

Vanadium Geochemistry in Contrasting Aquifers in the United States

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Vanadium (V) is a necessary trace element, which has also been shown to reduce the risk of breast cancer and alleviate cardiomyopathy complications from diabetes. At higher concentrations, however, V(V) impedes the functionality of Na⁺/K⁺-dependent ATPase and may also reduce photosynthetic rates in phytoplankton. In nature, V exists both as oxyanions and oxycations depending on its oxidation state. In oxic natural waters, the pentavalent V predominates, occurring as the vanadate oxyanion (e.g. H₂VO₄⁻, HVO₄²⁻), whereas the tetravalent form of V is found in more reducing waters as the vanadyl oxycation (e.g. VO²⁺, V(OH)₃⁺). Trivalent V also exists but is unlikely in aqueous solution. Although a number of studies have examined V in rivers, estuaries, and the ocean, the geochemistry of V in aquifer systems is poorly known. Here, V concentrations are presented for groundwater from two relatively well characterized, but geochemically different aquifer systems: the Oasis Valley aquifer (Nevada) and the Carrizo Sand aquifer (Texas). The Oasis Valley aquifer is a shallow, alluvial aquifer with oxic, alkaline groundwaters, whereas groundwater from the Carrizo sand aquifer is generally anoxic and becomes sulfidic. The behavior of V along the flow path in these two aquifer systems is described as a function of the important geochemical reactions (e.g. redox, dissolution of aquifer materials, adsorption/desorption from mineral surfaces) that occur. Geochemical modeling predicts that V occurs as the vanadate oxyanion in Oasis Valley groundwaters, which is relatively stable in solution along the entire flowpath. Concentrations of V increase down the flow gradient, likely due to dissolution of volcanic glasses and pH-induced desorption from mineral surfaces. In the Carrizo Aquifer, redox conditions change along the flowpath, becoming progressively more reducing farther from the point of recharge. Vanadium concentrations rapidly decrease about 7 km beyond the recharge zone, and subsequently remain low (0.21 nM) along the remainder of the studied flow path. Geochemical modeling predicts that V chiefly occurs as the vanadyl cation in Carrizo Sand groundwaters. Vanadyl is strongly adsorbed onto mineral surface sites as pH increases along the groundwater flow path owing to silicate weathering, microbial respiration, and calcite dissolution.