Lithium Evolution and Reservoir Sustainability in the Salton Sea Geothermal Reservoir from Reactive-Transport Modeling

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ABS TRACT

Assessing the extent and sustainability of the lithium (Li) resource in the Salton Sea Geothermal Field (SSGF) is aided by an understanding of reservoir water-rock reactions affecting lithium-rich brines. The purpose of this work is to examine the rates and extent of water-rock reactions involving Li in the SSGF, the rates of Li-rich brine replenishment into the reservoir after extraction/reinjection, and the effects of water-rock reactions on Li-depleted brine (+/- condensate) that are re-injected into the reservoir. Simulations were performed using an updated version of the reactive-transport simulator TOUGHREACT V4.13-OMP. Three-dimensional reactive-transport simulations over 4000 years using the SSGF reservoir model, considering hypersaline brine convection in unaltered reservoir rocks, results in alteration to hectorite at lower temperatures and primarily cookeite (Li-chlorite) at temperatures over 300°C. The high initial Li concentration in the hypersaline brine leads to small increases/decreases in reservoir bulk rock Li concentrations, and little change in brine Li concentrations except at the top of the reservoir model, and Li concentrations in the brine. The primary replenishment mechanism for Li is the upward flux of convecting Li-rich brine from below the producing reservoir, and unexploited brines in the reservoir. Assuming the calibrated upward basal fluxes in the reservoir model, and Li concentrations in the upwelling brine of about 200 ppm, Li enrichment of reinjected depleted brines at 2750 m depth is roughly 10 ppm per 100 years. At the bottomhole depths of deep production wells (~2000-2700 m), with brine temperatures exceeding 300°C, reactions of relatively stable Li-bearing metamorphic minerals (primarily cookeite-chlorite, feldspars, and micas) are slow, and thus injection of Li-depleted brine or condensate is not enriched by mineral-water reactions over time periods of hundreds of years.

1. INTRODUCTION

Assessing the extent and sustainability of the lithium (Li) resource in the Salton Sea Geothermal Field (SSGF) is aided by an understanding of the processes that led to the development of lithium-rich brines. Although there is extensive literature over the past 50 years on the origin, geologic history, and geochemistry of the SSGF, lacking are quantitative models that can be used to assess the rates at which Li concentrations evolve and are transported through the field. For the timescale of exploitation of the Li resource (10-100 years), the rates at which mineral-water reactions and transport processes (advection-diffusion) take place is essential to constraining the lifetime of the resource. The purpose of this work is to examine the rates and extent of water-rock reactions involving Li in the SSGF, the rates of Lirich brine replenishment into the reservoir, and the effects of water-rock reactions on Li-depleted brine (+/- condensate) that are re-injected into the reservoir.

The origin of Li-rich geothermal brines (200-400 ppm) produced in the SSGF has been attributed to deep circulation of evaporated nearsurface Li-rich brines, hydrothermal alteration of buried volcanic and sedimentary rocks, magnatic fluid contributions, and/or interaction of hydrothermal fluids with evaporites and/or mudstones (Helgeson, 1968; McKibben et al., 1988). The SSGF has undergone a complex tectonic history, magnatism, rapid sedimentation/burial, metamorphism, and climatic changes with concomitant formation/disappearance of large surface water bodies over tens of thousands to 0.5 million years (Cullen et al., 2021). Lithium concentrations in the unaltered rhyolites are relatively low (~40 ppm), suggesting that the magna body is not likely Li-enriched. The primary source of Li may be from brines formed through repeated evaporation events following Pleistocene high lake levels, supported by Li-rich surface mudstones from the Durmid Hills (Humphreys et al., 2023). To evaluate the roles of hydrothermal circulation, water-rock interaction, and surface evaporative concentration in the SSGF lithium evolution, reactive-transport models were developed for Salton Sea evaporation and hydrothermal alteration, using a 3-D calibrated SSGF reservoir model (Araya et al., 2022), as well as surface evaporation and 1-D reactivetransport models.

