



Open Research Online

The Open University's repository of research publications and other research outputs

Natural Analogue Constraints on Europa's Non-ice surface Material

Journal Item

How to cite:

Fox-Powell, Mark; Osinski, Gordon; Applin, Daniel; Stromberg, Jessica; Gázquez, Fernando; Cloutis, Ed; Allender, Elyse and Cousins, Claire (2019). Natural Analogue Constraints on Europa's Non-ice surface Material. *Geophysical Research Letters*, 46(11) pp. 5759–5767.

For guidance on citations see [FAQs](#).

© 2019 American Geophysical Union

Version: Accepted Manuscript

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1029/2018GL081339>

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online's data [policy](#) on reuse of materials please consult the policies page.

oro.open.ac.uk

Natural analogue constraints on Europa's non-ice surface material

Mark G. Fox-Powell¹, Gordon R. Osinski², Daniel Applin³, Jessica M. Stromberg^{3†},
Fernando Gázquez^{1‡}, Ed Cloutis³, Elyse Allender¹, Claire R. Cousins¹

¹ School of Earth and Environmental Sciences, University of St Andrews, Irvine Building, St Andrews, UK.

² Centre for Planetary Science and Exploration/Dept. Earth Sciences, University of Western Ontario, London, Ontario, Canada.

³ Department of Geography, University of Winnipeg, Winnipeg, Manitoba, Canada

Corresponding author: Mark G. Fox-Powell (mgfp@st-andrews.ac.uk)

† Current address: CSIRO Mineral Resources, Perth, WA, Australia

‡ Current address: Department of Geology and Biology, University of Almería, Almería, Spain

Key Points:

- Low-temperature hydrated salts from the Canadian Arctic provide geochemical and spectral analogues for euroman surface material.
- Qualitatively different deposits can form from fluids with similar major ion chemistry
- Endogenic sulfates on Europa would not rule out a chloride-dominated ocean.

22 **Abstract**

23 Non-icy material on the surface of Jupiter's moon Europa is hypothesised to have originated from
24 its subsurface ocean, and thus provide a record of ocean composition and habitability. The nature
25 of this material is debated, but observations suggest that it comprises hydrated sulfate and chloride
26 salts. Analogue spectroscopic studies have previously focused on single phase salts under
27 controlled laboratory conditions. We investigated natural salts from perennially cold (<0 °C)
28 hypersaline springs, and characterised their reflectance properties at 100 K, 253 K and 293 K.
29 Despite similar major ion chemistry, these springs form mineralogically diverse deposits, which
30 when measured at 100 K closely match reflectance spectra from Europa. In the most sulfate-rich
31 samples, we find spectral features predicted from laboratory salts are obscured. Our data are
32 consistent with sulfate-dominated european non-icy material, and further, show that the
33 emplacement of endogenic sulfates on Europa's surface would not preclude a chloride-dominated
34 ocean.

35

36 **Plain Language Summary**

37

38 Europa, a moon of Jupiter, has become a priority target in the search for life off the Earth, due to
39 the presence of a liquid water ocean under its icy shell. Salts on the moon's surface might originate
40 from this ocean, and therefore offer a way of studying the ocean without requiring direct access.
41 Our knowledge of these salts comes from comparing spacecraft measurements to pure salts
42 produced in laboratories. We have studied natural salts from hypersaline springs in the Canadian
43 Arctic as an alternative, complementary approach. Measuring samples from these deposits at
44 european surface temperatures, several unexpected properties were observed, including the absence
45 of spectral details predicted by previous laboratory studies. This challenges some of the estimates
46 of european surface composition. Natural analogues such as these will form part of an integrative
47 approach to understanding data from upcoming missions, such as NASA's Europa Clipper and
48 ESA's JUICE.

49 **1. Introduction**

50 In the coming decade, the European Space Agency's JUpiter ICy moons Explorer (JUICE) and
51 the NASA Europa Clipper will study the icy moon Europa to better understand its surface and
52 subsurface activity, and potential habitability. Europa hosts a liquid water layer beneath an icy
53 crust (Carr et al., 1998), with a depth of up to 100 km (Nimmo & Pappalardo, 2016). The
54 interaction between this ocean and a silicate core could generate the necessary chemical conditions
55 for life, meaning Europa may harbour the largest habitable volume of water in the solar system
56 (Nimmo & Pappalardo, 2016).

57 Constraining ocean composition is crucial to understanding the evolution and astrobiological
58 potential of Europa. The european surface is predominantly water ice (Carlson et al., 2009);
59 however spatially heterogenous, non-icy material exists, first studied by the Galileo spacecraft's
60 Near Infrared Mapping Spectrometer (NIMS) (McCord et al., 1999). This material is hypothesised
61 to have originated, either wholly or partly, from the subsurface ocean, becoming frozen into
62 exhumed ice or delivered directly to the surface through cryovolcanism (Schmidt et al., 2011;
63 Prockter et al., 2017; Howell & Pappalardo, 2018). The existence of putative cryovolcanic plumes
64 on Europa (Jia et al., 2018; Roth et al., 2014) further suggest that material from Europa's interior
65 is actively emplaced onto the surface. This surface material can provide a record of ocean
66 chemistry accessible to orbital or landed spacecraft.

67 Multiple observations of Europa's non-icy material exist, showing visible-near-infrared (vis-NIR)
68 evidence for hydrated compounds (Brown & Hand, 2013; Carlson et al., 2005; Dalton et al., 2012;
69 Fischer et al., 2015, 2016; Ligier et al., 2016; McCord et al., 1999). Such material can form through
70 exogenic and radiolytic processes, salt precipitation from subsurface brines, or a combination of
71 these two mechanisms. Previous studies have attempted to explain the shape of european non-icy

72 spectra with numerical linear mixes of pure salt spectra (Carlson et al., 2005; Dalton, 2007; Ligier
73 et al., 2016), or with experimentally-produced salt assemblages (Orlando et al., 2005). Based on
74 these works, hydrated sulfates such as mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and sulfuric acid hydrate have
75 been proposed as major components of deposits on the trailing hemisphere (Carlson et al., 2005;
76 Dalton et al., 2012; Shirley et al., 2010), whereas chloride salts may contribute to spectral
77 signatures of ‘chaos’ regions (Brown & Hand, 2013; Fischer et al., 2016).

78 The study of natural analogues provides a complementary approach, particularly for understanding
79 spectral behaviour of mineralogically heterogeneous precipitates. Axel Heiberg Island in the
80 Canadian Arctic hosts unique hypersaline, sub-zero ($< 0\text{ }^\circ\text{C}$) springs that precipitate hydrated
81 sodium sulfates and chloride salts, along with other low temperature phases (Battler et al., 2013;
82 Ward & Pollard, 2018). We investigated the vis-NIR spectral properties and geochemical context
83 of these natural hydrated salt assemblages and discuss their relevance for the exploration of
84 Europa.

