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1 **Askival: An Altered Feldspathic Cumulate Sample in** 2 **Gale Crater**

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ABSTRACT

26 Askival is a light toned, coarsely crystalline float rock, which was identified near
27 the base of Vera Rubin Ridge in Gale Crater. We have studied Askival, principally with
28 the ChemCam instrument but also using APXS compositional data and MAHLI
29 images. Askival and an earlier identified sample, Bindi, represent two rare examples
30 of feldspathic cumulate float rocks in Gale crater with >65% relict plagioclase. Bindi
31 appears unaltered whereas Askival shows textural and compositional signatures of
32 silicification, along with alkali remobilization and hydration. Askival likely experienced
33 multiple stages of alteration, occurring first through acidic hydrolysis of metal cations,
34 followed by deposition of silica and possible phyllosilicates at low T and neutral-
35 alkaline pH. Through LIBS compositional analyses and normative calculations, we
36 suggest that an assemblage of Fe-Mg silicates including amphibole and pyroxene, Fe
37 phases and possibly Mg-rich phyllosilicate are present. Thermodynamic modelling of
38 the more pristine Bindi composition predicts that amphibole and feldspar are stable
39 within an upper crustal setting. This is consistent with the presence of amphibole in
40 the parent igneous rocks of Askival and suggests that the paucity of amphiboles in
41 other known Martian samples reflects the lack of representative samples of the Martian
42 crust rather than their absence on Mars.

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1. INTRODUCTION

46 A series of igneous float rocks have been identified in Gale Crater that consist
47 predominantly of basalts and trachybasalts (Cousin et al., 2017; Edwards et al., 2017)
48 but with other examples of evolved bulk rock compositions having total alkali contents
49 up to 14 wt% (Sautter et al., 2015; Schmidt et al., 2013). These samples are likely the
50 result of fractionation of basaltic magma and are reminiscent of intraplate magmatism
51 on Earth (Edwards et al., 2017; Udry et al., 2018).

52 However, one sample - named Askival - is anomalous and represents a light
53 toned, coarsely crystalline float rock which was identified on sol 2018, at the Bressay
54 boulder field locality, near the base of Vera Rubin Ridge (Fig. 1, Fig. 2). The Curiosity
55 Rover was able to obtain MastCam, Mars Hand Lens Imager (MAHLI) and ChemCam
56 Remote Micro-Imager (RMI) imagery at high resolution and color, together with
57 ChemCam Laser Induced Breakdown Spectroscopy (LIBS) and Alpha Particle X-Ray
58 Spectrometer (APXS) compositional data on Askival. Data show an extremely high
59 silica-rich composition that is unlikely to be the result of purely igneous processes.

60 We describe the Askival sample using the rover data with the aim of
61 distinguishing between alteration overprints and its original mineral assemblage and
62 compositional signatures. To do this we compare to previously described samples
63 interpreted as pristine feldspar-rich igneous rocks, in particular the Bindi sample from
64 sol 544 (Cousin et al., 2017; Edwards et al., 2017) (location shown on Fig. 1). Bindi is
65 believed to be a feldspathic cumulate related to the basalt-trachybasalt igneous rocks
66 in Gale. A key part of the investigation of Askival is to reconstruct alteration processes
67 that significantly modified its original mineralogy. We use ChemCam laser spots to
68 analyze the sub-mm scale mineral intergrowths within the rock. We attempt to
69 constrain the primary and secondary mineral assemblages in Askival through
70 comparison of LIBS data with candidate mineral and normative compositions. On the
71 basis of the compositional and textural data informing phase equilibria modelling, we
72 also consider the stability of different mineral assemblages for the mafic phases in
73 Askival. We also discuss the processes that altered Askival. This is an important issue
74 as Askival is the first feldspathic rock found on Mars with such evidence for alteration.
75 Based on the discovery of its possible unaltered counterparts, it has been proposed
76 that feldspar-rich rocks could be a large fraction of the crust in the ancient highlands

77 (Sautter et al., 2015). Feldspathic rocks have been challenging to identify from orbit,
78 due to their paucity of spectral signatures. Their alteration products have been
79 predicted from orbit in specific localities (Ehlmann and Edwards, 2014) but there has
80 been no documentation of partial alteration on this type of rock on the surface of Mars.
81 Askival provides a first view of an alteration history for Martian feldspathic rocks.

82

83 **2. METHODS**

84 **2.1 ChemCam and Laser Induced Breakdown Spectroscopy**

85 The MSL ChemCam is a Laser-Induced Breakdown Spectroscopy (LIBS)
86 instrument with accompanying Remote Micro-Imager (RMI) for target characterization
87 through photographic imaging. ChemCam is the first LIBS instrument employed on a
88 space mission. The motivation for choosing this type of instrument on the MSL mission
89 was the need for a remote sensing instrument that could provide mineralogical data
90 through rock chemistry, improving on previous rover missions, which had carried
91 multispectral imaging cameras and infrared spectrometers for remote sensing and
92 relied on contact instruments for detailed chemical or mineralogical analysis. The
93 ability to gather this type of data through remote sensing carries large benefits to
94 science operations through both faster data collection and expansion of the range of
95 targets that are available as targets for investigation (Maurice et al., 2012; Wiens et
96 al., 2012).

97 The fundamental principle of LIBS is the use of a laser pulse to create a small
98 region of energetically excited plasma on the surface of a target. As the atoms return
99 to the ground state, characteristic photons are emitted which are observed using 3
100 spectrometers across Ultraviolet, Violet, and Visible/Near Infrared (UV-VIO-NIR) and
101 analyzed to determine the chemical content of the target. In order to create a LIBS
102 plasma on a typical Martian target, the required power density was determined to be
103 $>1 \text{ GW/m}^2$ (Maurice et al., 2012), which the ChemCam laser unit is capable of
104 delivering at distances up to several meters, although most analyses are done from
105 the optimal distance of $\sim 3 \text{ m}$ (including Askival which was performed at 2.5-2.7 m, and

106 Bindi which was performed at 2.74 m). The laser uses a wavelength of 1067 nm, with
107 an adjustable repetition rate set at 3 Hz.

108 Each target is analyzed by a raster pattern of observation points which in turn
109 consist of usually 30 laser pulses and corresponding spectral analyses. LIBS plasma
110 light is collected through the ChemCam telescope, which then delivers the incident
111 photons through fiber optic cable into the rover body unit, which contains three
112 Crossed Czerny-Turner spectrometers, each covering a portion of the total spectral
113 range, 240-850 nm (Wiens et al., 2012).

114 The repeated firing of the laser at a specific point on the incident target gradually
115 clears the ubiquitous Martian dust coating (Lasue et al., 2018; Maurice et al., 2016);
116 typically the first five pulses are sufficient to fully remove the dust covering from the
117 target surface (Wiens et al. 2012). These first five pulses are then excluded from the
118 compositional analysis of the observation point. Observation point analyses are
119 averages of the spectra conducted at a given raster point. Raster geometries are
120 typically planned in linear (5 by 1, 10 by 1, and less often 3 by 1 or 3 by 3)
121 configurations. Point footprints range from 350–750 μm in size depending on distance
122 from the rover (Maurice et al., 2016; Wiens et al., 2012). In this paper #1 refers to the
123 first point number in a LIBS raster, #2 to the second point, etc.

124

125 **2.2 Alpha Particle X-Ray Spectrometer**

126 The APXS instrument is a contact science instrument mounted on the end of
127 the Curiosity rover's robotic arm. The APXS uses a radioactive ^{244}Cm source to induce
128 X-ray emission in material contacted by the instrument. This instrument is an improved
129 version of those carried by the Mars Exploration Rovers and Pathfinder lander
130 (Campbell et al., 2012; Gellert and Clark, 2015; Gellert et al., 2006). Subjected to the
131 alpha particle and X-ray flux emitted by the radioactive source, the constituent atoms
132 of a contacted target emit characteristic X-rays, which are detected by the instrument's
133 X-ray detector, recording their energies. The APXS typically measures a sample area
134 1.7cm across, producing an averaged spectrum from all mineral grains in its field of
135 view (Gellert and Clark, 2015).

136 Due to the dust covering present across the Martian surface, the APXS is often
137 used in tandem with the Dust Removal Tool DRT brush to remove the dust (Berger et
138 al., 2020a; Berger et al., 2020b). However, DRT is not possible on small float rocks
139 like Askival and so we will consider the results for the potential to have dust
140 contamination. APXS analyzed Askival with 2 measurements with durations of 12
141 minutes and 15 minutes and 1 overnight measurement with a duration of 5 hours 30
142 minutes on sols 2018-2019. Bindi was not analyzed by APXS.

143

144 **2.3. Mars Hand Lens Imager and ChemCam RMI Imager**

145 The Mars Hand Lens Imager (MAHLI) is an optical imaging instrument mounted
146 on the Curiosity rover's robotic arm. MAHLI's capabilities as a high-resolution imager
147 were developed with the goal of providing images of targets with sufficient detail to
148 allow textural features such as grain size, shape, and structural features to be
149 observed. White and UV light are provided by light emitting diodes in tandem with the
150 imager, providing illumination and observation of target luster in visible light as well as
151 potential observations of fluorescence under UV light (Edgett et al., 2012). MAHLI
152 images are produced using a focus merging process and have a field of view of 1200
153 x 1600 pixels. At the closest operating distance of 2.1 cm, this corresponds to a pixel
154 scale of 14.3 μm , providing enough detail to image sub-millimeter scale textural
155 features and provide accurate depictions of grain shape and size.

156 The ChemCam analysis sequence also collects Remote Micro Imager (RMI)
157 images with a submillimeter resolution ($\sim 90 \mu\text{m}$ at the target distances for Askival)
158 before and after LIBS analyses (Le Mouélic et al., 2015; Maurice et al., 2012). Some
159 of the RMI images we use in this paper are colorized, using Mastcam images for the
160 color (Le Mouélic et al., 2015).

161 MAHLI and RMI images were annotated manually with the assistance of edge
162 detection tools in commercially available image editing software (Adobe Photoshop)
163 in order to categorize and quantify the visible area of different mineral phases.

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2.4 Data Analysis and Calibration of ChemCam Data

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Interpretation of ChemCam data is a multi-stage process. An initial pre-processing stage is required in order to subtract ambient light from the image, remove noise and the electron continuum signal, as well as to apply corrections to the data based on the wavelength, distance to target, and instrument response. Following pre-processing, multivariate analysis techniques are used to derive a set of chemical abundances from the received spectra. Historically, partial least squares algorithms have been used to analyze this information, starting with a PLS2 algorithm used in initial calibration and early rover operations (Clegg et al., 2009; Wiens et al., 2013). More recently, this has developed into a “sub-model” PLS technique (Anderson et al., 2017), which is used in conjunction with independent component analysis (ICA) (Forni et al., 2013) in order to provide a more accurate compositional analysis across the major oxides (Clegg et al., 2017).

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In order to support these analysis techniques, initial calibration of the ChemCam instrument was performed on a set of 69 geochemical standard targets to create a spectral library (Wiens et al., 2013). This library was updated later into the mission in order to better reflect the types of targets found in Gale Crater, expanding to 408 standard targets (Clegg et al., 2017). We use the LIBS analytical accuracy and precision as described in Bedford et al. (2019). Accuracy is determined by the root mean square error product of prediction (RMSEP) for representative geological samples that share abundances similar to those in the calibration dataset (Clegg et al., 2017). ChemCam instrument precision is calculated as the variation observed across the shots that make up the average spectrum for each observation point (Blaney et al., 2014; Mangold et al., 2015). These errors are displayed as error bars on the figures. The optimum distance for accurate LIBS analyses across the range of major elements is about 3 m from target to LIBS telescope (Maurice et al., 2016; Wiens et al., 2021).

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In some cases the unnormalized sum of oxide weights is significantly below or above 100%. This can be the result of statistical variation in the multivariate routine as well as target compositions which differ significantly to the reference compositions

196 used in the analysis. Spectral variation due to distance, matrix effects and laser
197 coupling can further compound this effect and cases where the modelled sum of
198 oxides is significantly below 100% are typically representative of targets with chemical
199 components which are not accounted for by the standard analysis routines (Maurice
200 et al., 2016); of particular relevance to the Askival sample are SO₃ and OH anions.

201

202 2.4.1. LIBS Hydrogen Analyses

203 The hydrogen signal was obtained from the spectra by fitting the Balmer alpha
204 emission peak at 656.6 nm. The processing used for Martian spectra has been
205 described first in Schröder et al. (2015) then revised with laboratory experiments in
206 Rapin et al. (2017b) and summarized here. It includes a multi-Lorentz fitting method
207 to extract the hydrogen peak area from the interference with a nearby carbon peak
208 and a linear baseline removal. The area of the carbon peak (C I at 247.9 nm), related
209 to the breakdown of the atmospheric CO₂, and the area of the oxygen triplet forming
210 a single peak (O I at 778.5, 778.6 and 778.8 nm) also partly related to the atmosphere,
211 are used for normalization of the hydrogen signal. Signal normalization, which here
212 consists of dividing the hydrogen peak area by the carbon peak area, is important to
213 compensate for undesired variations of the LIBS signal due to different parameters
214 (for instance, laser-target coupling, laser focus and distance to target). Normalization
215 to both the carbon and oxygen peaks were proven to be a satisfactory normalization
216 proxy for the hydrogen signal, even though precautions must be taken when
217 comparing different measurement conditions (Schröder et al., 2019). Finally, a
218 correction factor is applied to the normalized signal in order to account for the
219 difference of instrument response between the laboratory and flight model instruments
220 (Rapin et al., 2017b).

