

Thermodynamic evaporation and freshwater mixing models to test salinity proxies for late Pleistocene lake levels, Mono Lake, California

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ABSTRACT

Times of higher paleolake levels in Mono Lake basin correspond to higher abundances of authigenic minerals such as calcite and Mg-smectite in the Wilson Creek Formation, the lake sediments exposed around the modern lake that represent the persistent wetter conditions of the last glacial cycle. It has been suggested that precipitation of these minerals in Mono Lake is controlled by the flux of water (surface and ground), which replenishes Ca²⁺ and Mg²⁺ ions in the lake. This water is subsequently depleted due to the high rates of evaporation in the Mono Basin, resulting in precipitation of calcite and Mg-smectite mineral phases. Thermodynamic evaporation models starting with Sierra Nevada spring water can simulate the chemical composition

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of Mono Lake remarkably well. These models do not, however, consider the mixing of freshwaters in the lake that is hypothesized to result in precipitation of calcite and Mg-smectite. Here, we present the results of our empirical evaporation and mixing (E&M) model using simple thermodynamic approaches. Although this model is highly simplified, it provides a valuable test of the hypothesis.

INTRODUCTION

Elevated shorelines around lakes in the Great Basin of the western United States, such as those around Mono Lake (Russell, 1889; Lajoie, 1968), provide dramatic evidence of significant changes in the balance between precipitation and evaporation (Stine, 1990; Reheis, 1999). Understanding such changes in regional hydrology and their relationship to climate change can help to improve models used to make predictions about the impacts of future climate change in a warming world.

Geomorphic features such as shorelines are robust measures of lake level, but they provide only spot measurements in time. Lake sediments, on the other hand, potentially provide a more complete record. However, interpretation of proxy indicators in the sediments requires assumptions based on an understanding of the processes that control their characteristics in the sediments. We have previously interpreted the variation in geochemistry of the late Pleistocene sediments at Mono Lake to indicate past salinity variations. This was done by correlating the geochemical measurements with the physical evidence of lake-level variation (Zimmerman et al., 2011b; Sahajpal et al., 2011) based on the tephra stratigraphy and lake-level history from Lajoie (1968). Lajoie (1968) identified deep lake sediments deposited during highstands in exposures around Mono Lake. Authigenic carbonate and leachable lithium (Bischoff et al., 1997) are found in high abundances in these fine-grained lake sediments, which were deposited when Mono Lake stood at high levels (Zimmerman, 2006; Zimmerman et al., 2011b; Sahajpal et al., 2011). Initially, we considered this relationship counterintuitive, as we reasoned that, as in nearby Owens Lake, higher salinity during lake lowstands would lead to increased precipitation of minerals from the lake.

However, Mono Lake today has an extreme composition, with very high alkalinity and pH and very low Ca^{2+} and Mg^{2+} concentrations. We therefore reasoned that during dry times, as the lake evaporates, its Ca^{2+} and Mg^{2+} concentrations in the lake water limit the precipitation of calcite and Mg-smectite¹; in other words, its composition is beyond the chemical divides for those minerals (Eugster and Jones, 1979). During wet times, the increase in freshwater brings a greater flux of these ions into the lake, where they are incorporated into calcite and Mg-smectite throughout the lake. Zimmerman et al. (2011b) and Sahajpal et al. (2011) hypothesized that the input of these minerals to the

deep lake sediments is proportional to the flux of freshwater to the lake. The intent of this study was to test this hypothesis with thermodynamic constraints.

Here, we explored the application of simple thermodynamic approaches to evaporation and mixing of waters in the Mono basin and calculated the mineral equilibria in mixtures of fresh stream and spring water into the highly concentrated Mono Lake water, as well as evaporation of mixtures. The primary goal of this modeling was to test whether our previous interpretations of salinity changes derived from proxy records are reasonable and to explore sensitivity to compositional variations of the freshwaters. The approach presented here is broadly applicable to the understanding of sedimentary geochemistry proxies and the interpretation of changes in the hydrology of lakes and former lakes in arid lands.

MONO LAKE BASIN

Hydrology and Geochemistry

Most of the freshwater feeding Mono Lake today (postdiversion by the Los Angeles Department of Water and Power) is supplied by creeks (~85%) and springs (~15%), with negligible input from direct precipitation (Blevins et al., 1984; Neumann and Dreiss, 1995; Tomascak et al., 2003). The streams are fed by snowmelt from the Sierra Nevada, and their solute content is determined by weathering of the granodiorite and metasedimentary/metavolcanic bedrock (Fig. 1). Mono Lake basin has cold springs and hot springs. Cold springs have ion contents that result from interaction between creek water and the basin fill (Rogers and Dreiss, 1995), whereas the thermal spring waters have a deep source that has mixed with shallow groundwater (Neumann and Dreiss, 1995). For this study, we used a combined element budget supplied by these two end-member spring waters (Tomascak et al., 2003). The average spring waters are dominated by Na^+ and HCO_3^- (Fig. 2) and are important for the solute budget of the lake, despite being a small fraction of the total water input, due to their considerably higher concentration of these ions compared to the creek waters (Table 1).

Present-day Mono Lake is a $\text{Na}^+\text{-CO}_3^{2-}\text{-SO}_4^{2-}\text{-Cl}^-$ brine (Bischoff et al., 1993; terminology of Hardie and Eugster, 1970) with a very high alkalinity (~400 mM) and pH (9.8). The lake chemistry is the result of stream and spring contributions, as well as concentration through evaporation and loss of some elements due to precipitation of authigenic minerals. The average linear evaporation rate over the modern lake is ~1.14 m/yr (the modern area of Mono Lake is 180 km², so this would be equivalent to

¹Sahajpal et al. (2011) found evidence for Mg-smectite in the lake sediments, but the thermodynamic modelling typically uses sepiolite. For the purpose of this paper, the distinction is not important.

