

How to Make an Alkaline Lake: Fifty Years of Chemical Divides

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SEM-EDS map of lacustrine carbonate from the Cretaceous Barra Velha formation, offshore Brazil, showing calcite, dolomite, magnesite, silica, and Mg-silicates. Orange: Si; blue: Mg; black: Ca. PHOTO: NICHOLAS TOSCA.

Of all the surface environments on our planet, alkaline lakes are among the most distinctive and significant in terms of their biogeochemistry, climatic sensitivity, and associated mineral deposits. But how does the Earth produce alkaline lakes? Fifty years ago, Lawrence Hardie and Hans Eugster hypothesised that the bewildering complexity of non-marine evaporites could be explained by common successions of mineral precipitation events, or chemical divides. Since that time, the chemical divide concept has provided Earth scientists with an enduring framework within which to integrate new advances in mineral–water equilibria and kinetics, sedimentology, and paleoclimatology. These developments are painting an increasingly detailed picture of how alkaline waters form and interact with magmatic and atmospheric CO₂, now and in the distant past.

KEYWORDS: chemical divide; alkalinity; alkaline lake; Mg-carbonate; Mg-silicate; magmatic CO₂

INTRODUCTION

Most of the alkaline lakes now at the Earth's surface have originated from the evaporative concentration of dilute waters. This process translates relatively small chemical changes in dilute waters into profound differences as they become concentrated. To understand how alkaline lakes can be generated through evaporation, our discussion begins with major controls on solute acquisition and the alkalinity of natural waters. We then introduce the chemical divide concept and associated chemical criteria for generating concentrated alkaline waters. Because the behaviour of Mg strongly influences the chemical evolution of many alkaline waters, we highlight recent progress concerning Mg-carbonate and Mg-silicate precipitation, and how these developments can be accommodated in the chemical divide framework. Finally, because alkaline lakes are, by definition, associated with significant concentrations of inorganic carbon, their interactions with magmatic and atmospheric CO₂ highlight a special utility in reconstructing past CO₂ levels and reveal an outsized role in the modern (and perhaps ancient) carbon cycle.

CONTROLS ON SOLUTE ACQUISITION

The pathway to forming an alkaline lake begins with the acquisition of water. Water is supplied to lakes as precipitation, surface runoff, and groundwater, which itself encompasses local meteoric sources, interstitial water in sediments,

or deeper hydrothermally influenced basinal waters (Rosen 1994). Of the sources of water to alkaline lakes, the balance between surface runoff versus groundwater carries a strong influence on chemical evolution; runoff-dominated inflow imparts greater sensitivity to external geology and seasonal controls, whereas a dominant groundwater supply may impart greater sensitivity to internal biogeochemical processes (Rosen 1994). Importantly, if evaporation is critical for the development of many alkaline lakes, it follows that hydrological outflow must

be essentially absent or significantly restricted relative to inflow (Rosen 1994). This confers strong climatic sensitivity, with many modern alkaline lakes confined to arid or semi-arid climates.

Alkaline lakes of course also require solutes, which together control the alkalinity. Here, we focus on three important processes influencing the alkalinity of natural waters: (1) chemical weathering, (2) microbially mediated processes, and (3) circulation of basinal brines. A fourth process, the supply of dissolved CO₂ from magmatic sources, is discussed in the final section.

Chemical weathering controls the chemistry of waters that may feed alkaline lakes by modifying relative cation proportions, thus directly impacting their alkalinity. In their landmark study on the chemistry of spring waters draining the Sierra Nevada mountains, Garrels and Mackenzie (1967) showed that the cationic composition of these waters is dominated by chemical weathering reactions operating within local bedrock (dominantly granitic in composition), that is, reactions between CO₂-charged rainwater and rock-forming silicates. Although this conclusion may seem self-evident given our understanding of chemical weathering today, Garrels and Mackenzie's 1967 study provided the geochemistry community with a general mass balance approach to trace the origin of dissolved components in natural waters through specific reactions involving rock-forming silicates. They showed that plagioclase weathering accounted for much of the cation budget, producing waters dominated by Na and Ca, and that plagioclase and other rock-forming silicates were responsible for supplying most of the SiO₂(aq). Catchment geology, therefore, is crucial in shaping the chemistry of dilute waters through the rates and mechanisms of dissolving and precipitating solids involved in the weathering process.

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Chemical weathering also exerts strong control on the alkalinity of natural waters (TABLE 1). This is because chemical weathering of rock-forming silicates liberates 'conservative' cations (i.e., those that do not participate directly in acid–base reactions) and consumes protons, which together increase the alkalinity (see *Toolkit* on page 7 of this issue). Using the Garrels and Mackenzie (1967) waters as an example, the alkalinity framework in the *Toolkit* makes it clear that, because weathering in this locality contributes little SO_4 and Cl, yet liberates Na, Ca, and minor Mg and K, net charge balance is achieved through equilibration with atmospheric CO_2 , in turn supplying carbonate alkalinity. More broadly, this net effect applies to nearly all other rock-forming silicates, but the alkalinity generated per mole of reactant depends on the stoichiometry of weathering reactions operating in the catchment (TABLE 1). The chemical weathering of non-silicate minerals, on the other hand, is associated with variable effects on alkalinity. For example, weathering of carbonate-dominated lithologies increases alkalinity along with Ca and Mg (TABLE 1), whereas oxidation/chemical weathering of sulfide-bearing rocks (i.e., black shales) can strongly decrease alkalinity (TABLE 1). Even though sulfides tend to occur at low concentrations in many igneous and sedimentary lithologies, their reactions with water often prevent waters from becoming alkaline upon further evaporation (Nesbitt 1990).

Microbial metabolisms also generate or consume alkalinity in lake waters and sediment pore waters. These effects depend on specific metabolic processes (TABLE 1) and their quantitative importance in alkaline systems (Haines et al. 2023 this issue). For example, carbon fixation through photosynthesis increases net alkalinity; this is linked to the assimilation of phosphate, nitrate, or ammonium ions (TABLE 1). Although the stoichiometric alkalinity yield per mole of fixed carbon is low, the high rates of photosynthesis characteristic of many alkaline lakes can result in significant modifications to water column alkalinity and, in combination with decreases in dissolved inorganic carbon, increase the pH (Duarte et al. 2008; Haines et al. 2023 this issue). The effects of respiration may either magnify or offset this effect. For example, high-yielding metabolisms, such as microbial sulfate reduction, can end

up serving as the critical factor determining whether some water bodies become alkaline with further evaporation (Eugster and Hardie 1978).

