Adsorption/desorption of strontium on calcite*

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^{90}Sr has been released into the environment from nuclear power plants, submarines, accidents, and as fallout from nuclear testing. ^{90}Sr movement through soils and groundwaters is typically limited by interaction with mineral surfaces and soil organic material. Sr^{2+} appears to exchange for Ca^{2+} and, if exchange is extensive, Sr movement through a soil profile might be severely curtailed.

The primary Ca-bearing mineral in many soils is calcite ($CaCO_3$) and, although interaction with calcite may limit ^{90}Sr transport, the outcome of the interaction is impossible to predict due to the tendency for metal-calcite exchange to be incompletely reversible (e.g. Davis et al., 1987; Stipp and Hochella, 1991; Zachara et al., 1991). Our object here is to specifically examine adsorption and desorption K_ds for ^{90}Sr on calcite as a function of time in the early stages of metal-surface interaction where, presumably, exchange dominates surface processes. By measuring sorption equilibria under well-constrained conditions, we can: 1) assess the magnitude of the adsorption/desorption divide; and 2) identify how it varies over time. This in turn might give some insight into the macroscopic behaviour of Sr in calcite-rich soils.
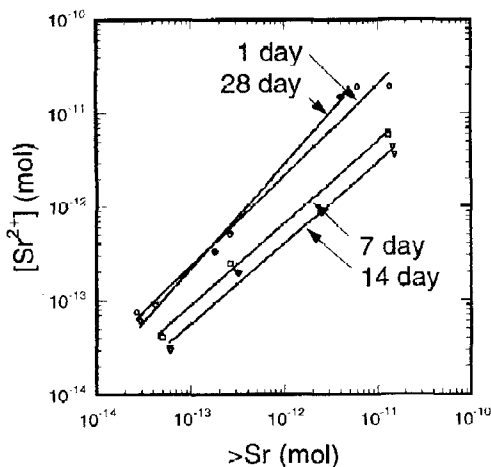
Experimental methods

Ultrapure calcite was equilibrated with 0.01 M NaCl and then brought into contact with ^{90}Sr ($4.3e^{-9}$, or $1.3e^{-10}$, or $8.7e^{-12}$ M) at near neutral pH. Adsorption K_ds were measured after 1, 7, 14 and 28 days of sorption. At the appropriate time, the test tubes were removed from the shaker table, the suspension allowed to settle and the $CaCO_3$ spun down by centrifugation. The supernatant was then poured off for analysis by gamma spectroscopy or liquid scintillation. In a number of cases the centrifuged $CaCO_3$ from the adsorption experiment was subsequently re-equilibrated with 0.01 N NaCl solutions containing no radioactive tracers. Re-equilibration 'desorption' runs lasted 1, 7, or 14 days, at the end of which the suspensions were centrifuged and the supernatants analysed for ^{90}Sr.

Results

Figure 1 shows sorbed ^{90}Sr as a function of the dissolved ^{90}Sr level and contact time. Note first of all that adsorption does not appear to depend on contact time, suggesting that sorption is rapid and occurs over time spans less than a day, the shortest experiment. There appears to be little long-term (1 < time < 28 days) movement of sorbed Sr to 'high-energy sites', followed by further uptake of Sr from solution, since the total amount of sorbed Sr remained reasonably constant, for a given level of Sr in solution.

Figure 2 shows desorption K_ds measured after 1, 7, 14 and 28 days of equilibration, followed by, respectively, 1, 7 and 14 days of equilibration with ^{90}Sr-free solutions. There is no systematic variation in K_d with ^{90}Sr levels at a given adsorption and desorption time period, yet desorption K_ds are routinely about an order of magnitude greater than adsorption K_ds. The difference points to an irreversible component of sorption that does not appear to change greatly when examined after 1, or 28, days of equilibration with desorbing solutions. This sorption hysteresis, therefore, is probably locked in very early in the sorption process, certainly within 24 hours.
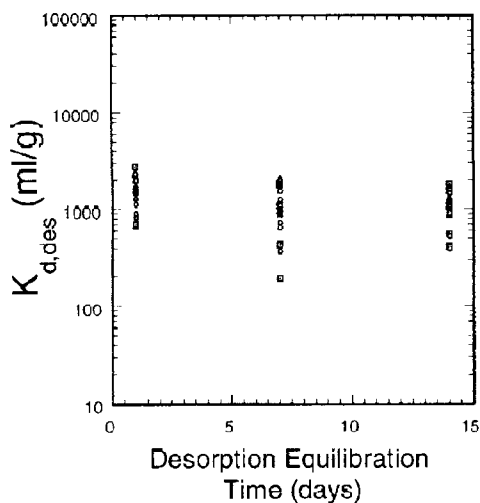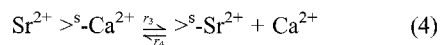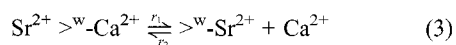

FIG. 1.

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$$Sr^{2+} >^{w}\text{-}Ca^{2+} \underset{r_2}{\overset{r_1}{\rightleftharpoons}} >^{w}\text{-}Sr^{2+} + Ca^{2+} \qquad (3)$$

$$Sr^{2+} >^{s}\text{-}Ca^{2+} \underset{r_4}{\overset{r_3}{\rightleftharpoons}} >^{s}\text{-}Sr^{2+} + Ca^{2+} \qquad (4)$$

If r_1, r_2, and r_3 are large, we would expect a rapid equilibration of the surface (both the strong and the weak sites) with the Sr in the spike. If the movement of strongly bound Sr back to weak sites in response to a shift in equilibrium were also rapid, we would observe equivalent adsorption and desorption K_ds equal to adsorption K_ds. We do not, though, and we hypothesize that this is a direct result of slow back-reaction from the strong to the weak sites.

We postulate that this hysteresis arises due to the existence of two distinct sorbate populations. Conceptually, Sr can sorb to either a 'weak' (denoted as $>^{w}$) or a 'strong' (denoted as $>^{s}$) site. The distribution of Sr between these sites and Sr solution occurs rapidly (within 1 days time). Two reactions occur:

References

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