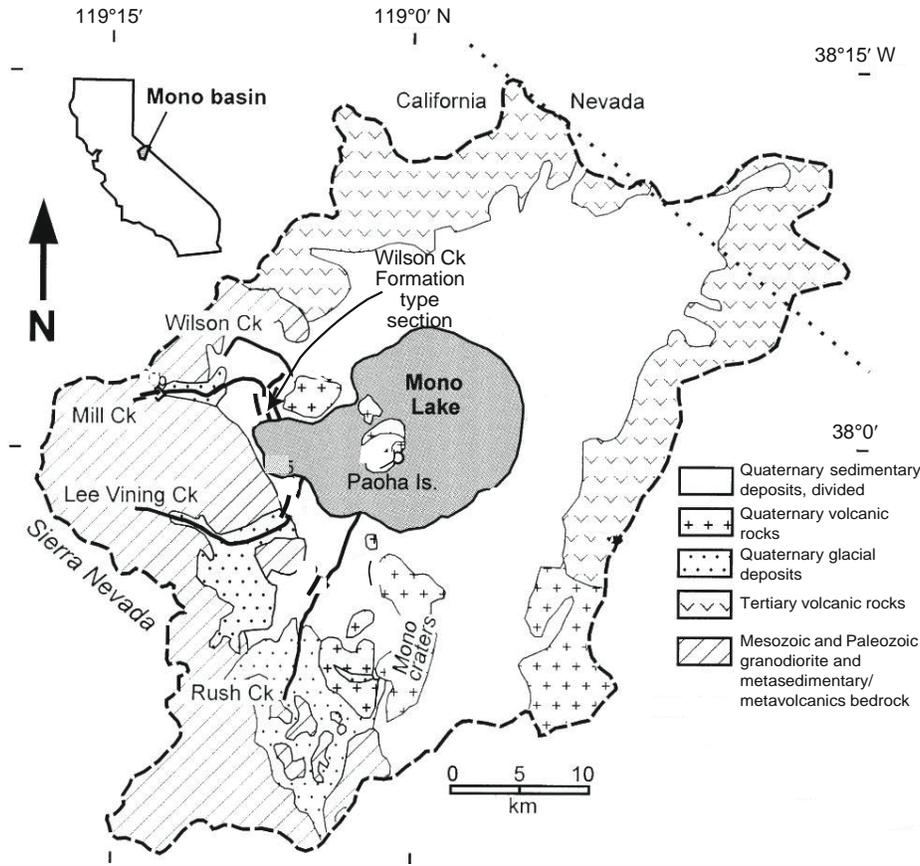


Figure 1. Simplified geology and hydrology of Mono Basin on western edge of the Great Basin. Wilson Creek Formation type section is as described by Lajoie (1968). Source map: Tomascak et al. (2003); modified from Blevins et al. (1984). Ck—Creek; Is—Island.

205 million m³/yr over the area of the lake), while freshwater input to the lake ranges from ~63 million m³/yr in extremely dry years to 126 million m³/yr in extremely wet years (Vorster, 1985; Mono Lake Committee, 2012). It is estimated that Mono Lake currently has ~50% of its natural volume (pre-1940 volume) under current climate conditions due to diversions of streams by

the Los Angeles Department of Water and Power (Blevins et al., 1984), although the lake level has generally been rising since the mid-1990s due to court-mandated reductions in these diversions (Tomascak et al., 2003). Mono Lake is currently ~1945 m above sea level, while the natural level under recent climate conditions would likely be ~12–15 m higher (Vorster, 1985). During the last

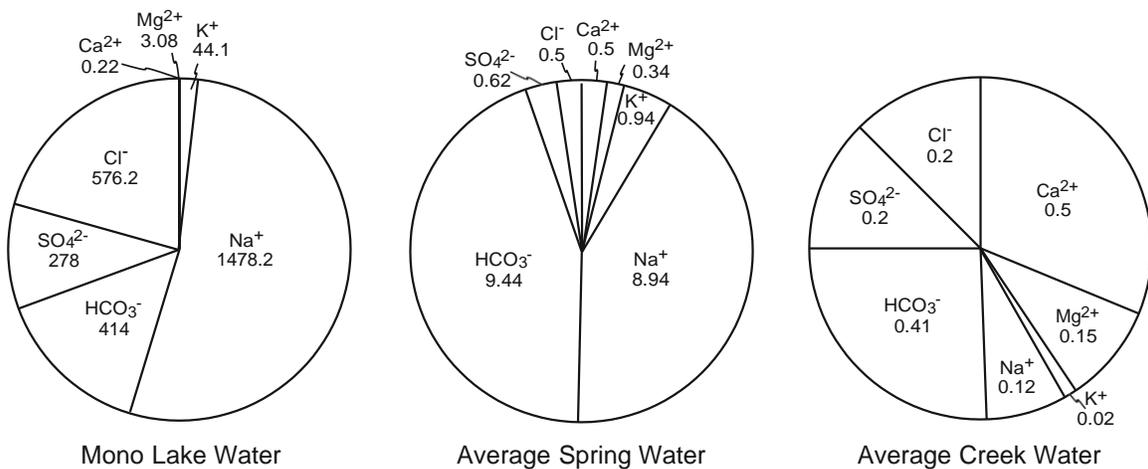


Figure 2. Pie charts showing the relative concentrations of cations and anions in milliequivalents per liter from creek and spring waters and Mono Lake water (data from Neumann and Dreiss, 1995; Tomascak et al., 2003).