85

86 **2. Field Areas**

87 Axel Heiberg Island (AHI), Nunavut, Canada (Fig. 1A) hosts Carboniferous evaporite diapirs
88 (Harrison & Jackson, 2014) and thick ($> 400\text{ m}$) permafrost (Andersen et al., 2002). Associated
89 with the diapirs are anoxic, perennially low-temperature ($-5\text{--}8\text{ }^\circ\text{C}$) hypersaline ($> 10\text{ wt. \%}$) springs
90 that form assemblages of hydrated sulfate and chloride salts (Battler et al., 2013; Pollard et al.,
91 1999). The precipitation of these Europa-relevant phases makes these springs compelling natural
92 laboratories for understanding analogous deposits on Europa. The waters of three springs, Lost
93 Hammer, Colour Peak and Stolz, were sampled along with their associated salt deposits in July

94 2017 (Fig. 1) (for further details of geologic setting see Battler et al., 2013, Ward and Pollard,
95 2018).

96

97 **2.1 Lost Hammer**

98 Lost Hammer (LH) Spring (also known as Wolf Spring; Battler et al., 2013) (79.076856, -
99 90.210472) emerges as a single outlet from the valley floor, approximately 500 m from the base
100 of Wolf Diapir (Fig. 1B). A large dome of salt exists around the vent, flanked by a salt apron with
101 terracing and layering. Brine samples and measurements were taken from the outlet, and at two
102 downstream points. Salt samples were taken from within the outlet dome and from the salt apron
103 (Fig. S1).

104

105 **2.2 Colour Peak**

106 Colour Peak (CP) springs (79.38, -91.27) emerge as several outlets from the side of Colour Peak
107 Diapir (Fig. 1C). Precipitates exist as sintered terraces exhibiting green and black colouration.
108 White crusts are visible at the edges of channels and pools. Brine samples and measurements were
109 taken at five spring outlets, and mineral samples were taken from terraces and peripheral
110 precipitates (Fig. S1).

111

112 **2.3 Stolz**

113 Stolz (STZ) springs (79.090117, -87.048248) emerges from two outlets on Stolz Diapir (Fig. 1).
114 The springs meet at a confluence 20 m downstream from the outlets, precipitating an extensive

115 salt apron with an approximate thickness of 5 m and downslope extent of ~800 m. During summer,
116 the drainage streams flow under this apron into a ‘salt cave’. Salts form grey and white terraces
117 (Fig. 1E), with the dry remains of large (~10 m diameter) pools on the apron. Brine samples and
118 measurements were taken at both outlets and at the confluence. Salts were sampled at the entrance
119 to the salt cave and from the apron surface (Fig. S1).

120

121 **3. Materials and methods**

122 **3.1 Sampling**

123 Brine samples were 0.22 µm-filtered into four 15 ml aliquots for stable isotopes, anion and cation
124 analysis, and aqueous sulfide measurements. Samples for cation analyses were acidified to a final
125 concentration of 1 % HNO₃. Temperature, pH and dissolved oxygen (DO) concentrations were
126 measured using a Mettler Toledo FiveGo probe. Salt mineral precipitates were collected into
127 sample bags and stored at ambient arctic temperatures, shipped chilled (4 °C), and stored at 4 °C
128 until analysis.

129

130 **3.2 Quantification of major ions**

131 Cations in spring fluids were measured with ICP-AES using a Prodigy7 (Teledyne-Leeman) AES
132 system at the Open University, UK. Chloride and sulfate were measured in triplicate with ion-
133 chromatography using a Metrohm 930 IC system fitted with a 150 mm Metrosep Asupp5
134 separation column (4 mm bore). Relative standard deviations of triplicate measurements were ≤ 0.1
135 % for all measured anions. Brines were diluted by a factor between 10^3 and 10^4 in ultrapure

136 deionised water prior to analysis. Aqueous sulfide was quantified spectrophotometrically in
137 triplicate using the methylene blue assay (Cline, 1969).

138

139 **3.3 Oxygen and hydrogen isotopes in waters**

140 Water-bound ^{16}O , ^{18}O , H, and D were measured simultaneously by cavity ringdown spectrometry
141 using a L2140-i Picarro water isotope analyser at the University of St. Andrews, United Kingdom.
142 Seven repeat measurements were averaged for each sample, with a typical precision of $\pm 0.013\%$
143 (1 SD.). See supplementary methods for more details.

144

145 **3.4 X-ray diffraction (XRD)**

146 Powder XRD patterns were recorded at Drochaid Research Services, Ltd. (St Andrews, UK) at
147 room temperature from 10° to 110° (2θ) using a Panalytical X'Pert Pro X-ray diffractometer.
148 Samples were equilibrated to room temperature and crushed as finely as possible prior to analysis.
149 In an effort to retain hydrated phases, samples were not fully dried, therefore sieving and grain
150 size normalisation was not possible. Because of this, Rietveld refinements are taken as semi-
151 quantitative, indicative of major and minor phases. See supplementary methods for more details.

152

153 **3.5 Visible-near-infrared reflectance spectroscopy**

154 Vis-NIR (0.35 to 2.5 μm) spectra from salt precipitates were collected at three temperatures: 293
155 K (room temperature), 253 K and approximately 100 K (simulating european surface temperature;
156 Nimmo and Pappalardo, 2016). Spectra were acquired with an Analytical Spectral Devices

157 FieldSpec Pro HR spectrometer at the Planetary Spectroscopy Facility, University of Winnipeg.
158 See supplementary methods for more details. Samples at 253 K were frozen in a chest freezer,
159 followed by active cooling with a Pelletier cooler after Bramble et al. (2014). Samples measured
160 at 100 K were held in an aluminium sample cup that was immersed in liquid nitrogen and
161 equilibrated until the liquid nitrogen ceased to boil vigorously.

162 The 100 K spectra were resampled to (1) Galileo NIMS spectral resolution, to precisely match
163 bandpasses in the G1ENNHILAT01 observation presented by Dalton et al. (2005) and others; (2)
164 the Europa Clipper Mapping Infrared Spectrometer for Europa (MISE) spectral resolution (10 nm
165 sampling from 0.8-5 μm) (Blaney et al., 2015), and (3) the JUICE Moons and Jupiter Imaging
166 Spectrometer (MAJIS) spectral resolution (2.3 nm sampling from 0.4-1.7 μm ; 6.6 nm sampling
167 from 1.7-5.7 μm) (Langevin et al., 2013).

