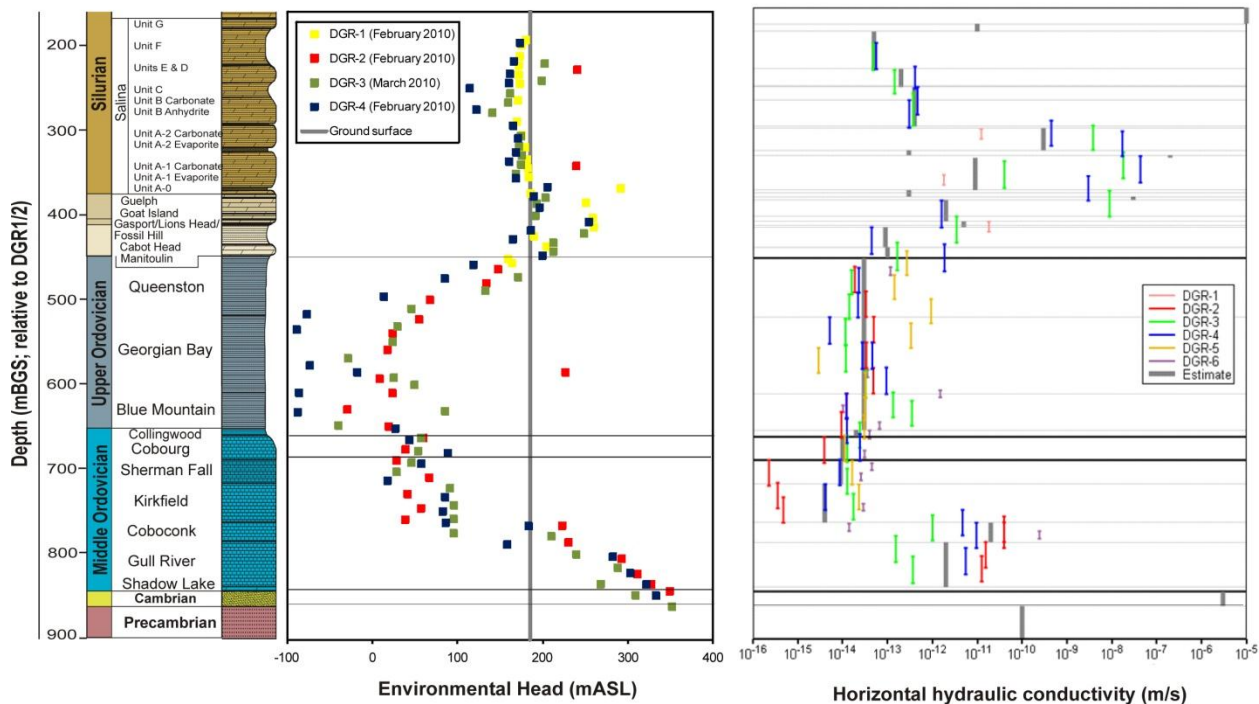


1 **SUPPLEMENTARY MATERIAL**2 **Paleozoic-age brine preserved in an Ordovician shale aquiclude**3 **I. D. Clark<sup>1</sup>, T. Al<sup>2</sup>, M. Jensen<sup>3</sup>, L. Kennell<sup>3</sup>, M. Mazurek<sup>4</sup>, R. Mohapatra<sup>1</sup> and K. G.**4 **Raven<sup>5</sup>**5 *<sup>1</sup>University of Ottawa, Ottawa, Ontario, Canada*6 *<sup>2</sup>University of New Brunswick, Fredericton, New Brunswick, Canada*7 *<sup>3</sup>Nuclear Waste Management Organization, Toronto, Ontario, Canada*8 *<sup>4</sup>Univeristy of Bern, Bern, Switzerland*9 *<sup>5</sup>Geofirma Engineering Ltd., Ottawa, Ontario, Canada*10 **ITEM DR1. HYDROSTRATIGRAPHY OF THE PALEOZOIC FORMATIONS**