2. MODELING APPROACH AND INPUT DATA

Simulations were performed using an updated version of the reactive-transport simulator TOUGHREACT V4.13-OMP (Sonnenthal et al., 2021; Spycher et al., 2021; Xu et al., 2006; 2011). For 3-D reservoir simulations, we used the EOS1sc module (supercritical water equation-of-state) derived from inverse TOUGH2 (iTOUGH2; Magnusdottir and Finsterle, 2015).

Simulations employ a parallel Pitzer implementation in TOUGHREACT v4.13-OMP (Spycher et al., 2021; Sonnenthal and Spycher, 2021; Zhang et al., 2008). The main extensions over the typical Debye-Huckel approach include: (1) Pitzer ion-interaction model (Pitzer and Mayorga, 1973; Pitzer, 1991) for ionic activity calculation of solutions over a broad range of concentrations; and (2) the coupling of

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the vapor-pressure-lowering effect of salinity to phase partitioning. The Pitzer formalism was implemented into TOUGHREACT using the Harvie-Moller-Weare (HMW) formulation (Harvie et al., 1984). The HMW formulation was developed from Pitzer's ion-interaction theoretical model and is equivalent to Pitzer's original model (Pitzer, 1973; Pitzer and Mayorga, 1973). The only difference is in the definition of interaction terms, interaction coefficients, and mathematical expressions (Rard and Wijesinghe, 2003).

2.1 Hydrological and Thermal Properties

The 3-D and 1-D thermal-hydrological-chemical (THC) reactive-transport models of the reservoir are based on the Araya & O'Sullivan (2022) 3-D model of the SSGF (pure water). Details of the calibrated porosities, permeabilities, and thermal properties are described in the latter paper.

2.2 Geochemical Data

2.2.1 Water Chemistry

The aqueous geochemical system was simplified into two endmember water compositions - the present-day Salton Sea (Holdren and Montaño, 2002) and the reservoir fluid (Table 1). The reservoir fluid was taken from one of the hotter deeper wells (State 2-14) with relatively high Li concentrations as characteristic of the deep brine convecting into the reservoir (McKibben and Hardie and, 1997). The concentrations of species that were not analyzed were determined through mineral equilibration (Table 1).

2.2.2 Thermodynamic Data for Minerals, Aqueous Species, and Gases

The thermodynamic databases used in the simulations are based on a conversion of the EQ3/6 *data0.ypf* Pitzer database (after Wolery et al., 2004; Alai et al., 2005), suitable for ionic strengths up to ~40 molal for some systems and temperatures ~150°C at solution vapor saturation pressures (see Spycher et al., 2021). Several modifications were made to the database (see notes in database and Spycher et al., 2021) prior to the additions made to simulate water-rock reactions involving Li. Additions for Li reactions included Li Pitzer ion interaction parameters from Lassin et al. (2015), taken after converting the PHREEQC Pitzer database *mmc4.dat* obtained in the supplemental information of Boschetti (2022a), as well as Li mineral data from the PHREEQC formatted file in the supplemental information of Boschetti (2022b). These data were then corrected for consistency with thermodynamic data for SiO₂(aq) and Al⁺³ in the *data0.ypf* database

Two ideal endmember solid solutions (Li-albite-albite and Li-K-feldspar-K-feldspar) were added to treat minor substitutions of Li in albite and K-feldspar in both primary and potential secondary minerals, similar to the approach used in Wanner et al. (2014), which also included isotopic fractionation of Li isotopes. One complicating factor is that most hydrothermal minerals are solid solutions potentially with several endmembers and substituting ions. Thermodynamics of solid solutions can be highly nonideal, and data are lacking for many highly complex minerals. Li-bearing chlorite can be considered as a solid solution between Mg-rich clinochlore, Fe-rich daphnite, cookeite, and potentially other substituting cations such as Mn and Sr.

