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DISCUSSION
SOURCE FLUIDS FOR THE SALTON SEA
GEOHERMAL SYSTEM

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ABSTRACT. The proposal by Helgeson (1968) that the source fluid for the Salton Sea geothermal brine was interstitial connate Colorado River water in the sediments is evaluated quantitatively in terms of the dynamics of the geothermal system and the isotopic composition of the various waters involved. Neither batch nor continuous evaporation processes operating on original interstitial water of present day Colorado River composition can produce the geothermal brine characteristics presently observed. The isotopic evidence indicates that the source fluid was meteoric water derived from local precipitation and circulating downward through the sediments.

Recent work on the isotopic and chemical relationships in the waters of the Salton Sea geothermal area (Craig, 1966) has shown that the thermal waters of this system display a regular pattern of increasing salinity, temperature, and oxygen-18 concentration with variations that are very large in comparison with those previously studied (Craig, 1963). But in spite of the fact that chloride concentrations vary by more than a factor of 100, these waters show the characteristic "oxygen isotope shift" observed in many other geothermal systems, that is, a progressive enrichment in oxygen-18 relative to local meteoric and ground waters with a constant deuterium concentration equal to that in the meteoric waters.

It is now rather generally accepted that such systems represent a continuous sequence of waters that have exchanged oxygen isotopes with carbonates and silicates to varying degrees; their common origin from local precipitation is shown by the constancy of the deuterium concentration which remains essentially unchanged because of the small amount of hydrogen in rocks. Recently Clayton, Muffler, and White (1968) have shown that the sub-surface sediments of the Salton Sea area show the expected reverse oxygen isotope shift with depletion of oxygen-18 which has enriched the circulating thermal waters.

In his very detailed description of this area, Helgeson (1968) proposes that the geothermal brines in the Salton Sea area originated from connate Colorado River water by an evaporative reflux mechanism in which hot water undergoes flash evaporation at the surface and drains back into the subsurface reservoir because the basin drainage is interior. Helgeson rightly recognizes the importance of understanding the mechanism by which such geothermal brines form, and it is particularly important to discover whether special or unique processes have operated in each such area, or whether, as I concluded earlier, geothermal brines result from basically similar dynamic circulation patterns of surface waters descending through sediments to subterranean reservoirs (Craig, 1966). Helgeson states that, in particular, the constant deuterium concentration in these waters does not rule out Colorado River water (which has a different deuterium concentration as it originates considerably

farther inland) as the source of the brine and that "flash evaporation of interstitial Colorado River water would tend to produce the isotopic characteristics of the brines".

Since Helgeson does not attempt to demonstrate quantitatively how this duplication would occur, it is necessary to set up a model for demonstration purposes. Helgeson postulates a "closed system" in which ascending hot pore fluids reach the surface through fractures or sand lenses, flash evaporate, and increase in salinity, and then recirculate back to the reservoir driven by their increased density. As described, this is essentially a batch distillation model for a brine which can be described by a modified Rayleigh equation:

$$\lambda - \lambda^0 = -n\epsilon^* \ln f \quad (1)$$

in which $\lambda = \ln(1 + \delta)$ where δ is the variation in the isotope ratio D/H or O^{18}/O^{16} relative to a standard, for example, $\delta D = [(D/H)/(D/H)_{std}] - 1$ and is customarily expressed in per mil units. The superscript o designates the initial fluid at the start of the process. The parameter ϵ^* is the single-stage enrichment, here defined as for example, $1 - [(D/H)_{vapor}/(D/H)_{liquid}]$ and similarly for oxygen-18 fractionation. The parameter n is the number of stages or theoretical plates attained in a multistage process, and equation (1) is actually an expansion of the function $[(1 - \epsilon^*)^n - 1]$ which is always valid in considering isotopic variations at the natural abundance level unless n is extremely large.

The fraction parameter f is the fraction of initial water left—it is related to the salinity by:

$$f = \frac{S^0(1 - S)}{S(1 - S^0)} \quad (2)$$

The mean salinity of these brines is about 250,000 ppm, so that $f = 3 \times 10^{-6} S^0$ when the initial salinity is not too large.