11 Shallow groundwater flow occurs in a variably permeable aquifer (horizontal hydraulic  
 12 conductivity,  $K_h$ , from  $10^{-8}$  to  $10^{-4}$  m s<sup>-1</sup>) that extends from surficial Quaternary deposits down to  
 13 the base of the Silurian Bass Islands Fm dolostone at 169 mbgs. A Silurian aquitard extends  
 14 through the Silurian Salina Fm to the base of the Silurian (447 mbgs) and is a low-permeability  
 15 ( $K_h = 10^{-14}$  to  $10^{-8}$  m s<sup>-1</sup>) series of dolostones, shales and evaporites. The aquitard hosts two thin  
 16 (3-5 m) aquifers: the Salina A1 Unit aquifer and the Guelph Fm aquifer. The Ordovician  
 17 aquiclude extends from the top of the Queenston Fm through to the base of the Trenton Group  
 18 limestones, and comprises low-permeability ( $K_h = 10^{-16}$  to  $10^{-14}$  m s<sup>-1</sup>) shales and argillaceous  
 19 limestones (Supplementary Figure DR1). The Black River Group is characterized by variably  
 20 dolomitized argillaceous limestones with slightly elevated hydraulic conductivity ( $K_h = 10^{-12}$  to  
 21  $10^{-10}$  m s<sup>-1</sup>) relative to the overlying Trenton Group. At the base of the Paleozoic stratigraphy,  
 22 the basal Cambrian aquifer displays a sharp increase in hydraulic conductivity ( $K_h = 10^{-6}$  m s<sup>-1</sup>).  
 23 Groundwater in the upper 200 m was collected from shallow drill holes equipped with WestBay

multilevel samplers. The two deep Silurian aquifers were sampled through packers deployed during drilling. The Cambrian groundwaters are flowing artesian, sampled under pressure at the well-head.



**Supplementary Figure DR1** Hydraulic conductivities determined from straddle-packer testing and environmental head profiles from Westbay sampling ports.

## ITEM DR2. NOBLE GAS EXPERIMENTS

Helium (He) and Neon (Ne) isotopic measurements were carried out using a MAP 215-50 noble gas mass spectrometer (MAPL) at the University of Ottawa. Samples were prepared by drilling 2 to 3 cm long 0.6 cm sub-cores from the central part of the parent core. In the case of DGR-2, the sub-cores were loaded into a stainless steel tube (~45cc), while all others were encapsulated in the field in annealed copper tubes (3/8" OD) and subsequently evacuation. Gas

extractions in the DGR-2 sub-cores were carried out by room temperature (20°C) diffusion in ~5 steps over a period of ~24 hours, followed by stepwise heating to 250°C to ensure complete degassing from diffusion-accessible porosity (Supplementary Figure DR2). Sub-cores in the DGR-3 copper tubes were stored for a period > 6 months at room temperature prior to analysis for He isotope ratios. The sample gas was cleaned for active volatiles by exposing it to a hot Ti sponge (600 °C) and an SAESTM getter, then to activated charcoal cooled by an external liquid nitrogen bath to trap the heavy noble gases. In the case of DGR-2 sub-cores, He and Ne were trapped on activated carbon at 10 Kelvin (K) and sequentially released sequentially to the mass spectrometer at 50K and at 90K. Typical experimental blanks were  $5 \times 10^{-15}$  ccSTP for  $^3\text{He}$ ,  $3 \times 10^{-9}$  ccSTP for  $^4\text{He}$ , and  $6 \times 10^{-9}$  ccSTP for  $^{20}\text{Ne}$ . Measured He was corrected for any atmospheric contributions by using  $^{20}\text{Ne}$ . Uncertainties involved in the corrections and the calibration parameters were propagated using standard statistical principles.

