Making Salt from Water: The Unique Mineralogy of Alkaline Lakes

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Sodium carbonates precipitating on the edge of Liberty Lake in the Cariboo Plateau, central British Columbia, Canada. Photo: Maija Raudsepp.

Alkaline lakes have some of the most unique and diverse known mineral assemblages as a result of their very high pH and dissolved inorganic carbon concentrations. In these closed-basin systems, aqueous geochemistry and mineralogy are intimately linked, whereby the removal of elements through mineral precipitation controls the lake water geochemistry. The resulting extreme water chemistry of alkaline lakes produces minerals that are rare in other environments, including low-temperature minerals that record valuable environmental information and that are commonly extracted as mineral resources. Alkaline lakes are also excellent environments to study various processes in mineral crystallization, growth, and transformation, including the formation of metastable phases, precipitation after extreme supersaturation, co-precipitation of minerals, and the influence of dynamic conditions.

KEYWORDS: alkaline lakes; carbonates; chemical sediments; crystallization; mineral behavior

INTRODUCTION

Alkaline lakes are extraordinary places to study the precipitation and stability of low-temperature minerals, partitioning of major and trace elements, and cycling of nutrients among minerals, solutions, and microbes. These environments have been well studied from a sedimentological perspective, but work remains to integrate recent discoveries in mineralogy, geochemistry, and geobiology into the study of alkaline lakes as complex biogeochemical systems. Every lake on Earth is a microcosm with a distinct evolutionary path—an opportunity to watch an ocean evolve in 117,000,000 different ways (Verpoorter et al. 2014). Alkaline lakes can have strikingly different water chemistry and mineralogy, even when they are in close proximity to one another, making them ideal environments to test hypotheses about how solution chemistry controls mineralogy and vice versa.

Broadly, more "moderate" alkaline lakes precipitate Ca- and Mg-carbonate minerals, whereas "extreme" alkaline lakes precipitate Na-carbonates. Accessory minerals contain other cations and anions that have accumulated in these highly saline closed basins. While the main principles of geochemical divides control the major cation and anion constituents of alkaline lakes (Tosca and Tutolo 2023

this issue), the specific mineral assemblage in a particular lake can have a more complex origin. For example, carbonate precipitation sometimes follows Ostwald's step rule, whereby the phase that first precipitates is the one that is most kinetically probable rather than most thermodynamically stable. Mineral precipitation and dissolution can also be affected by the dynamic equilibrium conditions that exist in lakes, including wetting and drying cycles, freezing and thawing, spring water discharge, and fluctuations in temperature and pCO_2. Alkaline lakes also have high biological productivity (Haines et al. 2023 this issue), which may result in enhanced biologically induced carbonate precipitation. Depending on the bedrock geology of the basin, alkaline lakes can become enriched in other cations and anions, which may result in co-precipitation of sulfates, borates, and fluorides alongside carbonate minerals.

Here, we review some characteristic and surprising mineral occurrences seen in alkaline lakes. We begin with carbonate mineralogy, starting with lakes with Ca- and Mg-rich compositions and finishing with more extreme Na-rich ones. This is followed by a brief description of other minerals that form in alkaline lakes. Finally, we discuss (1) how alkaline lakes can inform mineral behavior studies in the laboratory and field and (2) outstanding questions about the mineralogy of alkaline lakes and opportunities to use mineralogy to better understand their biogeochemistry.

Ca–Mg-CARBONATES IN ALKALINE LAKES: ROLE OF METASTABLE PHASES AND KINETICS

Ca-carbonate Phases

Terrestrial carbonate sedimentation generally occurs in two distinct environments: (1) closed-basin, evaporitic lakes and playas in arid environments and (2) fresh or brackish hard water (i.e., Ca + Mg > 1 mEq/L) in humid environments (Kelts and Hsü 1978). Calcite, the most stable polymorph of $CaCO_3$, is the dominant precipitate in fresh and brackish hard water. It often precipitates during the summer when water temperatures are warmer and there are blooms of photosynthesizing organisms (Kelts and Hsü 1978). Calcite precipitation in evaporitic lakes is the first geochemical control on the evolution of water chemistry and the formation of chemical divides (Tosca and Tutolo

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FIGURE 1 (**A**) Calcite tufa spires containing "thinolite" textures on the shores of Mono Lake, USA. REPRODUCED FROM DELLA PORTA (2015) WITH PERMISSION FROM THE GEOLOGICAL SOCIETY. (**B**) Sediment composed of magnesite and very high magnesium calcite (VHMC) in the dry season in Milne Lake, Australia. PHOTO: SASHA WILSON. (**C**) Seasonal formation of a natron crust in the autumn after almost complete evaporation of Last Chance Lake, Cariboo Plateau, Canada. PHOTO: NINA ZEYEN. (**D**) Formation of trona rafts on southern Nasikie Engida, Kenya. REPRODUCED FROM RENAUT ET AL. (2021) WITH PERMISSION FROM JOHN WILEY AND SONS.

