1. Introduction

Calcium isotope geochemistry ($\delta^{44}\text{Ca}$) has recently emerged as a promising tool for examining the chemical evolution of Earth’s atmosphere and oceans. To this end, most work has focused on the marine realm with the aim of reconstructing how climatic and tectonic processes have influenced the oceanic Ca cycle (Zhu and Macdonagh, 1998; De La Rocha and DePaolo 2000; Schmitt et al., 2003b; Fantle and DePaolo, 2005; Farkas et al., 2007a; Farkas et al., 2007b). Interpreting secular variations in the marine $\delta^{44}\text{Ca}$ record requires information about processes controlling the $\delta^{44}\text{Ca}$ composition of continental weathering inputs. Pioneering studies have revealed that calcite precipitation, ion-exchange, and plant uptake of Ca can preferentially remove light isotopes from solution. Thus, suggesting that development of a heavy isotope reservoir on the continents could impact the isotope balance of Ca in seawater (Russell and Papanastassiou, 1978a; Schmitt et al., 2003a; DePaolo, 2004; Lemarchand et al., 2004; Marriott et al., 2004; Wiegand et al., 2005; Tipper et al., 2006).

More recently, analyses of pore fluids within slowly recrystallizing marine carbonate sediments have demonstrated that no Ca isotope fractionation occurs during calcite precipitation under conditions of chemical equilibrium (Fantle and DePaolo, 2007). This implies that the equilibrium Ca isotope fractionation factor between calcite and water ($\Delta_{\text{cal-w}}$) equals 0‰ ($\alpha_{\text{cal-w}}=1.0000$) and that other instances of fractionation during calcite precipitation are kinetically controlled. On the continents, aquifers represent a comparable environment where relatively long water-rock interaction times and slow reaction kinetics may facilitate chemical and isotopic equilibration between water, calcite, and other phases involved in the distribution and transport of dissolved Ca. Hence, aquifers offer a powerful opportunity to test fundamental assumptions concerning Ca isotope fractionation effects while simultaneously providing direct insight into processes controlling $\delta^{44}\text{Ca}$ variability in terrestrial waters.

In this study, we examined the downgradient evolution of dissolved $\delta^{44}\text{Ca}$ values along a 236 km flow path in the Madison aquifer, South Dakota—a confined carbonate aquifer recharging in the igneous Black Hills. The Madison aquifer offers a unique opportunity to explore Ca isotope effects during water-rock interaction because...
(1) fluids and rock have chemically equilibrated over a much longer timescale (up to ~15 ky) than can be simulated in laboratory experiments and (2) previous studies have quantified the rates and mass-balances of geochemical reactions controlling bulk Ca concentrations along the aquifer flow path (Plummer et al., 1990; Jacobson and Wasserburg, 2005). Here, we use new δ⁴⁴Ca measurements and existing model rates for the addition and removal of Ca to evaluate the extent to which Ca isotope fractionation may be associated with calcite precipitation and Ca-for-Na ion-exchange. This work represents the first comprehensive analysis of Ca isotope transport in groundwater systems. We find that throughout most of the aquifer, δ⁴⁴Ca values trace mixing of Ca from dolomite and anhydrite dissolution, with no apparent isotope discrimination during calcite precipitation under conditions of chemical equilibrium.

2. Study site and methods

Detailed descriptions of the study site as well as the samples and their collection method are given in Jacobson and Wasserburg (2005). Briefly, the Madison aquifer is the middle of three Paleozoic aquifers in parts of MT, ND, SD, WY, and Canada. The aquifer is composed of Mississippian age Madison Limestone, which is a grey to buff colored shallow-water marine carbonate containing dolomite (70%), calcite (25%), and anhydrite (4%) with accessory goethite, halite, hematite, quartz, kaolinite, illite, and mixed layer illite-smectite (Thayer, 1983; Busby et al., 1991). Shale and siltstone belonging to the Englewood Formation confine the bottom of the aquifer, while shale and sandstone belonging to the Minnelusa Formation confine the top. The Madison Limestone was locally uplifted and tilted during the Laramide orogeny, which exposed Precambrian basement rocks and Tertiary syenite porphyry intrusions comprising the core of the Black Hills. Recharge to the aquifer primarily occurs by hydrologic loss as streams originating in gneissic and igneous watersheds cross karstified beds of Madison Limestone draping the flanks of the intrusion (Downey, 1984; Long and Putnam, 2002). Following recharge, groundwater flows in a west to east direction with velocities ranging from 2 to 25 m/yr (Downey, 1984; Plummer et al., 1990; Long and Putnam, 2002). Vertical water mass mixing is negligible (Downey, 1984).

