

Calcium isotopes in evaporites record variations in Phanerozoic seawater SO₄ and Ca

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ABSTRACT

Reconstructing variations in the major element chemistry of seawater provides constraints on how the global carbon and sulfur cycles have changed over geological time, but archives for this information are rare. This work generates a new independent record of ancient seawater composition, in particular the relative abundance of Ca and SO₄, through Ca isotope measurements in marine evaporites. Evaporite sequences that reach halite saturation record large Ca isotope variability if SO₄ > Ca, whereas a small range in Ca isotope ratios is observed if Ca > SO₄. Analyses of geological evaporites indicate SO₄-rich seawater in the Neogene and Permian and Ca-rich seawater in the Cretaceous and Silurian. These results agree with previous reconstructions using fluid inclusions in halite, and demonstrate a new approach for extending our understanding of oceanic and geochemical evolution.

INTRODUCTION

The major element chemistry of seawater is linked to the global carbon cycle and climate through weathering of silicate rocks, formation of clays, and burial of calcium carbonate, and to the oxidation of Earth's surface environment through cycling of seawater SO₄. Changes in seawater chemistry over the Phanerozoic have been proposed to explain a range of observations, including the occurrence of inorganic marine carbonates as either aragonite or calcite (Sandberg, 1983), the presence of MgSO₄ or KCl in late-stage evaporite minerals (Hardie, 1996), and the chemistry of fluid inclusions within evaporitic halite (Brennan and Lowenstein, 2002; Horita et al., 2002; Lowenstein et al., 2001, 2005). Many aspects of these records, however, remain untested. Several assumptions are required to transform fluid inclusion analyses into presumed seawater composition, due to the absence of certain ionic species, the evolved nature of the brine, and its extended storage in halite (Brennan et al., 2013). Other data sets, such as the composition of mid-ocean ridge flank veins (Coggon et al., 2010) and Mg/Ca ratios in well-preserved fossils (Dickson, 2002), generally confirm the direction of the fluid inclusion trends, but differences in the timing and magnitude of key changes suggest that the true seawater signatures contained in these records are yet to be resolved (Broecker, 2013).

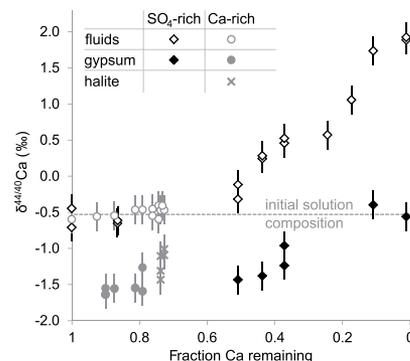
Ca isotope ratios in gypsum and anhydrite evaporites provide new independent evidence for intervals of Ca-rich seas and SO₄-rich seas. Seawater evaporation yields predictable mineral facies characterized by a progression from carbonates to sulfates to chlorides (Holser, 1979). Gypsum and anhydrite dominate the removal of Ca during these stages of evaporation in modern seawater, and previous work indicates that lighter Ca isotopes are preferentially removed while minerals from more advanced stages of evaporation become enriched in heavier isotopes (Harouaka et al., 2014; Hensley, 2006). In modern SO₄-rich seawater (SO₄/Ca = 2.7), nearly all the original Ca is depleted by sulfate minerals before reaching halite. Fluid inclusions within halite contain no Ca under these conditions, reflecting the excess of SO₄ over Ca (Lowenstein et al., 2001). This Rayleigh distillation of Ca yields a theoretical enrichment of >2‰ within sulfate evaporites, with mineral δ^{44/40}Ca values that may be greater than seawater [Ca isotope ratios are expressed as δ^{44/40}Ca, which equals $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$, where R is the ratio of ⁴⁴Ca/⁴⁰Ca in the analyte and the reference standard is modern seawater]. Such high δ^{44/40}Ca values are difficult to achieve by other means, as all major sources of Ca

are isotopically lighter than seawater, and all known mineral precipitation reactions are characterized by $\delta^{44/40}\text{Ca}_{\text{precipitate}} \leq \delta^{44/40}\text{Ca}_{\text{solution}}$ (Fantle and Tipper, 2014). In contrast, Ca-rich seawater with SO₄/Ca as low as 0.3, as predicted for the Silurian (Brennan and Lowenstein, 2002), would deplete SO₄ during gypsum and/or anhydrite precipitation while leaving excess Ca in the brine. Fluid inclusions record this chemical divide by the presence of Ca rather than SO₄. A smaller fraction of Ca removed from the brine yields a much smaller isotopic enrichment, <0.5‰, when halite saturation is reached. The degree to which Ca is distilled by SO₄, or vice versa, should be reflected in the δ^{44/40}Ca range observed in calcium sulfate minerals. This study analyzes Ca isotope behavior within evaporite formations from throughout the Phanerozoic to characterize oceanic chemistry during their periods of deposition.