2023 this issue). For lakes that evolve along the alkaline pathway (ALK > 2[Ca], where ALK indicates alkalinity), precipitation of Ca-carbonates sequesters Ca and enriches the remaining water in Mg, resulting in Mg/Ca ratios that are often much higher than that of seawater (i.e., Mg/Ca ≈ 5.2). This Mg enrichment is key to the formation of Ca–Mg- and Mg-carbonate minerals, and controls which Ca-carbonate polymorph precipitates in alkaline lakes. When the Mg/Ca ratio is high, aragonite often dominates. Precipitation of either calcite or aragonite is controlled in part by differences in their crystal structures. Whereas calcite-group minerals can incorporate both Ca and Mg, the crystal structure of aragonite almost completely excludes smaller Mg ions owing to the nine-fold coordination of its large cation sites. The often observed preferential formation of aragonite over Mg-calcite in waters with Mg/Ca ratios greater than 2 is not due to a difference in solubility between pure calcite and Mg-calcite (Sun et al. 2015). Instead, uptake of Mg into calcite increases its surface energy and inhibits nucleation and growth, thus favoring aragonite formation (Sun et al. 2015).

Calcium-carbonate minerals play a crucial role in the formation of microbialites (benthic sedimentary deposits consisting of carbonate mud formed through the mediation of microbes), such as stromatolites, which preserve much of the history of early life on Earth and are generally restricted to alkaline lakes today. In Turkey, the discharge of Ca-rich spring water into Lake Van, the world's fourth largest lake and largest alkaline lake (3570 km^2), has resulted in growth of the largest known modern microbialites, at an impressive height of 40 m (Kempe et al. 1991). Other metastable Ca-carbonate phases, such as vaterite (CaCO$_3$) and monohy-

drocalcite (CaCO$_3$·H$_2$O), can occur in laboratory synthesis experiments but are very rare or poorly preserved in alkaline lakes. For example, although monohydrocalcite has been reported in living microbialites in several volcanic lakes in Mexico, it is likely a transient phase that is ultimately replaced by aragonite or Mg-calcite (Zeyen et al. 2021).

The hydrated Ca-carbonate mineral, ikaite (CaCO$_3$·6H$_2$O), features in an interesting story of dynamic equilibrium involving the dramatic tufa mounds at Pyramid Lake and Mono Lake in the United States (FIG. 1A). These tufa pinnacles formed from the sublacustrine discharge of Ca-rich spring waters into the large alkaline lakes that existed during the Pleistocene (Della Porta 2015). For many years, the origin of "thinolite" textures (monoclinic prismatic forms of calcite) in these spires was unknown; however, documentation of ikaite formation in Mono Lake unraveled this mystery (FIG. 2D; Bischoff et al. 1993). Most common carbonate minerals have retrograde solubility, i.e., they are more soluble at low temperatures and less soluble at high temperatures, which controls everything from the formation of scale in your tea kettle to the carbonate compensation depth in the global oceans. In contrast, ikaite, a monoclinic hydrated Ca-carbonate, has prograde solubility, i.e., it is less soluble at low temperature. Ikaite is also more thermodynamically stable than calcite at low temperatures (Chaka 2018). Ikaite forms at near freezing temperatures in the winter during the mixing of sublacustrine springs and lake water, and builds carbonate spires over the course of years (Bischoff et al. 1993). When the temperature of the lake water increases in spring, ikaite transforms into calcite, preserving the original ikaite crystals as "thinolite" pseudomorphs. Because of a seasonal sampling bias brought about by researchers preferring to do fieldwork in the summer, and by poor preservation, we may be missing the role of ikaite precipitation in other temperate and polar alkaline lakes during the winter months.

### *Magnesite and Very High Magnesium Calcite (VHMC): Kinetically Inhibited Mg-containing Carbonates*

Some alkaline lakes and playa sediments contain modern low-temperature magnesite (MgCO$_3$) and very high magnesium calcite (VHMC; Ca$_{0.5}$Mg$_{0.5}$CO$_3$, also referred to as poorly ordered/disordered dolomite or protodolomite). These phases are kinetically inhibited from forming under Earth's ambient surface conditions because of the slow dehydration kinetics of the Mg^{2+} cation. There has been extensive interest in determining the biogeochemical processes and environmental conditions that promote the formation of these phases. The interest in VHMC is often related to it being a precursor to dolomite [CaMg(CO$_3$)$_2$], which formed abundantly from Earth's ancient Precambrian oceans, but not from the modern (i.e., Holocene) ocean despite it being supersaturated with

both VHMC and dolomite (i.e., the "dolomite problem"). Additionally, carbonate mineral formation in alkaline lakes is a natural analogue for accelerated CO_2 fixation. Advancing our mechanistic understanding of how highly stable carbonates form, particularly the most stable of the Ca- or Mg-carbonates, magnesite, is fundamental to developing economically viable CO_2 removal and carbon capture, utilization, and storage technologies (Power et al. 2009).