The suite of samples analyzed in this study consists of two surface water samples (S1 and S2) assumed to represent recharge waters to the aquifer and eight groundwater samples (W1–W8) assumed to lie along a 236 km hydrologic flow path between the Black Hills and central SD [see Fig. 1a,b in Jacobson and Wasserburg (2005)]. S1 was collected from a tributary stream draining the core of the Black Hills, whereas S2 was collected where the main stem of the tributary intersects outcrop of Madison Limestone. W1–W8 were collected from wells completed in the Madison aquifer. Groundwater ages range from ~0–30 yrs (W1–W4), ~70 yrs (W5), and ~15,000 yrs (W6–W8) (Plummer et al., 1990). All samples were filtered through acid-cleaned 0.45 μm filters, acidified to pH=2 with ultrapure HNO₃, and stored in acid-cleaned LDPE bottles prior to analysis. Two dolomite samples (DOL1 and DOL2) were collected near the location of S2, and two anhydrite samples (ANH1 and ANH2) were taken from Madison Limestone drill core currently stored at the USGS Core Research Center in Denver, CO (Blankennagel et al., 1979). All rock samples were reduced to a fine powder in a shatterbox, and 1-g sub-samples were completely digested in 6N ultrapure HCl.

Following the procedure outlined in Holm (2005), δ⁴⁴Ca values were measured using a Triton MC-TIMS at the Saskatchewan Isotope Laboratory and a ⁴⁴Ca/⁴⁰Ca double-spike to correct for instrumental mass discrimination. Care was taken to ensure complete spike-sample equilibration before purification of Ca from matrix elements using Teflon columns packed with AG MP-50 cation exchange resin. Total procedural blanks were negligible (~100 ng). Sample:blank ratios were 500:1. Approximately 5 to 8 µg of purified Ca was loaded onto out-gassed Ta filaments, using ultrapure H₂PO₄ acid, and measurements were made using a single filament assembly. Observation of the ⁴¹K beam demonstrated absence of an isobaric interference of ⁴⁰K on ⁴⁰Ca. All ⁴⁴Ca/⁴⁰Ca ratios are reported in delta notation (δ⁴⁴Ca)mol) after 1000. The internal precision (2σ) of the analyses ranged between ±0.030 and 0.045‰. Repeated analyses of samples and internal standards during the period of study yielded an external precision (2σcal) of ±0.08‰. The value obtained for NIST 915a was ~1.88‰.

3. Results

Table 1 reports data for the water samples, and Fig. 1 shows δ⁴⁴Ca values as a function of distance along the flow path. The surface water collected from the core of the Black Hills (S1) has δ⁴⁴Ca=−0.93‰, whereas the surface water collected at the hydrologic loss zone (S2) has δ⁴⁴Ca=−0.71‰. Following recharge, dissolved δ⁴⁴Ca values decrease from −0.72 to −1.31‰ with increasing downgradient distance between W1 and W7. The one exception to this trend is W8 (the oldest water sample collected), which has δ⁴⁴Ca=−0.74‰.

Table 2 shows δ⁴⁴Ca values for the dolomite and anhydrite samples. Within the uncertainty of the measurements, the dolomite samples are distinct from each other (~1.10 and ~0.88‰). The anhydrite samples yielded lower and more uniform δ⁴⁴Ca values (~1.29 to ~1.31‰).

