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Carbonate-associated sulfate as a proxy for lake level fluctuations: a proof of concept for Walker Lake, Nevada

William Berelson · Frank Corsetti · Brad Johnson · Toan Vo · Chris Der

Abstract Closed-basin alkaline lakes record climate change particularly well because they generally contain a sedimentary record that is high in carbonate mineral content from which climate proxies can be determined. Various approaches are used to estimate paleo-lake level and volume (δ^{18}O, dating of "shoreline" tufas, biotic proxies, etc.), yet all carry certain caveats that limit their usefulness. Ultimately, the relationship between the chemistry of the lake, the volume of the lake, and the response of the proxy will determine how well a proxy serves a paleolimnologic purpose. Here, we discuss the use of carbonate-associated sulfate (CAS), the sulfate contained within the lattice of carbonate minerals that precipitate in lake water, as a proxy for lake water chemistry and by extension, lake volume. Walker Lake, an alkaline closed-basin lake in western Nevada, has experienced a well-documented lake-level decline since 1880 and provides a test case for CAS as a lake-level proxy. By extracting the CAS from sedimentary carbonate and tufas that have been age dated, we can relate these values to lake sulfate content based on historical or other proxy data. We confirm that CAS tracks lake sulfate. Our study of sedimentary carbonates demonstrates that CAS is a linear function of lake sulfate

through a range of 10–25 mM, which corresponds to a change in lake level of 30 m. As confirmation of the CAS technique, we analyzed a stromatolitic tufa dated using AMS ^{14}C. The CAS trend in the stromatolite suggested that it grew during a lake-level decline, a result consistent with other proxy data. Finally, laboratory experiments were conducted that demonstrate CAS is monotonically correlated with sulfate concentration and that precipitation kinetics are not likely a major control on CAS in alkaline lakes, but that ionic strength of the solution exerts a strong control on CAS.

Keywords Carbonate · Sulfate · Paleoproxy · Walker Lake · Tufa

Introduction

Closed-basin alkaline lakes are particularly sensitive to climate change. The record of lake change is often recorded with excellent temporal resolution within carbonate-rich sediments (when there is a high accumulation rate) amenable to paleoclimatic studies (Li 1995; Yuan et al. 2004, 2006a, b). Many alkaline lakes also contain carbonate accretionary structures, commonly known as tufas, that provide another geological archive of information from which to investigate lake and climate history (e.g. Kelts and Hsu 1978; Benson 2004; Nelson et al. 2005).

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The ability to recognize past lake level is fundamental to understanding the evolution of the lake. A diagnostic measure of lake level can be lake chemistry, especially for elements and compounds whose concentration is closely related to lake-volume (conservative ions). A variety of lake-level proxies have been applied in the past, and they each carry with them some level of confidence and ambiguity. In Walker Lake, Nevada, our test case, the $\delta^{18}O$ of the lake sediments (Yuan et al. 2004, 2006b), biological proxies (Bradbury et al. 1989), "shoreline tufa" age dating (Benson 1978; Benson and Thompson 1987; Lao and Benson 1988; Benson et al. 1991) and physical stratigraphy of proximal lake sediments (Adams 2007) have been used to address lake-level change over the past 15,000 years. Unfortunately, different lake-level proxies agree at times and disagree at others (see discussion in Adams 2007) (Fig. 1), thus carrying with them some level of uncertainty.

Here, we propose a new lake-level proxy based on Carbonate Associated Sulfate (CAS; sulfate that is incorporated into the carbonate lattice during mineral precipitation). We investigate the ability of CAS to track lake sulfate concentration during a period of lake volume decline (sulfate concentration increase). We also investigate the sensitivity of this variable to other environmental factors and to mineral precipitation rates. These results suggest that CAS may be useful in other saline lake systems as well, and may find broad application as a lake-level indicator.
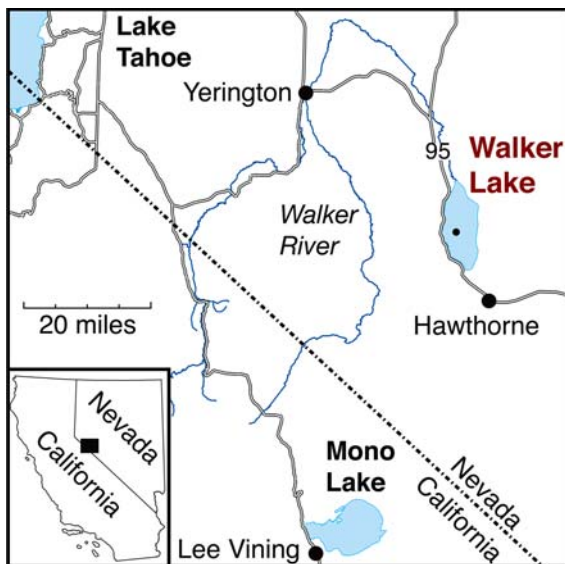
Study area: Walker Lake, Nevada

