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1 A temperature-controlled sample stage for *in situ* micro-X-ray diffraction: Application to
2 Mars analogue mirabilite-bearing perennial cold spring precipitate mineralogy.

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24 **Abstract**

25

26 A temperature-controlled sample stage with an operational range of ~60 °C above
27 or below ambient laboratory temperature (~ -35 to 85 °C) was constructed for *in situ* X-
28 ray diffraction of minerals and materials using a Bruker D8 Discover diffractometer with
29 theta-theta geometry. The stage was primarily designed for characterizing mirabilite-
30 bearing samples from a Mars analogue High Arctic perennial cold spring at an *in situ*
31 temperature. Operation of the stage was demonstrated through the analysis of a synthetic
32 sample of the hydrated sodium sulfate, mirabilite (Na₂SO₄·10H₂O). Mirabilite was held at
33 -25 °C for approximately two hours without significant dehydration and then
34 incrementally warmed to ambient laboratory temperature at 5 °C intervals, during the
35 acquisition of *in situ* diffraction data. At ambient laboratory temperature the mirabilite
36 dehydrated and only polycrystalline thenardite (Na₂SO₄) remained. Preliminary analysis
37 of the cold spring precipitates demonstrates that when mirabilite is present in the sample
38 the dehydration reaction is occurring between collection and analysis at ambient
39 laboratory temperature. This temperature-controlled stage was designed for versatility
40 and ease of X-ray access, with applications that can extend to many geological and
41 planetary settings, including Mars analogue environments.

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44 **Keywords:** micro-X-ray diffraction, sodium sulfate dehydration, Peltier-effect,
45 thermoelectric temperature-controlled stage, mirabilite, thenardite, Mars analogue.

46

47 **Introduction**

48

49 Wolf Spring is a perennial cold spring on Axel Heiberg Island, Nunavut, Canada
50 (Fig. 1a), produced by the flow of water through permafrost, which generates evaporitic
51 precipitate minerals around the main vent (Pollard et al. 2009). It has been proposed as a
52 terrestrial Mars analogue with implications for Martian mineralogy (Battler et al. 2013)
53 and astrobiology (Niederberger et al. 2010; Lay et al. 2012). A mineralogical study of the
54 cold spring carried out by powder X-ray diffraction (pXRD) at ambient laboratory
55 temperature by Battler et al. (2013) suggested that halite, thenardite, gypsum, mirabilite,
56 other Na-bearing sulfates, and presumed detrital minerals (such as quartz, plagioclase,
57 and clays), were abundant minerals at the spring site. However, a subset of mineral
58 samples underwent changes in mechanical and physical properties between sampling and
59 analysis in the laboratory, interpreted to be dehydration of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) to
60 thenardite (Na_2SO_4) (Battler et al. 2013). This suggested that mirabilite may be a more
61 abundant phase at the spring site than suggested by laboratory pXRD under ambient
62 conditions. In this study, we constructed a sample stage to enable *in situ* temperature-
63 controlled micro-X-ray diffraction (μXRD) of these mineral samples, as well as other
64 geological and planetary materials.

65 Beginning at approximately 0 °C and continuing with warming to 32.4 °C,
66 mirabilite dehydrates to thenardite, with both temperature and relative humidity (RH)
67 controlling the vigor of the transition (Hamad 1967; Cardell et al. 2007). An
68 approximately linear boundary between the stability fields of mirabilite and thenardite
69 exists between 0 °C and ~60 % RH and 32.4 °C and ~85 % RH, with mirabilite above

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70 this phase boundary, stable at the higher relative humidity, and thenardite below (Flatt
71 2002; Genkinger and Putnis 2007). Therefore, at ambient temperatures (~ 22 °C) and RH
72 (55-65%), mirabilite is unstable and does not retain water in its crystal structure. Wolf
73 Spring's average perennial vent water temperature is between -5.9 to -4.7 °C
74 (Niederberger et al. 2010), with the late-April to mid-July sediment temperatures
75 underlying the outflow channels ranging from -18 to 9.2 °C (Lay et al. 2012). The spring
76 site thus frequently remains in the stability field of mirabilite.