Alkaline lakes are able to overcome the kinetic constraints on low-temperature formation of VHMC and magnesite. Modern VHMC and magnesite are authigenic in alkaline lakes, precipitating directly from solution. For example, VHMC forms from the overlying surface water in Deep Spring Lake, USA (Meister et al. 2011), and magnesite forms from the porewaters of the Atlin playas, Canada (Power et al. 2019). Compared with alkaline lakes that accumulate Ca-carbonates, lakes precipitating VHMC and magnesite are generally more saline, have enriched carbonate alkalinity and Mg/Ca ratios in their surface and/or porewater, and typically undergo seasonal desiccation. These lakes are often associated with mafic and ultramafic bedrocks, and are thus coupled with the weathering of Mg-rich landscapes, such as the ophiolitic ultramafic bedrock of the Atlin playas (Power et al. 2009) and Lake Salda, Turkey (Balci et al. 2020), or the basaltic bedrock of the Cariboo Plateau, Canada (Renaut and Long 1987). Microbial activity, such as photosynthesis or sulfate reduction, generates further alkalinity, while carboxylated surfaces, such as exopolymeric substances and microbial cell walls, provide key nucleation sites for dehydrating and concentrating cations, such as Mg^{2+} and Ca^{2+}. Formation of VHMC and magnesite via non-classical crystallization pathways, such as through highly soluble amorphous precursor phases or growth by particle attachment, may be favored because of the slow kinetics of classical crystallization for Mg-carbonates. Non-classical crystallization has been proposed as the formation mechanism for these phases in the Coorong Lakes, Australia, as evaluated using high-resolution electron microscopy (Fig. 2C; Raudsepp et al. 2022). As such, saturation indices of waters relative to amorphous precursors can be a useful tool for understanding how the equilibrium chemistry of soluble amorphous phases may control (Ca–)Mg-carbonate formation (e.g., Zeyen et al. 2021; Raudsepp et al. 2022).

Magnesite is sometimes proposed to form via progressive transformation of crystalline hydrated Mg-carbonates, mainly based on high-temperature laboratory studies. Although this may occur on geologic timescales, several recent studies in alkaline lakes suggest otherwise. Magnesite in the Atlin playas, for example, is a nucleation-limited primary precipitate that does not form via dehydration of hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] despite their co-occurrence in sediments (Power et al. 2019). Likewise, magnesite in the microbialites of Lake Eras, Spain, forms via biologically induced primary precipitation, which excludes transformation from hydrated precursors (Sanz-Montero et al. 2019). Growth of magnesite by particle attachment, a non-classical growth mechanism, in Milne Lake, Australia, which does not contain hydromagnesite, also supports the hypothesis that magnesite commonly forms directly from an amorphous precursor rather than hydromagnesite (Fig. 1B; Raudsepp et al. 2022). It is also notable that Milne Lake magnesite can contain ~10 mol% Ca, while the crystal structure of hydromagnesite does not allow for Ca substitution. Precipitation and transformation of hydrated Mg-carbonates can alter porewater chemistry, and thus may be an important indirect control for magnesite formation
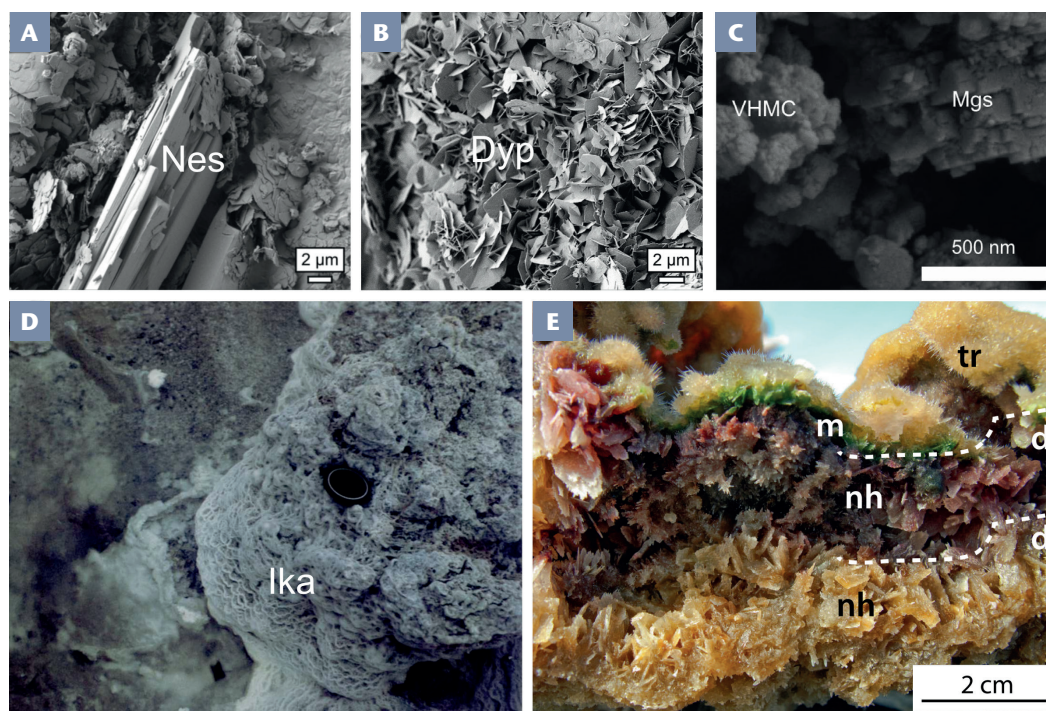
FIGURE 2 (**A–C**) Scanning electron microscopy images and (**D–E**) photographs of carbonates from various alkaline lakes. (**A**) Nesquehonite (Nes) and (**B**) dypingite (Dyp) from Atlin, Canada. Reproduced from Power et al. (2019) with permission from Elsevier. (**C**) Very high magnesium calcite (VHMC) and magnesite (Mgs) from Milne Lake, Australia. Modified from Raudsepp et al. (2022). (**D**) Ikaite (Ika) precipitation around a cold water spring in Mono Lake, USA. Reproduced from Bischoff et al. (1993) with permission from Elsevier Science & Technology Journals. (**E**) Trona (tr) and nahcolite (nh) precipitation resulting from volcanic CO_2 degassing at Nasikie Engida, Kenya. The boundaries between crystal layers (dashed lines), dissolution contacts (d), and green microbe-rich layers (m) are delineated. Reproduced from Renaut et al. (2021) with permission from John Wiley and Sons.

