

FIRST OCCURRENCE IN NATURE OF A MINERAL CONTAINING A DAWSON-TYPE HETEROPOLYANIONIC CLUSTER $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$: EVIDENCE FROM A CRYSTAL STRUCTURE DETERMINATION

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A highly unusual, new secondary molybdate mineral, $(X_6)^{6+}[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-} \cdot n\text{H}_2\text{O}$ (X = cations, including Cu^{2+} , H_3O^+ etc.), has been found at two localities in the Erzgebirge, Eastern Germany (Glückauf-Schacht, Grube Himmelsfürst, Langenau bei Brand-Erbisdorf and Kupfergrube Sadisdorf). The new species represents the first occurrence of a naturally formed compound that contains a discrete DAWSON (1953) type heteropolyanionic cluster $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ (which is closely related to the better known KEGGIN (1934) type cluster $[\text{X}_2\text{M}_{12}\text{O}_{40}]^{3-}$, where $X = \text{As}, \text{P}$; $M = \text{Mo}, \text{W}$). The molybdate occurs as deep blue, glassy, water-soluble prisms up to 0.2 mm in length. They have formed due to weathering of jordisite (amorphous MoS_2), and are associated with quartz, a halotrichite-pickeringite-group mineral, rozenite, a copiapite-group mineral and ilsemannite.

A single-crystal structure determination (Mo-K α X-radiation, CCD area detector, $R(F) = 7.4\%$) revealed a very large, monoclinic unit cell, space group $C2/c$ (no. 15), and $a = 36.348(7)$, $b = 15.603(3)$, $c = 29.349(6)$ Å, $\beta = 116.69(3)^\circ$, $V = 14871(5)$ Å³. The unique atomic arrangement contains isolated oval clusters with composition $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$, which are weakly connected to each other via charge-balancing X cations and H-bonded H_2O molecules. These cations and the H_2O groups are located on several partially occupied and disordered positions (at present, due to a lack of quantitative electron microprobe analyses, only the cation Cu^{2+} and traces of Na^+ and K^+ are unambiguously confirmed, but the presence of H_3O^+ appears probable). The oval cluster itself is composed of a 'shell' built of 18 distorted MoO_6 octahedra (Mo-O bond distances range from 1.665(14) to 2.385(13) Å), which completely encloses two distorted AsO_4 tetrahedra ($\langle \text{As-O} \rangle = 1.69$ Å). All atoms are on general positions.

The cluster will be compared to that in $(\text{CH}_6\text{N}_3)_6[\text{As}_2\text{Mo}_{18}\text{O}_{62}] \cdot 9\text{H}_2\text{O}$ (ICHIDA & SASAKI, 1983) and the analogous P-W-cluster in $(\text{K}_6)^{6+}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-} \cdot n\text{H}_2\text{O}$ ($n \sim 14$) (DAWSON, 1953) as well as $(\text{NH}_4)_6^{6+}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-} \cdot n\text{H}_2\text{O}$ ($n \sim 9$) and $(\text{Na}_4\text{H}_2)^{6+}[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-} \cdot n\text{H}_2\text{O}$ ($n \sim 20$) (D'AMOUR, 1976).

The new mineral appears to be the product of acidic weathering solutions. Because it is water-soluble, it may have been overlooked previously at other molybdenum deposits.

References

- D'AMOUR, H. (1976): Acta Crystallogr., B32, 729-740.
DAWSON, B. (1953): Acta Crystallogr., 6, 113-126.
ICHIDA, H. & SASAKI, Y. (1983): Acta Crystallogr., C39, 529-533.