77 Subsequent mineralogical sampling of the Wolf Spring vent (Fig. 1b) was
78 executed with the intention of keeping the samples below 0 °C to allow for any hydrated
79 sulfates to remain in the hydrated state for later temperature-sensitive laboratory analysis.
80 Figure 1c depicts the context of one of these samples, LH-11-01B, which was involved in
81 the experiment discussed below. The temperature-controlled stage for X-ray diffraction
82 would require the ability for analysis below 0 °C, preferably at temperatures down to -25
83 °C, and then allow for the warming of the sample to particular temperatures, such as the
84 average perennial spring water temperature of ~ -5 °C, and hold the sample at this
85 temperature while diffraction data were collected. A temperature-controlled sample stage
86 of this design, when paired with the versatility of theta-theta geometry μ XRD (Flemming
87 2007) would allow observation of the hydrated sodium sulfate mineral behavior at Wolf
88 Spring to be studied in a controlled setting.

89

90 **Temperature-Controlled Stage Design**

91

92 The temperature-controlled stage design was based on the Peltier effect (Fig. 2).
93 When an electric current is applied across a Peltier thermoelectric (TE) module, in its
94 simplest form a series of semiconductors electrically in series and thermally in parallel, a
95 thermal gradient is created between two ceramic plates. This thermal gradient (ΔT)
96 depends on the current, and varies depending on the conditions of operation, but, in
97 general, the colder the hot side of the module becomes, the colder the cold side is via the
98 thermal gradient. When the hot side of the module is attached to a heat sink, such as a
99 copper block cooled by water or liquid nitrogen, the heat is dissipated away allowing the
100 cool side to become colder.

101 Single stage TE modules (Marlow Industries DT12-8-01; Fig. 2a) with cooling
102 face dimensions of 40.13 mm by 40.13 mm were chosen with a maximum ΔT of 66 °C
103 operating at a temperature of 27 °C. The TE modules were connected to a temperature
104 controller (Tellurex TTC-12-24A) with a power supply module (Tellurex PS-12-12) that
105 provided 12 VDC at 12 A output, allowing for the full range of operation of the 7.4 A
106 modules.

107 Sample holders (Fig. 2b) were made of copper, selected due to its high thermal
108 conductivity, and consisted of two parts: a 40 x 40 x 3 mm block of copper that contacted
109 the TE module and a second copper plate of the same dimensions containing a 1 mm
110 depression 25 mm in diameter to contain the sample. The bottom copper block had a hole
111 of 1.6 mm diameter bored to its center to accommodate a temperature sensor and four
112 threaded holes to allow the sample holder to be fastened to the bottom block, ensuring
113 good thermal contact. As with the TE / copper block contact, a layer of thermal paste
114 separated the bottom block from the sample holder.

115 A quick disconnect thermocouple (Omega Engineering, Inc., TMQSS-062U-6;
116 Fig. 2c) was inserted into the bottom block of the sample holder to provide temperature
117 information from the sample holder to the temperature controller. This temperature
118 sensor was coated with a layer of thermal conductivity paste prior to injection. Future
119 applications would benefit from an additional thermocouple or remote infrared
120 thermometer analyzing the temperature at the incident X-ray beam location.

121 Beneath the hot side of the TE module, and a layer of thermal paste, sat the heat
122 sink (Fig. 2d). A 50.75 x 50.90 x 25.40 mm copper block was used with a 12.70 mm hole
123 bored through with copper hose couplings threaded-in on each end. Using hose clamps,
124 the system was plumbed into the μ XRD enclosure using 15 m of tubing connected to an
125 open water source and drainage (Fig. 2e). This dissipated heat via a flow of water at \sim 4
126 L/min.

127 The entire temperature-controlled stage was mounted on top of a remote-
128 controlled XYZ sample stage on a Bruker D8 Discover Diffractometer (Fig. 2), which
129 allowed for a 1000 cm³ volume available for analysis. Samples were prepared in the cold
130 storage room on a copper sample holder and then brought to the μ XRD and set up on the
131 temperature-controlled stage. The mineral of interest can be targeted in three dimensions
132 and focused using the existing laser and video camera system.

133

134 **Demonstration Experiment**

135

136 For this study, the temperature-controlled stage was mounted on a Bruker D8
137 Discover X-ray diffractometer which was configured for μ XRD at the University of

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138 Western Ontario with a two-dimensional HI-STAR detector and a General Area
139 Detection Diffraction System (GADDS). μ XRD is an effective tool for investigating
140 mineral structures and textures of Earth and planetary materials (Flemming 2007), and
141 the key feature for this study is the non-destructive, *in situ* nature of the technique. A
142 $\text{CoK}\alpha$ (1.78897 Å) radiation source operating at 35 kV and 45 mA, collimated through a
143 graphite monochromator and 300 μm monochromator (nominal beam diameter is 300 μm)
144 was used. The GADDS images were integrated and then analyzed with the Bruker-AXS
145 DiffracPlus Evaluation software (Bruker-AXS 2010), and phase identification was
146 verified using the International Center for Diffraction Data (ICDD) Powder Diffraction
147 File (PDF-4) database (rev. 2010).

