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Supporting Information for

Evidence of freezing pressure in sea ice discrete brine inclusions and its impact on aqueous-gaseous equilibrium

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Introduction
Supplementary material provides details on iterative calculation presented in the manuscript.

Table S1. The iterative computation used to calculate final pressure in a bubble in a discrete brine inclusion. The required input parameters for a numerical solution are the bubble and brine volumes. The total number of moles in the system (Nt) is established at the initial temperature of each sequence using Eq. 7 & 8 where the bubble inner pressure (P_{Bu} in atm) is derived from the Laplace relationship using Eq.4. For each successive temperature the number of mole of dissolved gas in brine is ($N_{Br\ sat}$) computed using Eq. 8. and the number of moles in the bubble (N_{Bu}) is deduced from the total number of moles of gas in the brine/bubble system (N_t) minus the number of moles of gas in brine at saturation ($N_{Br\ sat}$). First, we applied Eq. 9 to investigate the effect of bubble volume decrease on the bubble pressure. Secondly, because increased pressure in the discrete pocket increases the ability of brine to hold dissolved gases (Eq. 8), a fraction of the gas residing in the bubble dissolves in the brine, reducing N_{Bu} for the given volume and temperature. Therefore, to quantify the fraction of gas transferred from the bubble to brine, we recalculated $N_{Br\ sat}$ (Eq. 8) using the pressure from Eq. 9. Since the bubble has lost some of its content to the brine, the lowered N_{Bu} slightly decreases the pressure in Eq. 9, which in return modifies the ability of brine to hold dissolve gases therefore adjusting $N_{Br\ sat}$ and N_{Bu} for a given volume and temperature. Note that the volume of brine used in this computation is strictly the volume of liquid brine solution contained in the brine inclusion, computed as the volume of brine inclusion minus the volume of the bubble contained in the inclusion. Equilibrium concentration in mol L^{-1} of O_2 ($[O_2]_{sat}$), N_2 ($[N_2]_{sat}$), Ar, ($[Ar]_{sat}$), and air ($[_{Air}]_{sat}$) as the sum of $[O_2]_{sat}$,$[N_2]_{sat}$ and $[Ar]_{sat}$ in brine solution is computed from Henry's Law (Eq.1) for atmospheric standard condition ($P_{air}= P_{Ar} + P_{O2} + P_{N2} =1 =0.01+0.21+0.78$ in atm) using solubility coefficient ($K_{H(T,S)}$) in mol L^{-1} atm^{-1} from Garcia and Gordon (1992) for O_2 and from Hamme and Emerson (2004) for N_2 and Ar. The brine freezing (S_{Br}) point is calculated after Notz and Wortser (2009). The surface tension of the brine solution (γ in N m^{-1}) is computed after Sharquawy et al. (2010) using Eq.6.

Exp 1	Brine salinity (S_{Br})	$[O_2]_{sat}$	$[N_2]_{sat}$	$[Ar]_{sat}$	$[Air]_{sat}$	$K_{H(T,S)air}$
Temp (°C)	Notz and Worster (2009)	mol L^{-1}	mol L^{-1}	mol L^{-1}	mol L^{-1}	mol L^{-1} atm^{-1}
	$=-21.4T -0.886T^2-0.017T^3$	Garcia and Gordon (1992)	Hamme and Emmerson (2004)	Hamme and Emmerson (2004)	$=[O_2]_{sat}+[N_2]_{sat}+[Ar]_{sat}$ $=1 X K_{H(T,S)\ air}$	$= [Air]_{sat}/1$
-0.80	1.66E+01	4.11E-04	7.39E-04	2.01E-05	1.17E-03	1.17E-03
-2.30	4.48E+01	3.43E-04	6.06E-04	1.67E-05	9.66E-04	9.66E-04
-6.50	1.07E+02	2.32E-04	3.90E-04	1.13E-05	6.34E-04	6.34E-04
-8.00	1.24E+02	2.09E-04	3.46E-04	1.01E-05	5.65E-04	5.65E-04
-14.80	1.82E+02	1.51E-04	2.32E-04	7.19E-06	3.90E-04	3.90E-04
-17.90	2.03E+02	1.35E-04	2.01E-04	6.37E-06	3.42E-04	3.42E-04
-21.00	2.25E+02	1.19E-04	1.70E-04	5.56E-06	2.95E-04	2.95E-04

