

Apatite supergroup minerals of the solid solution

$\text{Ca}_5[(\text{PO}_4)_{3-x}(\text{AsO}_4)_x]_{\Sigma 3-2y}[(\text{SO}_4)_y(\text{SiO}_4)_y]_{\Sigma 2y}(\text{OH}, \text{F}, \text{Cl})$, $x = 0-3$, $y = 0-1.5$, from high temperature skarn of the Upper Chegem caldera, Northern Caucasus, Russia

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Minerals represented by $\text{Ca}_5[(\text{PO}_4)_{3-x}(\text{AsO}_4)_x]_{\Sigma 3-2y}[(\text{SO}_4)_y(\text{SiO}_4)_y]_{\Sigma 2y}(\text{OH}, \text{F}, \text{Cl})$ solid solutions, where $x = 0-3$, $y = 0-1.5$, have been detected in altered calcareous xenoliths within ignimbrite of the Upper Chegem caldera, Northern Caucasus, Russia. These minerals belonging to the apatite supergroup occur in all zones of skarn from the core to the contact with ignimbrite as follows: brucite-marble, spurrite, humite and larnite zone. They are associated with both high-temperature minerals: reinhardbraunsite, chegemite, wadalite, rondorfite, cuspidine, lakargiite, and srebrodolskite, corresponding to the sanidinite metamorphic facies, and secondary low-temperature minerals: calcium hydrosilicates (hillebrandite, awfillite, bultfonteinite), hydrogarnets, and minerals of the ettringite group. Minerals of the apatite supergroup often form elongated cracked hexagonal or pseudo-hexagonal crystals up to 250 μm in size as well as grain aggregates. A new solid solution series between ellestadite and svabite-johnbamite (\pm apatite) with ellestadite type isomorphic substitution according the following scheme: $2(\text{RO}_4)^{3-} \rightarrow (\text{SO}_4)^{2-} + (\text{SiO}_4)^{4-}$, where $\text{R} = \text{As}^{5+}$, P^{5+} is identified on basis of chemical composition. The As content in the investigated minerals decreases from the contact skarn zone with the ignimbrite towards the core of altered xenoliths (from 2.11 As pfu to 0), for example:

1) svabite $\text{Ca}_5[(\text{AsO}_4)_{2.01}(\text{PO}_4)_{0.33}(\text{SiO}_4)_{0.33}(\text{SO}_4)_{0.33}]_{\Sigma 3}[\text{F}_{0.58}(\text{OH})_{0.30}\text{Cl}_{0.12}]_{\Sigma 1}$,

2) As-bearing fluorapatite $\text{Ca}_5[(\text{PO}_4)_{1.56}(\text{AsO}_4)_{1.06}(\text{SiO}_4)_{0.19}(\text{SO}_4)_{0.19}]_{\Sigma 3}[\text{F}_{0.59}(\text{OH})_{0.35}\text{Cl}_{0.06}]_{\Sigma 1}$,

3) As-bearing hydroxyllestadite

$\text{Ca}_5[(\text{SiO}_4)_{1.25}(\text{SO}_4)_{1.25}(\text{AsO}_4)_{0.43}(\text{PO}_4)_{0.07}]_{\Sigma 3}[(\text{OH})_{0.70}\text{Cl}_{0.20}\text{F}_{0.10}]_{\Sigma 1}$,

4) Si, S-bearing hydroxylapatite $\text{Ca}_5[(\text{PO}_4)_{0.95}(\text{SO}_4)_{0.93}(\text{SiO}_4)_{0.93}(\text{AsO}_4)_{0.19}]_{\Sigma 3}[(\text{OH})_{0.67}\text{Cl}_{0.18}\text{F}_{0.15}]_{\Sigma 1}$,

5) hydroxyllestadite $\text{Ca}_5[(\text{SO}_4)_{1.49}(\text{SiO}_4)_{1.49}(\text{PO}_4)_{0.02}]_{\Sigma 3}[(\text{OH})_{0.74}\text{F}_{0.13}\text{Cl}_{0.13}]_{\Sigma 1}$.

The crystals of As-bearing phases belonging to the investigated solid solution are heterogeneous and small in size. Therefore, X-ray single-crystal data were obtained only for Si, S, As-bearing hydroxylapatite (see formula above): $P6_3/m$, $R1 = 0.0523$ for 991 reflections, $a = 9.5193(2)$ Å, $c = 6.9052(2)$ Å, $V = 541.90$ Å³, and $Z = 4$. Also Raman spectroscopy confirms that the investigated samples belong to the arsenate phosphate-silicate-sulfate multiple solid solution.