(Power et al. 2019). Magnesite with ~25 mol% Ca, often described as huntite (e.g., Sanz-Montero et al. 2019), has also been observed in alkaline lakes.

Hydrated Mg-carbonates

It remains unresolved why some alkaline lakes are dominated by magnesite, while others contain abundant hydrated Mg-carbonates (e.g., hydromagnesite). However, Mg/Ca ratios in solution have been linked to which Mg-carbonate phases precipitate (summarized by Zeyen et al. 2021). Hydrated Mg-carbonates include lansfordite ($MgCO_3 \cdot 5H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$), dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot \sim 5H_2O$], and hydromagnesite, in order of increasing stability and decreasing hydration state (Chaka 2018). Mineral formation and transformation through these phases is complex and dependent on a range of environmental variables, including temperature, pH, pCO_2, and humidity. Lansfordite and nesquehonite are too unstable for long-term preservation in the sediment of alkaline lakes and are not often documented. As an exception, in the subarctic Atlin playas, lansfordite forms abiotically as subsurface hardpans when capillary action draws $Mg-HCO_3$ groundwater toward the surface where it evaporates (Power et al. 2019). Lansfordite readily precipitates from alkaline waters at <10 °C, while nesquehonite, with its distinct needle-like morphology (Fig. 2A), forms at ambient temperatures, either as a dehydration product of lansfordite or as a primary precipitate from solution. For example, nesquehonite forms evaporative crusts on the surface waters at Atlin (Power et al. 2019) and on decaying microbial mats in Lake Eras, Spain (Sanz-Montero et al. 2019).

Dypingite and hydromagnesite are distinctive flakey minerals containing hydroxyl in their crystal structures, and thus their solubility is more pH dependent. For example, these phases can form via the release of hydroxyls during oxygenic photosynthesis, which can locally increase pH within a microbial mat, even in otherwise well-buffered alkaline water. Microscopy shows dypingite is strongly associated with cyanobacterial mats at Atlin (Fig. 2B; Power et al. 2009). Dypingite is structurally similar to hydromagnesite, while containing more H_2O, and can form either as an intermediate in the nesquehonite-to-hydromagnesite transformation or as a primary precipitate at ambient temperatures. Hydromagnesite is the most stable and abundant hydrated Mg-carbonate in alkaline lakes. Its formation is kinetically controlled at <40 °C, and it can form by the sequential transformation of metastable crystalline precursor phases via Ostwald's step rule, such as is observed at Atlin (Power et al. 2019). Hydromagnesite in microbialites from Lakes Alchichica and Atexcac, Mexico, also likely formed via the sequential transformation of amorphous magnesium carbonate and nesquehonite (Zeyen et al. 2021). Hydromagnesite also precipitates within microbialites that fringe other alkaline lakes, including Lake Eras, Spain (Sanz-Montero et al. 2019), and Lake Salda, Turkey (Balci et al. 2020).

While many alkaline lakes only contain a single carbonate phase, alkaline lakes can contain assemblages of co-occurring aragonite and hydrated Mg-carbonate minerals. In the modern wetland at Atlin, aragonite and dypingite precipitate within benthic cyanobacterial mats, with only the aragonite preserved in the sediment (Power et al. 2009). Other examples of the co-occurrence of aragonite and hydromagnesite include the sediment in North Stromatolite Lake, Australia (Raudsepp et al. 2022), and stromatolites in Lakes Alchichica and Atexcac, Mexico (Zeyen et al. 2021). It is unclear what geochemical conditions favor the splitting of cations into pure Ca-carbonate (aragonite) and

pure Mg-carbonate (e.g., hydromagnesite) phases over the precipitation of VHMC, which contains Ca and Mg in a single carbonate phase. The formation of mineral assemblages with two or more Ca- and/or Mg-carbonate minerals is likely due to kinetic limitations on the precipitation of Mg-containing carbonates, as discussed above, or perhaps sequential crystallization. Interestingly, laboratory experiments examining crystallization of a single amorphous Ca–Mg-carbonate phase often form multiple crystalline Ca- and/or Mg-carbonate minerals (reviewed by Raudsepp et al. 2022).

SODIUM CARBONATES AND DYNAMIC EQUILIBRIUM IN ALKALINE LAKES

## Effect of Temperature and CO₂ on Sodium Carbonate Mineralogy

In the most extreme alkaline lakes, hydrated Na-carbonate minerals (e.g., natron, trona, thermonatrite, nahcolite) can precipitate out of highly concentrated alkaline brines. Numerous large, highly alkaline lakes, also called soda lakes, exist in the East African Rift Valley. These lakes are important cultural and economic resources (Haines et al. 2023 this issue), and have informed our understanding of Na-carbonates. Unlike relatively insoluble Ca- and Mg-carbonate minerals, Na-carbonates experience cycles of dissolution and reprecipitation as a result of dynamic wetting and drying conditions. The most common Na-carbonate minerals incorporate both HCO_3^- and CO_3^{2-} anions into their crystal structures. As such, the temperature and pCO_2, which is the partial pressure of CO_2 equilibrated with carbonate alkalinity ($HCO_3^- + CO_3^{2-}$), have a strong control on Na-carbonate mineralogy (Fig. 3A; Eugster 1966, 1980; Jagniecki et al. 2015).