Walker Lake presently has an area of approximately 100 km^2 and a maximum depth of 28 m (Fig. 2); its salinity is currently 17 g/l and pH is 9.4. It is a closed-basin, sodium carbonate lake that has undergone cycles of expansion and contraction affected by climatic forcing and anthropogenic use of Walker River water (e.g. Benson et al. 1991; Yuan et al. 2004). Approximately 15,000 ybp, Walker Lake was joined with the large pluvial Lake Lahontan, with the highstand at 1,338 m elevation (e.g. Russell 1885; Benson et al. 1991; Adams and Wesnousky 1999). However, Walker Lake has the highest sill in the Lahontan system (1,310 m) and has remained separated from the rest of the Lahontan basin for
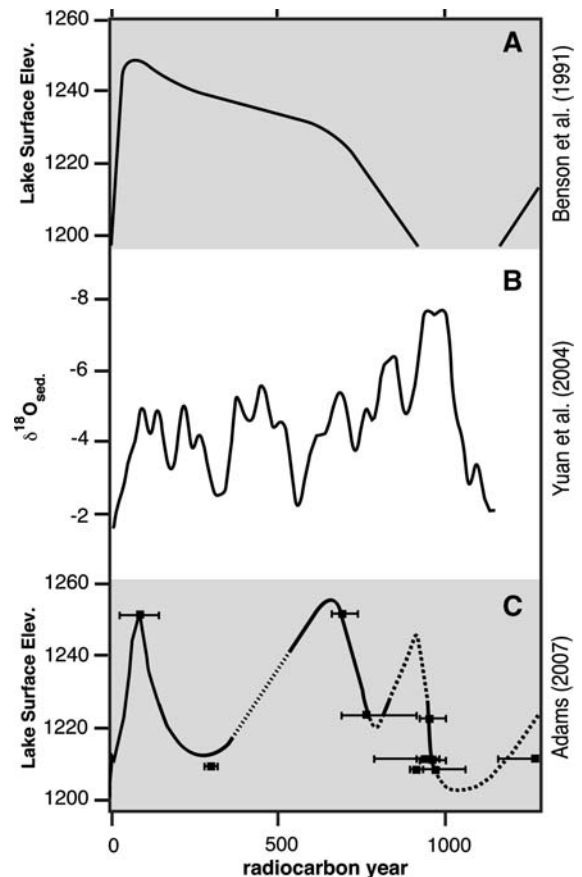
Fig. 1 Different lake-level proxies yield different degrees of detail and document different processes responsible for or related to changes in lake volume. This comparison of three accounts of Walker Lake level fluctuations demonstrates the range of interpretation and the need for more tools to help deconvolve lake level history

approximately the last 12,000 years. Presently, the lake level stands at ∼1,200 m; it has fallen ∼50 m since the early 1900s primarily because of agricultural diversion of Walker River water (Thomas 1995). Changes in lake level over the past 100 years are well documented (Yuan et al. 2006a) and the bathymetry and lake surface area to volume relationship is very well known in light of recent high-resolution bathymetric studies (Lopes and Smith 2007).

Lake stratification during the summer months results in depletion of oxygen in bottom water. Beutel et al. (2001) and Beutel (2001) document the decline in the trout fishery and the stress imposed by increasing lake salinity and other factors related to lake stratification. The anoxic bottom water

Fig. 2 Study area, Walker Lake, Nevada. Coring location indicated by solid circle

accumulates ammonia, sulfide, methane and phosphate, yet when the lake mixes, gradients in these species become more diffuse or disappear. The concentrations of sulfate, bicarbonate, magnesium and other salts are so high that changes in their concentrations during lake stratification are not detectable. The lake has been the subject of many USGS open file reports (e.g. Yount and Quimby 1988; Rice and Tuttle 1989; Yang 1989) describing aspects of lake chemistry and basin hydrology.

Methods

In this study, we report on analyses of Walker Lake sediments and tufas and experiments conducted using Walker Lake water and artificial solutions in the laboratory. Both the lake water and cores were collected from near the middle of the lake (Fig. 2) where the depth was ~25 m (38°42′ N, 118°43′ W). The water used in precipitation experiments was collected at a depth of 8 m in June, 2007 using a standard Niskin bottle. Sediment cores analyzed in this study were collected in September, 2005 using two coring techniques. One was obtained using a freeze-corer device (Shapiro 1958). The face of the freeze-corer captured sediments from 10 to 40 cm. Sediments from 0 to 10 cm were recognizable, but

somewhat smeared in the coring/recovery process. Freeze-core sediments adhered to the face of the corer during transport back to shore and the core was sampled within 2 h of collection, sections stored in plastic sample bags, kept cool in an ice chest and later refrigerated. The second core (WL GC2) was collected in September 2005 by gravity corer, using a 60-cm-long, 10-cm-diameter, polycarbonate tube attached to a weighted flapper valve. The valve kept suction as the core was retrieved by hand line and brought on board. Solid-phase material was obtained from core WL GC2 by extrusion and sectioning, and samples were kept cool in an ice chest and then refrigerated until analysis. All sediments analyzed were first rinsed with de-ionized water (DIW) to remove pore-water salts, dried at 45°C and lightly ground by mortar and pestle. S and N were measured using an Elantech EA CNS analyzer. Solid-phase material from GC2 was analyzed by a gamma detector (EGG Ortec) and the Cs-137 activity per gram dry sediment obtained. Some solid phase material from GC2 was analyzed on a Rigaku XRD for mineralogic assessment. Sediment was also examined by SEM using an Hitatchi TM1000 equipped with an Oxford EDS system.

Tufas were collected from boulders sitting near lake level at an elevation of ~1,200 m. The tufas collected have a stromatolitic texture and formed crusts on the tops and sides of boulders, 4–8 cm thick. Several dome-shaped tufa samples were cut with a rock saw; one face was cleaned and polished with a rock-polishing wheel. A series of samples were drilled from the tufa using a microdrill and the resulting carbonate powder was collected. Three to five holes were drilled to collect enough powder from a single horizon and each hole was located adjacent to the previous one. All the powder was pooled to represent a single 'stratigraphic horizon.' Various laminae defining the structure were drilled with a spacing of about 0.5 cm. The carbonate powder collected was rinsed with DIW and dried and CAS was analyzed as described below. One stromatolitic tufa was drilled at 6 horizons and carbonate powder was rinsed, dried and sent to the UC Irvine Keck Laboratory for ^{14}C radiometric dating (Table 1). In order to compare the age-dated stromatolite to ones on which CAS was analyzed, we defined a distinctive transition between laminated and non-laminated textures as a synchronous tie-point. All stromatolites

Table 1 ^{14}C dates on Walker Lake tufa

UCIAMS #	Sample name	USC ID	^{14}C age (BP)	±
18325	UCIT13431	fWLDL-8-A 0.5 mm	730	15
18326	UCIT13432	eWLDL-8-A 6.8 mm	2,285	15
18328	UCIT13433	DWLDL-8-A 13 mm	2,690	20
18329	UCIT13434	cWLDL-8-A 23 mm	2,985	15
18330	UCIT13435	bWLDL-8-A 33 mm	3,135	15
18331	UCIT13436	aWLDL-8-A 42 mm	3,150	20

Age dating from the Keck Carbon Cycle AMS Facility, UC Irvine

show this transition zone, approx. 0.5 cm thick. Other CAS samples were collected from laminae below this transition zone as described below.

