

hierarchical level is formed. In the same way the cluster of the 2nd level is formed, etc.

Thus, we interpret the formation of silica spheres as the process of hierarchical self-organization of matter at nanolevel.

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Modular structure of galuskinite $\text{Ca}_7(\text{SiO}_4)_3(\text{CO}_3)$

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The new mineral galuskinite (IMA2010-63) was detected in small, a few meters in diameter, altered silicate-carbonate xenoliths within the Birkhin gabbro massif in Eastern Siberia. Most surprisingly a synthetic analogue of galuskinite $\text{Ca}_7(\text{SiO}_4)_3\text{CO}_3$ is not known, neither from cement clinker production nor from studies of the $\text{CaO-SiO}_2\text{-CO}_2$ system.

The structure was solved on the basis of X-ray single-crystal data and refined to $R_1 = 3.1\%$. The mineral crystallizes in the monoclinic space group $P2_1/c$: $a = 18.7872(5)$, $b = 6.7244(2)$, $c = 0.4673(2)$ Å, $\beta = 90.788(1)^\circ$, $V = 1322.24(6)$ Å³, $Z = 4$. The structure of galuskinite represents an orthosilicate with additional CO_3 groups. There are 7 symmetry independent Ca sites with O coordination between seven and eight. The arrangement of the coordination polyhedra indicates modular character with strong similarities to spurrite $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$ [1] and larnite $\beta\text{-Ca}_2\text{SiO}_4$ [2]. A polyhedral model of the crystal structure of galuskinite is presented in figure 1. Dashed contours intersect the structure in layered modules parallel to (100). The structure is composed of three alternating modules. The central module with composition Ca_2SiO_4 contains eight-coordinate Ca polyhedra with SiO_4 tetrahedra and is analogous to a corresponding one in spurrite. The adjacent module on both sides is a mixed anion layer of $\text{Ca}_2\text{SiO}_4 \times \text{CaCO}_3$ composition with topologically different front- (Ca_2SiO_4) and backside (CaCO_3). The sequence is completed by one perfect larnite layer of Ca_2SiO_4 composition. Adding up the modular units, the composition of galuskinite becomes $\text{Ca}_7(\text{SiO}_4)_3\text{CO}_3$.

The mineral galuskinite is named in honour of the couple Irina O. Galuskina and Evgeny V. Galuskin, University of Silesia, Poland for their outstanding contributions to skarn mineralogy.

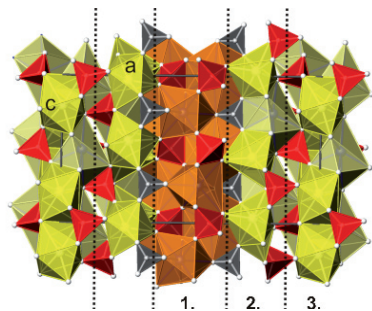


Fig. 1 Layered modules in the galuskinite structure: 1) Ca_2SiO_4 layer analogous to the one in spurrite 2) $\text{Ca}_2\text{SiO}_4 \times \text{CaCO}_3$ mixed anion layer analogous to spurrite 3) larnite layer with Ca_2SiO_4 composition.

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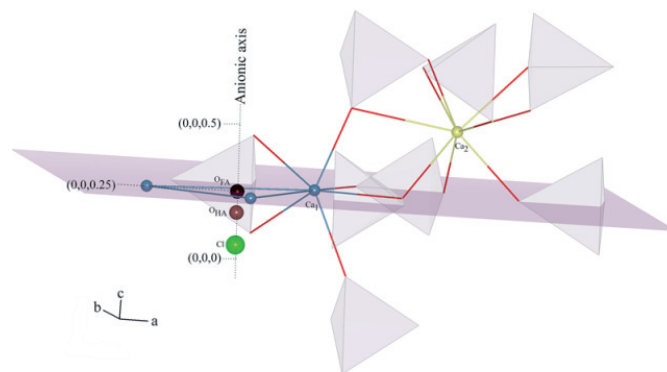
Chlorapatite to Hydroxiapatite ion-exchanging, single-crystal point of view

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There is an interest in obtaining biocompatible crystals of Calcium phosphates (CaPs) because they have a composition very similar to the mineral component of bones, [1]. This property makes them excellent candidates for very broad applications such as a reinforcing phase in composite bioceramics, [2]. Elliot and Young, [3] have provided the first evidence of solid-state ion exchange in CaPs into the apatite crystal structure.

Chlorapatite (ClAp) millimeter-size crystals were heated in atmosphere conditions from 1300 to 1500°C, leading to a systematic conversion from ClAp to Hydroxyapatite (HA) structure by an ion exchange reaction. Under these experimental conditions, the ClAp and annealed samples are single crystals suitable for SXR analysis. We provide a detailed description of the evolution of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}(\text{OH})_{1-x}$ single-crystals decreasing systematically its chlorine content. The results obtained from SXR were extrapolated for bulk samples by Le Bail refinement of powder XRD data.

We have described the ion-exchange procedure in terms of systematic ionic substitution of the Cl^- anion by OH^- along the anionic axis (see Fig). It has been necessary to include two kinds of OH^- ions into the refined atomic models: one into the OH^- site which is assigned at the pure HA (O_{HA} at Fig.) and the other has been positioned into the Ca_1 triangle plane (O_{FA}), which has not been ever described for this kind of HA-ClAp system. This ionic substitution affects the anionic position of all chemical species included in the apatite type structure. A detailed geometric evolution is presented, trying to compare many different geometric values with those previously reported.



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