221 Rapin et al. (2017a) have shown that the hydrogen LIBS signal can be affected
222 by surface texture roughness effects. The hydrogen signal is enhanced by a factor that
223 varies depending on laser-surface geometry at the LIBS target point when the
224 roughness scale approaches the size of the laser beam, notably near the millimeter
225 scale. This effect is specific to the hydrogen signal and does not affect the emission
226 of other elements (Rapin et al., 2017a). Nevertheless, in spite of the complications of

227 roughness, a consistently observed increase of hydrogen signal cannot be attributed
228 solely to the effect of roughness. Indeed, the roughness effect does not only yield high
229 hydrogen signal points, it also produces points without an enhanced hydrogen signal.
230 Therefore if a group of points on a specific target material all present elevated
231 hydrogen it likely represents real enhanced hydration in the target material.

232

233 2.4.2 Hierarchical Clustering Analysis

234 In addition to the comparison of the abundances by pair of elements, and to
235 take into account the multivariate dimension of the chemical measurements, a
236 clustering analysis was conducted on the 23 ChemCam analyses from Askival. The
237 calculation is based on the ICA products, one of the two components going into the
238 calculation of ChemCam abundances as explained above, using the DIANA divisive
239 hierarchical clustering method (Kaufman and Rousseeuw, 2009). This is implemented
240 in the Cluster package (Maechler et al., 2022) for the statistical software R 3.5.2 (R.
241 Core Team, 2018). Dissimilarity between clusters was determined using Euclidian
242 distance. The main output is a dendrogram tree showing how the data points can be
243 best split in two groups, then each group in two subgroups, and repetitively until all the
244 points are separated. The comparison of each step with the major oxide compositions
245 (see section 2.4.1) indicates which chemical elements drive the division in subgroups.

246

247 2.4.3 Normative Calculations

248 In order to assess the possible mineralogical assemblage of Askival, we have
249 used a normative calculation, starting from the composition of each data point of
250 interest. These calculations are a method of predicting the idealized set of minerals
251 that constitute material in the LIBS point. This methodology is usually applied to largely
252 anhydrous, igneous rocks, via the CIPW technique which gives molar mineral
253 estimates.

254 Here we have used an approach based on the same computational sequence
255 as the CIPW norm (Kelsey, 1965), but have included likely hydrated phases such as

256 a ferrohastingsite amphibole (hornblende), muscovite and have excluded certain
257 minerals that would otherwise compete with these additional minerals for chemical
258 assignment, e.g., orthoclase was replaced in the sequence by muscovite in some
259 calculations, in order to better simulate the Askival composition. We also included the
260 compositions of two known examples of Mg-rich phyllosilicates from the Lafayette
261 Martian meteorite (Hicks et al., 2014). Because our analysis deviated from standard
262 methodology, multiple alternate normative calculations were performed for each LIBS
263 point composition so that the viability of different assemblages could be assessed.

264 As an indicator of the quality of calculations, residuals were calculated for each
265 assemblage, with the goal of keeping residual chemistry below 2 wt%. The normative
266 calculations attempt to assign all available chemistry to crystalline mineral phases,
267 which assumes there is no amorphous phase, despite this being a common product
268 of altered mafic minerals in Gale crater (Rampe et al., 2020). Therefore normative
269 mineral molar abundances are not definitive identifications, but they are a guide to
270 which mineral phases may be present. The normative calculations are documented
271 on a spreadsheet within the supplementary materials to this paper.

272 **2.5. Perple_X Modelling**

273 On the basis of major element compositions and the normative calculations we
274 explore the possible presence of some amphibole content in Askival with phase
275 equilibria modelling to predict stability conditions. Phase diagrams were calculated
276 with the Gibbs free energy minimization software Perple_X 6.9.0 (Connolly, 2005)
277 using the internally consistent thermodynamic data set of (Holland and Powell, 1998;
278 Holland and Powell, 2011). The oxides MnO, Cr₂O₃, P₂O₅ were not included in the
279 calculation because of their low abundance. Halogens were not included due to their
280 absence in available solid solution models. Sulfur was excluded since it is not
281 quantified by the ChemCam data and all sulfur detected by APXS in Askival is
282 interpreted to be associated with low temperature alteration as calcium sulfate. The
283 bulk water content in Martian igneous samples is estimated to be low (e.g. Leshin et
284 al. (1996); Usui et al. (2012, 2015)); however, Martian magmas may have lost water
285 due to partial degassing (e.g. McSween Jr and Harvey (1993)) and the estimated pre-
286 eruptive water content ranges from dry to 2 wt% H₂O (Giesting et al., 2015; McCubbin
287 et al., 2012; McCubbin et al., 2010; Usui et al., 2012, 2015). As a starting composition,

288 we used the Bindi light phase composition (Bindi #5), normalized to 100%, and with
289 the addition of 0.5 wt% of H₂O. Ten wt% of the total iron was assumed to be Fe₂O₃
290 (e.g. Edwards et al. (2017)) which was added to Perple_X by the following existing
291 components: 2 FeO + 0.5 O₂. The starting composition of our calculations is hence (in
292 wt %): 50.5 SiO₂, 0.94 TiO₂, 13.4 Al₂O₃, 2.06 Fe₂O₃, 16.8 FeO, 1.96 MgO, 10.2 CaO,
293 3.38 Na₂O, 0.99 K₂O, 0.5 H₂O, which was then normalized by Perple_X. Phase
294 stability fields were calculated in the temperature range of 500-1000 °C at pressures
295 of 1-2000 bars. The following solid solution models were used: basaltic melt, augite
296 (clinopyroxene), and amphibole (Green et al., 2016); olivine (Holland and Powell,
297 1998); ilmenite (White et al., 2000); spinel (White et al., 2002); and feldspar (Holland
298 and Powell, 2003). The amphibole model uses the formula
299 A[M1]₃[M2]₂[M4]₂[T1]₄(OH)₂Si₄O₂₂ allowing for mixing on the following sites: A = Na, K
300 (and with vacancies); M1 = Mg, Fe²⁺; M2 = Mg, Fe²⁺, Fe³⁺, Al, Ti; M4 = Mg, Fe²⁺, Na,
301 Ca; T1 = Al, Si; OH = O, OH (Green et al., 2016). The composition of the modelled
302 amphibole will hence vary with pressure and temperature. Biotite end-endmembers
303 annite, phlogopite, and eastonite were excluded from the calculation to focus on
304 amphibole formation. Quartz and H₂O were included as pure phases.

305

306 **3. RESULTS**

307 The Askival and Bindi samples described in this paper were investigated at two
308 separate localities on the rover's traverse: Askival was identified at Bressay (sols
309 2018-2020) and Bindi on the Gale plains at the approach traverse to the Kimberley
310 site (sol 544), as shown in Fig. 1. Williams et al. (2020) described the geomorphology
311 of the Bressay area. They noted that Bressay is a roughly elliptical (<200 m²) grouping
312 of heterolithic float rocks forming an apron of material on top of the Vera Rubin Ridge,
313 arranged orthogonally to the long axis of the Vera Rubin Ridge, (Fig. 1). The largest
314 stones are concentrated in an area <3 m², with clast dimensions 15-25 cm across.
315 Float rock types present at Bressay are diverse, with both igneous (one quarter of float
316 rocks), and sedimentary (three quarters of float rocks) (Williams et al., 2020) (Fig. 2).

317 **3.1. TEXTURES**

318 3.1.1 Askival

319 Askival is a partially buried rock of approximately 10 cm visible diameter. The
320 surface is uneven and angular, consisting of light and dark toned phases of up to cm
321 scale (Fig. 3). There is evidence of extensive fracturing throughout the sample, with
322 veins in the light-toned phase that are infilled with darker material (Fig. 3, Fig. 4)

323 Four distinct phases have been identified based on RMI and MAHLI images
324 (Fig. 3, Fig. 4, Fig.5). Phase 1, the most abundant phase is light toned and coarse-
325 grained. Exact grain size at formation is difficult to constrain due to fracturing of phase
326 1, but some examples of single crystals up to 15 mm in length are preserved (Fig. 3,
327 Fig. 4). In addition, examples of triclinic crystal termination are also seen in phase 1
328 (Fig. 3). Phase 2 consists of dark toned patches, which appear as interstitial material
329 between phase 1 grains. The size of the interstitial areas varies significantly, with some
330 areas of phase 2 material extending to over 1 cm in diameter (Fig. 3) while others are
331 less than 1 mm. In MAHLI images (Fig. 3) phase 2 appears to have a fine-grained
332 texture with multiple components of slightly varying dark tone.

333 Two other phases are significantly less abundant: phase 3 is a grey/brown
334 toned, phase that occurs between phase 1 crystals. Phase 4 is a light toned phase
335 (brighter than phase 1) and observed as small veins around phase 2, occupying small
336 interstitial areas. One of the notable features of the Askival texture is the presence of
337 mm-sized and smaller pits (Fig. 3, Fig. 4). These are sometimes seen to be lined with
338 a layer of light brown dusty material. The origin of these and the relationship to
339 alteration are discussed in a later section.

340 Pixel counting of the four phases on MAHLI images (Fig. 4) using Adobe
341 Photoshop indicates that the approximate abundances by visible area of the four
342 phases are as follows: 64% phase 1, 30% phase 2, 5% phase 3 and 1% phase 4.

343 3.1.2 Bindi

344 Bindi is an angular, blocky rock, approximately 5 cm in diameter. The RMI
345 image of Bindi (Fig. 5A) show two distinct phases. Bindi phase 1 consists of subhedral
346 and euhedral light toned ≤ 1 cm crystals, comprising approximately 80% of the rock

347 (Cousin et al., 2017). Crystals appear to be better formed than those seen in Askival
348 phase 1, with clear elongated tabular crystals, in some cases aligned to give a roughly
349 planar fabric. The remaining 20% of the resolvable texture consists of phase 2, a dark
350 interstitial phase. Further subdivision of phase 2 is not possible with the imagery
351 available. The high proportion of one phase and roughly planar fabric are consistent
352 with an origin as a cumulate (Cousin et al., 2017).

353

354 **3.2. ELEMENTAL COMPOSITION**

355 3.2.1 Askival

356 The Askival target was sampled using three separate LIBS rasters: Askival
357 (10x1), Askival_2 (3x1) and Askival_3 (10x1), the positions of which are shown on Fig.
358 5 (B-D). The Askival and Askival_3 rasters were performed with the typical 30 laser
359 analyses per point, whereas Askival_2 used an extended sequence of 150 laser
360 analyses. Of the total of 23 sampling points between the 3 rasters, fifteen have
361 sampled the Phase 1 light-toned phenocrysts, three have sampled the phase 2 dark-
362 toned assemblages, one has analyzed the phase 4 white veins and border of dark
363 material, only one point has sampled the green/brownish phase 3 (as an individual
364 grain, in the border) and three have sampled the interface between phase 1 and 2.
365 Unfortunately, there is no sampling point on the greenish/brownish material located at
366 the border of the dark assemblages.

367 Major oxide compositions are provided in Table 1, from which a clear distinction
368 can be seen between Askival's 4 texturally distinct phases. We also plot these phase
369 compositions, with the exception of phase 4 (discussed below), on a set of Harker
370 plots (Fig. 6) alongside bulk ChemCam data from igneous and sedimentary samples
371 from Gale crater, as well as a meteorite composition and the Adirondack class basaltic
372 composition from Gusev crater for comparison.

373 Phase 1 (Table 1) is highly enriched in SiO₂ (58 - 86.6 wt %) but relatively low
374 in Al₂O₃ (4.9 - 16.6 wt%), CaO (0.5 - 3.9 wt%) and alkalis (<5 wt%). FeO is low (<8.7
375 wt %), as well as MgO (<7 wt%) - but both are variable. The Cl spectral line is observed

376 in all of these points (see supplementary material). Phase 1 also exhibits a stronger H
377 signal compared to all the other phases observed in Askival (Fig. 7). The silica and
378 hydrogen enrichments are close to an opal endmember with 9 wt% H₂O, and some
379 points (Askival_3 #4, #5, #7 and #10) having an even stronger signal, corresponding
380 to around 13 wt % of H₂O, with slightly lower SiO₂ but increases in other elements
381 (Fig. 8) which could be related to the combined presence of other hydrated minerals
382 in this phase.

383 Phase 2 (Table 1) has a variable chemistry. Three points have sampled
384 the interface between phase 2 and phase 1 (Askival #8, Askival_2 #3, Askival_3 #1).
385 The CaO content in these three points is >10 wt % also varies with depth in most
386 cases. These three points enriched in CaO exhibit the S lines and Cl lines (see
387 supplementary material figures 1-3), indicating that as well as a mix of phase 1 and 2
388 these points may also be sampling CaSO₄ at the phase boundary. Askival #1 also
389 contains a high proportion of CaO despite not being visibly placed at the boundary of
390 two phases.

