

Temperature, charge and radius dependence of multivalent cation adsorption on rutile (α -TiO₂) in aqueous 1:1 electrolytes

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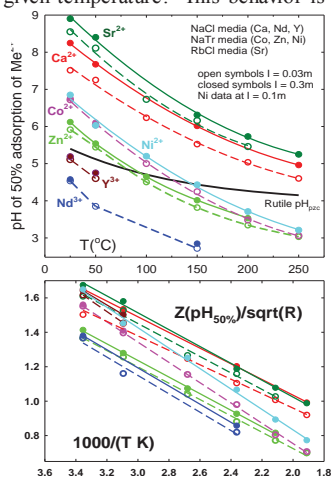
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Sorption isotherms – percent adsorption of trace amounts (typically 10⁻³ molal) of multivalent cations (Ca²⁺, Sr²⁺, Co²⁺, Ni²⁺, Zn²⁺, Nd³⁺, Y³⁺) in 0.03 to 0.3 molal aqueous, non-complexing 1:1 electrolytes (NaCl, RbCl, NaTrifluoromethanesulfonate) – on (Tiioxide Corp.) rutile submicron powder suspensions were collected at approximately constant solution/solid ratio (~50 g solution/1 g of 15 m²/g rutile). The pH at temperature was measured using a hydrogen-electrode concentration cell, and samples were taken through an *in situ*, submicron filter for analysis of unadsorbed cation concentration by ICP-AES. Under these conditions, the pH of 50% adsorption, readily extracted from the sigmoidal sorption isotherms, represents a model-independent measure of the relative sorption affinity of the multivalent cations, which are shown in the figure below to be remarkably systematic and increase strongly (lower pH_{50%}) with increasing cation charge and temperature (linear with inverse temperature) and decreasing ionic radius. Alkaline earth cations sorb weakly and show ionic strength dependence, while smaller divalent transition metals and especially trivalent rare earths sorb much more strongly and do not exhibit significant ionic strength dependence. Multiplication of the pH_{50%} sorption value by (Z²/R)^{1/2}, (Z=cation charge; R=bare cation radius in pm), greatly reduces the total variance at a given temperature. This behavior is also found for uraninite (UO₂) and may be typical of multivalent ion sorption on high-bulk-dielectric solids that exhibit inner-sphere cation sorption, as we have demonstrated for rutile by combined X-ray reflectivity and molecular modeling studies. The results have important implications for contaminant migration in subsurface environments and suggest a simple approach for recovery of rare earth elements from phosphate production waste streams, and separation from actinides.

Research sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.



VARIATION IN THICKNESS OF THE CHEMICAL WEATHERING ZONE AND IMPLICATIONS FOR EROSIONAL AND CLIMATIC CONTROLS ON EARTH'S GLOBAL WEATHERING THERMOSTAT

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The variability of weathering fluxes on the modern Earth surface provides key information about how associated CO₂ consumption may have varied in Earth's geologic past. Understanding the functioning of the planet's thermostat rests on unravelling the range of parameters that are empirically observed to influence weathering. This has not proved to be an easy task, partly because little is known about where the most important weathering reactions take place. Indeed, the locus of weathering, and the depth at which weathering reactions take place, is difficult to measure directly. In this work, a new approach is used to try to infer how the thickness of the weathering zone varies, and how this influences variability in weathering and CO₂ drawdown.

The approach taken in this work centers on inverse analysis of a parametric model describing weathering, with respect to previously compiled data on weathering fluxes derived from the solute load of headwater catchments draining felsic bedrock [1]. Though there are significant uncertainties inherent in this approach, the results provide first-order constraints on the variability in the depth over which weathering takes place. Results suggest that the effective weathering thickness varies relatively little across several orders of magnitude of denudation rate. At low to moderate erosion rates, reactions in the soil zone dominate weathering fluxes at the catchment scale, but the contribution from soil weathering decreases significantly at higher erosion rates. Continually increasing silicate weathering fluxes at higher denudation rates are sustained by progressively greater contributions from weathering in bedrock.

These results have important implications for understanding the climatic and erosional forcing of weathering fluxes, with broad repercussions for models of carbon cycle evolution. Broadly speaking, increases in erosion lead to increases in weathering, but this effect becomes progressively less significant at the highest denudation rates. The weathering model used here implies that the effect of climate (temperature and runoff) on weathering fluxes is appreciably weaker at relatively low denudation rates on the modern Earth (the supply limited case), such that erosion is critical to maintaining climate-stabilizing feedbacks in the global carbon cycle. Whether these feedbacks continue to strengthen as denudation rates increase is not completely clear, because of the changing locus of reaction. In rapidly eroding settings, bedrock weathering at depth appears to become dominant, and the effect on climate-weathering feedbacks may be more complicated in this case, since it is not known how weathering at depth may respond to changes in climate at the Earth's surface. This question demands further attention.

[1] West et al. (2005) *Earth Plan. Sci. Lett.* **235**, 211-218.