Finally, extra-basinal or deep-basinal inflow can strongly modify the chemical evolution of evaporating waters. These concentrated waters are commonly featured in tectonically active basins and reflect subsurface hydrothermal and diagenetic interactions between fluids and sediments or rocks (Lowenstein and Risacher 2009). Dolomitisation, albitisation of plagioclase, sulfate reduction/anhydrite precipitation, and K metasomatism can all contribute to a distinctively alkalinity-poor Ca–Cl signature (Lowenstein and Risacher 2009). These brines typically circulate in response to regional thermal and/or topographic anomalies, ultimately reaching the surface through fracture and fault systems where they may mix with surface waters, decrease alkalinity, and result in widely variable pathways upon further evaporation.

CHEMICAL DIVIDES AND THE GENERATION OF ALKALINE WATERS

As evaporation removes H_2O from solution, all components increase in concentration until the fluid becomes saturated with respect to a solid phase. Mineral precipitation therefore serves as a principal control on the subsequent chemical evolution of evaporating waters. In one of the first examples of what is now known as reaction path modelling, Garrels and Mackenzie (1967) numerically predicted the chemical evolution of Sierra Nevada spring waters as they became concentrated through evaporation (maintaining equilibrium with respect to an atmospheric pCO_2 of $10^{-3.5}$ bar). Their results showed that, upon evaporation, initially dilute waters influenced by plagioclase weathering first reached calcite saturation. Because the waters were assumed to remain in equilibrium with calcite with continued evaporation, calcite continued to precipitate until essentially all of the Ca was removed from solution. Garrels and Mackenzie (1967) also found that hydrous Mg-silicate (sepiolite) precipitated after calcite and that this consumed alkalinity, Mg, and $\text{SiO}_2(aq)$. Once sepiolite stopped forming, the alkalinity increased and the pH increased to ~ 10 at a concentration factor of 1000 times

TABLE 1 MAJOR CHEMICAL WEATHERING AND BIOGEOCHEMICAL PROCESSES AND THEIR INFLUENCE ON THE ALKALINITY (ALK) OF NATURAL WATERS.

Process	Reaction	$\Delta\text{ALK} / \text{mol}^*$	$\Delta\text{Ca} / \text{mol}^*$	$\Delta\text{Mg} / \text{mol}^*$
Weathering of alkali feldspar	$\text{NaAlSi}_3\text{O}_8 + 0.5\text{H}_2\text{O} + \text{H}^+ = \text{Na}^+ + 0.5\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2(aq)$	+1	0	0
Weathering of plagioclase feldspar	$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{O} + 2\text{H}^+ = \text{Ca}^{2+} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	+2	+1	0
Olivine dissolution	$\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Mg}^{2+} + \text{SiO}_2(aq) + 2\text{H}_2\text{O}$	+4	0	+2
Pyroxene dissolution	$\text{CaMgSi}_2\text{O}_6 + 4\text{H}^+ = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{SiO}_2(aq) + 2\text{H}_2\text{O}$	+4	+1	+1
Calcite dissolution	$\text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$	+2	+1	0
Magnesite dissolution	$\text{MgCO}_3 + 2\text{H}^+ = \text{Mg}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$	+2	0	+1
Mg-silicate precipitation	$3\text{Mg}^{2+} + 4\text{H}_2\text{O} + 4\text{SiO}_2(aq) = 6\text{H}^+ + \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	-6	0	-3
Pyrite oxidation	$\text{FeS}_2 + 3.75\text{O}_2 + 3.5\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$	-4	0	0
Photosynthetic production	$\text{CO}_2 + 0.15\text{HNO}_3 + 0.01\text{H}_3\text{PO}_4 + 1.15\text{H}_2\text{O} = (\text{CH}_2\text{O})(\text{NH}_3)_{0.15}(\text{H}_3\text{PO}_4)_{0.01} + 1.3\text{O}_2$	+0.16	0	0
Denitrification	$(\text{CH}_2\text{O})(\text{NH}_3)_{0.15}(\text{H}_3\text{PO}_4)_{0.01} + 0.8\text{HNO}_3 = 0.15\text{NH}_3 + 0.4\text{N}_2 + \text{CO}_2 + 0.01\text{H}_3\text{PO}_4 + 1.4\text{H}_2\text{O}$	+0.94	0	0
Mn reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_{0.15}(\text{H}_3\text{PO}_4)_{0.01} + 2\text{MnO}_2 + 4\text{H}^+ = \text{CO}_2 + 0.15\text{NH}_3 + 0.01\text{H}_3\text{PO}_4 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$	+4.14	0	0
Fe reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_{0.15}(\text{H}_3\text{PO}_4)_{0.01} + 2\text{Fe}_2\text{O}_3 + 8\text{H}^+ = \text{CO}_2 + 0.15\text{NH}_3 + 0.01\text{H}_3\text{PO}_4 + 4\text{Fe}^{2+} + 5\text{H}_2\text{O}$	+8.14	0	0
Sulfate reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_{0.15}(\text{H}_3\text{PO}_4)_{0.01} + 0.5\text{H}_2\text{SO}_4 = \text{CO}_2 + 0.15\text{NH}_3 + 0.01\text{H}_3\text{PO}_4 + 0.5\text{H}_2\text{S} + \text{H}_2\text{O}$	+1.14	0	0
Methanogenesis	$(\text{CH}_2\text{O})(\text{NH}_3)_{0.15}(\text{H}_3\text{PO}_4)_{0.01} = 0.5\text{CO}_2 + 0.15\text{NH}_3 + 0.01\text{H}_3\text{PO}_4 + 0.5\text{CH}_4 + \text{H}_2\text{O}$	+0.14	0	0
Sulfide oxidation	$\text{H}_2\text{S} + 2\text{O}_2 = \text{SO}_4^{2-} + 2\text{H}^+$	-2	0	0

* Per mole of mineral reacted or per mole of carbon

relative to the initial dilute spring water. The resulting alkaline Na-carbonate brines showed strong similarities to the chemistry of several lakes formed in the western US. These results supported the hypothesis that evaporation of water derived from weathering felsic rocks of the Sierra Nevada could explain basic geochemical features of some of these alkaline lakes.