148 To demonstrate the operation of the temperature-controlled stage with the
149 diffractometer, synthetic crystals of mirabilite (Sigma-Aldrich 403008-100G), stored at –
150 25 °C, were raised in increments of 5 °C to ambient conditions, with μ XRD data
151 collected at each temperature after a thermal equilibration period of three minutes. Prior
152 to the experiment, the top sample holder blocks were brought to thermal equilibrium
153 inside a –25 °C cold storage room. Once this occurred, the synthetic mirabilite crystals
154 were appropriately sized and placed inside the 1 mm depression in the sample holder.
155 The mirabilite crystals as obtained were not powdered but were coarse granular. Crystals
156 less than ~3 mm were selected for the experiment. To achieve a selection of smaller
157 crystals, it was necessary to reduce the size of some of the larger crystals by applying
158 pressure with an agate pestle. This provided enough crystals of the correct size for a layer
159 covering the entire sample area (~490 mm²). Pressure was applied only once. Using a
160 transport container, the sample in the holder was brought to the μ XRD laboratory where

161 the temperature-controlled stage was already operating and pre-cooled to $-25\text{ }^{\circ}\text{C}$. The
162 prepared sample and holder were removed from the container, placed on top of the lower
163 sample holder block at the top of the temperature-controlled stage with a layer of thermal
164 paste in between the blocks. Transport and mounting took ~ 2 minutes. To prevent
165 condensation on the temperature-controlled stage as well providing an experimental
166 constraint on the humidity, a flow of dry nitrogen gas was directed at the center of the
167 sample holder.

168 Measures were taken to achieve the highest quality data in the shortest amount of
169 time due to the time- and temperature-sensitive nature of this experiment. Due in part to
170 the coarse grained nature of the crystals, a $300\text{ }\mu\text{m}$ nominal beam diameter was used and
171 data was collected from only one detector position (one GADDS image), using omega
172 scan mode (rotating optics). The parameters were $\theta_1 + \theta_2 = 36^{\circ}$, with $\theta_{1(\text{start})} = 10^{\circ}$ and
173 $\theta_{2(\text{start})} = 26^{\circ}$, and scanning through an omega angle of $\omega = 14^{\circ}$. This yielded data from
174 $15\text{-}56^{\circ} 2\theta$, at a detector distance of 12 cm. The sample was oscillated by 2 mm in the xy -
175 plane, to maximize the number of crystallites sampled for the dataset, somewhat akin to
176 bulk pXRD of the sample. Each frame of data was collected for 10 minutes.

177 The experiment began by holding the mirabilite crystals at $-25\text{ }^{\circ}\text{C}$ for
178 approximately two hours and collecting data every 15 minutes to demonstrate the
179 capability of the temperature-controlled stage to maintain the mirabilite crystal structure
180 under these conditions. At this temperature the crystal structure is ‘frozen’ in place, and if
181 exposed suddenly to ambient conditions from this temperature the mirabilite would
182 presumably begin a rapid transition to thenardite. After reaching $23\text{ }^{\circ}\text{C}$, data were

183 collected at 30 minute intervals as the entire temperature-controlled stage system was
184 brought to equilibrium at ambient conditions within the enclosure.

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Results and Discussion

187

188 Synthetic mirabilite demonstration

189 Representative GADDS images of the data collected during this experiment can
190 be seen in Figure 3. Figure 3a was collected within approximately 20 minutes of the
191 mirabilite being placed on the operating temperature-controlled stage at $-25\text{ }^{\circ}\text{C}$. The
192 diffracted X-ray spots are indicative of the coarse crystal size of the initial mirabilite
193 crystals. Note the faint Debye rings seen in the GADDS image. These rings are indicative
194 of polycrystalline thenardite and their intensity increases slightly over the two hours that
195 the experiment is held at $-25\text{ }^{\circ}\text{C}$ on the μXRD .

196 The thenardite likely formed during transport from the cold storage room to the
197 laboratory, where the ambient conditions would induce a vigorous transition. The
198 thenardite may also have formed during sample preparation as handling the crystals or
199 simply pressing hydrated sulfate minerals into sample holders can induce dehydration,
200 even under constant temperature and RH (Cardell et al. 2007). The minimal sample
201 preparation required for μXRD minimizes the preparation-induced dehydration.