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance (km)</th>
<th>Ca (mol/l)</th>
<th>δ⁴⁴Ca ± 2σcal/uniFB01</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0</td>
<td>1023</td>
<td>−0.93 ± 0.03</td>
</tr>
<tr>
<td>S2</td>
<td>12</td>
<td>958</td>
<td>−0.71 ± 0.04</td>
</tr>
<tr>
<td>W1</td>
<td>10</td>
<td>1307</td>
<td>−0.72 ± 0.03</td>
</tr>
<tr>
<td>W2</td>
<td>17</td>
<td>873</td>
<td>−0.78 ± 0.04</td>
</tr>
<tr>
<td>W3</td>
<td>20</td>
<td>1180</td>
<td>−0.93 ± 0.03</td>
</tr>
<tr>
<td>W4</td>
<td>23</td>
<td>1073</td>
<td>−0.04 ± 0.05</td>
</tr>
<tr>
<td>W5</td>
<td>38</td>
<td>1859</td>
<td>−1.12 ± 0.04</td>
</tr>
<tr>
<td>W6</td>
<td>150</td>
<td>5714</td>
<td>−1.25 ± 0.04</td>
</tr>
<tr>
<td>W7</td>
<td>189</td>
<td>7136</td>
<td>−1.31 ± 0.03</td>
</tr>
<tr>
<td>W8</td>
<td>236</td>
<td>5739</td>
<td>−0.74 ± 0.04</td>
</tr>
</tbody>
</table>

*Data taken from Jacobson and Wasserburg (2005).*

2σ cal/uniFB01 = internal precision.
Ca isotope geochemistry of dolomite (DOL) and anhydrite (ANH) samples from the Madison aquifer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca (μmol/g)</th>
<th>δ⁴⁴Ca ± 2σ_{int}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOL1</td>
<td>4618</td>
<td>−0.89±0.03</td>
</tr>
<tr>
<td>DOL2</td>
<td>3076</td>
<td>−1.10±0.04</td>
</tr>
<tr>
<td>ANH1</td>
<td>7401</td>
<td>−1.21±0.05</td>
</tr>
<tr>
<td>ANH2</td>
<td>7293</td>
<td>−1.29±0.04</td>
</tr>
</tbody>
</table>

The lighter value for DOL1 relative to DOL2 cannot be explained by the presence of trace anhydrite with low δ⁴⁴Ca, because the anhydrite concentration in DOL1 is small (~4 × 10⁻⁴ g/g) (Jacobson and Wasserburg, 2005). At present, Ca isotope data for dolomite and anhydrite are scarce. Relative to our values for seawater and NIST 915a, Carboniferous dolomite has δ⁴⁴Ca = −0.76‰ (n = 2 Steuber and Buhl, 2006), and Neoproterozoic cap carbonate dolomictite has δ⁴⁴Ca = −0.87‰ (Kasemann et al., 2005). Similarly, Russell and Papanastassiou (1978b) reported values of −1.5 and −2.1‰ for anhydrite, whereas in a more recent survey, Hensley (2006) reported values for both anhydrite and gypsum ranging from −0.20 to −2.40‰. According to batch precipitation experiments, the δ⁴⁴Ca value of anhydrite is lower by −1% relative to the fluid from which it precipitates (Hensley, 2006).

### 4. Discussion

Previous researchers have shown that groundwater in the Madison aquifer chemically evolves by dedolomitization (Plummer and Back, 1980; Back et al., 1983; Plummer et al., 1990; Naus et al., 2001; Jacobson and Wasserburg, 2005). In this reaction, the irreversible dissolution of anhydrite in waters in equilibrium with respect to dolomite and calcite leads to dolomite dissolution and calcite precipitation according to the following generalization reaction:

\[
\text{CaSO}_4 + \text{CaMg(CO}_3\text{)}_2 \rightarrow 2\text{CaCO}_3 + \text{Mg}^{2+} + \text{SO}_4^{2-}
\]