The ϵ^* factors for each isotope are functions of temperature; these functions are plotted for D and O^{18} in figure 1. Because multi-stage processes may occur, values for $\lambda - \lambda^0$ and $\ln f$ inserted in (1) do not define a temperature, but the ratio of the λ functions for the two isotopes, which is equal to the ϵ^* ratios, is uniquely correlated with temperature over most of the range, as shown in figure 1. The temperature of 224°C at which $\epsilon^*(D)$ goes through zero is the well-known "cross-over" temperature for hydrogen; the oxygen isotopic species do not have such a cross-over (Bottinga and Craig, 1968). For each isotope, ϵ^* goes to zero at the critical temperature.

The characteristic δ values in the system at hand (relative to the SMOW standard, Craig, 1966) are:

	δD (‰)	δO^{18} (‰)
Local meteoric water	-75	-11
Geothermal brine	-75	+3
Colorado River water	-120	-16

The oxygen shift in this system is seen to be 14 per mil. The intermediate waters varying in O^{18} content from meteoric water to brine are

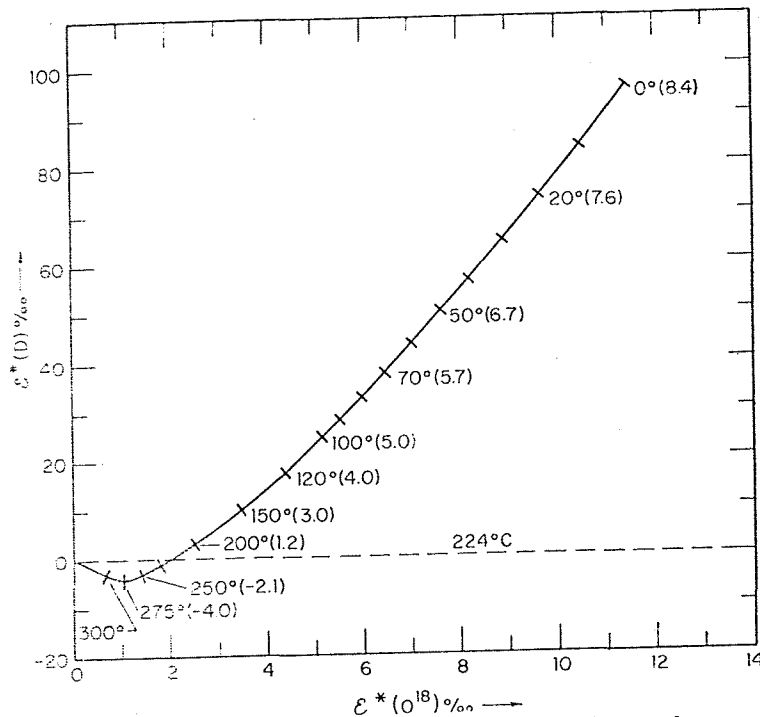


Fig. 1. Single-stage isotopic enrichment factors for deuterium and oxygen-18 in evaporation. The numbers in parentheses after the temperatures are the ratio $\epsilon^*(D)/\epsilon^*(O^{18})$ at that temperature. Above 224°C deuterium concentrates preferentially in the vapor phase instead of the liquid.

not listed, as they do not enter the calculations. (The value of Colorado River water assumed is extrapolated from observed values of about -11.4, -14.5, down the low temperature evaporation slope connecting Lake Mead and Salton Sea values in fig. 1 of Craig, 1966, to the intersection with the meteoric water line. This difference is not critical).

Now Helgeson makes one numerical calculation, on cycling times, in which he flash evaporates the connate river water at 230°C—and then goes on to state that flash evaporation will account for the isotopic composition of the brine. It is immediately obvious that this at least cannot be done at 230° because removal of steam will only make the river water decrease in deuterium, rather than increase as required (see fig. 1). This effect is actually observed in the steam-water relationships in the Salton Sea wells where Helgeson and I collected brine and steam (Craig, 1966, fig. 1, shows the isotopic cross-over effects). So flash evaporation cannot produce these effects anywhere near temperatures of 200° where the deuterium fractionation vanishes and then changes sign.

