1	REVISION 1
2	Celestine discovered in Hawaiian basalts
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6	ABSTRACT
7	We report here the first occurrence of celestine in recent oceanic basalts. Celestine was
8	found in moderately altered accidental volcanic blocks from Ka'ula Island, a rejuvenated tuff
9	cone in the northern Hawaiian Islands. This occurrence is novel not only for the presence of
10	celestine but also for the absence of barite, the sulfate mineral most commonly found in oceanic
11	hydrothermal deposits. Celestine was found lining vesicles and partially fillings voids within the
12	matrix of several high Sr (2200-6400 ppm) Kaʻula basalts. High-quality wavelength dispersive
13	microprobe analyses of celestine are reported here for near end-member celestine (>90%). The
14	Ka'ula celestine deposits are compositionally heterogeneous with large variations in Ba content
15	(0.9-7.5 wt.%) within single mineral aggregates. The mostly likely source of the Sr for celestine
16	in the Kaʻula basalts was the host basalt, which contains ~1200 ppm. This is about 10 times
17	higher than normally found in mid-ocean ridge basalts and 4 times greater than commonly
18	observed in Hawaiian basalts. Hydrothermal alteration by S-bearing fluids related to the eruption
19	that transported these accidentally fragments probably mobilized Sr in the blocks. These S-rich
20	solutions later precipitated celestine during or following the eruption. We were unable to confirm
21	the origin for the Sr via Sr isotope measures because the Ka'ula celestine was too fine grained,
22	friable and widely dispersed to be concentrated for Sr isotope analyses. Future studies of
23	basalts from active volcanoes on oceanic islands, especially for basalts with elevated Sr
24	contents (>1000 ppm), should be aware of the possible presence of celestine in moderately
25	altered lavas.
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27 Keywords: Hawaii, volcanic rocks, celestine, hydrothermal alteration, strontium

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### INTRODUCTION

31 Celestine ( $SrSO_4$ ) is normally associated with continental evaporate deposits, although it is 32 also reported in hydrothermally altered continental volcanic and intrusive rocks (even kimberlites 33 and lamproites) as well as in some metamorphic rocks (eclogites; Hanor, 2000; Karakaya et al. 34 2001; Bailey and Lupulescu, 2007; Nakamura et al., 2010; Rukhlov et al., 2013; Anenburg et al. 35 2014; Nickschick et al., 2014; Enkhbayar et al., 2016). In sedimentary environments, celestine is 36 thought to form by reaction of hypersaline Sr-rich fluids with gypsum and/or anhydrite (Hanor, 2000). In continental igneous settings, celestine is commonly associated with barite and the two 37 38 are interpreted to be the product of interaction of a hydrous silicate fluid (rich in Sr and Ba) with a sulfur-rich fluid (Hanor, 2000). Celestine is an important ore mineral (the principle commercial 39 40 source for Sr). The principal uses of celestine in the USA are: drilling fluids (70%); ceramic ferrite magnets, and pyrotechnics and signals (9% each), electrolytic production of zinc, master 41 42 alloys, pigments and fillers, and other applications, including glass (3% each; U.S. Geological 43 Survey, 2019). Celestine is apparently unreported from active oceanic volcanic regions (e.g., mid-ocean ridge hydrothermal vents) and was unknown in the Hawaiian rocks prior to its 44 accidental discovery in high Sr content (2200-6400 ppm) lavas from Ka'ula Island (Fig. 1; Garcia 45 et al., 2016). However, high Sr content barite (11-12 wt.% SrO) was reported in hydrothermal 46 deposits related to the 1996 eruption of Loihi volcano, a seamount located south of the island of 47 Hawai'i (Davis and Clague, 1998; Davis et al., 2003), and in mid-ocean ridge hydrothermal vent 48 49 deposits (e.g., Loki's Castle; Eickmann et al., 2014). Celestine was not reported at either of these areas. The Ka'ula occurrence presents a rare opportunity where an explosive eruption 50 51 tapped moderately hydrothermally altered submarine basalts (Garcia et al., 1986). Although no 52 barite was found in these Ka'ula rocks, earlier formed, Ba-bearing zeolite (phillipsite with up to 2 53 wt% BaO) is present (Garcia et al., 2016).