These results inspired Hardie and Eugster (1970) to adopt a similar approach to predicting equilibrium fluid chemistries and mineral assemblages with evaporation, but they extended their investigation to a wide variety of natural waters. In their analysis, Hardie and Eugster (1970) noted that the precipitation of minerals along the evaporation sequence served as a 'critical evolutionary step' in the generation of concentrated waters. This is because mineral precipitation will consume cations and anions from solution in a stoichiometric ratio dictated by the solid. When these ions are present in solution at a ratio that differs from that in the solid, further evaporation will lead to an increase in the concentration of ions present in greater relative concentration in solution, and a decrease in the concentration of ions present at lower relative concentration. This forms the basis of the principle of chemical divides: of the two ions involved in precipitation, one will increase in solution as evaporation proceeds and the other will decrease to the point of near complete depletion.

Hardie and Eugster went on to systematically document similarities between various calculated evaporation pathways and the mineral precipitation sequences recorded in the sedimentary deposits of saline lakes (Hardie and Eugster 1970; Eugster and Hardie 1978). They proposed that the evolution of evaporating waters could be viewed as a succession of chemical divides and that, depending on the ratio of relevant components in solution, could explain the extreme variability of brine chemistries observed in saline lakes worldwide.

In the Hardie and Eugster model, the critical threshold in generating alkaline waters is the precipitation of CaCO_3 , which serves as the first chemical divide for most natural waters (FIG. 1). Because CaCO_3 precipitation consumes two equivalents of alkalinity (ALK) per mole of Ca, CaCO_3 precipitation will, in theory, determine whether waters influenced by evaporative concentration are associated with high alkalinity or whether that alkalinity is largely consumed. This process leaves three possible evolutionary trajectories for Ca-bearing dilute waters. When $\text{ALK} > 2[\text{Ca}]$, Ca is largely consumed and ALK continues to increase (FIG. 1). If $\text{ALK} = 2[\text{Ca}]$, ALK, [Ca], and pH become largely invariant upon CaCO_3 precipitation and as evaporation proceeds (FIG. 1). If $\text{ALK} < 2[\text{Ca}]$, ALK is consumed as CaCO_3 precipitates and pH begins to decrease (FIG. 1). This introduces a critical requirement for the development of an alkaline lake: any dilute water undergoing evaporative concentration must have $\text{ALK} > 2[\text{Ca}]$.

The $\text{ALK} > 2[\text{Ca}]$ condition implies that relatively minor modifications to the alkalinity of inflow waters often become decisive factors in whether alkaline lakes develop. For instance, because chemical weathering of rock-forming silicates tends to release cations other than Ca to solution, catchments hosting these minerals are most likely to develop alkaline fluids upon evaporation (FIG. 2). For felsic lithologies, it is the release of Na and K (and Mg) in addition to Ca that typically results in fluids where $\text{ALK} > 2[\text{Ca}]$ (Garrels and Mackenzie 1967). By contrast, evaporation of modern seawater will not lead to the production of alkaline fluids, nor will the evaporation of waters where the alkalinity budget has been modified by sulfide weath-

ering/oxidation (Hardie and Eugster 1970; Eugster and Hardie 1978; Nesbitt 1990) or basinal brines (Lowenstein and Risacher 2009).

After CaCO_3 precipitation, the chemical pathways of evaporating brines can vary widely depending on the ionic proportion (FIG. 3). For example, for dilute waters that have precipitated CaCO_3 , and have $\text{ALK} > 2[\text{Ca}]$, precipitation of Mg-carbonates (and, for $\text{SiO}_2(\text{aq})$ -bearing systems,