Precipitation experiments

Two types of precipitation experiments are described; $CaCO_3$ was precipitated in artificial solutions containing K_2SO_4 made in DIW to a concentration of sulfate between 0 and 50 mM. The volume was generally between 900 and 980 ml. To this solution was added 10–50 ml of 1 M Na_2CO_3, mixing occurred, and then 10–50 ml of 1 M $CaCl_2$ was added and mixed. This final solution was allowed to sit overnight at a controlled temperature (all the solutions were brought to the experimental temperature before mixing) and the precipitate collected, rinsed 3×, dried and analyzed as described below. The other precipitation experiments used Walker Lake water that had been collected in Niskin bottles and filtered through a 0.2 μm cartridge filter (Pall Life Sciences 0.2-μm Versapor filter). A volume of 500 ml of lake water was kept at the desired temperature, as was the single reagent solution, 1 M $CaCl_2$. About 5 ml of $CaCl_2$ solution was added to lake water, shaken and allowed to sit for 24 h, at which time the solution was decanted, the precipitate was collected in a 50 ml Falcon tube, rinsed with DIW 3×, dried and analyzed for CAS.

Analysis of CAS

The pure carbonate samples from the precipitation experiments were weighed to determine the total amount of carbonate, and approximately 100 mg was dissolved in 1.5 N HCl. This solution was analyzed

for sulfate using the $BaCl_2$ turbidimetric method described by Tabatabai (1974). Sediment-core material was first analyzed for wt.% $CaCO_3$ both by calculating the difference between total C and organic C as analyzed on the EA, and also by weight loss following acidification. These two approaches yield similar results, ±10% with respect to one another. An aliquot of sediment was weighed and a quantity sufficient to provide ~100 mg of $CaCO_3$ was placed in a 5 ml test tube. All the following procedures were performed within a N_2 glove bag. About 1.5 N HCl was added to the sediment in a quantity sufficient to dissolve all the carbonate (typically 3 ml). The acid was added in 0.1–0.3 ml increments to keep the dissolution bubbling under control. Following each acid addition, the sediment was mixed and 5 min to 1 h later, more acid added. After all acid was added, the sediment solution was allowed to sit overnight. The next day, the sample was well mixed, allowed to settle, and 1–2 ml of solution was taken in a glass syringe and filtered into a test tube through a 0.2-μm filter. A check was performed to ascertain that $CaSO_4$ was not precipitated in the solution by pushing 1 ml DIW through the filter after the step described previously. If anhydrite were present on the filter, the DIW would be enriched in sulfate, hence we analyze this solution as well as our acid solution. We found that as long as the acid was not stronger than 3 N, there was not a problem with $CaSO_4$ precipitation. Both solutions were removed from the glove bag before performing the standard turbidimetric analytical procedure. Standards bracketed the sample concentrations and a typical run included sulfate standards ranging from 0 to 5 mM, including standards that were 250 and 750 μM. Our standard curve was linear with an r^2 value of better than 0.99, and replicate analyses of the same solution yielded precisions of ±2% or better. Replicate analyses of sediment yielded precisions of ±7% or better.

Walker lake hydrology and sediment chemistry

Walker Lake surface water temperature fluctuates between 5 and 25°C, its present chloride concentration is ~115 mM, carbonate ion is ~20 mM, Na ~210 mM, Mg ~7 mM and sulfate ~40 mM. With such a large carbonate ion concentration, calcium

concentrations are low (<100 μM) and carbonate precipitation is thought to require inputs of Ca from either dust, riverine or groundwater sources. Productivity in Walker Lake is N-limited, although ammonia can build up in the bottom water to >30 μM during anoxic stratification. Orthophosphate concentrations in the lake exceed 25 μM year round.

Walker Lake sulfate content is so large ($\sim$40 mM) that it does not fluctuate on account of sulfate reduction within sediments. This can be demonstrated with the following calculation: assuming a sediment accumulation rate of 0.3 cm/year (Benson et al. 1991; Yuan et al. 2004), a sediment porosity of 0.85 and average sediment density of 2.7 g/cm^3 yields a sediment accumulation rate of 0.13 g/cm^2 year. The concentration of solid phase S in Walker Lake sediments (Fig. 3) averages 0.15 wt.%, hence net S burial (if all due to sulfate reduction) can remove sulfate at a rate of 0.2 mmolS/m^2 day. At this rate, the standing stock of sulfate in a 25-m lake-water column would take >10,000 years to deplete, or, in half a year, the sulfate concentration may be reduced by 0.003%, clearly a negligible process with respect to the sulfate budget of Walker Lake on annual, decadal or century time scales.

The major control on sulfate ion concentration in Walker Lake is the dilution with riverine water and concentration due to net evaporation. This is clearly demonstrated by the linear relationship ($r^2 = 0.94$) between lake chlorinity, a stable conservative tracer of water volume, and sulfate (Fig. 4). For example, lake level fluctuated between 1991 and 2004 by 25 feet with an increase in lake volume from 2.1×10^9 to 3.0×10^9 m^3 and then a return to 2.0×10^9 m^3 (USGS Scientific Investigations Report 2007-5012). Concentrations of total dissolved solids, chlorinity and sulfate increase in proportion to lake volume decrease as would be expected from evaporative loss and conservative ion behavior.

