# Short Note Modelled composition of cryogenically produced subglacial brines, Antarctica

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Received 26 September 2018, accepted 28 January 2019

### Introduction

Polar subglacial hydrologic systems have garnered much interest since the recognition of Lake Vostok in 1996. In Antarctica, these environments are hydrologically diverse, including isolated lakes of different sizes, riverlake flow-through systems, "swamps" and groundwater (Siegert 2016). The refreezing of subglacial meltwater is also an important process beneath a large portion of the East Antarctic Ice Sheet (Bell et al. 2011). As subglacial water refreezes it exsolves salts, potentially leaving behind saline and hypersaline brines. Brines thought to derive from this cryoconcentration process have been observed in the northern polar permafrost regions and in the McMurdo Dry Valleys (MDVs) region of Antarctica. Additionally, sediments in the Victoria Land Basin have diagenetic signatures produced by brine movement dating from 3-11 m.y.a, suggesting hypersaline brines have existed in the McMurdo region since at least this time (Staudigel et al. 2018).

Two other processes are known to produce subglacial hypersaline brines. Brines along the Antarctic coast are thought to come from the cryoconcentration of seawater (e.g. Frank *et al.* 2010). An isolated complex of hypersaline subglacial lakes was discovered beneath the Devon Ice Cap in the Canadian Arctic, probably originating from a local salt-bearing geologic unit (Rutishauser *et al.* 2018).

Antarctic subglacial lakes can support viable microbial ecosystems (Christner *et al.* 2014). The geochemistry of subglacial brines is inextricably linked to the structure and function of possible subglacial ecosystems where coupled biogeochemical cycles may support life. This short note demonstrates the variability of geochemical compositions of subglacial Antarctic inland brines potentially formed through cryoconcentration.

## Methods

The chemical thermodynamic model FREZCHEM version 13.3 (Marion & Kargel 2008) and previously published subglacial fresh water data from Antarctica were used to model the chemical evolution of these waters as they are

cryoconcentrated to -8°C. This temperature was used because it is the approximate temperature of the observed Taylor Glacier englacial brine (Lyons *et al.* 2019). Data came from Lake Whillans (LW) (Christner *et al.* 2014, Michaud *et al.* 2016), pore waters from the Kamb (KIS) and Bindshadler (BIS) ice stream sediments in West Antarctica (Skidmore *et al.* 2010), the predicted water chemistry of Lake Vostok (LV) in East Antarctica (Siegert *et al.* 2003) and subglacial outburst waters near Casey Station (CS) (Goodwin 1988). Recently measured geochemistry of the englacial brine associated with Taylor Glacier (TG) in the MDVs is included for comparison, and is interpreted as having derived from the cryoconcentration of seawater modified by chemical weathering (Lyons *et al.* 2019).

## **Results and discussion**

The compositions of these brines are diverse (Table I). Although the LW, LV, TG, and CS brines are classified as Na-Cl waters, LW and CS have much higher Na:Cl ratios (1.26 and 1.36, respectively) than LV (0.74) and the observed TG brine (0.82). The LW and CS brines are similar, having much lower Ca and Mg concentrations, higher HCO3 concentrations than LV and TG, and similar elemental ratios. LW solutes are thought to come primarily from microbially mediated silicate mineral weathering with an additional seawater input (Michaud et al. 2016). The modelled KIS and BIS brines are  $Mg-SO_4 > Cl$  waters. These may reflect different water-rock interactions, such as an influence of bedrock, reactivity, biogeochemical weathering or hydrological flow path. Provenance work on the tills in the Ross Embayment shows diverse geology (Lang Farmer et al. 2006). Skidmore et al. (2010) argued that the solute concentrations in KIS and BIS pore waters are the result of both cryoconcentration and biogeochemical weathering through sulphide and organic matter oxidation. All the original subglacial waters have Na as the primary cation; initial KIS and BIS waters have Na:Cl ratios approximately an order of magnitude higher than the others. The higher sulphate concentrations in BIS and KIS lead to removal of Na and Ca though

	Lake Whillans (LW)		Casey Station outburst (CS)		Lake Vostok estimated (LV)		Kamb Ice Stream (KIS)		Bindschadler Ice Stream (BIS)		Taylor Glacier englacial brine TG*
	meas	model	meas	model	est	model	meas	model	meas	model	meas
Na	5.3	2430	6.4	2471	0.7	1641	20	676	35	669	1683
K	0.2	105	0.2	180	-	-	0.6	551	0.7	400	30
Ca	0.43	0.0015	0.05	0.0013	0.14	34	6.4	14	9	13	78
Mg	0.26	0.03	0.09	0.03	0.18	343	3.1	1459	8.6	1436	199
Cl	3.5	1934	2.1	1817	0.46	2216	1.1	1011	2	1134	2043
$SO_4$	0.55	54	0.28	60	0.22	89	17	1580	31	1417	58
HCO <sub>3</sub>	2.1	151	3.4	192	0.29	0.85	4.1	1.4	7.5	1.3	108
Modelled	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O		Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O		Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O		Na2SO4·10H2O		Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O		
Solid	CaCO <sub>3</sub>		CaCO <sub>3</sub>		CaSO <sub>4</sub> ·2H <sub>2</sub> O		CaSO <sub>4</sub> ·2H <sub>2</sub> O		CaSO <sub>4</sub> ·2H <sub>2</sub> O		
phases	MgCO <sub>3</sub>		MgCO <sub>3</sub>		$CaMg(CO_3)_2$		MgSO <sub>4</sub> ·11H <sub>2</sub> O		MgSO <sub>4</sub> ·11H <sub>2</sub> O		
	$CaMg(CO_3)_2$		Na2CO3·10H2O					MgCO <sub>3</sub>		gCO <sub>3</sub>	
								CaMg(CO <sub>3</sub> ) <sub>2</sub>		$g(CO_3)_2$	

Table I. Measured geochemistry and modelling results\*\* of five subglacial waters cryoconcentrated to -8°C with modelled precipitated solid phases.