202 After approximately two hours, the only change in the GADDS image (Fig. 3b) is
203 a minor increase in intensity of the polycrystalline thenardite Debye rings. This may be
204 due to a minor amount of uncontrolled dehydration occurring at the top of the sample due

205 to the μ XRD enclosure being at ambient laboratory temperature and RH. Figures 3a and
206 3b are representative of the frames collected during the incremental warming to 0 °C.

207 Figure 3c shows the data collected at 5 °C. This frame shows significant change
208 from all the previous frames collected below 0 °C; for the first time, Debye rings of
209 mirabilite are seen. This transition may be the result of a small amount of water seeping
210 into the sample holder depression, thus stabilizing mirabilite in contact with water. While
211 the nitrogen gas flow was able to keep ice crystals from forming on the surface of the
212 mirabilite, ice crystals did form around the edges and the top of the sample tray.
213 Subsequently, the top portion of the sample holder was beveled with a 1° slope away
214 from the center of the sample holder which greatly mitigated melt water pooling in the
215 sample holder.

216 The presence of water in contact with portions of the sample caused mirabilite to
217 crystallize along with thenardite in the sample holder during the warming from 0 to 23 °C
218 (Fig. 3c). Homogeneous Debye rings indicate that the secondary mirabilite is fine grained
219 (<5 μ m) (Klug and Alexander 1962). At 25 °C, the warming experiment was terminated
220 and a small number of the thenardite and mirabilite crystals grew to 15-50 μ m in size as
221 seen by the appearance of diffraction spots along the Debye rings in the GADDS images.
222 The experiment was allowed to sit at ambient conditions inside the enclosure for another
223 12 hours.

224 After termination of the warming experiment and as the entire system reached
225 equilibrium with the ambient conditions of the laboratory, the number and intensity of the
226 diffraction spots decreased and finally disappeared altogether as the primary mirabilite
227 crystals reacted to form thenardite. This was accompanied by the growth in intensity of

228 polycrystalline thenardite Debye rings, with continued formation of fine-grained
229 secondary thenardite (see Figure 3d).

230 The GADDS images were integrated to give conventional X-ray diffraction
231 patterns plotting peak intensity versus 2θ as seen in Figure 4. Figure 4a shows the
232 integrated diffraction pattern collected at 0 °C. Mirabilite, ICDD card 01-075-1077, is
233 matched, showing preferred orientation due to the omega scan mode and large crystallite
234 size. Thenardite, ICDD card 00-037-1465, is matched in Figure 4b. This data was
235 collected after 90 minutes under ambient laboratory conditions with the cold stage turned
236 off and demonstrates the polycrystalline nature of the crystals, consistent with the Debye
237 rings mentioned above.

238 All of the peaks in the data could be fit by the ICDD cards for either mirabilite or
239 thenardite except for two. These peaks were at 18.23 and 32.91 ° 2θ and only occurred in
240 a few transient frames during the warming experiment (Fig. 4a). The two unidentified
241 peaks do not exactly line up with 2θ literature values for sodium sulfate heptahydrate
242 ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), but 18.23 and 32.91 ° 2θ fall within 0.33 and 2.14 percent difference,
243 respectively, of the Hamilton and Hall (2008) experimental values for sodium sulfate
244 heptahydrate and 4.41 and 1.08 percent difference, respectively, of the Genkinger and
245 Putnis (2007) experimental values.

246 The transitory and elusive appearance of sodium sulfate heptahydrate in the data,
247 appearing and disappearing unexpectedly in separate frames would correlate with its
248 metastable existence in the transition zone of mirabilite and thenardite. This experiment
249 was designed to mimic the temperature variations seen at Wolf Spring and further study

250 is needed to see if the heptahydrate of sodium sulfate is an important phase at Wolf
251 Spring.

252 **Application to Wolf Spring samples**

253 This temperature-controlled stage has been used for preliminary μ XRD studies of
254 the Wolf Spring samples, which have been stored in cold storage since they were
255 collected in the summers of 2011 and 2012. Preliminary data show that the abundant
256 phases match those determined by prior pXRD (Battler et al. 2013), such as halite,
257 thenardite, and gypsum, but in selected samples to date, mirabilite is found as the major
258 phase at low temperature, which was not commonly seen in the previous work. At
259 ambient laboratory temperatures only thenardite remains, this is consistent with previous
260 work. Figure 1b shows the context for sample LH-11-01B, the sample analyzed in Figure
261 5. When analyzed with the temperature-controlled stage, this sample demonstrates the
262 occurrence of the dehydration reaction as seen in the diffraction data shown in Figure 5.
263 When present, the stable phases—halite, thenardite, and gypsum—are present throughout
264 the data collection at all temperatures.

