Poster Presentation

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Crankshaft chains of LEP cations as a solution to the cation size misfit

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In Pb-As and Pb-Sb sulfosalts, columns of large coordination prisms of Pb combine with intervening slabs of As- or/and Sb coordination polyhedra. The LEP of these elements dictate the configurations resembling SnS (especially for As) or inflated PbS (especially for Sb). The size misfit of cation polyhedra forces the short As-S and Sb-S bonds to form crankshaft chains. In the homologues with thicker slabs, parallel crankshaft chains and incorporation of Pb in the slabs compensate for the misfit. In the low homologues, N = 3 for sartorite series and N = 4 for andorites, the misfit becomes critical and requires special arrangements. In sartorite (~PbAs2S4), two subsets of parallel short crankshaft chains in a slab are (approximately) mirror-related via two contacts. One contact has a missing S atom with valence compensation by Tl; the other one differs between the two structurally analyzed varieties, sartorite (9a) [1] and sartorite (11a) [new], which are type structures for two homologous subseries: (13a; 9a;5a) and (15a;11a;7a;3a). Structures of andorites VI and IV(~PbAgSb3S6) [2,3], and arsenquatrandorite [new] allow to construct a predictive scheme of zig-zag crankshaft chain arrangement. The 4c superstructure of andorite (IV) contains simple zig-zag sequences of As3S7 chains; in 6c andorite (VI) parallel and perpendicular chains alternate. Andorite (VI) unites, in one slab, two different stackings of perpendicular chains which are present, as separate 3c intervals, in two adjacent slabs in andorite (IV). An additional 1c interval gives the 4c structure. Further varieties, such as 10c roshchinite, are derived from these unit sequences. The fourfold varieties either have slight surplus of Pb or As replaces a part of Sb (arsenquatrandorite).

[1] *Berlepsch, P. et al. (2003) Am. Miner.88, 450-461.,* ***[2]*** *Sawada, H. et al. (1987) Z.Kristallogr. 180, 141-150.,* ***[3]*** *Nespolo, M. et al. (2012) J.Miner.Petrol.Sci. 107,226-243.*

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