The stepwise diffusion and heating experiments for DGR-2 samples were developed to quantify the rate of gas release from the cores in order to make corrections for the loss of He during sample encapsulation in the lab. Stepwise room-temperature He data typically describe a gas release profile that follows an exponential decay function,

$$y_t = a * \exp(-b * t) + c * \exp(-d * t), \quad (1)$$

where, y represents the rate of degassing measured at different times t; a, b, c and d are constants obtained from curve fitting (Sigma Plot<sup>TM</sup>). Extrapolation to the time of sub coring in the laboratory provided an estimate of the gas loss during the sample preparation. The total pore

space He in a sample was obtained by the following relation (Supplementary Table DR1),

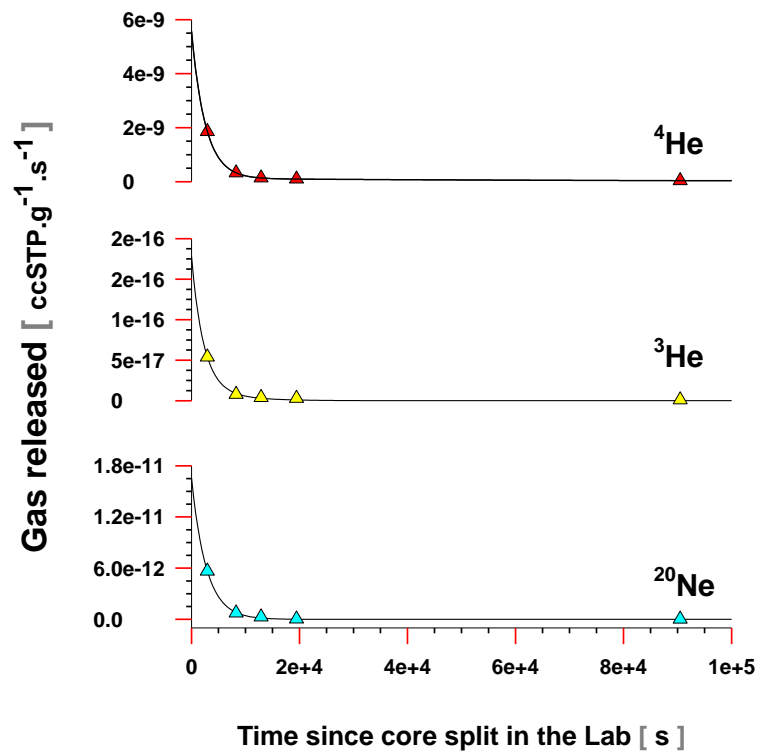
$$\text{Total He} = [\text{diffusion}] + [\text{stepwise heating}] + [\text{loss during sample preparation}]. \quad (2)$$

The time for accumulation is determined from the total measured helium ( $^4\text{He}$ ) and the

production rate for  $^4\text{He}$  from U and Th decay as calculated with the following equation from Ballentine and Burnard (2002).

$$^4\text{He atoms g}^{-1} \text{ yr}^{-1} = (3.115 \times 10^6 + 1.272 \times 10^5) [\text{U}] + 7.710 \times 10^5 [\text{Th}]$$

Consideration was given to the time required to replace an initial He content equivalent to the autochthonous content of the underlying limestones ( $1\text{E}-5 \text{ cc g}^{-1}$ ). Ingrowth of authigenic He in the shales over a period of 60 Ma would bring the in-situ xRa value to within the range measured for the shales and Cobourg limestone.



**Supplementary Figure DR2** Stepwise release of He and Ne by room temperature diffusion.

**Supplementary Table DR1** Measured and modelled initial (in-situ) He concentrations for stepwise diffusion experiments.