Sediments within the lake are fine grained, $\sim$50% silts and clays and up to 35 wt.% CaCO$_3$. The primary form of carbonate in the upper 1 m of sediments is monohydrocalcite (CaCO$_3 \cdot$ H$_2$O). Distinct layers and laminae are visually detectable within the upper 45 cm. These layers and a well-preserved bomb Cs-137 peak indicate that bioturbation of sediments is minimal (Fig. 5). Carbonate content generally increases between depths of 10–35 cm and the sediments contain 2–3 wt.% organic C (Fig. 3).
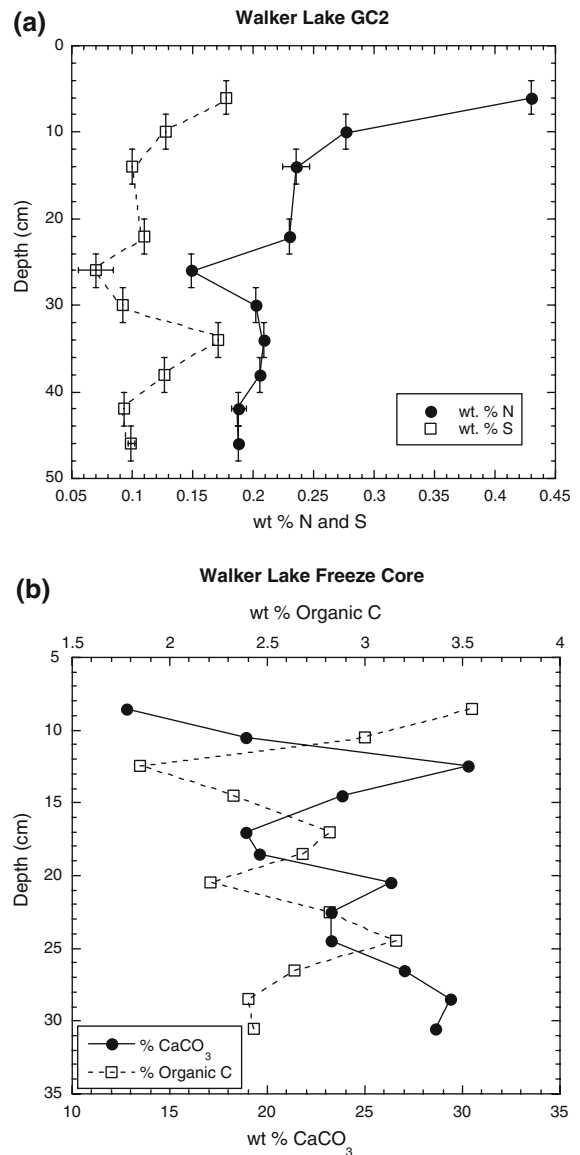

Fig. 3 (a) Weight % solid-phase S and N from Walker Lake sediments. X-axis error bars represent ±s.d. of replicate analyses of separate splits of sediment. Y-axis bars represent sediment interval spacing (2 cm). (b) Weight % CaCO$_3$ and organic C down core from Walker Lake sediments
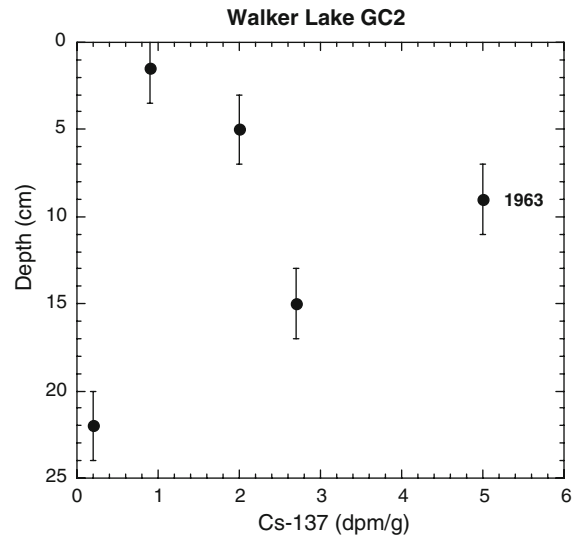
Previous lake-level proxies

Several key approaches typify past attempts to determine Walker Lake level history, with varying degrees of resolution, integration and success (Fig. 1). Benson et al. (1991) reconstructed lake level over the past 5,000 years using an integrative approach, combining the dating of presumed

(a)

(b)
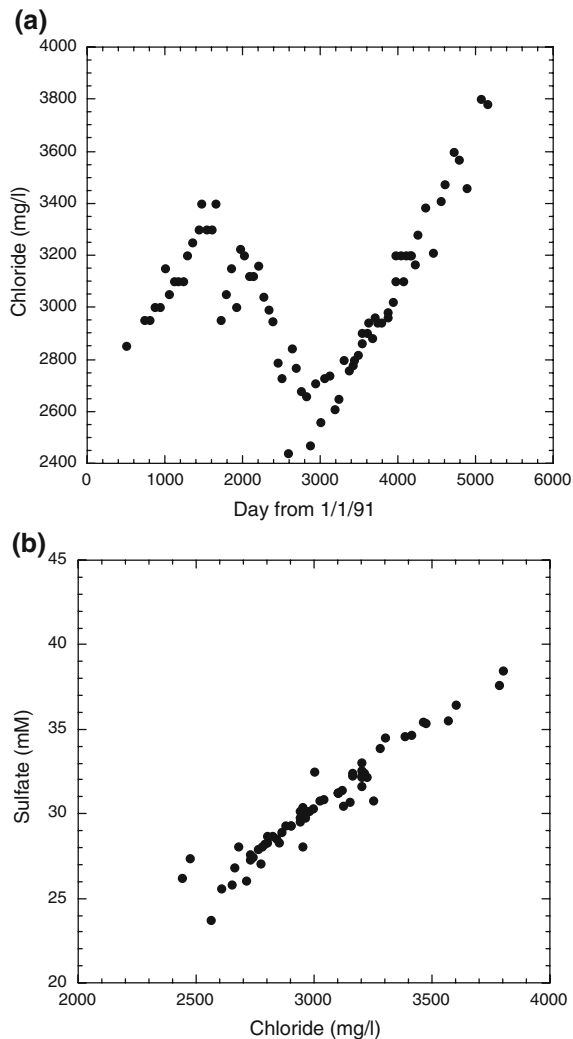
Fig. 4 (**a**) Chlorinity of Walker Lake surface water as monitored between 1991 (Day = 0 is Jan. 1991) and 2004 (Nevada EPA). Notable fluctuations in Cl content relate to the general lake-level decline (increase in Cl) with an interval of 3 years where lake level was rising. (**b**) Sulfate concentration in surface samples plotted against chlorinity from the period noted in panel **a**. Sulfate is linearly related to chlorinity ($r^2 = 0.94$), suggesting conservative behavior for both of these ions