168

169 **3.6 Spectral mixing**

170 To investigate the loss of spectral detail caused by the presence of anhydrous phases, linear spectral
171 mixes were generated to compare directly with the LH outlet sample, which has four phases in
172 XRD patterns: anhydrous thenardite (Na_2SO_4) and halite (NaCl), and their hydrous counterparts
173 mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$). Semi-quantitative XRD indicates
174 sulfates form the major salt phase (approximately 80%) with a minor chloride salt phase
175 (approximately 20%), and this ratio was maintained in each mix, varying the anhydrous component
176 from 0% (fully hydrated; i.e. mirabilite and hydrohalite) to 100% (fully anhydrous; i.e. thenardite
177 and halite). Pure phase spectra were taken from Hanley et al. (2014), Shirley et al. (2010) and the
178 USGS spectral library (Supplementary Methods).

179 **4. Results**

180 **4.1 Aqueous geochemistry and salt mineralogy**

181 Brine compositions and salt mineralogy at the springs are consistent with published data (Battler
182 et al., 2013; Lay et al., 2013; Omelon et al., 2006; Ward & Pollard, 2018). Across all springs, fluids
183 are dominated by sodium and chloride and contain significant concentrations of sulfate (Fig. 2A;
184 Table S1). LH brines contain the highest sulfate concentration of the three springs (60 mM), and
185 the lowest temperature (-3.6 °C). CP brines are relatively warm (3.8-8.4 °C), neutral alkaline (pH
186 6.98-7.75) and contain higher dissolved Ca²⁺ levels than either LH or STZ (Fig. 2B; Table S1).
187 STZ brines are the most saline with respect to sodium (3790-3868 mM) and chloride (5213-5216
188 mM) and possess sub-zero temperatures (-1.7 and -2.9° C). Sulfide concentrations ranged from
189 highs of 1.86 mM at CP to lows of 0.04 mM at STZ (Table S1). The δD and δ¹⁸O of the spring
190 brines plot close to the local meteoric water line (LMWL) (Fig. 2C). LH brine shows the lowest
191 δ¹⁸O and δD values of the springs but is comparable to that of nearby permafrost. CP brine isotope
192 values plot close to snowmelt on Colour Peak Diapir, in agreement with Pollard et al. (1999) (Fig.
193 2C). The isotopic values of two snowmelt pools sampled on Stolz Diapir fall below the LMWL
194 and show higher δ¹⁸O and δD than the STZ brines (Fig. 2C).

195 Mineralogy (measured by XRD after raising samples to 20 °C) is dominated at LH by Na-sulfates,
196 notably mirabilite and thenardite, with lesser contributions from chlorides (Table S2). The low-
197 temperature chloride hydrohalite is present in several samples, which had not previously been
198 reported by Battler et al. (2013). White crusts at CP are dominated by halite, while dark precipitates
199 consisted primarily of gypsum (CaSO₄·2H₂O) and calcite (CaCO₃), which are not considered likely
200 phases at Europa. White salt assemblages at STZ contained higher abundances of Na-chloride

201 salts, predominantly anhydrous halite. The darker banded salts were composed of thenardite and
202 halite, as approximately equal major phases.

203

204 **4.2. Visible-near-infrared spectral characteristics**

205 Representative spectra from salt precipitates at all three measured temperatures are plotted in Fig.
206 3. The largest spectral differences are observed between 253 K and 273 K. ‘CP-green’ (dark green
207 precipitates) show a sharpening of the major water absorption bands at 1.5 (triplet), 2.0 (doublet)
208 and 2.2 μm (triplet) at 253 and 100 K, consistent with gypsum (Cloutis et al., 2006), which
209 dominates this sample (Table S2) and is stable at room temperature. Spectra from ‘STZ-white’ at
210 253 K and 100 K are consistent with hydrohalite; particularly the doublet 1.5 and 2.0 μm features
211 (Light et al., 2016; measured at 243 K), and the 1.75 μm feature in frozen NaCl brine (Hanley et
212 al., 2014). ‘STZ-dark’ salts display muted versions of these features. Spectra from CP-white, and
213 all LH and STZ salts have minimal hydration features at 293 K, with overtone absorptions at 1.2
214 and 2.2 μm absent entirely. LH spectra exhibit the 2.2 μm absorption feature as a slight shoulder
215 to the larger and broader 2.0 μm feature, consistent with the presence of mirabilite. Salts from the
216 interior of the outlet dome show broader absorptions, and exhibit hydration features at 1.0 and 1.2
217 μm that are absent in salts from the surface of the salt apron. Numerical linear mixes failed to
218 recreate LH spectra, even when all components identified by XRD were included (Fig. 4). For
219 example, hydrohalite details were not observed in LH spectra, but were evident in spectral mixes
220 designed to simulate LH phase abundances.

221

222 **4.3. Comparisons with mission data**

223 100 K spectra resampled to match spacecraft instrument capabilities are plotted in order of
224 decreasing resolution in Fig. 3C, D. Major absorption features in LH salts show similar asymmetry
225 and broadening to the NIMS data from European non-icy material. Furthermore, minima for the
226 1.75 μm band in LH salts very closely matches the corresponding minimum of Europa's non-icy
227 material observed by NIMS. Band minima of the major 1.5 and 2.0 μm absorptions tend to shift
228 to shorter wavelengths at lower spectral resolution (Fig. 3D). Spectral details such as the diagnostic
229 gypsum triplets in CP salts and the hydrohalite doublets in STZ salts (1.5, 2.0 μm) are represented
230 at MISE and MAJIS resolutions, but at NIMS resolution these become difficult to resolve or are
231 absent entirely. The hydrohalite doublet at 2.0 μm in STZ-white appears as a single feature at
232 NIMS resolution with a band minimum that closely matches data from Europa.

233

234 **5. Discussion**

235 **5.1. Environmental controls on spring geochemistry**

236 The AHI springs provide geochemical analogues for the formation of hydrated salt deposits from
237 subsurface fluids on icy moons. Constraining their geologic and geochemical context as well as
238 their stability is crucial for understanding which aspects can be extrapolated for planetary
239 exploration. The brine $\delta^{18}\text{O}$ and δD values support the hypothesis that the AHI springs are
240 recharged by meteoric water. Anderson et al. (2002) suggested that evaporite diapirs create
241 conduits through permafrost that allow meteoric waters to infiltrate and dissolve deep evaporites,

242 buffering the spring temperatures via a dynamic equilibrium between the sub-permafrost geotherm
243 and the permafrost itself. The behaviour of the STZ and LH systems are consistent with this idea.
244 At both sites, $\delta^{18}\text{O}$ and δD values of the spring brines are significantly more depleted than local
245 snowmelt, and at LH are similar to permafrost values. This indicates a complex mechanism of
246 water recharge to the system, potentially including local permafrost melts and more distal meteoric
247 sources that could have experienced a longer residence time in the evaporites. At CP however,
248 similar δD and $\delta^{18}\text{O}$ values in the brine and snow show that contemporary melt is likely feeding
249 the springs, consistent with interpretations by Omelon et al. (2006). This challenges the notion
250 (Pollard et al., 1999) that long residence times are required within the evaporites and permafrost
251 to acquire a high solute load and to buffer the spring temperatures.