265 **Temperature-controlled stage versatility**

266 This temperature-controlled stage extends the capability of μ XRD to enable X-ray
267 diffraction analysis of many solids for which studies would benefit from non-destructive
268 XRD at non-ambient temperatures. The possibilities beyond the Wolf Spring samples
269 include analogue experiments designed to reflect aspects of Martian or icy satellite
270 surfaces, material investigations that would benefit from a controlled sample temperature,
271 or even historical or precious materials being preserved by cold storage.

272 The temperature-controlled stage design was designed in part for its versatility. In
273 addition to functioning for cooling experiments, this temperature-controlled stage can be
274 used to heat a sample with only minor alterations of the current setup. It is possible to
275 heat to ~ 80 °C with the current configuration and higher if the water flow was warmed
276 prior to entering the heat sink.

277 To reach colder temperatures than the temperature range in this experiment,
278 simply exchanging the water flow into the copper heat sink with a liquid nitrogen-based
279 cooling system would allow for temperatures in the realm of -200 °C to be reached. The
280 TE module and controller would allow for a controlled working temperature range
281 spanning ~ 60 °C.

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325 High Arctic. *Planetary and Space Science*, 57, 646-659.
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Figures

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329 Figure 1. The Wolf Spring perennial cold spring is located on Axel Heiberg Island,
330 Nunavut, Canada, near Strand Fiord (a). The island's situation within Canada is shown in
331 the insert. The spring vent (b) is ~2.5 m in height and ~3 m in diameter (Battler et al.
332 2013). The area sampled for LH-11-01B is shown (c) along with the sample tube used
333 during transportation and storage.

334 Figure 2. The temperature-controlled stage mounted on the μ XRD XYZ stage. Visible in
335 this image are the a) thermoelectric module, b) sample holder, c) thermocouple, d) heat
336 sink, and e) water hosing.

337 Figure 3. Two-dimensional GADDS images of the diffracted X-rays from the
338 demonstration experiment taken (a) immediately, (b) after ~2 hours at $-25\text{ }^{\circ}\text{C}$, (c) at $5\text{ }^{\circ}\text{C}$,
339 and (d) after equilibration to ambient conditions. For (a), (b), and (d) the polycrystalline
340 Debye rings match thenardite (ICDD-00-037-1465) and the diffracted X-ray spots match
341 mirabilite (ICDD-01-075-1077). In addition to the above, (c) shows the formation of
342 secondary mirabilite (m).