Walker Lake GC2

Fig. 5 Cs-137 activity in sediments from Walker Lake core collected in 2005. The peak in bomb-produced Cs-137 occurred in ∼1963, which could be anywhere between 5 and 15 cm, but most likely lies near 10 cm. The uncertainty in the Cs-137 activity is roughly ±5%

shoreline tufas and sedimentary indicators of salinity (Fig. 1a). Oxygen isotopes from carbonate lake sediments have also been used to reconstruct lake level (Fig. 1b). Using $\delta^{18}O_{carbonate}$, Yuan et al. (2004, 2006b) produced a different Walker Lake level history compared to previous studies. The benefit of $\delta^{18}O_{carbonate}$ is the temporal resolution afforded by a high-resolution sampling of lake sediments.

However, it is well known that $\delta^{18}O_{carbonate}$ is both temperature and salinity sensitive, and thus, depending on how well the parameters at which the carbonate formed are known, this proxy may be somewhat problematic, as discussed in detail by Yuan et al. (2006a). Furthermore, Li et al. (1997) conducted precipitation experiments with Mono Lake water and found that ionic strength as well as temperature of the solution imparts a strong effect on the $\delta^{18}O$ of carbonate precipitates in alkaline lakes, forcing them well off equilibrium (see also "Discussion" in Rosen et al. 2004). The effect was even stronger when the experiments were conducted at low temperatures. Thus, there is reason to be cautious when using $\delta^{18}O_{carbonate}$ as a lake-level indicator in Walker Lake as well as other alkaline lakes.

Adams (2007) used an entirely different approach by examining the physical stratigraphy of proximal lake sediments (Fig. 1c). By investigating when the Walker River incised into previously deposited sediments or when the lake sediments transgressed over the river deposits, a lake-level history was reconstructed. As demonstrated in Fig. 1, the Adams (2007) reconstruction differs from other previous attempts. Although this method does not suffer from the same kinds of ambiguities as the $\delta^{18}O$ record, it

does provide a less detailed history, as incision and erosion remove parts of the sediment record.

CAS as a lake level proxy

Sulfate is a common ion in many closed-basin lakes, and in many cases, such as Walker Lake, it behaves conservatively with lake volume (Fig. 4). A premise of this study is that carbonates incorporate sulfate proportionally to the sulfate concentration in the fluid from which they precipitate. As the sulfate concentration in the fluid changes, the concentration of CAS in the mineral phase will change. Changes in CAS should be recorded in the carbonate sediments accumulating on the lake bottom, e.g., as lake level rises and lake water freshens, CAS concentration should fall; as lake level falls and lake water becomes more saline, CAS concentration should rise. As a test case, we carried out preliminary studies comparing an excellent historical record of sulfate in the lake to the CAS recorded in the recently deposited sediments. To further corroborate our findings, a tufa deposit was age-dated and CAS determined.
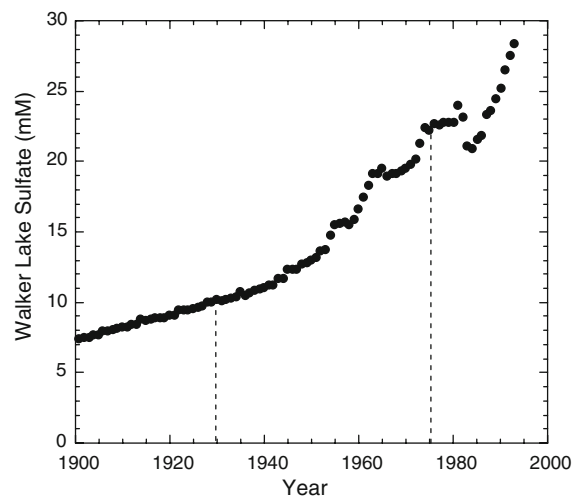
CAS-lake sediments

CAS was determined on sediments from the freeze core collected in 2005. Only sediments from 10 to 35 cm were analyzed due to poor sediment recovery from the upper 10 cm (Fig. 6). We relate this CAS-versus-depth data to CAS versus age (years AD) by using the sediment age model developed by Yuan et al. (2004). These authors describe a linear and polynomial fit to sediment depth/age data and suggest that the polynomial fit provides the better relationship for sediments <100 years old. Our ^{137}Cs data is consistent with their age model, and our pattern of wt.% carbonate is similar to theirs, suggesting we have a sediment record reasonably well age constrained for the years between 1925 and 1975. Given that sediment samples represent an average from a 2-cm-thick section, a ±7 year uncertainty on the age model is appropriate.

   A good salinity record exists for Walker Lake spanning the time interval in question (Thomas 1995). Over this time period, there are a few actual sulfate measurements. Thus, the salinity record was translated into a sulfate record, based on the tight
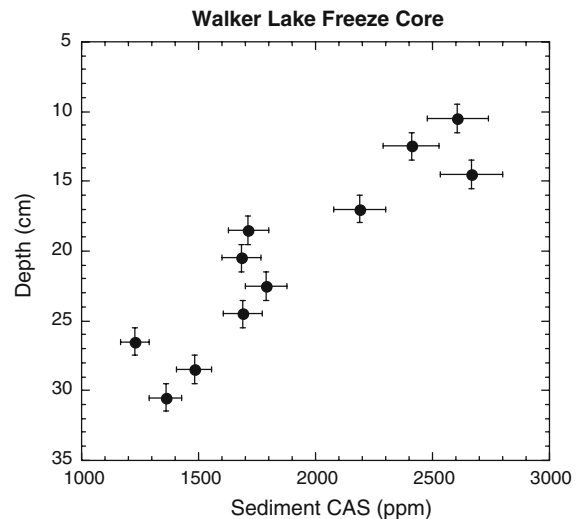

