ELECTRONIC ANNEX

Geo- and Biogeochemical Processes in a Heliothermal Hypersaline Lake

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EA.1. Gas syringe samplers and gas chromatography analysis

Each MLS dialysis cell (polypropylene, 3.1 cm diameter, 7 cm length) contained a 0.2 micron filter membrane (cellulose nitrate membrane) on its ends to permit diffusive equilibration with surrounding Hot Lake water. The diffusion gas sampler was constructed with a 2 mL or 5 mL size gas syringe with a built-in shutoff valve (Gas-tight, #050054 or #050055, VICI Precision Sampling, Inc., Baton Rouge, LA). The plunger of the syringe was pulled out to fill the syringe completely with air. A 5 cm long section of Tygon silicone tubing (#3350, 0.25" O.D., Saint-Gobain Performance Plastics, Inc.) with a polyethylene plug at one end was attached to the outlet of the syringe with a plastic cable tie. The Tygon silicone tubing served as the gas diffusion medium. Gas samples obtained from the syringe were analyzed using two different gas chromatographs in the laboratory (see below). For some samples, dilutions were required. Dilutions were made by injecting an aliquot of gas into 25 mL glass vials with a septum stopper containing UHP nitrogen (#P34385, Oxarc, Inc.).

Oxygen concentrations were determined with a HP 5890 series II gas chromatograph using a Thermal conductivity detector (TCD) detector and a Supelco column (#1-2392-U, 15 feet x 1/8" SS support, 60/80 Carboxen 1000, lot 1202200) with initial temperature of 180 °C, a final temp of 235 °C, °C/min = 20.0, and a final time of 2.00 min. The nitrogen carrier input pressure was 60 psi and the column head pressure was 30 psi. Injection volume was 1 mL. The oxygen retention time was 2.1 minutes. Calibration gas standards were diluted using a 1 L gas syringe (#S-1000, Hamilton CO., Reno, NV) and 3 L Tedlar gas bags (SKC Inc. #232-03). For calibration, ambient air was diluted with UHP nitrogen (#P34385, Oxarc, Inc.). The calibration range was between 1 and 20.9% oxygen.

Methane gas concentrations were determined with a HP 5890 series II gas chromatograph using a flame ionization detector (FID) and a Chrompack capillary column (#7516, plot fused silica 10MX0, 53 MM ID with an Al₂O₃/KCl coating). The initial temperature was 35 °C, the final temp was 120 °C,

°C/min = 20.0, and the final time was 2.00 min. The nitrogen carrier inlet pressure was 45 psi with a column head pressure of 4 psi. The injection volume was 0.2 mL. The methane retention time was 12 seconds. Calibration gas standards were diluted using a 1 L gas syringe (#S-1000, Hamilton CO., Reno, NV) and 3 L Tedlar gas bags (SKC Inc. #232-03). For calibration, a 10,000 ppm methane standard (#G0123, lot 109-14-04699-A, Grace Inc., Deerfield, IL) was diluted with UHP nitrogen (#P34385, Oxarc, Inc.). The calibration range was between 1 and 10,000 ppm methane.

EA.2. Temperature corrections to Pitzer parameters

The necessary ion-interaction parameters for the $\text{Na}^+\text{-Cl}^-\text{-SO}_4^{2-}$ and $\text{Ca}^{2+}\text{-Cl}^-$ ion-interactions were corrected for temperature using the temperature dependent expressions of Greenberg and Møller (1989), valid over the temperature range 0-250 °C. Parameters for $\text{Mg}^{2+}\text{-Cl}^-$ were corrected for temperature using the temperature dependent expression of DeLima and Pitzer (1983b), evaluated over the temperature range 25-200 °C (Delima and Pitzer, 1983a, b). Parameters for $\text{Mg}^{2+}\text{-SO}_4^{2-}$, $\text{Na}^+\text{-CO}_3^{2-}$ and $\text{Na}^+\text{-HCO}_3^-$ were corrected for temperature using the first derivative with respect to temperature expressions given by Pitzer (1991). Parameters for $\text{Mg}^{2+}\text{-HCO}_3^-$ and $\text{Ca}^{2+}\text{-HCO}_3^-$ ion-interactions were taken from the recent critical evaluation by De Visscher et al. (2012). Interactions between the divalent ions $\text{Ca}^{2+}\text{-CO}_3^{2-}$ and $\text{Mg}^{2+}\text{-CO}_3^{2-}$ were described by the use of $\text{CaCO}_{3(\text{aq})}$ and $\text{MgCO}_{3(\text{aq})}$ ion pairs. Equilibrium constants for these species were taken from De Visscher and Vanderdeelen (2012) and De Visscher et al. (2012), respectively. $\text{Ca}^{2+}\text{-SO}_4^{2-}$ ion interactions were also described by the use of a $\text{CaSO}_{4(\text{aq})}$ ion pair using the temperature dependent expression given by Greenberg and Møller (1989) valid from 0-150 °C.