Trona [$Na_3(HCO_3)(CO_3) \cdot 2H_2O$] is the most common mineral that precipitates at ~20–30 °C in Na-rich alkaline lakes at equilibrium with modern atmospheric CO_2 (Fig. 1D; Eugster 1966, 1980; Warren 2010). At Lake Magadi, Kenya, trona crystals grow as rosettes of clear 2–5 cm blades, forming a banded deposit, although the net yearly accumulation of trona is likely less than 0.4 cm/y (Eugster 1980). If the temperature is below ~20 °C, natron ($Na_2CO_3 \cdot 10H_2O$) is the thermodynamically stable Na-carbonate phase (Jagniecki et al. 2015). In Lake Magadi, natron has been observed to crystallize during cool nights and redissolve in the morning as the temperature increases (Eugster 1980). Trona and natron are often found interbedded as a result of this fine temperature control. Natron also forms via freeze-out crystallization, as observed in Last Chance Lake, Canada (Fig. 1C; Renaut and Long 1987). Thermonatrite ($Na_2CO_3 \cdot H_2O$), the least common lacustrine Na-carbonate mineral, requires both temperatures over 35 °C and a low pCO_2, but is reported in alkaline lakes in the East African Rift Valley (Eugster 1966, 1980; Nielsen 1999).

Precipitation of nahcolite ($NaHCO_3$) requires high pCO_2, which may occur in environments with volcanic CO_2 degassing, a large amount of degradation of organic matter, or during geologic periods with a high concentration of atmospheric CO_2. Thus, specific mineral assemblages preserved from Na-carbonate lakes have been used to interpret paleoenvironmental conditions. For example, nahcolite in the Green River Formation has been used to constrain the atmospheric pCO_2 of the Eocene to <680 ppm (Jagniecki et al. 2015). Similarly, the predominance of trona in sediments from Searles Lake, USA, is consistent with an atmospheric pCO_2 of ~190–270 ppm during the Pleistocene and Holocene (Olson and Lowenstein 2021). The presence of anomalous layers of nahcolite with thénardite (Na_2SO_4) in Searles Lake has been interpreted to reflect localized,
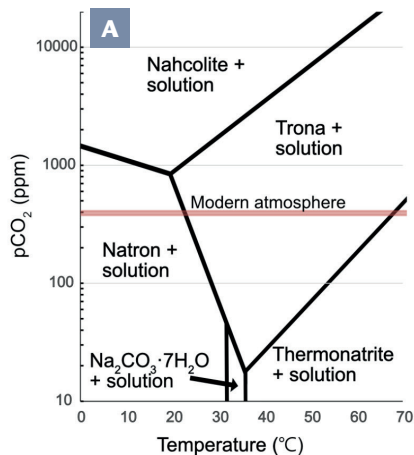
Figure 3 (**A**) pCO$_2$–temperature stability of Na-carbonates. Phase diagram modified from Eugster (1966) to include the updated triple point for the stability of nahcolite–trona–natron from Jagniecki et al. (2015).
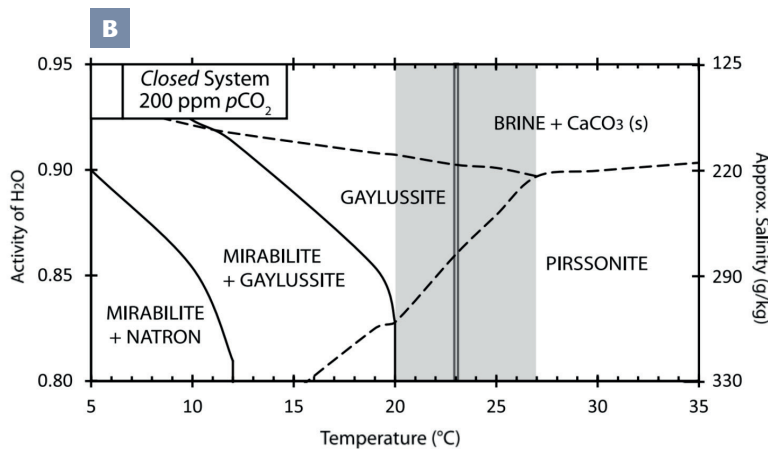
(**B**) Example of a H$_2$O–temperature–salinity stability diagram of Ca–Na-carbonates in the sediment of Searles Lake under low pCO$_2$. REPRODUCED FROM OLSON AND LOWENSTEIN (2021) WITH PERMISSION FROM THE GEOLOGICAL SOCIETY OF AMERICA.

periodic injections of volcanic CO$_2$ into the lake (Olson and Lowenstein 2021). Modern nahcolite precipitation in Nasikie Engida, Kenya, only occurs in areas where volcanic CO$_2$ degases (FIG. 2E; Renaut et al. 2021).

In the 19th century, prior to the invention of the Solvay (or ammonia–soda) process (which is the major industrial process for producing sodium carbonate, or soda ash, Na$_2$CO$_3$, developed by the Belgian chemist Ernest Solvay during the 1860s), soda ash, an important raw ingredient for soap, glass, and ceramics, was produced by either burning seaweed or by mining Na-carbonate deposits (Kostick 1983). Both early Egyptian and Roman cultures used Na-carbonate deposits in small alkaline lakes for the manufacture of glass and as a food additive (Kostick 1983). Sodium-carbonates from alkaline lakes were also used as a desiccant in the mummification process. Mining of trona deposits accounts for about one third of modern soda production, with the remaining two thirds of soda ash being synthetically produced. The Green River Formation is the world's largest natural deposit of Na-carbonate minerals, but mining of modern alkaline lake sediment also occurs (Warren 2010).