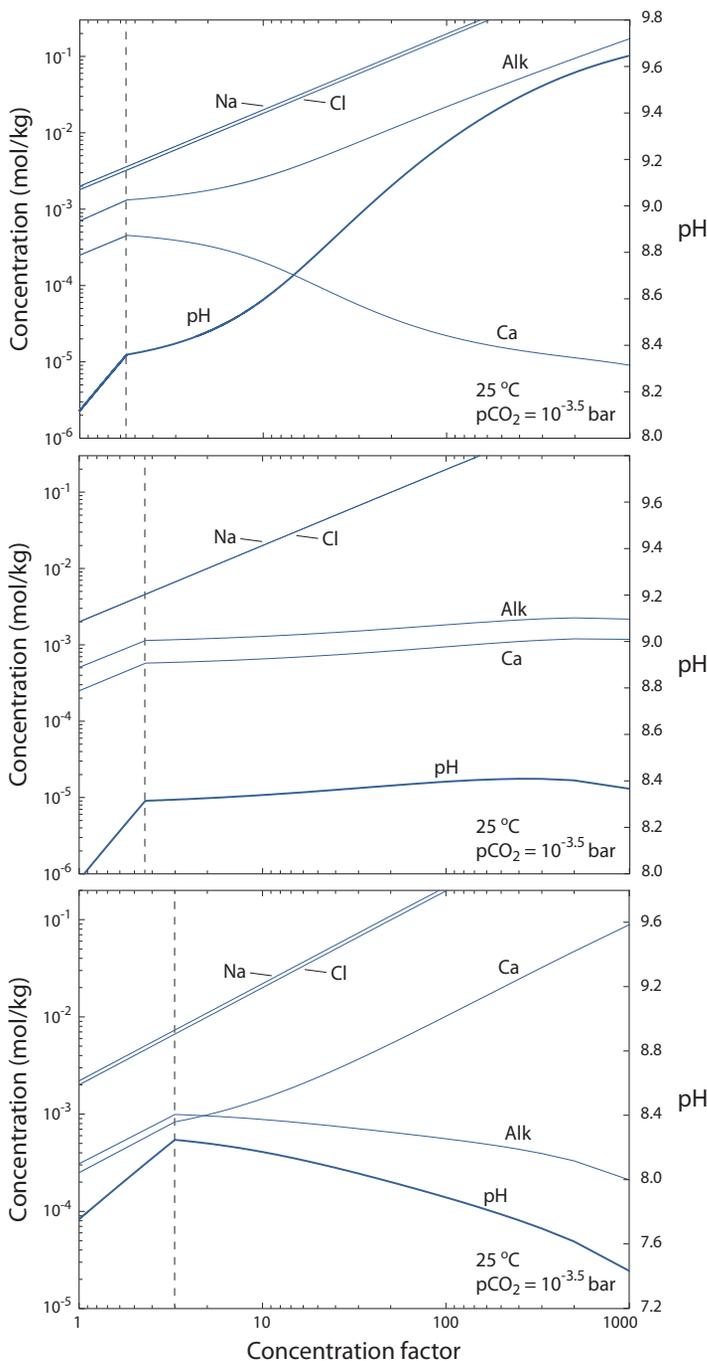


FIGURE 1 Calcite chemical divide, commonly the first step in the generation of alkaline waters. (TOP) Evaporation of a dilute water with $\text{ALK} > 2[\text{Ca}]$, where ALK indicates alkalinity. (MIDDLE) Evaporation of a dilute water with $\text{ALK} = 2[\text{Ca}]$. (BOTTOM) Evaporation of a dilute water with $\text{ALK} < 2[\text{Ca}]$. Dashed lines indicate the onset of calcite precipitation. All calculations maintain equilibrium with atmospheric $p\text{CO}_2 = 10^{-3.5}$ bar and with precipitated calcite. Calculations were performed with the Geochemist's Workbench using thermodynamic data from Plummer et al. (1988).

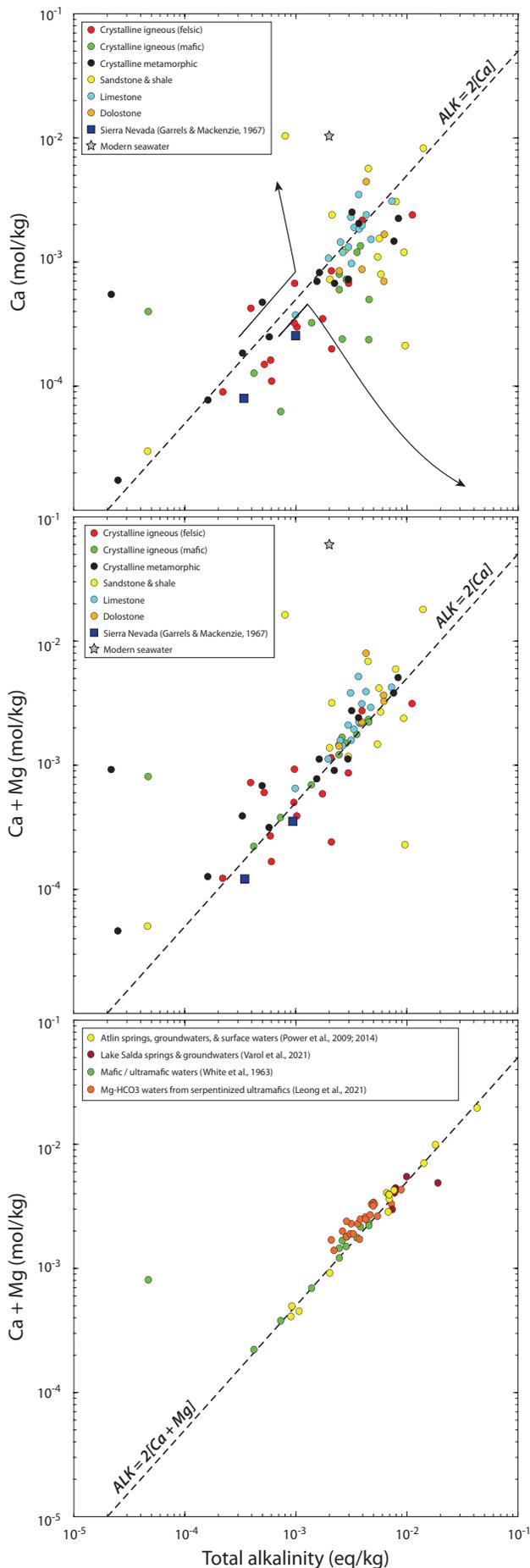


FIGURE 2 Alkalinity and alkaline earth cation concentrations in dilute subsurface waters. **(TOP)** Calcium and alkalinity for waters associated with various aquifer lithologies. Black lines correspond to evaporation pathways shown in FIG. 1. MODIFIED FROM HARDIE AND EUGSTER (1970). **(MIDDLE)** $[Ca + Mg]$ and alkalinity for waters associated with various aquifer lithologies. **(BOTTOM)** $[Ca + Mg]$ and alkalinity for dilute inflow to alkaline lakes and playas where authigenic Mg-carbonates have been documented, and for comparison, Mg-HCO₃ waters derived from serpentinised ultramafic bodies, which dominate catchment geology for these alkaline lakes and playas. EXCEPT WHERE INDICATED, ALL DATA ARE FROM WHITE ET AL. (1963).

Mg-silicate) becomes possible. If sufficient alkalinity remains, the resulting fluids can precipitate a distinctive suite of sodium carbonate and/or sodium sulfate minerals in addition to halite (Eugster and Hardie 1978; Olson and Lowenstein 2021). Where $ALK < 2[Ca]$, further evaporation often results in gypsum precipitation, which introduces another chemical divide, separating waters where $Ca > SO_4$ and $Ca < SO_4$ (FIG. 3; Eugster and Hardie 1978). The development of Pitzer's ion interaction model for estimating ion activity coefficients and mineral solubility in concentrated solutions, and its application to geochemical systems, has provided a means to accurately estimate the effects of late-stage brine evolution (Plummer et al. 1988; Olson and Lowenstein 2021).