391 Excluding the mixed phase points from our analysis, phase 2 contains a
392 moderate amount of SiO₂ (35.1 – 54.5 wt %), it is relatively poor in Al₂O₃ (<3.4 - 6.8
393 wt %) and MgO (2.1 - 4.6 wt %) but contains a higher FeO content (13.2 - 28.4 wt %)
394 as well as K₂O (0.7 - 1.6 wt %) compared to phase 1. The CaO content varies from 3
395 to 14.2 wt %, with the highest CaO content corresponding to Askival #1.

396 Askival #1 also shows the highest FeO content with the lowest SiO₂ content
397 (<35 wt% - Table 1). Shot-to-shot analysis of Askival #1 (Fig. 9) shows an anti-
398 correlation between SiO₂ and FeO. Askival #6 and #7 are enriched in Ti at 1.3 and 1.4
399 wt % respectively and contain the highest K₂O content for this class (0.9 wt % and 1.6
400 wt %, respectively). These two points also exhibit the CaF molecular line, which means
401 that they contain at least 0.2 wt % F (Forni et al., 2015). Other points from the dark-
402 toned material could contain some F but below or close to the limit of detection.

403 All 6 points that wholly or partially sampled phase 2 are enriched in Cr and Mn
404 compared to other points (see supplementary material). Cr is particularly elevated in
405 Askival #6 and #7, and Mn in Askival #1, #6, #7 and Askival_3 #1. These points are
406 also enriched in Rb compared to phase 1, probably due to their relatively high K₂O

407 content. This dark-toned material shows the lowest H signal among phases sampled
408 on Askival. Nevertheless, this dark-toned material has the same hydration level as
409 previous igneous rocks observed at Gale (Fig. 7).

410 Phase 3 (Table 1) was only sampled by one point (Askival_3 #9, Fig. 5). Phase
411 3 has significantly higher Al₂O₃ compared to phase 2, at 11.3 wt % compared to 6.8
412 wt % and 3.5 wt% in points Askival #6 and #7, respectively. It contains a moderate
413 amount of SiO₂ and CaO. FeO is depleted and lower than that of phase 2 (5.4 wt %)
414 whereas this point shows one of the highest MgO content of the dataset (4.9 wt %).
415 As observed in Askival #6 and #7 (phase 2), the phase 3 K₂O content is relatively high
416 (1.1 wt %). S and Cl were detected, whereas the F signal seems to be observed but
417 is close to the limit of detection (see supplementary material). The H signal is elevated,
418 similar to phase 1, with an equivalent 9 wt% of H₂O (Fig. 7).

419 Phase 4 (Table 1) displays extremely high CaO and low SiO₂, with very low
420 abundances for all other quantified oxides, leading to a lower oxide sum than the other
421 sampled phases. The only point that has sampled the light toned phase 4 material
422 (Askival #2) shows the highest CaO content in the dataset (31 wt%). Analyzing the 30
423 individual laser shots, we can observe that the CaO content increases with depth, up
424 to 35.9 wt% on the last shot. This point also shows the highest S detection observed
425 on Askival (see supplementary material).

426 The independent component analysis dendrogram (Fig. 10) produced from the
427 3 Askival ChemCam rasters separates the phases into groupings which correspond
428 well to the visually and compositionally identified phases described above, with the
429 exception that the light toned phase 1 points are partitioned into two clusters which
430 vary primarily in the extent of their SiO₂ enrichment. One group contains all phase 1
431 points which have SiO₂ contents <70 wt% and the other contains all points with SiO₂
432 content >70 wt%. The former group is also associated in the dendrogram with the
433 single point Askival_3 #9, although a clear compositional distinction is present
434 between the two from CaO content, which is at 7.6 wt% in phase 3 whereas the highest
435 CaO in the associated phase 1 points is 3.8 wt%. There is also raised K₂O (1.1 wt%)
436 and lower Na₂O (2.4 wt%) in the Askival_3 #9 point compared to this set of phase 1
437 points. We will therefore continue to classify the light-toned material in Askival as a

438 single phase (phase 1), but this analysis highlights the extent of variation in silicification
439 of this phase.

440 3.2.2 APXS Analyses of Askival

441 The APXS instrument field of view (~1.7 cm) means that the analyses of Askival
442 represent a mixed composition of the phases identified, with contributions from phases
443 1, 2 and 4. The placement of the APXS analyses avoids any visually identified phase
444 3 material. Taking these analyses as representing an average composition of Askival,
445 we compare them to a modally calculated ChemCam composition (Table 2, Figs 4, 7),
446 which was calculated using the abundances of each phase as measured on MAHLI
447 images (64% phase 1, 30% phase 2, 5% phase 3 and 1% phase 4), and the average
448 composition of each phase across all ChemCam LIBS analyses. Similar calculations
449 were also performed for Bindi, using 85% phase 1 and 15% phase 2 material.

450 Comparing this to the APXS analyses, which measure 61-68 wt% SiO₂ in
451 Askival, implies approximately a 6-10% increase in silica from a modally calculated
452 composition for Bindi, despite Bindi having greater (85%) felsic material in our modal
453 calculations, which would increase the silica abundance in a pristine feldspar cumulate
454 sample.

455 There are, however, some points of disagreement between the APXS analyses
456 and the ChemCam LIBS results. Primarily, APXS analysis includes SO₃, which is
457 excluded from ChemCam analysis. We include some SO₃ in our modal calculations
458 from ChemCam results in the form of phase 4, the calcium sulfate phase, which is
459 added using an assumed pure CaSO₄ molecular formula rather than directly from
460 sample analysis. However, this does not account for the quantity of SO₃ measured by
461 APXS, which is approximately 8% higher across the analyses than in our calculations.

462 Terrestrial experiments with an analogue instrument have shown that the APXS
463 system is prone to overestimating the sulfur component present in sulfate-silicate
464 mixtures by approximately 1.5 times (Berger et al., 2020b), which is of particular
465 relevance in the case of an SiO₂ enriched sample such as Askival. Furthermore, the
466 SO₃ measured by APXS scales proportionally with the CaO content in the three
467 analyses, consistent with a calcium sulfate source. As such, it seems likely that the

468 APXS CaSO_4 measurement is somewhat overestimated in line with Berger et al.
469 (2020b), but still indicates that there may be additional calcium sulfate deposited on
470 the surface of Askival that is not clearly visible in the MAHLI or RMI images. Although
471 the SO_3 is not systematically quantified with ChemCam, this is also consistent with the
472 total weight percentages throughout Askival's LIBS analysis being below 100%.

473 Other major elements have a variety of agreement between APXS and our
474 modal calculations from ChemCam results. Al_2O_3 , MgO and alkali elements are
475 generally close to matching although K_2O varies significantly between APXS analyses
476 and only the lower end of this range is close to the modal calculations.

477 However, our modal calculation predicts significantly higher FeO content in
478 Askival's composition than the APXS analyses show. Comparing the high FeO points
479 in phase 2 to igneous geochemistry from other targets in Gale crater (Fig. 5) we see
480 that Askival #1's FeO content is significantly above the usual range and shot to shot
481 data from this point (Fig. 9) indicates an iron oxide component is present. As there are
482 only four points sampling phase 2 to any extent from ChemCam data, our modal
483 analysis may be overestimating the FeO content due to this outlier composition, as
484 compared to the wide field of view analysis performed by APXS.

485 3.2.3 Bindi

486 Bindi was sampled using a single 5x1 LIBS raster, leading to a less extensive
487 sampling of its chemistry than of Askival. However, all phases identified from RMI
488 imagery are sampled by at least one LIBS point. In contrast to Askival, the equivalent
489 light toned phase 1 in Bindi shows very little variation in SiO_2 (Fig. 6,) or any other
490 major elemental oxides (Table 3), indicating that it did not undergo the same post-
491 formation silicification process. This is reinforced by the near-stoichiometric $\text{An}_{38}\text{-An}_{40}$
492 plagioclase feldspar composition seen in this Bindi phase 1 (Table 3). Target points 3
493 and 5 have higher mafic oxide abundances but retain relatively high Al_2O_3 and in the
494 case of point 3, similar SiO_2 . In combination with the ChemCam targeting RMI (Fig.
495 5A) which shows point 3 located at a boundary between phase 1 and the more mafic
496 phase 2, we classify point 3 as representing a linear combination of the two phases
497 and point 5 as being representative of phase 2 chemistry in Bindi.

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4. INTERPRETATION AND DISCUSSION

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4.1. Mineralogical assessment

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The LIBS technique gives chemical information about the different phases of the target, their mineralogy can be assessed by combining both the chemistry and visual observations. It is usually easier for feldspars as their shape, texture and chemistry are easily distinguished. It is more challenging to distinguish the mafic phases, as they have less distinct shapes and colors in the RMI and MAHLI images. Also, their chemistry can vary significantly among each mineral. In the specific case of Askival, the mineralogical assessment is even more complex as the chemical and visual analyses suggest that this sample has recorded at least one and possibly several hydrous alteration overprints.

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Combining the chemical data with the textural description in Section 3.2, we identify phase 4 as calcium sulfate bearing points (measurement of sulfur with ChemCam presents a number of difficulties, discussed in Dyar et al. (2011), and therefore is not included in our elemental oxide measurements here). Phase 1 has a texture and color, consistent with plagioclase feldspar. However, the variably high SiO₂ content (Fig. 6, Table 1) means that phase 1 does not present a stoichiometric feldspar composition. In addition, the negative correlation between major elements including Al₂O₃ and SiO₂ shown in Fig. 6 trends away from stoichiometric albite-anorthite compositions (Fig. 8). We interpret this as evidence of post-crystallization alteration, which makes Askival's composition harder to interpret from a purely magmatic perspective. We consider alkali remobilization and silica enrichment in more detail in a later section.

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Half of the phase 2 points are enriched in Ca and have an S detection. These points were located on the border of the dark-toned material, which means they could correspond to a mixture between the phase 1, phase 2 and phase 4. Here we will focus our mineralogical assessment on points that are not mixed with a CaSO₄ component.

527 Phase 2 has a more variable chemistry than phase 1, but broadly consists of
528 more FeO_T and MgO-rich minerals. SiO₂ varies by almost 20 wt% across the 3 points
529 classified as phase 2, correlating positively with increased H₂O peak area (Fig. 7). It
530 is unclear if this hydration is native to the mineral compositions or is the result of the
531 same post-formation alteration event that increased the silica content of phase 1. Point
532 #1 in the Askival raster has the lowest SiO₂ content of phase 2. Examination of the
533 individual LIBS shots on this point reveal higher FeO and CaO contents in early shots,
534 with FeO being anti-correlated with SiO₂ indicating the presence of iron oxide and
535 calcium sulfate grains in the shot area.

536 Three phase 2 points do not seem to be mixed with the highly altered phase 1
537 or sulfates: Askival #1, Askival #6 and Askival #7. However, their chemistry does not
538 match with any pure mafic mineral such as olivine (SiO₂, CaO, Al₂O₃ and alkalis are
539 all too high) or pyroxenes (Al, Ca, and alkalis are too high, Mg is too low relative to
540 Fe). MAHLI images (Fig. 3, Fig. 4) also reveal some variation in the tone across
541 regions identified as phase 2, supporting interpretation as a fine-grained mixture of
542 mafic minerals.

543 The presence of amphiboles or clays is a possibility suggested by detection of
544 F in these points, as well as their relatively high Al and K contents. The hydration state
545 of these two points is relatively low (compared to the light-toned material), but still
546 around 2 wt % H₂O, which is consistent with such phases. Clays and amphiboles cover
547 such a wide variety of compositions that it is not possible to test all the possibilities.
548 Several normative calculations were made, taking into account different types of
549 phases: oxides (ilmenite), feldspars using albite and/or orthoclase, pyroxenes with
550 wollastonite, ferrosilite and enstatite, saponite (composition as observed in nakhlite
551 meteorite alteration veins, see Hicks et al. (2014)), amphibole (Ca-Mg and Ca-Mg-Fe
552 hornblende, actinolite) and quartz. Results are listed in Table 4. The best match was
553 obtained using a mixture dominated by pyroxenes (ferrosilite, wollastonite, enstatite –
554 45 mol% for Askival #6 and 85 mol% for Askival #7), albite (5 and 4 mol% resp.),
555 ilmenite (3 mol%), saponite (4 and 0 mol% resp.) and some quartz (44 mol% for
556 Askival #6 and 8 mol% for Askival #7). The presence of saponite is consistent with
557 the detection of F in #6. Phase 3, which was only sampled in one LIBS point, has a
558 unique chemistry compared to the other phases, with intermediate SiO₂ and FeO_T,

559 high Al₂O₃, CaO and K₂O. A similar approach as for phase 2 was performed by doing
560 some normative calculations (Table 4).

561 Askival_3 #9 is a distinct data point within phase 3. This type of material has
562 been observed around most of the dark material, but also as a whole – that is the case
563 for Askival_3 #9, but we have sampled the border only by LIBS. From the images (Fig.
564 3, Fig. 4), this type of texture and morphology suggests that phase 3 could be a result
565 of the alteration of the dark material phase 2. As noted above, these dark phases in
566 Askival #6 and #7 have shown to be a mixture, likely including pyroxenes.

