Large calcium isotope fractionations by zeolite minerals from Iceland

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Zeolites are secondary tectosilicates produced during the hydrothermal alteration of basalt. The minerals serve as major sinks of calcium, which readily exchanges with calcium from surrounding groundwater. However, no studies have specifically investigated the calcium isotope geochemistry ($\delta^{44/40}$Ca) of zeolites. Here, we report $\delta^{44/40}$Ca values for zeolites from East Iceland, where the minerals form during progressive burial of the lava pile. The zeolites show a $\delta^{44/40}$Ca range of 1.4‰, which strongly correlates with average mineral calcium-oxygen bond lengths. As this correlation appears most consistent with equilibrium isotope partitioning, our findings point toward developing a novel geothermometer for studying low-grade basalt metamorphism. The results also have significance for using calcium isotopes to trace basalt weathering, including its role in long-term climate regulation and application in carbon capture and storage, a leading strategy for mitigating anthropogenic climate change.
Calcium (Ca), the fifth most abundant element in the Earth’s crust, plays a key role in regulating climate over geologic timescales and is essential for biological processes, such as biomineralization, plant growth, and cellular regulation. Due to the ubiquitous occurrence of Ca in Earth and extraterrestrial materials, as well as major geochemical cycles, stable Ca isotopes have emerged as a promising tool for investigating processes in geochemistry, cosmochemistry, biology, and archaeology. Calcium isotope ratios are reported in delta notation as $\delta^{44/40}\text{Ca}_{\text{std}}(\%o) = \left(\frac{{^{44}\text{Ca}}}{{^{40}\text{Ca}}}_{\text{sample}} / {^{44}\text{Ca}}/{^{40}\text{Ca}}_{\text{std}} - 1\right) \times 1000$, where $\text{std}$ refers to the sample and $\text{std}$ refers to the normalizing standard, which in this study is OSIL Atlantic Sea-water or ASW ($\delta^{44/40}\text{Ca}_{\text{ASW}} = 0\%o$).

In the ongoing effort to develop and apply the $\delta^{44/40}\text{Ca}$ tracer, research has focused on quantifying mechanisms that fractionate isotopes according to their masses and produce isotopic offsets. Studies have used Ca isotopes to examine mid-ocean ridge systems, and water or ASW ($\delta^{44/40}\text{Ca}_{\text{ASW}} = 0\%o$) during low-grade metamorphism.

Hydrothermal alteration commonly leads to the formation of zeolites, which is a leading carbon capture and storage (CCS) strategy. Application of the Ca isotope tracer to these and other intermediate temperature systems requires a thorough examination of all secondary minerals that may fractionate Ca isotopes and contribute to the $\delta^{44/40}\text{Ca}$ values of circulating waters. In addition, a better understanding of both equilibrium and kinetic effects on Ca isotope fractionation at intermediate temperatures is essential for improving knowledge about Ca isotope cycling and identifying novel applications for the $\delta^{44/40}\text{Ca}$ tracer.

Hydrothermal alteration commonly leads to the formation of zeolites. Zeolite mineral structures comprise frameworks of linked Si- or Al-O tetrahedra, creating voids and channels that contain H$_2$O, Ca, and other cations, which are readily exchangeable. The minerals serve as sizeable Ca$_2^+$ sinks during low-grade metamorphism. In basaltic settings such as Iceland, equilibrium-controlled ion-exchange reactions with zeolites strongly regulate Ca$_2^+$ concentrations in natural hydrothermal waters, as well as those produced in CCS experiments. Calcium cycling during basalt weathering in subsurface hydrothermal systems also plays a major role in regulating Earth’s long-term carbon cycle. Moreover, owing to their properties as ion-exchangers, absorbents, molecular sieves, and catalysts, zeolites have numerous environmental, industrial, and medical applications, including drinking water purification, nuclear waste management, contaminant transport mitigation, automotive emission reduction, and cancer treatment.

Nonetheless, despite the widespread occurrence and applicability of zeolites, their Ca isotope geochemistry has been neglected. Only one study has reported Ca isotope data for zeolites. Coexisting heulandite and stilbite from Iceland are isotopically lighter and heavier, respectively, relative to basalt.

Icelandic hydrothermal water and calcite also have $\delta^{44/40}\text{Ca}$ values higher than basalt. Heavy calcite is highly unusual because most carbonate minerals form kinetically and incorporate lighter isotopes relative to their Ca source reservoir.

Uptake of lighter Ca isotopes during zeolitization may elevate the relative abundance of heavier Ca isotopes in hydrothermal waters from which calcite precipitates, but no systematic understanding has been established.

To better understand the Ca isotope geochemistry of zeolites, we used a high-precision thermal ionization mass spectrometry (TIMS) method to measure $\delta^{44/40}\text{Ca}$ values of six zeolite mineral species. We also analyzed bulk basalt, primary mineral separates, and calcite. Specimens were collected from the Berufjörður–Breiðdalur region of East Iceland, which is type-locality for the zeolitization of basaltic lava flows due to burial metamorphism. Here, increasing temperature with depth below the surface of the lava pile has generated distinct zeolite zones where two zeolite mineral types, referred to as coinex coin mineral pairs, distinctly form and thus are diagnostic of each depth zone (Fig. 1). Depth-controlled zeolite zones have been identified worldwide in active geothermal systems, as well as in extinct systems now exposed at the surface. We report a large range of zeolite $\delta^{44/40}\text{Ca}$ values, which is best explained by equilibrium isotope partitioning, given a strong observed correlation with Ca–O bond lengths. Our findings point the way for developing entirely new tools for investigating low-grade basalt alteration. They also broadly illustrate how future efforts focused on the Ca isotope geochemistry of zeolites could have implications for numerous other topics, such as understanding the compositional evolution of hydrothermal waters, quantifying elemental cycling in the oceans, and improving CCS strategies.