2.2.3 Kinetic Data

Kinetic data were derived from a variety of sources, most based originally on Palandri and Kharaka (2004), and others estimated based on similar mineral structures. Because the reactive surface area is a major factor in the effective rate and can vary by many orders of magnitude, uncertainties in the rate constants are combined into the effective rate. Determining the effective rate generally is best done by "calibration" of reactive surface areas (RSA), and sometimes by modifications to kinetic parameters/rate laws. Where the ages of the rocks and their geologic histories are known at least approximately, calibration was done by running forward-looking "native-state" models and comparing to observed secondary mineral abundances and measured present-day water chemistry. To simulate the nativestate evolution, the model considered the initial unaltered mineral abundances to be the same everywhere. Initial mineral volume fractions are given in Table 2. For the 3-D reservoir simulation a "low-reactivity" and "high-reactivity" case, with the latter having reactive surface areas ten times higher than those given in Table 2.

	Salton Sea ¹	Salton Sea (speciated)	S 2-14 ²	S 2-14 (speciated)
T (°C)	25	25	330	349.565
pН	8.12	6.9842	-	4.000
Ionic str.	-	0.88983	-	4.797
H ₂ O activity	-	0.98101	-	0.904
Osmotic P (bar)	-	26.403	-	291.48
EC(uS_cm)	-	55.101	-	3508.52

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Component	ppm	mol/kg H ₂ O	ppm	mol/kg H ₂ O
Na ⁺	12369.93	5.381E-01	54800	2.382E+00
K+	258.00	6.599E-03	17700	4.524E-01
Li+	3.00 ³	4.322E-04	209	3.009E-02
Ca ⁺²	944.00	2.355E-02	28500	7.107E-01
M g+2	1399.99	5.760E-02	49	2.015E-03
Ba ⁺²	0.07	5.097E-07	210	1.528E-03
Sr ⁺²	22.00	2.511E-04	421	4.802E-03
M n+2	0.03	5.461E-07	1500	2.729E-02
Fe ⁺²	0.07	1.253E-06	1710	3.060E-02
Zn ⁺²	0.02	3.059E-07	507	7.749E-03
Al+3	0.06	2.039E-09	-	3.704E-06
Cŀ	17239.92	4.863E-01	157500	4.440E+00
Br	13.00	1.627E-04	111	1.388E-03
F-	2.10	1.105E-04	-	1.105E-04
HCO3-	245.00	4.015E-03	1580 (CO ₂ )	3.588E-02
SO4-2	10499.93	1.093E-01	53.00	5.514E-04
HS-	na	3.594e-18	10 (H ₂ S)	2.844E-17
HPO ₄ -2	0.05	5.209E-07	-	5.206E-07
SiO ₂ (aq)	9.87	1.643E-04	588.00	2.824E-02
B(OH) ₃ (aq)	63.50	1.027E-03	1550.00	2.505E-02

¹Holdren and Montaño (2002); ²McKibben and Hardie (1997); ³Synthesis of analyses from Werner and Olson (1970) and Sturz (1989).

fable 2. Mineral kinetic parameters,	reactive surface areas,	Li contents in minerals	s and bulk rock (l	ow-reactivity case)
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Mineral	k _{0,25C} (1/s)	Ea (J/mol K)	RSA (cm ² /g)	Li (ppm)	Initial Vol Fraction	Li in Rock (ppm)
hectorite-1	1.6596e-13	35.	1.e-4	36.60	-	-
hectorite-2	1.6596e-13	35.	1.e-4	210.43	-	-
cookeite	1.6596e-13	35.	1.e-4	13292.7	-	-
ephesite	2.5119E-15	66.2	1.e-4	17887.2	-	-
lepidolite	1.6596e-13	35.	1.e-4	-	-	-
taeniolite	2.5119E-15	66.2	1.e-4	-	-	-
elbaite	2.37e-13	58.	1.e-4	-	-	-
Li-mica	1.6596e-13	35.	1.e-4	8912.54	1.9e-4	1.78
Li-albite (ss)	2.75e-13	69.8	1.e-5	26.47	0.237	6.41
albite (ss)	2.75e-13	69.8	1.e-5	-	-	-
Li-K-feldspar (ss)	3.8905e-13	38.	1.e-5	49.88	0.275	13.70
K-feldspar(ss)	3.8905e-13	38.	1.e-5	-	-	-
quartz	6.4E-14 3.2E-12	77. 50.	1.e-5	-	0.474	-
halite	equilibrium	-	-	-	-	-
barite	equilibrium	-	-	-	-	-
gypsum	equilibrium	-	-	-	-	-
anhydrite	6.4565e-04	14.3	1.e-4	-	-	-
calcite	1.6E-6/1.8E-7	24./66.	1.e-4	-	-	-
magnesite	4.571E-10	23.5	1.e-4	-	-	-