EXPERIMENTAL RESULTS

A controlled laboratory precipitation experiment demonstrates the large δ^{44/40}Ca range possible from Rayleigh distillation of Ca during evaporite formation (Fig. 1). Artificial SO₄-rich and Ca-rich solutions were created to replicate modern and Silurian seawaters, respectively (Brennan and Lowenstein, 2002; Kester et al., 1967). Beakers were left to evaporate 1 kg of solution at room temperature, with regular sampling of fluid and crystals. The δ^{44/40}Ca of SO₄-rich seawater became enriched by 2.4‰ from its initial composition to the onset of halite precipitation, whereas the δ^{44/40}Ca of a Ca-rich solution evolved by only 0.2‰. These results are consistent with theory and indicate that Rayleigh distillation occurs in the brine. Gypsum crystals show a smaller range than predicted, likely due to inadvertent sampling of younger crystals during late-stage sulfate precipitation. The gypsum crystals are offset from the fluids by 1.0‰–1.3‰, with larger apparent offsets occurring with the most extreme isotopic enrichments. This fractionation may be dependent on additional factors such as temperature, precipitation rate, and crystal morphology (Harouaka et al., 2014), but the steady enrichment of the fluid suggests an apparent average fractionation of ~1.0‰. These experiments neglect the dynamic balance of evaporation and recharge of geological basins, but facies changes in evaporite sequences represent relatively fixed markers for seawater concentration and ensure that threshold concentration levels are reached. The appearance of halite indicates that seawater has been concentrated by a factor of 10–11. At this point, due to the solubilities of gypsum and anhydrite, either Ca or SO₄ will have become depleted in the brine, and the δ^{44/40}Ca value will reflect the degree of Ca distillation that has occurred.

Figure 1. Laboratory precipitation experiments. Black markers show progression of SO₄-rich seawater; gray markers show evaporation of Ca-rich seawater. Both experiments ran over 19 days, and attained halite saturation on the same day. Horizontal dashed line represents initial Ca isotope composition of the sol



GEOLOGICAL RESULTS

Massive subaqueous evaporite formations were analyzed from proposed periods of Ca-rich or SO_4 -rich seawater to identify the alternating pattern of Phanerozoic seawater chemistry. Sequences ideally contained intervals of halite, assuring maximum distillation of Ca, and also include the earliest evaporites within the stratigraphy. The youngest samples represent the Messinian Salinity Crisis, a period of evaporite deposition in the Mediterranean that commenced at 6.0 Ma (Krijgsman et al., 1999). The general basin stratigraphy contains a lower evaporite unit overlain by the main salt layer, followed by an upper evaporite unit (Hsü and Montadert, 1978). Ca isotope ratios were measured on upper evaporite samples from several DSDP (Deep Sea Drilling Project) and ODP (Ocean Drilling Program) expeditions (Fig. 2A). Site 654A (ODP Leg 107) on the upper Sardinian margin yielded 11 intervals of pure laminated gypsum (Kastens et al., 1987) with a range in $\delta^{44/40}\text{Ca}$ of 1.3‰. The highest, i.e., most isotopically enriched, values occurred at the base of the sampled interval. This stratigraphic ordering is opposite to the expectation of progressive enrichment upsection, but is likely due to basin recharge, rather than evaporation, during the period after major salt deposition. Site 654A evaporites likely record some nonmarine influence, based on Sr isotopic data (Hensley, 2006; Müller and Mueller, 1991), but the existence of highly enriched values, even above the $\delta^{44/40}\text{Ca}$ of modern seawater, cannot be achieved with terrestrial Ca sources and points to the influence of an evolved brine on the Ca isotopes of these deposits. Additional Messinian gypsum and anhydrite from Sites 374Z, 372Z, 376Z, 134Z, and 124Z (DSDP Legs 13 and 42) do not offer a coherent evaporitic stratigraphy on the scales we sampled (1 m to tens of meters), but yield a collective $\delta^{44/40}\text{Ca}$ range of 1.1‰ with a maximum value of +0.24‰. Enriched values during the Messinian in multiple Mediterranean basins are diagnostic of substantial Rayleigh distillation of Ca, indicating excess SO_4 in the seawater of the Neogene.