**Geologic setting**

Iceland is an exposed section of the Atlantic mid-ocean ridge overlying a mantle plume, which has caused extensive rifting and volcanism over the past 50–60 Myr. Rocks increase in age away from the active rift zone, with the oldest rocks at the edges of Iceland dating to ~16 Ma. Samples analyzed in this study were collected from Berufjörður–Breiðdalur region described in detail by Walker (1960) (Fig. 1). Successive eruptions of a Tertiary volcano supplied lava that piled to a minimum total thickness of ~2000 m at the eastern end. The central volcano comprises highly altered rhyolite, while the flows are predominantly tholeiitic basalt, with lesser amounts of olivine basalt. Within ~1 Myr after the eruptions ceased, heat from burial, as well as the volcanic center and associated dike swarms, extensively zeolitized the lava pile, filling up to 90% of the primary porosity. Pleistocene glacial erosion carved deep valleys and fjords into the lava pile and exposed the top ~1000 m of the altered sequence, where the depth-controlled zeolite zones are clearly delineated.
and accessible above sea level (Fig. 1). The shallowest zone studied here is the chabazite–thomsonite zone (~30–70 °C), followed by the mesolite–scolecite zone (~70–90 °C) and the stilbite–heulandite zone (~90–150 °C), which reaches a maximum depth of ~1500 m below the top of the lava pile31,39,64,73.

### Results

**Bulk basalt and primary minerals.** Table 1 presents elemental and Ca isotope data for bulk basalt and primary mineral separates. Bulk basalt samples from the Berufjörður–Breiðdalur region yield an average δ⁴⁴/⁴⁰Ca of −1.04 ± 0.08‰ (2σSD, n = 5), which agrees well with the average of −1.06 ± 0.02‰ (2σSD, n = 6) for basalt sampled from other regions throughout Iceland21. The primary minerals have a narrow range of δ⁴⁴/⁴⁰Ca values, which bracket those for bulk basalt. Olivine has the highest average δ⁴⁴/⁴⁰Ca (−1.02 ± 0.14‰, 2σSD, n = 3), followed by clinopyroxene (−1.05 ± 0.06‰, 2σSD, n = 3), apatite (−1.12 ± 0.06‰, 2σSD, n = 3), and plagioclase (−1.14 ± 0.04‰, 2σSD, n = 3).

**Calcite.** Table 1 presents elemental and Ca isotope data for calcite samples. The average δ⁴⁴/⁴⁰Ca equals −0.80 ± 0.20‰ (2σSD, n = 4), which is similar to the average of −0.79 ± 0.34‰ (2σSD, n = 13) for zeolite–zone calcite reported in Jacobson et al. (2015). Calcite consistently has higher δ⁴⁴/⁴⁰Ca than basalt and primary minerals.

**Zeolites.** Table 2 provides elemental and Ca isotope data for bulk zeolites. Stilbite has the highest average δ⁴⁴/⁴⁰Ca (−0.72 ± 0.24‰,

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### Table 1 Elemental and Ca isotope data for bulk basalt, primary mineral separates, and calcite.

| Sample ID | Ca (µmol/g) | Na (µmol/g) | Sr (nmol/g) | Mg (µmol/g) | δ⁴⁴/⁴⁰Ca (‰)  |
|-----------|-------------|-------------|-------------|-------------|---------------|
| ILR_D_6   | 1997        | 701         | 2845        | 1582        | −1.00         |
| ILR_D_13  | 1833        | 656         | 3168        | 1275        | −1.10         |
| ILR_12_f  | 1280        | 792         | 3145        | 1008        | −1.02         |
| ILR_12_m  | 1748        | 668         | 3049        | 1371        | −1.02         |
| ILR_12_l  | 1723        | 759         | 2894        | 1201        | −1.05         |
| Plagioclase|             |             |             |             |               |
| ILR_PL_16 | 3206        | 437         | 2139        | 69.1        | −1.12         |
| ILR_SJ_22 | 2800        | 753         | 8084        | 47.5        | −1.15         |
| ILR_SV_2  | 3212        | 460         | 2293        | 62.7        | −1.16         |
| Clinopyroxene|          |             |             |             |               |
| ILR_PL_16 | 3405        | 134         | 299         | 3633        | −1.03         |
| ILR_SJ_22 | 4023        | 141         | 560         | 3369        | −1.05         |
| ILR_SV_2  | 3873        | 94.7        | 189         | 3260        | −1.08         |
| Apatite   |             |             |             |             |               |
| ILR_PL_16 | 3162        | 448         | 2384        | 158         | −1.09         |
| ILR_SJ_22 | 2390        | 811         | 7883        | 56.5        | −1.14         |
| ILR_SV_2  | 3105        | 539         | 2589        | 185         | −1.14         |
| Olivine   |             |             |             |             |               |
| ILR_PL_16 | 344         | 51.9        | 119         | 9269        | −0.95         |
| ILR_SJ_22 | 2416        | 127         | 497         | 4605        | −1.08         |
| ILR_SV_2  | 900         | 51.4        | 104         | 6878        | −1.03         |
| Calcite   |             |             |             |             |               |
| ILM_C_15  | 9182        | —           | 140         | 0.72        | −0.66         |
| ILM_C_35  | 9120        | —           | 2428        | 3.37        | −0.89         |
| ILM_C_44  | 8802        | —           | 1916        | 23.6        | −0.86 (−0.87) |
| ILM_C_49  | 8710        | —           | 174         | 1.04        | −0.80         |

Duplicate analyses are shown in “( )”. Elements not detected are marked with “—”.

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**Fig. 1** Map of Iceland showing sample locations. a Mineral separates were obtained from basalts sampled throughout Iceland. The Berufjörður–Breiðdalur region of East Iceland is outlined. b Sampling locations of bulk rocks, calcite, and zeolites collected from the main region of study. c Zeolite sampling locations correspond to different elevations or depths below the original surface of the lava pile. Depth-controlled zeolite zones, adapted from Walker (1960), are overlain on a photograph of the Berufjörður volcanic sequence taken from the north.
Table 2 Elemental and Ca isotope data for bulk zeolite minerals.