Fig. 6 CAS (as ppm SO_4^{2-} within $CaCO_3$) down core in Walker Lake sediments

correlation between these conservative properties (Fig. 7). This reconstructed record of sulfate concentration for the years between 1925 and 1975 was used to compare with our sediment CAS record. Figure 8 reveals our striking result: CAS abundance in the sediments tracks lake-water sulfate concentration excellently, suggesting that CAS may indeed constitute a proxy for lake level. The CAS versus sulfate data are not only linear, but it appears to trend on a line that passes very close to the origin. That the trend

Fig. 7 Walker Lake sulfate concentration between 1900 and 1995 AD. The dashed lines indicate the range of years sampled for CAS in the sediment core
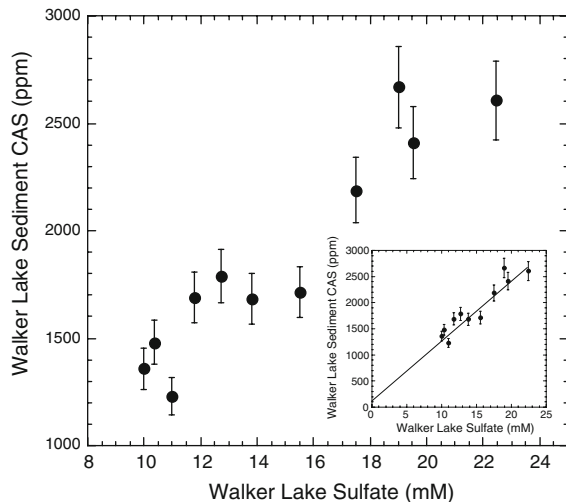
Fig. 8 CAS versus Walker Lake sulfate concentration. CAS versus depth (Fig. 6) was translated into CAS versus sediment age, and lake sulfate versus year was merged with CAS versus sediment age to achieve this plot. The insert plot shows the linear regression of CAS versus lake sulfate extrapolated to the origin ($r^2 = 0.88$). There is a small positive intercept


Fig. 9 Photograph of stromatolitic tufa with location and values of ^{14}C ages (years before present, adjusted for reservoir affect). Letters correspond to the transition zone (d) and the two zones below that ("c" and a combination of "b" and "a") that were sampled for CAS (see Fig. 10). The distance between "a" and "f" is 40 mm

in CAS and sulfate is linear ($r^2 = 0.88$) and defines a line intersecting very near the origin is taken as confirmation that Walker Lake carbonates capture a quantity of sulfate in proportion to the amount present in lake water.

CAS-tufas

The ^{14}C dates acquired on a stromatolitic tufa from Walker lake show a consistent trend of growth between 2,900 and 2,400 ybp (these ages have been corrected for a 285-year residence time of C in Walker Lake, Broecker and Walton 1959). At or near the horizon dated at 2,405 BP, the stromatolitic texture transitions from well laminated to poorly laminated (Fig. 9). Above this transition zone, the stromatolite is made of carbonate that shows no layering, below this zone, the carbonate is very finely laminated, with each lamina ~ 100 μm thick. CAS was determined on carbonate collected at the transition zone (d in Fig. 9) and from two horizons below this zone (c and both a and b).

Each zone has a distinctive CAS value, the largest CAS comes from the transition zone where the value is $1,320 \pm 300$ ppm (s.e. of the mean of $n = 3$

measurements). Below this zone the CAS value averaged 790 ± 90 ($n = 4$), and even further below this zone, CAS averaged 605 ± 50 ($n = 8$). Thus, the tufa reveals an increase in CAS with growth. Based on our assumptions, we would predict that the tufa grew during lake-level decline—but what was the lake doing between $\sim 2,900$ and 2,400 BP? Our reconstruction of lake level for this time period is based on both the data of Adams (2007) and Yuan et al. (2006b) and both of these reconstructions indicate lake level was falling between 2,900 and 2,400 ybp (Fig. 10). Qualitatively, the fall in lake level is consistent with the rise in CAS, as would be expected if CAS were a proxy for lake sulfate concentration. Moreover, the lake height at $\sim 2,900$ ybp was about twice the lake height at $\sim 2,400$ ybp. Hence, the change in sulfate concentration would be expected to double because the relationship between lake elevation and volume for this time period is generally linear. This is what is observed in the CAS data.

Both lake sediment and tufa analyses suggest CAS holds great promise as a lake-volume proxy, however, in the paragraphs below, we discuss some of the potential artifacts and pitfalls that must be considered in applying this technique.
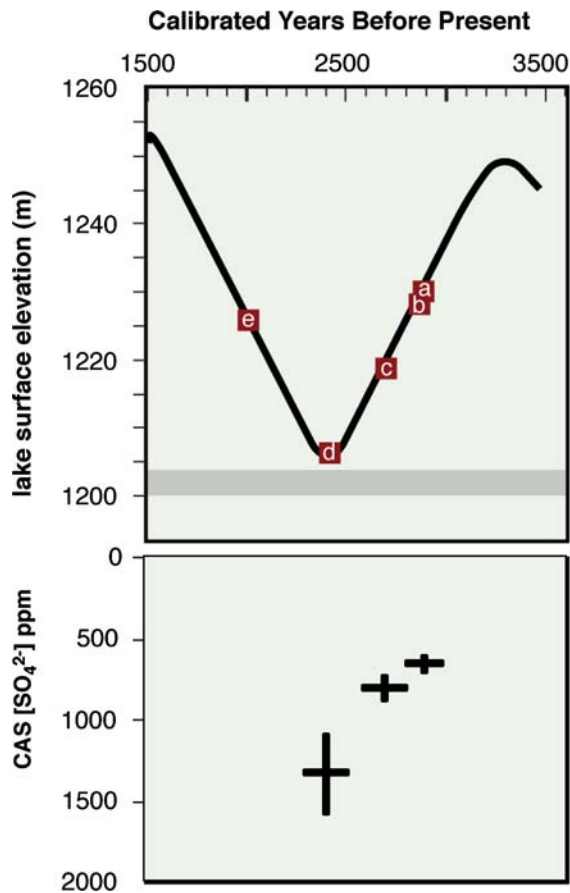
Fig. 10 Upper panel shows paleo-lake level based on reconstructions of Adams (2007) and Yuan et al. (2006a, b). The letters a–e correspond to the locations and values of AMS ^{14}C dates shown in Fig. 9. The lower panel places our CAS data on the correlative time scale. Range in CAS is ±1 s.e. of the mean and range in age corresponds to the thickness of the zone from which carbonate was extracted for CAS analysis. Notice the inverted scale in CAS and how the CAS increase tracks lake level fall