TABLE 1. INITIAL COMPOSITION OF FRESHWATER AND MONO LAKE WATER BASED ON ESTIMATES OF NEUMANN AND DREISS (1995) AND TOMASCAK ET AL. (2003)

	Spring water (average) (mmolal)	Creek water (average) (mmolal)	Mixed water (spring + creek) (mmolal)	Mono Lake water (mmolal)
Ca ²⁺	0.25	0.25	0.25	0.11
Mg ²⁺	0.17	0.075	0.1	1.54
Na ⁺	8.94	0.12	1.91	1478.2
K ⁺	0.47	0.02	0.36	44.1
Li ⁺	0.002	0.0002	0.001	1.43
Sr ²⁺	0.006	0.004	0.0003	0.0001
HCO ₃ ⁻	9.44	0.41	7.81	414.7
Cl ⁻	0.25	0.20	0.21	576.2
SO ₄ ²⁻	0.31	0.1	0.26	139.0
SiO ₂ (aq)	1.1	0.14	0.84	0.22
B	0.04	0.002	0.01	0.001

glacial period, the lake level reached elevations as high as 2155 m above sea level (Lajoie, 1968). There is no indication that the lake spilled over its sill (at ~2195 m) at any time in at least the last 70,000 yr (Zimmerman et al., 2006). This is in contrast to the nearby Owens Lake basin, which has a different basin geometry than Mono Lake basin, because it routinely flushes its ions into low-lying Searles and China Lake basins during glacial periods (e.g., Bischoff et al., 1997). The lake-level variations have left a geomorphic and physical stratigraphic record that has been used to infer past changes in the lake level (Russell, 1889; Lajoie, 1968; Benson et al., 1990; Stine, 1990, 1991; Ali, 2018).

The fluvial and lacustrine deposits of the last glacial period at Mono Lake were named the Wilson Creek Formation after the type section in Wilson Creek canyon (Lajoie, 1968). The Wilson Creek Formation is exposed in artificial stream cuts and some natural exposures near Mono Lake to elevations as high as 2070 m above sea level. The physical evidence for lake-level variations has been tied to geochemical proxy evidence by using tephrostratigraphy and the lake-level history of Lajoie (1968) to correlate between exposures around the basin (Zimmerman et al., 2006, 2011b; Sahajpal et al., 2011). This empirical evidence provides a first-order test of the geochemical proxy interpretation.

Paleohydrology Proxies

Authigenic calcite, inorganic pisoliths, and ostracodes form a significant portion of the Wilson Creek Formation lacustrine sediments in the Mono Lake basin. Zimmerman et al. (2006, 2011b) demonstrated that times of high lake level are times of high carbonate abundance in Wilson Creek Formation sediments (Fig. 3). Sahajpal et al. (2011) used the method applied by Bischoff et al. (1997) to Owens Lake sediments to determine the concentrations of leachable Li, Mg, and Sr and found these elements were also higher in the Mono Lake sediments deposited during times of higher lake levels. In contrast, Bischoff et al. (1997) found higher concentrations of carbonate and leachable ions in sediments deposited during lowstands of Owens Lake.

The difference in the abundance of leachable ions and calcium carbonate in Mono Lake and Owens Lake is due to the low sill and frequent flushing of saline water that occurred at Owens Lake. In contrast, Mono Lake did not overflow during the last glacial period (Zimmerman et al., 2011a; Sahajpal et al., 2011). In other words, the precipitation of authigenic minerals in Mono Lake is limited by the supply of Ca²⁺ and Mg²⁺ from the freshwater sources. The Ca²⁺ and Mg²⁺ fed to the lake precipitate out as calcite and Mg-smectite, so during times of high lake levels, which we associate with periods of high freshwater input, more Ca²⁺ and Mg²⁺ are supplied to the lake as compared to times of lower freshwater input (less rainfall and/or more evaporation).

EVAPORATION-BASED MODELS

Evaporation-based models have long been used to explain the geochemistry of arid basin lakes and the mineral phases that precipitate from these waters (Garrels and Mackenzie, 1967; Hardie and Eugster, 1970). These models predict the behavior of various chemical species with a reasonable accuracy. Ions that are not structural constituents of minerals that are precipitating are conservative, and their concentration increases in solution with increasing concentration factor (CF). Ions that are precipitating into mineral phases may increase in concentration more slowly, remain unchanged, or even decrease in concentration. Since its conception, this model has undergone several revisions in order to make it more inclusive of the phenomena that are generally witnessed in waters of arid basins (Hardie and Eugster, 1970; Eugster and Hardie, 1978; Eugster and Jones, 1979; Harvie and Weare, 1980; Harvie et al., 1984; Eugster and Maglione, 1979).

Garrels and Mackenzie (1967) used the evaporation of Sierra Nevada spring water to explain the composition of Mono Lake water in their classic paper, and they modeled the main features with remarkable accuracy. In our current study, we started with a similar approach to simulate the evaporation of three freshwater sources from the Mono Lake basin, creek and spring end members and a creek/spring mix in proportions

based on estimates by Tomascak et al. (2003). In our simulations, we made the evaporation models more comprehensive than those of Garrels and Mackenzie (1967) and Hardie and Eugster (1970) by including Sr^{2+} and Li^+ ions and B species (e.g., $\text{B}(\text{OH})_4^- + \text{B}(\text{OH})_3$), and by extending the modeled CF

range to 3000× to include the current conditions of the Mono Lake basin, which are beyond the CF range of the previously published studies. In addition, to understand the proxy records of the Wilson Creek Formation, we also simulated the mixing of each of these freshwater compositions into the saline Mono Lake water. We assumed that the pre-Wilson Creek (last interglacial) Mono Lake was similar to the modern lake, so modeling the mixing of creek + spring inputs with an existing (highly evaporated) lake is therefore a better representation of the real history of Mono Lake than simple evaporation of freshwaters.

METHODS

To simulate the behavior of various chemical species as freshwater is progressively evaporated (Table 1), we used the REACT subprogram of Geochemist's Workbench (Bethke and Yeakel, 2008; Lawrence Livermore National Laboratory [LLNL] database). The REACT subprogram is capable of tracing reaction paths of fluids, minerals, and gases, in addition to calculating the distribution of species in aqueous solution, mineral saturation, and gas fugacity. The modeled freshwaters for our study were evaporated through a CF range of 1× to 3000×, where a CF of 1× ($\log \text{Cl}^- 10 \times 10^{-4}$) was taken as the initial freshwater (average spring, creek, or creek/spring mix water) and a CF of 3000× was taken as approximately the current CF of Mono Lake water. For simplicity, we used temperature (T) = 25 °C and CO_2 (g) = 350 ppm. We did some sensitivity tests on these parameters, and they had very little impact on the trends presented here.