	Depth m below ground	He from outgassing at 23°C (cc <sub>STP</sub> g <sup>-1</sup> )	He from heating to 250°C (cc <sub>STP</sub> g <sup>-1</sup> )	Total measured He (cc <sub>STP</sub> g <sup>-1</sup> )	Error	Total Corrected He (cc <sub>STP</sub> g <sup>-1</sup> )	Error	Total measured Ne (cc <sub>STP</sub> g <sup>-1</sup> )	Error
Queenston	453.95	4.16E-05	2.09E-05	6.25E-05	4.16E-06	8.18E-05	2.66E-06	1.15E-08	4.05E-10
Queenston	485.40	3.66E-05	4.13E-05	7.79E-05	3.66E-06	9.65E-05	2.82E-06	6.57E-09	2.30E-10
BM/GB	612.09	8.85E-05	5.57E-05	1.44E-04	8.85E-06	1.57E-04	5.24E-06	1.78E-08	6.22 E-10
Cobourg	663.34	1.48E-05	3.03E-05	4.50E-05	1.48E-06	4.62E-05	1.71E-06	1.48E-07	5.16E-09
Cobourg	670.48	2.24E-05	3.61E-05	5.85E-05	2.24E-06	5.99E-05	2.12E-06	4.17E-08	1.46E-09
Cobourg	681.45	3.18E-05	1.25E-05	4.43E-05	3.18E-06	4.71E-05	1.71E-06	4.73E-08	1.66E-09
Sherman Fall	689.45	1.21E-06	1.12E-05	1.24E-05	1.22E-07	1.34E-05	5.66E-07	6.35E-09	2.22E-10
Sherman Fall	694.63	2.53E-06	2.78E-06	5.31E-06	2.54E-07	7.41E-06	2.57E-07	8.25E-09	2.89E-10
Sherman Fall	699.58	4.06E-06	3.20E-06	7.26E-06	4.07E-07	8.43E-06	2.68E-07	2.41E-08	8.45E-10
Kirkfield	748.92	5.54E-06	1.47E-05	2.03E-05	5.55E-07	5.47E-06	2.51E-07	2.04E-08	7.14E-10
Gull River	797.50	3.27E-06	9.18E-06	1.25E-05	3.32E-07	2.16E-05	7.87E-07	1.64E-07	5.72E-09
Gull River	822.42	1.42E-05	3.99E-05	5.41E-05	1.42E-06	1.28E-05	4.88E-07	1.32E-08	4.63E-10

