PERGAMON

Applied Geochemistry 14 (1999) 569–579

SAND 95-1620J

**Applied
Geochemistry**

Metal sorption to dolomite surfaces[☆]

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Received 14 December 1997; accepted 7 September 1998

Editorial handling by P. Raiswell

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AUG 17 2000

OSTI

Abstract

Potential human intrusion into the Waste Isolation Pilot Plant (WIPP) might release actinides into the Culebra Dolomite where sorption reactions will affect of radiotoxicity from the repository. Using a limited residence time reactor the authors have measured Ca, Mg, Nd adsorption/exchange as a function of ionic strength, P_{CO_2} , and pH at 25°C. By the same approach, but using as input radioactive tracers, adsorption/exchange of Am, Pu, U, and Np on dolomite were measured as a function of ionic strength, P_{CO_2} , and pH at 25°C. Metal adsorption is typically favored at high pH. Calcium and Mg adsorb in near-stoichiometric proportions except at high pH. Adsorption of Ca and Mg is diminished at high ionic strengths (e.g., 0.5M NaCl) pointing to association of Na^+ with the dolomite surface, and the possibility that Ca and Mg sorb as hydrated, outer-sphere complexes. Sulfate amplifies sorption of Ca and Mg, and possibly Nd as well. Exchange of Nd for surface Ca is favored at high pH, and when Ca levels are low. Exchange for Ca appears to control attachment of actinides to dolomite as well, and high levels of Ca^{2+} in solution will decrease K_{ds} . At the same time, to the extent that high P_{CO_2} s increase Ca^{2+} levels, K_{ds} will decrease with CO_2 levels as well, but only if sorbing actinide-carbonate complexes are not observed to form (Am-carbonate complexes appear to sorb; Pu-complexes might sorb as well. U-carbonate complexation leads to desorption). This indirect CO_2 effect is observed primarily at, and above, neutral pH. High NaCl levels do not appear to affect to actinide K_{ds} . © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Dolomite surfaces might control potential releases of buried actinides to the environment at the Waste Isolation Pilot Plant (WIPP), a potential repository for transuranic defense-waste located approximately 42 km E of Carlsbad, New Mexico (Sandia National Laboratories, 1992a,b). The WIPP is located approximately 655 m below the surface in a massive halite (NaCl) interval within the Permian Salado Formation. Groundwaters associated with the WIPP consist of high-ionic strength NaCl brines, with various concentrations of Mg^{2+} , Ca^{2+} , K^+ , and SO_4^{2-} . One poten-

tial mechanism for transport of radioelements to the biosphere involves a breach of the repository by drilling during prospecting for natural resources. Repository brines would be transported up the intrusion boreholes in the disposal area, and some of the radioelements (of relative importance $Pu > Am > U > Th > Np$) might reach the surface. Others could migrate laterally, principally through the Culebra Dolomite member of the Rustler Formation (Culebra), a thin fractured microcrystalline unit consisting primarily of dolomite, clay minerals, and gypsum. If dolomite surfaces in this layer sorb the actinide inventory appreciably the calculated dose to the biosphere will be small. However, if little affinity exists between actinides and the dolomite the export of radioactivity might be quite large. Because of its importance to predicted doses, the controls on actinide sorption to dolomite are examined in detail here.

This work supported by the United States Department of Energy under contract DE-AC04-94AL85000.

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PII: S0883-2927(98)00085-7

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1.1. Metal retardation

Metal retardation arises due to the combined effect of electrostatic (non-specific) and chemical forces experienced by aqueous species when they approach hydroxylated mineral surfaces. Whereas the thermodynamics of metal association with metal (hydro)oxides and clays is reasonably well understood (see reviews of e.g., Davis and Kent, 1990; Dzombak and Morel, 1990) the controls on metal carbonate surface chemistry remain a source of continuing debate. A number of conflicting interpretations have been advanced to explain calcite (CaCO_3) surface charge measured potentiometrically or electrokinetically (Charlet et al., 1990; Thompson and Pownall, 1989; Van Cappellen et al., 1993; Wersin, 1990). Metal adsorption to calcite is somewhat less controversial. Exchange and/or adsorption of metals to the calcite surface causes an initial rapid uptake of metals from solution. This is followed by a slower incorporation of metals with the formation of surface precipitates and/or solid solutions (e.g., Comans and Middelburg, 1987; Franklin and Morse, 1983; McBride, 1979a,b; Stipp and Hochella, 1991; Wersin, 1990). The latter step is favored as adsorbed metal concentrations approach lattice limits and involves the possible diffusion of metals through a hydrated surface layer (Davis et al., 1987), water loss and the formation of MeCO_3 bonds, and the nucleation and precipitation of a solid solution.

