The crystal structure of turneaureite, $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$, the arsenate analog of chlorapatite, and its relationships with the arsenateapatites johnbaumite and svabite

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**Abstract**

The crystal structure of turneaureite, ideally $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$, was studied using a specimen from the Brattfors mine, Nordmark, Värmland, Sweden, by means of single-crystal X-ray diffraction data. The structure was refined to $R_1 = 0.017$ on the basis of 716 unique reflections with $F_o > 4\sigma(F_o)$ in the $P6_3/m$ space group, with unit-cell parameters $a = 9.9218(3)$, $c = 6.8638(2)$ Å, $V = 585.16(4)$ Å$^3$. The chemical composition of the sample, determined by electron-microprobe analysis, is (in wt%; average of 10 spot analyses): $\text{SiO}_2$ 0.22, $\text{P}_2\text{O}_5$ 0.20, $\text{V}_2\text{O}_5$ 0.01, $\text{As}_2\text{O}_3$ 51.76, $\text{SiO}_2$ 0.06, $\text{CaO}$ 41.39, $\text{MnO}$ 1.89, $\text{SrO}$ 0.12, $\text{BaO}$ 0.52, $\text{PbO}$ 0.10, $\text{Na}_2\text{O}$ 0.02, $\text{F}$ 0.32, $\text{Cl}$ 2.56, $\text{H}_2\text{O}_{\text{calc}}$ total 99.04. On the basis of 13 anions per formula unit, the empirical formula corresponds to $(\text{Ca}_{4.82}\text{Mn}_{0.17}\text{Ba}_{0.02}\text{Sr}_{0.01})\{\text{Cl}_{0.02}\text{F}_{0.11}\text{O}_{\equiv 0.71}\}$. Turneaureite is topologically similar to the other members of the apatite supergroup: columns of face-sharing $\text{M}_1$ polyhedra running along $c$ are connected through $\text{TO}_4$ tetrahedra with channels hosting $\text{M}_2$ cations and $X$ anions. Owing to its particular chemical composition, the studied turneaureite can be considered as a ternary calcium arsenate apatite; consequently it has several partially filled anion sites within the anion columns. Polarized single-crystal FTIR spectra of the studied sample indicate stronger hydrogen bonding and less diverse short-range atom arrangements around (OH) groups in turneaureite as compared to the related minerals johnbaumite and svabite. An accurate knowledge of the atomic arrangement of this apatite-remediation mineral represents an improvement in our understanding of minerals able to sequester and stabilize heavy metals such as arsenic in polluted areas.

**Keywords:** Turneaureite, calcium arsenate, apatite supergroup, crystal structure, infrared spectroscopy, Sweden, Apatite: A common mineral, uncommonly versatile

**Introduction**

Calcium arsenate apatites belong to the apatite supergroup, a series of minerals having the general formula $[\text{M}_1^{1IV}\text{M}_2^{1VI}]_2[\text{AsO}_4]_2X$ (Pasero et al. 2010). Three calcium arsenate members are known: johnbaumite, svabite, and turneaureite, differing for the nature of the $X$ anion, that is (OH), $F$, and Cl, respectively. Whereas the crystal structures of johnbaumite and svabite were recently investigated (Biagioni and Pasero 2013; Biagioni et al. 2016), the structural features of turneaureite have not been described so far, even if the crystal structure of synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$ was reported by Wardojo and Hwu (1996). In addition, natural specimens of turneaureite usually show a complex anion composition, allowing a better understanding of the crystal chemistry of binary and ternary calcium arsenate apatites. Indeed, whereas binary and ternary calcium phosphateapatite samples have been accurately studied (e.g., Hughes et al. 1989, 1990, 2014), few data are available for their arsenate analogs. This paper aims at filling this gap.

Turneaureite was first described by Dunn et al. (1985) from three different localities, i.e., Franklin, New Jersey, U.S.A.; Balmat, New York, U.S.A.; and Långban, Värmland, Sweden, as the arsenate analog of chlorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, and the calcium analog of mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$. Only the specimen from the Swedish locality allowed the full-characterization of the species and was designated as the holotype. Although the symmetry of apatites is typically hexagonal (space group $P6_3/m$), several phases have been reported with lower symmetry (e.g., White et al. 2005; Baikie et al. 2007), sometimes showing superstructure reflections (e.g., Chakhmouradian and Medici 2005). This is particularly true for Cl-bearing apatites. As a matter of fact neither deviation from the hexagonal symmetry nor any superstructure reflections in turneaureite were reported by Dunn et al. (1985). The specimen from Långban has chemical composition $(\text{Ca}_{4.85}\text{Mn}_{0.16}\text{Pb}_{0.02})\{\text{AsO}_4\}_{2.42}\{\text{PO}_4\}_{0.54}\{\text{Cl}_{0.56}\text{F}_{0.39}\}_{2.95}$, with unit-cell parameters $a = 9.810(4)$, $c = 6.868(4)$ Å, $V = 572.4$ Å$^3$. The crystal structure of synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$ was refined by Wardojo and Hwu (1996) in the space group $P6_3/m$, with unit-cell parameters $a = 10.076(1)$, $c = 6.807(1)$ Å, $V = 598.4$ Å$^3$. Dai and Harlow (1991) presented, as a communication at a meeting, the results of the single-crystal X-ray diffraction study for the