In order to simulate evaporation and the mixing of waters (E&M) together, we used the PHREEQC version 2 (LLNL database; Parkhurst and Appelo, 1999) geochemical modeling program developed by the U.S. Geological Survey. To simulate the geochemical evolution of the lake water since the last glacial period, we increased the proportion of freshwater to initial lake water in our E&M model to proportions that are equivalent to a rise in the lake from the present-day level (~1945 m) up to its deglacial highstand level of 2155 m by keeping the evaporation rate constant (4% of the lake volume in each iteration) and adding a constant flux of freshwater (7% of the lake volume) in each iteration, such that filling exceeded the evaporation rate. We chose the present-day lake as a starting point for our model because the current water budget and mass balance of different chemical species in the Mono Lake basin are well constrained (Neumann and Dreiss, 1995; Tomascak et al., 2003) and because we assumed that the lake composition was likely similar to today during previous interglacials. This simulation was also performed using $T = 25$ °C and CO_2 (g) = 350 ppm.

In order to understand how changes in the flux of freshwaters from different sources may affect the resulting lake chemistry and precipitation of authigenic mineral phases, we examined two scenarios. The first scenario used the freshwater mix and compositions estimated by Tomascak et al. (2003) (85% creek water and 15% spring water) and assumed that (just like today) the creeks and springs were both feeding the lake, with the streams supplying the

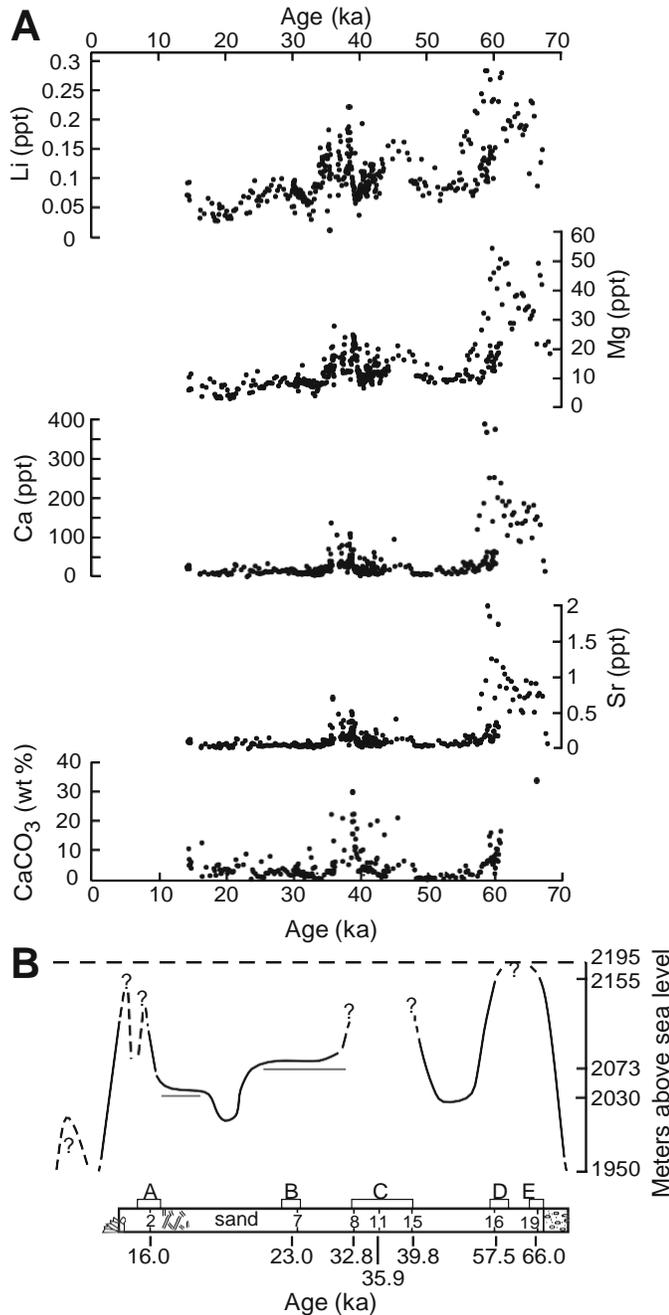


Figure 3. (A) Abundance of leachable Li, Mg, Ca, Sr (Sahajpal et al., 2011), and CaCO_3 (Zimmerman et al., 2006) in the lacustrine Wilson Creek Formation sediments. (B) Lake level interpretation from Sahajpal et al. (2011); used with permission. Letters (A–E) and numbers (1–19) represent tephra packages and tephra layers, respectively (from Lajoie, 1968).

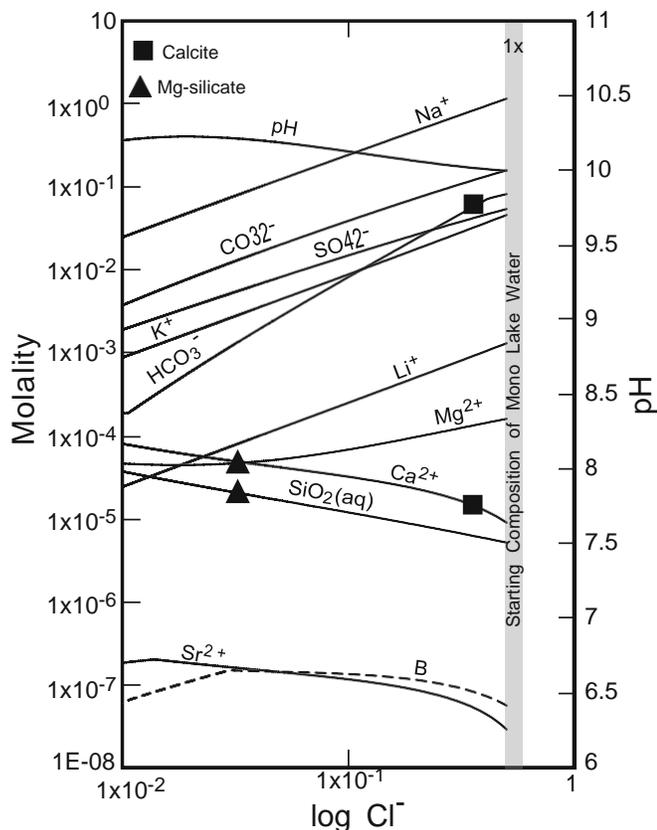


Figure 4. Calculated results of various chemical species plotted against Cl^- concentration from evaporation and mixing-based model predicting the evolution of Mono Lake from the present-day lake to its spill level at 25 °C and $\text{CO}_2 = 350$ ppm. The evaporation model predicts that the pH of Mono Lake water remains close to 10.