567 Askival_3 #9 has an Al₂O₃ content of 11.1 wt%, higher than either Askival #6
568 (6.8 wt%) or #7 (3.5 wt%), whereas its FeO_T content is significantly lower (5.4 wt%
569 compared to 13.2 wt% and 19.6 wt% respectively). As such, our normative
570 calculations of this observation point could be a mixture of silica (66.6 mol%),
571 wollastonite (17.5 mol%), hornblende (2.4 mol%), albite (7.9 mol%), saponite (3.8
572 mol%) and ilmenite (1.9 mol%).

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574 **4.2 Aqueous Alteration**

575 Numerous compositional features of Askival are beyond the expected
576 chemistry for purely igneous production of a feldspathic cumulate, as exhibited by
577 Bindi. The silicification of the primary feldspar phase, leaching of aluminum and alkalis
578 and remobilization of magnesium, as well as the increased hydration signal, point to
579 extensive alteration under aqueous conditions. Elevated temperatures trigger the
580 transformation of opal into crystalline, anhydrous quartz (Williams et al., 1985), even
581 with little to no burial (Lynne et al., 2005). Therefore, silicification of Askival most likely
582 did not occur in high temperature conditions. Instead, it formed at relatively low
583 temperatures as evidenced by the amount of water found in the altered light-toned
584 phase at near opal composition (Fig. 7).

585 The alteration seen in Askival bears some geochemical similarity with alteration
586 halos observed in lacustrine mudstone of the Murray sedimentary unit and overlying
587 aeolian sandstone of the Stimson sedimentary unit. At the Marias Pass, Williams and

588 Bridgr Basin locations, silica-enriched material is associated with fractures that cross
589 the unconformity between the two units (Frydenvang et al., 2017). Yen et al. (2017)
590 and (Hausrath et al., 2018) concluded that the presence of these silica-rich fracture-
591 associated halos crosscutting bedding in both the Murray and Stimson units are the
592 result of a multiple-stage alteration process that both passively (through cation
593 leaching) and actively (through precipitation of dissolved silica) enrich the silica
594 content of the constituent minerals. This process would have involved an initial stage
595 of interaction with acidic fluids, with changing pH into neutral to alkaline conditions
596 during precipitation of silica. Neutralization of acidic fluids through contact with basaltic
597 rock types common to Mars has previously been suggested as a result of acidic
598 weathering in Gusev crater (Hurowitz et al., 2006; Zolotov and Mironenko, 2007) and
599 Gale crater (Rampe et al., 2017; Yen et al., 2017).

600 This occurrence of late, and localized, acidic leaching and remobilization of
601 silica within Gale is a potential route for the Askival float sample to have been silicified.
602 However, unlike the sedimentary outcrops studied in these works, there is no pristine
603 material directly available for comparison to Askival, with Bindi providing our primary
604 example of a possibly similar pre-alteration rock. Furthermore, geochemical trends in
605 these sedimentary alteration halos indicate that the feldspar grains are more resilient
606 to the silicification process than mafic minerals (Bedford et al., 2020; Hausrath et al.,
607 2018).

608 The shot-to-shot variation on points in the light-toned phase 1 reveals the
609 complexity of the mixtures observed with several points deviating from a simple opal-
610 feldspar binary mixture, defining a trend which is lower than the trachybasalt Na_2O ,
611 K_2O , Al_2O_3 compositions on the low SiO_2 end (Edwards et al., 2017) and indicating the
612 possibility of Mg-enriched phases (Fig. 11). In the absence of a pristine feldspar
613 composition in Askival the exact remobilization of these elements cannot be quantified,
614 but comparison to Bindi as an equivalent pristine cumulate sample as well as the range
615 of feldspar compositions throughout Gale crater indicates that Askival's feldspar phase
616 would have lost about 25% of its alkali and Al_2O_3 content by feldspar dissolution (Fig.
617 8). Although the proportion of silica enrichment is highly heterogeneous at near mm-
618 scale as observed by the spread of points along the silica trend, an average 30%
619 increase in silica along with minor Ca-sulfate recreates the phase 1 composition

620 observed by ChemCam. The extensive leaching of aluminum and alkalis from phase
621 1 is also consistent with acidic alteration (Chardon et al., 2006; Oelkers et al., 1994),
622 which has been hypothesized to be present during the late Noachian and early
623 Hesperian (Berger et al., 2009; Treguier et al., 2008).

624 Combined Mg and H enrichment specifically on the low SiO₂ end of phase 1
625 (Fig. 7, Fig. 8) indicates the presence of an Mg-bearing secondary mineral phase in a
626 mixture with the silicified feldspars. Clay minerals typically precipitate from solution
627 following feldspar dissolution, forming kaolinite from leached Al and alkali ions (Yuan
628 et al., 2019) and in some cases a further phase of Mg-rich smectite (Zhu et al., 2006).
629 In the case of Askival, we hypothesize that an Mg-enriched fluid, either from dissolution
630 of surrounding mafic phases during the acidic alteration or transported from
631 elsewhere, led to the precipitation of an Mg-phyllsilicate secondary mineral phase on
632 the surface of phase 1. This could have occurred concurrently with the later
633 precipitation of Si as the pH of the fluid evolved into neutral to alkaline conditions.

634 Phases 2 and 3 are likely relicts of mafic phases that were also partially altered.
635 Whereas the light-toned crystals are silicified and present a composition consistent
636 with an intimate mixture of feldspars and Mg-phyllsilicates, the surrounding other
637 phases were in places entirely dissolved as observed with the voids filled by light-
638 toned Ca-sulfate (Fig. 4). In the dark-toned phase 2 the high FeO_T point (28.3 wt.%)
639 shows shot-to-shot Fe to be negatively correlated with silica (Fig. 9), evidence that the
640 iron may be present as Fe-oxide mixed with relict silicates or silica deposits.

641 Askival also contains visible small fills of calcium sulfate (phase 4). Such
642 precipitates are common within Gale crater, suggesting that Askival was likely
643 subjected to the same late-stage alteration identified elsewhere in Gale during the
644 Curiosity traverse and, hypothesized to have been the result of late-stage dissolution
645 of earlier sulfate deposits (Schwenzer et al., 2016).

646 In summary, we hypothesize that the alteration of Askival began with hydrolysis
647 of Al, K, Na from the feldspar phase 1, and of Mg from the mafic phase 2, under acidic,
648 conditions. Following this, precipitation of Mg-bearing clay minerals and additional
649 silica onto the relict feldspar surfaces occurred, producing a surface layer that is
650 heavily enriched in SiO₂ and has a thin coating of Mg-phyllsilicate. This stage

651 occurred under low temperatures, preserving the hydration state of the high SiO₂ layer,
652 and may have been driven by an influx of neutral to alkaline Si-enriched groundwater,
653 as observed in the diagenetic silica-enriched halos at Marias Pass (Frydenvang et al.,
654 2017). Finally, Askival was altered by a sulfur-rich fluid, precipitating the phase 4
655 calcium sulfate into the voids left behind by prior dissolution, as is seen throughout
656 Gale crater (Schwenzer et al., 2016). This hypothesis is supported by the textural and
657 geochemical measurements made of Askival, but without an *in situ* example of pre-
658 alteration minerals, further constraint of the conditions of alteration cannot be made.

659 The other float samples at the Bressay boulder site do not feature the same
660 increase in hydration signal as Askival across any of their ChemCam analysis points
661 (Fig. 7), indicating that the alteration of Askival took place prior to its emplacement at
662 Bressay.

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665 **4.3. Amphibole in Askival?**

666 Our normative calculations and some point analyses such as Askival #1 (once
667 FeO and CaSO₄ components have been removed) suggest that there may be an
668 amphibole component within the mafic phases. The exact composition of an
669 amphibole is difficult to identify. In our normative calculations (Table 4), we have used
670 a Ca-Mg hornblende. Phase 3 could also be mainly secondary amphiboles formed
671 from alteration of phase 2 pyroxenes. This seems consistent with the fact that the relict
672 plagioclase grains observed in Askival are also altered by a silicification process. We
673 explore the possible presence and significance of amphibole further with calculated
674 phase relationships relevant to calculated phase stabilities for the Bindi composition
675 at a fixed H₂O content of 0.5 wt %. As mentioned in 2.4.3, normative identification of
676 mineral phases is not definitive, and our modelling is performed to support the possible
677 presence of amphibole in the mafic phase of Askival.

678 The phase diagram in Fig. 12 covers the range 1-2000 bars and 500-1000 °C,
679 consistent with an upper crustal setting. The predicted mineral assemblages are

680 dominated by feldspar and clinopyroxene at most conditions, with amphibole stable in
681 the lower temperature range, and melt towards higher temperatures. Feldspar is the
682 most abundant phase with close to 60 vol. % in the field where neither amphibole nor
683 melt are stable but decreases in proportion with increasing melt towards higher
684 temperatures (~20 vol. % at the highest temperatures). Feldspar at temperatures
685 below the solidus is albite rich (An_{50-60}), while the anorthite component increases with
686 increasing temperature and melt formation due to its higher solidus.

687 Clinopyroxene is present in amounts of 20-30 vol% enriched in diopside
688 component (X_{Di} . 0.7-0.8). Up to 10 vol% are olivine with $X_{Fa} > 0.8$. Amphibole is stable
689 in the lower temperature range up to 740 °C at 2000 bars. At pressures above 1400
690 bars, amphibole coexisting with melt is the most Fe^{3+} rich (Fig. 13) and is similar in
691 composition to hastingsite (Hawthorne et al., 2012; Locock, 2014). Close to the
692 solidus, modal amounts of amphibole are in the range of 2-7 vol%. Melting starts at
693 temperatures of ~680 °C at 2000 bars and >800 °C at 1 bar. Spinel, ilmenite, and
694 quartz are accessory phases with <2 vol%.

695 Uncertainties in the modelling derive from uncertainties in the thermodynamic
696 data and solid solution models. The influence of oxides (MnO , Cr_2O_3 , P_2O_5) not
697 considered in the calculation is estimated to be relatively small. Halogens, however,
698 which are currently not included in available solid solution models, have shown to be
699 an important component in Martian meteorites (Filiberto et al., 2014; Giesting and
700 Filiberto, 2016) and amphibole would be the dominant host for Cl and F at conditions
701 considered here (Kendrick, 2019). Experimental and analytical studies have
702 concluded that Cl is preferentially retained in the fluids and therefore more
703 incompatible compared to H_2O and F (e.g. Fabbrizio et al. (2013); Hecker et al. (2020);
704 Kendrick (2019)), which are therefore expected to have more influence on amphibole
705 stability.

706 While the water content is fixed to 0.5 wt% in the calculations, higher or lower
707 values do not significantly influence phase stability fields shown in Fig. 12 but may
708 change the phase proportions of hydrous phases such as amphiboles and melt. To
709 focus on amphibole formation, biotite end members have been excluded from the
710 calculations. Thermodynamically, biotite is a stable phase at temperatures close to the
711 solidus and amphibole may therefore not be the first OH-bearing phase to form from

712 melt. However, data and observations of the rock samples do not suggest the
713 presence of biotite, justifying its exclusion from the models.

714

715 **4.4. Askival-Bindi: Differentiation and Alteration of the Gale Crust**

716 The Gale Crust reveals evidence in its igneous float rocks and conglomerate
717 clasts for low pressure crystal fractionation, including cumulates, from an Adirondack-
718 type melt (Edwards et al., 2017). This may also represent early feldspar-enriched
719 crust on Mars (Sautter et al., 2015). The unaltered Bindi cumulate sample is part of
720 this igneous series. The Askival sample has a more complex history, principally its
721 overprint of silicification and hydration, probably occurring during its residency on the
722 surface of Gale Crater or within its near-surface regolith. Despite that late, intense
723 alteration, particularly of the plagioclase, Askival has preserved a coarse cumulate
724 texture. Although not as clearly defined as the planar cumulate texture in Bindi, the
725 similarity of relict plagioclase alkali ratios (even taking into account some
726 remobilization) to those of the Gale igneous suite (Edwards et al., 2017; Payré et al.,
727 2020) suggest that Askival is an igneous cumulate sample rather than a fragment of a
728 hydrothermal vein.

729 Amphiboles on Mars are below the detection limits from orbital spectroscopy
730 (Bandfield, 2002) and are absent from mineral assemblages reported from surface
731 missions. However, a lack of orbital detection may not necessarily imply the complete
732 absence of amphiboles. Amphiboles may not be detected due to their relatively low
733 abundance, or because VNIR spectra are typically dominated by one or two phases,
734 thus contributing non-linearly to the observed spectra (Ehlmann and Edwards, 2014;
735 Ehlmann et al., 2011). This observed lack of amphiboles is in contrast to Earth, where
736 amphiboles are common in both alteration and magmatic mineral assemblages
737 (Filiberto et al., 2019). However, based on our phase equilibria model, amphibole may
738 be a significant Mars crustal reservoir of volatiles after all, their perceived absence
739 being a product of our as yet limited sampling of the Mars lithosphere by meteorites
740 and landers.

741 Feldspathic igneous float rocks have been previously observed at Gale and
742 hypothesized to form a significant fraction of the crust on Noachian Mars which was
743 later buried by more basaltic upper volcanic deposits (Sautter et al., 2015). If these
744 feldspathic materials were part of the early crust, it is possible that a significant fraction
745 was not directly buried but exposed to surface or near surface conditions for some
746 time. While Bindi likely represents unaltered buried feldspathic rock, Askival provides
747 a first example of an altered feldspathic rock by fluids that led to the partial dissolution
748 of both felsic and mafic minerals, and the possible formation of Mg-phylosilicates
749 (Peretyazhko et al., 2016). Askival represents a possible feldspathic bedrock near-
750 surface exposure partially altered during that time in Mars history.