Over the last 50 years, the application of the chemical divide concept to many natural systems has been met with a number of conceptual and technological advances that have extended its utility far beyond what Hardie and Eugster may have envisioned. For instance, the application of stable Ca isotopes to the CaCO₃-water and gypsum-water systems has uncovered isotopic expressions associated with different chemical divides, establishing a key tool in the reconstruction of ancient marine and non-marine chemistry (Nielsen and DePaolo 2013; Blättler and Higgins 2014). At the same time, the combination of Pitzer-based reaction path modelling and sedimentological analysis has resulted in a sophisticated understanding of brine generation and mineral deposition in the Hardie-Eugster framework, clarifying the role of partial evaporation/dilution cycles, and the degree to which saline mineral-water systems are most appropriately treated as open (i.e., fractional crystallisation) or closed (i.e., equilibrium crystallisation; Olson and Lowenstein 2021).

THE BEHAVIOUR OF Mg IN ALKALINE SYSTEMS

If there could be any fly in the ointment for Hardie and Eugster's model, it may have been the behaviour of Mg in alkaline waters. Hardie and Eugster recognised that, in alkaline systems, Mg may be incorporated into calcite, Mg-carbonates (i.e., dolomite, magnesite), or authigenic/diagenetic Mg-silicates (Hardie and Eugster 1970; Eugster and Hardie 1978; Darragi and Tardy 1987; Nesbitt 1990; Power et al. 2009, 2019). However, the influence of these minerals on evolving fluid chemistry was not easy to ascertain, in part because they formed early in some evaporation sequences and late in others, and because thermodynamic calculations employed at the time could not address complex salts in concentrated multicomponent aqueous systems. Hardie and Eugster thus regarded the relative positions of Mg-carbonate and Mg-silicate in alkaline evaporation sequences as 'problematic', foretelling much subsequent research (Raudsepp et al. 2023 this issue).

From a mass balance perspective, both Mg-carbonates and Mg-silicates generally consume alkalinity and Mg in 2:1 molar ratios (TABLE 1). Thus, regardless of which mineral forms, residual alkalinity must be present after precipi-

tation for a given Mg-bearing system to develop into an alkaline lake. It follows that, in addition to $ALK > 2[Ca]$, the development of alkaline lakes should also require $ALK > 2[Ca + Mg]$.

Despite this theoretical requirement, many natural waters strongly influenced by the weathering of crystalline rocks lie close to, or on the wrong side of, this threshold (i.e., $ALK < 2[Ca + Mg]$; FIG. 2). This is particularly true of mafic and ultramafic rocks and likely reflects (1) the stoichiometry of chemical weathering reactions involving ultramafic silicates, (2) the maintenance of electroneutrality for SO_4 - and Cl-poor waters dominated by Mg and Ca, and (3) dissolution and/or precipitation of Mg and Ca carbonates present in altered ultramafic host rocks. If $ALK > 2[Ca + Mg]$ must be satisfied for all alkaline waters, it is puzzling that mafic and ultramafic lithologies should develop such waters at all.

One reason why Mg-rich waters are often associated with high alkalinity on evaporation may relate to when Mg-carbonates form, which is controlled in part by the Mg/Ca ratio. As Hardie and Eugster pointed out, for HCO_3 -bearing waters with low Mg/Ca, alkaline waters can initially be generated through evaporation if $ALK > 2[Ca]$, but Mg can be partially or completely removed through early precipitation of Mg-silicates or alkaline earth carbonates (FIG. 3; Hardie and Eugster 1970; Eugster and Hardie 1978; Nesbitt 1990; Power et al. 2009, 2019). In this case, Ca- and Mg-carbonate formation can be efficient in consuming alkalinity from solution, causing the resulting brine to evolve toward a Na–Mg– SO_4 –Cl-rich composition (FIG. 3; Nesbitt 1990).

However, for ultramafic waters with high Mg/Ca, $CaCO_3$ formation consumes little alkalinity but much of the Ca. As Mg-rich carbonates become supersaturated, their sluggish precipitation kinetics leads to the development of highly alkaline waters sometimes with relatively high concentrations of Mg (Fukushi and Matsumiya 2018; Power et al. 2019). These conditions appear to persist until metastable hydrous Mg-carbonate phases precipitate (Power et al. 2019). However, data seem to indicate that this process is not efficient in removing alkalinity, allowing alkaline waters to be generated from inflow with $ALK < 2[Ca + Mg]$ (FIG. 2). In fact, in a thermodynamic assessment of the geochemistry of alkaline lakes, Fukushi and Matsumiya (2018) showed that many lakes are poised near apparent saturation with respect to amorphous magnesium carbonate, hinting toward common precipitation pathways and strong kinetic control associated with Mg-carbonate formation in alkaline systems.

The effects of Mg-silicate precipitation on the evolution of alkaline Mg-rich systems most obviously depend on the $SiO_2(aq)$ concentration but also on when precipitation occurs (Eugster and Hardie 1978). Geochemical and sedimentological studies have long documented that Mg-silicates often precipitate directly from the water column and/or syndepositionally in alkaline lake sediments (Hardie and Eugster 1970; Darragi and Tardy 1987). More recently, laboratory studies have shown that pH appears to serve as the strongest control on Mg-silicate precipitation because of both thermodynamic and kinetic factors (Tutolo and Tosca 2018). Thus, the relative timing of Mg-silicate precipitation is most strongly controlled by pH as a function of evaporation.

In theory, depending on the $SiO_2(aq)$ concentration, Mg-silicate precipitation can consume residual alkalinity and prevent the development of alkaline waters, as Hardie and Eugster (1970) hypothesised. However, given the strong role of pH in governing Mg-silicate precipitation (Tutolo and Tosca 2018), and evidence suggesting that poorly crystalline Mg-silicates may rapidly dissolve when under-saturated (Cerling 1996; Wright 2022), these phases may be efficient in consuming Mg and promoting the generation of alkaline conditions upon evaporation (Darragi and Tardy 1987), but not necessarily the reverse. This is because, if $SiO_2(aq)$ is non-limiting, precipitation of Mg-silicate when $ALK < 2[Mg]$ may consume alkalinity but lead to pH decreases, which would trigger rapid dissolution and return of alkalinity to solution (Cerling 1996). The precipitation and preservation of Mg-silicates in modern and ancient sediments, therefore, is more likely a consequence of *persistent* alkaline conditions. Where these minerals are preserved, they offer potentially sensitive and valuable records of the geochemistry of alkaline waters (Chase et al. 2021).