majority of the water, but with an increased flux from both creeks and springs due to much wetter conditions than today. The second scenario predicted the behavior of chemical species if the present-day Mono Lake were to be filled up to the highest level it attained during the last glacial period (2155 m) using only the average creek water end member (Figs. 4, 5A, and 5B). The latter scenario, in our estimate, should more closely reflect the conditions during glacial times, when we would expect the concentration of ions in the freshwater, including springs, to be much lower.

In its current form, PHREEQC version 2 limits the number of mixing and evaporation scenarios that can be performed, so in order to increase the ability of PHREEQC to run a desired number of mixing scenarios, a Python language-based computer program was developed to carry out multiple mixing and evaporation scenarios until the desired lake volume was achieved (see Supplemental Material²).

²Supplemental Material. A Python-based computer code used for automating the simulation used to predict the geochemical evolution of Mono Lake waters since the last glacial period. Please visit <https://doi.org/10.1130/SPE.S.14632977> to access the supplemental material, and contact editing@geosociety.org with any questions.

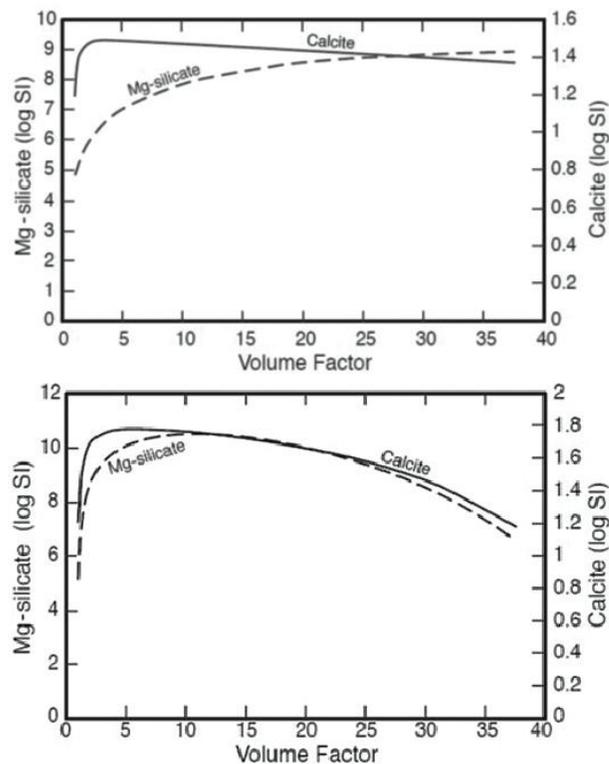


Figure 5. (A) Results of the evaporation and mixing model using a constant flux of water with average creek composition. Calcite and Mg-silicate remain saturated in the Mono Lake water. $\text{Log SI} > 1$ indicates that the mineral is saturated, where saturation index is given by: $\text{SI} = \log(\text{IAP})/\text{K}_{\text{sp}}$, where IAP is ion activity product, and K_{sp} is solubility product. The model output shows that even when water as dilute as the average creek water is evaporated, calcium carbonate and Mg-silicate remain saturated. Volume factor (VF) is an indication of the extent of the lake. The modern-day lake is assumed to have $\text{VF} = 1$, while the VF values at past lake levels (in meters above sea level) are: 7 at 2030 m (lower Pleistocene terrace); 12 at 2073 m (upper Pleistocene terrace); 24 at 2155 m (highest lake level attained during last glacial); and 31 at 2195 m (Mono Lake basin spill level). The VFs are based on the paleovolume estimates of Ali et al. (2011). (B) Results of the evaporation and mixing model using a constant flux of water with proportional mix of average creek and spring composition based on estimates by Tomascak et al. (2003). The model shows that calcium carbonate and Mg-silicate remain saturated during the evaporation and mixing of the more accurate composition (average creek and spring water) of water in the Mono Lake basin.

RESULTS

Chemical Evolution during Evaporation of Freshwaters

The model results of our three evaporation scenarios (Table 2) using Geochemist's Workbench (creek water; spring water; creek/spring mix) are presented in Figures 6, 7, and 8. We plotted all the modeled chemical species against Cl^- concentration.

TABLE 2. SUMMARY OF THE PROCESSES MODELED AND THE TYPES OF WATER USED FOR EACH EXPERIMENT

Process modeled	Water type	Software	Figure
Evaporation	Average creek water	Geochemist's Workbench	Figure 6
Evaporation	Average spring water	Geochemist's Workbench	Figure 7
Evaporation	Creek + spring water	Geochemist's Workbench	Figure 8
Evaporation and mixing	Creek + spring water	PHREEQC	Figure 4

Modeled Na^+ , K^+ , and Li^+ increase as the water evolves to a CF of 3000 \times in all three scenarios (Figs. 6, 7, and 8). The SO_4^{2-} ion increases initially but begins to decrease above 1000 \times ($\log \text{Cl}^- 10 \times 10^{-1}$; Fig. 7) in the spring water end member. Sulfate increases throughout the calculations in a proportional mix of creek and spring waters (Fig. 8). For the creek end member, SO_4^{2-} concentration increases up to a 100 \times ($\log \text{Cl}^- 10 \times 10^{-2}$) concentration, and then between 100 \times and 1000 \times ($\log \text{Cl}^- 10 \times 10^{-3}$ to $\log \text{Cl}^- 10 \times 10^{-2}$), it increases at a lower rate, and then it shows signs of titrating out beyond 3000 \times (Fig. 6).

