

B- and As-bearing galuskinite and B-analog of galuskinite from Upper Chegem caldera, Northern Caucasus, Russia

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Recently, a new mineral galuskinite, $\text{Ca}_7(\text{SiO}_4)_3\text{CO}_3$ ($P2_1/c$, $a = 18.79$, $b = 6.72$, $c = 10.47$ Å, $\beta = 90.79^\circ$, $Z = 4$), was described from thin veins cutting larnite skarns of the Birkhin Massif (Baikal, Russia). The galuskinite structure can be viewed as built by spurrite $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$ and larnite $\beta\text{-Ca}_2\text{SiO}_4$ modules (Lazić et al. 2011). A skarn zone of galuskinite-larnite composition was also noted in an altered carbonate-silicate xenolith within ignimbrite of the Upper Chegem caldera (Northern Caucasus, Russia). Within this rock As-bearing hydroxylellestadite, chegemite, reinhardbraunsite, rondorfite, killalaite and srebrodolskite show spotty distribution. Galuskinite from Caucasus is characterized by significant content of B (1-4 wt.% of B_2O_3) and occasionally As (up to 4 wt.% As_2O_5). Boron was measured using CAMECA SX100 electron probe micro analyzer equipped with PC2 crystal at 5 kV and 200 nA. As-free galuskinite is characterized by low boron content: $(\text{Ca}_{6.96}\text{Na}_{0.04})_{\Sigma 7}[(\text{SiO})_{2.76}(\text{HSiO}_4)_{0.17}(\text{SO}_4)_{0.04}(\text{PO}_4)_{0.03}]_{\Sigma 3}[(\text{CO}_3)_{0.76}(\text{BO}_3)_{0.24}]_{\Sigma 1}$ ($\text{CO}_2 \approx 5.8$ wt.%, $\text{B}_2\text{O}_3 \approx 1.3$ wt.%). The crystal structure of As- and B-bearing galuskinite with the crystal chemical formula $(\text{Ca}_{6.94}\text{Na}_{0.06})_{\Sigma 7}[(\text{SiO})_{2.53}(\text{HSiO}_4)_{0.25}(\text{AsO}_4)_{0.15}(\text{SO}_4)_{0.05}(\text{PO}_4)_{0.02}]_{\Sigma 3}[(\text{CO}_3)_{0.54}(\text{BO}_3)_{0.46}]_{\Sigma 1}$ ($\text{CO}_2 \approx 3.8$ wt.%, $\text{B}_2\text{O}_3 \approx 2.6$ wt.%) was refined from X-ray single crystal data in space group $P2_1/c$ ($a = 18.82$, $b = 6.76$, $c = 10.47$ Å, $\beta = 90.56^\circ$ and $Z = 4$). High boron content in this galuskinite increases the mean distance (C, B)-O = 1.34 Å whereas in B-free galuskinite from Baikal C-O = 1.29 Å. Galuskinite crystals (100-200 µm in size) from Caucasus are inhomogeneous in their marginal zones with B > C: $(\text{Ca}_{6.92}\text{Na}_{0.08})_{\Sigma 7}[(\text{SiO})_{2.40}(\text{HSiO}_4)_{0.41}(\text{AsO}_4)_{0.11}(\text{SO}_4)_{0.06}(\text{PO}_4)_{0.02}]_{\Sigma 3}[(\text{BO}_3)_{0.58}(\text{CO}_3)_{0.42}]_{\Sigma 1}$ ($\text{CO}_2 \approx 3$ wt.%, $\text{B}_2\text{O}_3 \approx 3.2$ wt.%). Incorporation of boron in galuskinite follows the schemes: $(\text{SiO}_4)^{4-}(\text{CO}_3)^{2-} \rightarrow (\text{HSiO}_4)^{3-}(\text{BO}_3)^{3-}$ and $\rightarrow (\text{AsO}_4)^{3-}(\text{BO}_3)^{3-}$. Thus existence of the possible end-members: $\text{Ca}_7(\text{SiO}_4)_2(\text{HSiO}_4)(\text{BO}_3)$ and $\text{Ca}_7(\text{SiO}_4)_2(\text{AsO}_4)(\text{BO}_3)$ is expected. Maximum contents of these end-members in B-bearing minerals of the galuskinite series reach 65% and 25%, respectively. In the Raman spectrum of the boron analog of galuskinite the intensity of the band at 1077 cm^{-1} (C-O stretching vibration) decreases strongly and new bands at about 3600 cm^{-1} (O-H stretching vibration) and 650 cm^{-1} (B-O bending vibration) become obvious. Our investigations indicate the existence of a potential new mineral with the end-member crystal chemical formula $\text{Ca}_7(\text{SiO}_4)_2(\text{HSiO}_4)(\text{BO}_3)$ in Caucasian skarn.

Lazić et al. (2011) Min.Mag., 75, 2631-2648.