252

253 **5.2 Implications for spectroscopic detection of salts on Europa**

254 The natural salts studied here show complex behaviours, not fully predictable from the behaviours
255 of pure laboratory salts. Some samples, notably CP-green, CP-white and STZ-white, show
256 sharpening of spectral detail at 253 and 100 K, predicted from pure salts. However, for most
257 samples the main temperature-related spectral changes are associated with the loss of hydration at
258 293 K, and not the narrowing or sharpening effects seen at low temperature with pure salts. For
259 example, the mirabilite-dominated LH salts lack the sharpened details observed in pure mirabilite
260 (Dalton et al., 2005), instead exhibiting smooth absorptions that span the 1.3-1.7 and 1.8-2.3 μm
261 ranges. Achieving this ‘smoothing’ effect in previous linear mixing efforts was achieved by adding
262 up to 65 % sulfuric acid hydrate (Carlson et al., 2005; Dalton et al., 2012). Based on LH salt
263 spectra, which contain only Na-sulfates and chloride salts (plus trace detrital quartz), ‘smooth’ low
264 temperature spectra do not require the addition of sulfuric acid hydrate. This does not rule out its

265 presence at Europa, but demonstrates it need not be such a significant component to produce the
266 observed spectral features.

267 Overall, LH salt spectra measured at 100 K most closely recreate the shape, breadth and depth of
268 absorption features in NIMS non-icy spectra, including the 1.75 μm band minimum (Fig. 3D).
269 These data therefore are consistent with an LH-like sulfate-rich composition at Europa. However,
270 they do not rule out the presence of chlorides salts, as data from Europa show some similarity to
271 the chloride-rich STZ samples when viewed at the lower spectral resolution of mission data. The
272 hydrohalite doublet at 2.0 μm in STZ-white disappears at NIMS resolution, meaning that this
273 feature would not have been detectable, even if hydrohalite were present. Recent ground-based
274 observations with greatly improved spectral resolution (*e.g.*, Fischer et al., 2015) lack data in the
275 1.80-1.95 μm region, so also cannot be used to definitively eliminate hydrohalite. Future spacecraft
276 instruments such as MISE (Europa Clipper) and MAJIS (JUICE) have sufficient resolution to
277 capture this, and other diagnostic features, therefore these missions will reveal if european non-icy
278 deposits bear closer resemblance to a “LH-“ or “STZ-like” composition.

279 Hydrohalite was detected in some LH samples by XRD (Table S2) as a minor phase, including
280 LH-outlet. Spectral linear mixing predicts that hydrohalite should be observable in the near-
281 infrared in this sample, however apart from a subtle reflectance minimum at 1.983 μm , hydrohalite
282 features were absent, even when the sample was measured at 100 K (Fig. 4). Incorporating
283 spectrally featureless anhydrous phases at proportions above 50% into the mix produces similar
284 smoothing effects, but causes features at 1.5 and 2.0 μm to lack the depth and breadth observed in
285 LH-outlet spectra (Fig 4b). Moreover the approximate anhydrous proportion measured by XRD at
286 room temperature (20%) provides an upper limit on anhydrous phase abundance in LH-outlet
287 material, which will be heavily hydrated at 100 K. This demonstrates that the behaviour of natural

288 assemblages, which can be complex intimate mixtures of compounds and hydrations states, cannot
289 be predicted from the additive properties of pure salts alone. If ocean-derived hydrated chlorides
290 are present on the surface of Europa (Brown and Hand, 2013), they could be spectrally obscured
291 by sulfates. Importantly, if sulfates are exogenic in origin (i.e., from Io's plasma torus), this could
292 present a problem for identifying endogenic material within surface deposits. In this case, the 1.983
293 μm band minimum could be an important diagnostic feature of hydrohalite that is retained, albeit
294 subtly, in sulfate deposits.

295

296 **5.3 Geochemical implications for Europa from natural analogues**

297 The deposits at AHI springs show that natural brines with similar major ion chemistry can
298 precipitate different mineralogical deposits, ranging from calcite and gypsum at CP, to mirabilite
299 and hydrohalite at LH. These differences are accounted for by minor variations in the
300 sulfate:chloride ratio of the brines, and by dissolved calcium and alkalinity (Fig. 2; Fig S2). CP
301 exhibits minerals not considered likely at Europa, however their formation demonstrates how
302 minor differences in geochemistry can produce varied mineralogies. The same may be true on a
303 geologically diverse world such as Europa. Additionally, CP can be a useful analogue for
304 cryovolcanic precipitates on bodies with more alkaline and carbonate-rich aqueous chemistries,
305 such as Enceladus (Glein et al., 2015).

306 The compositions of AHI deposits do not reflect equilibrium salt assemblages that would form if
307 the spring brines fully crystallised, rather they represent a snapshot during this evolution (Fig. S2;
308 Table S3). For example, despite bearing a high chloride : sulfate ratio (25; Table S1), LH salts are
309 dominated by mirabilite and thenardite, showing that a dominantly chloride brine can form sulfate-

310 dominated deposits. Thermodynamic models show that mirabilite forms early upon freezing or
311 evaporation-driven concentration, while chlorides are retained in late-stage brines that can be
312 transported away from the deposit (Fig. S2). On Europa, a chloride-dominated ocean in which
313 sulfate is only a minor constituent may form sulfate-rich salt assemblages in a similar manner, at
314 the surface or within the ice, while denser chloride-enriched brines migrate away (Zolotov &
315 Shock, 2001). The discovery of endogenous sulfate salts on Europa would therefore not preclude
316 a chloride-dominated ocean.

317 The composition of Europa's ocean is not well constrained, and the relative contributions of
318 exogenic and endogenic processes to surface non-ice material are not known. Different
319 geographical regions may harbour different compositions, reflecting different processes (Fischer
320 et al., 2015). In one proposed scenario, chloride-dominated subsurface fluids are delivered to the
321 surface and become progressively altered by exogenous sulfur ion bombardment (Brown and
322 Hand, 2013). Under these circumstances, STZ-white salts represent pristine deposits, with STZ-
323 dark and the LH salt assemblages representing more altered, sulfate-rich deposits where the vis-
324 NIR signature of hydrohalite is obscured. Alternatively, if the ocean is sulfate-rich, (Kargel et al.,
325 2000) then LH salts would represent suitable analogue material for pristine endogenic deposits.
326 The study of natural environments such as the AHI springs forms part of an integrative theoretical,
327 experimental and analogue approach that will be critical to interpreting future mission data, both
328 from upcoming fly-by missions as well as the under-development NASA Europa Lander project.