Modeled Ca^{2+} and Sr^{2+} ion concentrations increase with increasing CF in creek water, showing only a slight drop in concentration at CF of $\sim 10 \times$ ($\log \text{Cl}^- 10 \times 10^{-3}$) when calcite begins to precipitate (Fig. 6). In the case of the spring water end member and the creek/spring mix, Ca^{2+} and Sr^{2+} show distinctive nonconservative behavior, with negligible Sr^{2+} above 100 \times ($\log \text{Cl}^- 10 \times 10^{-3}$), and negligible amounts of Ca^{2+} remaining in the water beyond CF of 1000 \times ($\log \text{Cl}^- 10 \times 10^{-1}$) (Figs. 7 and 8). The concentrations of HCO_3^- and CO_3^{2-} show conservative behavior up to $\sim 10 \times$ evaporation ($\log \text{Cl}^- 10 \times 10^{-3}$) but deviate significantly

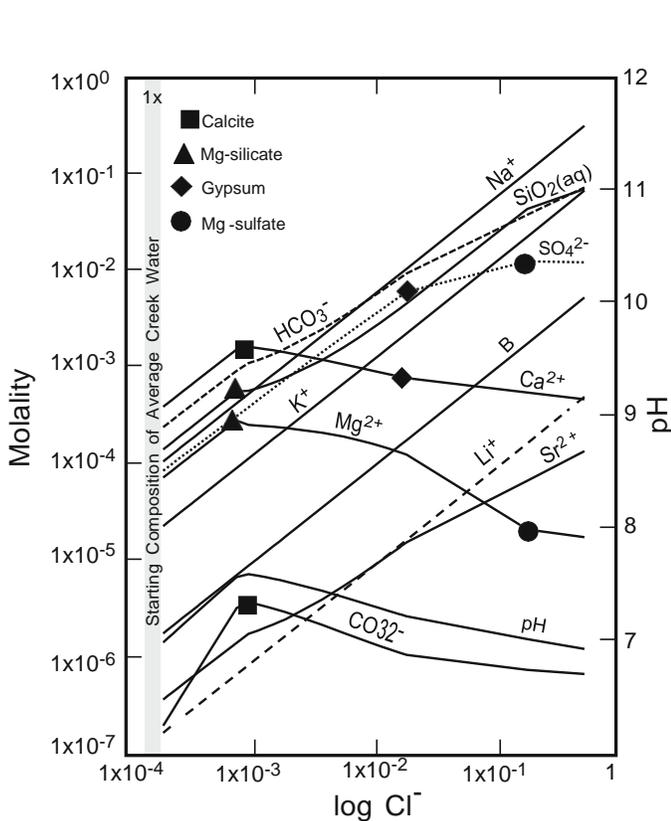


Figure 6. Calculated results of various chemical species plotted against Cl^- concentration ($\log 0.0001 = 1 \times$ and $\log 1 = 10,000 \times$) with evaporation of average creek water feeding Mono Lake at 25 °C and $\text{CO}_2 = 350$ ppm. The inflection point for any element indicates the conditions under which it starts to precipitate. The symbols indicate the conditions under which minerals like calcium carbonate and Mg-silicate precipitate.

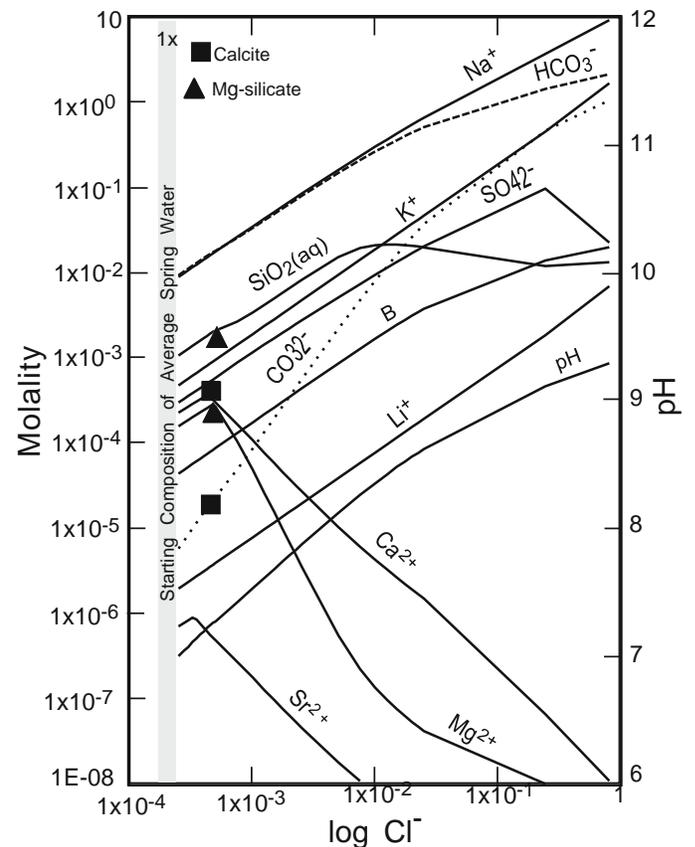


Figure 7. Calculated results of various chemical species plotted against Cl^- concentration ($\log 0.0001 = 1 \times$ and $\log 1 = 10,000 \times$) with evaporation of average spring waters feeding Mono Lake at 25 °C and $\text{CO}_2 = 350$ ppm. These results from our simulation of evaporation of spring water closely match the theoretical results of evaporation of spring water proposed by Garrels and Mackenzie (1967).