Formation of Na–Ca-carbonates in Mixing Zones

Because of the strong control of calcite over geochemical divides, Na-alkaline lakes have very low Ca concentrations (Tosca and Tutolo 2023 this issue). Thus, the formation of Na–Ca double salts, such as gaylussite [Na$_2$Ca(CO$_3$)$_2$·5H$_2$O] or pirssonite [Na$_2$Ca(CO$_3$)$_2$·2H$_2$O], requires dynamic equilibrium conditions, either by mixing waters or reacting a pre-existing mineral with a new fluid phase. For example, in Nasikie Engida, gaylussite only forms in the mixing zone between more Ca-rich streams and Na-carbonate-rich sediment and lake water (Renaut et al. 2021). In Mono Lake, the dispersion and dissolution of ikaite likely provides the Ca for the subsequent formation of gaylussite on the lake shore (Bischoff et al. 1993). In contrast, in the sediment of Searles Lake, gaylussite and pirssonite (which is less hydrated than gaylussite) are diagenetic and partially to fully replace laminated aragonite and calcite during periods when a Na-carbonate-rich brine infiltrates the sediment porewater (Olson and Lowenstein 2021). The crystallization of anhydrous Na–Ca-carbonate, shortite

[Na$_2$Ca$_2$(CO$_3$)$_3$], likely only occurs at elevated temperatures, thus it is found in the Green River Formation but not in modern alkaline lake sediment (Warren 2010).

NON-CARBONATE MINERALOGY OF ALKALINE LAKES

Sulfate Minerals in Alkaline Lakes

The most saline alkaline lakes can also have high aqueous concentrations of Cl$^-$ and/or SO$_4{}^{2-}$ in addition to high HCO$_3{}^-$ and CO$_3{}^{2-}$, resulting in the precipitation of Na-chloride and sulfate minerals, such as halite (NaCl), mirabilite (Na$_2$SO$_4$·10H$_2$O), and thénardite (Na$_2$SO$_4$). A heptahydrate of sodium sulfate (Na$_2$SO$_4$·7H$_2$O) has also been observed in laboratory syntheses but has yet to be identified in nature. Highly saline Na–Mg–SO$_4$ lakes, on the other side of the calcite geochemical divide (Tosca and Tutolo 2023 this issue), precipitate nine species of Mg–sulfate minerals with seven hydration states and two polymorphs, ranging from kieserite (MgSO$_4$·H$_2$O) to meridianiite (MgSO$_4$·11H$_2$O). Hydration states of sulfate minerals are extraordinarily sensitive to temperature and atmospheric humidity (Chipera and Vaniman 2007), and it is very likely that many hydrated sulfate minerals transform between sampling and laboratory analysis. Little is known about the temperature–humidity stability of most hydrated sulfates (or other hydrated minerals) that form in lakes, with only the stability of Ca- and Mg-sulfates having been studied in detail. This is important for the mineralogy of saline lakes on both Earth and Mars (Hurowitz et al. 2023 this issue).

In the most extreme Na–HCO$_3$–CO$_3$–SO$_4$–Cl lakes, double and triple salt minerals with two or three anions or cations of different types can precipitate. These minerals, including northupite [Na$_3$Mg(CO$_3$)$_2$Cl], burkeite [Na$_4$(SO$_4$)(CO$_3$)], and hanksite [KNa$_{22}$(SO$_4$)$_9$(CO$_3$)$_2$Cl], are only well characterized from the sediment of Searles Lake, where their sequential crystallization has been used to interpret the chemical evolution of lake and porewater during diagenesis (FIG. 3B; Olson and Lowenstein 2021).

Lithium, Borates, and Fluorides in Alkaline Lakes

Highly saline, closed-basin, alkaline lakes can accumulate trace elements at high concentration. Examples include (1) accumulation of B and the subsequent precipitation of borates such as borax [$Na_2B_4O_5(OH)_4 \cdot 8H_2O$], including in Searles, Owens, and Soda lakes (USA); (2) accumulation of Li and the subsequent precipitation of zabuyelite (Li_2CO_3) in Zhabuye Salt Lake, Tibetan Plateau, China (Warren 2010); and (3) accumulation of F and the subsequent precipitation of kogarkoite [$Na_3(SO_4)F$] and villiaumite (NaF) at Lakes Natron and Magadi in the East African Rift (Nielsen 1999). Fluoride-rich brines and minerals from some Na-carbonate lakes in the East African Rift are associated with fluorosis (fluoride toxicity) when used for cooking (Nielsen 1999). Borax and Li-bearing minerals from these lakes can be mined as economic resources. For example, lacustrine evaporites of Miocene age in the Jadar Basin, Serbia, contain the largest greenfield (i.e., project lacking constraints imposed by prior work; green = new) Li deposit in the world with the recently characterized Li–Na-borosilicate mineral jadarite $LiNaB_3SiO_7(OH)$, which could be used to supply Li for the electric vehicle industry.