The focus here is the initial metal uptake by adsorption, particularly Ca, Mg, trivalent cations, and actinides. Zachara et al. (1988) showed that Zn adsorbed to calcite by exchanging for Ca. Exchange was greatest when Ca levels were lowest, which was generally at high pH and low P_{CO_2} . The sorbing aqueous species were thought to be Zn^{2+} and $\text{Zn}(\text{OH})^+$. Adsorption follows the trend of decreasing ionic radii $\text{Cd} > \text{Mn} > \text{Zn} > \text{Co}$ (Davis et al., 1987; Kornicker et al., 1985; McBride, 1979a,b; Zachara et al., 1991; Zachara et al., 1988). Am^{3+} adsorption onto calcite was measured by Shanbhag and Morse (1982) and found to be largely irreversible. Similar results were seen by Higgo and Rees (1986), suggesting the precipitation of an Am-rich phase at the mineral surface. Carroll et al. (1992) measured Th and uranyl exchange on calcite surfaces and found pH to have little effect on the latter. Carroll (1993) found minimal sorption or exchange of Nd at calcite surfaces, but rather observed the formation of $\text{NdCO}_3(\text{OH})$ – CaCO_3 solid solutions.

It is impossible to predict the degree to which metal-carbonate interactions depend on the identity of the carbonate mineral (e.g., dolomite, magnesite (MgCO_3), siderite (FeCO_3), etc.) as calcite has been the object of the vast majority of metal adsorption experiments. The structural mineralogy of dolomite is very similar to the

calcite structure, except that Mg substitutes for Ca in every other cation layer, which results in lower symmetry. Lippmann (1973) and Reeder (1983) point out the dolomite structure can be visualized as alternating layers of calcite and magnesite. The tendency for Ca and Mg to exist in separate layers stems from the large difference in ionic radii of those metal ions (0.99 vs. 0.66 Å, respectively). To accommodate that difference, the carbonate groups are displaced slightly in the dolomite structure compared to their positions in the rhombohedral single-metal carbonate structure.

Like calcite and magnesite, dolomite has perfect $\{10\bar{1}4\}$ cleavage (Miller-Bravais indices with hexagonal X-ray smallest cell; $Z = 6$), and also shares many of the same crystal habits, such as the common $\{10\bar{1}4\}$ and $\{10\bar{1}1\}$ habits. As with calcite, the common cleavage planes, as well as the growth planes, are sub-perpendicular to the metal-containing layers. As a result, Ca and Mg sites should be exposed in near-stoichiometric proportions at the dolomite surface, prior to any reactions with solute species.

Perhaps due to differences in structural mineralogy, the adsorptive behavior of carbonates differs from mineral to mineral. For example, Mucci and Morse (1985) showed that Mg has a greater affinity for the aragonite (CaCO_3) surface relative to calcite. Metal sorption is also found to differ among carbonate minerals (e.g., Wersin, 1990). The adsorptive behavior of carbonate surfaces has long been linked with their rates of dissolution and growth. Here again calcite and dolomite behave differently. The surface-controlled dissolution of dolomite occurs at a rate that is much less than that of calcite (Chou et al., 1989). Calcite growth at low temperatures is controlled by adsorption reactions and is generally fast, whereas dolomite growth at the same temperatures is very slow (see e.g., Morrow, 1982).

Here the authors present measurements of metal ion (Mg^{2+} , Ca^{2+} , Nd^{3+} , Am^{3+} , UO_2^{2+} , NpO_2^+ , and PuO_2^+) adsorption onto pure, clean dolomite at 25°C in NaCl solutions. Experiments were done with clean, reagent dolomite minerals in chemically simple solutions, containing no other components other than the various radionuclide spikes, and Ca, Mg, and HCO_3^- derived from the dissolution of the dolomite substrate and the atmosphere (HCO_3^-). By performing experiments in well-characterized fluids whose chemistry is relatively simple it is possible to roughly isolate potentially complex reaction mechanisms at the surface. By then adding the various components of WIPP brines (e.g., SO_4 for the Nd measurements) one can begin to account for the effects of the latter on sorption in the Culebra. These results might ultimately allow us to set some limits on the mechanisms of sorption which might be expected in the case of human intrusion into the WIPP.

Fig. 1. Experimental setup (after Wersin, 1990). The volume of reactors A and B is 1 liter. The volume of reactor C is 10 mL.

2. Experimental methods

Equilibrium adsorption onto carbonate minerals is difficult to measure compared to metal (hydr)oxides because dissolution and growth occur more rapidly, making pH control difficult. To get around this obstacle the authors follow the approach of Wersin (1990) and use a limited residence time reactor to measure metal adsorption (see Fig. 1). A saturated dolomite slurry (vessel B) is continuously pumped to a reaction chamber (vessel C) where it is mixed with a mineral-free solution containing the metal adsorbate(s) (vessel A). Overnight equilibration was typically enough time to roughly saturate the solution in vessel B with respect to dolomite. P_{CO_2} is controlled in each input solution, as well as in the reaction chamber, by continuously bubbling ultra-pure CO_2 - N_2 mixtures. pH was monitored in each chamber using Orion 940/Ross combination pH electrodes calibrated (and verified) with Fisher Scientific (Pittsburgh, PA) pH 4 and 10 buffers. The mineral-free solution is titrated with either dilute HCl or $NaHCO_3$. Because the mean residence time of dolomite surfaces in the reaction chamber is $\sim 1/2$ min, the results are assumed to monitor adsorption without the complications of dissolution or irreversible surface precipitation. Because in natural systems subsequent occlusion of sorbed metals is often observed on metal carbonate minerals, the authors

believe the metal sorption results reported here represent a reasonably conservative assessment of uptake.