329

330 **Acknowledgements**

331

332 This work was funded by The Leverhulme Trust (RPG-2016-153) and the Natural Sciences and
333 Engineering Research Council of Canada. The Planetary Spectroscopy Facility, University of

334 Winnipeg, is supported by the University of Winnipeg, the Canada Foundation for Innovation, the
335 Manitoba Research Innovation Fund and the Canadian Space Agency. Thanks to The Polar
336 Continental Shelf Program (Natural Resources Canada) for logistical field support in Nunavut.
337 Geochemical and spectral data presented in this manuscript are available in Supporting
338 information. Finally, we thank two anonymous reviewers for constructive comments.

339

340 **6. References**

341 Andersen, D. T., Pollard, W. H., McKay, C. P., & Heldmann, J. (2002). Cold springs in permafrost
342 on Earth and Mars. *Journal of Geophysical Research*, 107(E3). doi:10.1029/2000JE001436

343 Battler, M. M., Osinski, G. R., & Banerjee, N. R. (2013). Mineralogy of saline perennial cold
344 springs on Axel Heiberg Island, Nunavut, Canada and implications for spring deposits on Mars.
345 *Icarus*, 224(2), 364–381. doi:10.1016/j.icarus.2012.08.031

346 Blaney, D. L., Clark, R., Dalton, J. B., Davies, A. G., Green, R., Hedman, M., et al. (2015)
347 Mapping Imaging Spectrometer for Europa (MISE). Paper presented at European Planetary
348 Science Congress, Nantes, France

349 Bramble, M. S., Flemming, R. L., Hutter, J. L., Battler, M. M., Osinski, G. R. & Banerjee, N. R.
350 (2014). A temperature-controlled sample stage for in situ micro-X-ray diffraction: Application to
351 Mars analog mirabilite-bearing perennial cold spring precipitate mineralogy. *American*
352 *Mineralogist*, 99, 943–947. doi:10.2138/am.2014.4629

353 Brown, M. E., & Hand, K. P. (2013). Salts and radiation products on the surface of Europa. *The*
354 *Astronomical Journal*, 145, 110–7. doi:10.1088/0004-6256/145/4/110

- 355 Carlson, R. W., Anderson, M. S., Mehlman, R., & Johnson, R. E. (2005). Distribution of hydrate
356 on Europa: Further evidence for sulfuric acid hydrate. *Icarus*, *177*(2), 461–471.
357 doi:10.1016/J.ICARUS.2005.03.026
- 358 Carlson, R. W., Calvin, W. M., Dalton, J. B., Hansen, G. B., Hudson, R. L., Johnson, R. E., et al.
359 (2009). Europa's Surface Composition. In R. T. Pappalardo, W. B. Mckinnon, & K. Khurana
360 (Eds.), *Europa* (pp. 283–327). University of Arizona Press.
- 361 Carr, M. H., Belton, M. J., Chapman, C. R., Davies, M. E., Geissler, P., Greenberg, R., et al.
362 (1998). Evidence for a subsurface ocean on Europa. *Nature*, *391*, 363–365. doi:10.1038/34857
- 363 Cloutis, E. A., Hawthorne, F. C., Mertzman, S. A., Krenn, K., Craig, M. A., Marcino, D., et al.
364 (2006). Detection and discrimination of sulfate minerals using reflectance spectroscopy. *Icarus*,
365 *184*, 121-157. doi:10.1016/j.icarus.2006.04.003
- 366 Dalton, J. B. (2007). Linear mixture modeling of Europa's non-ice material based on cryogenic
367 laboratory spectroscopy. *Geophysical Research Letters*, *34*(21), 2–5. doi:10.1029/2007GL031497
- 368 Dalton, J. B., Prieto-Ballesteros, O., Kargel, J. S., Jamieson, C. S., Jolivet, J., & Quinn, R. (2005).
369 Spectral comparison of heavily hydrated salts with disrupted terrains on Europa. *Icarus*, *177*, 472–
370 490. doi:10.1016/j.icarus.2005.02.023
- 371 Dalton, J. B., Shirley, J. H., & Kamp, L. W. (2012). Europa's icy bright plains and dark linea:
372 Exogenic and endogenic contributions to composition and surface properties. *Journal of*
373 *Geophysical Research: Planets*, *117*(E03003). doi:10.1029/2011JE003909
- 374 Doran, P. T., McKay, C. P., Adams, W. P., English, M. C., Wharton, R. A., & Meyer, M. A.
375 (1996). Climate forcing and thermal feedback of residual lake-ice covers in the high Arctic.

- 376 *Limnology and Oceanography*, 41(5), 839–848. doi:10.4319/lo.1996.41.5.0839
- 377 Fischer, P. D., Brown, M. E., & Hand, K. P. (2015). Spatially resolved spectroscopy of Europa:
378 The distinct spectrum of large-scale chaos. *The Astronomical Journal*, 150(164).
379 doi:10.1088/0004-6256/150/5/164
- 380 Fischer, P. D., Brown, M. E., Trumbo, S. K., & Hand, K. P. (2016). Spatially resolved spectroscopy
381 of Europa's large-scale compositional units at 3–4 μm with Keck NIRSPEC, 153(13).
382 doi:10.3847/1538-3881/153/1/13
- 383 Glein, C. R., Baross, J. A., & Waite, J. H. (2015). The pH of Enceladus' ocean. *Geochimica et*
384 *Cosmochimica Acta*, 162, 202–219. doi:10.1016/j.gca.2015.04.017
- 385 Hand, K. P., & Carlson, R. W. (2015). Europa's surface color suggests an ocean rich with sodium
386 chloride. *Geophysical Research Letters*, 42, 3174–3178. doi:10.1002/2015GL063559
- 387 Hanley, J., Dalton, J. B., Chevrier, V. F., Jamieson, C. S., & Barrows, R. S. (2014). Reflectance
388 spectra of hydrated chlorine salts: The effect of temperature with implications for Europa. *Journal*
389 *of Geophysical Research: Planets*, 119(11), 2370–2377. doi:10.1002/2013JE004565
- 390 Harrison, J. C., & Jackson, M. P. A. (2014). Exposed evaporite diapirs and minibasins above a
391 canopy in central Sverdrup Basin, Axel Heiberg Island, Arctic Canada. *Basin Research*, 26(4),
392 567–596. doi:10.1111/bre.12037
- 393 Howell, S. M & Pappalardo, R. T. (2018) Band formation and ocean-surface interaction on Europa
394 and Ganymede. *Geophysical Research Letters*, 45(10), 4701–4709. doi:10.1029/2018GL077594
- 395 Jia, X., Kivelson, M. G., Khurana, K. K., & Kurth, W. S. (2018). Evidence of a plume on Europa
396 from Galileo magnetic and plasma wave signatures. *Nature Astronomy*, 2(6), 459–464.

