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Re-Os Isotopic Analyses of Wulfenite (PbMoO4) in the Oxidation Zone of the Alpine Zn(Pb) Deposits

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The lead molybdate mineral, wulfenite ($PbMoO_4$), is a relatively rare mineral that usually occurs in oxidized zones of Zn(Pb) deposits. Wulfenite is generally observed to be one of the last mineral species formed in the oxidation zone, on top of other non-sulfides (e.g., cerussite, anglesite, smithsonite, hemimorphite, mimetite, pyromorphite, and Fe- and Mn-(hydr)oxides). Wulfenite is found in several mines in Triassic carbonates of the Alpine realm in Austria and Italy (Bleiberg, Raibl, Gorno) and is particularly abundant at Mežica (Slovenia). Wulfenite mines were a source of Mo through WWII.

Wulfenite forms xenomorphic aggregates that can replace host carbonates or surround altered galena crystals. Cavities formed in the oxidation zone may contain zoned wulfenite laths of up to 30 mm. Crystals vary from colorless, yellow, yellow-red, and red-brown to brown-black. Trace element analyses show As, Hg, V, W, Bi, and U in wulfenites, especially in earlier-precipitated, darker varieties. Since these elements are not known in the precursor sulfide minerals nor in the host carbonates, oxidizing fluids external to Triassic carbonates may be involved.

In this study, we analyzed pure handpicked wulfenite crystals from three localites (Bleiberg, Mežica, Gorno) for their Re-Os isotopic composition. None of the data was isochronous, which we attribute to different and varying Os isotopic compositions in wulfenite-precipitating fluids. Changing fluid compositions during wulfenite deposition are readily observed in zoning at the macroscale (see photo). All analyses show that 80 to 97% of the total Os is common Os. For two of the deposits (Bleiberg, Mežica), Re ranged from 1.6 to 4.9 ppb, whereas the two analyses from Gorno were much higher, 48.3 and 48.5 ppb Re. Extremely low $^{187}Re/^{188}Os$ for Bleiberg and Mežica preclude calculation of model ages, but with so little radiogenic ^{187}Os, it can be assumed that wulfenite ages must be very young (post-Alpine). A much higher Re content and $^{187}Re/^{188}Os$ for Gorno coupled with Os that is 95% common Os also suggests a very young wulfenite age, perhaps <10 Ma. For all samples, measured $^{187}Os/^{188}Os$ ratios are very high (Mežica ~5, Bleiberg ~14, Gorno ~26). Therefore, the initial $^{187}Os/^{188}Os$ ratios for fluids responsible for wulfenite deposition are highly radiogenic, perhaps representing shale units in much older (Precambrian) basement. More likely, however, shales with highly anomalous $^{187}Re/^{188}Os$ (>2000), as are known in the upper Permian, can explain the wulfenite data (Georgiev et al., 2011). These shales also have very high Mo.

Based on Re-Os data for Triassic (Carnian) shales (Xu et al., 2014), present day measured Os isotopic ratios ($^{187}Os/^{188}Os$) are about 3-4, thereby making derivation of wulfenite-depositing fluids from Triassic shales unlikely.

Georgiev, S., Stein, H.J., Hannah, J.L., Bingen, B., Weiss, H.M., and Piasecki, S. (2011) Hot acidic Late Permian seas stifle life in record time: *EPSL*, 310: 389-400.

Xu, G., Hannah, J.L., Stein, H.J., Mørk, A., Vigran, J.O., Bingen, B., Schutt, D., and Lundschien, B.A. (2014) Cause of Upper Triassic climate crisis revealed by Re-Os geochemistry of Boreal black shales: *Palaeogeography-Palaeoclimatology-Palaeoecology*, 395: 222-232.

Mežica, Slovenia
zoned wulfenite crystals
2 cm