Equilibrium constants as a function of temperature for the formation of HCO_3^- and CO_3^{2-} were taken from the recent review by De Visscher et al. (2012). Thermodynamic data for sodium chloride, sodium sulfate and calcium sulphate minerals: halite (NaCl), anhydrite (CaSO_4), gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$), and thenardite (Na_2SO_4) were taken from the compilation

of Greenberg and Møller (1989). Thermodynamic data for the calcium and magnesium carbonate phases magnesite (MgCO_3), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), calcite (CaCO_3), and aragonite (CaCO_3) were taken from the recent review of De Visscher et al. (2012) and De Visscher and Vanderdeelen (2012) respectively. Thermodynamic data for other possibly important solid phases including brucite ($\text{Mg}(\text{OH})_2$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), nahcolite (NaHCO_3), portlandite ($\text{Ca}(\text{OH})_2$), and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) were corrected for variations in temperature using the Van Hoff equation using data for the enthalpy of reaction from Robie and Hemingway (1995) and Archer and Rard (1998).

Thermodynamic data for amorphous magnesium silicate, as well as data for sepiolite, antigorite and chrysotile are from Gunnarsson et al. (2005). Pitzer ion-interaction parameters for $\text{H}_4\text{SiO}_{4(\text{aq})}$ with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , HCO_3^- and SO_4^{2-} valid from 25 °C to 250 °C were taken from Azaroual et al. (1997).

EA.3. Thin section preparation

Thin sections were made by placing freeze-dried sediment sample in an aluminum pipe, 1.6 cm inside diameter 1.6 cm long, with one end sealed with Parafilm (American Can Company, Greenwich, CT). EpoThin epoxy was added to cover the sample (Buehler Inc., Lake Bluff, Illinois, resin cat #20-8140-032, hardener, cat #20-8142-016). The sample was then vacuum-degassed from ambient pressure to minus 1 atmosphere for a total of ten cycles, and the epoxy allowed to harden. The ends of the samples were cut flush with an Isomet 1000 diamond blade thin sectioning saw (Buehler, Inc., # cat 11-1280-160) with Isocut fluid (Buehler cat#11-1193-032). The flush-cut end of the sample was epoxied to a quartz spectroscopic grade microscope slide 25.4 mm x 25.4 mm x 1 mm thick (SPI supplies, West Chester, PA, cat #1016). The slide surface was scuffed with 400 grit sand paper before cementing so that the epoxy would adhere. The orientation of the core pieces was recorded with respect to the core top. The epoxy was allowed to dry overnight.

The thin sectioning saw was used to remove unwanted sample off the quartz slide leaving a thickness of approximately 300 microns. The samples were then thinned to about 50 μm using aluminum oxide sand paper and Isocut fluid. A progression of sandpapers [400 grit (Buehler Carbimet disk #30-5118-400-100) , 600 grit (Buehler Carbimet disk #30-5118-600-100, and finally 1200 grit (Buehler Carbimet disk cat #30-5118-1200-100)] was used for thickness reduction. The samples were then polished for 15 minutes using TEXMET 1500 (Buehler #40-8618) and 1 μm diamond polish (Metadi II, Buehler cat #40-6244). The sample surfaces were cleaned with methanol before EMP analysis.

References

- Archer, D.G., Rard, J.A. (1998). Isopiestic investigation of the osmotic and activity coefficients of aqueous MgSO_4 and the solubility of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ at 298.15 K: Thermodynamic properties of the $\text{MgSO}_4 + \text{H}_2\text{O}$ system to 440 K. *J Chem. Eng. Data* **43**, 791-806.
- Azaroual, M., Fouillac, C., Matray, J.M. (1997). Solubility of silica polymorphs in electrolyte solutions. 1. Activity coefficient of aqueous silica from 25° to 250°C, Pitzer's parameterisation. *Chem. Geol.* **140**, 155-165.
- De Visscher, A., Vanderdeelen, J. (2012). IUPAC-NIST solubility data series. 95. Alkaline earth carbonates in aqueous systems. Part 2. Ca. *J. Phys. Chem. Ref. Data* **41**.
- De Visscher, A., Vanderdeelen, J., Königsberger, E., Churagulov, B.R., Ichikuni, M., Tsurumi, M. (2012). IUPAC-NIST Solubility data series. 95. Alkaline earth carbonates in aqueous systems. Part 1. Introduction, Be and Mg. *J. Phys. Chem. Ref. Data* **41**.
- Delima, M.C.P., Pitzer, K.S. (1983a). Thermodynamics of saturated aqueous-solutions including mixtures of NaCl, KCl, and CsCl. *J. Solution Chem.* **12**, 171-185.
- Delima, M.C.P., Pitzer, K.S. (1983b). Thermodynamics of saturated electrolyte mixtures of NaCl with Na_2SO_4 and with MgCl_2 . *J. Solution Chem.* **12**, 187-199.