751

752 **5. CONCLUSIONS**

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754 1. Askival and Bindi represent two rare examples of feldspathic cumulate float
755 rocks in Gale crater with >65% relict plagioclase. Bindi appears unaltered and provides
756 a pre-alteration comparison for Askival which shows textural and compositional
757 signatures of aqueous alteration and low temperature silicification.

758 2. Askival's alteration occurred through a post-formation alteration process, in
759 which localized acidic fluids led to the dissolution and leaching of aluminum and alkali
760 cations from the feldspar phase, followed by precipitation of dissolved silica as the
761 conditions changed to a more neutral pH. This occurred at low temperatures, allowing
762 for the silica-enriched phase to remain hydrated. Additional silica was likely
763 transported to Askival via neutral to alkaline fluids such as those related to alteration
764 halos at Marias Pass. The acidic fluids also partially dissolved the mafic phase 2
765 mineral assemblage, remobilizing cations which were incorporated into phyllosilicate
766 secondary minerals and creating voids which were later infilled with Ca sulfate during
767 a more recent late-stage alteration event, coinciding with similar sulfate precipitation
768 throughout the crater.

769 3. A pre-silicification mafic assemblage, interstitial to the relict plagioclase
770 cumulate grains, is present in Askival. Through a combination of LIBS compositional

771 analyses and normative calculations, we suggest that an assemblage of Fe-Mg
772 silicates including amphibole and pyroxene, Fe oxides and possibly phyllosilicates
773 may be present although we could not exclude other secondary phases due to the
774 general evidence for alteration in Askival.

775 4. Phase equilibria modelling of the Bindi composition (which has not been
776 affected by the later silicification) predict that amphibole and feldspar are stable within
777 an upper crustal setting. This is consistent with the possible presence of amphibole in
778 the parent igneous rocks of Askival and the Martian crust.

779 5. Compared to Bindi, Askival possibly represents a fragment of an altered
780 feldspathic bedrock at or near the surface in the late Noachian or Hesperian when
781 aqueous alteration was widespread on Mars.

782

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787 aboard Curiosity. RCW acknowledges NASA contracts # NNH15A35I and
788 NNH13ZDA018O. CCB acknowledges funding from USRA. We thank the engineering
789 and science teams of Mars Science Laboratory for the successful operations and
790 acquisition of ChemCam and other data.

791

Table 1: Askival ChemCam oxide measurements

Raster	Point	Phase	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	FeO _T (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	Total (wt%)
Askival	1	2	35.1	0.62	6.7	28.3	2.1	14.2	1.3	0.73	89.2
Askival	2	4	0.1	0.2	0.6	6.3	2.3	30.8	0.7	n.d.	41.1
Askival	3	1	63.3	0.72	13	8.7	2.9	3	4.0	0.92	96.5
Askival	4	1	86.6	0.56	5	n.d.	2.1	0.4	1.0	0.1	95.8
Askival	5	1	67.1	0.59	11.5	1.7	4.4	2.9	3.5	0.45	92.0
Askival	6	2	54.5	1.44	6.8	13.2	2.4	3	2.1	1.57	85.0
Askival	7	2	49.1	1.31	3.4	20.1	4.6	9.2	1.6	0.93	90.3
Askival	8	Interface	42.6	0.81	8.8	10.5	2.5	19	1.7	0.78	86.7
Askival	9	1	74.1	0.6	9.4	0.4	2.7	2.5	2.0	0.28	91.9
Askival	10	1	77.4	0.71	8.6	0.4	2.5	1.6	2	0.27	93.4
Askival_2	1	1	78	0.55	10.1	0.2	1.9	2	1.7	0.13	94.6
Askival_2	2	1	70.3	0.64	10.1	1.5	3.6	2.7	2.8	0.28	91.8
Askival_2	3	Interface	32.6	0.89	11.5	8.3	2	23.3	2.4	0.44	81.3
Askival_3	1	Interface	54.5	0.82	6.8	14.3	3.4	9.9	2.3	0.85	92.9
Askival_3	2	1	59	0.74	16.2	5.1	6.7	3.4	3.9	0.73	95.8
Askival_3	3	1	73.2	0.37	10.5	0.6	3.4	2.2	2.2	0.28	92.8
Askival_3	4	1	70.4	0.32	10.3	1.6	4.5	2	2.1	0.48	91.7
Askival_3	5	1	79.8	0.47	7.3	0.3	3.2	1.3	1.4	0.08	93.8
Askival_3	6	1	75.6	0.56	8.7	0.5	3.7	1.8	1.9	0.27	93.0
Askival_3	7	1	76.8	0.71	6.7	1.3	3.7	1.3	1.7	0.22	92.4
Askival_3	8	1	79	0.54	9.8	0.1	1.9	1.8	2.0	0.29	95.5
Askival_3	9	3	58.2	0.75	11.1	5.5	5.3	7.6	2.5	1.1	92.0
Askival_3	10	1	64.4	0.63	14	2.6	4.4	3.8	3.3	0.85	94.0
Reference Compositions											
Plagioclase An ₄₀	-	-	58.0	-	26.5	-	-	8.3	6.33	0.87	100
Ferrohastingsite	-	-	36.4	-	10.3	37.0	-	11.3	3.13	-	98.18

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Table 2: Askival APXS oxide measurements

	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	FeO _T (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	SO ₃ (wt%)	Total (wt%)
Askival_raster1 ^a	66.4 ± 1.0	0.46 ± 0.05	7.8 ± 0.3	3.3 ± 0.1	3.2 ± 0.2	5.3 ± 0.1	2.9 ± 0.2	1.0 ± 0.1	7.7 ± 0.3	97.9
Askival_raster2 ^a	61.8 ± 0.6	0.39 ± 0.02	9.2 ± 0.2	3.4 ± 0.1	2.4 ± 0.1	6.3 ± 0.1	3.3 ± 0.1	1.6 ± 0.1	9.7 ± 0.1	98.0
Askival_raster3 ^a	61.1 ± 1.0	0.52 ± 0.05	8.3 ± 0.3	4.0 ± 0.1	3.0 ± 0.2	6.3 ± 0.1	3.1 ± 0.2	1.2 ± 0.1	9.8 ± 0.3	97.3
Calculated modal composition	68.6	0.80	9.4	8.3	3.7	5.6	2.4	0.7	0.61	100

^a Gellert, R., Mars Science Laboratory Alpha Particle X-Ray Spectrometer RDR Data V1.0, MSL-M-APXS-4/5-RDR-V1.0, NASA Planetary Data System, 2013.

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Table 3: Bindi ChemCam oxide measurements

Target	Point	Phase	SiO ₂	TiO ₂	Al ₂ O ₃	FeO _T	MgO	CaO	Na ₂ O	K ₂ O	Total
			(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
Bindi	1	1	58.3	0.68	23.3	0.1	0.7	7.1	6.1	0.59	96.8
Bindi	2	1	56.9	0.7	23.9	0.1	0.7	8.6	6.7	0.51	98.1
Bindi	3	1 & 2	56	0.89	18.1	9.9	1.4	7.5	4.2	1.6	99.6
Bindi	4	1	58.5	0.68	23.2	0.2	0.4	7.7	6.4	0.75	97.9
Bindi	5	2	46.3	0.86	12.3	17.1	1.8	9.4	3.1	0.91	91.8

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Table 4: Mafic phase normative compositions

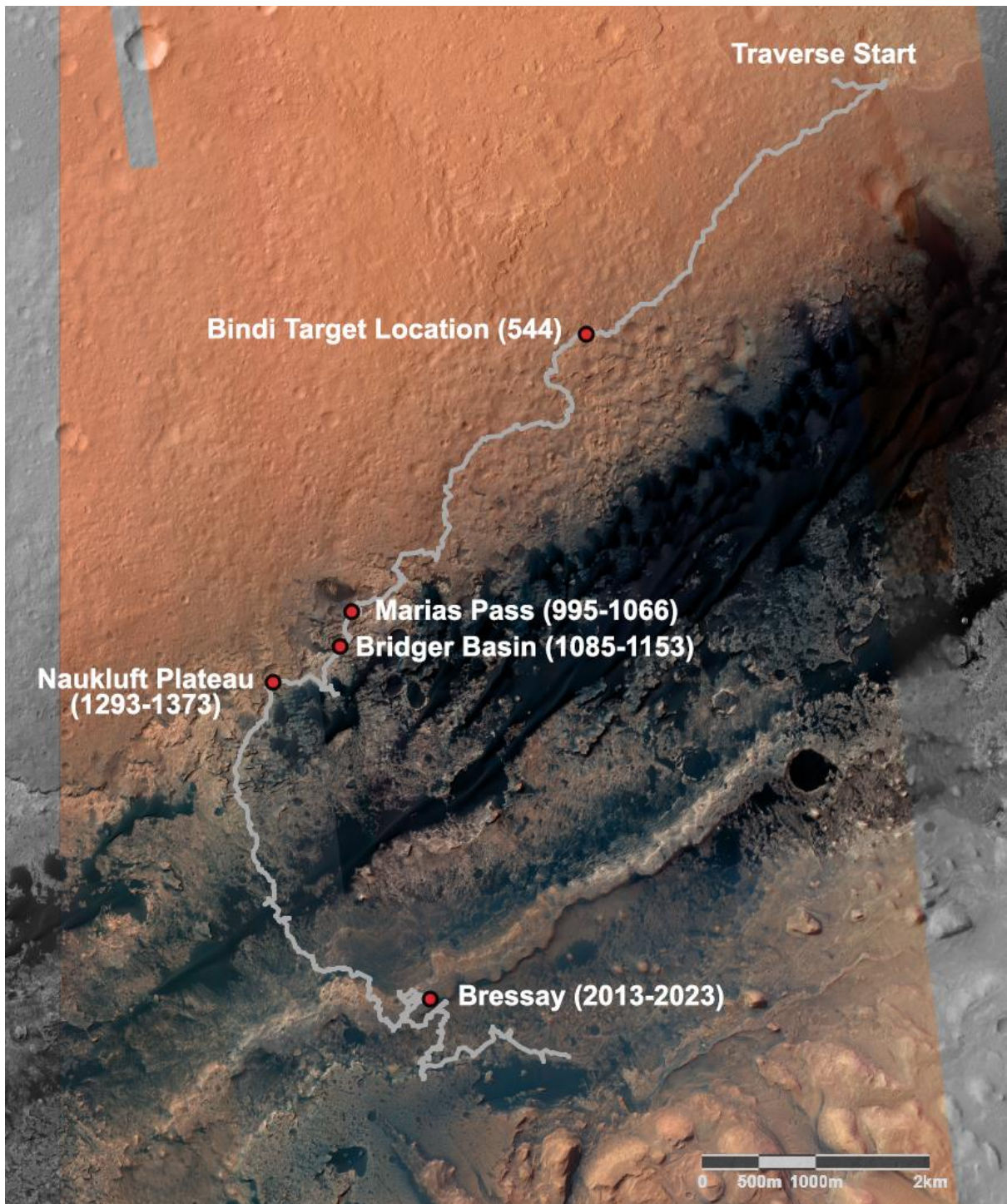
Target	Point	Ilm ^a	Ab ^a	Sap ^a	Hbl ^a	Fs ^a	Wo ^a	Qz ^a	Mag ^a	En ^a	Or ^a	An ^a	Msc ^a
		(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)
Askival	#1	1.2	3.3	2.7	1.1	n.d	33.3	n.d	58.4	n.d	n.d	n.d	n.d
Askival	#6	2.9	5.5	3.5	n.d	26.7	8.6	43.6	n.d	9.2	n.d	n.d	n.d
Askival	#7	2.6	4.1	n.d	n.d	40.3	26.3	8.4	n.d	16.8	1.6	n.d	n.d
Askival_3	#9	1.9	7.9	3.8	2.4	n.d	17.5	66.6	n.d	n.d	n.d	n.d	n.d
Bindi (a) ^b	#5	2.4	11.1	n.d	1.8	36.9	29.7	n.d	13.4	2.5	n.d	n.d	2.1
Bindi (b) ^b	#5	2.1	9.8	n.d	n.d	27.3	20.9	n.d	17.3	8.8	1.9	12.0	n.d

^aInternational Mineralogical Association abbreviations from (Whitney and Evans, 2010)

Bindi (a) calculation was performed using hornblende and muscovite endmembers in place of orthoclase and anorthite, which Bindi (b) includes.