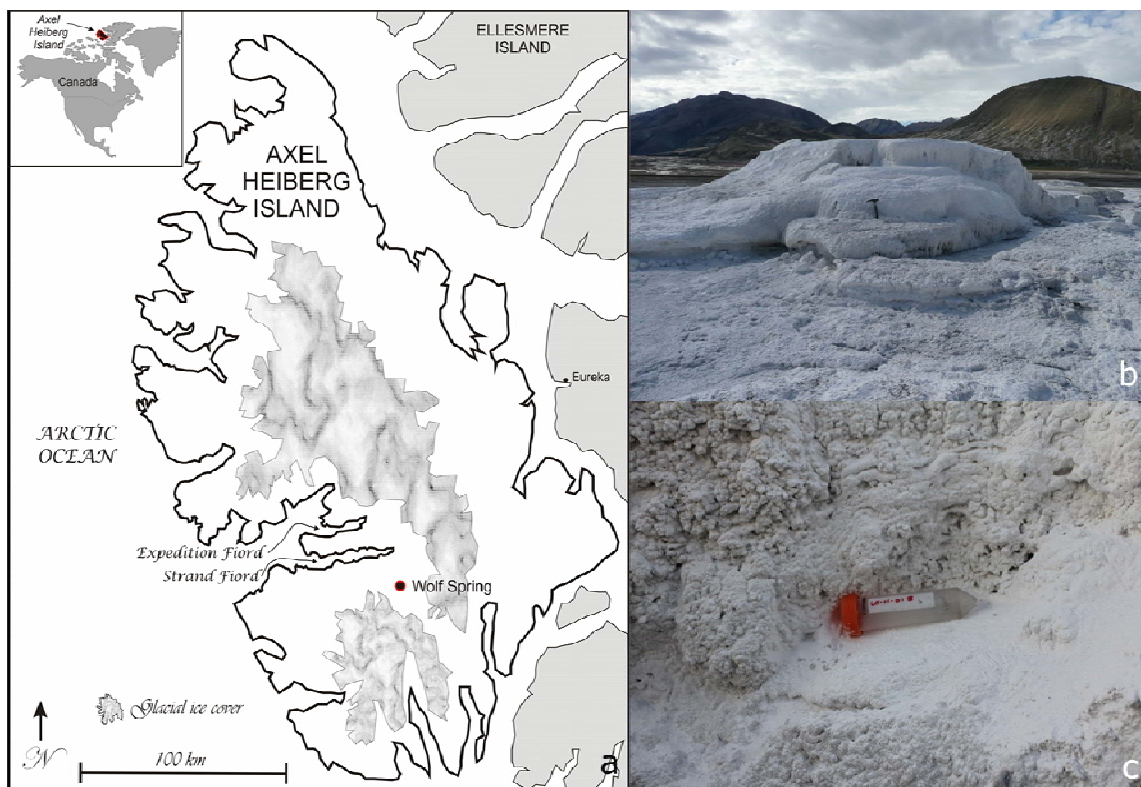
343 Figure 4. (a) Synthetic mirabilite of the demonstration experiment at $0\text{ }^{\circ}\text{C}$. Standard
344 integrated X-ray diffraction pattern plotting peak intensity versus 2θ , with ICDD mineral
345 pattern matches: mirabilite-01-075-1077 (blue) displaying preferred orientation, and
346 thenardite-00-037-1465 (red). (b) Synthetic mirabilite of the demonstration experiment
347 after 90 minutes under ambient laboratory conditions with the cold stage turned off.
348 Integrated X-ray diffraction pattern with ICDD mineral pattern match: thenardite-00-
349 037-1465 (red).

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350 Figure 5. Integrated X-ray diffraction patterns of Wolf Spring sample LH-11-01B.
351 Pattern (a) was collected at 0 °C, and (b) after 24 hours of adjusting to ambient laboratory
352 conditions. ICDD mineral pattern matches: mirabilite–01-075-1077 (blue), and
353 thenardite–00-037-1465 (red). The peak at 35.97° 2θ has not been unambiguously
354 identified. Pattern (b) has a correction applied for a sample displacement of –1.33 mm
355 caused by the sample moving out of focus during dehydration.
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357 Figure 1.



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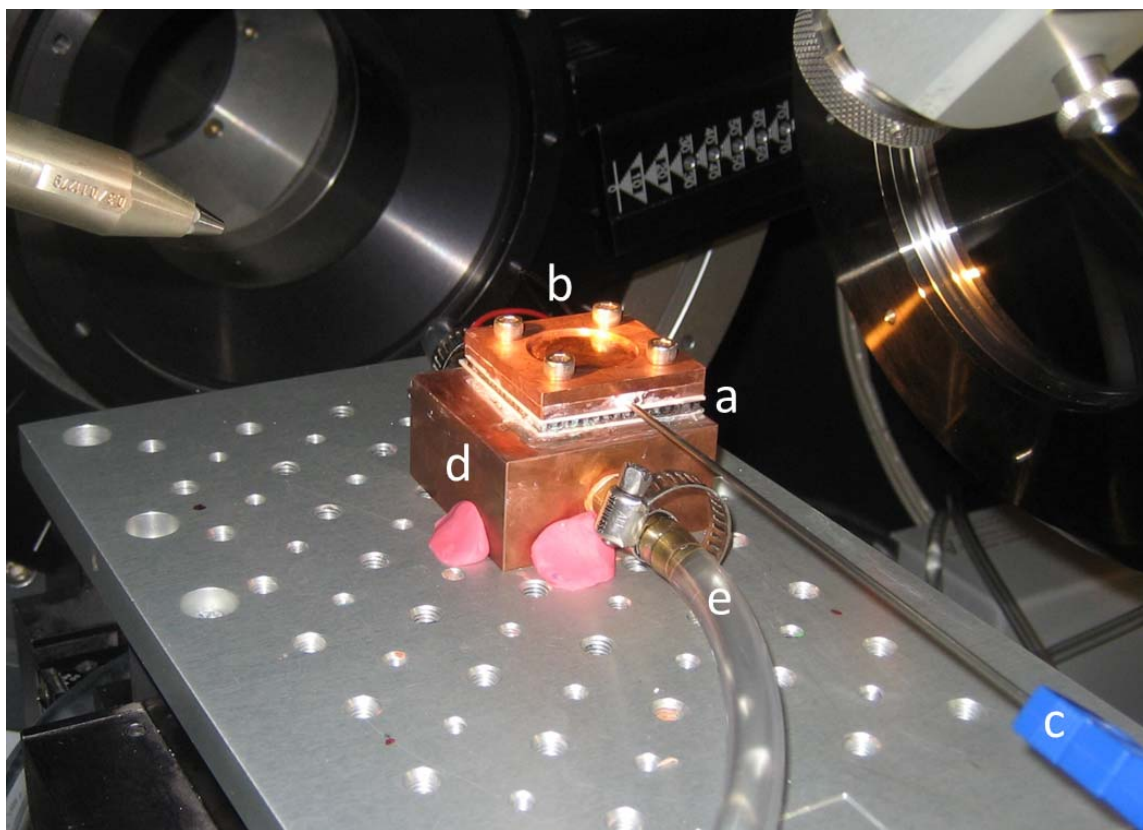
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370 Figure 2.