Highly pure dolomite from Norway (purchased from Wards Scientific, Inc./Rochester, NY) was crushed in an Fe sleeve, the clearest pieces separated by hand. The latter were crushed with a shatterbox and sieved to a diameter less than $106 \mu m$. A magnet was used to remove any Fe particles remaining from the crushing. The dolomite was then repeatedly etched in dilute HCl to remove any disturbed surfaces caused by grinding, and dried at $40^\circ C$. All input solutions were made from reagent grade materials. BET N_2 -adsorption isotherm (5 point) measurements indicated a surface area of $0.46 m^2/g \pm 5\%$ (the surface area measurement was done using a Micromeritics ASAP-2000 Surface Area Analyzer calibrated against NIST reference material #8570 (calcined kaolinite, $10.9 m^2/g$), lot #492206).

Each experimental run was done as follows. Ten grams of dolomite were allowed to equilibrate overnight with 1 liter of solution in a fleaker beaker (vessel B), stirred with a Teflon magnetic stirring bar. Ultrapure N_2 - CO_2 gas was bubbled through vessel B overnight, and in each reactor during the experiments. Vessel A contained the same solution, but no dolomite. Immediately before each experimental run, Orion Ross glass combination pH electrodes were calibrated and inserted into each vessel. During the experiments fluid (slurry in the case of B) was pumped through peristal-

tic tubing from reactors A and B at 10 ml/min. Reactor C had a steady state volume of 5 ml which was maintained with a peristaltic pump, and stirred with a Teflon-coated magnetic stirrer. The pH in each reactor was measured before the experiment. At the same time a ~5 ml sample was extracted from reactor B, filtered (0.45 µm) and analysed for base level Ca and Mg with an ICP-AES (Thermo Jarell Ash Atomscan 25). There is a possibility that particles smaller than this might have been included in the Ca and Mg analyses. It was assumed that the early HCl wash destroyed many of the smaller particles during preparation of the solid, and that minimal small particles were produced by subsequent collisions in the reaction vessel. Concentrations of Ca and Mg were typically $\sim 10^{-4}$ M. Compensation for any background interferences were made by matrix-matching. From the known inputs from A and B the initial concentrations of each dissolved metal Me in reactor C is calculated, as per:

$$[\text{Me}]_c = \frac{P_A[\text{Me}]_A + P_B[\text{Me}]_B}{P_A + P_B} \quad (1)$$

where $[\text{Me}]_{in}$ is the concentration of Me in reactor C before reaction (adsorption, desorption, dissolution, growth, etc.) and P is the pumping rate (ml/min) from the subscripted vessel. Output Me concentrations (and SO_4) were measured periodically from filtered samples by ICP-AES. To measure pH effects, titrations were performed by adding small amounts of acid or base to vessel B during the run with a syringe, and pH readings were taken after they stabilized (acid and base solutions were prepared by diluting more concentrated standards). Steady state was assumed to exist in vessel C after titrant addition to reactor A when the pH in reactor C stabilized (< 0.4 mV/min). For each point thus defined, input and output species concentrations for reactor C were subsequently calculated.

For the radionuclide K_d measurements, a multi-element tracer was added to vessel A. Its composition was: $[\text{Np}^{\text{VI}}] = [\text{U}^{\text{VI}}] \sim 10^{-7}$ mol L^{-1} ; $[\text{Pu}^{\text{VI}}] = [\text{Am}^{\text{III}}] \sim 10^{-8}$ mol L^{-1} , and made up to the ionic strength (NaCl solution) desired. Specifically, the spike was made up of U in HNO_3 , and Np, Pu, and Am perchlorate solutions. Input solution concentrations were measured by ICP-MS (VG-elemental). Analyses were done and actinide reagents processed following the CST-STP-ANC5-073/1 protocol at Los Alamos National Laboratory. Total actinide levels in output solutions were likewise measured by ICP-MS. It is assumed that no redox reactions occurred during the experiments, in light of the general absence of other redox-sensitive substances in the mineral and solution. The actual redox state of the actinides was not continuously monitored or verified. The total amount

of a given metal sorbed, $[>\text{Me}]$ in mol L^{-1} was calculated by difference:

$$[>\text{Me}] = [\text{Me}]_{in} - [\text{Me}]_{out} \quad (2)$$

K_{ds} were calculated as:

$$K_d(\text{ml g}^{-1}) = [\text{ml of fluid/g of dolomite}][>\text{Me}]/[\text{Me}]_{out} \quad (3)$$

The first bracketed term was for all experiments equal to ~ 200 ml g^{-1} . ICP-MS analyses for a number of the actinides showed a great deal of scatter. Uranium analyses were particularly spotty. This uncertainty is translated into uncertainty in the K_{ds} calculated by Eq. (3). For the K_{ds} shown below input Me levels measured at the same time as the output values were measured. These values were generally close to the input solution composition predicted from the recipe. Uranium was the primary exception to this. Four of the input solution analyses were significantly different from the recipe value, and different from ICP-MS analyses done on the input solutions independently as well. For these cases ($P_{\text{CO}_2} = 0.00032$ and 0.05 atmospheres) the average of the replicates done for the latter independent measurement were used instead. Overall, the uncertainty in the ICP-MS analyses sometimes resulted in calculated negative K_{ds} .

