

RADIOCARBON RESERVOIR AGES AS FRESHWATER-BRINE MONITORS IN LAKE LISAN, DEAD SEA SYSTEM

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ABSTRACT. A continuous and high-resolution record of the radiocarbon reservoir age (RA) has been recovered from the primary aragonites that were deposited from the last glacial Lake Lisan. The RA is calculated as the difference between the measured ¹⁴C “apparent” age in the aragonite and the atmospheric age at any particular time. The RA shows temporal decreases during the time interval of ~28 to ~18 ka cal BP. This behavior is attributed to a continuous addition of low RA-high bicarbonate freshwater into the high RA-Ca-chloride (low bicarbonate) brine solution filling the lake. The mixing of the brine with freshwater drives the precipitation of CaCO₃ in the form of aragonite from the lake epilimnion (surface layer). The run-off-brine mixture in Lake Lisan is also reflected by the Sr/Ca ratios that are positively correlated with the RA. Nevertheless, the ¹⁴C content in the epilimnion did not drop at the same rate as the atmospheric value but rather remained nearly constant. We suggest that turbulent mixing with the much saltier hypolimnion (lower layer) across the hypolimnion/epilimnion interface at a depth of about 390 m below sea level, buffered the ¹⁴C content as well as the Sr and Ca concentrations in the aragonite precipitating solution. The RA-Sr/Ca related limnological model developed here opens the way to determine the reservoir-age-corrected atmospheric ages of Lisan Formation aragonites beyond 28 ka cal BP.

INTRODUCTION

Radiocarbon dating, which is based on the measurement of the ratio of ¹⁴C/¹²C organic and inorganic carbon-bearing material, has to take into account the variations in ¹⁴C level in atmospheric carbon, which reflects changes in the cosmogenic production and/or changes in the exchange between the various carbon reservoirs. The secular variations in the atmospheric ¹⁴C have been well established since ~12 ka by using tree rings. However, for older ¹⁴C ages, other archives have been used: corals (e.g. Barbados, Bard et al. 1998); speleothems (e.g. Bahamas, Beck et al. 2001; Hoffman et al. 2010); foraminifera (e.g. Iceland Sea, Voelker et al. 2000); marine varves (e.g. Cariaco Basin, Hughen et al. 1998); and laminated carbonate lake sediments (e.g. lakes Suigetsu and Lisan, Kitagawa and van der Plicht 2000; Schramm et al. 2000; Bronk Ramsey et al. 2012). ¹⁴C dating of carbonates, however, requires an estimation of the ¹⁴C “reservoir age” (RA), which accounts for contribution of old (¹²C-enriched) carbon in the deposited material. This problem is not severe for corals, where the RA of the surrounding ocean is estimated to be around 400 yr (cf. Bard et al. 1998; Fairbanks et al. 2005), but is often complicated in the case of speleothems and laminated lake sediments (cf. Schramm et al. 2000; Beck et al. 2001; Belmaker et al. 2007).

The efforts to define the RA for Lake Lisan trace back to the work of Schramm et al. (2000), who set up a preliminary U-Th and ¹⁴C chronology for the aragonite sequences of the PZ1 (Perazim Valley) and M1 (Massada plain) sections (Figure 1). They compared ¹⁴C ages of organic debris and its host aragonite laminae from the upper part of the section at the calendar time interval (determined by U-Th) of ~20 to ~17 ka cal BP and obtained low RA values of almost zero to 1000 yr. Subsequently, Stein et al. (2004) used pairs of aragonite and organic debris collected from the same stratigraphic horizons in the sedimentary sections of the Holocene Dead Sea and obtained significantly older reservoir ages ranging from ~6 to 2.2 ka. They proposed that the high RA values (~6 ka) are related to enhanced contributions from the Ca-chloride brine of the hypolimnion (the deep-water

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brine layer), via discharge of saline springs after a significant lake level drop (e.g. at ~8.1 ka cal BP), while low RA values (~2 ka) reflect enhanced runoff, which was equilibrated with atmospheric ^{14}C , into the epilimnion (the surface layer). Prasad et al. (2009) compared the ^{14}C ages of aragonites from the M1 Massada section (Figure 1) to the IntCal09 (Reimer et al. 2009) values and showed that reservoir ages in the lake declines systematically by 2000 yr during the time interval 21–17.4 ka cal BP.