Potential issues with CAS as a lake level proxy

It has been shown in laboratory experiments that the rate of crystallization has an effect on CAS incorporation (e.g. Busenberg and Plummer 1985), and this observation has fostered a reticence to accept CAS concentration as meaningful (the focus has been on sulfur isotopes of CAS). Further, Marenco et al. (2008) conducted experiments demonstrating that pyrite mixed with carbonate can, if oxidized, contribute to a sulfate reading that is not CAS. These and other aspects of the correlation between CAS and lake sulfate concentration are examined so as to

provide the reader with a balanced picture of the strengths and limitations of this approach.

Experiments with simple solutions

In a lake with such high alkalinity, the kinetics of carbonate precipitation may be reasonably simulated by the batch mixing experiments we conducted in the laboratory. Although not a strict measure of precipitation kinetics, we did conduct batch mixing experiments adding known concentrations of carbonate and calcium ions dissolved in DIW in which the Ion Concentration Product (ICP) of these two species varied over a range of 25. The CAS of the carbonate (calcite) produced in these experiments did not appear to be a function of ICP (Fig. 11). However, another parameter that varied during this experiment was the $[CO_3^-]$ to $[SO_4^{-2}]$ ion ratio (see Fig. 11 caption) and this ratio may impart some influence on CAS. Further work is necessary to determine how sensitive CAS is to the carbonate/sulfate ratio and how sensitive it is to precipitation kinetics, but if these laboratory experiments simulate batch mixing of lake water with its high carbonate ion content and
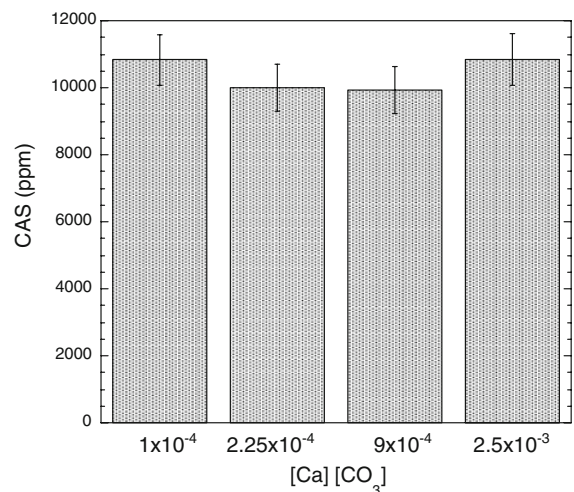
Fig. 11 Results of four batch-mixing precipitation experiments with a solution containing 25 mM sulfate. The experiment was conducted at room temperature at roughly the same ionic strength, the major variable was the concentration product of calcium and carbonate ion (shown along the *x*-axis). Over a change of ICP of 25×, the CAS value remained constant at ∼10,000 ppm. These experiments were conducted over a range of carbonate-to-sulfate concentration ratios, 0.4 for the ICP = 1×10^{-4} and 2 for ICP = 2.5×10^{-3}

fresh water with high calcium content, our results suggest that the rate of calcium addition is not a fundamental controlling factor on CAS.
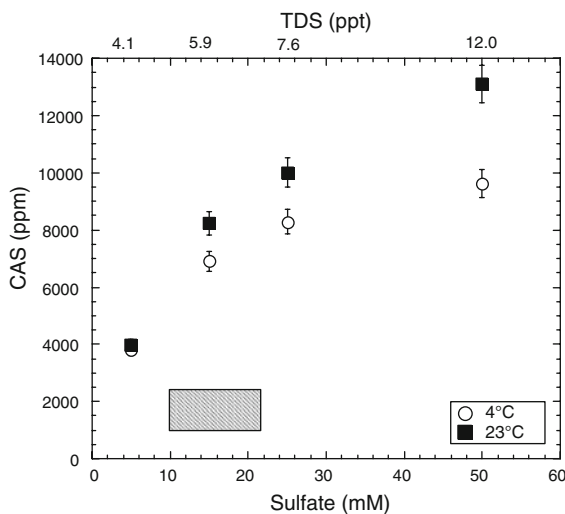
There is both a temperature and ionic strength effect on CAS as demonstrated by experiments conducted with DIW spiked with sulfate and carbonate and calcium (Fig. 12). Precipitation experiments conducted at 4° and 23° show that CAS incorporation is not a simple function of temperature. Generally, at lower temperatures carbonate incorporates lower sulfate concentrations than at higher temperatures. However, at low sulfate concentrations, this discrimination is minimal. In these laboratory experiments, carbonate precipitated at 4°C has between 5% and 25% less CAS than carbonate precipitated at 23°C over a range of sulfate concentrations 2–50 mM. The difference is 5% at low sulfate and 25% at high sulfate concentrations. Although these experiments demonstrate non-linear incorporation of CAS as a function of sulfate concentration over a very wide range, CAS is linear with sulfate concentration through concentrations of 0–30 mM, above this