In fact, the maximum temperature at which this process can have operated can be calculated by assuming that no oxygen isotope shift by exchange has occurred, so that all the O¹⁸ enrichment in the brine is due to evaporation. Then the λ enrichments in (1) are 49.9 and 19.1

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per mil (using ϵ^* in ‰ and expressing λ as 1000 times the decimal value, for consistency with δ notation), with a ratio of 2.61 which corresponds to a process temperature of 159°C. If we set $n = 1$, then $S^\circ = 900$ ppm (a reasonable value) but $f = 2.7 \times 10^{-3}$, that is, all but 0.27 percent of the water of the system has been evaporated away as steam. This seems like a highly inefficient way to make geothermal brines. We can suppose that $n = 2$, requiring that in some crevices or fumarole throats the steam trajectory became non-adiabatic due to conductive losses, and enough cooling took place so that condensation, and thus counter-current two-phase flow, occurred giving us two theoretical plates of separation. In this case f becomes 0.50, not much help, but S° is now required to have been 17,000 ppm, meaning that we have almost a brine to begin with and have to account for that also.

The values of n , f , and S° are all correlated by (1) and (2); for this case of no exchange isotope shift and 159°C a few values follow:

n	f	S° (ppm)
1.00	0.0027	900
1.26	0.009	3000
1.69	0.030	10000
2.00	0.052	17000

As n increases we can evaporate less water for a given enrichment, but this requires the initial salinity to have been higher in order to achieve the observed salinity of the brine. It is very difficult to get more than two or three theoretical plates in such a natural process and even more difficult to assume an initial salinity of more than say 3000 ppm (Helgeson assumes 1000 ppm). (It should perhaps be stated that the kinetic isotope effects in water evaporation, which I have discussed elsewhere, are encountered only at temperatures below 100°C in open air. Many analyses of steam and liquid in geothermal bores, separators, and large fumaroles have been made, and isotopic equilibrium is always attained because of the high temperature and vapor pressure.)

Of course an oxygen isotope shift by exchange with rock *has* occurred, as demonstrated by (A) the progressive enrichment in O^{18} , at constant D , of waters in the system, and (B) the reverse oxygen shift in the rocks (Clayton, Muffler, and White, 1968). Helgeson (p. 162) uses the evidence of the reverse shift to conclude that the O^{18}/O^{16} ratio in the brine is depth independent; he would have to admit, then, that his flash evaporation process is not responsible for *all* the isotope enrichment but only part of it. Therefore, the $\epsilon^*(D)/\epsilon^*(O^{18})$ ratio has to be *greater* than the value of 2.61 obtained above, so that for the given D enrichment of the brine relative to Colorado River water, the evaporation trajectory produces less O^{18} enrichment. In table 1 are shown some values of the parameters for oxygen shifts by exchange ranging from 0 to 9 per mil, the latter value corresponding to a temperature of 100°C for the evaporation process. All calculations are for $n =$ one stage. The "volume loss ratio" shown is the function $(1 - f)/f$, the number of volumes of present brine water which have been evaporated away.

We see that at high temperatures, near 159°, the isotope separation is low, so that S° can be a reasonable value, but we have to evaporate away several hundred volumes equivalent to the present value of brine, and we have no allowance for the oxygen shift. At lower temperatures

TABLE 1

Values of the evaporation process parameters for $n = 1$ theoretical plate

$T^\circ\text{C}$	$f(\%)$	Volume loss ratio	S° (ppm)	O^{18} shift (‰)
159*	0.27	370	900	0
140	1.8	55	6100	4
120	5.8	16.2	18900	6.5
100	13.5	6.4	43000	9

* Maximum temperature for the process, corresponding to zero oxygen shift.

the separation factors are larger, and we have a reasonable isotope shift (which allows a finite and reasonable ratio of water to rock), but then S° very quickly becomes unreasonably high, already 6000 ppm higher for a temperature drop of 20°. This is a sort of "anti-bootstrap" operation, and it appears that we have to settle on a very closely defined temperature range of, say, 140 to 150° to have any reasonable compromise. Even here, we have to evaporate of the order of 100 volumes of present brine away and demand a fairly high initial salinity of several thousand ppm and a very high water to rock ratio in the reservoir. Increasing the value of n is equivalent to dropping the temperature, with respect to the resulting values of f and S° and does not help. (A value of n less than one in this context means that osmotic loss or membrane filtration is taking place, so that some water is leaving the system with no isotope fractionation by phase separation and no salt content; there is a very real case to be made for this, but it will be related elsewhere, as it does not correspond to the process we are considering.)