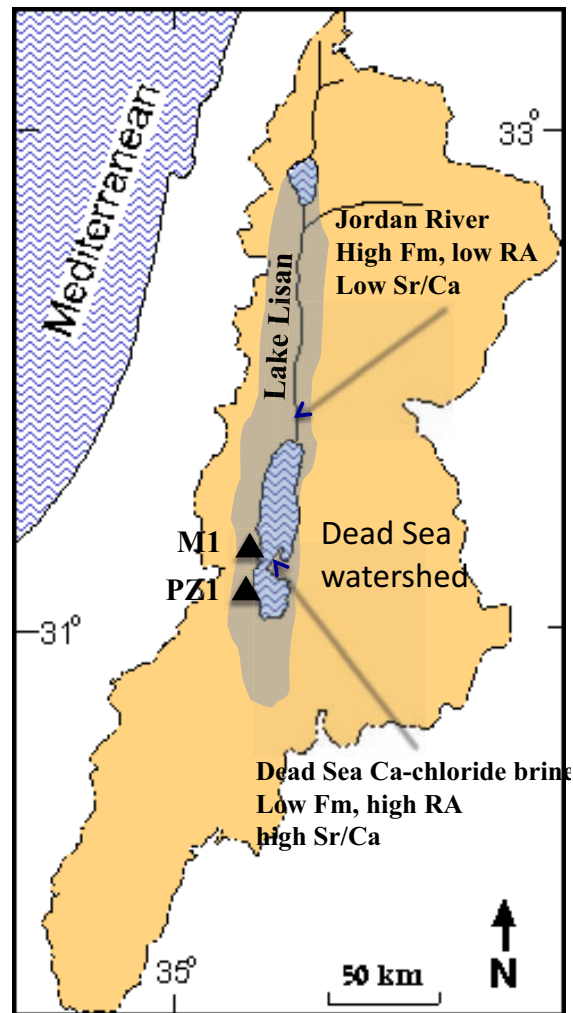


Figure 1 The Dead Sea watershed showing the northern freshwater Sea of Galilee (Lake Kinneret) the hypersaline southern Dead Sea (filled with Ca-chloride solution), and the location of the PZ1 stratigraphic section at the Perazim Valley.

Here, we follow the approach of Prasad et al. (2009) and calculate the RA values in Lake Lisan and the Holocene Dead Sea by comparing the primary aragonite ^{14}C ages with the IntCal09 calibration curve over the time interval ~28–18 ka cal BP. The RA values show temporal decreases during this time interval. We interpret the decrease as reflecting the mixing between the incoming freshwater and brines in the lake, which dictate the precipitation of the primary aragonite.

SAMPLES AND METHODS

Samples were collected from the exposed stratigraphic sections of the last glacial Lisan Formation at the Perazim Valley (PZ1 section, SW of Mt. Sedom, Figure 1). Detailed lithological descriptions of the Lisan PZ1 section are given in Machlus et al. (2000) and Haase-Schramm et al. (2004). The chronology of the PZ1 section was established by U-Th dating of the primary aragonite (Haase-Schramm et al. 2004; Torfstein et al. 2013). Aragonite samples for ¹⁴C analyses were obtained from individual sediment samples taken from the exposures or from the cores.

The aragonite samples were treated with acid in an evacuated glass line in order to release and collect the CO₂. In a separate step, the CO₂ was converted into graphite, in which form it was used for analysis. Accelerator mass spectrometry (AMS) analyses were carried in the ¹⁴C laboratory of University of Utrecht (van der Borg et al. 2004). In the AMS analyses, the yields of the carbon isotopes were measured and converted to ¹⁴C/¹²C ratios, which were used to calculate conventional ¹⁴C ages.