CONNECTIONS BETWEEN ALKALINITY AND CO_2

Although we have highlighted some key controls on how alkaline lakes develop, the geographic distribution of alkaline waters on Earth today is closely tied to volcanically active tectonic settings, including the East African Rift zone, western North America and Mexico, and parts of Asia. This distribution suggests an important connection between magmatically derived CO_2 and the development of alkaline water bodies. How might magmatic CO_2 contribute to the formation of alkaline lakes?

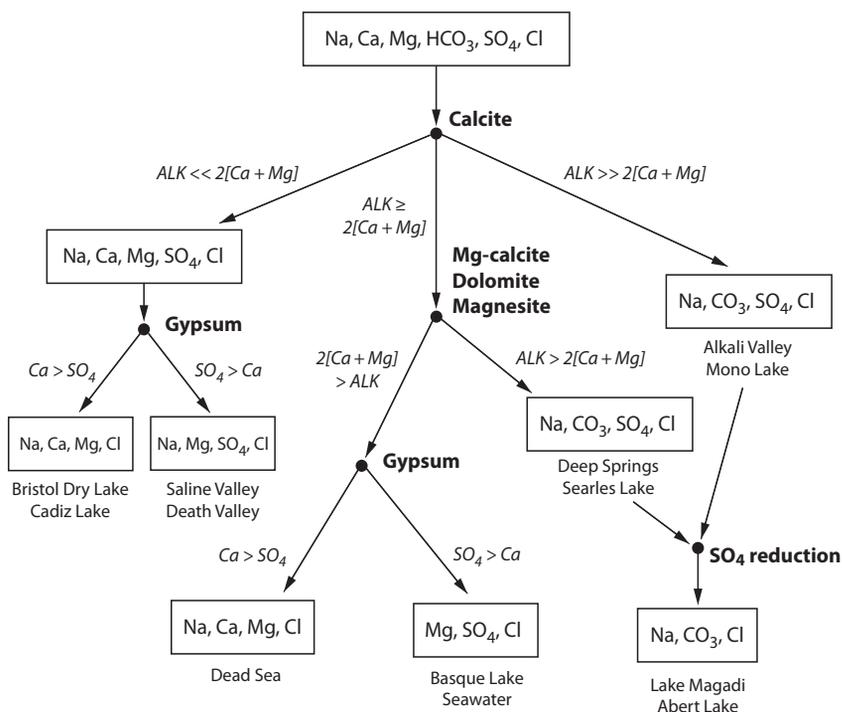


FIGURE 3 Some possible paths for the evaporation of natural waters. Alkaline waters commonly precipitate Mg-carbonates although the timing of their formation depends largely on the Mg/Ca ratio in the fluid. Poorly crystalline hydrous Mg-silicates (not shown) also form in systems with sufficient $SiO_2(aq)$, and are possible for most pathways, but the relative timing of their formation is principally dependent on the pH. MODIFIED FROM EUGSTER AND HARDIE (1978).

Strictly speaking, the dissolution of $\text{CO}_2(\text{g})$ cannot by itself increase the alkalinity of a water body because it is a neutral molecule, but conversion of $\text{CO}_2(\text{g})$ to HCO_3^- can, depending on associated interactions that influence pH. For example, increases in $\text{CO}_2(\text{g})$ generally lead to more acidic fluids that yield alkalinity through silicate hydrolysis (e.g., Renaut et al. 2021). In addition, CO_2 -rich hydrothermal fluids may be released along fracture networks and faults and effuse directly into sediment pore or lake waters (Milesi et al. 2020; Renaut et al. 2021), which may then trigger a variety of complex biogeochemical interactions. Dziani Dzaha, an alkaline lake in Mayotte (Indian Ocean), provides an interesting example. Major element geochemistry and halogen ratios suggest that this crater lake may have filled with seawater in association with a phreatomagmatic eruption (Milesi et al. 2020), but evaporation of seawater itself cannot have supplied alkalinity to the system (FIG. 2). Radiocarbon measurements indicate that magmatic inputs account for more than 50% of the dissolved inorganic carbon, which is thought to both exsolve and fuel intense primary production when reaching the sunlit surface of the lake, in turn increasing the pH (Milesi et al. 2020). This may support methanogenesis (generation of methane by microbes known as methanogens) and fermentation in the water column and in sediments, where authigenic silicate and carbonate minerals precipitate and dissolve. Although this together suggests strong biogeochemical responses to the injection of magmatic CO_2 , this carbon cycle appears to carry a small overall influence on alkalinity, which remains high (~200 mEq/kg) and invariant throughout. Though the alkalinity source remains unconstrained, it may ultimately derive from interactions between felsic materials and hydrothermal waters charged with magmatic CO_2 (Earman et al. 2005; Milesi et al. 2020; Renaut et al. 2021).

The connection between magmatically derived CO_2 and the development of alkaline waters may be recorded, at least in part, by extensive trona (a non-marine evaporite mineral) deposits preserved in some sedimentary basins. Although chemical weathering is crucial in providing alkalinity to inflow waters that feed many alkaline lakes, Earman et al. (2005) showed that silicate hydrolysis and subsequent evaporation is insufficient to produce signifi-

cant trona deposits and suggested that ‘excess’ CO_2 must be supplied. The association of large modern and Pleistocene trona deposits with magmatic activity supports this model, though Lowenstein et al. (2017) note that there is little evidence for a similar magmatic source contributing to the Na– HCO_3 waters that formed the trona deposits of the Green River Formation, one of the most significant in the geologic record. Lowenstein et al. (2017) hypothesised that, aside from magmatic CO_2 sources, accelerated rates of silicate weathering under elevated atmospheric CO_2 , or the decay of large accumulations of organic matter, may have provided the necessary alkalinity; however, there are no known modern analogues in support of the latter process.

