

Dissolved Mo, W and V at redox interface in the Black Sea

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Transition elements molybdenum, tungsten, and vanadium mainly occur as oxyanions (MoO_4^{2-} , WO_4^{2-} и HVO_4^{2-}) in oxic seawater. Despite they exhibit similar speciation in seawater and close geochemical behavior, their molar ratio in seawater indicates different rates of input and removal in the ocean.

We measured dissolved Mo, W and V concentration in the upper part of the seawater column at the redox interface zone of the Black Sea. The major fractionation of these elements occurs in anoxic zone. The molar ratio of Mo/W in water column changes from 224 in surface waters to 19 in the anoxic zone on the depth of 320 m (σ_t ca. 16.8 kg/m³).

Mo concentrations are nearly constant (~37 nmol/kg) in oxygenated water downward to the upper boundary of the anoxic zone. In the anoxic waters, Mo concentrations gradually decrease as Fe-Mo sulfidic phase precipitate [1]. In oxygenated waters of the Black Sea, tungsten concentrations are two times higher than in Atlantic seawater [2]. They decrease from 160 pmol/kg in the surface water to 110 pmol/kg at the depth just above the sulfidic boundary with maximum particulate manganese concentration. Below redox interface, after the dissolution of particulate manganese W reaches a maximum of 220 pmol/kg, then sharply decreases downward. Tungsten strongly correlates to dissolved manganese ($R^2=0.92$). Vanadium behaves in a similar way with tungsten: its surface concentration is the lowest (9 nmol/kg), then reaches a maximum of 15 nmol/kg in 10-20 m below the redox interface as H_2S appears, and then decreases downward.

Apparently, tungsten concentration in oxic and suboxic waters is strongly influenced by manganese cycle. During particulate manganese dissolution tungsten and probably vanadium are released. Molybdenum, in turn, is presented as oxyanion in oxygenated water and behaves conservatively. In the lower part of the sulfidic zone, molybdenum and to a lesser extent vanadium are scavenged with Fe sulfides.

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[1] Helz *et al.* (2011) *Chem.Geol.* **284**, 323-332. [2] Rimskaya-Korsakova *et al.* (2013) *Min.Mag.* **77**, 2018-2296.