SALT CRYSTALLIZATION TEMPERATURES IN SEARLES LAKE, CALIFORNIA¹

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Abstract

The D/H ratios in natural samples of borax, gaylussite, nahcolite and trona were compared with minerals synthesized in the laboratory to deduce temperatures of crystallization in Searles Lake. During most of the Early Holocene, trona in the Upper Salt was deposited during warm summers, average 32° C, similar to the present. Crystallization temperatures of the Middle Wisconsin Lower Salt inferred from D/H ratios are in the range -12° to $+8^{\circ}$ C; by consideration of phase relations these are assigned to winter crystallization. Winter temperatures much colder than those of the present are inferred for the upper and lower thirds of this Lower Salt unit; summer temperatures for these units inferred from mineral aspublished elsewhere.

INTRODUCTION

Searles Lake, which is dry today, was one of a chain of large lakes that formed in the Great Basin segment of southeast California during pluvial periods of late Quaternary time (Gale, 1914; Flint and Gale, 1958; Smith, 1968). The number of lakes in the chain, and the size of the last lake in the chain, were governed by the regional climate. A knowledge of the geologic history of these lakes thus provides a record of climatic fluctuations during late Quaternary time.

The history of lakes in Searles Valley is recorded in the stratigraphy of sediments deposited in the center of the basin. The sediments have been divided into six stratigraphic units that are informally designated (Flint and Gale, 1958) as the Mixed Layer (of pre-Wisconsin age), Bottom Mud (Early Wisconsin), Lower Salt (Middle Wisconsin), Parting Mud (Late Wisconsin), Upper Salt (Early Holocene), and Overburden Mud (Late Holocene). Wet periods caused the lakes to expand and deposit muds over a large area. Dry periods caused the lakes to shrink or disappear, and to produce layers of mixed salts in the center of the basin. The salts were permeated by brine, and both phases were apparently in chemical and isotopic equilibrium with each other. The chemical and isotopic composition of certain salt minerals should, therefore, reflect the temperatures at which they were deposited. This paper summarizes new isotopic temperature data, and compares these with phase data to deduce paleoclimate. Details will be published elsewhere.

Phase Data on Paleotemperatures

Paleotemperatures are derived from phase data by comparing the assemblages of primary minerals in the saline layers with phase diagrams representative of certain temperatures. For example, at or above 20°C, Searles Lake brines that crystallize trona and halite should also produce burkeite (Smith and Haines, 1964). Natural assemblages that contain major quantities of trona, halite, and burkeite are therefore considered to have crystallized well above 20°C, and assemblages lacking burkeite are considered to have formed at lower temperature. Similarly, assemblages that contain nahcolite, borax, thenardite, and mirabilite, whose solubilities are also greatly affected by temperature, are used to estimate crystallization temperatures. The initial composition of the brine is estimated from the present bulk composition of the deposit.

It is important to realize, however, that mineral assemblages are only an approximate indicator of crystallization temperature. For example, certain minerals tend to form only in summer or in winter, so their existence may reflect only seasonal extremes. Also, suites of such minerals are stable over a moderate range of temperature, pressure, and concentration of the involved ions; this means that crystallization temperatures can be expressed only in terms of a range or limit, and also helps explain how saline layers that formed during one season persist even though their salts are subjected to seasonal and longer term changes in temperatures and brine concentration. Further uncertainties exist because natural crystallization processes do not generally occur under conditions of nearly constant temperatures, salinity, and CO₂ pressures as do the laboratory processes with which they are compared, nor are temperatures in a crystallizing body of brine identical with those of the atmosphere.

ISOTOPIC DATA ON PALEOTEMPERATURES

Isotopic estimates of paleotemperatures for Searles Lake saline layers are based on data obtained by the laboratory synthesis of borax (Na₂B₄O₇·10H₂O), gaylussite (CaCO₃· Na₂CO₃·5H₂O), nahcolite (NaHCO₃), and trona (Na₂CO₃· NaHCO₃·2H₂O) from aqueous solutions having a known deuterium-to-hydrogen (D/H) ratio. We found that deuterium is depleted in gaylussite, nahcolite, and trona relative to the solutions from which they were crystallized, and that borax contains about the same percentage relative to its solution. We also found that the fractionation factors of the trona-water and nahcolite-water systems are dependent on temperature, and that the factors for borax and gaylussite are not. A coexisting pair of these minerals (such as trona and borax) therefore provides a means of judging the temperature at which they formed.