Now we have to ask what the meaning is of evaporating away hundreds of times the volume of the reservoir water and of requiring a very small isotope shift in the water (which means a large water/rock ratio) when the water itself is only a small part of the system, dispersed in the rock rather than in a large single chamber. The water, after all, fills the reservoir space available now, so that initially we require an infinite amount. The meaning is that the process cannot be a batch distillation in Helgeson's closed system (1968, p. 162); it must be a continuous distillation in an open system with continual input of new feed water flowing in.

At this point equation (1) is wiped out and the situation is much clearer—the isotopic composition of the reservoir fluid changes until it reaches the steady state composition—and the steam evaporating away has the same isotopic composition as the input water supplying the reservoir. The liquid in the reservoir is then one equilibrium-stage enrichment factor (or, more precisely, n factors) removed from the input-output fluid. In Helgeson's model the input fluid is interstitial connate Colorado River water in the pores of the sediments surrounding the thermal hot-spot. So the reservoir itself is always full, and the water can exhibit only

a small oxygen isotope shift. The driving force for flow into the system is simply the volume loss of water by evaporation.

The open system process is, in contrast to the closed system batch evaporation, a possible process. It is, in fact, the process I proposed for the general origin of geothermal brines from normal meteoric waters of low salinity (Craig, 1966). The question remains as to the source of the input water. In the actual calculation for O^{18} balance, the flux of O^{18} into the fluid, from rock, has to be entered (the actual fluid is an oxygen-shifted river water, as it were), but we can get the temperature directly from the deuterium data and the separation factors in figure 1. For $n =$ one stage, the process must operate at $50^{\circ}C$ to produce the 51 per mil enrichment of brine relative to Colorado River water. For $n =$ two stages, the temperature can be $100^{\circ}C$. The maximum temperature is still 159° , but this now requires $n = 6$. The salinity of the input water can have any value. But it is clearly unreasonable, unless one is willing to postulate some very special circumstance, that n could ever be more than about 1.5 for a natural process, and since Clayton, Muffler, and White (1968) have shown temperatures were much higher, the source fluid cannot have been water of the isotopic composition of the present Colorado River.

One final point that should be made is that, as I pointed out previously (Craig, 1966), any proposed process for these geothermal fluids in which the source fluid has a different deuterium value than the brine requires the simultaneous operation of *two* coincidences: the correct initial composition for the process to produce the observed brine composition and the correct process "intensity", that is, the degree of separation obtained, corresponding to number of stages or extent of a transient process, which will just give a final composition with the same deuterium concentration as the local meteoric water.

Helgeson (1968) objects to my conclusion that the salts have been derived from sediments, because the isotopic analyses have been made on "relatively few samples, most of which were taken from surface features such as mud pots". Actually, my figure 2 (Craig, 1966) shows 17 analyses of which 9 are brines and associated steam. Most of the analyses are on other waters simply because the brines are all very similar, one to another, and it is the more dilute thermal waters that show the range of properties from meteoric water to brine. Helgeson also states that "Craig (1966) claims to have documented a linear relation between O^{18}/O^{16} and the logarithm of chloride concentration" in these waters and objects to this because Clayton has now found one dilute brine sample at an intermediate depth which does not fit the relationship. The relationship is actually doubly-logarithmic as shown in my text and figure; secondly, Clayton's sample actually is one point compared to 17 which fit the relationship over a range from 500 to more than 100,000 ppm; and finally, Helgeson himself devotes a two-paragraph footnote to discussing his belief that this aberrant sample is the result of contamination by drilling fluid!

With respect to the actual extent of the leaching process by these intermediate waters of the system, White (personal commun.) has convinced me that membrane-filtration has to be seriously considered as a mechanism for salt concentration. The process responsible for producing these intermediate waters is of great importance for understanding their relationship to the end members of the system: if it is leaching, they represent waters circulating downward from shallow levels toward the reservoir; if it is membrane-filtration they represent filtered brine fluid moving up and out and mixing with dilute waters in the process. It can be shown that either of these processes will produce the doubly-logarithmic relation I observed, and a quantitative discussion of these effects will be presented elsewhere.

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