Typically, the amount of Ca added to solution, mostly by anhydrite dissolution and to a lesser extent dolomite dissolution, exceeds the amount of Ca removed by calcite precipitation such that dissolved Ca accumulates during downward gradient water transport (Plummer and Back, 1980; Back et al., 1983; Plummer et al., 1990; Naus et al., 2001; Jacobson and Wasserburg, 2005). Calcite precipitation occurs during small fluctuations about the equilibrium state. Indeed, intrinsic carbonate mineral reaction rates in the Madison aquifer are extremely slow (~10⁻⁹–10⁻¹⁰ yr⁻¹; Jacobson and Wasserburg, 2005) and comparable to those reported for recrystallizing marine carbonate sediments (Fantle and DePaolo, 2007). Halite dissolution and Ca-for-Na ion-exchange also occur, but for the bulk of the flow path (S1–W7), these reactions are negligible. The one exception is the flow path segment between W7 and W8, where ion-exchange and calcite precipitation remove Ca at nearly equivalent rates. The net effect is that Ca concentrations linearly increase between S1 and W7 but then moderately decline between W7 and W8 (Jacobson and Wasserburg, 2005).

As waters approach equilibrium with respect to anhydrite with increasing downgradient distance, their δ⁴⁴Ca composition approaches that of anhydrite. We therefore interpret the bulk of the data to reflect the progressive addition of anhydrite-derived Ca during groundwater flow. However, notable exceptions to this overall pattern exist, especially at the extremes of the flow path. Waters in the immediate vicinity of the recharge zone appear to be supersaturated with respect to calcite and dolomite, whereas all groundwater samples (W1–W8) are in equilibrium (Jacobson and Wasserburg, 2005). As shown in Fig. 2b and c, however, an immediate correlation between δ⁴⁴Ca and the calcite and dolomite saturation state of the waters is not evident. Removal of δ⁴⁴Ca by plants could also explain the relatively high δ⁴⁴Ca values of infiltrating waters (Schmitt et al., 2003a; Bullen et al., 2004; Wiesand et al., 2005; Holmden and Belanger, 2006). In the case of W8, which is δ⁴⁴Ca enriched relative to the samples that precede it, we reason by inference to previous laboratory experiments that Ca-for-Na ion-exchange could fractionate Ca isotopes (Russell and Papanastassiou, 1978a). As discussed above, the flow path segment between W7 and W8 experiences a large effect from ion-exchange relative to the preceding segment.

To better understand the δ⁴⁴Ca evolution of the aquifer waters, we adopt the steady-state 1D reactive-transport model presented in Jacobson and Wasserburg (2005). Consistent with previous studies of the Madison aquifer, the model implicitly assumes that the composition of recharge waters has not changed appreciably over the time span represented by the samples (Plummer et al., 1990). The equation describing the rate of change in the dissolved Ca in water (w) over distance (dx) is:

\[
v \frac{dC_w}{dx} = F_{\text{dol}} + F_{\text{anh}} - F_{\text{exc}},
\]

where v is the water velocity, \(F_{\text{dol}}\) and \(F_{\text{anh}}\) are the rates of Ca addition by dolomite and anhydrite dissolution, respectively, and \(F_{\text{exc}}\) are the rates of Ca removal by calcite precipitation and Ca-for-Na ion-

---

**Fig. 2.** δ⁴⁴Ca vs. the saturation state of waters (log2) with respect to anhydrite (a), calcite (b), and dolomite (c). Surface- and ground-water samples shown with open and filled circles, respectively. Error bars show 2σ_{int}=±0.08‰. Dashed lines show ±0.25 uncertainty of saturation state calculations. Saturation state data taken from Jacobson and Wasserburg (2005).
exchange, respectively. Similarly, the equation describing the
down-gradient evolution of dissolved $\delta^{44}$Ca values is:

$$
v_{Ca}(x) \frac{d(\delta^{44}Ca_{x})}{dx} = F_{dal}(\delta^{44}Ca_{dal} - \delta^{44}Ca_{x}) + F_{ahh}(\delta^{44}Ca_{ahh} - \delta^{44}Ca_{x}),$$

$$-F_{cal}(\delta^{44}Ca_{cal} - \delta^{44}Ca_{x}) = F_{exc}(\delta^{44}Ca_{exc} - \delta^{44}Ca_{x})$$