| Sample ID    | Ca (µmol/g) | Na (µmol/g) | Sr (nmol/µmol) | Si (µmol/g) | Al (µmol/g) | δ⁴⁴/⁴⁰Ca (%) |
|--------------|-------------|-------------|----------------|-------------|-------------|--------------|
| Heulandite   |             |             |                |             |             |              |
| HD_1         | 1243        | 426         | 23,551         | 9706        | 3130        | -1.74        |
| HD_11        | 1350        | 468         | 26,254         | 9713        | 3209        | -1.72        |
| HD_18        | 1219        | 456         | 24,593         | 9753        | 3062        | -1.69        |
| HD_23        | 1280        | 447         | 26,143         | 9674        | 3107        | -1.90        |
| HD_28        | 1305        | 429         | 21,213         | —           | —           | -2.00        |
| Chabazite    |             |             |                |             |             |              |
| CZ_54        | 1698        | 163         | 17,815          | 7995        | 3662        | -1.72        |
| CZ_56b       | 1644        | 317         | 12,881          | 8240        | 3621        | -1.49        |
| CZ_62        | 1734        | 199         | 18,117          | 8003        | 3729        | -1.62        |
| Thomsonite   |             |             |                |             |             |              |
| TM_57        | 1368        | 328         | 515.1           | 9293        | 3240        | -0.91        |
| TM_58        | 1415        | 474         | 38.1            | 9263        | 3211        | -0.87        |
| TM_63        | 1412        | 680         | 120             | 8960        | 3483        | -1.04        |
| Scolecite    |             |             |                |             |             |              |
| SB_17        | 1417        | 161         | 41.1            | 9796        | 2946        | -0.62        |
| SB_69        | 1401        | 157         | 95.5            | 9543        | 2750        | -0.68        |
| SB_73        | 1462        | 209         | 535             | 9651        | 3015        | -0.85        |
| Mesolite     |             |             |                |             |             |              |
| MS_50        | 1786        | 1689        | 3951            | 7183        | 5604        | -1.78        |
| Scolecite    |             |             |                |             |             |              |
| SC_3         | 1857        | 80.2        | 53.7            | 7940        | 4907        | -0.84        |

Analyses not made due to limited sample sizes are marked with “-“.

Fig. 2 Zeolite δ⁴⁴/⁴⁰Ca versus burial depth. δ⁴⁴/⁴⁰Ca of bulk zeolites versus approximate burial depth in the Berufjörður-Breiðdalur region64. The orange line shows the average value for all basalt analyzed here and by Jacobson et al. (2015), with the width encompassing the standard deviation (−1.05 ± 0.06‰, 2σSD, n = 11). Error bars show external reproducibility (+0.05‰, 2σSD).

2σSD, n = 3), followed by scolecite (−0.84‰, n = 1), thomsonite (−0.94 ± 0.18‰, 2σSD, n = 3), chabazite (−1.58 ± 0.22‰, 2σSD, n = 4), mesolite (−1.78‰, n = 1), and heulandite (−1.81 ± 0.28‰, 2σSD, n = 5). δ⁴⁴/⁴⁰Ca for stilbite and heulandite agree with previously reported values21.

Discussion

Controls on zeolite δ⁴⁴/⁴⁰Ca: kinetic isotope effects. A striking observation is that for each zeolite zone64, coindex pairs have contrasting δ⁴⁴/⁴⁰Ca that bracket basalt, with one mineral lower and the other higher (Fig. 2). Relative to basalt, the zeolites chabazite, mesolite, and heulandite have low δ⁴⁴/⁴⁰Ca, while their respective pairs (thomsonite, scolecite, and stilbite) have high δ⁴⁴/⁴⁰Ca. Chabazite, mesolite, and heulandite represent some of the isotopically lightest minerals thus far measured6,26,74, neglecting those that host appreciable ⁴⁰Ca additions from the radioactive decay of ⁴⁰K75. The data provide good evidence that zeolites fractionate Ca isotopes, as bulk basalt and primary mineral separates show effectively no isotopic variability (Fig. 3).

Many studies have shown that kinetic fractionation during mineral precipitation causes preferential uptake of lighter Ca isotopes relative to the main Ca reservoir11,74. Other minerals measured thus far with low δ⁴⁴/⁴⁰Ca values similar to zeolites are mainly carbonates, which have experienced kinetic fractionation due to either variable precipitation rates13,14 or biogenic vital effects during mineral growth74. Kinetic effects resulting in low δ⁴⁴/⁴⁰Ca have also been observed in some high-temperature silicate minerals25,76,77. However, unlike carbonates and primary rock-forming silicate minerals, all Ca in zeolites is exchangeable34, therefore, it cannot be assumed a priori that kinetic fractionation mechanisms identified for the former minerals apply to zeolites. Kinetic isotope fractionation during mineral precipitation from solution mainly occurs due to incomplete exchange of ions or molecules, when transfer from solution to the solid proceeds more quickly than the reverse reaction9,11,78. Calcium ion exchange in zeolite minerals is equilibrium-controlled34,43, thus implying that forward and backward reaction rates are equal. Nevertheless, we consider below potential transport-related kinetic isotope effects.

Zeolites consist of an aluminosilicate tetrahedral framework, where cations occupy specific exchange sites within void channels33. Isomorphic substitution of Al³⁺ for Si⁴⁺ in the tetrahedra creates a net negative charge in the zeolite framework, which is balanced by the uptake of monovalent cations,
including Ca\(^{2+}\), from the coexisting solution\(^{33}\). Thus, coulombic forces related to charge density could in theory kinetically \(\delta^{44/40}\text{Ca}\) values support our assumption that bond lengths are shorter for zeolites with lower $\delta^{44/40}\text{Ca}$, consistent with the observation that stilbite (CN = 7) has nearly identical average Ca–O bond lengths and $\delta^{44/40}\text{Ca}$ values support our assumption that bond length better approximates the effect of bond strength for this particular mineralogical system. Therefore, we calculated an average Ca–O bond length for each unique Ca site and used this as a proxy for the average Ca–O bond length per mineral, assuming Ca is evenly distributed across all potential sites (Table 3).

When zeolite $\delta^{44/40}\text{Ca}$ values are plotted versus average Ca–O bond length per mineral (Fig. 4), five of the six zeolites studied generate a significant correlation ($R^2 = 0.93$, $p < 0.001$). In general, zeolites with lower $\delta^{44/40}\text{Ca}$ have longer approximate bonds (Fig. 2), consistent with previous research that reported similar trends. However, this pattern is not observed. For example, heulandite and thomsonite only need to break three hydration spheres containing lighter Ca isotopes\(^{80,101}\). If such a mechanism is applied here, then minerals with higher charge densities and more readily take up cations relative to those with higher Si/Al ratios and lower charge densities\(^{34,83}\). If kinetic effects related to rates of Ca uptake or diffusion fractionated Ca isotopes, then a trend between zeolite Si/Al ratios and $\delta^{44/40}\text{Ca}$ values should exist. However, we observe no trend for the present dataset, suggesting that charge density does not elicit kinetic isotope effects for these minerals (see Fig. S1).