397 doi:10.1038/s41550-018-0450-z

398 Kargel, J. S., Kaye, J. Z., Head, J. W. III, Marion, G. M., Sassen, R., Crowley, J. K., Ballesteros,
399 O. P., Grant, S. A. & Hogenboom, D. L. Europa's crust and ocean: Origin, composition, and the
400 prospects for life. *Icarus* 148, 226-265. doi:10.1006/icar.2000.6471

401 Langevin, Y., Piccioni, G. & the MAJIS Team. (2013) MAJIS (Moons and Jupiter Imaging
402 Spectrometer) for JUICE: objectives for the Galilean satellites. Paper presented at European
403 Planetary Science Conference, London, United Kingdom

404 Lay, C.-Y., Mykytczuk, N. C. S., Yergeau, É., Lamarche-Gagnon, G., Greer, C. W., & Whyte, L.
405 G. (2013). Defining the Functional Potential and Active Community Members of a Sediment
406 Microbial Community in a High-Arctic Hypersaline Subzero Spring. *Applied and Environmental*
407 *Microbiology*, 79(12), 3637–3648. doi:10.1128/AEM.00153-13

408 Light, B., Brandt, R. E., & Warren, S. G. (2009). Hydrohalite in cold sea ice: Laboratory
409 observations of single crystals, surface accumulations, and migration rates under a temperature
410 gradient, with application to “Snowball Earth.” *Journal of Geophysical Research*, 114(C07018).
411 doi:10.1029/2008JC005211

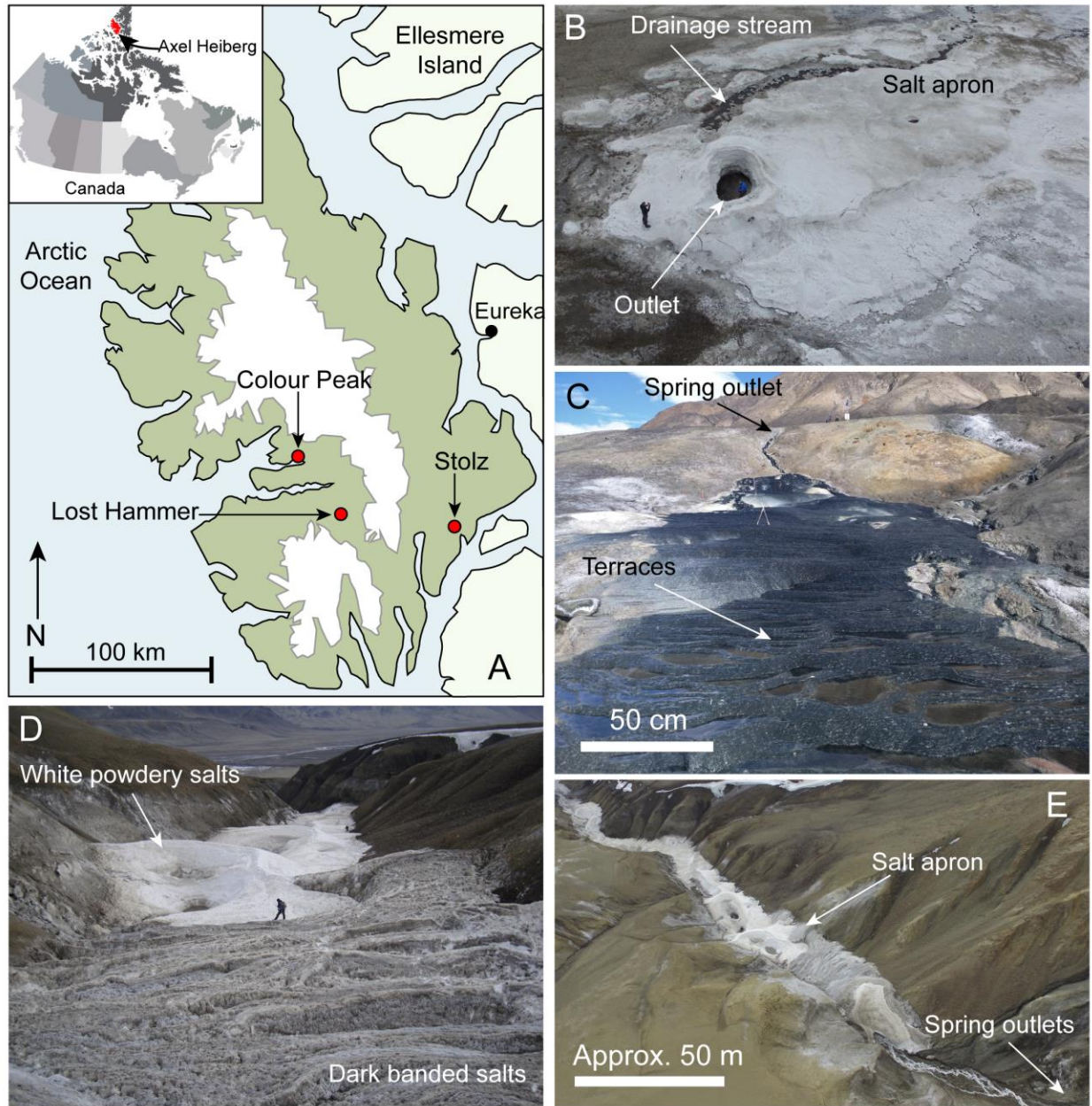
412 Light, B., Carns, R. C., & Warren, S. G. (2016). The spectral albedo of sea ice and salt crusts on
413 the tropical ocean of Snowball Earth: 1. Laboratory measurements. *Journal of Geophysical*
414 *Research: Oceans*, 121(7), 4966–4979. doi:10.1002/2016JC011803

415 Ligier, N., Poulet, F., Carter, J., Brunetto, R., & Gourgéot, F. (2016). VLT/SINFONI observations
416 of Europa: New insights into the surface composition. *The Astronomical Journal*, 151(163) doi:
417 10.3847/0004-6256/151/6/163