K_{ds} were essentially measured simultaneously for all of the actinides, and it was assumed that there was no competition between them for surface sites. This was assumed to be reasonable because the actinides were present in quantities which were at least two orders of magnitude less than the available number of surface sites (~ 30 sites/ nm^2 – see below). The experimental conditions for each of the non-actinide titrations are shown in Table 1.

3. Sorption/exchange of Ca and Mg

Because exchange of metal ions for Ca exposed at calcite surfaces is commonly observed, it is important to first examine the controls on Ca and Mg adsorption/exchange on dolomite. Me adsorption as a function of pH and P_{CO_2} at $I = 0.05$ M for the runs la-cNd is shown in Fig. 2. Dolomite dissolution into reactor B was found to be highly stoichiometric. The ratio of bound Ca to Mg, $>\text{Ca}/>\text{Mg}$, is close to unity when the Ca and Mg levels in solution are similar, indicating that Ca and Mg adsorbed stoichiometrically (i.e., equimolar) to the dolomite surface from an equimolar supernatant. This was found to be the case for most of the experiments (see below), and, for this reason, Ca and Mg are considered jointly as Me ($=\text{Ca} + \text{Mg}$) in much of the subsequent discussion.

Table 1
Experimental conditions

Expt.	Matrix	P _{CO₂} (atm)	Adsorbate	Variable
1a	0.05 M NaCl	10 ^{-3.5}		pH
2a	0.05 M NaCl	10 ^{-2.3}		pH
3a	0.05 M NaCl	10 ^{-1.3}		pH
1b	0.5 M NaCl	10 ^{-3.5}		pH
2b	0.5 M NaCl	10 ^{-2.3}		pH
3b	0.5 M NaCl	10 ^{-1.3}		pH
1aNd	0.05 M NaCl	10 ^{-3.5}	6.9 μM Nd	pH
2aNd	0.05 M NaCl	10 ^{-2.3}	6.9 μM Nd	pH
3aNd	0.05 M NaCl	10 ^{-1.3}	6.9 μM Nd	pH
1aSO ₄ 1	0.05 M NaCl	10 ^{-3.5}	10 mM SO ₄	pH
2aSO ₄ 1	0.05 M NaCl	10 ^{-2.3}	10 mM SO ₄	pH
3aSO ₄ 1	0.05 M NaCl	10 ^{-1.3}	10 mM SO ₄	pH
1aSO ₄ 2	0.05 M NaCl	10 ^{-3.5}	100 mM SO ₄	pH
2aSO ₄ 2	0.05 M NaCl	10 ^{-2.3}	100 mM SO ₄	pH
3aSO ₄ 2	0.05 M NaCl	10 ^{-1.3}	100 mM SO ₄	pH
1aCa	0.05 M NaCl	10 ^{-3.5}	1 mM Ca	pH
1aMg	0.05 M NaCl	10 ^{-3.5}	1 mM Mg	pH
1bNd	0.5 M NaCl	10 ^{-3.5}	6.9 μM Nd	pH
2bNd	0.5 M NaCl	10 ^{-2.3}	6.9 μM Nd	pH
3bNd	0.5 M NaCl	10 ^{-1.3}	6.9 μM Nd	pH
2bNd, [Mg]	0.5 M NaCl, free drift pH	10 ^{-2.3}	6.9 μM Nd	[Mg]; 0 to ~0.2 M
2bNd, [K]	0.5 M NaCl, free drift pH	10 ^{-2.3}	6.9 μM Nd	[K]; 0 to ~0.2 M
2bNd, [SO ₄]	0.5 M NaCl, free drift pH	10 ^{-2.3}	6.9 μM Nd	[SO ₄]; 0 to ~0.2 M

3.1. Effects of pH and CO₂

Metal adsorption increases slightly with increasing pH. Note from Fig. 2 that Ca and Mg adsorption is negative at the lower pH's. At low pH, Ca and Mg adsorption is written as negative because adsorption is referenced to adsorbate levels at the starting point of the titration (high pH). Calcium + Mg levels at the

dolomite surface are always positive as they are the sum of the relative sorption, shown in Fig. 2, plus the number of Ca + Mg-occupied sites existing at the beginning of the titration, i.e.:

$$[> \text{Me}] = [\text{Me}]_{\text{out}} - [\text{Me}]_{\text{in}} + [> \text{Me}_0] \quad (4)$$

[Me]_{out} and [Me]_{in} are, respectively, the Ca + Mg levels measured as output and input for reactor C. [> Me₀] is

Fig. 2. Me adsorption onto dolomite as a function of P_{CO₂} for the runs 1–3aNd. A 3% error in the Nd analyses, combined with an uncertainty of 5% in the surface area, suggests 2σ error bars of ±22%. The horizontal line near the top of the graph corresponds to 6 × 10⁻⁵ moles/m² of surface sites, or roughly 30 sites per nm⁻² of dolomite.