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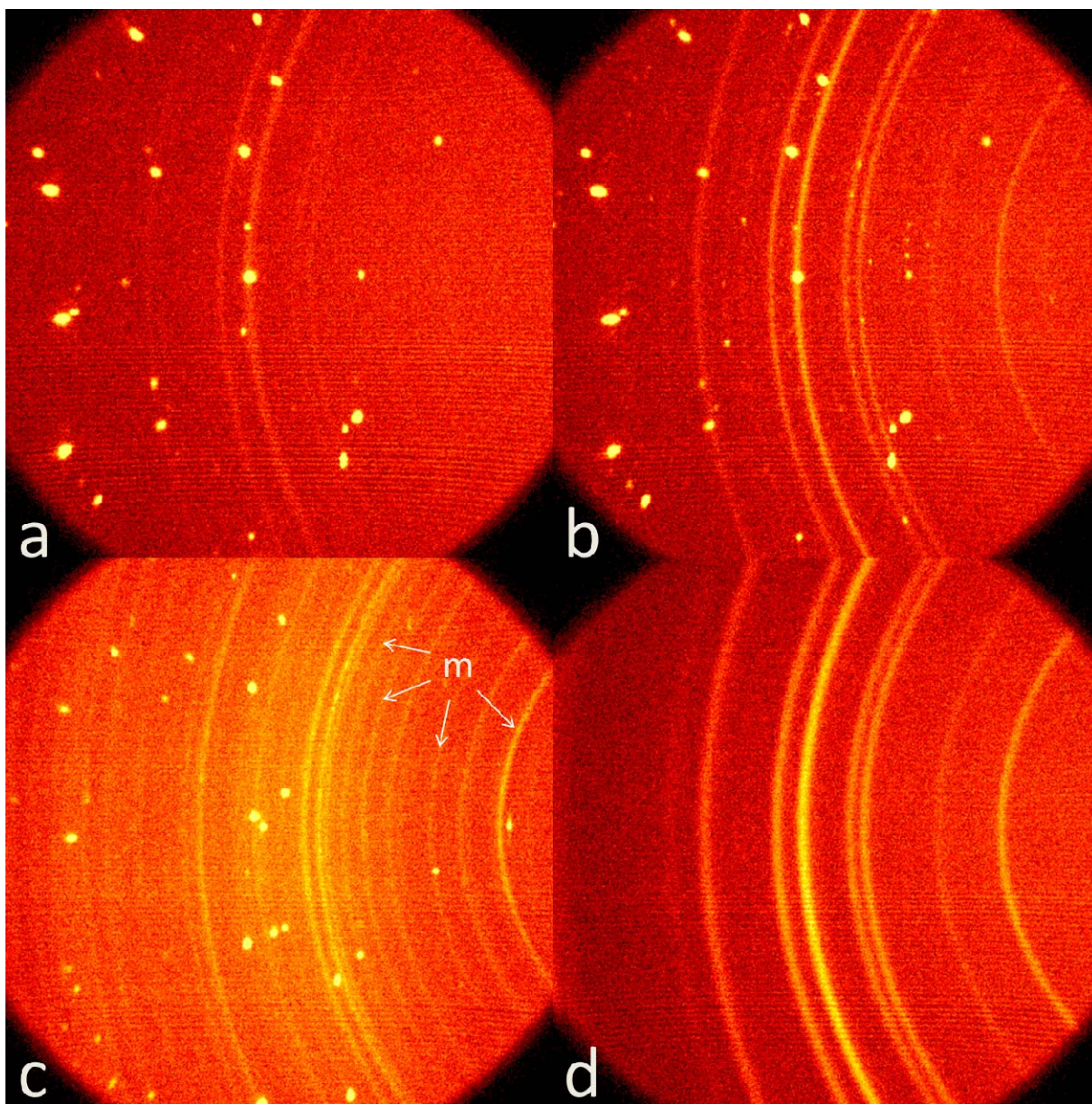
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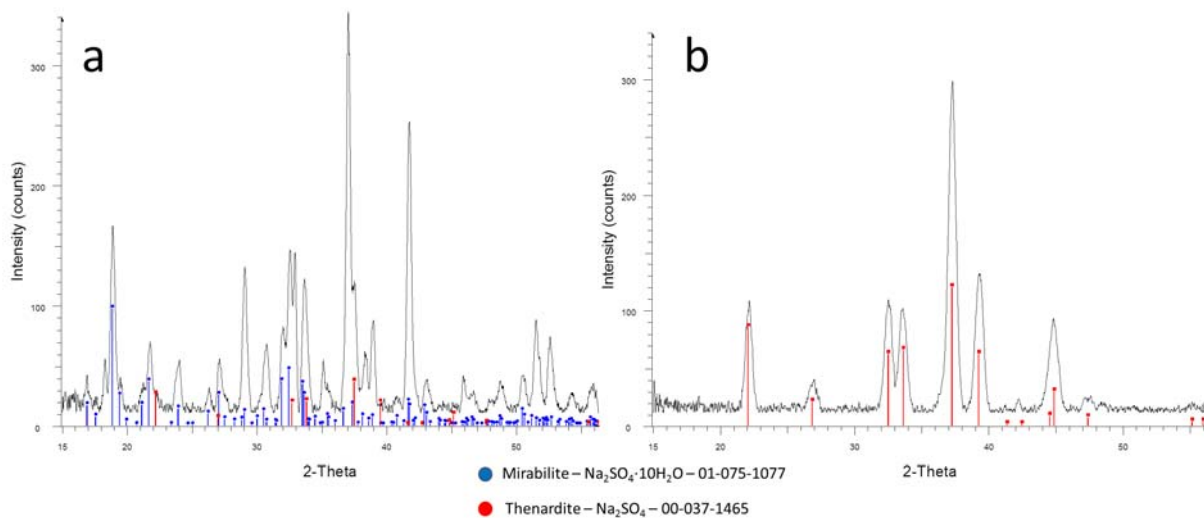
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383 Figure 3.