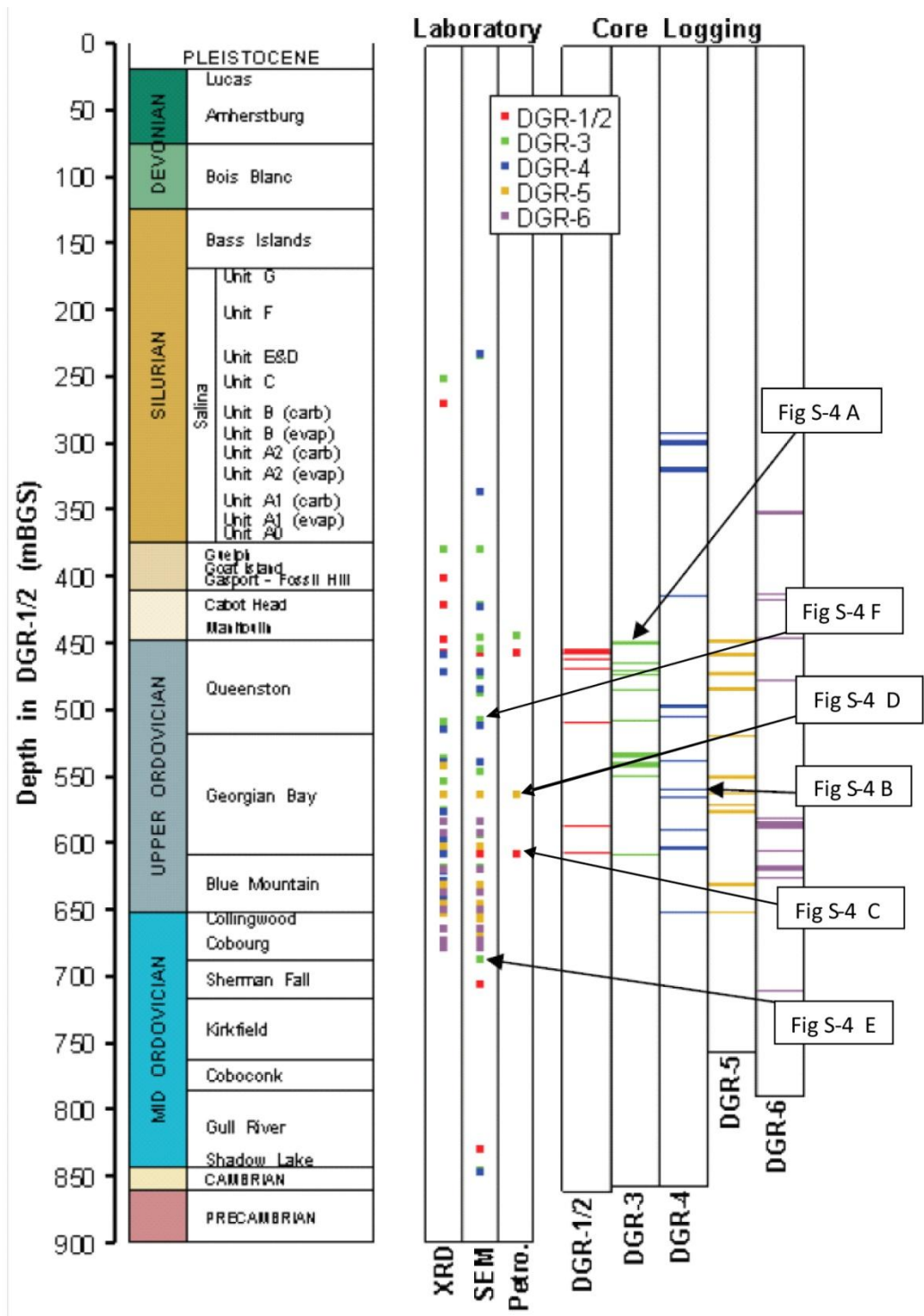
The in-situ <sup>3</sup>He/<sup>4</sup>He ratio, as xRa, was calculated for comparison with the measured xRa according to the ratio of the respective <sup>3</sup>He and <sup>4</sup>He production rates. The <sup>3</sup>He production rate was calculated according to Ballentine and Burnard (2002), based on U, Th and Li concentrations (Intera Engineering Ltd., 2011) and using the whole rock abundance of Na, Mg, Al, Si and C (Intera Engineering Ltd., 2011), which are the elements having significant cross sections for α-n production reactions (Supplementary Table DR2).

**Supplementary Table DR2** Measured whole-rock concentrations for U, Th and Li (ppm) and for the principal nuclides contributing to neutron production through α-n reaction (percent).

Formation	Depth m bgs	U	Th	Li	Na	Mg	Al	Si	C	av n capture	<sup>4</sup> He atoms a- lg-l	<sup>3</sup> He atoms a- lg-l	xRa
Queenston	446.25	2.32	13.2	76	0.40	2.58	8.16	23.1	1.33	9.87E-03	1.77E+07	5.70E-01	2.33E-02
Queenston	451.33	1.67	7.12	37	0.28	2.60	5.01	14.0	5.79	9.87E-03	1.09E+07	1.35E-01	8.96E-03
Queenston	455.45	2.23	8.58	57	0.30	2.26	6.20	17.0	4.01	9.87E-03	1.38E+07	2.79E-01	1.46E-02
Queenston	456.01	2.21	9.11	58	0.80	2.35	6.01	16.7	4.06	9.87E-03	1.42E+07	3.10E-01	1.58E-02
Queenston	460.77	1.81	7.31	52	0.27	2.19	5.24	14.7	5.37	9.87E-03	1.15E+07	1.98E-01	1.24E-02
Queenston	482.45	2.36	8.53	62	0.29	3.06	7.02	19.6	3.53	9.87E-03	1.42E+07	3.46E-01	1.76E-02
Queenston	508.93	2.48	8.73	50	0.36	3.03	6.08	18.5	4.20	9.87E-03	1.48E+07	2.78E-01	1.36E-02