Site 627B from ODP Leg 101 on the southern Blake Plateau, north of the Little Bahama Bank, provides an example of evaporites from the purported Ca-rich sea of the Cretaceous (Lowenstein et al., 2001). The laminated, organic-rich dolomite and gypsum of Albian age (Austin et al., 1986) show a small range of <0.4‰ in gypsum $\delta^{44/40}\text{Ca}$ (Fig. 2B). The absence of halite prevents the full range of evaporative Ca distillation from being expressed, so these $\delta^{44/40}\text{Ca}$ values cannot be entirely diagnostic of a Ca-rich sea in the Albian.

Another Cretaceous evaporite sequence from the Sergipe-Alagoas Basin in Brazil also results in a $\delta^{44/40}\text{Ca}$ range of <0.4‰, and as this formation contains halite, is a stronger indication of a Cretaceous Ca-rich sea. The Ibura Member of the Muribeca Formation, of Aptian age (Timofeeff et al., 2006), contains anhydrite both below and above the major interval of salt deposition. The upper evaporites, deposited during basin recharge and consisting of nodular and massive anhydrites within muddy shales, were sampled within 15 m of halite in a core from Vale Potássio Nordeste near Aracaju. The small $\delta^{44/40}\text{Ca}$ range and lack of isotopic enrichment suggest that Ca was in excess of SO_4 in Aptian seawater (Fig. 2B).

The Castile Formation in the western Texas Delaware Basin (southwest United States) evinces a clear relationship between stratigraphy and

