

## Kolbeckite, $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$ , isomorphous with metavariscite

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This study presents the first structural report of kolbeckite, with the ideal formula  $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$  (scandium phosphate dihydrate), based on single-crystal X-ray diffraction data. Kolbeckite belongs to the metavariscite mineral group, in which each  $\text{PO}_4$  tetrahedron shares four vertices with four  $\text{ScO}_4(\text{H}_2\text{O})_2$  octahedra and *vice versa*, forming a three-dimensional network of polyhedra.

### Comment

A number of phosphates and arsenates belong to the orthorhombic (*Pbca*) variscite and monoclinic ( $P2_1/n$ ) metavariscite mineral groups with a general chemical formula  $\text{AXO}_4 \cdot 2\text{H}_2\text{O}$ , where  $A = \text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{In}^{3+}$  or  $\text{Ga}^{3+}$ , and  $X = \text{P}^{5+}$  or  $\text{As}^{5+}$ . The crystal chemistry of these compounds has been investigated extensively because of the biological and geochemical importance of phosphorus and arsenic, especially their roles in soils, water, and waste management (*e.g.* Huang & Shenker, 2004; O'Day, 2006). Recent studies have also revealed that variscite- and metavariscite-type materials possess interesting microporous and absorption properties (Tang *et al.*, 2002, and references therein). To date, structural determinations have been conducted for the following variscite- and metavariscite-type materials: *Pbca* and  $P2_1/n$   $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Kniep & Mootz, 1973; Kniep *et al.*, 1977), *Pbca* and  $P2_1/n$   $\text{Fe}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Moore, 1966; Song *et al.*, 2002; Taxer & Bartl, 2004),  $P2_1/n$   $\text{In}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Sugiyama *et al.*, 1999; Tang *et al.*, 2002), *Pbca*  $\text{Al}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$  (Harrison, 2000),  $\text{Fe}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$  (Hawthorne, 1976),  $\text{In}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$  (Tang *et al.*, 2002), and  $\text{Ga}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Loiseau *et al.*, 1998). The structural relationships between the two groups of compounds have been discussed by Moore (1966), Loiseau *et al.* (1998), and Taxer & Bartl (2004). Kolbeckite, which was also previously called eggonite or sterrettite, is a scandium phosphate mineral with the ideal chemical formula  $\text{Sc}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  and a monoclinic unit cell comparable with that of metavariscite [see the review

by Hey *et al.* (1982)]. However, in spite of the long time since its first description (Schrauf, 1879), the crystal structure of kolbeckite remained undetermined. This study presents the first structure refinement of kolbeckite based on single-crystal X-ray diffraction data.

The structure of kolbeckite, which is homologous with metavariscite, consists of two basic polyhedral units, *viz.*  $\text{PO}_4$  tetrahedra and  $\text{ScO}_4(\text{H}_2\text{O})_2$  octahedra. Each  $\text{PO}_4$  tetrahedron shares four vertices with four  $\text{ScO}_4(\text{H}_2\text{O})_2$  octahedra and *vice versa*, forming a three-dimensional network of polyhedra (Fig. 1). The two  $\text{H}_2\text{O}$  molecules (O5 and O6) coordinated to  $\text{Sc}^{3+}$  are in *cis* positions, and the  $\text{Sc}-\text{O}5$  and  $\text{Sc}-\text{O}6$  distances are noticeably longer than the other four  $\text{Sc}-\text{O}$  bond lengths. The average interatomic  $\text{P}-\text{O}$  (1.527 Å) and  $\text{Sc}-\text{O}$  (2.080 Å) distances in kolbeckite are in agreement with those reported in the literature. Nevertheless, the bond-valence-sum calculations (Brown, 1996) indicate that  $\text{P}^{5+}$  is slightly underbonded (4.926 valence units, v.u.), whereas  $\text{Sc}^{3+}$  is overbonded (3.24 v.u.). The  $U_{33}$  parameter of atom O5 in kolbeckite is significantly larger than the  $U_{11}$  or  $U_{22}$  parameters. A similar observation has been reported for other metavariscite-type materials, such as  $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Kniep & Mootz, 1973),  $\text{In}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Sugiyama *et al.*, 1999) and  $\text{Fe}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Song *et al.*, 2002), thus suggesting a possible disordered distribution of this water molecule in the channels along the *c* axis.

As observed in other metavariscite-type compounds, the  $\text{Sc}1-\text{O}5$  and  $\text{Sc}1-\text{O}6$  bond distances of 2.116 (4) and 2.178 (4) Å, respectively, are significantly different, indicating distinct bonding environments for the two  $\text{H}_2\text{O}$  molecules. In fact, the hydrogen bonds involving atoms H1A and H1B are both shorter than those involving atoms H2A and H2B.