One key point is that basalt represents the initial source of Ca in this system\(^{37,38}\). If the occurrence of zeolites with $\delta^{44/40}\text{Ca}$ higher than basalt was the result of a kinetic fractionation mechanism during mineral formation, then this would require that zeolites with lower $\delta^{44/40}\text{Ca}$ either precipitate faster or form first, thereby creating an isotopically enriched solution from which zeolites with higher $\delta^{44/40}\text{Ca}$ later precipitate, as no kinetic fractionation mechanism could result in the preferential uptake of heavier Ca isotopes. Calculations and experiments employing solution chemistry and thermodynamic conditions have been used to predict the progression of zeolitization\(^{84–87}\), and while petrographic evidence in some locations points to possible chronologic sequences of zeolites\(^{32,40,88,89}\), studies in Iceland indicate that the coindex pairs form simultaneously under similar conditions\(^{37,38,41,90}\). Furthermore, some coindex zeolite pairs analyzed here were intergrown and collected from a single amygdule, suggesting simultaneous precipitation. The absence of clear evidence for kinetically controlled reservoir effects is unsurprising, as all zeolite-bound Ca is extra-framework, with ion-exchange reactions between zeolites and fluids continuing after initial growth of the aluminosilicate framework\(^{43,66}\). Calculated equilibrium elemental compositions of zeolites, as well as those produced experimentally under equilibrium conditions, agree with geochemical analyses of natural Icelandic zeolites, which strongly indicates that the ion-exchange reactions are equilibrium-controlled\(^{43,44,66}\). Because zeolites with identical formation conditions have contrasting $\delta^{44/40}\text{Ca}$ and the ion-exchange processes governing Ca uptake are equilibrium-controlled, kinetic effects are unlikely to contribute to the $\delta^{44/40}\text{Ca}$ variations observed here.

Another interesting observation is that zeolites with lower $\delta^{44/40}\text{Ca}$ also have higher Sr/Ca (Fig. 3). During calcite precipitation, rate-dependent shifts in Ca isotope fractionation and Sr partitioning produce linear correlations between $\delta^{44/40}\text{Ca}$ values and Sr/Ca ratios\(^{13}\); however, the pattern observed in Fig. 3 for zeolites is nonlinear. In general, the understanding achieved for simple ionic solids does not immediately apply to more complex minerals, such as zeolites. Each zeolite studied here has a unique aluminosilicate framework. Incorporation of Sr into chabazite and heulandite, for example, is widely documented to reflect underlying structural characteristics, where zeolite framework topology and local bonding conditions give rise to larger exchange sites that prefer Sr relative to Ca\(^{33,43,91–93}\). The trend shown in Fig. 3 provides evidence that structural properties known to control Sr incorporation may also discriminate Ca isotopes as well.

**Controls on zeolite $\delta^{44/40}\text{Ca}$: equilibrium isotope effects.** We deduce that a fractionation mechanism related to mineral-specific Ca bonding conditions likely explains zeolite $\delta^{44/40}\text{Ca}$ variability. Previous research has shown that Ca isotope fractionation varies as a function of coordination number (CN)\(^{63,94–97}\), and relationships between $\delta^{44/40}\text{Ca}$ and Ca–O bond length have been identified for carbonates, phosphates, hydrox minerals, silicates, and aqueous calcium\(^{23,95–98}\). Both a function of bond length and CN, bond strength (stiffness) determines isotope fractionation, where stronger bonds preferentially concentrate heavier isotopes\(^{99}\).

The CN of Ca in zeolites can vary widely within each mineral because the minerals support a variety of exchange sites with unique Ca–O bonding conditions\(^{33}\). For example, Ca in chabazite could have a CN of 6 or 12 depending on which exchange site Ca occupies (Table 3)\(^{100}\). Moreover, within a given zeolite exchange site, Ca can coordinate to either framework oxygens (O\(_{\text{framework}}\)), those composing molecular water also contained within the framework (O\(_{\text{water}}\)), or some combination thereof. In general, Ca–O\(_{\text{framework}}\) bonds are considerably longer than Ca–O\(_{\text{water}}\) bonds at a given site; thus, Ca–O bond lengths can vary greatly within one individual site, as well as between sites within a single mineral (Table 3). The effect of CN on bond strength is documented for mineral systems where most of the bonds contributing to the CN of Ca have nearly equal lengths, relative to zeolites, which support highly different Ca–O bond lengths\(^{25,95–97}\). As the average CN of Ca per zeolite cannot take into account nonuniform bond lengths, the average Ca–O bond length per zeolite likely better approximates bond strength for this particular mineralogical system. Therefore, we calculated an average Ca–O bond length for each unique Ca site and used this as a proxy for the average Ca–O bond length per mineral, assuming Ca is evenly distributed across all potential sites (Table 3).

When zeolite $\delta^{44/40}\text{Ca}$ values are plotted versus average Ca–O bond length per mineral (Fig. 4), five of the six zeolites studied generate a significant correlation ($R^2 = 0.93$, $p < 0.001$). In general, zeolites with lower $\delta^{44/40}\text{Ca}$ have longer approximate Ca–O bond lengths, while zeolites with higher $\delta^{44/40}\text{Ca}$ have shorter approximate Ca–O bond lengths, consistent with equilibrium isotope fractionation theory\(^9,10\). While CN can adequately predict bond strength for many mineral systems\(^{26,63,74,94,95,97}\), the observation that stilbite (CN = 8) and scolecite (CN = 7) have nearly identical average Ca–O bond lengths and $\delta^{44/40}\text{Ca}$ values supports our assumption that bond length better approximates the effect of bond strength on Ca isotope fractionation for zeolites. We suggest that differences in zeolite Ca–O bond energies underlie the trend between $\delta^{44/40}\text{Ca}$ and bond length shown in Fig. 4, which we interpret as evidence for equilibrium isotope partitioning.

