0.21 0.14			1.33	0.49			2.17
O(5)	0.10	0.28 $\times 2 \downarrow$	1.35		0.47			2.20
O(6)	0.09			1.26		0.14	0.56	2.05
O(7)						0.50 0.47	0.51 0.46	1.94
O(8)	0.17			1.30	0.47			1.94
O(9)	0.15	0.23 $\times 2 \downarrow$	1.27			0.42		2.07
$\Sigma$	1.10	1.16	5.00	5.08	2.01	2.01	2.46	

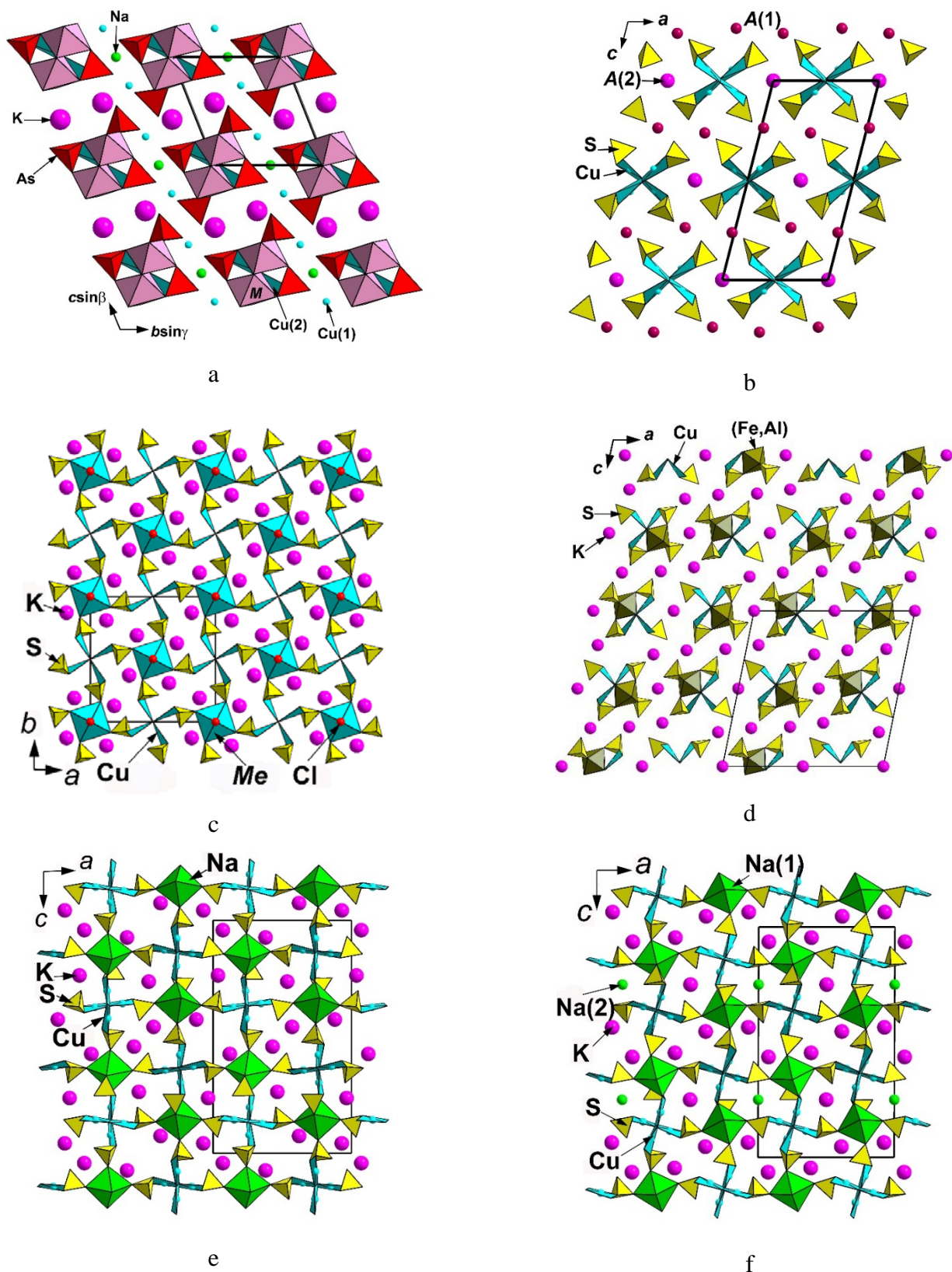


Figure S1. The crystal structures of edtolite/alumoedtolite (our data; for legend see text and Table 6) (a) and structurally related sulfates: eleomelanite (IMA2015-118: our data) (b), piypite (c: drawn using data by Effenberger and Zemmann, 1984), klyuchevskite (d: drawn using data by Gorskaya *et al.*, 1992), wulffite (e) and parawulffite (f) (drawn using data by Pekov *et al.*, 2014c). The unit cells are outlined. Cu-centred polyhedra in all structures [except of Cu(1) in edtolite/alumoedtolite] are shown as almost planar squares for better clarity; the *Me* site in piypite can be occupied by K, Na or Cu.

Effenberger H. and Zemann J. (1984) The crystal structure of caratiite. *Mineralogical Magazine*, 48, 541–546.

Gorskaya M.G., Filatov S.K., Rozhdestvenskaya I.V. and Vergasova L.P. (1992) The crystal structure of klyuchevskite,  $K_3Cu_3(Fe,Al)O_2(SO_4)_4$ , a new mineral from Kamchatka volcanic sublimates. *Mineralogical Magazine*, 56, 411–416.

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Belakovskiy D.I., Chukanov N.V., Lykova I.S., Saveliev D.P., Sidorov E.G. and Pushcharovsky D.Yu. (2014c) Wulffite,  $K_3NaCu_4O_2(SO_4)_4$ , and parawulffite,  $K_5Na_3Cu_8O_4(SO_4)_8$ , two new minerals from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia. *The Canadian Mineralogist*, 52, 699–716.