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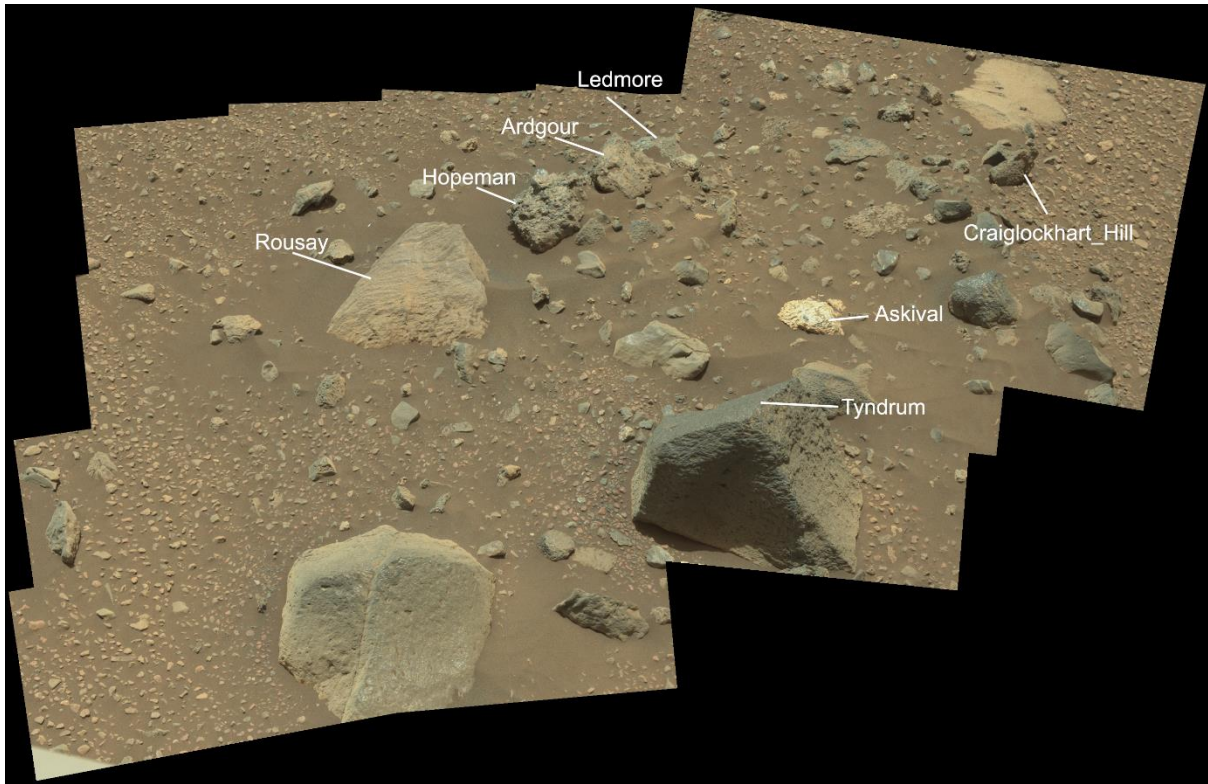
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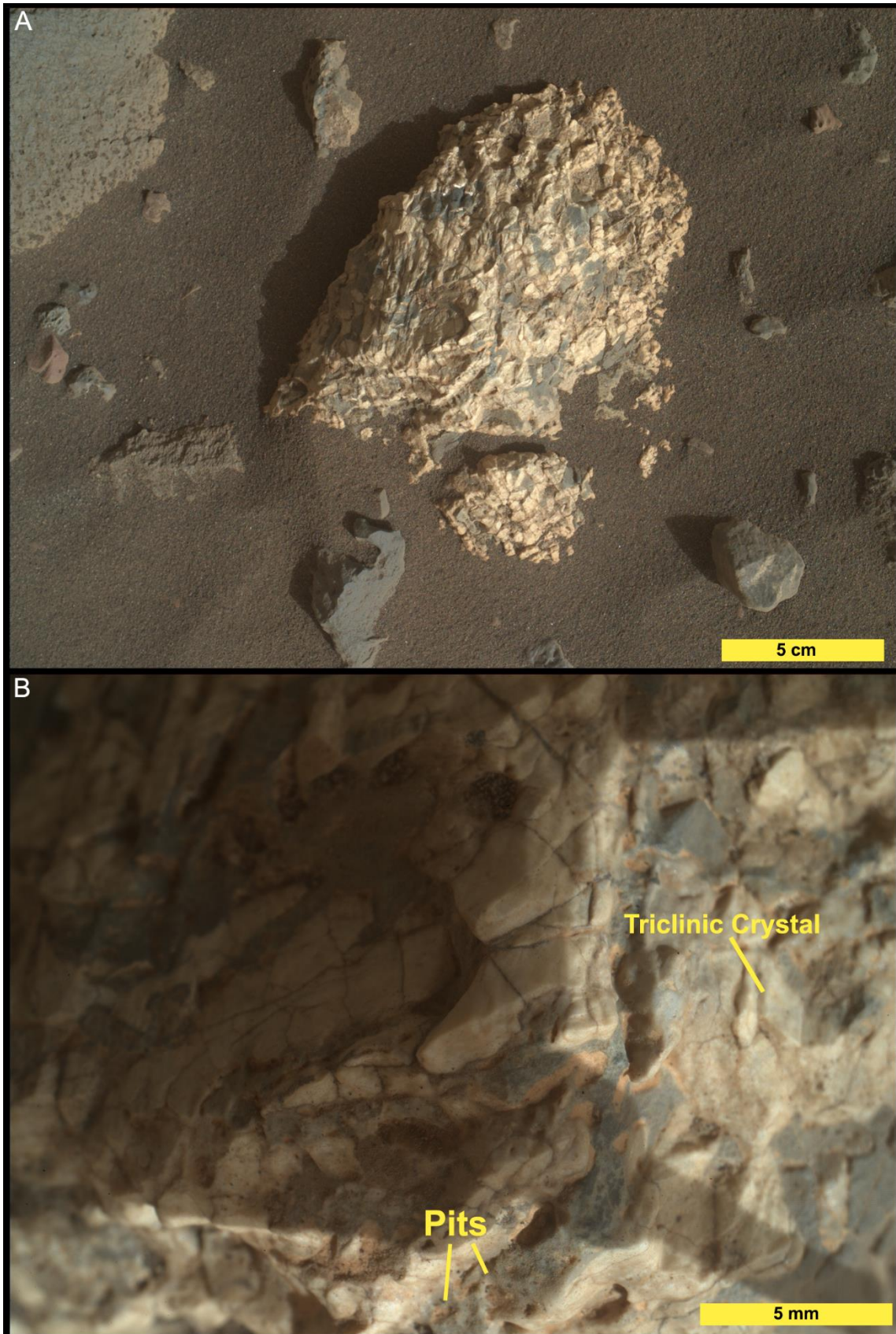
807 Figure 1: Traverse map showing the Bressay site where Askival is located, as well
808 as the location of Bindi. In addition, the Marias Pass, Bridger Basin and Naukluft
809 Plateau locales, at which evidence of diagenetic silica enrichment was encountered
810 (Frydenvang et al., 2017) are marked. Parentheses indicate mission sols covering
811 each area.

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813

814 Figure 2: MastCam mosaic CX02016MR0691552 of Bressay workspace with
815 labelled scientific targets. The Askival sample is ~20cm in length. Source images:
816 NASA/JPL-Caltech/MSSS, DOI 10.17189/1520328. Context mosaic produced by
817 Mars Analyst's Notebook.



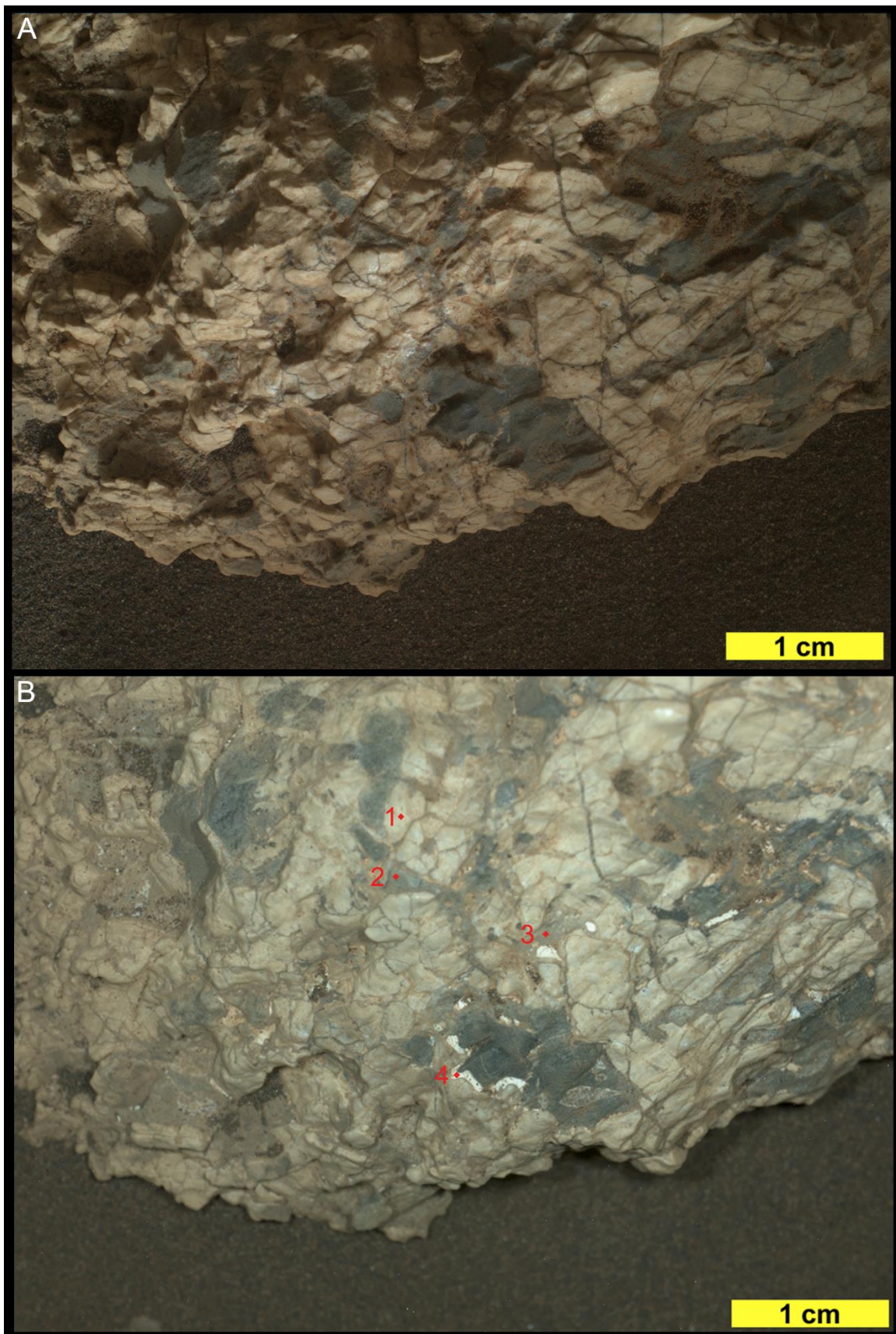
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Figure 3: MAHLI Images of Askival. A) Context image from ~25cm standoff (sequence ID 000706). B) Close-up image showing surface texture (sequence ID 00656). Examples of pitting in dark material and of triclinic crystal termination are labelled.



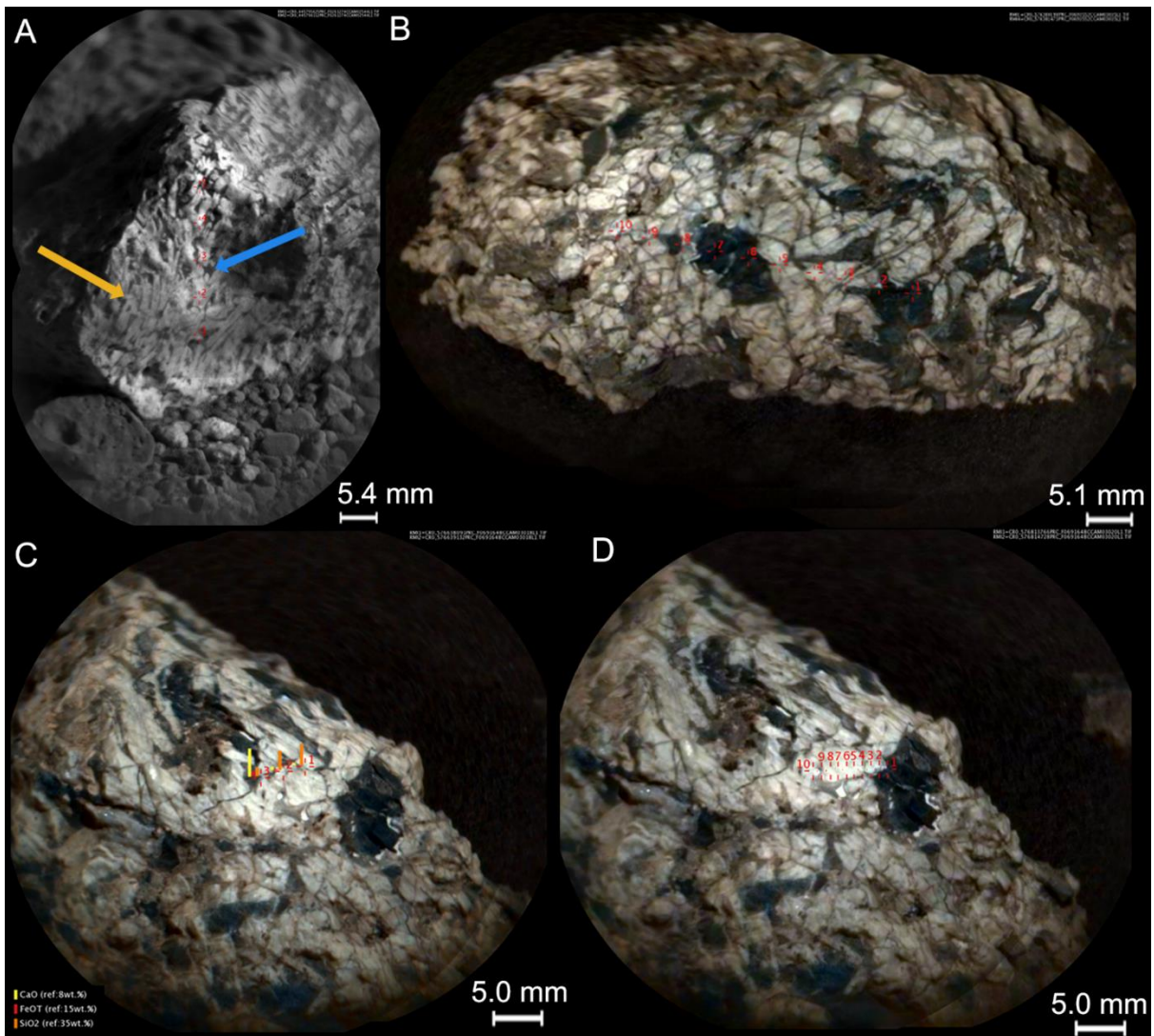
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Figure 4: MAHLI images of Askival with differing illumination. A) Daytime illumination (sequence ID 000458). B) Night time with LED illumination (sequence ID 000739) Red markers indicate examples of phases 1-4 (see section 3.1.1 and Table 1).



