

Modular crystal chemistry of sulfosalts with large cations: Thallium

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Crystal structures of complex sulfides, the 'sulfosalts' of mineralogy, which contain cations larger than Pb, are rare in terrestrial environments because the majority of these cations are included in oxygen-based structures. The only prominent candidate is univalent thallium which is a significant constituent of a broad spectrum of natural sulfosalt structures. Still, unlike the other large cations, such as K, Rb, Cs, Ba, Sr, and the limiting cases like Na, thallium combines its large crystal radius and low valence with a character of a lone electron pair cation. Because of its size, Tl mostly does not fit into archetypal arrays which form many homologous series (SnS archetype being more susceptible) so that one has to involve less strictly constructed types of series – merotypes, plesiotypes, etc. The arsenic- and antimony-based structures dominate the system, bismuth-based ones are much less frequent. The relative size and shape of As, Sb, and Bi coordination polyhedra is of increased importance when Tl is a principal element. Combination Tl – Pb in one structure is frequent; their roles mostly differ in a rather subtle way. Combination Tl – Hg results in interesting crystal structures.

With the exception of TlSb_3S_5 , lillianite homologues contain only traces of Tl. Sartorite homologues can have substantial Tl in some positions; the structurally ordered members of the $N = 3$ Pb-As-(Ag,Tl) solid solution lead to philrothite, TlAs_3S_5 , as the Tl-As endmember. The $N = 3$ Pb-As-Tl series contains four anion-omission derivatives, with a distinct role of Tl and with large superstructures, the so-called M-sartorites ($M = 7, 9, 11, 13$). The hutchinsonite merotypes represent intergrowths of SnS like slabs, with marginal Tl sites, with interlayers of diverse kinds. The above quoted crystal-chemical properties of Tl result in several subtypes of layer structures or in similar rod structures with a chess-board distribution of channels. The interlayers or channels in them are either Tl-filled or Tl-lined. Structural details of layer structures are mostly complicated, and the simplicity of design observed for phyllosilicates is not reached, making classification difficult. Beside a Tl-filled layer, these structures contain additional layer types, either formed by Ag- or Cu- coordinations or by a complicated As-S and Sb-S framework. A special group among Tl-sulfosalts are cage structures based on tetrahedral framework, represented by the routhierite group and (partly) by galkhaite.

Presence of one or two Tl – S bonds shorter than the rest of Tl-S bonds is fairly common for Tl coordination polyhedra. Short Tl – Me interactions, where Me = Tl, As, Cu, Ag, Hg, etc., are rather rare but ubiquitous in the family. The observed range and crystal chemistry of natural Tl sulfosalts is strongly influenced by geochemical factors – Tl is mostly a member of a few selected cation combinations found in ore deposits and cases of unusual element compositions – like the recently described tsyngankoite which contains Tl, Hg, Mn, Pb, and Sb - are rare. The considerable work of the predecessors in this field will be evaluated and references to the structures used will be given in the presentation itself.