(3)

where $Ca_{x}(x)$ is the Ca concentration in water at position $x$
determined from Eq. (1), $\delta^{44}Ca_{dal}$ and $\delta^{44}Ca_{ahh}$ are the Ca isotope
compositions of dolomite and anhydrite, respectively; $\Delta_{cal-x}$ and $\Delta_{ahh-x}$ are
the approximate isotope fractionation factors associated with
calcite precipitation and Ca-for-Na ion-exchange, respectively; and
the remainder of the parameters are described above. As discussed
here, $\delta_{x}=\delta^{44}Ca_{x} - \delta^{44}Ca_{w} = 10^{-3}\ln_{10}q_{x}$, where $j$ refers to either calcite
precipitation or Ca-for-Na ion-exchange, and $\alpha_{x}$ is the isotope
fractionation factor. The model only considers fractionation during
removal of dissolved Ca because at present, no evidence exists for
isotope fractionation during weathering.

We use Eqs. (1) and (2) to estimate $\Delta j$ values that could best
explain the observed water data. We set $v$ = 2 m/yr (Jacobson and
Waterbury, 2005); $\delta^{44}Ca_{dal} = -0.99\%$ (the average of DOL1
and DOL2); and $\delta^{44}Ca_{ahh} = -1.25\%$ (the average of ANH1 and
ANH2). The rate parameters ($F$ values) are given in Table 3. These rates, which
were determined via inverse mass-balances for Cl, Na, Mg, SO$_4$2-, and
total inorganic carbon ($C_T$), are “effective”, in that they describe the
rate at which dissolution, precipitation, and ion-exchange either add
or remove Ca to produce the observed water chemistry for a specified
value of $r$. As discussed in Jacobson and Waterbury (2005), two sets of $F$ values exist,
one for flow path segment S1–W7 and one for W7–W8. To evaluate the apparent $^{44}$Ca enrichment of the recharge
waters relative to the bedrock $^{44}$Ca values, we divide segment S1–W7 into
two smaller segments, S1–S2 and S2–W7. This is permissible because
the reaction rates are linear. The $F$ values that apply to segment S1–W7
also apply to any smaller segment between S1 and W7. The high
$^{44}$Ca value for S2 superimposed on the otherwise decreasing
trend between S1 and W7 (Fig. 1) dictates that we divide S1–W7 into
a minimum of two smaller segments. We could further subdivide S1–S2
and S2–W7, but because the reaction rates are linear, this would not
change the model $\Delta_{x}$ values obtained.

For S1–S2, the best fit is obtained by setting $\Delta_{cal-x} = -2.1\%$ (Fig. 1; solid
curve). This suggests that calcite precipitation could enrich
infiltrating water in $^{44}$Ca by preferentially removing $^{44}$Ca. The dissolved
$^{44}$Ca values cannot be attributed to ion-exchange because the model
shows that the relatively modest rate of Ca removal by ion-exchange
(a factor of $\sim 40$ lower than that attributed to calcite precipitation)
would require an unreasonably high fractionation factor.