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dolomite	2.9512e-08	52.2	1.e-4	-	-	-
ankerite	2.24e-09	48.	1.e-4	-	-	-
strontianite	1.2598e-09	62.76	1.e-4	-	-	-
talc	1.00e-12	42.0	1.e-4	-	-	-
kaolinite	6.9183e-14	22.2	1.e-4	-	-	-
illite	1.6596e-13	35.	1.e-4	-	-	-
clinochl-30	1.6596e-13	35.	1.e-4	-	-	-
Ca-montmor	1.6596e-13	35.	1.e-4	-	-	-
Na-montmor	1.6596e-13	35.	1.e-4	-	-	-
K-montmor	1.6596e-13	35.	1.e-4	-	-	-
Mg-montmor	1.6596e-13	35.	1.e-4	-	-	-
smectite-FeMg	1.6596e-13	35.	1.e-4	-	-	-
hematite	2.5119E-15	66.2	1.e-4	-	-	-
magnetite	3.98e-14	90.9	1.e-4	-	0.0095	-
fluorapatite	2.37e-13	58.	1.e-4	-	0.0047	-
sphalerite	1.e-15	50.	1.e-4	-	-	-
pyrite	$\begin{array}{ccc} H^+ & 3.02 \text{E-} 08 \\ O_2(\text{aq}) & 2.8184 \text{E-} \\ 05 \end{array}$	56.9	1.e-4	-	-	-
pyrrhotite	1.4e-09	100.	1.e-4	-	-	-
Bulk Rock	-	-		-	1.0	21.89

## **3. SIMULATION RESULTS**

The native-state geochemical evolution of the SSGF is approximated by starting with a steady -state EOS1sc fluid and heat flow simulation run for over 1 My, without considering reactive transport. Water and heat are injected into the base of the reservoir, and the fluxes are determined through calibration of the initial EOS1 model from Araya and O'Sullivan (2022) to wellbore temperatures and pressures. Note that this was a pure water EOS, which differs in density and viscosity from a saline brine. However, because the fluid is injected into the base of the reservoir, rather than allowing it to convect above the deeper magma body, it is closer to a forced convection system than a naturally convecting system. As a forced convection system, the flow rates are boundary conditions that are not affected by the density and viscosity of the fluid as in a buoyancy-driven system.

In the 3-D reactive-transport simulation, the rocks and fluid are already at high temperatures, so minerals begin to react immediately, particularly at temperatures over 300°C, but also near the surface (Figure 1). Lithium is introduced only in the brine injected at the base of the model, and therefore slowly replaces the fluids in the reservoir, reacting with the rock over time. Figure 1 also shows the evolution of the lowest temperature minerals in the cooler region and near the surface (barite), trending to hydrothermal dolomite at moderate temperatures, then anhydrite over a wide temperature range, followed by hectorite-1, cookeite, and then hectorite-2 at the highest temperatures. This order is a little different for the high-reactivity case over longer time periods (see below), where cookeite is more dominant at the highest temperatures. This is expected given that cookeite is a chlorite, rather than a smectite.





Figure 1. Distribution of mineral volume faction changes after 200 years; brine convection and reaction for the low reactivity case. In order (left to right, top down): dolomite, anhydrite, hectorite-2, and cookeite.