Authigenic Silicate Minerals in Alkaline Lakes

Aluminum-poor, nanocrystalline, authigenic Mg-phyllosilicate minerals such as kerolite [$Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$] and stevensite [$(M^+_{2y} \cdot nH_2O)(Mg_{3-y}\square_y)Si_4O_{10}(OH)_2$, where $\square$ denotes a vacancy or unoccupied atomic position] are common in more moderate alkaline lakes, where they co-occur with Ca- and Mg-carbonates. These Mg-phyllosilicates are likely the first minerals to precipitate in microbialites in alkaline lakes, providing the foundation for the microbialite architecture that has preserved geological records of the early biosphere (Zeyen et al. 2021).

Authigenic silicate minerals such as zeolites and borosilicates can precipitate from the most extreme, Na-alkaline lakes as aqueous silica is mobilized at high pH. Jadarite and accompanying searlesite [$NaBSi_2O_5(OH)_2$] are among the borosilicates that form in Na-carbonate lakes. Three rare Na-silicate minerals were first characterized in Lake Magadi: magadiite [$Na_2Si_{14}O_{28}(OH)_2 \cdot 8H_2O$], kenyaite [$Na_2Si_{22}O_{41}(OH)_8 \cdot 6H_2O$], and makatite [$Na_2Si_4O_8(OH)_2 \cdot 4H_2O$]. New minerals can provide inspiration for materials science. For example, the structure of magadiite, a phyllosilicate, could be used as a drug carrier and precursor phase for producing commercially valuable synthetic zeolites (Krysiak et al. 2021). Precipitation of silica gels in alkaline lakes in the East African Rift Valley may also help us understand the silicification and preservation of microbial fossils in Precambrian cherts.

LESSONS FROM THE MINERALOGY OF ALKALINE LAKES

Alkaline lakes can be used as testing grounds for field-based mineral behavior experiments and as model systems for controlled laboratory experiments (FIG. 4). Some conditions are challenging to emulate in the laboratory, such as natural microbial diversity, seasonal wetting and drying cycles, the composition of natural organic matter, and changing aqueous geochemistry. Instead, laboratory-synthesized minerals can be transported into the field to study processes such as mineral growth and dissolution, the amorphous-to-crystalline transition, phase transformations, and isotopic and elemental resetting. On the other hand, reproductions of lake water chemistry and climatic variables in the laboratory can be used to study mineral behavior, and the geochemical records minerals preserve, under conditions more relevant to natural systems.

Alkaline lakes provide a stark contrast to the geochemical conditions that are commonly used to study the nucleation and growth of crystals in the laboratory. These lakes can have outrageously high concentrations of dissolved inorganic carbon (DIC) while having only several ppm-level concentrations of the cations needed to make the most abundant carbonate minerals in their sediments. For example, Last Chance Lake contains an alkalinity as high as 3.1 mol/L (as HCO_3^-) (Renaut and Long 1987), which is more than 22 times the DIC concentration of soda pop (i.e., carbonated soft drinks) and more than 1000 times the DIC of seawater. Alternatively, alkaline lakes can have hundreds of ppm of dissolved cations and mineral precipitation may instead be controlled by degassing of CO_2 (e.g., the Atlin playas; Power et al. 2019). This is a far cry from the ideal equimolar proportions of cations and anions and extreme supersaturations typically employed in laboratory models, e.g., mixing equal parts of 1.8 mol/L K_2CO_3 and 1.8 mol/L $MgCl_2$ to synthesize nesquehonite.

A. Winter **B. Spring/Summer** **C. Fall**
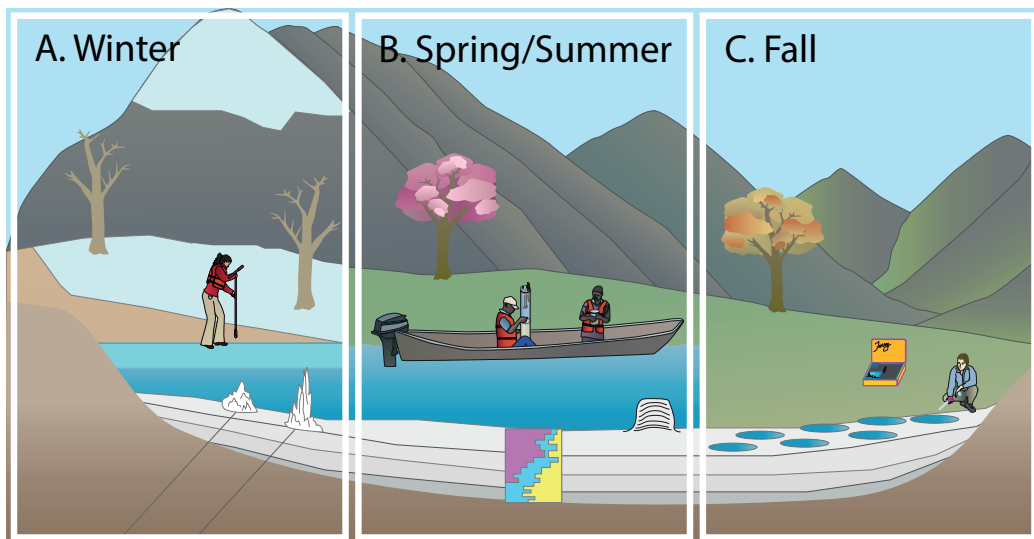
FIGURE 4 Geoscientists sampling a temperate alkaline lake during different seasons. (**A**) Winter: Ice coring to sample spring-fed spires of ikaite. (**B**) Spring/summer: Sediment coring for analysis of solids, porewater, and microbes. A stromatolite is shown alongside a graphical depiction of the down-profile mineral abundances. (**C**) Fall: Using a portable X-ray diffractometer to identify evaporite minerals forming from brine in a spotted lake. SOME GRAPHICAL ELEMENTS ARE COURTESY OF THE INTEGRATION AND APPLICATION NETWORK, UNIVERSITY OF MARYLAND CENTER FOR ENVIRONMENTAL SCIENCE (IAN.UMCES.EDU/MEDIA-LIBRARY/).