the sorbed Ca + Mg concentration at the start of the titration. The Ca + Mg sorption edges are reversible as little hysteresis was observed when the direction of the titration was reversed. The trends shown for runs 1a-cNd are typical for all of the experimental runs. There appears to be, at best, only a slight amplification of metal sorption by increasing P_{CO_2} . Experiments 1aCa and 1aMg, which were run with a high [Me] background, exhibit elevated Me sorption (see below). Metal levels were generally $\sim 40\%$ higher in the $P_{CO_2} = 10^{-1.3}$ runs relative to the atmospheric P_{CO_2} runs. Note from Fig. 2 that Ca + Mg sorption approaches 1.2×10^{-4} moles, which, considering that there were 5 g of 0.46 m^2 surface per liter of solution, corresponds to 6×10^{-5} moles/ m^2 of surface sites, or roughly 30 sites per nm^{-2} of dolomite in our experiments. This value is at least a factor of 4 higher than the site density observed for flat metal (hydroxide) surfaces, suggesting that adsorption occurs in a semi-porous, exchange layer.

3.2. Adsorption and $[Ca^{2+}]/[Mg^{2+}]$

Fig. 3 shows $>\text{Me}$ adsorption measured in high (mM) Ca and Mg solutions (runs 1aCa and 1aMg) at $P_{CO_2} = 10^{-3.5}$ atm, $I = 0.05 \text{ M NaCl}$. Raising the Ca or Mg level in the solution causes a decrease in the desorption of the other cation only at high pH, and then, only to a minor extent. Brätter et al. (1972) observed one-for-one Ca to Mg co-adsorption at the dolomite surface. $[Mg^{2+}]/[Ca^{2+}]$ was equal to 5 in Brätter et al. (1972) experiments. Mucci and Morse (1985) measured a value of $[>\text{Mg}]/[>\text{Ca}] \sim 3$ using Auger spectroscopy. Mucci and Morse (1985) argued that exposed Mg layers specifically sorbed more Mg, but exposed Ca layers adsorbed both Ca and Mg. There is some independent evidence suggesting that dolomite surfaces

Fig. 3. Ca and Mg adsorption as a function of the Ca/Mg ratio in solution (from runs 1aCa and 1aMg). To calculate the surface Ca/Mg ratio a starting site density of 30 sites nm^{-2} was assumed. The ICP analyses for Ca and Mg are on the order of 6% which translates to 2σ error bars of $\pm 20\%$.

remain fairly stoichiometric in the face of changing Ca/Mg solution contents. Berner (1967) found that dolomite, dissolved up to saturation in solutions of widely varying Ca/Mg, always maintained a stoichiometric surface. We see roughly one-to-one Ca:Mg stoichiometry (see Fig. 3) though it may approach 3 at high pH. (Note that the Ca/Mg ratios in Fig. 2 of Brady et al. (1996) were incorrectly calculated.)

The simplest explanation for Ca and Mg adsorption is through the reaction:

$>CO_3^-$ is an exposed anionic carbonate group at the mineral surface adjacent to a Mg or Ca site. The anionic nature of metal binding sites is an assumption, justified primarily on electrostatic considerations. The metal adsorption data does not, in itself, point to the stoichiometry of the metal binding site (e.g., the latter could equivalently be written as $>CO_3H$). The slight pH-dependence of metal adsorption suggests that the affinity of the carbonate site for metals does not change appreciably over the pH range of the experiments. Eq. (5) predicts an increase in metal sorption with increasing metal content over the concentration range where sorption is linear.

3.3. Ionic strength

Fig. 4 shows Me adsorption in 0.05 and 0.5 M NaCl at $P_{CO_2} = 10^{-3.5}$, $10^{-2.3}$ and $10^{-1.3}$ atm. The one order-of-magnitude increase in ionic strength systematically shifts the metal sorption edges upward approximately one pH unit for all values of P_{CO_2} . At the same time initial [Me] was $\sim 60\%$ higher in the 0.5 M NaCl runs. If Me had been the same for both ionic strengths the shift in the adsorption isotherms with ionic strength would probably have been larger still.

Fig. 4. Me adsorption as a function of ionic strength (runs 1–3aNd, 1–3b). The ICP analyses for Ca and Mg are on the order of 6% which translates to 2σ error bars of $\pm 20\%$.

Fig. 5. Me adsorption as a function of P_{CO_2} in 10^{-3} and 10^{-2} M SO_4 solutions (runs 1-3aSO41 and 1-3aSO42). The ICP analyses for Ca and Mg are on the order of 6% which translates to 2σ error bars of $\pm 20\%$.