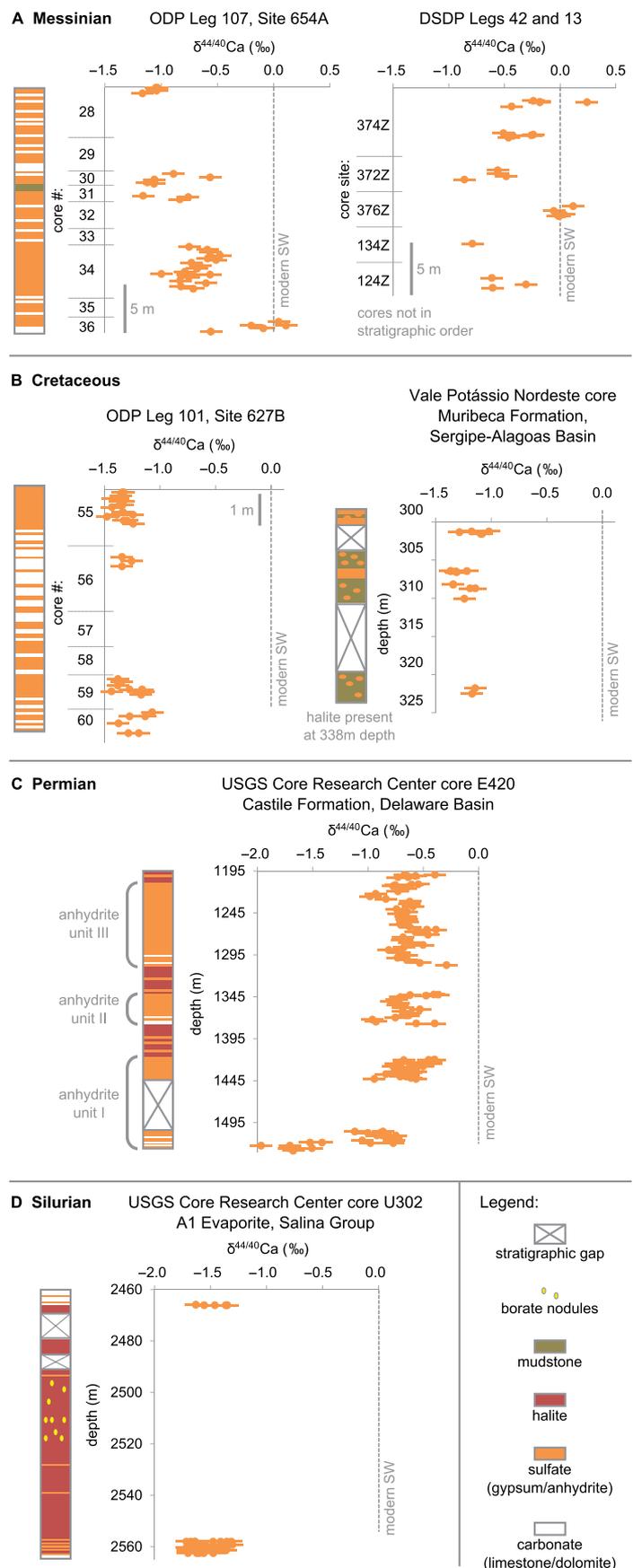


Figure 2. Ca isotope data from geological evaporite formations. **A:** Messinian upper evaporite samples from various Mediterranean basins. Vertical scales represent relative depth of recovered core material. Cores 374Z, 372Z, 376Z, 134Z, and 124Z (Deep Sea Drilling Project [DSDP] Legs 13 and 42) are not in vertical stratigraphic order. ODP—Ocean Drilling Program; SW—seawater. **B:** Gypsum from Cretaceous evaporites at Ocean Drilling Program Site 627B and anhydrite from the Muribeca Formation in the Sergipe-Alagoas Basin (Brazil). **C:** Anhydrite from the Permian Castile Formation in west Texas (USA). USGS—U.S. Geological Survey. **D:** A1-Evaporite from the Salina Group in the Michigan Basin (USA).

$\delta^{44/40}\text{Ca}$ indicating a SO_4 -rich sea during the Permian (Fig. 2C). Samples from the Union Oil 37-4 Univ core at the U.S. Geological Survey (USGS) Core Research Center include carbonate-anhydrite sequences separated by halite units tens of meters thick, reflecting massive subaqueous evaporite deposition (Dean and Anderson, 1978). The $\delta^{44/40}\text{Ca}$ range during carbonate-anhydrite intervals is 1.7‰. The lowest values are observed at the base of the core, and become enriched by 1.6‰ up to the first halite unit at 1420 m. In the next anhydrite interval from 1377 to 1342 m, $\delta^{44/40}\text{Ca}$ values initially drop by 0.6‰ before increasing again, and this pattern repeats in the next anhydrite unit starting at 1307 m. These trends in $\delta^{44/40}\text{Ca}$ follow the concentration and recharging of the basin that is expected according to the evaporite facies changes. The most evaporative anhydrites record the largest enrichment from the $\delta^{44/40}\text{Ca}$ at the base of the core, with a large range indicating an excess of SO_4 over Ca in Permian seawater.

The Silurian Salina Group in the Michigan Basin (Michigan and surrounding states, USA) records different Ca isotope behavior than the Messinian and Permian sections (Fig. 2D). The JEM Bruggers 3-7 core from the USGS Core Research Center is predominantly halite, and has yielded fluid inclusions that suggest a low Mg/Ca calcite sea (Brennan and Lowenstein, 2002). Ca isotope ratios from anhydrite intervals within the halite show very little variation; values are between -1.7‰ and -1.3‰. Samples from the carbonate-anhydrite layer just overlying the halite unit record similar values, giving no evidence for enriched evaporative brines. This narrow range of 0.4‰, similar to that of the Cretaceous, suggests that Ca was in excess of SO_4 during the Silurian.

DISCUSSION

The behavior of Ca isotopes in evaporite formations is a clear indication of large changes in the relative concentrations of the major ions of seawater throughout the Phanerozoic (Fig. 3). With Ca-rich seas, the degree of $\delta^{44/40}\text{Ca}$ enrichment in sulfate evaporites should be sensitive to the magnitude of Ca excess over SO_4 , but the difficulty in observing the full range of Rayleigh enrichment in sulfate precipitates likely limits the ability to reconstruct seawater Ca and SO_4 concentrations quantitatively. Complications may also arise from local and/or regional dolomitization, as the Ca released during secondary dolomitization could have a $\delta^{44/40}\text{Ca}$ value much lower than seawater. In general, other sources of Ca, such as riverine input, must be small relative to seawater-derived Ca in order to express the full $\delta^{44/40}\text{Ca}$ range. However, the introduction of nonmarine Ca from dolomitization, riverine input, or other water-rock interaction is expected to be isotopically light and therefore likely to reduce the observed $\delta^{44/40}\text{Ca}$ range, such that a reduced range is less clearly indicative of high Ca, but a large range and highly enriched values are strongly diagnostic of high SO_4 .