Magmatic CO_2 is also thought to have played a role in sustaining what may have been one of the most extensive non-marine alkaline systems preserved in the rock record, but here too the specific source of the alkalinity has proven challenging to identify. The Lower Cretaceous carbonates of the Barra Velha Formation were formed in association with the rifting and opening of the South Atlantic Ocean (Wright 2022). These extensive accumulations include distinctive shrubby, dendritic, and spherulitic calcite textures that were precipitated in association with authigenic Mg-silicates, together implying that $\text{ALK} > 2[\text{Ca} + \text{Mg}]$ (Tutolo and Tosca 2018; Wright 2022). However, direct evidence for accelerated silicate weathering and/or significant contributions from organic matter decay has remained limited (Wright 2022). Magmatic CO_2 and its interactions with regional crystalline lithologies may have supplied Ca, Mg, and alkalinity from a suite of lithologies compatible with $^{87}\text{Sr}/^{86}\text{Sr}$ data, but the sheer volume and extent of the system challenges our basic understanding of the alkalinity cycle and the development of alkaline systems on the modern and ancient Earth.

Finally, the Barra Velha Formation and similar examples from the geological record highlight the possibility that alkaline systems developed in volcanically active tectonic settings may themselves have served as significant geological repositories for magmatic and perhaps atmospheric CO_2 (Edmonds et al. 2020). As waters with $\text{ALK} > 2[\text{Ca} + \text{Mg}]$ evaporate, alkalinity and pH both increase, but so too does the carbon storage capacity (FIG. 4). Alkaline waters

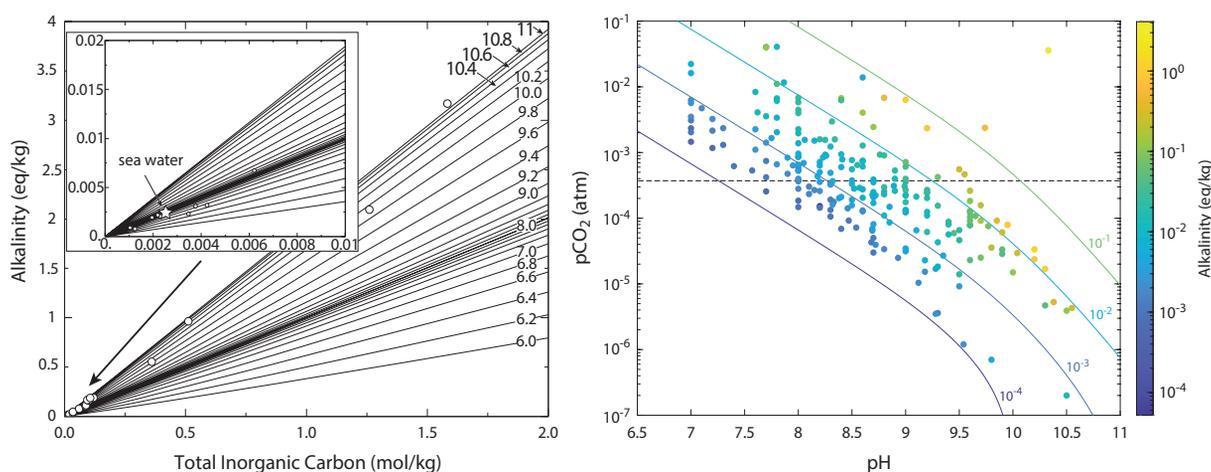


FIGURE 4 (LEFT) Relationship between pH, alkalinity, and total inorganic carbon concentration, calculated by speciating the solution along the axes using the Geochemist’s Workbench. Labels on lines indicate the pH of the solution, and circles indicate analyses of East African Rift lake samples collected by Cerling (1979). The inset emphasises the magnitude of the difference in the carbon and alkalinity concentrations between seawater and alkaline rift lakes. REPRODUCED FROM EDMONDS ET AL. (2020) WITH PERMISSION FROM THE MINERALOGICAL SOCIETY OF AMERICA.

(RIGHT) pCO₂ of water as a function of pH and alkalinity, illustrating that waters tend to be more undersaturated with respect to atmospheric CO₂ (dashed line) at low alkalinity and high pH. Data points are for saline lakes from Duarte et al. (2008), showing that individual lakes can emit and/or absorb CO₂ from the atmosphere depending on the alkalinity and pH. MODIFIED FROM DUARTE ET AL. (2008).

may then intercept and sequester significant quantities of CO₂ from outgassed rifted margins, potentially impacting the global carbon cycle (Edmonds et al. 2020). However, depending on the relative fugacity of aqueous to atmospheric CO₂, the production of alkaline lakes may initiate net transfer of carbon either to or from lake waters and together can account for a globally significant C flux (Duarte 2008). The sedimentary record has shown, in fact, that individual alkaline lakes interact in varied and complex ways with magmatic and atmospheric CO₂, serving, at different times, as both source and sink (Olson and Lowenstein 2021). Unravelling how alkaline systems interact with magmatic and atmospheric pCO₂ remains an important research objective; it is only one of the many that have spawned from a robust geochemical framework established by two visionary Earth scientists some 50 years ago.