Carbonates		Halides	
calcite	$CaCO_3$	villiaumite	NaF
aragonite	$CaCO_3$	halite	$NaCl$
vaterite	$CaCO_3$	**Sulfates**	
monohydrocalcite	$CaCO_3 \cdot H_2O$	thénardite	Na_2SO_4
ikaite	$CaCO_3 \cdot 6H_2O$	mirabilite	$Na_2SO_4 \cdot 10H_2O$
dolomite	$CaMg(CO_3)_2$	**Double & Triple Salts**	
very high Mg calcite	$Ca_{0.5}Mg_{0.5}CO_3$	northupite	$Na_3Mg(CO_3)_2Cl$
magnesite	$MgCO_3$	burkeite	$Na_4(SO_4)(CO_3)$
hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	hanksite	$KNa_{22}(SO_4)_9(CO_3)_2Cl$
dypingite	$Mg_5(CO_3)_4(OH)_2 \cdot \sim 5H_2O$	kogarkoite	$Na_3(SO_4)F$
nesquehonite	$MgCO_3 \cdot 3H_2O$	**Borates & Borosilicates**	
lansfordite	$MgCO_3 \cdot 5H_2O$	borax	$Na_2B_4O_5(OH)_4 \cdot 8H_2O$
shortite	$Na_2Ca_2(CO_3)_3$	searlesite	$NaBSi_2O_5(OH)_2$
pirssonite	$Na_2Ca(CO_3)_2 \cdot 2H_2O$	jadarite	$LiNaSiB_3O_7(OH)$
gaylussite	$Na_2Ca(CO_3)_2 \cdot 5H_2O$	**Silicates**	
trona	$Na_3(HCO_3)(CO_3) \cdot 2H_2O$	kerolite	$Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$
nahcolite	$NaHCO_3$	stevensite	$(M^+{}_{2y} \cdot nH_2O)(Mg_{3-y}\square_y)Si_4O_{10}(OH)_2$
thermonatrite	$Na_2CO_3 \cdot H_2O$	magadiite	$Na_2Si_{14}O_{28}(OH)_2 \cdot 8H_2O$
natron	$Na_2CO_3 \cdot 10H_2O$	makatite	$Na_2Si_4O_8(OH)_2 \cdot 4H_2O$
zabuyelite	Li_2CO_3	kenyaite	$Na_2Si_{22}O_{41}(OH)_8 \cdot 6H_2O$

Because carbonates can be dated radiometrically, for example, using ^{14}C dating for Holocene and Pleistocene lakes (e.g., Olsen and Lowenstein 2021), equilibrium fractionation of stable isotopes can be used to reconstruct temporal changes in atmospheric pCO_2, temperature, and pH. Kinetic isotope fractionation records information about the roles of evaporation, biogenic carbon cycling, and CO_2 degassing during carbonate precipitation while providing occasional insights into the relative rates of mineral precipitation. Alkaline lakes contribute an important record of regional climatic change, which can be read in part using stable isotopes; however, even less is known about stable isotope fractionation in these minerals than about their stability. In the most recent thorough review of mineral H, C, and O stable isotope fractionation factors, Chacko et al. (2001) summarized fractionation factors for common carbonate minerals, including aragonite, calcite, and dolomite, and provide references to the few studies that have focused on other carbonate and sulfate minerals found in alkaline lakes. At that time, oxygen isotope fractionation factors were only available for hydromagnesite (a single data point) and temperature-dependent carbon isotope fractionation factors were only known for gaylussite, pirssonite, and trona. Carbon and magnesium isotopic fractionation factors have only recently been measured for dypingite (Harrison et al. 2021), and there are still no such data for most of the Mg-, Ca-, and Na-carbonate minerals (listed in TABLE 1) that preserve environmental records in lakes.

Mineralogical studies of alkaline lakes have long been frustrated by the temperature-, humidity-, and oxygen-sensitive nature of their hydrated, and sometimes reduced, phases (e.g., ikaite, monohydrocalcite, lansfordite). This has presented a challenge with respect to characterizing these phases, or even identifying that they exist, let alone preserving the structural, elemental, and isotopic infor-mation they contain. Recent advances in portable mineralogical and geochemical analysis are making it possible to obtain detailed and accurate measurements in the field and to improve the preservation of samples for analysis in the laboratory and at synchrotron light sources. Portable X-ray diffraction and Raman spectroscopy, for example, allow in situ characterization and quantification of mineral abundances under environmental conditions while cryoshippers (designed for safe transportation of biological samples at −150 °C or colder using liquid nitrogen) and anoxic containers enable better sample preservation. At the start of this new golden age of field-based mineralogy, there has never been a better time to study the diverse mineralogy of alkaline lakes.

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