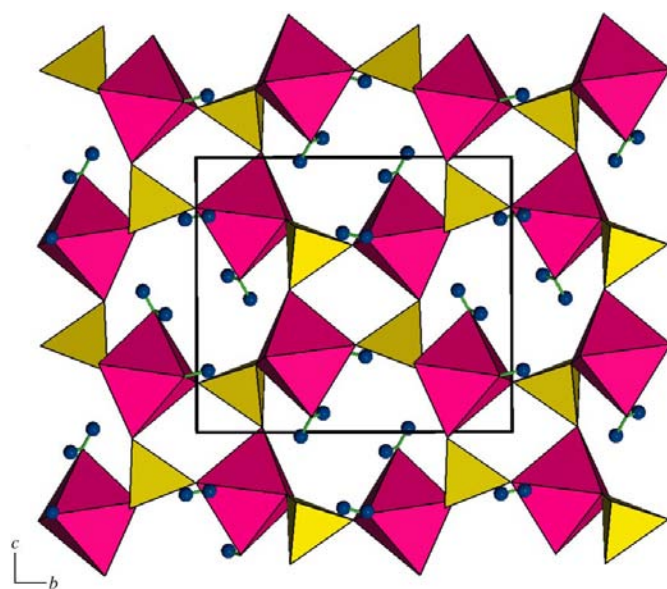


Figure 1

The crystal structure of kolbeckite, viewed along the *a* axis. The tetrahedra and octahedra represent the  $\text{PO}_4$  and  $\text{ScO}_4(\text{H}_2\text{O})_2$  groups, respectively. Small spheres indicate the H atoms.

Experimental

The kolbeckite specimen used in this study is from Hot Springs County, Arkansas, USA, and is in the collection of the RRUFF project (deposition No. R060981; <http://rruff.info>). The average chemical composition (15 point analyses),  $(\text{Sc}_{0.94}\text{V}_{0.03}\text{Fe}_{0.02}\text{Al}_{0.01})_{\Sigma=1}\text{P}_{1.00}\text{O}_4 \cdot 2\text{H}_2\text{O}$ , was determined with a CAMECA SX50 electron microprobe (<http://rruff.info>). All crystals examined are severely twinned, with the twin axis along *a*. Kolbeckite crystals from another locality, viz. Christy Pit, Magnet Cove, Arkansas, USA (RRUFF deposition No. R061040), display the same feature.

Crystal data

ScPO<sub>4</sub>·2H<sub>2</sub>O V = 493.08 (7) Å<sup>3</sup>  
*M<sub>r</sub>* = 175.96 Z = 4  
 Monoclinic, *P*2<sub>1</sub>/*n* Mo Kα radiation  
*a* = 5.4258 (4) Å μ = 1.76 mm<sup>-1</sup>  
*b* = 10.2027 (8) Å T = 293 (2) K  
*c* = 8.9074 (7) Å 0.07 × 0.06 × 0.06 mm  
 β = 90.502 (5)°

Data collection

Bruker SMART CCD area-detector 8954 measured reflections  
 diffractometer 1858 independent reflections  
 Absorption correction: multi-scan 1600 reflections with *I* > 2σ(*I*)  
 (SADABS; Sheldrick, 2005) *R*<sub>int</sub> = 0.042  
*T*<sub>min</sub> = 0.887, *T*<sub>max</sub> = 0.902

Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.052 H atoms treated by a mixture of  
*wR*(*F*<sup>2</sup>) = 0.168 independent and constrained  
*S* = 1.11 refinement  
 1858 reflections Δρ<sub>max</sub> = 1.13 e Å<sup>-3</sup>  
 90 parameters Δρ<sub>min</sub> = -1.21 e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H1A...O1 <sup>i</sup>	0.78 (6)	1.89 (6)	2.658 (5)	169 (10)
O5—H1B...O4 <sup>ii</sup>	0.78 (6)	1.95 (6)	2.704 (4)	165 (10)
O6—H2A...O3 <sup>iii</sup>	0.81 (5)	2.16 (6)	2.874 (5)	147 (9)
O6—H2B...O2	0.80 (6)	2.27 (6)	3.029 (7)	168 (10)

Symmetry codes: (i)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

The twin refinement with the twin law (100, 010, 001) reduced the *R*<sub>1</sub> factor from 0.105 to 0.052. The chemical analysis showed the presence of small amounts of V<sup>3+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> in the sample, but the final refinement assumed a full occupancy of the octahedral site by Sc<sup>3+</sup> only, as the overall effects of these trace amounts of elements on the final structure results are negligible. Four H atoms were located in the difference Fourier syntheses and their positions

refined freely. The isotropic displacement parameters of the H atoms, however, were refined with the constraint that the *U*<sub>iso</sub> values of atoms H1A and H1B were 1.2 times *U*<sub>eq</sub> of their parent atom O5, and those of atoms H2A and H2B were 1.2 times *U*<sub>eq</sub> of their parent atom O6. The highest residual peak in the difference Fourier map was located at (0.248, 0.662, 0.740), 1.28 Å from atom O3, and the deepest hole at (0.100, 0.831, 0.252), 0.45 Å from Sc1.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Xtal-Draw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: SHELXTL (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3100). Services for accessing these data are described at the back of the journal.

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