Increasing solution ionic strength results in (e.g., Dzombak and Morel, 1990): a decrease in Me activity in solution: a decrease in the surface potential and the Coulombic work required for sorption; and a change in the acid-base speciation of the surface. The activity coefficients for aqueous Ca^{2+} and Mg^{2+} decrease by roughly a factor of 2 from 0.05 M NaCl to 0.5 M NaCl. The change in the Me activity therefore accounts for about a third of the isotherm shift. A decrease in interfacial potential would lead to increased charge buildup and would therefore tend to favor adsorption. Because the opposite is seen another explanation is needed. One plausible rationale for decreasing Me sorption at high ionic strength, despite the otherwise favorable change in coulombic energy, is that counterion binding occurs. On the basis of electrostatic considerations Na^+ should sorb less strongly than divalent cations. Nevertheless, the greater abundance of Na in the high ionic strength experiments (Na was roughly 500 times more abundant on a molar basis than either Ca or Mg) probably compensates for the difference in charge. One important implication of the ionic strength dependence of Me sorption is that Me sorption appears to be primarily outer-sphere in nature. As Na^+ ions are thought to be hydrated, the fact that they can displace Me ions from the surface makes it highly likely that the adsorbed Me ions are hydrated as well.

3.4. Effects of sulfate

To test the effect of SO_4 on Ca and Mg sorption Na_2SO_4 was added to reactor B in a number of exper-

Fig. 6. Me adsorption as a function of SO_4 concentration - run 2bNd[SO4]. The ICP analyses for Ca and Mg are on the order of 6% which translates to 2σ error bars of $\pm 20\%$.

iments (see Table 1). Sulfate levels were set at either 10^{-2} or 10^{-3} M. In Fig. 5 are shown Me sorption curves as a function of pH, P_{CO_2} , and SO_4 concentration. In Fig. 6 is shown Me sorption for an experiment where pH was held constant and SO_4 added to reactor B. The results in Fig. 5 and Fig. 6 show that SO_4 at low concentrations ($< 10^{-3.5}$ M) diminishes sorption, but at higher concentrations amplifies sorption. The latter possibly points to co-adsorption of Me and SO_4 at the mineral surface. How this might affect dolomite growth rates has been outlined elsewhere (Brady et al., 1996). Since Ca^{2+} levels were typically $\sim 10^{-4}$ M, and the solubility product of gypsum is $10^{-4.59}$, solutions would approach saturation with gypsum only if SO_4 concentrations exceeded 0.1 M.

4. Adsorption of Nd

Nd has been used frequently as an analog for trivalent transuranic actinides, including Pu and Am, in a number of investigations (see e.g., Stout and Carroll, 1993). Like the lanthanides, actinides of a given oxidation state generally exhibit similar chemical behaviors. As f-elements, the trivalent lanthanides, and particularly Nd, are chemically similar to at least some of the trivalent actinides. The slight decrease in ionic radii with increasing atomic number, and differences in the filling of molecular orbitals, accounts for subtle differences in their chemical behaviors, such as solubility, aqueous speciation, and surface complexation. Because the latter are reasonably predictable, rare earth elements (REE's) are important tracers for geochemical processes. There is considerable interest in the ability of carbonate surfaces to scavenge REE's. As carbonate minerals record the conditions of their formation they are an important tool for understanding fluid-rock interaction. The degree to which carbon-

ate minerals incorporate REE's by sorption/growth is therefore an obvious avenue for research on diagenesis and paleoclimatology (see e.g., Zhong and Mucci, 1995).

4.1. Ion pairing

In natural solutions Nd forms ion pairs with hydroxyls, CO_3^{2-} , HCO_3^- , Cl^- and SO_4^{2-} . Insoluble Nd hydroxy-carbonate salts become stable above neutral pH (see below). For the experimental conditions examined here the primary aqueous forms of Nd are: Nd^{3+} , NdCl^+ , NdCO_3^+ and NdSO_4^+ . NdSO_4^+ is only important in solutions having $[\text{SO}_4^{2-}]$ greater than 100 μM . NdCl^+ must be considered when $[\text{Cl}^-]$ is greater than 1 mM. In solutions poorer in SO_4^{2-} and Cl^- than this Nd^{3+} and NdCO_3^+ dominate except at very high pH.

4.2. Effects of pH and P_{CO_2}

Fig. 7 shows the results of Nd sorption experiments done as a function of pH and P_{CO_2} in 0.05 M NaCl. K_d s range from 300 to 3000 ml/g, increasing with pH. Appreciable sorption occurs at all pH's, though sorption is most pronounced at $\text{pH} > 5$. In general the experiments were calculated to have exceeded saturation with respect to hydroxycarbonate Nd salts at $6 < \text{pH} < 8$. The authors assume that the decrease in $[\text{Nd}]_{\text{tot}}$ measured in the experiments represents short-term sorption due to the very short residence time of the fluid-solid mixture in reaction vessel C and that negligible masses of Nd salts formed. Nd^{3+} and NdCO_3^+ are the most reasonable sorbing species for the low Cl^- and SO_4^{2-} -free experiments. At near neutral pH, adsorption of NdCO_3^+ probably precedes the nucleation and growth of Nd-hydroxy-carbonate solids.