We note that the $\Delta_{cal-x}$ Value of $-2.1\%$ is larger than that
determined in prior studies of inorganic calcite precipitation in both field
and laboratory settings (e.g., $-0.92\%$, Timper et al., 2006; $-1.5 \pm 0.25\%$
Lemarchand et al., 2004). This discrepancy could arise because the
model attributes all fractionation to calcite precipitation, whereas $^{40}$Ca
uptake by plants might also be important. Moreover, the model
fractionation factor greatly depends on the Ca concentration and
isotope composition of the initial input water (S1). Sample S1 was
collected during the summer, when stream flow is lowest and
 evaporative concentration is highest. However, most recharge occurs
during peak discharge in the spring, when water from melting snow
is expected to be more dilute. As such, a lower initial Ca concentration
would yield a lower model $\Delta_{cal-x}$ value. If we set $\Delta_{cal-x} = -1.5\%$, then
the model predicts an input water Ca concentration of $-400$ mol/l,
which is a factor of $\sim 2.5$ lower than the concentration for S1. As
described above, it is also conceivable that we incompletely
characterized $^{44}$Ca in dolomite and that the actual average value is closer to
S2 and W1. This scenario decreases the importance of calcite
precipitation and points to dolomite dissolution as the cause for the
isotopic increase between S1 and S2. In either case, while apportioning
isotopic effects among calcite precipitation versus biological
processes, and determining seasonal and spatial variability in surface
$^{44}$Ca values presently hampers reliable estimation of $\Delta_{cal-x}$ in
the Black Hills recharge zone, our data qualitatively suggest that some
form of Ca isotope redistribution could occur during the initial stages
of water transport and infiltration.

Given that ion-exchange is unimportant for Ca isotope transport in
segment S1–S2, we set $\Delta_{exc-x} = 0\%$, for segment S2–W7. However, the same logic
does not hold for $\Delta_{cal-w}$. Setting $\Delta_{cal-w} = -2.1\%$, or even as low as $-1.5\%$, produces a large offset between the measured
and modeled data (Fig. 1; dashed curves A and B). Although
groundwater temperatures increase downgradient from a minimum
of $10\, ^{\circ}C$ to a maximum of $70\, ^{\circ}C$ at a rate of $0.25\, ^{\circ}C$/km, the offset
persists even if we account for the effect of temperature on $\Delta_{cal-w}$
(0.02‰/°C) (Lemarchand et al., 2004) (Fig. 1; dashed curves B and C).
In general, Ca isotope fractionation during inorganic calcite precipita-
tion is only weakly dependent on temperature (Marriott et al., 2004;
Cusson et al., 2005; Sime et al., 2005; Steuber and Buhl, 2006).

The closest match is obtained by setting $\Delta_{cal-w} = 0\%$, which indi-
cates that calcite precipitation under conditions of chemical equilib-
rium does not fractionate Ca isotopes in this region of the aquifer
(soluble curve in Fig. 1). This is consistent with the absence of a
correlation between the calcite saturation state of the groundwater
samples and their $^{44}$Ca composition (filled circles in Fig. 2b). When
$\Delta_{cal-w}$ is set to $0\%$, the resulting theoretical $^{44}$Ca values are largely
insensitive to assumed changes in the dolomite weathering contribu-
tion. For example, the difference between the “best fit” model output
(soluble curve in Fig. 1) and model output obtained by setting
$^{44}$Ca in dolomite equal to one of the two values measured (either $-1.10$ or $-0.88\%$)
is much smaller than the $\pm 0.08\%$ uncertainty of the measurements.
The same holds by eliminating the dolomite weathering contribution
entirely ($F_{exc} = 0$). These sensitivity analyses confirm that
anhydrite dissolution dominates the $^{44}$Ca evolution of groundwater.
Dolomite dissolution imparts only a small effect in the “best fit” case because
the rate of Ca addition by dolomite dissolution is a factor $-5$ lower than the
corresponding rate for anhydrite dissolution (Table 3). A slightly better
fit is obtained by setting the initial input Ca concentration to the model
predicted value of $400$ mol/l (Fig. 1; dashed curve E). Regardless, the
majority of data analyzed in this study clearly demonstrate that $^{44}$Ca
conservatively tracks the progressive effect of anhydrite dissolution in
a manner exactly identical to $^{87}Sr/^{86}Sr$ (Jacobson and Waterbury,
2005).