\*Taylor Glacier englacial brine concentrations as measured at ~-8°C (Lyons et al. 2019).

\*\*Units are mmol 1<sup>-1</sup>; meas = measured; est = estimated; model = modelled at -8°C.

mirabolite  $(Na_2SO_4 \cdot 10H_2O)$  and gypsum  $(CaSO_4 \cdot 2H_2O)$  precipitation, leaving Mg-SO<sub>4</sub>-rich brines.

There is evidence of microbial sulphide oxidation in both LW (Michaud et al. 2016) and the KIS and BIS pore waters (Skidmore et al. 2010). The modelling discussed here illustrates the potential for sulphate mineral precipitation (primarily mirabolite and gypsum) to control the chemistry of brines undergoing cryoconcentration, and the diversity of geochemical compositions that may occur in subglacial regions of Antarctica where meltwater freeze-on has occurred. Hypersaline waters as demonstrated in Table I could exist in various subglacial features, from lakes to much smaller cavity fillings, and even groundwater. Diverse brines have been documented in subaerial evaporative environments where subtle differences in the initial freshwater can occur. Evolution of brines and precipitation of salts are well understood theoretically. The modelling here suggests the possibility of a wide range of brine compositions in Antarctica's subglacial environments.

#### Acknowledgments

This work was supported in part by NSF grant ANT-1144176.

#### Author contribution

C.B. Gardner performed FREZCHEM modelling and both authors contributed to manuscript preparation.

#### References

BELL, R.E., FERRACCIOLI, F., CREYTS, T.T., BRAATEN, D., CORR, H., DAS, I., DAMASKE, D., et al. 2011. Widespread persistent thickening

of the East Antarctic Ice Sheet by freezing from the base. *Science*, **331**, 10.1126/science.1200109.

- CHRISTNER, B.C., PRISCU, J.C., ACHBERGER, A.M., BARBANTE, C., CARTER, S.P., CHRISTIANSON, K., et al. 2014. A microbial ecosystem beneath the West Antarctic Ice Sheet. *Nature*, **512**, 10.1038/ nature13667.
- FRANK, T.D., GUI, Z. & ANDRILL SMS SCIENCE TEAM. 2010. Cryogenic origin for brine in the subsurface of southern McMurdo Sound, Antarctica. *Geology*, 38, 10.1130/G30849.1.
- GOODWIN, I.D. 1988. The nature and origin of a jökulhlaup near Casey Station, Antarctica. *Journal of Glaciology*, **34**, 95–101.
- LANG FARMER, G., LICHT, K., SWOPE, R.J. & ANDREWS, J. 2006. Isotopic constraints on the provenance of fine-grained sediment in LGM tills from the Ross Embayment, Antarctica. *Earth and Planetary Science Letters*, 249, 10.1016/j.epsl.2006.06.044.
- LYONS, W.B., MIKUCKI, J.A., GERMAN, L.A., WELCH, K.A., WELCH, S.A., GARDNER, C.B., et al. 2019. The geochemistry of englacial brine from Taylor Glacier, Antarctica. Journal of Geophysical Research -Biogeosciences, 10.1029/2018JG004411.
- MARION, G.M. & KARGEL, J.S. 2008. Cold Aqueous Planetary Geochemistry with FREZCHEM. Berlin: Springer, 251 pp.
- MICHAUD, A.B., SKIDMORE, M.L., MITCHELL, A.C., VICK-MAJORS, T.J., BARBANTE, C., TURETTA, C., *et al.* 2016. Solute sources and geochemical processes in subglacial Lake Whillans, West Antarctica. *Geology*, 44, 10.1130/G37639.1.
- RUTISHAUSER, A., BLANKENSHIP, D.D., SHARP, M., SKIDMORE, M.L., GREENBAUM, J.S., GRIMA, C., *et al.* 2018. Discovery of a hypersaline subglacial lake complex beneath Devon Ice Cap, Canadian Arctic. *Science Advances*, **4**, 10.1126/sciadv.aar4353.
- SIEGERT, M.J. 2016. A wide variety of unique environments beneath the Antarctic ice sheet. *Geology*, **44**, 10.1130/focus052016.1.
- SIEGERT, M.J., TRANTER, M., ELLIS-EVANS, J.C., PRISCU, J.C. & LYONS, B.W. 2003. The hydrochemistry of Lake Vostok and the potential for life in Antarctic subglacial lakes. *Hydrological Processes*, 17, 10.1002/hyp.1166.
- SKIDMORE, M., TRANTER, M., TULACZYK, S. & LANOIL, B. 2010. Hydrochemistry of ice stream beds – evaporitic or microbial effects? *Hydrological Processes*, 2274, 10.1002/hyp.7580.
- STAUDIGEL, P.T., MURRAY, S., DUNHAM, D.P., FRANK, T.D., FIELDING, C.R. & SWART, P.K. 2018. Cryogenic brines as diagenetic fluids: reconstructing the diagenetic history of the Victoria Land Basin using clumped isotopes. *Geochimica et Cosmochimica Acta*, 224, 10.1016/j.gca.2018.01.002.