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REFERENCES

- Blättler CL, Higgins JA (2014) Calcium isotopes in evaporites record variations in Phanerozoic seawater SO₄ and Ca. *Geology* 42: 711-714, doi: 10.1130/g35721.1
- Cerling TE (1979) Paleochemistry of Plio-Pleistocene Lake Turkana, Kenya. *Palaeogeography, Palaeoclimatology, Palaeoecology* 27: 247-285, doi: 10.1016/0031-0182(79)90105-6
- Cerling TE (1996) Pore water chemistry of an alkaline lake: Lake Turkana, Kenya. In: Johnson TC, Odada EO (eds) *Limnology, Climatology and Paleoclimatology of the East African Lakes*. Routledge, London, pp 225-240, doi: 10.1201/9780203748978
- Chase JE, Arizaleta ML, Tutolo BM (2021) A series of data-driven hypotheses for inferring biogeochemical conditions in alkaline lakes and their deposits based on the behavior of Mg and SiO₂. *Minerals* 11: 106, doi: 10.3390/min11020106
- Darragi F, Tardy Y (1987) Authigenic trioctahedral smectites controlling pH, alkalinity, silica and magnesium concentrations in alkaline lakes. *Chemical Geology* 63: 59-72, doi: 10.1016/0009-2541(87)90074-x
- Duarte CM and 6 coauthors (2008) CO₂ emissions from saline lakes: a global estimate of a surprisingly large flux. *Journal of Geophysical Research: Biogeosciences* 113: G04041, doi: 10.1029/2007jg000637
- Earman S, Phillips FM, McPherson BJOL (2005) The role of “excess” CO₂ in the formation of trona deposits. *Applied Geochemistry* 20: 2217-2232, doi: 10.1016/j.apgeochem.2005.08.007
- Edmonds M, Tutolo B, Iacovino K, Moussallam Y (2020) Magmatic carbon outgassing and uptake of CO₂ by alkaline waters. *American Mineralogist* 105: 28-34, doi: 10.2138/am-2020-6986ccby
- Eugster HP, Hardie LA (1978) Saline Lakes. In: Lerman A (ed) *Lakes: Chemistry, Geology, Physics*. Springer-Verlag, Berlin, pp 237-293
- Fukushi K, Matsumiya H (2018) Control of water chemistry in alkaline lakes: solubility of monohydrocalcite and amorphous magnesium carbonate in CaCl₂-MgCl₂-Na₂CO₃ solutions. *ACS Earth and Space Chemistry* 2: 735-744, doi: 10.1021/acsearthspacechem.8b00046
- Garrels RM, Mackenzie FT (1967) Origin of the chemical compositions of some springs and lakes. In: Strumm W (ed) *Equilibrium Concepts in Natural Water Systems*. American Chemical Society, Washington DC, pp 222-242, doi: 10.1021/ba-1967-0067.ch010
- Haines M, Khot V, Strous M (2023) The vigor, futility, and application of microbial element cycles in alkaline soda lakes. *Elements* 19: 30-36
- Hardie LA, Eugster HP (1970) The evolution of closed-basin brines. *Mineralogical Society of America Special Paper* 3: 273-290
- Leong JAM and 7 coauthors (2021) Theoretical predictions versus environmental observations on serpentinization fluids: lessons from the Samail ophiolite in Oman. *Journal of Geophysical Research: Solid Earth* 126: e2020JB020756, doi: 10.1029/2020jb020756
- Lowenstein TK and 5 coauthors (2017) The Green River salt mystery: what was the source of the hyperalkaline lake waters? *Earth-Science Reviews* 173: 295-306, doi: 10.1016/j.earscirev.2017.07.014
- Lowenstein TK, Risacher F (2009) Closed basin brine evolution and the influence of Ca-Cl inflow waters: Death Valley and Bristol Dry Lake California, Qaidam Basin, China, and Salar de Atacama, Chile. *Aquatic Geochemistry* 15: 71-94, doi: 10.1007/s10498-008-9046-z
- Milesi VP and 13 coauthors (2020) Early diagenesis of lacustrine carbonates in volcanic settings: the role of magmatic CO₂ (Lake Dzirani Dzaha, Mayotte, Indian Ocean). *ACS Earth and Space Chemistry* 4: 363-378, doi: 10.1021/acsearthspacechem.9b00279
- Nesbitt HW (1990) Groundwater evolution, authigenic carbonates and sulphates, of the Basque Lake No. 2 Basin, Canada. In: Spencer RJ, Chou I-M (eds) *Fluid-Mineral Interactions: A Tribute to H. P. Eugster*. The Geochemical Society, Special Publication Number 2, pp 355-371
- Nielsen LC, DePaolo DJ (2013) Ca isotope fractionation in a high-alkalinity lake system: Mono Lake, California. *Geochimica et Cosmochimica Acta* 118: 276-294, doi: 10.1016/j.gca.2013.05.007
- Olson KJ, Lowenstein TK (2021) Searles Lake evaporite sequences: indicators of late Pleistocene/Holocene lake temperatures, brine evolution, and pCO₂. *GSA Bulletin* 133: 2319-2334, doi: 10.1130/b35857.1
- Plummer LN, Parkhurst DL, Fleming GW, Dunkle SA (1988) A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines. USGS Numbered Series, Water-Resources Investigations Report 88-4153, 315 pp, doi: 10.3133/wri884153
- Power IM and 5 coauthors (2009) The hydromagnesite playas of Atlin, British Columbia, Canada: a biogeochemical model for CO₂ sequestration. *Chemical Geology* 260: 286-300, doi: 10.1016/j.chemgeo.2009.01.012
- Power IM and 5 coauthors (2019) Magnesite formation in playa environments near Atlin, British Columbia, Canada. *Geochimica et Cosmochimica Acta* 255: 1-24, doi: 10.1016/j.gca.2019.04.008
- Raudsepp MJ, Wilson S, Morgan B (2023) Making salt from water: the unique mineralogy of alkaline lakes. *Elements* 19: 22-29
- Renaut RW and 6 coauthors (2021) The role of hydrothermal fluids in sedimentation in saline alkaline lakes: evidence from Nasikie Engida, Kenya Rift Valley. *Sedimentology* 68: 108-134, doi: 10.1111/sed.12778
- Rosen MR (1994) The importance of groundwater in playas: a review of playa classifications and the sedimentology and hydrology of playas. In: Rosen MR (ed) *Paleoclimate and Basin Evolution of Playa Systems*. Geological Society of America Special Papers 289: 1-18, doi: 10.1130/SPE289-p1
- Tutolo BM, Tosca NJ (2018) Experimental examination of the Mg-silicate-carbonate system at ambient temperature: Implications for alkaline chemical sedimentation and lacustrine carbonate formation. *Geochimica et Cosmochimica Acta* 225: 80-101, doi: 10.1016/j.gca.2018.01.019
- Varol S and 6 coauthors (2021) Assessment of groundwater quality and usability of Salda Lake Basin (Burdur/Turkey) and health risk related to arsenic pollution. *Journal of Environmental Health Science and Engineering* 19: 681-706, doi: 10.1007/s40201-021-00638-5
- White DE, Hem JD, Waring GA (1963) Chemical composition of subsurface waters. USGS Numbered Series, Professional Paper 440-F, 66 pp, doi: 10.3133/pp440F
- Wright VP (2022) The mantle, CO₂ and the giant Aptian chemogenic lacustrine carbonate factory of the South Atlantic: some carbonates are made, not born. *Sedimentology* 69: 47-73, doi: 10.1111/sed.12835 ■