Figure 2 (left) shows the vertical distribution of Li abundances in brine, mineral changes, and temperatures up to 1000 years for the low reactivity case in the high temperature core of the upflow zone. Note the large amount of gypsum forming at the surface, and the large amount of hydrothermal anhydrite forming a cap at the top of the reservoir. As brine advects from the base of the reservoir, Li increases from about 10-20 ppm per 100 years in the upper parts of the reservoir, and close to 40 ppm per 100 years at 3 km. Where hectorite and cookeite are precipitating at about 950 m depth, there is a sharp inflection in Li in the brine where Li is being removed from the fluid. At depth, Li in the reservoir is getting close to the maximum value injected and is not increasing or decreasing significantly due to waterrock reactions.

Figure 2 (right) shows the vertical distribution of Li abundances in brine, changes in the bulk rock Li concentrations, and temperatures at different times up to 4000 years for the low reactivity case in the high temperature core of the upflow zone. Curves for changes in the bulk rock Li concentration illustrate the "extraction" of Li from the brine through much of the reservoir, but only significantly affecting the brine composition shallower than about 1400 m. Below 1500 m depth, Li in the reservoir has attained the maximum value injected and has not increased or decreased noticeably due to water-rock reactions. Two regions show very small net removals of Li from the rock: between about 200 m and 400 m depth, and at the very base of the model where brine is injected. The base of the model involves more uncertainty because the injection temperature is fixed while the bottom temperatures vary, so minor thermal disequilibria may be the cause of the Li removal. However, the trend toward less Li removal from the rock with depth is smoothly vary ing and is not an effect of the boundary temperature disequilibrium.



#### Figure 2. Left: Vertical profile of Li abundances in brine, changes in mineral abundances, and temperatures at different times up to 1000 years for the low reactivity case. Right: Vertical profile of Li abundances in brine and rock up to 4000 years for the low reactivity case.

Another simulation was run using reactive surface areas that are 10 times higher to capture some of the possible uncertainty in the rates. Distributions of individual mineral changes with depth are shown in Figure 3 (left). The dissolution of K-feldspar and albite are quite pronounced at 900 to 1100 m depth, along with precipitation of hectorite and cookeite, leading to greater removal from the brine. The small pink bars at the left (upper scale) show where Li (on the order of ppm) is being added to the rock. Distributions of bulk rock Li changes and brine compositions with depth are shown in Figure 3 (right) for times up to 3000 years for the high reactivity case. Also plotted are measured bulk rock Li concentrations. Whereas measured Li concentrations in bulk rock do not span the entire depth range,

they are higher in the depth range of 300 to 1000 m where modeled Li is depleted in the brine by mineral precipitation. Maximum simulated enrichments of about 10 ppm (starting from 22 ppm) over 3000 years are seen at 950 m depth, with measured concentrations of about 120 ppm. If 40,000 years is an approximate time for the reaction, and Li is added at the same rate, that corresponds to an increase of 133 ppm (total=155 ppm), which is roughly consistent with observed values.



# Figure 3. Left: Vertical profile of changes in mineral volume fractions, changes in Li in the bulk rock (ppm), brine Li concentrations, and temperature up to 1000 years for the low reactivity case. Right: Vertical profile of Li abundances in brine and bulk rock, and temperature up to 3000 years for the high reactivity case. Measured Li abundances in cores/sediments are shown for a few wells.

In summary, the 3-D results show that Li in brine is not replenished by Li-bearing minerals within the reservoir footprint. Specifically, Li-rich smectite (hectorite) forms at lower temperatures, and Li-rich chlorite (cookeite) at slightly higher temperatures. Although dissolution of Li-bearing albite and K-feldspar drives hectorite and cookeite formation, most Li is derived from the hot upwelling Li-rich brine. Li is extracted from brine into minerals above 1200 m depth.