Neodymium binding increases with pH, paralleling the behavior observed for Ca and Mg. Increasing P_{CO_2} tends to decrease adsorption at any given pH. This shift is almost certainly caused by the higher $[\text{Ca}^{2+}]_0$ values attendant with higher P_{CO_2} 's. Order-of-magni-

tude reductions in Nd adsorption result from similar increases in $[\text{Ca}]$ and decreases in pH. Because the ionic radius of Nd^{3+} is nearly identical to that of Ca^{2+} it is reasonable to assume that Nd^{3+} (and possibly NdCO_3^+) compete with Ca^{2+} for surface sites. Exchange for the much smaller Mg is less favored sterically. Increased $[\text{Ca}^{2+}]$ should cause Nd desorption through the simple exchange reaction:

$> \text{REE}$ denotes either Nd^{3+} or NdCO_3^+ , its sorbed form having charge Z . Formation of poorly sorbed Nd-carbonate species above pH 6 may also account for some of the decrease in K_d s with increasing P_{CO_2} .

4.3. Effects of K^+ , SO_4^{2-} and Mg^{2+}

A series of experiments were undertaken to establish the sensitivity of Nd binding to K^+ , SO_4^{2-} and Mg^{2+} . KCl, Na_2SO_4 , or MgCl_2 , respectively, were added to reactor B. The starting pH was approximately 7 and the drift less than 0.2 pH units, and, therefore a second order effect on Nd sorption. Sulfate concentrations, varied from 0 to 0.2 M, caused minimal ($< 20\%$) change in the amount of Nd adsorbed. At high $[\text{SO}_4^{2-}]$, NdSO_4^+ was the predominant Nd-containing species, which may mean that NdSO_4^+ adsorbs as well. Potassium does not appear to compete with Nd for surface sites, at least over the range 0 to 0.2 M. Magnesium causes Nd to desorb, but only when present at very high concentrations (> 0.05 M). This is consistent with the interpretation presented above, namely that Nd (and probably the other REE's as well) are sterically hindered from adhering to the Mg plane. At very high $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ levels Mg may potentially be able to compete with Nd for Ca sites, and cause desorption of the former. Except at $\text{P}_{\text{CO}_2} = 10^{-3.5}$ and $\text{pH} < 6$ ionic strength does not appear to greatly affect Nd sorption.

5. Actinide sorption

In Fig. 8 are shown actinide K_d s. The values are useful primarily in an order of magnitude sense due to the uncertainty coming from the ICP-MS analyses. The standard deviation for the Np analyses is roughly 3%. With the exception of the runs done under atmospheric conditions in 0.05 M NaCl (where the standard deviation is between 3 and 51%) the standard deviation for the U analyses is, like Np, roughly 3%. The standard deviation in the Pu analyses varies between one and 12%, with 6% as a rough average. The Am analyses are similar to the Pu values in their associated error. These averages can give an approximate estimate

Fig. 7. Calculated K_d s for Nd adsorption to dolomite as a function of pH and P_{CO_2} in 0.05 M NaCl solutions (runs 1–3aNd): (circles: $\text{P}_{\text{CO}_2} = 0.5\%$; open triangles: $\text{P}_{\text{CO}_2} = 5\%$; filled triangles: $\text{P}_{\text{CO}_2} = \text{atmospheric}$).

Fig. 8. Calculated K_d s for Am, Np(V), Pu(V), and U(VI) adsorption to dolomite as a function of pH and P_{CO_2} in 0.5 (X: P_{CO_2} = 0.5%; +: P_{CO_2} = 5%) and 0.05 M NaCl solutions (circles: P_{CO_2} = 0.5%; squares: P_{CO_2} = 5%; diamonds: P_{CO_2} = atmospheric).

of the error associated with the K_d s. Specifically, the standard deviation in the amount of metal sorbed is equal to the square root of the sum of the squared deviation in the input and output analyses. For the case of Np, where the deviation in analyses was approximately 3%, the standard deviation in K_d is ~4%. Given that the standard deviation in the surface area measurement is 5%, the compounded standard deviation in the Np (and the majority of the U) K_d s are calculated to be on the order of 11%. A 2σ error bar on the Np K_d s, and all but the 0.05 M NaCl atmospheric CO_2 U K_d s, would be $\pm 22\%$. Using the average Pu and Am analytical uncertainty of 6%, the 2σ error bar on the K_d s is calculated to be $\pm 28\%$.

5.1. Americium

The results in Fig. 8 are interpreted to indicate exchange of Am for calcium sites at the dolomite surface. K_d s are near zero at low pH (pH ~3) but rise to ~400 ml g⁻¹ at pH 6. Experiments were done at higher pH, though K_d s were unmeasurable due to the

lack of any Am signal. In other words, because no Am was detected, no K_d could be calculated. K_d s are high (>400 ml g⁻¹) at pH >6. The primary aqueous forms of Am in low pH Cl⁻ solutions is $AmCl_2^+$ and Am^{3+} (Silva and Nitsche, 1995). Chloride does not appear to have a clearly discernible role on Am sorption under the pH conditions where sorption was quantifiable. Therefore Am^{3+} appears to be the primary sorbing species over the pH range where sorption was measurable. The adsorption reaction for Am is therefore envisioned to be:

where $>Ca^{2+}$ denotes an exchangeable Ca at the dolomite surface. The earlier mechanistic sorption studies done with Nd as an Am analogue pointed to exchange of Ca (but not Mg) sites in reactions such as Eq. (7). Higher concentrations of Ca in solution should cause increased desorption of Am, and lower K_d s. This is consistent with the picture observed for Nd. At low pH, Ca (and Mg) concentrations were higher in the experimental runs due to the dissolution of the dolomite

substrate. Dolomite dissolution is an important feature which affected adsorption for a number of the radionuclides (see below).