- 418 Marion, G .M. & Kargel, J. S. (2008) Cold Aqueous Planetary Geochemistry with FREZCHEM.
419 *Advances in Astrobiology and Biogeophysics*. Springer-Verlag Berlin Heidelberg
420
- 421 McCord, T. B., Hansen, G. B., Matson, D. L., Johnson, T. V, Crowley, J. K., Fanale, F. P., et al.
422 (1999). Hydrated salt minerals on Europa’s Surface from the Galileo near-infrared mapping
423 spectrometer (NIMS) investigation. *Journal of Geophysical Research*, *104*, 11827–11851.
424 doi:10.1029/1999JE900005
- 425 Nimmo, F., & Pappalardo, R. T. (2016). Ocean worlds in the outer solar system. *Journal of*
426 *Geophysical Research: Planets*, *121*(8), 1378–1399. doi:10.1002/2016JE005081
- 427 Omelon, C. R., Pollard, W. H., & Andersen, D. T. (2006). A geochemical evaluation of perennial
428 spring activity and associated mineral precipitates at Expedition Fjord, Axel Heiberg Island,
429 Canadian High Arctic. *Applied Geochemistry*, *21*(1), 1–15. doi:10.1016/j.apgeochem.2005.08.004
- 430 Orlando, T. M., McCord, T. B., & Grieves, G. A. (2005). The chemical nature of Europa surface
431 material and the relation to a subsurface ocean. *Icarus*, *177*(2), 528–533.
432 doi:10.1016/j.icarus.2005.05.009
- 433 Pollard, W., Omelon, C., Anderson, D., & McKay, C. (1999). Perennial spring occurrence in the
434 Expedition Fiord area of western Axel Heiberg Island, Canadian High Arctic. *Canadian Journal*
435 *of Earth Science*, *36*, 105–120. doi:10.1139/e98-097
- 436 Prockter, L. M., Shirley, J. H., Dalton, J. B. & Kamp, L. (2017) Surface composition of pull-apart
437 bands in Argadnel Regio, Europa: Evidence of localized cryovolcanic resurfacing during basin
438 formation. *Icarus* *285*, 27-42. doi:10.1016/j.icarus.2016.11.024

- 439 Rodriguez-Navarro, C., Doehne, E., & Sebastian, E. (2000). How does sodium sulfate crystallize?
440 Implications for the decay and testing of building materials. *Cement and Concrete Research*, *30*,
441 1527–1534. doi:10.1016/S0008-8846(00)00381-1
- 442 Roth, L., Saur, J., Retherford, K. D., Strobel, D. F., Feldman, P. D., McGrath, M. A., & Nimmo,
443 F. (2014). Transient Water Vapor at Europa’s South Pole. *Science*, *343*(6167), 171–174.
444 doi:10.1126/science.1247051
- 445 Schmidt, B. E., Blankenship, D. D., Patterson, G. W. & Schenk, P. M. (2011) Active formation of
446 ‘chaos terrain’ over shallow subsurface water on Europa. *Nature* *479*, 502-505.
- 447 Shirley, J. H., Dalton III, J. B., Prockter, L. M., & Kamp, L. W. (2010). Europa’s ridged plains
448 and smooth low albedo plains: Distinctive compositions and compositional gradients at the leading
449 side-trailing side boundary. *Icarus*, *210*, 358–384. doi:10.1016/j.icarus.2010.06.018
- 450 Ward, M. K., & Pollard, W. H. (2018). A hydrohalite spring deposit in the Canadian high Arctic:
451 A potential Mars analogue. *Earth and Planetary Science Letters*, *504*, 126–138.
452 doi:10.1016/J.EPSL.2018.10.001
- 453 Zolotov, M. Y., & Shock, E. L. (2001). Composition and stability of salts on the surface of Europa
454 and their oceanic origin. *Journal of Geophysical Research: Planets*, *106*(E12), 32815–32827.
455 doi:10.1029/2000JE001413

456



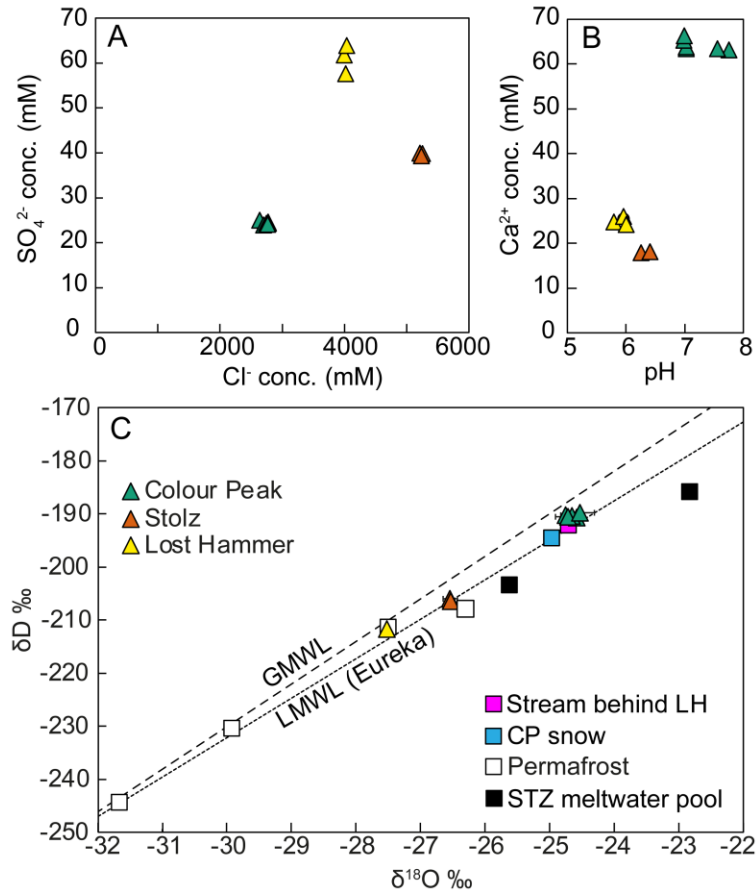
457

458 **Fig. 1:** (a) Map of Axel Heiberg Island, location of the three springs studied, and icecaps (white).

459 (b) Aerial view of Lost Hammer spring, showing outlet and salt apron. Person for scale. (c)