## 4. DISCUSSION: CONSTRAINTS ON REACTION RATES

The rates of reaction of minerals interacting with brine are a key factor in predicting the potential for Li to be "extracted" from Li-bearing minerals. Whereas the high-reactivity case seems more consistent with the observed changes in the rock, it needs further validation. From the high reactivity case we can sum the maximum volume fractions of primary minerals (Li-albite, albite, Li-K-feldspar, K-feldspar, Limica, and quartz) dissolved (at around 950 meters depth and 300°C) over 1000 years of brine convection in the highest temperature up flow zone. This yields approximately  $1.42 \times 10^{-6}$  volume fraction of primary minerals dissolved per year. An estimated observed reaction rate can be deduced as follows.

Helgeson (1968) noted that about 25% of the rock in the SSGF geothermal reservoir is hydrothermally altered. Ages of rhyolites at depths ranging from 1600-2700 m are from 420-479 thousand years ago (ka), with a 770 ka age for the Bishop Tuffin State Well 2-14 (Schmitt and Hulen, 2008). These ages and depths give subsidence rates of roughly 3-6 mm/yr. Subsidence rates over the last 40,000 years have been estimated at 10-20 mm/yr (Brothers et al., 2009); which, assuming 15 mm/yr for 40,000 years, gives 600 m subsidence. If repeated intrusions below the Salton Sea took place over at least the last 40,000 years, then these rocks have been above approximately 300°C for 40,000 years, since a depth of 600 meters is still in the hot geothermal reservoir. Assuming a volume fraction reacted of 0.25 over 40,000 years, the reaction rate of the bulk rock is  $6.25 \times 10^{-6}$  volume fraction/year. Extrapolating to a depth of 950 m and assuming the same subsidence rate increases the time above 300°C to 63.3 ky and reduces the reaction rate to  $3.95 \times 10^{-6}$  volume fraction per year. Certainly, water-rock reactions were taking place at temperatures below 300°C for a longer time period, albeit at a lower rate, so this value is certainly an overestimate of the true rate. The approximate minimum rate can be estimated using the time period for reaction of about 400 ky, which reduces the reaction rate to  $6.25 \times 10^{-7}$  volume fraction/year.

Given that the high-reactivity simulation case yields a value of  $1.42 \times 10^{-6}$  volume fraction of rock per year, it is in the range of the minimum and maximum estimates. It is possible that the simulated rate is slightly low, but it is not likely to be an order of magnitude higher. If the simulated rates were much higher, Li concentrations in the brine would be significantly depleted in the reservoir over a few thousand years.

## CONCLUSIONS

3-D reactive-transport simulations over 4000 years using the SSGF reservoir model, considering hypersaline brine convection in unaltered reservoir rocks results in alteration to hectorite at lower temperatures and primarily cookeite (as a rough approximation for Li incorporation into chlorite) at temperatures over 300°C. Although cookeite is not observed in the SSGF, Li concentrations up to 500 ppm are found in the chlorite (Humphreys et al., 2023), indicating some solid-solution of Li in chlorite. The high initial Li concentration in the hypersaline

brine leads to small increases/decreases in reservoir bulk rock Li concentrations, and little change in brine Li concentrations except at the top of the reservoir where more Li is removed from the brine. Under most conditions, Li-bearing minerals formed through hydrothermal interactions with Li-bearing evaporitic brines. Reaction of Li-bearing minerals with Li-poor fluids generally results in dissolution of some Li-bearing minerals and co-precipitation of other more stable minerals without much change in the brine Li concentration. The primary replenishment mechanism for Li is the upward flux of convecting Li-rich brine from below the producing reservoir, and unexploited brines in the reservoir. Assuming the calibrated upward basal fluxes in the reservoir model, and Li concentrations in the upwelling brine of about 200 ppm, Li enrichment of depleted brines at 2750 m depth is roughly 10 ppm per 100 years. At the bottomhole depths of deep production wells (~ 2000-2700 m), and brine temperatures exceeding 300°C, reactions of relatively stable Li-bearing metamorphic minerals (primarily cookeite-chlorite, feldspars, and micas) are slow and thus injection of Li-depleted brine or condensate is not enriched by mineral-water reactions over time periods of hundreds of years.