RADIOCARBON IN THE DEAD SEA HYDROLOGICAL SYSTEM

Lake Lisan, which occupied the Dead Sea basin (Figure 1) during the last glacial period (70–14 ka cal BP, Haase-Schramm et al. 2004; Torfstein et al. 2013), deposited sequences of laminated primary aragonite and silty detritus, gypsum, and clastics (Machlus et al. 2000; Haliva-Cohen et al. 2012). The deposition of the primary aragonite reflects the supply of Ca and bicarbonate to the lake by freshwater, and some Ca and Mg from the underlying Dead Sea brine (Katz et al. 1977; Stein et al. 1997). The continuous and the annual mode of deposition of primary aragonite from the epilimnion, and the possibility to obtain U-Th ages on the aragonites, make the Lisan aragonite a potential high-resolution archive for atmospheric ¹⁴C calibration (Schramm et al. 2000; Haase-Schramm et al. 2004; Torfstein et al. 2013). Yet, the ¹⁴C of the dissolved inorganic carbon content of the lake solution, from which the primary aragonite precipitates, is a mixture of 3 reservoirs: dissolved atmospheric CO₂ supplied mainly through runoff entering the lake (Belmaker et al. 2007); “dead carbon” (¹⁴C-depleted) dissolved from the surrounding Phanerozoic carbonate terrains (e.g. the Cretaceous Judean Mountain wall-rocks of the Dead Sea basin); and ¹⁴C provided by saline springs that underwent water-rock interaction and ¹⁴C “aging” within the aquifers (e.g. Belmaker et al. 2007). Thus, the fresh and saline solutions that enter the lake are characterized by different amounts of ¹⁴C reflecting their primary source, dissolution processes, and exchange processes with the atmosphere. While the runoff water in the Judean Desert can reach atmospheric values (e.g. ~0.9–1.0 Fm), the Jordan River water entering the Sea of Galilee has ~0.85 Fm and the saline springs comprising the Dead Sea Ca-chloride brine are characterized by low to very low Fm values (e.g. ~0.05 Fm, Belmaker et al. 2007).

TEMPORAL CHANGES IN THE RESERVOIR AGE IN LAKE LISAN

The ¹⁴C content in the primary (chemical) aragonites deposited from Lake Lisan is compared in Figure 2 with corals and Cariaco Basin sediments that were used to construct calibration curve beyond the dendrochronology range. Here, we discuss the time interval between 18 and 28 ka BP, which is included in IntCal09. The ¹⁴C in the Lisan aragonites differs from the corals and the Cariaco data, but the difference in the apparent ¹⁴C ages declines regularly from ~3 kyr at 28 ka cal BP to ~1 kyr at 18 ka cal BP. The older ¹⁴C ages at each point in time in the Lisan aragonites, compared to the corals and Cariaco data, stems from higher reservoir age (RA) in the Lisan aragonites. Accordingly, the temporal decline in the difference between the Lisan aragonite and the coral-Cariaco data reflects a continuous decrease in the RA. The temporal decrease in RA reflects a change in the hydrological-limnological conditions of the lake and a change in the reservoirs contributing ¹⁴C to the lake layer

that precipitated the aragonite. We construct a hydrological-limnological model that describes a continuous replenishment of the lake water, which is initially composed of the Dead Sea Ca-chlorine brine with incoming fresh runoff waters. The Lisan aragonite is deposited from the epilimnion, comprised of a mixture of the Ca-chlorine brine and freshwater loaded with bicarbonate (Stein et al. 1997). Low RA values are attributed to freshwater runoff that rapidly exchanges ^{14}C with the atmosphere (Belmaker et al. 2007). High RA values are attributed to the brines that are discharged to the lake from the Judean Mountain aquifers. The RA declines as long as freshwaters loaded with bicarbonate enter the lake and aragonite is being deposited. The RA rises when the supply of runoff declines and mainly the Ca-chloride brines (either from the hypolimnion or saline springs) feed the epilimnion. The RA rises appear to occur during or after major declines in lake levels. Thus, the RA reflects the hydrological-limnological configuration of the lake, which is modulated by the climate regime in the drainage area, declining during wet phases and increasing during arid phases.

