

Crustal Sources of Molybdenum

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As a bioessential and redox-sensitive trace element, Mo has been the focus of numerous studies linking the rise of atmospheric oxygen with the evolution of early life. It is generally assumed that Mo is hosted in common igneous sulfides (e.g. pyrite) within the continental crust, and that these sulfides break down during weathering by atmospheric O₂. Therefore, Mo will be sequestered within continents under a reducing atmosphere and will be enriched in oceans under an oxidizing one, as is observed after the Great Oxidation Event. Here we test the assumption that Mo is contained in common igneous sulfides using *in-situ* laser ablation ICP-MS to determine the mineralogical hosts of Mo in typical lithologies of the upper continental crust (UCC).

Phanerozoic granitoids, Hawaiian basalts, and Archean Tonalite-Trondhjemite-Granodiorites were studied to determine where Mo resides. The average UCC [Mo] is ~1 ppm, yet the granitic rocks fell well below this (0.16 – 0.84 ppm) while the enriched Hawaiian basalts range from 0.56 – 4.6 ppm. Molybdenum concentrations in common igneous sulfides (pyrite, chalcopyrite) frequently fell below the detection limits (~10 ppb) within granitoids. Immiscible sulfides within basaltic glasses contain <6 ppm Mo. In both granitoids and basalts, titaniferous phases such as titanite (CaTiSiO₅) and ilmenite (FeTiO₃) were the predominant hosts of Mo with concentrations ranging from 1 – 40 ppm. Basaltic glasses are also a volumetrically significant host of Mo. Thus, common igneous sulfides are not a significant host of Mo in the crust, while glass and titaniferous phases are.

Titaniferous minerals are fairly resistant to weathering and their decomposition is not expected to vary with partial pressure of oxygen in the atmosphere. Therefore, Mo will remain sequestered in these phases in the continental crust regardless of the fO₂ state of the atmosphere, requiring another mechanism of continental Mo release to deliver it to the oceans. Rare molybdenite (MoS₂) deposits may provide a source of weatherable Mo from the crust, however the amount of atmospheric oxygen needed to break down MoS₂ is unknown. Experimental studies are needed to determine the oxidation rates of glasses and minerals that host Mo.