In the context of isotope fractionation between solution and mineral, it is important to consider Ca–O bonding dynamics in the surrounding fluid. Aqueous Ca\(^{2+}\) coordinates to water O atoms in coordination or hydration spheres, which have shorter Ca–O bond lengths than zeolites\(^{96}\). Icelandic groundwater has higher $\delta^{44/40}\text{Ca}$ values than zeolites (Fig. 4), consistent with predictions from equilibrium fractionation theory that stronger bonds preferentially concentrate heavier isotopes\(^{8–10}\). The exchange of Ca between groundwater and zeolite frameworks involves breaking a certain number of Ca–O\(_{\text{water}}\) bonds in the hydration spheres (desolvation) to create Ca–O\(_{\text{framework}}\) bonds\(^{82}\). Theoretical studies focusing on calcite have argued that desolvation can elicit kinetic isotope effects due to faster bond breaking of hydration spheres containing lighter Ca isotopes\(^{80,101}\). If such a mechanism is applied here, then minerals requiring more bond breaking of hydration spheres (i.e., those comprising fewer Ca–O\(_{\text{water}}\) bonds) should preferentially incorporate lighter Ca isotopes. However, this pattern is not observed. For example, heulandite and thomsonite only need to break three
| Mineral type | Site          | Number of Ca–Ow bonds, $N_w$ | Number of Ca–O$_{f_{mwk}}$ bonds, $N_{f_{mwk}}$ | Coordination number for site, $CN_s$ | Average Ca–Ow bond length, $l_w$ (Å) | Average Ca–O$_{f_{mwk}}$ bond length, $l_{f_{mwk}}$ (Å) | Average site Ca–O bond length, $l_s$ (Å) | $f_{Ca}$ in each site | Weighted average mineral Ca–O bond length, $L$ (Å) |
|--------------|--------------|-----------------------------|-----------------------------------------------|-------------------------------------|----------------------------------|------------------------------------------|------------------------------------------|----------------------|--------------------------------------------|
| Stilbite     | Ca-only      | 8                           | 0                                             | 8                                  | 2.45                             | 2.45                                     | 2.45                                     | 1                    | 2.45                                       |
| Mesolite     | Ca-only      | 3                           | 4                                             | 7                                  | 2.34                             | 2.51                                     | 2.44                                     | 1                    | 2.44                                       |
|              | Na-only      | 2                           | 4                                             | 6                                  |                                  |                                          |                                          | 0                    |                                            |
| Scolecite    | Ca-only      | 3                           | 4                                             | 7                                  | 2.34                             | 2.53                                     | 2.45                                     | 1                    | 2.45                                       |
| Thomsonite   | Ca-only      | 2                           | 4                                             | 6                                  | 2.39                             | 2.52                                     | 2.48                                     | 0.5                  | 2.52                                       |
|              | Ca or Na     | 4                           | 4                                             | 8                                  | 2.56                             | 2.57                                     | 2.57                                     | 0.5                  | 2.52                                       |
| Chabazite    | Cl- Ca-only  | 0                           | 6                                             | 6                                  | 3.05                             | 3.05                                     | 3.05                                     | 0.25                 | 3.05                                       |
|              | C2           | 0                           | 6                                             | 6                                  |                                  |                                          |                                          |                      |                                            |
|              | C3           | 8                           | 4                                             | 12                                 | 2.36                             | 2.82                                     | 2.51                                     | 0.25                 | 2.76                                       |
|              | C4- Ca-only  | 0                           | 8                                             | 8                                  |                                  |                                          |                                          |                      |                                            |
| Heulandite   | Ca2          | 5                           | 3                                             | 8                                  | 2.63                             | 2.85                                     | 2.71                                     | 0.333                | 2.79                                       |
|              | Ca or Na     | 4                           | 5                                             | 9                                  | 2.65                             | 2.81                                     | 2.74                                     | 0.333                | 2.79                                       |
|              | K3           | 2                           | 6                                             | 8                                  | 2.92                             | 2.93                                     | 2.93                                     | 0.333                | 2.93                                       |

The calculation accounts for different cation bonding sites within tetrahedral frameworks specific to each zeolite, as well as different lengths of Ca–O bonds that vary with the type of O atom participating in the bond. See “Methods” section for equations and supplementary information Table S2 for data sources.
Also shown are $\delta^{44/40}\text{Ca}$ data for calcite from this study and zeolite-zone calcite from Jacobson et al. (2015), as well as the average of natural groundwaters and pre-injection groundwaters from the CarbFix1 site, which circulate through active zeole zones analogous to the extinct system studied here. Calcite and groundwater Ca-O bond lengths are approximate. The black dashed line shows the average value for Icelandic basalt (−1.05‰) determined from this study and Jacobson et al. (2015). Average Ca-O bond lengths and $\delta^{44/40}\text{Ca}$ values of bulk zeolites strongly correlate ($R^2 = 0.93, p < 0.001$), when mesolite is excluded from the regression. The grey shading represents the confidence interval of this regression (see Supplementary information (S1) for details of the statistical model).

Fig. 4 Zeolite $\delta^{44/40}\text{Ca}$ versus estimated average Ca-O bond length.
Symbol size encompasses the external reproducibility (±0.05‰, 2σfl). Also shown are $\delta^{44/40}\text{Ca}$ data for calcite from this study and zeolite-zone calcite from Jacobson et al. (2015), as well as the average of natural groundwaters and pre-injection groundwaters from the CarbFix1 site, which circulate through active zeolite zones analogous to the extinct system studied here. Calcite and groundwater Ca-O bond lengths are approximate. The black dashed line shows the average value for Icelandic basalt (−1.05‰) determined from this study and Jacobson et al. (2015). Average Ca-O bond lengths and $\delta^{44/40}\text{Ca}$ values of bulk zeolites strongly correlate ($R^2 = 0.93, p < 0.001$), when mesolite is excluded from the regression. The grey shading represents the confidence interval of this regression (see Supplementary information (S1) for details of the statistical model).

Fig. 4. This zeolite and scolacite support identical Ca-site structures, but the mesolite framework also comprises alternating channels of Ca and Na sites. Our bond length estimate assumes that all Ca in mesolite resides in the Ca channel; however, Ca can substitute into the Na channel, where it coordinates to O$_{\text{inwk}}$ with much longer bonds than in the Ca channel. For this particular sample, it is possible that a substantial proportion of the Ca occupies the Na channel, where Ca–O$_{\text{inwk}}$ bond lengths are longer than our calculation estimates. Thus, the accumulation of lighter Ca isotopes in the Na channel could explain the sample’s lower $\delta^{44/40}\text{Ca}$ value. Similar observations of bond lengths varying with elemental substitutions have been made for calcite and other silicates, where Mg/Ca ratios discernably correlate with $\delta^{44/40}\text{Ca}$. An alternative explanation is that mesolite experienced kinetic isotope effects. The Ca sites in mesolite and scolacite have identical framework topologies, Ca–O bond lengths, and CNs. Theory for this scenario dictates that contrasting Ca isotope ratios could reflect kinetic isotope effects. However, because precipitation rate effects observed for other types of minerals do not apply to zeolites, which participate in equilibrium-controlled ion exchange after initial precipitation, the exact mechanism that would produce kinetic isotope effects is uncertain. Nevertheless, the data imply that mesolite is the most likely candidate of all zeolites examined here to have experienced kinetic fractionation. If correct, then our observation that mesolite plots off the line in Fig. 4 only supports equilibrium isotope partitioning for the other minerals.