Reactions that convert gypsum to anhydrite, and more rarely the reverse, are not expected to alter original $\delta^{44/40}\text{Ca}$ values, as these are dewatering-watering transitions and do not involve significant mass transport of Ca or SO_4 (Holser, 1979). A marine origin for evaporites is also essential for this approach (see the GSA Data Repository¹), because playa evaporite $\delta^{44/40}\text{Ca}$ appears to reflect different processes (Fantle et al., 2012). The importance of carbonate deposition on the $\delta^{44/40}\text{Ca}$ range of sulfate minerals is expected to be small, as carbonates currently account for <10% Ca removal and therefore <0.1‰ enrichment in $\delta^{44/40}\text{Ca}$. The very similar fractionation factors for carbonate and gypsum precipitation, and the experimental results that closely match the theory, suggest that carbonate does not significantly affect gypsum $\delta^{44/40}\text{Ca}$ ranges. As the Ca: CO_3 ratio rises in evaporative brines and reduces the fractionation for carbonate precipitation (Nielsen et al., 2012),

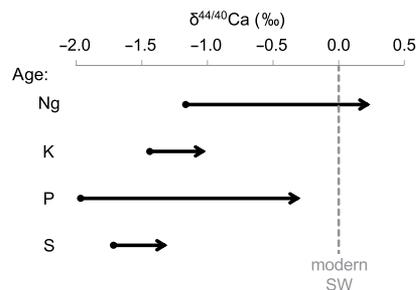


Figure 3. Summary of Ca isotope evaprites in geological evaporites. Ng—Neogene, K—Cretaceous, P—Permian, S—Silurian; SW—seawater. Large ranges for Neogene and Permian samples suggest SO_4 -rich seas, while restricted ranges in the Cretaceous and Silurian suggest Ca-rich seas.

carbonate phases are expected to have an even smaller effect on overall brine $\delta^{44/40}\text{Ca}$ enrichment.

In addition to providing a constraint on the relative abundance of seawater Ca and SO_4 , the lowest $\delta^{44/40}\text{Ca}$ values measured in sulfate evaporites, representing the first gypsum and/or anhydrite deposition, may be offset from seawater by a constant factor and thus provide a constraint on the evolution of Phanerozoic seawater Ca isotopes. Reconstructions of the $\delta^{44/40}\text{Ca}$ of seawater using the lowest $\delta^{44/40}\text{Ca}$ values in each of the evaporite sequences and a fractionation of 1.0‰ yield seawater Ca isotope ratios (Fig. DR1 in the Data Repository) that differ somewhat from records of carbonate fossils (Farkaš et al., 2007). A study of Ordovician limestone and anhydrite also conflicts somewhat with the carbonate fossil $\delta^{44/40}\text{Ca}$ curve and suggests that Ordovician seawater was isotopically heavier than predicted (Holmden, 2009). The cause of these discrepancies is currently unclear, although the effects of dolomitization and groundwater discharge on regional or global scales are possible sources for divergence of these records (Holmden et al., 2012). Further sampling of Phanerozoic evaporite sequences, using analyses from sulfate facies, can provide an independent record to test the evolution of seawater $\delta^{44/40}\text{Ca}$.

CONCLUSIONS

This work establishes a new archive for determining the extent and timing of the SO_4 -Ca chemical divide. Evaporite formations that are not rich in fluid inclusions or that do not contain halite can also be useful in determining the chemistry of ancient seawater, although evidence of the former presence of halite in the form of molds, casts, or pseudomorphs would be most effective. In the deeper geological record, where halite is rare and the history of marine SO_4 is central for understanding surface redox conditions, analyses of gypsum and anhydrite could yield unique records of seawater composition. This previously untapped archive of evaporitic sulfates can reveal the history of major geochemical cycles and their feedbacks on the marine environment.

APPENDIX: METHODS

Batch evaporation experiments were set up with artificial seawater solutions and evaporated over approximately three weeks. Samples of fluid and gypsum or halite crystals were taken regularly, and major ion concentrations were determined on a Thermo Dionex 5000+ ion chromatography system. Geological evaporites were powdered, analyzed by X-ray diffraction, and dissolved for ion chromatography. Other samples were directly dissolved or diluted in 2N HCl. Dissolved samples were prepared for Ca isotope analysis with two-stage column chemistry (Blättler et al., 2011). Ca isotope measurements were performed on a Neptune Plus multicollector-inductively coupled plasma-mass spectrometer in medium resolution with an ESI Apex-IR sample introduction and desolvation system. Standard-sample-standard bracketing is used to define $\delta^{44/42}\text{Ca}$ relative to an in-house standard, which is converted to $\delta^{44/40}\text{Ca}$ relative to seawater. Long-term external reproducibility on $\delta^{44/40}\text{Ca}$ is 0.1‰, based on replicate measurements of standards. (For extended descriptions of methods, see the Data Repository.)

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¹GSA Data Repository item 2014265, extended methods, supplemental Figures DR1–DR3, and data tables DR1–DR7, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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