

ЭКСПЕРИМЕНТАЛЬНАЯ МИНЕРАЛОГИЯ

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LOW HYDROTHERMAL GROWTH OF SINCOSITE



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 СИНКОЗИТА  $\text{Ca}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

Синкозит  $\text{Ca}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  был синтезирован при 200 °С путем реакции монокристалла кальцита с раствором, содержащим  $\text{VOCl}_2$  и  $\text{H}_3\text{PO}_4$ . Описана кристаллическая структура.

The rare  $\text{V}^{4+}$  containing mineral sincosite from Sincos, Peru was first described by W. T. Schaller (1922). He assumed it to be isostructural to the uranium mica meta-autunite with  $\text{VO}^{2+}$  ions replacing the  $\text{UO}_2^{2+}$  units. Natural crystals are of poor quality due to turbostratic nature. Only M. E. Zolensky (1985) obtained a  $hk0$  precession photograph of a crystal from South Dakota, Black Hills; he interpreted the structure to be tetragonal with  $a = 8.895 \text{ \AA}$ ,  $c = 12.727 \text{ \AA}$ .

We obtained light green crystals by the slow reaction of a single crystal of calcite at 200 °C in an autoclave with a solution containing  $\text{VOCl}_2$  and  $\text{H}_3\text{PO}_4$  (0.01 mol). Rectangular platelets approximately of  $200 \times 150 \mu\text{m}$  size grew perpendicular to the wall of the glass container. Sincosite was obtained also at 100 °C, but the crystal quality was very poor, the X-ray powder diffraction data of both grains fitted to JCPDS 39-318 sincosite.

Already M. E. Zolensky (1985) presumed the existence of isotypic compounds. Such isotypic compounds were synthesized substituting Mg for Ca, and As for P.

Single crystal analysis revealed for sincosite a structure indeed similar to meta-autunite, but forming a triclinic cell (sp. gr.  $P1$ ,  $Z = 1$ ). The formula unit contains only four  $\text{H}_2\text{O}$  instead of five as presumed by M. E. Zolensky. It is seen from the following unit cell data, that only the Mg compound is tetragonal:

Compound	a, Å	b, Å	c, Å	$\alpha$ , °	$\beta$ , °	$\gamma$ , °	Pointgroup
$\text{Ca}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	6.354	6.329	6.598	106.72	94.10	90.06	1
$\text{Ca}(\text{VO}/\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	6.502	6.484	6.719	106.43	85.49	90.36	1
$\text{Mg}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	6.251	6.251	13.448	90	90	90	4/m

$\text{PO}_4$  and VO are forming dense packed layers in the plane (001), these layers are tied together by Ca fourfold coordinated by  $\text{H}_2\text{O}$ . The coordination number of Ca is seven:

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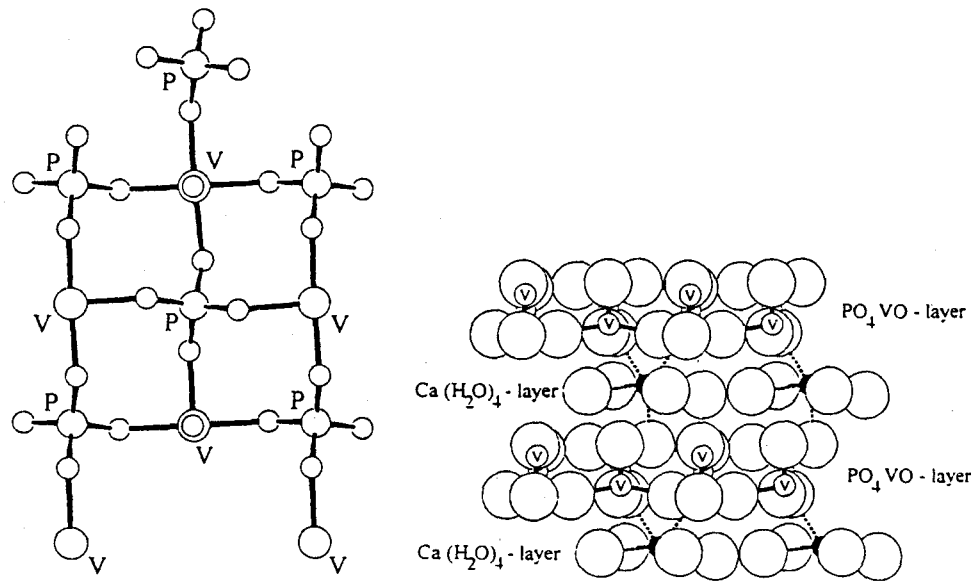


Fig. 1. Arrangement of the  $\text{PO}_4$  tetrahedra and VO groups in the plane (001), Ca and  $\text{H}_2\text{O}$  are omitted.

Рис. 1. Распределение тетраэдров  $\text{PO}_4$  и групп VO в плоскости (001), Ca и  $\text{H}_2\text{O}$  не показаны.

Fig. 2. Sincosite structure viewed in the direction [100]. Dense packing is demonstrated by showing four unit cells with oxygen size close to the real ionic radius (black circles: Ca).

Рис. 2. Вид структуры синкозита в направлении [100]. Плотность упаковки видна из показанных четырех элементарных ячеек с размерами кислорода, близкими к его реальному ионному радиусу; черные кружки — Ca.

4 oxygen from water, 2 oxygen from  $\text{PO}_4$  tetrahedra from different layers and 1 oxygen from VO. No oxygen of  $\text{H}_2\text{O}$  is a next neighbour to V; thus V is fivefold coordinated.

The pseudotetragonal arrangement of  $\text{PO}_4$  tetrahedra and VO groups is shown by fig. 1, whereas fig. 2 illustrates the dense packing of the whole structure.

The refractive indices measured  $n\alpha' = 1.692$  and  $n\beta' = 1.700$  are very similar to the values given by W. T. Schaller (1924), the direction of extinction for crossed nicols is [110].

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