Fig. 12 Two precipitation experimental results are shown which demonstrate the sensitivity of CAS to temperature of precipitation and solution ionic strength (TDS is total dissolved solids, upper *x*-axis). These results are similar to those of Busenberg and Plummer (1985) in which they demonstrated a relationship between CAS and rate of carbonate precipitation. Our experiments demonstrate that the effect of temperature on mineral precipitation kinetics and hence on CAS is minimized at low sulfate concentrations. Experiments conducted with DIW yield carbonates with much higher CAS values than found in natural lake sediments. The hatched box shows the range in CAS and sulfate values determined in this study

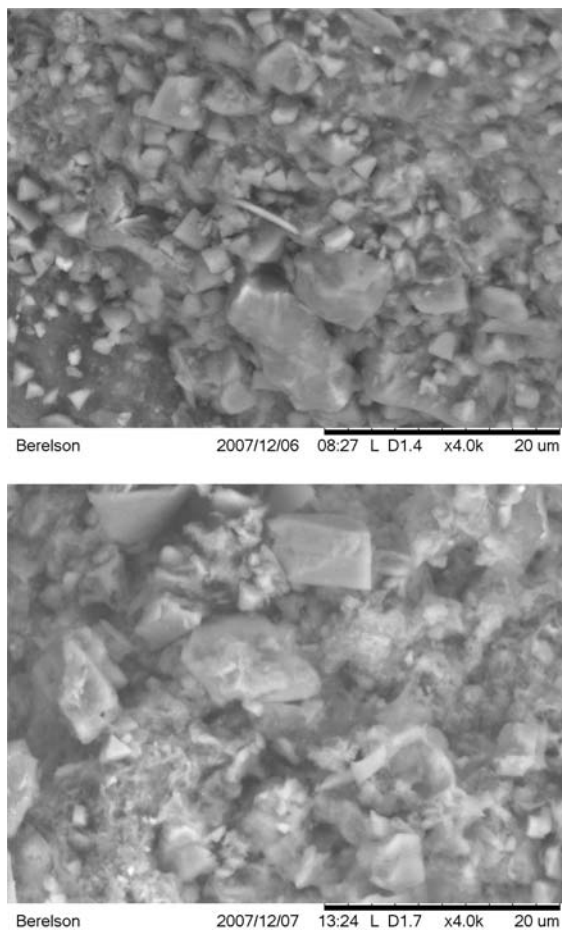value, the CAS-versus-sulfate concentration gradient changes slope.

Experiments with Walker Lake water

It is clear that carbonate from Walker Lake contains much less CAS than carbonate precipitated experimentally in a solution made from DIW (typical results from above produced CAS values of 6,000–8,000 ppm, whereas Walker Lake carbonates typically recorded values of 1,500–2,500 ppm, Fig. 12). In addition, the slope of CAS-versus-sulfate concentration recreated from the Walker Lake core data is about one third the slope of CAS versus sulfate for batch experiments in a solution made from DIW. Further demonstrating this difference, when we added dissolved calcium to Walker Lake water and recovered the carbonate precipitate, it had a CAS value ∼2,000 ppm, similar to the natural samples. Clearly, the ionic strength of Walker Lake water contributes to attenuating the CAS signal. We think it reasonable to assume that the linear relationship between CAS and sulfate from the experimental work, within the range of sulfate concentration 10–25 mM, suggests that the Walker Lake sediment CAS values can be interpolated linearly to derive lake sulfate concentrations.

More work remains to be done to further establish the veracity of CAS as a lake sulfate recorder. The mineralogy of Walker Lake sediment carbonate is monohydrocalcite, $CaCO_3 \cdot H_2O$, the mineralogy of carbonate precipitated experimentally is calcite and the carbonate precipitated by adding calcium-enriched solutions into Walker Lake water is Mg-enriched calcite. Busenberg and Plummer (1985) have shown that biogenically-precipitated carbonate can have very high values of CAS and marine organisms today produce carbonate with a wide range of CAS values. During our inspection, carbonate shells were not found in Walker Lake sediments, although Yuan et al. (2006a) demonstrated that ostracod shells do exist. An SEM image of Walker Lake sediments shows that the predominant carbonate mineral form is small (1–2 μm) rhombic crystals (Fig. 13), which are absent after treating the sediment with acid. This observation supports the hypothesis that carbonate within Walker Lake sediments is formed as precipitated crystals rather than shell hash or other biogenic sources.

Fig. 13 SEM images of Walker Lake sediment that had been rinsed with DIW, dried and lightly ground. The upper image shows the abundance of rhombic crystals, presumed to be carbonate as indicated by EDS analysis. These crystals are on the order of 1–2 μm. The lower panel shows the same sediment after treatment with 1.5 M HCl overnight. The small rhombic crystals are absent in the acidified sediment

If pyrite in the sediments contributes sulfate during the processing of samples, then we would expect the lake-sediment CAS to correlate with lake-sediment S content (e.g. Marenco et al. 2008). We do not see a systematic relationship between these variables, as expected if there were an artifact dominating our signal (Figs. 3, 6), and our processing of lake sediment in an anaerobic glove bag was designed to minimize this effect.

Finally, the nuances of lake-volume changes and lake sulfate concentration are not lost on us—a lake that fills to a certain elevation continuously as opposed to one that gets to that elevation through a series of fill-evaporation-fill steps will have different

final sulfate concentrations. Further, the relationship between lake elevation and lake volume is not a linear function (Lopes and Smith 2007) and this hypsometric condition will also impact CAS interpretation. The pilot study we conducted here does demonstrate a good relationship between lake sulfate concentration and CAS, in part because we focused on a time period when the lake was in fairly steady, unidirectional decline in volume, and because the relationship between lake elevation and volume for this time period is generally linear. Testing in other alkaline lakes may further demonstrate the nuances of the CAS method.

Summary

Lake-level change can be one of the most dramatic effects of climate change, yet proxies for determining past lake-level changes have their strengths and weaknesses. We tested a new lake-level proxy in Walker Lake, Nevada by comparing the carbonate associated sulfate (CAS) record in the sediments to the historic lake-chemistry record, and by comparing a laminated tufa with an age-correlative lake-level history. The CAS proxy worked well in our study. With further testing, CAS may find application in other saline lakes where sulfate behaves as a conservative ion.

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