Georgian Bay	535.56	3.19	12.0	67	0.42	2.43	8.63	23.9	0.98	9.87E-03	1.96E+07	5.53E-01	2.04E-02
Georgian Bay	550.28	3.29	11.5	61	0.33	2.14	8.04	25.0	1.29	9.87E-03	1.95E+07	4.82E-01	1.78E-02
Georgian Bay	570.73	3.26	11.8	69	0.33	2.22	8.26	24.0	1.19	9.87E-03	1.97E+07	5.51E-01	2.03E-02
Georgian Bay	590.10	3.64	11.9	64	0.57	2.03	8.14	25.2	1.27	9.87E-03	2.10E+07	5.57E-01	1.92E-02
Georgian Bay	606.62	2.03	6.36	55	0.42	1.98	8.27	25.9	6.47	9.87E-03	1.15E+07	2.82E-01	1.77E-02
Blue Mountain	626.29	3.66	11.7	59	0.37	1.87	8.73	25.6	1.79	9.87E-03	2.09E+07	5.15E-01	1.78E-02
Blue Mountain	644.49	3.84	11.5	52	0.36	1.70	8.34	24.8	2.09	9.87E-03	2.13E+07	4.48E-01	1.52E-02
Collingwood	659.31	1.54	2.13	11	0.09	1.24	1.23	3.91	10.7	6.58E-03	6.64E+06	2.39E-02	2.60E-03
Cobourg	669.27	1.51	3.12	16	0.12	1.30	1.75	5.59	10.1	6.58E-03	7.30E+06	4.03E-02	3.99E-03
Cobourg	677.93	0.84	1.24	7.0	0.07	1.21	0.66	2.35	11.3	6.58E-03	3.68E+06	7.88E-03	1.55E-03
Sherman Fall	695.51	0.34	1.32	7.0	0.07	1.98	0.53	1.95	11.4	6.58E-03	2.12E+06	4.58E-03	1.56E-03
Sherman Fall	704.87	0.61	3.17	21	0.12	1.13	2.04	6.53	9.40	6.58E-03	4.42E+06	3.16E-02	5.17E-03
Kirkfield	745.97	0.61	2.80	24	0.11	0.91	1.50	5.51	10.0	6.58E-03	4.14E+06	3.14E-02	5.49E-03
Gull River	816.85	0.60	0.78	3.0	0.09	7.67	0.17	1.15	11.8	6.58E-03	2.55E+06	3.49E-03	9.91E-04
Cambrian	844.95	1.17	1.20	5.0	0.12	11.5	0.24	3.29	11.4	1.02E-02	4.72E+06	8.55E-03	1.31E-03