Barring the one mesolite sample, bulk zeolite $\delta^{44/40}\text{Ca}$ values inversely vary with approximate Ca–O bond lengths. While we interpret this pattern to reflect inter-mineral equilibrium isotope partitioning, more research is needed to better constrain zeolite fractionation mechanisms. The correlation between zeolite Ca–O bond lengths and $\delta^{44/40}\text{Ca}$ values reported here is consistent with theoretical and laboratory, and field studies of other mineral types. To the best of our knowledge, our study is the first to report such effects for zeolites, as few studies have investigated $\delta^{44/40}\text{Ca}$ variability in minerals that form in nature at intermediate temperatures. Zeolites with low $\delta^{44/40}\text{Ca}$ values incorporate more Sr relative to Ca (Fig. 3). As Sr$^2+$ has a larger ionic radius than Ca$^{2+}$, these minerals presumably support larger exchange sites, consistent with Ca isotope evidence that the minerals have longer Ca–O bond lengths. We also note that zeolites appear to fractionate Sr isotopes, with heulandite and stilbite bracketing the composition for bulk basalt. Our overall interpretation is further consistent with an early investigation reporting that fractionation of Li and K isotopes by zeolites during ion exchange is largely equilibrium-controlled.

While structural differences between zeolite frameworks adequately explain $\delta^{44/40}\text{Ca}$ variability, we do note that Ca isotope offsets between the coindex pairs increases with depth (Fig. 2), which counters the expectation that higher temperatures diminish isotopic fractionation. This only underscores the first-order control of the mineral structure. Each zeolite has a unique framework structure, which gives rise to the positive correlation between the magnitudes of isotopic contrast and Ca–O bond-length differences between the coindex pairs. Zeolite $\delta^{44/40}\text{Ca}$ values may indirectly relate to formation temperature, as temperature determines which frameworks crystallize as a function of depth and structural properties appear to control Ca isotope fractionation (Fig. 4). However, the Ca isotope geochemistry of the minerals could more directly relate to the temperature of coexisting groundwater, as zeolites participate in equilibrium-controlled ion-exchange reactions after formation. Thus, calcium isotopes could be developed as a proxy for circulating fluid temperature; however, more studies are needed to better elucidate equilibrium versus kinetic controls on fractionation and fully quantify fractionation factors for each mineral relative to solution. Nevertheless, our present findings illustrate the potential for developing an entirely new geothermometer for investigating low-grade basalt metamorphism, as well as probing a diverse range of other environments where zeolites form.

Controls on hydrothermal water $\delta^{44/40}\text{Ca}$. Primary minerals display limited Ca isotope contrast and bracket $\delta^{44/40}\text{Ca}$ values of bulk basalt (Fig. 3). This confirms previous suggestions that the limited Ca isotope variability of Icelandic basalt is due to a narrow range of primary mineral $\delta^{44/40}\text{Ca}$. The source of fluid in the system studied here is meteoric, which implies that its initial $\delta^{44/40}\text{Ca}$ value is rock-dominated (~1‰). No evidence exists for
preferential Ca isotope release during primary silicate mineral dissolution for any silicate rock type. Therefore, hydrothermal waters and calcite in Iceland must be driven heavy as a byproduct of secondary light Ca sinks. During hydrothermal alteration of basalt, Ca-bearing zeolites and calcite are the two main sinks of aqueous Ca2+45,113, with zeolites forming distinctly prior to calcite38,45,48,90,114. Smectite and mixed layer clays form before zeolites, but they incorporate little Ca by comparison38,41,45,63,115. The low δ44/40Ca values of chabazite, mesolite, and heulandite indicate that fractionation by zeolites overshadows any effects due to Ca2+44 adsorption onto clays. If an appreciable amount of clay with low δ44/40Ca values formed prior to zeolites, then all zeolites would have elevated δ44/40Ca values, due to a reservoir effect, which is not the observed pattern. Thus, either clays are negligible Ca sinks or they have negligible Ca isotope fractionation factors. Recent research has attributed elevated δ44/40Ca values in CCS waters to the formation of isotopically light calcite29, but no such calcite, whether anthropogenic or natural, has been measured in the Icelandic system. However, similar to natural hydrothermal water65,116–119, CCS waters are supersaturated with respect to zeolites after periods of CO2 injection45,48,90. While some zeolites do show higher δ44/40Ca than basalt, the depth trend presented here is clearly asymmetric, where negative fractionations are larger (Fig. 2). Thus, it follows that progressive ion exchange with zeolites would elevate groundwater δ44/40Ca, supporting previous suggestions that uptake of lighter Ca isotopes by zeolites enriches hydrothermal waters in heavier isotopes21,50,120.

Studies of other groundwater systems have suggested that preferential uptake of lighter Ca isotopes by anhydrite or calcite elevates water δ44/40Ca values relative to source rocks19,20,121,122. Zeolites form ubiquitously at temperatures ranging from ~30 to 150 °C during the hydrous alteration of silicates in many diverse environments31,123. Our results emphasize a need to consider Ca uptake by zeolites in studies aimed at understanding the geochemical evolution of natural groundwater, as well as CCS waters monitored during mineral carbonation of basalt26,29,122,124.

**Controls on calcite δ44/40Ca.** The overlapping range of calcite and hydrothermal water δ44/40Ca values in Iceland suggests that Δ44/40Ca_cal-sol is close to 0‰21, similar to patterns documented in other natural systems, where calcite slowly forms about the state of chemical equilibrium125,126. Equilibrium isotope effects appear to control the Ca isotope composition of zeolites, given the strong linear correlation between zeolite Ca–O bond lengths and δ44/40Ca (Fig. 4). Many hydrothermal calcite samples also have δ44/40Ca values that closely approach this line, suggesting a similar control by Ca–O bond length. We, therefore, propose that the unusually high δ44/40Ca of Icelandic hydrothermal calcite reflects the influence of zeolites on hydrothermal water δ44/40Ca. Because calcite samples display a range of δ44/40Ca values (Fig. 4), it is possible that the lighter calcite samples may have precipitated from hydrothermal waters that isotopically evolved to differing degrees. Alternatively, kinetic isotope effects due to variable precipitation rates may have contributed to the lower δ44/40Ca of some calcites relative to hydrothermal water. Regardless, it is likely that many Icelandic hydrothermal calcites have δ44/40Ca values consistent with equilibrium isotope control.

