

## **Te(IV) reduction by siderite: Kinetics, mechanism and Te isotopic fractionation**

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Tellurium (Te) has a wide range of industrial uses, particularly in the photovoltaic cells, electronic and metallurgy industry. Extensive industrial use has effectively redistributed Te in the environment despite its low crustal abundance (1–2  $\mu\text{g}/\text{kg}$ ), and influenced its global biogeochemical cycle. Environmental Te mobility is controlled by the large solubility difference between the oxidized and reduced Te species. Oxidized species of Te, particularly Te(IV) is toxic and mobile in aqueous environments because of its higher solubility. Reduction to insoluble Te(0) may immobilize Te but because Te(IV) is highly toxic to most bacteria, it is important to determine whether Te(IV) may be reductively immobilized in soils and sediments by abiotic reductants. Additionally, any naturally occurring immobilization may also lead to Te accumulation in soils and sediments which can be used for future resource extraction.

Here, we experimentally determine the kinetics of Te(IV) reduction by synthetic siderite ( $\text{FeCO}_3$ ) at 3 different pH (pH 7, 8, and 9). We also determine Te isotopic fractionation factor during Te(IV) reduction by siderite to establish Te isotope ratios as a reliable indicator of Te(IV) reduction. Our results show that siderite effectively reduces Te(IV) to Te(0) under the tested pH conditions via a surface catalyzed reaction by which siderite surfaces are oxidized to magnetite. The reaction product, magnetite, may be able to reduce Te(IV) at a slower rate. The first order rate constants of Te(IV) reduction decreases with increasing Te(IV) concentration and with increasing pH. In each experiment, the systematic increase in  $\delta^{130/126}\text{Te}$  of the remaining Te(IV) indicate a kinetic fractionation of Te isotopes during reduction by siderite. The fractionation factor ( $\epsilon$ ) is determined as 0.2‰, which does not vary with the reaction rate in our experiments. Our results reveal that Te(IV) is efficiently immobilized under mildly reducing ferruginous conditions in soils, sediments and aquifers under environmentally relevant pH (7-9) which can be monitored by measuring Te isotope ratios.