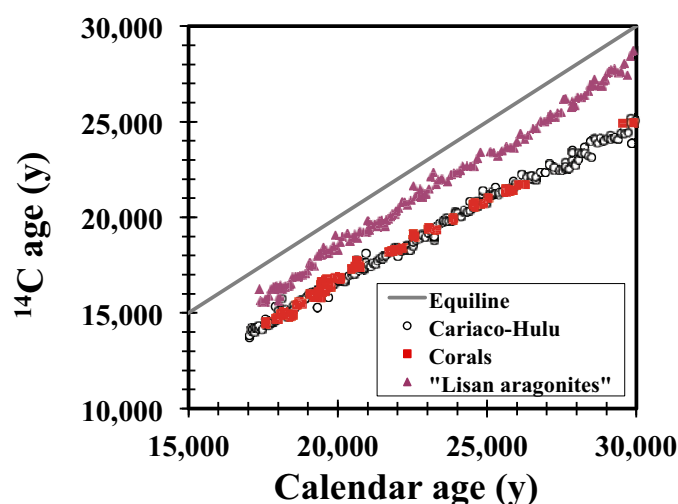


Figure 2 ^{14}C ages of Lake Lisan aragonites compared to Cariaco Basin sediments (ages tuned to Hulu Cave speleothems), corals, and Bahamas speleothem (data: Hughen et al. 1998; Schramm et al. 2000; van der Borg et al. 2004; Fairbanks et al. 2005).

Coeval Changes in the Sr/Ca Ratio and RA in the Lake

The precipitation of primary aragonite from Lake Lisan requires the input of freshwater containing significant bicarbonate to the lake and its mixing with the Ca-chloride brine (Stein et al. 1997). The Sr/Ca ratio in the aragonite is a sensitive tracer of the brine-freshwater mixing, because the distribution coefficient for aragonite/water is about unity, and the Sr/Ca ratio is high in the Ca-chloride brine and low in the freshwater runoff (Katz et al. 1977). The continuous supply of freshwater by runoff to Lake Lisan, mainly via the paleo-Jordan River, and the mixing of these waters with the brine, are reflected in the temporal decrease of the Sr/Ca ratio in the precipitating aragonite (Katz et al. 1977; Stein et al. 1997). The Sr/Ca ratio displays an almost monotonous decline through the time interval ~28–18 ka cal BP (Figure 3), when the lake was at its highest stand. Yet, Machlus (1997) noted that the rate of decline in the Sr/Ca ratio in the Upper Member of the Lisan Formation would be much greater if the Sr and Ca were controlled just by runoff, and suggested that the ratio is buffered by supply of the Ca-chloride brine via the saline springs to the lake. Stein et al. (1997) argued that replenishment of the lower layer by the hypersaline Ca-chloride brine is required to maintain the

meromictic (layered) lake configuration. At the highest stand of lake level, the deep brine layer was replenished by sinking of epilimnion brine, after being evaporated to high density at the shallow margins of the lake (Stein et al. 1997).