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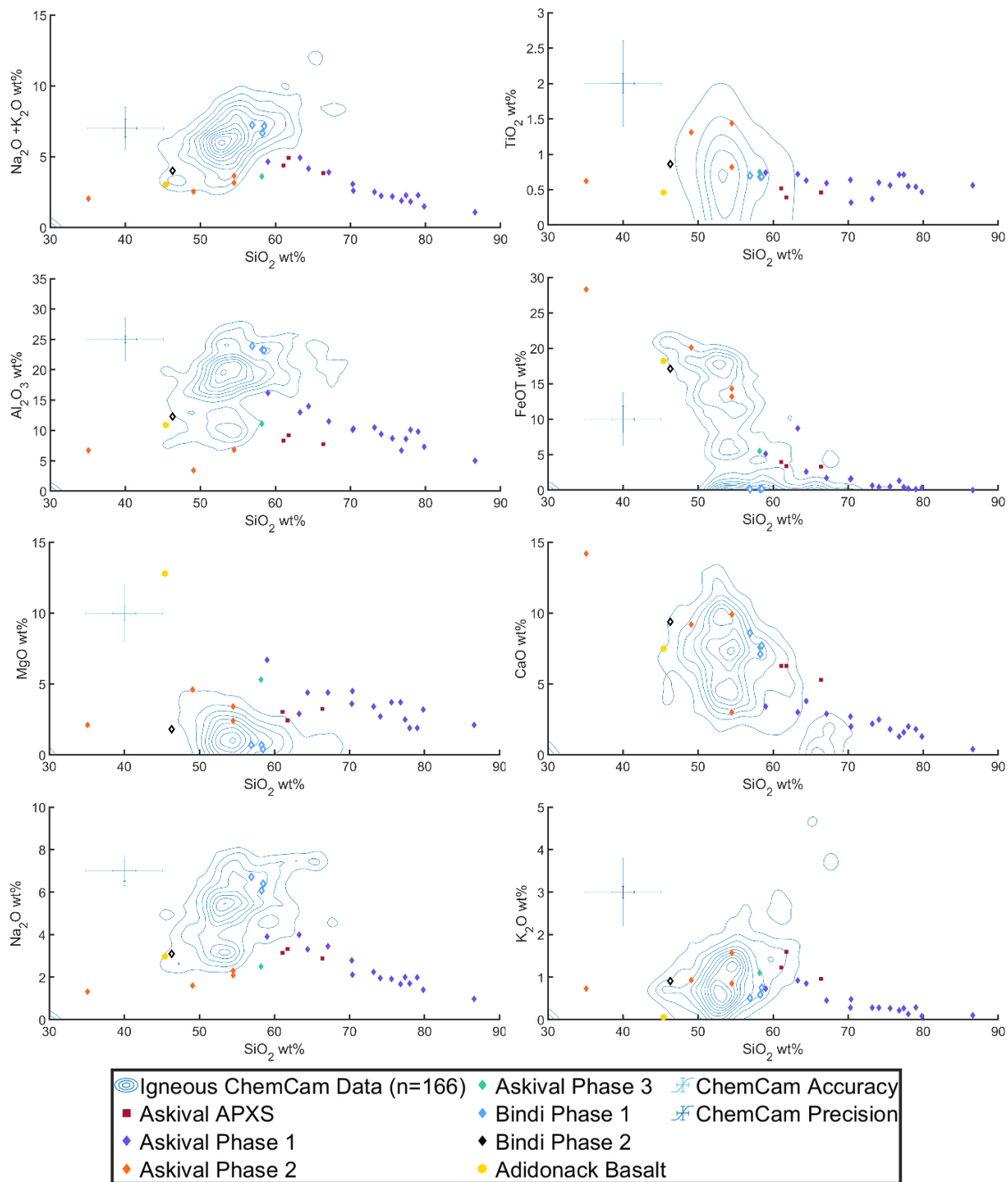
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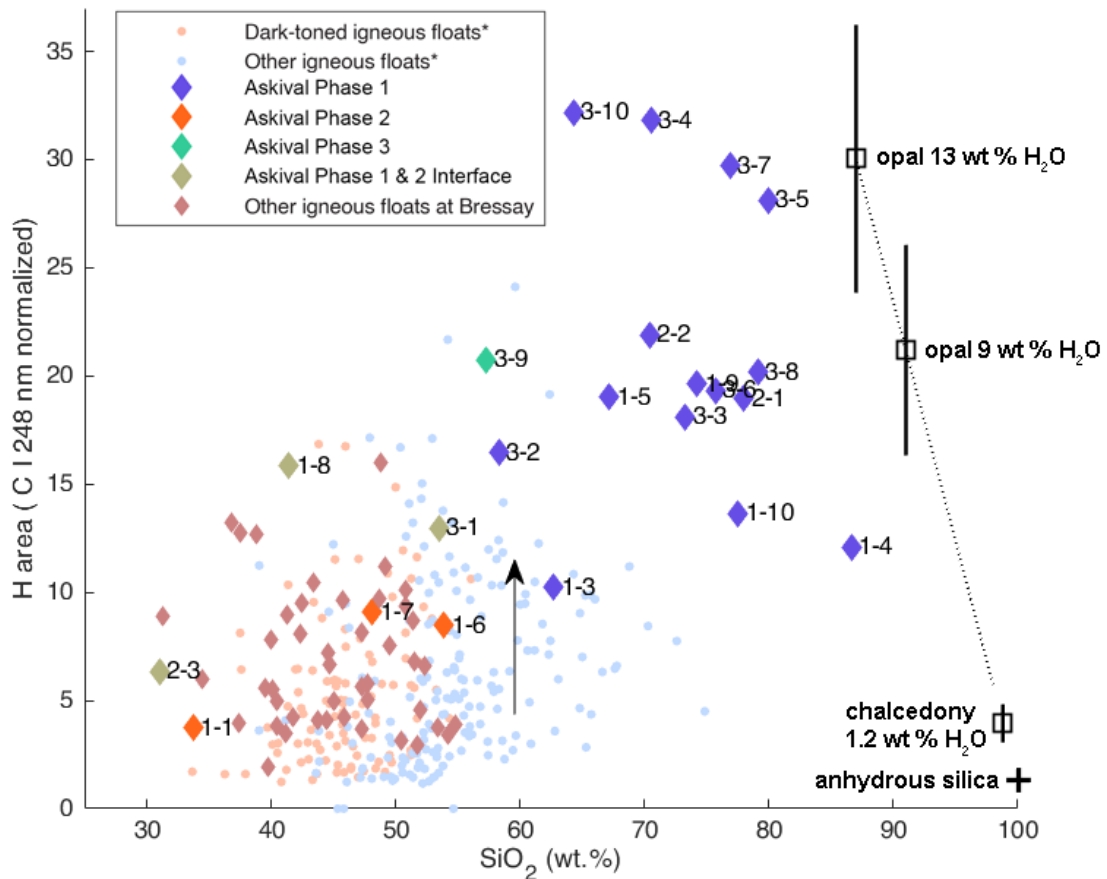
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Figure 5: A: ChemCam RMI image of Bindi, with markers showing location of ChemCam target points. Yellow arrow indicates characteristic plagioclase lathe forms in phase 1. Blue arrow indicates darker interstitial phase 2. B-D: Colorized RMI images from Mastcam color merge (Le Mouélic et al., 2015) of Askival, with markers showing location of ChemCam target points in sequences Askival (B), Askival_2 (C) and Askival_3 (D).



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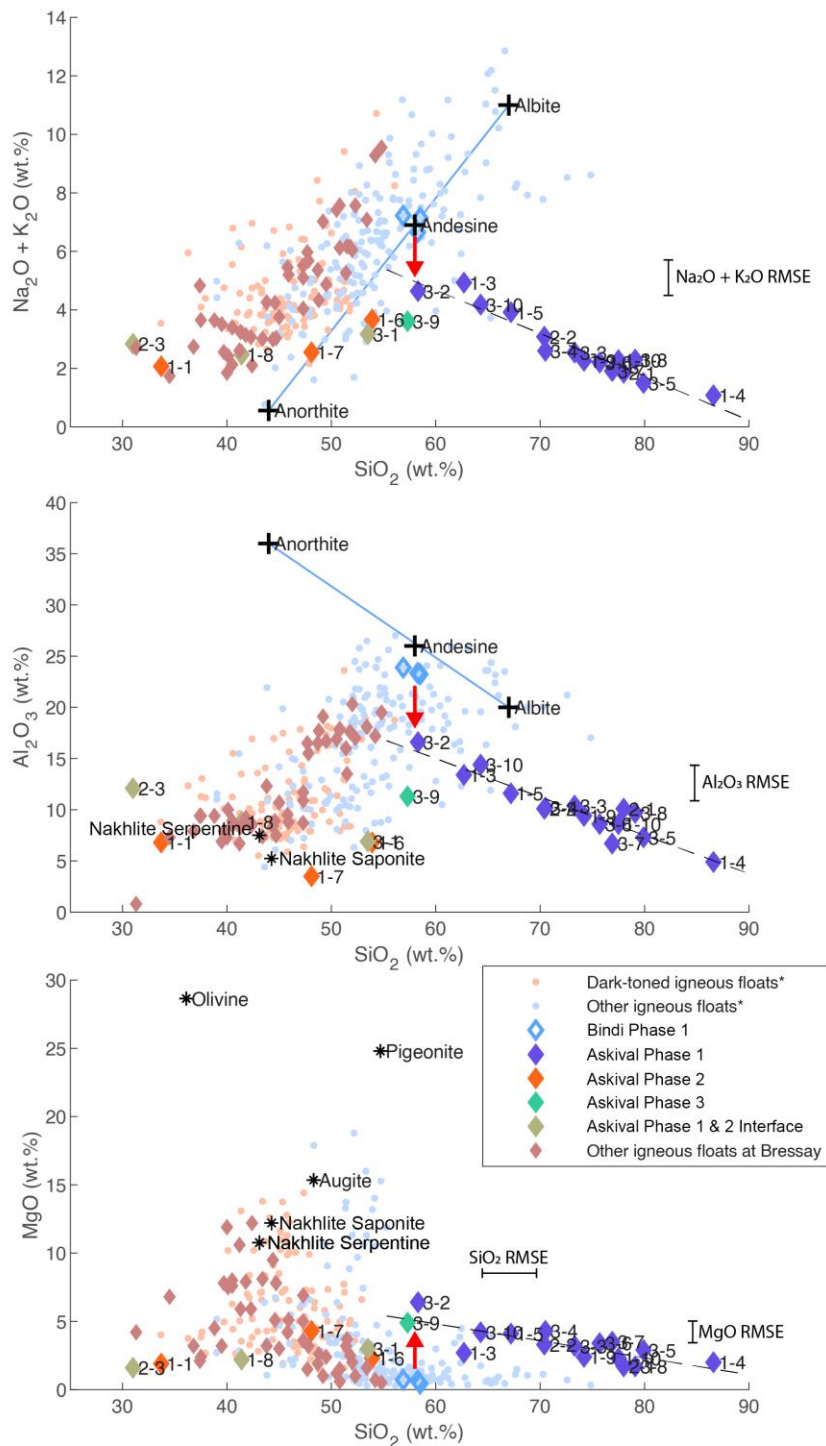
834 Figure 6. Major oxide plots for Askival, Bindi ChemCam and Askival APXS data.
 835 Igneous contours represent bulk ChemCam data (Edwards et al., 2017). Askival's
 836 light toned phase 1 shows an enrichment of silica correlating with a decrease in
 837 other elements, representing an alteration trend away from Bindi's composition. This
 838 is shown in more detail in Fig. 8. Adirondack basalt composition from (McSween et
 839 al., 2004) Error bars show ChemCam precision and accuracy from (Bedford et al.,
 840 2019).