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FIG. 1. Diagram showing for each layer the average isotopic and phase data paleotemperatures for selected stratigraphic intervals in the Lower Salt and Upper Salt, Searles Lake, Also shown are data representing the present climate in the area.

Samples for isotopic study were collected from cores. Most trona and nahcolite samples came from beds of finegrained material; borax samples were from more coarsely crystalline material. We interpret all samples to be original precipitates formed in, or within a few inches of the bottom of, a saline lake. Although the brines now in these saline beds are in chemical equilibrium, they are not in isotopic equilibrium with the present salts. Therefore, we have used coexisting crystals of borax to reconstruct the approximate isotopic composition of the water that was present when the salts in each layer crystallized.

The possibility was considered that some or all of the crystals used in our work were products of postburial recrystallization from the younger and isotopically lighter brines, or affected by isotopic diffusion from such brines. However, for a number of reasons we conclude that these possibilities can be disregarded. For example, microscopic crystals of primary trona and much larger cystals of secondary trona from the same specimen have maintained isotopic differences even though they have always been immersed in the same brine, and neither type has reached isotopic equilibrium with the present brine. Attempts to alter the isotopic composition of natural trona in the laboratory resulted in less than 1 percent change. Using the D/H ratios in mineral samples collected from all major horizons, we estimate their crystallization temperatures. The assumptions applied are (1) that the deuterium content of the original brine that produced each salt layer is reflected in the deuterium content of borax crystals from that layer, and (2) that crystallization of hydrogen-bearing minerals took place under equilibrium conditions.

Paleotemperature determinations from the Upper Salt (early Holocene) are shown in Figure 1. Samples from the basal layer indicate isotopic and phase data crystallization temperatures near 15°C. The remaining samples from the lower half of the unit have isotopic temperatures that average 33°C, and samples from the upper half average 32°C. These and other geologic data suggest that all but the basal horizons represent a saline lake that was warm and shallow, and that trona was deposited from this lake during summers that were similar to present summers.

Samples from the Lower Salt (Middle Wisconsin) generally indicate crystallization temperatures below those of the Upper Salt. The average isotopic paleotemperatures for the seven salt units in the Lower Salt, shown individually in Figure 1, range from -12° C to $+8^{\circ}$ C. The temperature coefficient of solubility for trona is such that the mineral probably crystallized during winter from all but very shallow lakes. The mineral assemblages of the salt units show that of the layers in the Lower Salt sequence, which are numbered S-1 to S-7 in Figure 1, only S-5 and possibly S-4 were likely to have been deposited in lakes that were shallow enough to crystallize trona during the summer. Isotopic paleotemperatures for the remaining lavers are thus considered indicative of winter conditions. Because the abundance or near-absence of burkeite in trona-halite assemblages is used as the criterion, we consider crystallization temperatures derived from phase data for units S-4, S-5, S-6, and S-7 to represent summer crystallization temperatures. The presence of borax-trona assemblages accompanied by virtually no halite is the criterion used for units S-1, S-2, and S-3, so we consider these limits indicative of winter temperatures. Summer and winter temperatures during the times represented by S-6 and S-7 were thus clearly below present temperatures; summer and winter temperatures during S-4 and S-5 times could have been nearly the same as at present; and winters during the times represented by S-1, S-2, and S-3 were distinctly colder than present winters but summer temperatures are not inferred.

The winter temperatures indicated by the isotopic measurements from the lower and upper beds in the Lower Salt are especially important because the layers were deposited under transitional conditions between an interstade of which they are a part, and the early and late Wisconsin glacial stades for which we have no isotopic paleotemperature control. Relative to the present climate, they indicate substantially greater cooling than is commonly inferred for glacial stades.

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