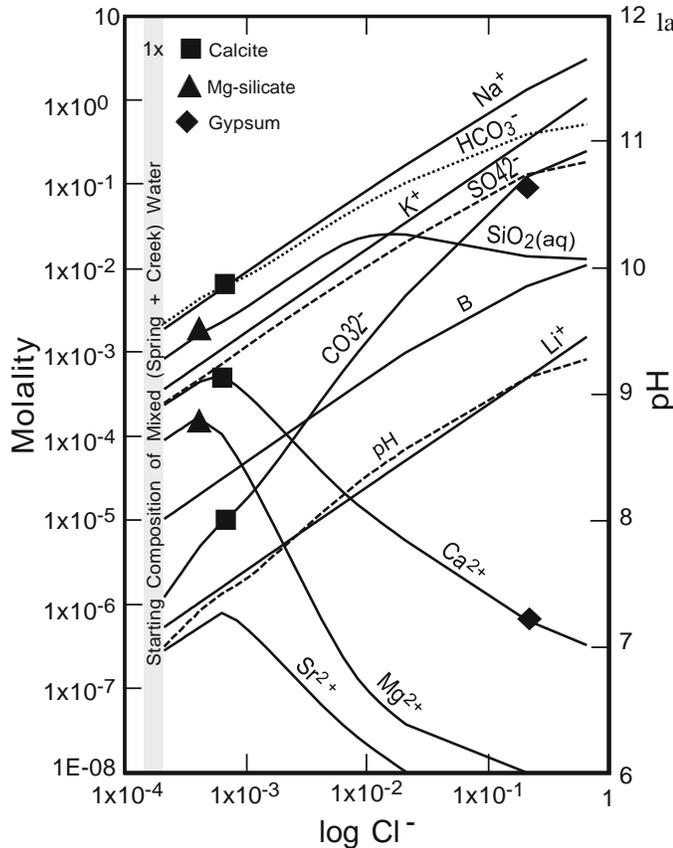


Figure 8. Calculated results of various chemical species plotted against Cl^- concentration ($\log 0.0001 = 1\times$ and $\log 1 = 10,000\times$) with evaporation of a mix of average creek and spring waters (based on estimates from Tomascak et al., 2003) feeding Mono Lake at 25°C and $\text{CO}_2 = 350$ ppm.

from this conservative behavior with increases above $10\times$ evaporation (Fig. 6). However, in the case of the spring water and the creek/spring mix, values increase with increasing CF after Ca^{2+} and Sr^{2+} have been titrated out (Figs. 7 and 8). Mg^{2+} exhibits non-conservative behavior in all three scenarios, starting to decrease with increasing CF above $\sim 10\times$, and it is reduced to extremely low concentrations at a CF of $\sim 1000\times$ ($\log \text{Cl}^- 10 \times 10^{-1}$) in the spring water and the creek/spring mix (Figs. 7 and 8). In the creek end member, some Mg^{2+} still remains at $3000\times$.

Evaporation and Mixing of Lake and Freshwaters

The results of our E&M model are shown in Figures 5A and 5B. Na^+ , K^+ , Li^+ , SO_4^{2-} , HCO_3^- , and CO_3^{2-} continually increase with increasing CF, whereas Ca^{2+} , Sr^{2+} , Mg^{2+} , and $\text{SiO}_2(\text{aq})$ precipitate in the authigenic phases of calcite and Mg-silicate and thus show strongly nonconservative trends (Fig. 4). The saturation indices [SI = $\log(\text{IAP}/\text{K}_{\text{sp}})$, where IAP is ion activity product, and K_{sp} is solubility product] of the authigenic mineral phases produced by this model plotted against the volume factor of the

lake (a measure of how expanded the lake would be compared to current lake volume) demonstrate that these phases remain saturated in the lake water and are not sensitive to the composition of the freshwater mixed into the lake, which is simulated to rise during the glacial period highstand (Figs. 5A and 5B).

DISCUSSION

Evaporation-Based Models

In almost all natural waters, calcite is the first mineral to precipitate during progressive evaporation (Garrels and Mackenzie, 1967). However, in high-alkalinity waters such as Mono Lake, after all the Ca^{2+} has been removed as calcium carbonate, the alkalinity is still higher than the Mg^{2+} concentration. It is possible that magnesite (MgCO_3) or hydromagnesite, denoted $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is precipitating or has precipitated in Mono Lake sediments, but we know that Mg-smectite is a prominent phase present in the X-ray diffraction and scanning electron microscope scans (Sahajpal et al., 2011), so we assume this is the main path for removal of Mg^{2+} from the water. In waters like Mono Lake, this leads to a situation where the lake water is almost always saturated with respect to calcite and Mg-silicate but contains low concentrations of Ca^{2+} and Mg^{2+} (e.g., in modern Mono Lake, $\text{Ca}^{2+} = 4$ ppm). Ions like Li^+ and Sr^{2+} replace Mg^{2+} and Ca^{2+} in the mineral phases due to their similar ionic size. This is why Li^+ and Sr^{2+} ion concentrations mimic the Ca^{2+} and Mg^{2+} ion concentration curves in the lake sediments (Fig. 3). It has been reasoned out in Sahajpal et al. (2011) that, since Li^+ ion is a conservative ion and tends to remain in the water at concentration factors past the precipitation of Mg-silicate, it serves as a better proxy for a lake that evolves from being relatively fresh to brine (salinity $\sim 8.1\%$, alkalinity 400 mM) conditions.

Evolution of Mono Lake Based on the E&M Model

Since Mono Lake is a closed basin lake, any change in the lake chemistry is a result of the flux of freshwater input, rate of evaporation, mineral precipitation, and mixing with the preexisting lake water. Thus, geochemical models need to include both evaporation and mixing processes. The model that we developed for this study is a first step in this direction.

The results of the first E&M scenario, assuming the modern balance between creek and spring water but with increased overall flux, show that calcite and Mg-silicate remain saturated in the lake through the dilution necessary to raise the lake to its glacial period highstand (Figs. 5A and 5B). The outcome of the second E&M scenario, filling the lake to the highest level of the last glacial period with only creek water, demonstrates that even when waters as dilute as the creek water end member are fed to the lake, authigenic minerals like calcite and Mg-silicate continue to remain oversaturated in the water.

This model supports our initial hypothesis that the greater freshwater flux, regardless of its chemical composition, provides

greater amounts of elements (Li, Ca, Mg, and Sr) that are then concentrated in carbonate and Mg-smectite in the sediments (Figs. 4, 5A, and 5B).