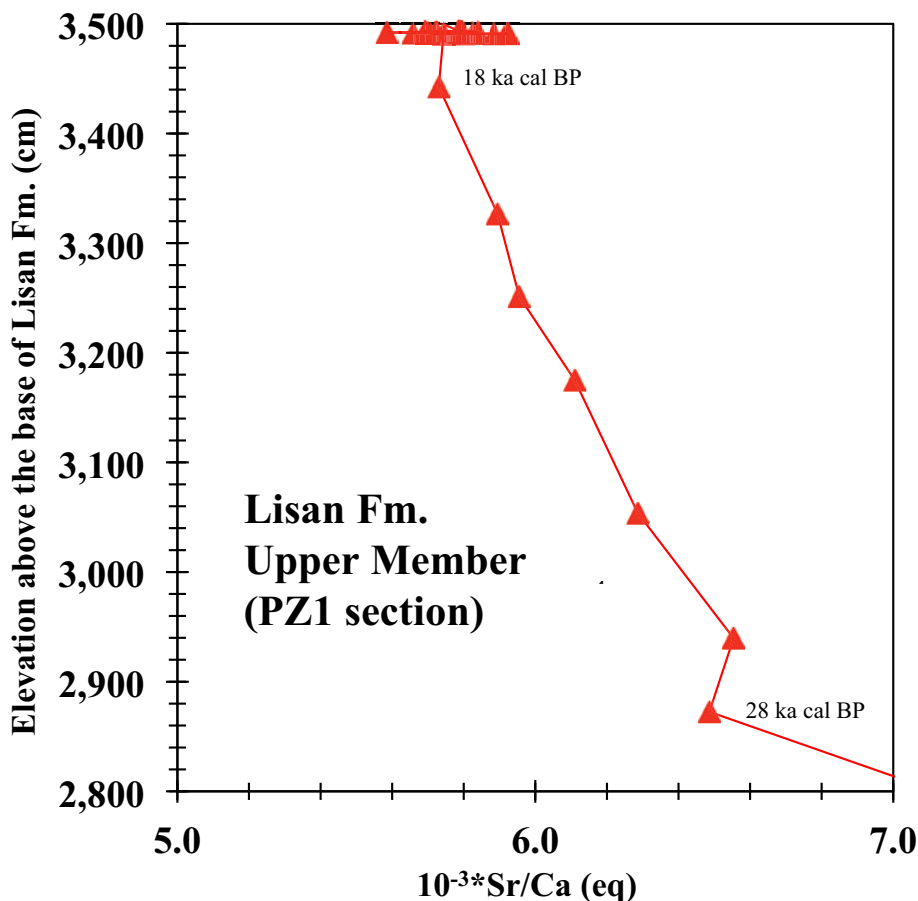


Figure 3 Sr/Ca vs. height in the Upper Member of the Lisan Formation at the PZ1 section. The continuous decline in the Sr/Ca ratio reflects continuous input of low Sr/Ca freshwater loaded with bicarbonate that replenish the lake and led the precipitation of the primary aragonite.

The ¹⁴C content of the lake's epilimnion at time of aragonite deposition, ¹⁴C₀, is calculated from the RA and the atmospheric ¹⁴C (IntCal09) by the equation:

$$\ln(^{14}\text{C}_0) = \ln(^{14}\text{C}_{\text{IntCal09}}) - \lambda_{14} \times \text{RA}$$

The aragonite laminae and the lake epilimnion represented by open circles in Figure 4 show that during the deposition of the Upper Member the lake's ¹⁴C content remained almost uniform. Thus, it appears that the RA decrease during most of this time interval does not reflect the temporal drop in the atmospheric ¹⁴C content. Apparently, there was a buffering mechanism that balanced the anticipated ¹⁴C drop in the lake due to atmospheric exchange. The buffering of the ¹⁴C content in the epilimnion is probably furnished by turbulent mixing with the hypolimnion brine. This mixing is reflected also by the contemporaneous decrease in the Sr/Ca ratio in the aragonites (Figure 4). The

steep drop in the Sr/Ca ratio toward the end of this period, at ~21 ka BP, likely resulted from relatively weaker vertical mixing with the hypolimnion, causing the lake's epilimnion ^{14}C to approach the atmospheric ^{14}C value. This possibly reflects the increase in the density gradient across the epilimnion/hypolimnion interface when the supply of freshwater input increased towards the end of the high-stand Upper Member period. A more elaborate discussion of the limnological-geochemical history of Lake Lisan during its high and low stands conditions is beyond the scope of this paper, however, and will be discussed in a future publication.