			Initial Number of mole of gas				Number of mole of gas		
γ	Bubble radii (r)	P_{Bu}	in Brine **$N_{Br\ sat}$**	in Bubble **N_{Bu}**	Total **Nt**	$[air]_{sat}$	in Brine **$N_{Br\ sat}$**	in Bubble **N_{Bu}**	Total **Nt**
$N\ m^{-1}$	m	atm	mol	mol	mol	$mol\ L^{-1}$	mol	mol	mol
γ = [75.59-0.13476T+0.021352S$_{B}$ 0.00029529T S_{Br}]/100		= 1+2γ/r	= $[air]_{sat}*V_{Br}$	= $P_{Bu}V_{Bu}/RT$	= $N_{Br\ sat}+N_{Bu}$	= $P_{Bu} * K_{H(T,S)air}$	= $[air]_{sat} *V_{Br}$	= Nt-$N_{Br\ sat}$	
0.076	1.69E-05	1.09	5.58E-13	9.81E-13	1.54E-12	1.28E-03	5.58E-13	9.81E-13	1.54E-12
0.077	1.18E-05	1.13				1.09E-03	1.61E-13	1.37E-12	1.54E-12
0.079	8.01E-06	1.20				7.59E-04	3.93E-14	1.50E-12	1.54E-12
0.080	7.32E-06	1.22				6.88E-04	2.72E-14	1.51E-12	1.54E-12
0.082	6.03E-06	1.27				4.97E-04	1.32E-14	1.53E-12	1.54E-12
0.083	5.25E-06	1.32				4.51E-04	1.00E-14	1.53E-12	1.54E-12
0.085	4.12E-06	1.41				4.16E-04	8.83E-15	1.53E-12	1.54E-12

Bubble (V_{Bu})	Brine (V_{Br})	P'_{Bu}	$[air]'_{sat}$	$N'_{Br\ sat}$	N'_{Bu}	P''_{Bu}
L	L	atm	$mol\ L^{-1}$	mol	mol	atm
image derived	image derived	=$N_{Bu}RT/V_{Bu}$	= P'_{Bu} * $K_{H(T,S)(air}$	=$[air]'_{sat}$ *V_{Br}	=Nt-$N'_{Br\ sat}$	= $N'_{Bu}RT/V_{Bu}$
2.01E-11	4.38E-10	1.09	1.28E-03	5.58E-13	9.81E-13	1.09
6.80E-12	1.48E-10	4.50	4.34E-03	6.41E-13	8.99E-13	2.93
2.15E-12	5.18E-11	15.24	9.66E-03	5.01E-13	1.04E-12	10.55
1.64E-12	3.95E-11	19.97	1.13E-02	4.46E-13	1.09E-12	14.45
9.17E-13	2.65E-11	35.22	1.37E-02	3.64E-13	1.18E-12	27.13
6.05E-13	2.23E-11	52.83	1.81E-02	4.02E-13	1.14E-12	39.20
2.94E-13	2.12E-11	107.73	3.18E-02	6.74E-13	8.65E-13	60.89

$[air]''_{sat}$	$N''_{Br\ sat}$	N''_{Bu}	P'''_{Bu}	$[air]'''_{sat}$	$N'''_{Br\ sat}$	N'''_{Bu}	P''''_{Bu}
$mol\ L^{-1}$	mol	mol	atm	$mol\ L^{-1}$	mol	mol	atm
= P''_{Bu}*$K_{H(T,S)air}$	= $[air]''_{sat}$*V_{Br}	= Nt-$N''_{Br\ sat}$	= $N''_{Bu}RT/V_{Bu}$	= P'''_{Bu} * $K_{H(air)}$	= $[air]'''_{sat}$ *V_{Br}	= Nt-$N'''_{Br\ sat}$	= $N'''_{Bu}RT/V_{Bu}$
1.28E-03	5.58E-13	9.81E-13	1.09	1.28E-03	5.58E-13	9.81E-13	1.09
2.83E-03	4.18E-13	1.12E-12	3.66	3.53E-03	5.21E-13	1.02E-12	3.32
6.69E-03	3.47E-13	1.19E-12	12.12	7.68E-03	3.98E-13	1.14E-12	11.60
8.16E-03	3.22E-13	1.22E-12	16.08	9.08E-03	3.59E-13	1.18E-12	15.60
1.06E-02	2.80E-13	1.26E-12	29.06	1.13E-02	3.00E-13	1.24E-12	28.60
1.34E-02	2.99E-13	1.24E-12	42.85	1.46E-02	3.26E-13	1.21E-12	41.91
1.79E-02	3.81E-13	1.16E-12	81.53	2.40E-02	5.10E-13	1.03E-12	72.43