- Greenberg, J.P., Møller, N. (1989). The prediction of mineral solubilities in natural-waters: A chemical-equilibrium model for the Na-K-Ca-Cl-SO₄-H₂O system to high-concentration from 0°C to 250°C. *Geochim. Cosmochim. Acta* **53**, 2503-2518.
- Gunnarsson, I., Arnórsson, S., Jakobsson, S. (2005). Precipitation of poorly crystalline antigorite under hydrothermal conditions. *Geochim. Cosmochim. Acta* **69**, 2813-2828.
- Lobo, V.M.M., Quaresma, J.L. (1981). Electrolyte Solutions : Literature data on thermodynamic and transport properties. Departamento de Quimica da Universidade de Coimbra, Coimbra, Portugal.
- Pitzer, K.S. (1991). Activity Coefficients in Electrolyte Solutions. CRC Press, Boca Raton.
- Robie, R.A., Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ pascals) pressure and at higher temperatures. U.S. Geological Survey, Denver, CO.

Table EA-1. Parameters (A) to convert pH meter reading to the molality of H^+ , see equation (1).

Solution Composition (mol/L)	Temperature (degrees C)	A value
0.1 $MgSO_4$	25	-0.021
0.5 $MgSO_4$	25	-0.102
1.0 $MgSO_4$	25	-0.069
2.0 $MgSO_4$	25	0.129
0.5 $MgSO_4$ + 0.1 Na_2SO_4	25	-0.133
1.0 $MgSO_4$ + 0.2 Na_2SO_4	25	-0.078
1.5 $MgSO_4$ + 0.3 Na_2SO_4	25	0.026
2.0 $MgSO_4$ + 0.4 Na_2SO_4	25	0.184
0.5 $MgSO_4$ + 0.1 Na_2SO_4	50	-0.402
1.0 $MgSO_4$ + 0.2 Na_2SO_4	50	-0.383
1.5 $MgSO_4$ + 0.3 Na_2SO_4	50	-0.315
2.0 $MgSO_4$ + 0.4 Na_2SO_4	50	-0.136
2.5 $MgSO_4$ + 0.5 Na_2SO_4	50	-0.005

Table EA-2. Select solute mass balances for 2012, 2013, and 2014.

Date	TDS (g)	DIC (gC)	Ca²⁺ (g)	Volume (m³)
10/21/2012				
Mixo	3.19×10^7	2.89×10^4	7.16×10^4	218.0
Meta	9.62×10^8	7.48×10^5	1.56×10^6	3215
Mono	<u>1.5×10^8</u>	<u>1.14×10^5</u>	<u>9.24×10^4</u>	<u>336.4</u>
Total	1.14×10^9	8.91×10^5	2.56×10^6	3769
10/10/2013				
Mixo	1.89×10^8	1.62×10^5	1.47×10^6	3170
Meta	9.44×10^8	5.53×10^5	1.92×10^6	3855
Mono	<u>1.54×10^8</u>	<u>1.14×10^5</u>	<u>9.24×10^4</u>	<u>336.4</u>
Total	1.29×10^9	8.29×10^5	3.48×10^6	7361
9/16/2014				
Mixo	0	0	0	0
Meta	9.05×10^8	5.98×10^5	1.62×10^6	3215
Mono	<u>1.54×10^8</u>	<u>1.14×10^5</u>	<u>9.24×10^4</u>	<u>336.4</u>
Total	1.06×10^9	7.12×10^5	1.72×10^6	3551

Table EA-3. Measured densities of MgSO₄ solutions as function of concentration (molality) and temperature (Lobo and Quaresma, 1981).

MgSO ₄ mol/kg	15.00°C	20.00°C	25.00°C	30.00°C	35.00°C	40.00°C	45.00°C
$\rho/\text{kg m}^{-3}$							
0.050	1005.37	1004.38	1003.20	1001.76	1000.14	996.31	991.78
.100	1011.40	1010.40	1009.16	1007.69	1006.05	1002.21	997.65
.500	1057.75	1056.47	1055.02	1053.37	1051.60	1047.58	1042.88
1.000	1112.59	1111.16	1109.26	1107.46	1105.55	1101.38	1096.66
1.500	1164.41	1162.82	1160.97	1159.04	1157.05	1152.67	1147.93
2.000	1212.95	1211.10	1209.14	1207.17	1205.12	1200.59	1195.85
2.500	1260.71	1258.76	1256.82	1254.81	1252.87	1248.60	1243.81

Figure EA-1. Quantification of x-ray diffraction patterns by standard addition (corundum).

Figure EA-2. Dissolved Mg^{2+} (a) and SO_4^{2-} (b) for 2013.

Figure EA-3. Dissolved inorganic carbon (DIC) concentrations in the mixolimnion during 2013.

Figure EA-4. Electron microprobe X-ray maps for S, Ca, Mg, and Si. Characteristic X-ray intensities for each map were normalized to have equal area mean and variance to exhibit similar apparent contrasts. These elements represented the most abundant compositional components of the sediments.

Figure EA-5. Cumulative precipitation measured in Oroville, WA for years 2012, 2013, and 2014. Dates are given in Julian days beginning with Jan. 1, 2012.

Figure EA-6. Multi-year concentration data for Mg^{2+} (a) and DIC (b) for select sampling dates in 2012, 2013, and 2014.

Figure EA-7. Temperature comparisons for select monitored dates in 2013 and 2014.