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#### REFERENCES

- Alai, M., Sutton, M., and Carroll, S.: Evaporative evolution of a Na–Cl–NO₃–K–Ca–SO₄–Mg–Si brine at 95 °C: Experiments and modeling relevant to Yucca Mountain, Nevada, Geochemical Transactions, 6 (2), (2005), 31–45.
- Araya, N., and O'Sullivan, J.: A 3D Conceptual and Natural-State Model of the Salton Sea Geothermal Field, GRC Transactions 46, (2022), 2123–2159.
- Boschetti, T.: A revision of lithium minerals thermodynamics: Possible implications for fluids geochemistry and geothermometry, Geothermics 98, (2022a), 102286.
- Boschetti, T.: Comments on "Lithium-rich geothermal brines in Europe: An up-date about geochemical characteristics and implications for potential Li resources" by Sanjuan et al. (2022), Geothermics 105, (2022b), 102518.
- Brothers, D.S., Driscoll, N.W., Kent, G.M., Harding, A.J., Babcock, J.M., and Baskin, R.L. Tectonic evolution of the Salton Sea inferred from seismic reflection data, Nat. Geosci. 2, (2009), 581–584.
- Cho, M., Liou, J.G., and Bird, D.K.: Prograde phase relations in the State 2-14 well metasandstones, Salton Sea geothermal field, California, J. Geophys. Res. 93, (1988), 13,081–13,103.
- Cullen, J.T., Hurwitz, S., Barnes, J.D., Lassiter, J.C., Penniston-Dorland, S., Meixner, A., Wilckens, F., Kasemann, S.A., and McCleskey, R.B.: The Systematics of Chlorine, Lithium, and Boron and δ³⁷Cl, δ⁷Li, and δ¹¹B in the Hydrothermal System of the Yellowstone Plateau Volcanic Field, Geochemistry, Geophys. Geosystems 22, (2021), 1–24.
- Harvie, C.E., Moller, N., and Weare, J.H.: The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-H₂O System to High Ionic Strengths at 25°C, Geochimica et Cosmochimica Acta, 48(4), (1984), 723–751.
- Helgeson, H.C.: Geologic and thermodynamic characteristics of the Salton Sea geothermal system, Am. J. Sci. 266, (1968), 129-166.
- Holdren, G.C., and Montaño, A.: Chemical and physical characteristics of the Salton Sea, California, Hydrobiologia 473, (2002), 1–21.
- Humphreys, J., Brounce, M., McKibben, M.A., Dobson, P., Planavsky, N., and Kalderon-Asael, B.: Distribution and isotopic composition of Li in the Salton Sea Geothermal Field. GRC Transactions, 47, (2023), 225–240.
- Kaspereit, D., Mann, M., Sanyal, S., Rickard, B., Osborn, W., and Hulen, J.: Updated conceptual model and reserve estimate for the Salton Sea geothermal field, Imperial Valley, California, GRC Transactions 40, (2016), 57–66.
- Lassin, A., Christomir, C., Andre, L., and Mohamed, A.: A thermodynamic model of aqueous electrolyte solution behavior and solidliquid equilibrium in the Li-H-Na-K-Cl-OH-H₂O system to very high concentrations (40 molal) and from 0 to 250 °C, Am. J. Sci. 315, (2015), 204–256.
- Magnusdottir, L., and Finsterle, S.: An iTOUGH2 equation-of-state module for modeling supercritical conditions in geothermal reservoirs, Geothermics 57, (2015), 8–17.
- McKibben, M.A., and Hardie, L.A.: Ore-forming brines in active continental rifts. In: Geochemistry of Hydrothermal Ore Deposits, 3rd Ed., H.L. Barnes, ed., (1997), 877–935.
- McKibben, M.A., Williams, A.E., and Okubo, S.: Metamorphosed Plio-Pleistocene evaporites and the origins of hypersaline brines in the Salton Sea geothermal system, California: Fluid inclusion evidence, Geochim. Cosmochim. Acta 52, (1988), 1047–1056.
- Palandri, J., and Kharaka, Y.: A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling, U.S. Geological Survey Open File Report 2004-1068, (2004).
- Pitzer, K.S.: Thermodynamics of electrolytes, I. Theoretical basis and general equations, J. Phys. Chem., 77, (1973), 268-277.
- Pitzer, K.S.: Ion Interaction Approach: Theory and Data Correlation, Chapter 3 of Activity Coefficients in Electrolyte Solutions, 2nd Edition, Pitzer, K.S., ed. Boca Raton, Florida: CRC Press, (1991), TIC: 251799.

