

Reactions of Tc with Fe(II) and O₂ in Hanford redox-sensitive sediments

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Technetium-99 is a fission product of uranium-235 and plutonium-239 and has been introduced in Hanford site as a result of disposal of spent nuclear fuel and tank waste leakage. Under oxic conditions, Tc exists as the pertechnetate anion which is weakly sorbed. The reduced form of technetium, Tc (IV), is stable in anoxic environments, and often forms a sparingly soluble precipitate TcO₂·nH₂O. Therefore, Tc redox transformations are crucial in controlling its migration in subsurface environments. The objective of this work was to investigate abiotic electron transfer reactions of Fe, O₂, and Tc in mineralogically heterogeneous sediment obtained from a subsurface redox transition zone including their reaction products and kinetics. Technetium (VII) reaction experiments were performed with anoxic sediments collected from Hanford's unconfined aquifer (~18 to 55 m bgs). Wet chemical, X-ray diffraction, Mössbauer, X-ray absorption and electron microscopy measurements were performed to identify the ferrous minerals that might control Tc (VII) reduction. The results revealed complex Fe (II) mineralogy, including Fe (II)-smectites, pyrites, magnetites and still unidentified Fe (II) discrete phases. Batch experiments with 10 μM Tc (VII) and six different sediments demonstrated that all anoxic sediments reduce Tc (VII), but with different rates. All Tc (VII) was reduced to Tc (IV) and immobilized as TcO₂·nH₂O. The residual Tc (IV)-containing sediment suspensions were used in stirred flow reactors to study their reaction with dissolved O₂. Ongoing experiments reveal that O₂ reacts preferentially [over Tc (IV)], albeit slowly, with sediment Fe (II). Effluent Tc solution is at nanomolar concentration level and consists of Tc (VII) and up to 5% Tc (IV). The data suggest that both non-oxidative and oxidative dissolution of TcO₂·nH₂O occur.

Geochemical dispersion of weathered copper mineralised dolomitic rocks in tropical environment, Dos Parecis Basin, Amazon Craton, Brazil

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The Dos Parecis basin is located in the south-western part of the Amazon Craton, Brazil. The Dos Parecis Basin is composed of two parallel sub-basins: Basin of Colorado in the north and Pimenta Bueno Basin in the south. A dolomitic layered unit is exposed in the northern limit of the Colorado Basin and hosts copper sulphides, which are mainly chalcocite. Chip samples from outcrops, samples of drainage sediments and pan concentrates of heavy minerals were collected. All samples were analyzed with acid digestion and ICP finish. Chemical analysis was undertaken on the fine fraction (-270# and +400#), on the coarse fraction (-35# and +65#) and on whole-pan concentrates.

The highest copper concentrations are found in white dolomites (4, 137 ppm Cu on average). The dolomitic unit also has the highest concentrations of manganese (0.56% to 2.6% MnO). Basement rocks contain high local copper concentrations (1, 529 ppm maximum). This unit locally has copper sulphides and oxides.

Weathering has produced oxidation of rocks. Anomalous concentrations of copper in soils in the B horizon range from 51 ppm to 98 ppm, up to 2, 580 ppm. Barium and manganese anomalies are also found within 40 m to 160 m of the mineralised outcrops.

Sediments in creeks cutting the non-mineralised sedimentary rocks contain low copper concentrations: 7 ppm to 17 ppm in the coarse fraction; 21 ppm to 25 ppm in the fine fraction and variable concentrations between 34 ppm and 108 ppm in the whole-pan concentrates. Anomalous values for stream sediment samples containing detritus with copper oxides range from 51 ppm to 145 ppm in the fine fraction and 44 to 830 ppm in the pan concentrates. Copper concentration in the coarse fraction varies from 19 ppm to 39 ppm, up to anomalous values of 193 ppm and 290 ppm.

The observed copper concentrations in the fine fraction, related to the distance downstream from the mineralised outcrops, is 39 ppm to 77 ppm between 0 and 500 m; 99 ppm to 135 ppm between 500 and 1000 m; 90 ppm between 1000 and 2500 m and less than 53 ppm at distances greater than 2500 m.