841

842 Figure 7: Scatter plot showing normalized hydrogen peak area against SiO₂ content.
 843 Data is plotted for all ChemCam points in Askival as well as other igneous material
 844 from the Bressay locality and across the Bradbury sedimentary group. Data point
 845 annotations indicate raster (first number) and point number (second number). The
 846 vertical arrow illustrates the bias from random enhancement in hydrogen signal related
 847 to the roughness of the target surface (Rapin et al., 2017a). The black cross to the
 848 lower right of the plot represents ChemCam limit of detection for water for anhydrous
 849 silica (about 0.2 wt.%), and black squares show end-members for chalcedony,
 850 microcrystalline quartz which may contain 1 wt.% water (Flörke et al., 1982), and
 851 example of opals with various possible water content. The dotted line represents
 852 calibration to opaline silica, with 1-sigma uncertainty related to the laboratory
 853 calibration and instrument response function correction factor (Rapin et al., 2018;
 854 Rapin et al., 2017b). *Igneous float rocks from Bradbury described in (Cousin et al.,
 855 2017).

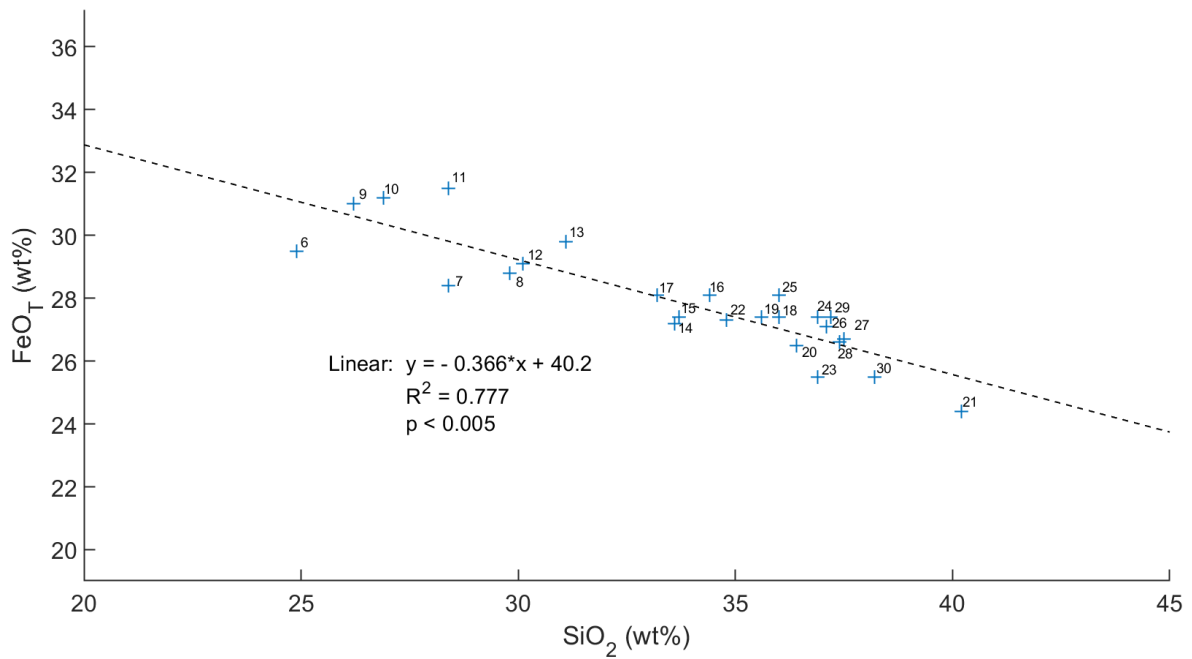
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858 Figure 8: Scatter plots of total alkali, Al₂O₃ and MgO vs Silica showing linear
 859 projections of stoichiometric plagioclase feldspar (Or₀₅, blue line) as well as chemical
 860 trends due to modelled linear dissolution of feldspar (loss of alkali and aluminum) and
 861 enrichment in Mg (red arrow) from a Bindi-like plagioclase starting composition. It then
 862 shows the silicification trend highlighting the enrichment in silica of the altered feldspar
 863 (dashed line). Nakhilite serpentine composition as reported in (Hicks et al., 2014;
 864 Piercy et al., 2022). *Igneous float rocks from Bradbury described in (Cousin et al.,
 865 2017)

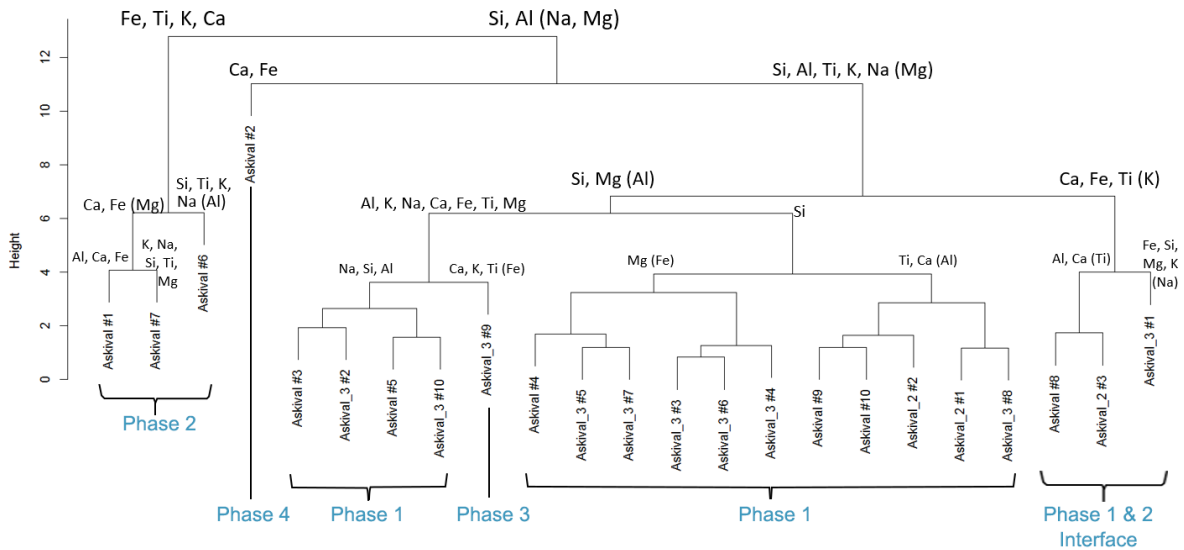
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868 Figure 9: Shot-to-shot analysis of FeO_T and SiO₂ content at target point Askival#1.
869 Number labels indicate shot order, first five shots are excluded due to dust cover.
870 Linear regression indicates a negative correlation between FeO_T and SiO₂, with earlier
871 points (6-13) having higher FeO_T and lower SiO₂.

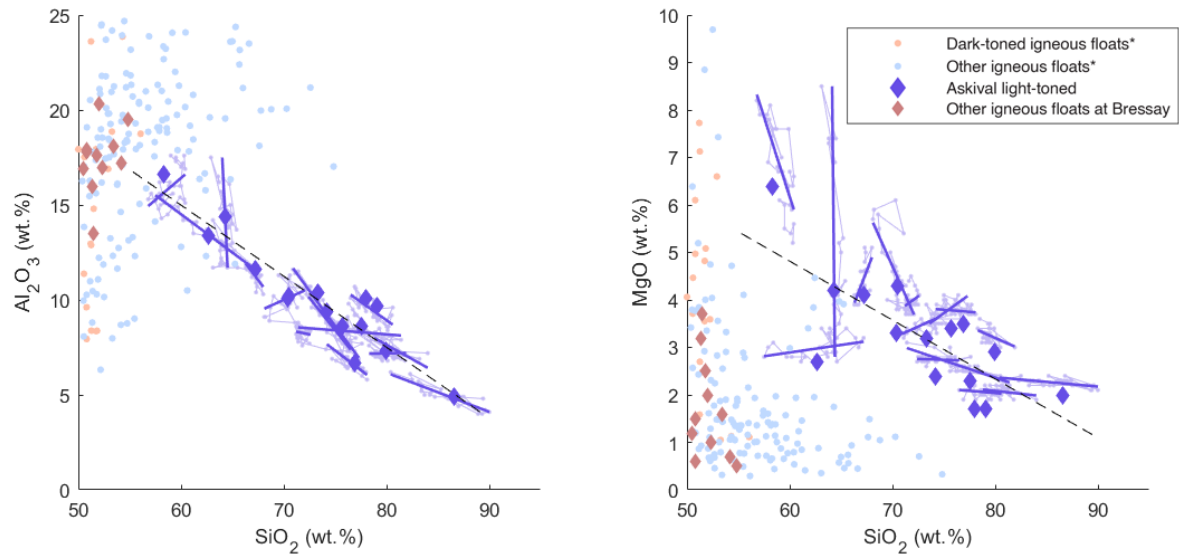
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874 Figure 10: Independent component analysis dendrogram displaying hierarchical
 875 clustering of Askival target points from all 3 rasters, based on major oxide composition.
 876 Elemental labels on each branch show the components which are higher in that
 877 cluster, with parentheses indicating that there is significant overlap in an element
 878 between the two clusters at that dividing step. Blue text phase classification based on
 879 RMI images (see Figure 3). A clear compositional distinction between texturally
 880 identified phases 1-3 is present. The light toned phase is divided into two halves,
 881 primarily differing in SiO₂ content (see section 3.2.1).

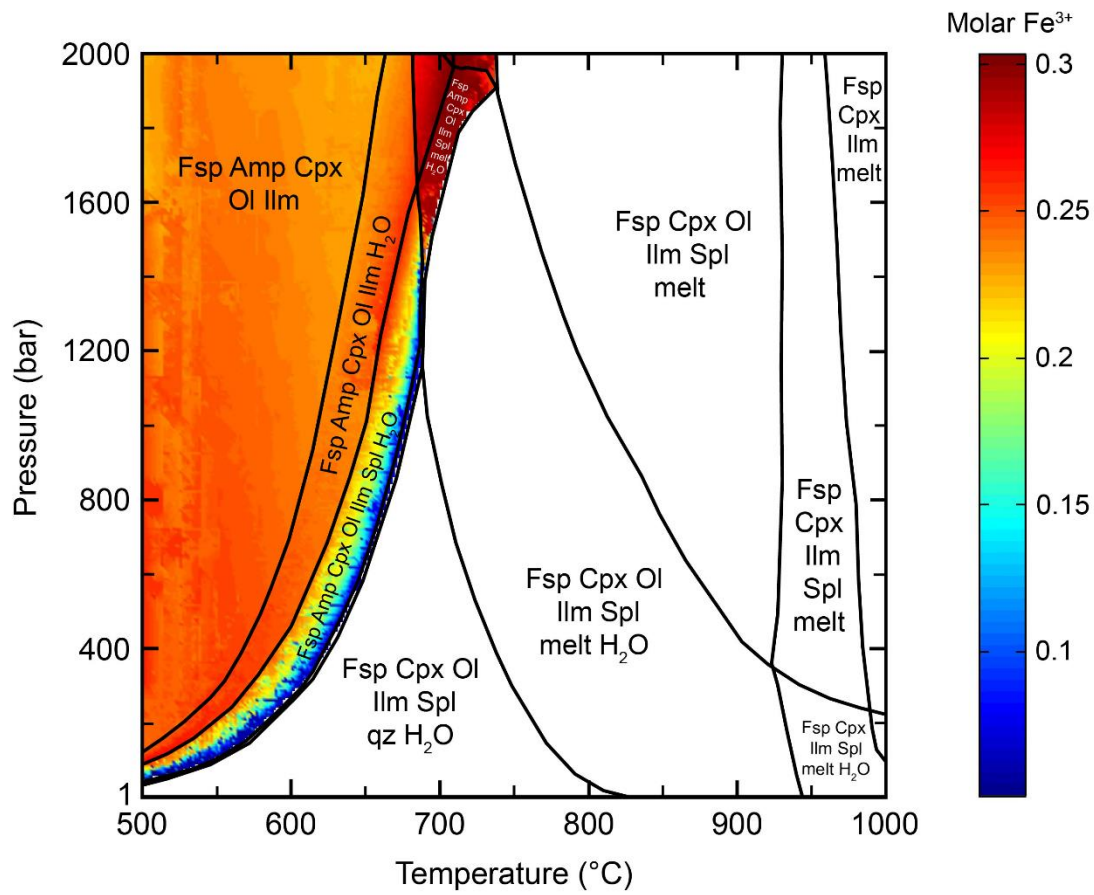
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884 Figure 11: Scatter plots of Al_2O_3 and MgO vs Silica focusing on Askival phase 1. Shot-
 885 to-shot composition data (light-blue dots and lines) is displayed along with shot-to-shot
 886 linear regression (dark blue lines) for each phase 1 point. *Igneous float rocks from
 887 Bradbury described in (Cousin et al., 2017)

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894 Figure 13. Modelled molar proportions of Fe^{3+} in amphibole for the Bindi
 895 composition. Amphibole with the highest Fe^{3+} content coexist with melt at pressures
 896 above ~ 1400 bars.

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