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- Pitzer, K.S., and Mayorga, G.: Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, J. Phys. Chem., 77, (1973), 2300–2307.
- Pruess, K., Oldenburg, C., and Moridis, G.: TOUGH2 user's guide, Version 2.0, Lawrence Berkeley Laboratory Report LBL-43134, Berkeley, California, (1999).
- Rard, J.A., and Wijesinghe, A.M.: Conversion of parameters between different variants of Pitzer's ion-interaction model, both with and without ionic strength dependent higher-order terms, J. Chem. Thermodynamics, 35, (2003), 439–473.
- Schmitt, A.K., and Hulen, J.B.: Buried rhyolites within the active, high-temperature Salton Sea geothermal system, J. Volcanol. Geotherm. Res. 178, (2008), 708–718.
- Sonnenthal, E., Spycher, N., Xu, T., and Zheng, L.: TOUGHREACT V4.12-OMP and TReactMech V1.0 Geochemical and Reactive-Transport User Guide, LBNL Report 2001410. (2021) https://tough.lbl.gov/software/toughreact.
- Spycher, N., Zhang, G., and Sonnenthal, E.: TOUGHREACT-Brine: Supplement to TOUGHREACT-V4.0-OMP User's Guide for Modeling Concentrated Solutions and Osmosis Using the Pitzer Ion-Interaction Model. LBNL-2001-387, (2021).
- Sturz, A.: Low-temperature hydrothermal alteration in near-surface sediments, Salton Sea Geothermal Area, Journal of Geophysical Research: Solid Earth, 94(B4), (1989), 4015–4024.
- Wanner, C., Sonnenthal, E.L., and Liu X.-M.: Seawater δ7Li: A direct proxy for global CO₂ consumption by continental silicate weathering? Chemical Geology, 381, (2014), 154–167.
- Werner, S.L., and Olson, L.J.: Geothermal wastes and the water resources of the Salton Sea area, California Department of Water Resources Bulletin 143-7, 123 p, (1970).
- Williams, A.E., and McKibben, M.A.: A brine interface in the Salton Sea Geothermal System, California: Fluid geochemical and isotopic characteristics, Geochim. Cosmochim. Acta 53, (1989), 1905–1920.
- Wolery T., Jove-Colon C., Rard, J., and Wijesinghe, A.: Pitzer Database Development: Description of the Pitzer Geochemical Thermodynamic Database data0.ypf. Appendix I in In- Drift Precipitates/Salts Model (P. Mariner) Report ANL-EBS-MD-000045 REV 02. Las Vegas, Nevada: Bechtel SAIC Company, (2004).
- Xu, T., Sonnenthal, E., Spycher, N., and Pruess, K.: TOUGHREACT: A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO₂ geological sequestration, Computers & Geosciences 32, (2006), 145–156.
- Xu, T., Spycher, N., Sonnenthal, E., Zhang, G., Zheng, L., and Pruess, K.: TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions, Computers & Geosciences 37, (2011), 763–774.
- Zhang, G., Spycher, N., Sonnenthal, E., Steefel, C., and Xu, T.: Modeling reactive multiphase flow and transport of concentrated solutions, Nuclear Technology, 164, (2008), 180–195.