While several studies have identified how variable Ca coordination controls inter-mineral equilibrium isotope partitioning63,108, few have determined the effects of CN on mineral–fluid Ca isotope partitioning during natural calcite growth127. Calcite supports only one Ca site having Ca–O bonds of uniform length97,128–130 therefore, unlike zeolites, the CN for calcite adequately approximates bond strength and related isotopic effects. Calcium in calcite coordinates to six O atoms128. Thus, calcite has a lower CN than any of the zeolites examined in this study, as well as shorter Ca–O bond lengths. It follows that calcite should have higher δ44/40Ca than zeolites, which is the relationship observed in Fig. 4. Experimental results and calculations have demonstrated that Ca isotope fractionation during mineral precipitation depends on the CN of mineral Ca, as well as the CN of aqueous Ca2+, which can range from six to ten80,95–97,131. Because Icelandic calcite appears to imprint the δ44/40Ca of hydrothermal waters and plot near the equilibrium-controlled zeolite Ca–O bond-length line, we suggest that aqueous Ca2+ in this system likely has a CN of six. Calcite, which has a known CN and a well-constrained Ca–O bond length, shows similar δ44/40Ca and bond length to Icelandic groundwater; thus, it follows that these reservoirs likely have similar CN. The isotopic offset between water and zeolites further implies that the CN of aqueous Ca2+ must be lower than those of zeolites (lowest CN = 7) and more similar to that of calcite (CN = 6). The apparent offset between Ca–O bond lengths for calcite and hydrothermal water (Fig. 4) is likely a consequence of our assumptions, as bond lengths in calcite vary with impurities97,98, and bond lengths for sixfold coordinated aqueous Ca2+ vary with temperature, ion pairing, and fluid ionic strength among other factors80,95,96,131,132.

Our results suggest that equilibrium-controlled calcite δ44/40Ca values could be used to identify the CN of aqueous Ca2+, and that laboratory studies able to control the CN of aqueous Ca2+ could better constrain equilibrium isotope effects in synthesized calcites. In this context, the equilibrium isotope offset between calcite and water (Δ44/40Ca_cal-sol), which is generally accepted to be ~0‰ given small Δ44/40Cacal-sol observed in natural settings where calcite precipitates at or near chemical equilibrium15,125,126, could be interpreted not only as an absence of kinetic isotope effects but also as an indication that aqueous Ca2+ and calcite both have a CN of six. This potentially has implications for various applications of the Ca isotope tracer, as the CN of aqueous Ca2+ can vary with ionic strength and temperature131,132, which could theoretically impact the equilibrium isotope fractionation factor between calcite and water. For example, if fluid Ca2+ was coordinated to eight oxygens instead of six (likely resulting in longer bond lengths in the hydration sphere134, Δ44/40Cacal-sol at equilibrium would be nonzero and positive, resulting in calcite that is enriched in heavier Ca isotopes95–97. Further work is needed to explore these ideas; however, our findings provide a valuable perspective on mineral–fluid isotope equilibrium, which could have implications for interpreting the δ44/40Ca values of marine carbonates deposited throughout geologic history.

**Conclusions**

This study reports Ca isotope data for natural zeolite minerals from Iceland, as well as hydrothermal calcite, bulk basalt, and primary mineral separates. Zeolite minerals display a δ44/40Ca range of ~1.4‰, which is on the order of the range exhibited by all igneous rocks thus far measured8,26. Zeolite δ44/40Ca values strongly correlate with average Ca–O bond lengths, which we interpret to reflect equilibrium isotope partitioning. The bond-length hypothesis presented here also provides some evidence that equilibrium isotope effects control Δ44/40Ca between hydrothermal calcite and waters, given that these reservoirs support similar Ca–O bond lengths and display small isotopic offsets. As equilibrium isotope fractionation factors strongly depend on temperature10, our findings suggest that the Ca isotope geochemistry of zeolite minerals could be developed into an entirely new geothermometer for investigating low-grade basalt
metamorphism. Moreover, zeolites should be considered in Ca isotope studies of other continental and oceanic hydrothermal systems where the minerals pervasively occur. Calcium isotopes hold particular promise for quantifying the mineralization of injected CO₂ during mineral carbonation of basalt, which is a leading CCS strategy 29,30. Our study characterizes the composition of key mineral reservoirs necessary for interpreting and modeling Ca isotope variations in both field and theoretical CCS studies. More research dedicated to the Ca isotope geochemistry of zeolites could help improve numerous environmental, industrial, and medical applications of the minerals.

Methods

Field collection. During the summer of 2017, zeolites, bulk basalt, and calcite were collected from various outcrops in the Berufjörður–Breiðdalsvík region of East Iceland. No permissions were required for sampling in this location. Mineral types were identified in the field and later confirmed by X-ray diffraction (XRD), as described below. Where possible, coindex zeolite pairs were collected from a single outcrop for every depth-zone described by Walker (1960), and calcite samples were collected from all rocks. Rock samples for primary mineral separates were collected from basaltic flows throughout Iceland (Fig. 1).

Sample preparation. Heavy liquids (Apatite-to-Zircon Inc., Viola, ID, USA) were used to separate mostly pure fractions of plagioclase, clinopyroxene, olivine, and apatite from three basalt samples with different ages and geologic histories. Intergrown zeolite samples from the same amygdaloidal basalt were physically separated. All basalt and mineral specimens, including primary minerals, calcite, and zeolites, were washed with MilliQ water and sonicated to remove excess sediment and impurities. Samples were dried in an oven at 50 °C and powdered by hand using a Diamonite mortar and pestle. Zeolites fundamentally differ from typical rock-forming silicate minerals, as their frameworks only comprise Al, Si, and O, that is, the minerals do not contain structurally bound Ca. All Ca is extra-framework, as it occurs in voids and channels created by the frameworks. Therefore, bulk measurements are most appropriate for characterizing the Ca isotope geochemistry of zeolites. Subsamples of basalt, primary mineral, and zeolite powders were completely digested using HF and HNO₃ acids. No insoluble residues were observed. Calcite powders were completely dissolved in 5% HNO₃. To further interrogate the Ca isotope geochemistry of zeolites, a sequential leaching and digestion procedure was applied. Supplementary information (S2) more completely describes this experiment, and the results are summarized in Table S3 and Fig. S2. The leaching solution clearly fractionated Ca isotopes, as indicated by correlations between δ⁴⁴/⁴⁰Ca and δ¹⁸O, δ¹³C, and δ¹⁵N (Fig. S4); therefore, leachate and residual digest δ⁴⁴/⁴⁰Ca values were excluded from the main interpretations of this study.