There appears to be no clear effect of P_{CO_2} on Am sorption. Near and above neutral pH Am forms carbonate complexes in solution, and fairly insoluble hydroxycarbonate mineral phases. Am-carbonate complexes appear to sorb even more strongly than $Am(OH)_2^+$ as evidenced by the absence of Am in solution under high pH conditions. An alternative explanation is that the Am precipitated out in the input flask to begin with, and was therefore unavailable for sorption. Above $\sim$ pH 8 the solution became over saturated with respect to pure, well-crystalline $AmCO_3OH$. The short residence time of the Am in reactor C ($\sim$ 1/2 minute) probably limited nucleation and growth of all but the least crystalline phase (if that). It is, therefore, more reasonable to ascribe the high K_{ds} at alkaline pH to adsorption of Am-carbonate complexes.

5.2. Neptunium and plutonium

Np and Pu are treated together as their solution speciation and adsorption characteristics appear to be very similar. To begin with, both were in the pentavalent oxidation state when introduced into the input solution at low pH where they exist as the cations NpO_2^+ and PuO_2^+ . In general, the K_d trends are very similar for Np and Pu, suggesting that the oxidation state analogy is not a bad predictor for sorption (see e.g., Langmuir, 1996). K_{ds} approach zero below pH 6, but rise to around 200 ml g^{-1} at alkaline pH. Neptunium and Pu sorb less strongly than Am at all pH's. And Np sorbs roughly a factor of 3 less than Pu. It is hypothesized that an exchange reaction involving Pu (or Np) and surface Ca sites explains sorption similar to the case of Am. K_{ds} increase with pH due to the lower concentrations of Ca at high pH. The effects of ionic strength and P_{CO_2} are unclear. In a few cases, high pH K_{ds} increase with P_{CO_2} . This may indicate that Pu-carbonate species are potentially important sorbates. Because increasing P_{CO_2} generally causes high Ca concentrations, the increase in K_d seen for example, for Pu, suggests that the Pu-carbonate species might interact with the mineral surface as well.

5.3. Uranium

Keeping in mind the wide scatter caused by the uncertainty in the ICP-MS analyses of the U input solutions, an otherwise consistent trend is seen in the U K_{ds} . At low pH, where Ca concentrations are high, U sorption is minimal. Around pH 5 to 7 U K_{ds} are maximal and approach 2000 ml g^{-1} . At higher pH sorption attenuates and approaches zero. Increasing P_{CO_2} at any given pH may cause a decrease in K_d ,

though the 0.05 M NaCl runs do not agree completely with this. It is hypothesized that the exchange reaction controls sorption at pH < 7.

At pH > 7 complexing of uranyl by carbonate occurs. This appears to cause a net desorption hence lower K_{ds} .

6. Summary

The primary conclusions of the work described above are:

1. Ca and Mg adsorb independently on separate, exposed crystallographic planes and do not appear to mix appreciably on those planes, except perhaps at high pH.
2. Ca and Mg adsorption/exchange is, at least initially, done with the aid of a non-trivial number of water molecules.
3. Na^+ , and presumably other univalent cations as well, are able to compete with Mg and Ca for surface sites, if present in great enough quantities ($>0.5\text{ M}$).
4. REE's (and their carbonate and sulfato complexes) apparently exchange for Ca. REE's do not exchange for Mg.
5. Exchange for Ca appears to control attachment of actinides to dolomite. High levels of Ca^{2+} in solution will decrease K_{ds} . At the same time, to the extent that high P_{CO_2} s increase Ca^{2+} levels, K_{ds} will decrease with CO_2 concentrations as well, but only if sorbing actinide-carbonate complexes are not observed to form. This indirect CO_2 effect is observed primarily at, and above, neutral pH.
6. Am-carbonate complexes appear to sorb; Pu-complexes might sorb as well. U-carbonate complexation leads to desorption.
7. High NaCl levels do not appear to have a significant effect on actinide K_{ds} . The order of magnitude change in salt content (from 0.05 to 0.005 M NaCl) caused minor shifts in K_{ds} .
8. The oxidation state analogy for pentavalent actinides works in an order-of-magnitude sense, reproducing trends and absolute K_{ds} within about a factor of 3.
9. In the mildly alkaline conditions of the Culebra the primary control over adsorption is likely to be Ca^{2+} concentrations, and, to a lesser extent, carbonate concentrations. Mg^{2+} concentrations may also be important.

Acknowledgements

Thanks to Phil Harrigan for doing the experimental work at LANL, and to Larry Brush for back seat driving on the rest of it. We greatly appreciate the constructive comments of J. J. W. Higgo and J. J. Middelburg. Thanks also for helpful internal reviews from Larry Brush, Deborah Coffey, John Holmes, and Malcolm Siegel (twice).

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