460 Terraces at Colour Peak springs and outlet channel. (d) Salt apron at Stolz Spring. Person for scale.

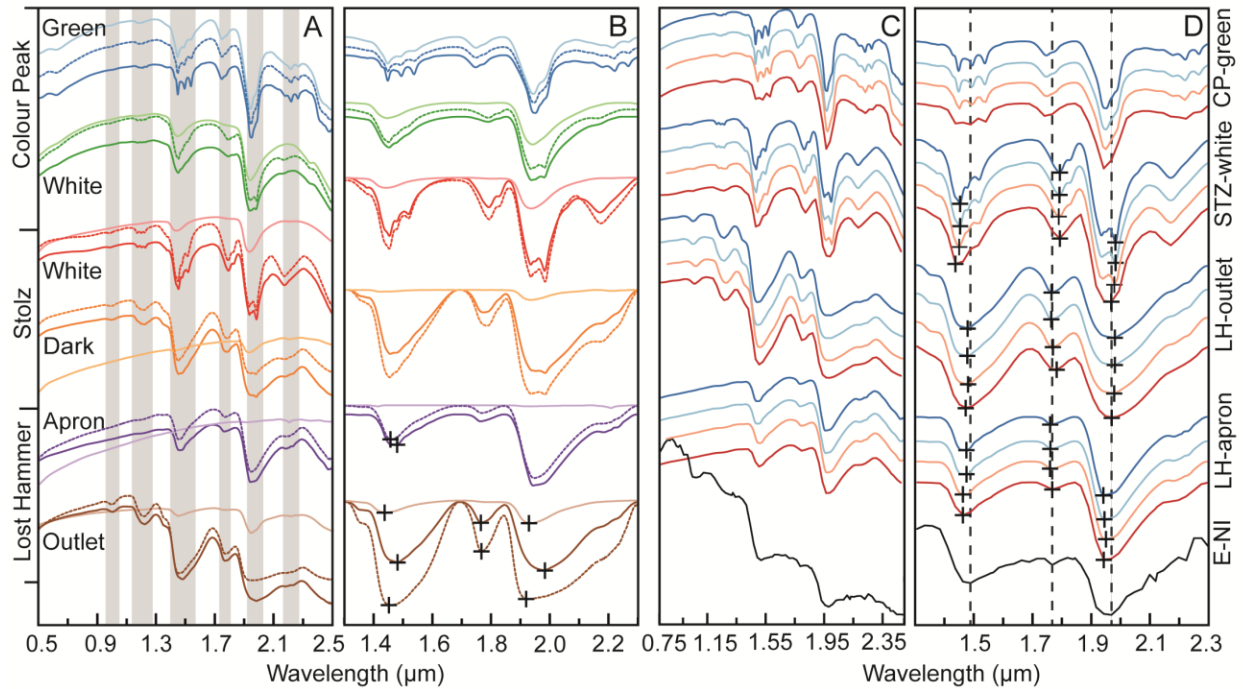
461 (e) Aerial view of Stolz Springs, showing the outlets on the side of Stolz Diapir



462

463 **Figure 2:** AHI spring geochemistry. (a) Major anions; (b) Calcium concentration vs. pH; (c) Water
 464 isotopic composition of the springs and potential source waters. Global (G) and local (L) meteoric
 465 water lines (MWL) plotted for reference (Pollard et al., 1999).

466



467

468 **Figure 3:** Representative vis-NIR reflectance spectra of salts from the AHI saline springs.469 Reflectance offset for clarity. **(a-b):** Full (a) and continuum-removed (b) spectra at 100K (darkest),470 253 K (dashed) and 293 K (lightest). Grey lines highlight $\text{H}_2\text{O}/\text{OH}$ water bands. **(c-d):**

471 Representative full (c) and continuum-removed (d) spectra resampled to instrument bandpasses,

472 ordered from top to bottom: full nm-resolved spectra, MAJIS resolution, MISE resolution, NIMS

473 resolution. Europa non-icy endmember spectrum (black), acquired by Galileo NIMS, is

474 reproduced from Carlson et al. (2005). Dashed lines and crosses in (b) and (d) show the positions

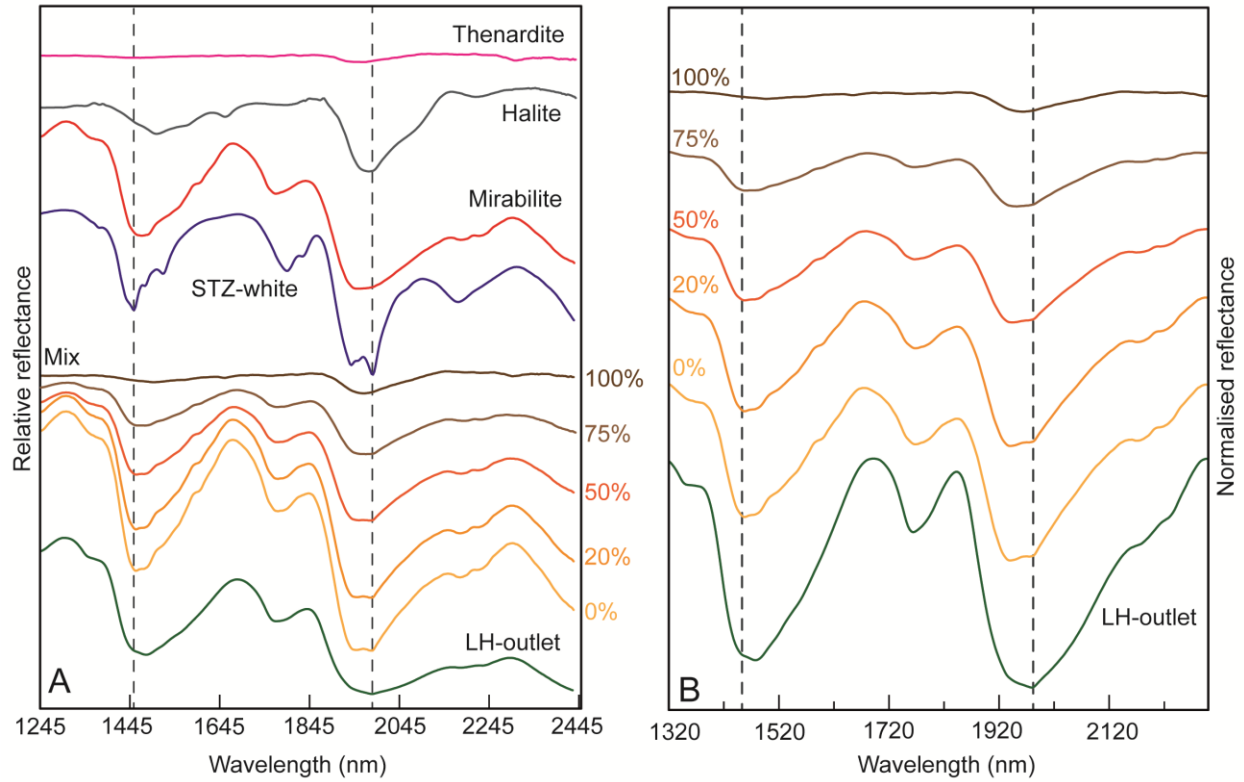
475 of absorption band minima for NIMS data and AHI data, respectively.

476

477

478

479



480

481 **Figure 4:** Comparison of numerically mixed spectra with LH-outlet spectra (measured at 100 K).
 482 STZ-white (at 100 K) provides the hydrohalite spectral endmember. Each mix represents an
 483 anhydrous percentage; 20% anhydrous corresponds to that measured in LH-Outlet by XRD at 20
 484 °C. (a) Vis-NIR reflectance spectra of spectral endmembers and their mixes; (b) continuum-
 485 removed spectral mixes. Grey dashed lines denote the position of major hydrohalite band minima
 486 at 1452 and 1983 nm (visible in STZ-white).

487