Comparison of Evaporation and Mixing Model with Evaporation-Only Models

The approach we used in developing our model is opposite of that of evaporation-based models. The E&M model starts with a concentrated brine like Mono Lake water and dilutes the lake with enough freshwater proportionally (average creek end member and creek and spring mixed water) to raise the lake to its glacial period highstand. Besides explaining the evolution of Mono Lake, the E&M model also predicts the oversaturation, and therefore the potential for precipitation of authigenic mineral phases like calcite and Mg-silicate (Figs. 5A and 5B). The following section briefly discusses the end-member evaporation scenarios followed by a discussion and comparison of the E&M model to the evaporation models.

It is impossible to attain concentrated brine with a composition like Mono Lake through evaporation of the creek water end member alone (Fig. 6), as this model shows the buildup of ions like Ca^{2+} , Sr^{2+} , and $\text{SiO}_2(\text{aq})$ in the brine and a drawdown in the concentrations of ions like HCO_3^- and CO_3^{2-} . The opposite is true in the actual lake waters—low Ca^{2+} , Sr^{2+} , and $\text{SiO}_2(\text{aq})$, but high alkalinity.

In contrast, the evaporation of the average spring water end member (Fig. 7) closely matches the actual behavior of different chemical species during the evolution of Mono Lake, and these results are in broad agreement with the theoretical model proposed by Garrels and Mackenzie (1967). The model was run using other ratios of creek to spring water, but since springs are much more concentrated than the creeks in their ionic content, the results were not different from what is reported in this study.

Zimmerman et al. (2006, 2011b) and Sahajpal et al. (2011) have shown that high Mono Lake levels correspond to high concentrations of leachable ions like Ca^{2+} , Mg^{2+} , Sr^{2+} , and Li^+ . The model that best describes these findings is the E&M model, which considers the continuous addition of ions from freshwater sources along with evaporation in the closed basin lake. During wet conditions, when there is a higher flux of water and thus ions, the concentrations of these ions build up compared to times when drier conditions prevail, as these ions persist in the lake due to the high sill elevation (Zimmerman et al., 2011b). Thus, the E&M model explains the geochemical evolution of Mono Lake water since the last glacial period and thus supports the interpretation of the proxy record of Zimmerman et al. (2006, 2011b) and Sahajpal et al. (2011). More realistic conditions, including varying the evaporation rate with climate changes, and including estimates of temperature and CO_2 variability, might improve the details, but the record that exists is not of sufficient resolution at this point to make such calculations practical.

We suggest that our empirical evaporation and mixing model provides a robust explanation for the current chemistry

of Mono Lake, and it further offers support for the geochemical proxy records for Mono Lake basin. Our model predicts that, just like in evaporation-based models, Na^+ , K^+ , Li^+ , and SO_4^{2-} are conservative in the water. However, it appears that SO_4^{2-} may start to precipitate out beyond a CF of 3000 \times . The HCO_3^- and CO_3^{2-} concentrations are so enriched in the lake water that their concentration always remains high, even after these ions titrate out along with Ca^{2+} and Sr^{2+} in the carbonate phase. Our findings concerning Ca^{2+} ion behavior in Mono Lake are similar to those of Garrels and Mackenzie (1967), wherein almost all of the Ca^{2+} ion brought to the lake is consumed in the formation of calcite. The concentration of Mg^{2+} starts to increase in the water after most of the $\text{SiO}_2(\text{aq})$ gets precipitated out as Mg-silicate. This observation is in agreement with the findings of Tomascak et al. (2003), who showed that Mg^{2+} has a longer residence time than Ca^{2+} in the water.

FUTURE IMPROVEMENTS TO THE EVAPORATION AND MIXING MODEL

Our evaporation and mixing-based model aims to create a more accurate depiction of the conditions that led to the brine evolution in the Mono Lake basin. This model is based solely on thermodynamics and does not take into account the kinetics, nor does it take into account the role that algae play in the CO_2 and silica cycles in the lake. It is also constrained by the accuracy of the mineral data that are used in its construction; nonetheless, a carefully constructed thermodynamic model can give us valuable insight into the geochemical evolution of Mono Lake. The main shortcomings of this model are the fact that it assumes a constant evaporation rate and a constant flux of water to the lake in order to increase the lake level, which is not what is expected in a natural situation. Since our assumptions are based on observations made in the present-day Mono Lake, they do serve as a reasonable starting point for developing more accurate geochemical models. The obvious next step toward understanding brine evolution in Mono Lake will be to integrate this with a hydrologic model to better account for water budgets throughout the history of the lake. In addition, experiments using other values for the temperature, evaporation rate, $p\text{CO}_2$, and other environmental factors will refine the representation of the glacial-age lake. Improvement in existing geochemical models and their integration with hydrologic and climate models will ultimately lead to better grounded geochemical proxies and enable us to use them for refining the climate records.

CONCLUSIONS

In carrying out this study, we developed a theoretical model of continuous mixing of freshwater into the saline Mono Lake, along with the significant evaporation in this arid basin. The evaporation of an 85:15 mix of stream and spring waters yields a result similar to the modern composition of Mono Lake, and mixing and evaporation in proportions that allow the lake

volume to increase to its maximum level provide a geochemical explanation for the evolution during freshening of Mono Lake during glacial periods and support the proxy record in the Mono Lake basin. Based on this study, we can make the following general conclusions:

- (1) A combined evaporation and mixing-based model provides an explanation for the calcite proxy record for lake level and Mg-silicate (leachable Li) proxy record for paleosalinity, specifically, their positive correlation with physical evidence for lake levels in the last glacial period.
- (2) The precipitation of authigenic calcite and Mg-silicate is controlled by the flux of ions supplied by the freshwater, and they should have remained saturated in the lake water throughout the last glacial period, when the lake volume was up to ~30 times greater, independent of the composition of the freshwater mixed into the lake.
- (3) Our evaporation and mixing model is a first step toward explaining the geochemical evolution of this arid lake basin, and the approach should be portable to other closed basin lakes with known or inferable hydrologic budgets. A significant future improvement will be to integrate the evaporation and mixing model with hydrological models in order to make more realistic estimates of water budgets.

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