Lastly, for segment S7–S8, we set $\Delta_{cal-x} = 0\%$, because calcite precipi-
tation under conditions of chemical equilibrium does not fractionate Ca
isotopes in the preceding segment. This leaves Ca-for-Na ion-exchange
as the most plausible mechanism to explain the large isotopic enrichment
in W8 relative to W7, even at the relatively high temperature of $70\, ^{\circ}C$.
The model yields $\Delta_{exc-x} = -1.0\%$, which is consistent with previous
laboratory experiments showing that ion-exchange preferentially selects
$^{40}$Ca over $^{44}$Ca (Russell and Papasastassiou, 1978a). Although we cannot
entirely rule out the delivery of $^{44}$Ca enriched fluids by cross-formational
mixing, we view this scenario as unlikely. Firstly, previous work has
demonstrated that cross-formational mixing is minimal (Downey, 1984).
Secondly, both underlying and overlying formations contain anhydrite,

Table 3 Reaction rates controlling the input and output of dissolved Ca to Madison aquifer groundwater$^{a,b}$

<table>
<thead>
<tr>
<th>Segment</th>
<th>$F_{dal}$</th>
<th>$F_{ahh}$</th>
<th>$F_{cal}$</th>
<th>$F_{exc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1–W7</td>
<td>1.88</td>
<td>8.88</td>
<td>-4.20</td>
<td>-0.0980</td>
</tr>
<tr>
<td>W7–W8</td>
<td>5.60</td>
<td>14.1</td>
<td>-12.0</td>
<td>-15.8</td>
</tr>
</tbody>
</table>

$^{a}$Calculated according to data presented in Jacobson and Waterbury (2005).

$^{b}$Negative sign indicates removed from solution.

$^{c}$S1–S2 and S2–W7 experience the same reaction rates as S1–W7; see text.
which presumably has low δ⁴⁴Ca values. Highly evolved waters in these aquifers should therefore be isotopically indistinguishable from those in the Madison aquifer. This is the first evidence that Ca isotope fractionation by ion-exchange may be occurring in nature with an apparent net isotope effect similar to many reported instances of biotic and abiotic calcite precipitation. Because ion-exchange is a ubiquitous phenomenon, it could be important for generating Ca isotope variability in other settings. However, we caution that further investigations are required to confirm this hypothesis.

5. Conclusions and implications

Throughout most of the Madison aquifer, δ⁴⁴Ca dynamically tracks mixing between anhydrite- and dolomite-derived Ca, with no apparent isotope fractionation when calcite precipitates during small fluctuations about the state of chemical equilibrium. Modeling suggests that calcite precipitation and Ca-for-Na ion-exchange could fractionate Ca isotopes during the initial and final stages of water transport, respectively. However, given the limited number of samples characterizing these regions of the aquifer, these findings are less robust than the main conclusion of the study demonstrating that the equilibrium fractionation factor between calcite and water is very close to zero. We attribute the absence of Ca isotope fractionation to the long time transit of water (∼15 ky) and relatively slow rate of calcite precipitation, which have permitted chemical and isotopic equilibration between calcite and water. Our study supports the contention that the equilibrium Ca isotope fractionation factor between calcite and water (∆δ⁴⁴Ca) is very close to zero (Fantle and DePaolo, 2007). We therefore reason that instances of ⁴⁴Ca enrichment on the continents attributed to calcite precipitation (e.g., Tipper et al., 2006) must originate from kinetic effects, most likely controlled by the magnitude of the intrinsic precipitation rate and/or the degree of supersaturation of the fluid with respect to calcite (Gussoni et al., 2003; Steuber and Buhl, 2006; Fantle and DePaolo, 2007). Although additional work is required to understand the possible role of ion-exchange in creating δ⁴⁴Ca variability, our findings imply that in aquifers where ∆δ⁴⁴Ca = 0‰ groundwater δ⁴⁴Ca values can be predicted by simple mixing, in a manner identical to other widely utilized radiogenic isotope tracers (e.g., δ⁸⁷Sr/δ⁶⁰Sr). We therefore suggest that groundwater can be discounted as a significant source of ⁴⁴Ca enriched water in carbonate-rich settings, and propose instead that simple dilution and mixing during surface-groundwater interactions might serve to reduce the range of δ⁴⁴Ca variability imparted to surface waters by rapid calcite precipitation and plant uptake.

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