X-ray diffraction. The identities of zeolite specimens collected in the field were confirmed by XRD in the Integrated Molecular Structure Education and Research Center at Northwestern University. Powder XRD data were collected at room temperature on an STOE-STAII-P powder diffractometer equipped with an asymmetrical curved germanium monochromator (Csl(Kα) radiation, λ = 1.5406 Å) and a one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. Intensity data from 2θ ranges of 1°–10° were collected over a period of 30 min. The instrument was calibrated against a NIST Si standard (640d) prior to measurement.

Elemental analysis. Sample solutions were diluted with 5% HNO₃, and analyzed for concentrations of Na, Mg, and K, and Sr using a Thermo Scientific iCAP 6500 ICP-OES at Northwestern University. The concentrations have an uncertainty of ±5% (relative standard deviation), as determined by repeated analyses of NIST SRM 1643d. Concentrations of Si and Al were measured using a lithium metaborate fusion procedure and an Enviro II ICP-AES (Activation Laboratories, Ancaster, ON). These data have an uncertainty of ±5%.

Ca isotope ratios. Calcium isotope ratios (⁴⁴Ca/⁴⁰Ca) were measured with a Thermo Fisher Triton MC-TIMS in the Radiogenic Isotope Laboratory at Northwestern University, using an optimized ⁴⁴Ca–⁴⁰Ca double-spike procedure 31. Sample mixing was accomplished with Bi + Ag MP-50 cation-exchange resin. Approximately 12.5 µg of purified Ca was loaded onto outgassed, single Ta filament assemblies together with 0.5 µL of 10% H₂PO₄. Total procedural blanks (n = 4) determined with a ⁴⁰Ca isotope dilution method were negligible (65–117 ng). Reported δ⁴⁴Ca/⁴⁰Ca have an internal precision of ±0.02–0.03‰ in δ⁴⁴Ca/⁴⁰Ca relative to the ⁴⁰Ca double-spike standard, as determined by analyzing at least 8 OSIL ASW standards and 2 NIST 915b standards every 30 or fewer samples. During the period of study, repeated analyses of the standards yielded δ⁴⁴Ca/⁴⁰Ca = 0.00 ± 0.005‰ (2σ; n = 68) and δ⁴⁰Ca/⁴⁰Ca = −1.147 ± 0.012‰ (2σ; n = 17). These data correspond to a short-term external reproducibility (2σ) of ±0.045‰ for OSI ASW and ±0.049‰ for NIST 915b. Long-term records for the laboratory yield δ⁴⁴Ca/⁴⁰Ca = 0.000 ± 0.002‰ (2σ; n = 661) and δ⁴⁰Ca/⁴⁰Ca = −1.135 ± 0.003‰ (2σ; n = 263). These data point to a 2σ of ±0.04‰ for OSI ASW and ±0.048‰ for NIST 915b. Based on all standard measurements, we adopt a 2σ of ±0.05‰ for the present dataset. As shown in the data tables, duplicate analyses of sample unknowns are better than ±0.03‰. Long-term records for the laboratory yield an SRM915a value of δ⁴⁴Ca/⁴⁰Ca = −1.86 ± 0.01‰ (2σ; n = 68) relative to ASW; therefore, data reported here can be converted to the SRM915a scale using the following equation: δ⁴⁴Ca/⁴⁰Ca (%SMR915a) = δ⁴⁴Ca/⁴⁰Ca (%SMR915a) + 1.86‰.

Bond-length calculation. The weighted average bond length per zeolite mineral (l) was approximated by compiling published data on lengths for the two types of bonds (either Ca–Ow or Ca–Omw) specific to each exchange site containing Ca (Table S2). For some zeolites, Ca occupying a given exchange site can coordinate to both water O atoms and framework O atoms (Table 3). Because, in general, bond lengths differ depending on whether Ca coordinates to water O or framework O atoms, we calculated weighted average, site-specific bond lengths (l'), which account for differences in Ca–Ow bond lengths (l') and Ca–Omw bond lengths (l') according to the number of water O atoms (Nw) and framework O atoms (Nmw) available for coordination.

The equations are:

\[ l = \left( \frac{N_{\text{w}}}{N_{\text{w}} + N_{\text{mw}}} \right) l' + \left( 1 - \frac{N_{\text{w}}}{N_{\text{w}} + N_{\text{mw}}} \right) l'' \]

\[ l' = \left( \frac{l_{\text{w}} - L_{\text{w}}}{C_{\text{w}}} \right) + \left( \frac{l_{\text{mw}} - L_{\text{mw}}}{C_{\text{mw}}} \right) \]

\[ CN_{\text{w}} = N_{\text{w}} + N_{\text{mw}} \]

Where l is the estimated bond length per mineral (Å), l' is the weighted average site-specific bond length (Å), l'' is the average Ca–Ow bond length in a given site (Å), l' is the average Ca–Omw bond length in a given site (Å), Nw is the number of Ca–Ow bonds in a given site, Nmw is the number of Ca–Omw bonds in a given site, and CN is the coordination number of Ca in a given site.

The calculations adopted for Fig. 4 assume even distribution of Ca across all potential Ca-bearing sites (Table 3). Sensitivity to this assumption was tested by changing l'' to values that produce the minimum and maximum possible estimates of l for each mineral. The correlation remains significant for all scenarios (R² > 0.80, p < 0.001). See Supplementary information (S1) for more details on statistical analysis (Table S1).

Data availability

The authors declare that all data supporting the findings of this study are available within the paper and its Supplementary information files. Data used to generate Figs. 1–4 can also be found on Dryad (datadryad.org) using the following DOI link: https://doi.org/10.5061/dryad.dfn2z352s.

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Author contributions

C.J.N. conducted fieldwork, carried out laboratory analyses, interpreted the data, and wrote the manuscript. A.D.J. contributed to data interpretation and helped write the manuscript. G.D.K. contributed to data interpretation, edited the manuscript, and conducted statistical analyses and data visualization. T.B.W. provided support during fieldwork, contributed to data interpretation, and edited the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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