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390 Figure 4.



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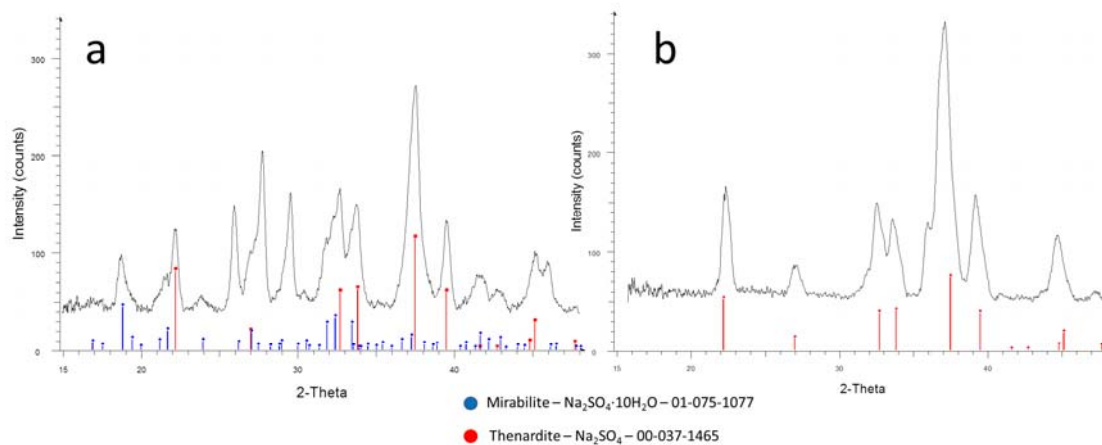
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