$[air]''''_{sat}$	$N''''_{Br\ sat}$	N''''_{Bu}	P'''''_{Bu}	$[air]'''''_{sat}$	$N'''''_{Br\ sat}$	N'''''_{Bu}	P''''''_{Bu}
mol L^{-1}	mol	mol	atm	mol L^{-1}	mol	mol	atm
= P''''_{Bu} * $K_{H(T,S)air}$	= $[air]''''_{sat}$ *V_{Br}	= Nt-$N''''_{Br\ sat}$	= $N''''_{Bu}RT/V_{Bu}$	= P'''''_{Bu} * $K_{H(T,S)air}$	= $[air]'''''_{sat}$ *V_{Br}	= Nt-$N'''''_{Br\ sat}$	= $N'''''_{Bu}RT/V_{Bu}$
1.28E-03	5.58E-13	9.81E-13	1.09	1.28E-03	5.58E-13	9.81E-13	1.09
3.21E-03	4.73E-13	1.07E-12	3.48	3.36E-03	4.96E-13	1.04E-12	3.41
7.35E-03	3.81E-13	1.16E-12	11.77	7.46E-03	3.87E-13	1.15E-12	11.71
8.81E-03	3.48E-13	1.19E-12	15.74	8.89E-03	3.51E-13	1.19E-12	15.70
1.12E-02	2.95E-13	1.24E-12	28.71	1.12E-02	2.96E-13	1.24E-12	28.68
1.43E-02	3.19E-13	1.22E-12	42.16	1.44E-02	3.21E-13	1.22E-12	42.09
2.13E-02	4.53E-13	1.09E-12	76.44	2.25E-02	4.78E-13	1.06E-12	74.67

$[air]''''''_{sat}$	$N''''''_{Br\ sat}$	N''''''_{Bu}	P'''''''_{Bu}	$[air]'''''''_{sat}$	$N'''''''_{Br\ sat}$	N'''''''_{Bu}	P''''''''_{Bu}
mol L^{-1}	mol	mol	atm	mol L^{-1}	mol	mol	atm
= P''''''_{Bu}*$K_{H(T,S)air}$	= $[air]''''''_{sat}$ *V_{Br}	= Nt-$N''''''_{Br\ sat}$	= $N''''''_{Bu}RT/V_{Bu}$	= P'''''''_{Bu}*$K_{H(T,S)air}$	= $[air]'''''''_{sat}$ *V_{Br}	= Nt-$N'''''''_{Br\ sat}$	= $N'''''''_{Bu}RT/V_{Bu}$
1.28E-03	5.58E-13	9.81E-13	1.09	1.28E-03	5.58E-13	9.81E-13	1.09
3.29E-03	4.85E-13	1.05E-12	3.44	3.32E-03	4.90E-13	1.05E-12	3.42
7.42E-03	3.85E-13	1.15E-12	11.73	7.43E-03	3.85E-13	1.15E-12	11.72
8.87E-03	3.50E-13	1.19E-12	15.71	8.87E-03	3.50E-13	1.19E-12	15.70
1.12E-02	2.96E-13	1.24E-12	28.69	1.12E-02	2.96E-13	1.24E-12	28.69
1.44E-02	3.20E-13	1.22E-12	42.11	1.44E-02	3.20E-13	1.22E-12	42.11
2.20E-02	4.67E-13	1.07E-12	75.45	2.22E-02	4.72E-13	1.07E-12	75.11

Table S2 show the Van der Waals constants used in Figure S1.

Compound	*a (L^2 atm mol^{-2})*	*b (L mol^{-1})*
Ar	1.345	0.03219
O_2	1.36	0.03803
N_2	1.39	0.03913

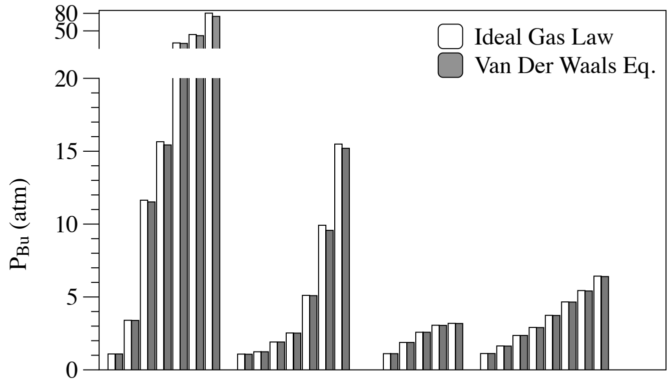

Figure S1. Final pressure computed with the iterative calculation presented in table S1 using (a) the Ideal Gas Law and (b) the Van der Waals Equation $\left(P = \frac{nRT}{(V-bn)} - \frac{an^2}{v^2}\right)$, where n is number of moles of gas, R = 0.0821 mol atm^{-1} L^{-1} K^{-1}, T is the temperature in K, V is the volume in L, a and b are the Van der Waals constants in L^2 atm mol^{-2} and L mol^{-1}, respectively (see table S2).

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