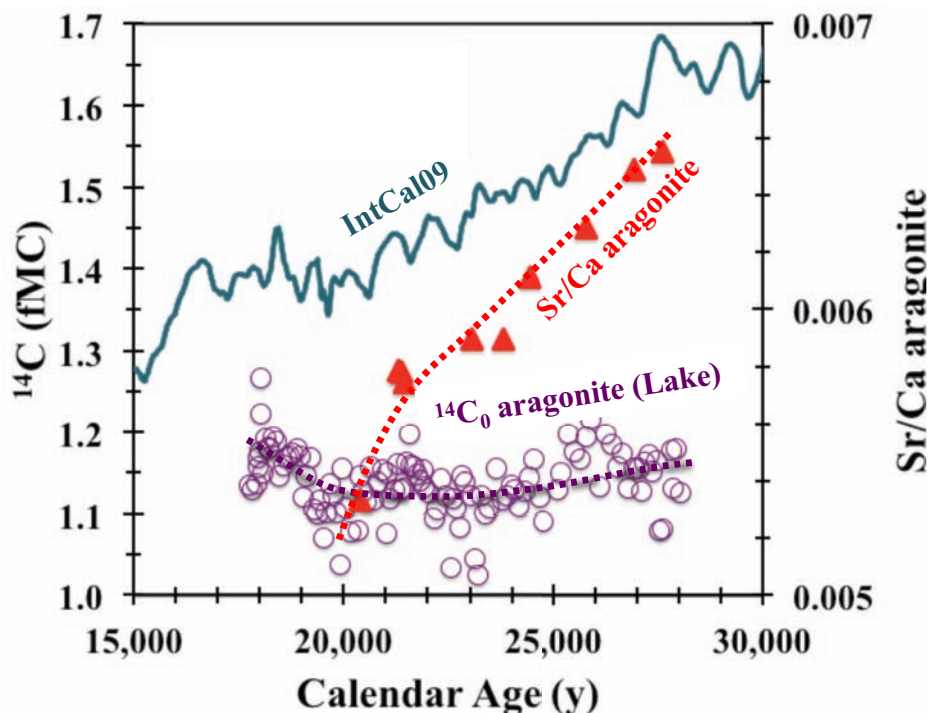


Figure 4 The calculated $^{14}\text{C}_0$ (the calculated ^{14}C value at the ^{14}C age in units of fraction modern carbon, Fm) and Sr/Ca ratio of aragonite laminae from the upper member of Lisan Formation versus the U/Th calendar age. The $^{14}\text{C}_0$ and the Sr/Ca ratio are assumed to be the Fm value and the Sr/Ca ratio of the lake's epilimnion at the time of deposition. The ^{14}C of the atmosphere at that time is taken as the IntCal09 Northern Hemisphere atmospheric ^{14}C calibration curve (<http://www.radiocarbon.org/IntCal09%20files/intcal09.14c>) recalculated in Fm units. Note that after 21 kyr BP, the Sr/Ca ratio dropped steeper than before and the $^{14}\text{C}_0$ starts to increase towards the contemporaneous atmospheric value.

The RA-Sr/Ca related limnological model developed here opens the way to determine the reservoir-age-corrected atmospheric ages of Lisan Formation aragonites beyond 28 ka cal BP. Combined with the U-Th chronology, and the possibility to count the annually deposited laminae, we expect that the Lisan Formation will be established as a high-resolution archive of atmospheric ^{14}C variations during the last glacial period.

SUMMARY

^{14}C ages were obtained from primary aragonites that were deposited in the last glacial Lake Lisan between ~28 to 18 ka cal BP, during Marine Isotope Stage 2, when the lake level averaged ~200 m

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higher than typical Holocene levels. The ages display a declining deviation from the IntCal09 calibration curve through time, which reflects a temporal decrease in the lake reservoir age (RA). The decrease in RA is accompanied by a decrease in the Sr/Ca ratios in the aragonite laminae reflecting the decreasing Sr/Ca ratio in the surface layer of the lake (the epilimnion).

The chemical composition of the epilimnion was dictated by freshwater input that continuously replenished the lake with high bicarbonate, low Sr/Ca and high Fm runoff, and by Ca-chloride brine, with low bicarbonate, high Sr/Ca, and low Fm. We suggest that turbulent mixing across the hypolimnion/epilimnion interface buffered the ¹⁴C, Sr, and Ca contents in the epilimnion, slowing the rate of decrease in the Sr/Ca ratio in the aragonite precipitating solution and causing the ¹⁴C content to remain nearly constant.

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