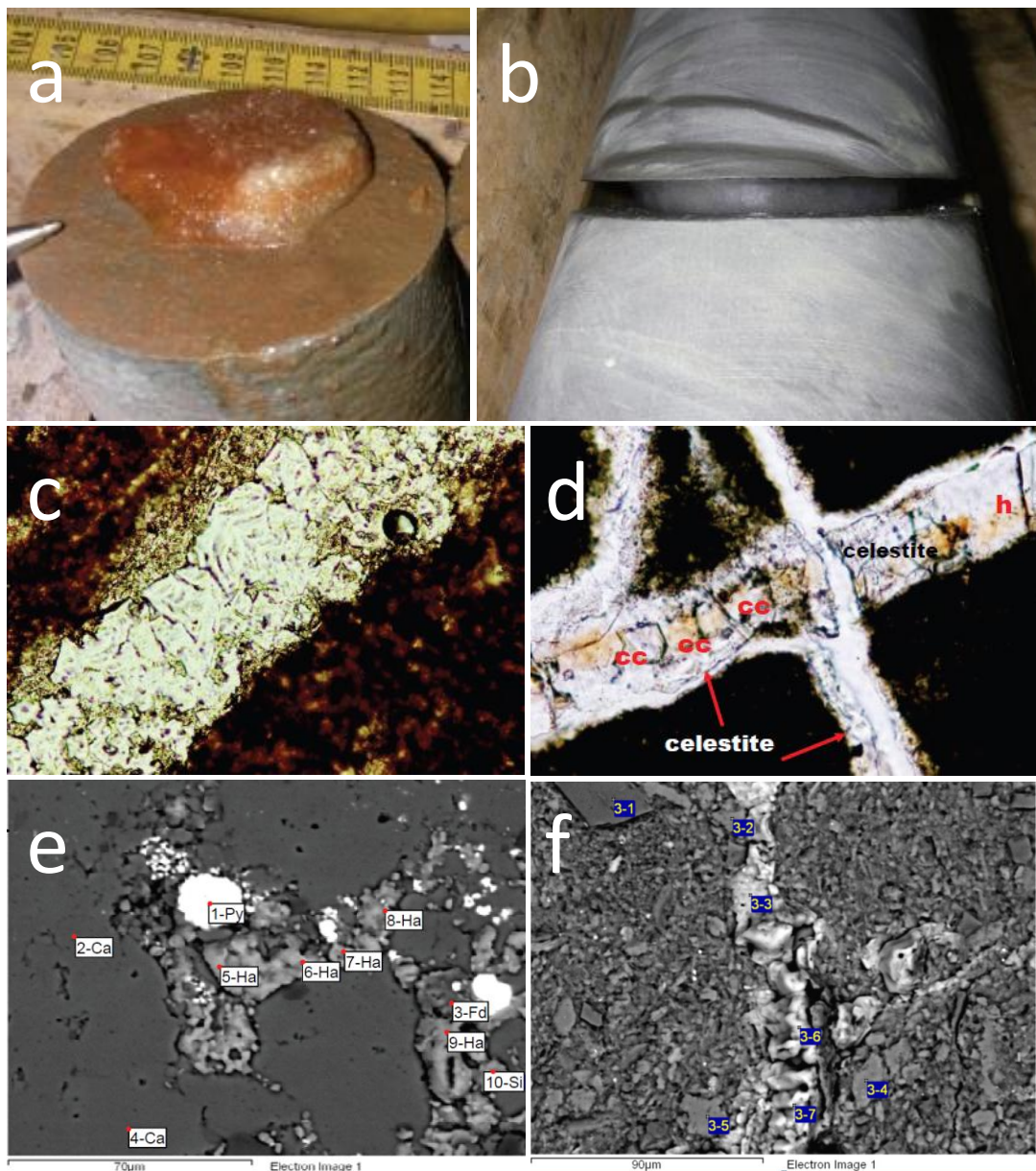
88     **ITEM DR3. SECONDARY HALITE OCCURRENCES IN DGR CORE**



89

90     **Supplementary Figure DR3** Halite occurrences in boreholes, noted from core logging and

91     laboratory testing (Intera Engineering Ltd., 2011).



**Supplementary Figure DR3a-f** **a:** Halite infilling fracture in the Queenston Fm shale, **b:** halite in Georgian Bay Fm, **c:** halite vein filling in Georgian Bay Fm shale, photo width: 0.34 mm, plane polarized light, **d:** vein filling in Georgian Bay Fm shale (h = halite, cc = calcite) photo width: 0.45 mm, plane polarized light, **e:** interstitial halite in Cobourg Fm Limestone (Ha = halite, Ca = calcite, Py = pyrite, Si = quartz), **f:** halite in Queenston Fm Shale (SEM EDS points 3-3, 3-6 and 3-7, other spot measurements - calcite).

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