Here we document the mode of occurrence of celestine in Ka'ula Island basalts using 54 backscattered electron imagery, present high precision electron microprobe analyses of 55 56 celestine, examine the effects of alteration on the geochemistry of Ka'ula basalts, and discuss possible origins for the formation of celestine in these rocks. High precision analyses of near 57 58 endmember celestine are rare in the scientific literature; most reported compositions are based on lower precision, EDS analyses (e.g., Anenburg et al., 2014; Garcia et al., 2016) or 59 60 wavelength dispersive (WDS) analyses with undocumented analytical conditions or poor totals 61 (<99 wt.% or >100.8 wt.%; e.g., Fernández-Cortés et al., 2006; Xu et al., 2010; Burtseva et al., 62 2013). Celestine is normally undersaturated with respect to hydrothermal solutions in marine

environments, suggesting that the presence of celestine is not the result of thermodynamically
controlled precipitation (Hanor, 2000; Singer et al., 2016). However, the very high Sr content of
these unaltered Ka'ula basalts (~1200 ppm) compared to other oceanic basalts (e.g., 100-150
ppm in mid-ocean ridge basalts; Hemond et al., 2006) may be the key factor in favoring
precipitation of celestine over barite in the Ka'ula basalts. Hydrothermal S-rich solutions related
to the eruption that carried the basalt blocks to the surface was probably responsible for the
formation of celestine at Ka'ula.

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# **GEOLOGICAL SETTING**

71 Ka'ula Island is a small (~1 km long), crescent-shaped remnant of a tuff cone that forms the 72 crown of a small, independent Hawaiian shield volcano (Fig. 1), the oldest of the main Hawaiian 73 volcanoes (~6.25 Ma; Garcia et al., 1986; 2016). The island is located near the summit of Ka'ula 74 shield volcano and along its southeast rift zone (Fig. 1). The cone is part of an extensive field of rejuvenation stage volcanoes that formed more than 2 Myrs after the underlying shield volcano 75 76 stopped erupting (Garcia et al., 2016). An extensive field of rejuvenation stage cones and associated lava flows forms a broad apron ~50 km wide surrounding the shield (Garcia et al., 77 78 2008; 2016). An accidental basalt block from the island and seven submarine basalts collected during two JASON ROV dives on the broad apron vielded <sup>40</sup>Ar-<sup>39</sup>Ar ages of 0.55-1.95 Ma for 79 Ka'ula rejuvenation stage volcanism (Garcia et al., 2016). The age of the eruption that formed 80 Ka'ula island is unknown but <0.66 Ma based on dating of an accidental block from the tuff 81 82 cone. The high Sr content basalt samples (2270 to 6400 ppm) examined in this study (KA-17, KA-19 and KA-34) were accidental blocks in the tuff cone derived from earlier rejuvenation 83 84 stage eruptions. The composition of these blocks is strongly alkaline basalts (basanite and foidite; Garcia et al., 1987; 2016), which are typical of Hawaiian rejuvenate stage lava (e.g., 85 86 Clague and Frey, 1982). The Sr content of fresh basanite and foidites from other Hawaiian Islands (Kaua'i and O'ahu) ranges from 500 to 1600 ppm, although a strongly alkaline lava from 87 O ahu, a melilite-bearing foidite with  $\sim$ 36 wt.% SiO<sub>2</sub>, has up to 3000 ppm Sr (e.g., Clague and 88 89 Frey, 1982; Fekiacova et al., 2007; Garcia et al., 2010). Finding a lava with more than twice the Sr content ever reported in a Hawaiian basalt (KA-19 with 6400 ppm Sr) was surprising (Garcia 90 91 et al., 2016). The cause of anomalously high Sr in these Ka'ula rocks was the subject of this 92 study.

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#### METHODS

Backscattered electron (BSE) images and compositional analyses were acquired using the
 University of Hawai'i JEOL 8500 Hyperprobe electron microprobe equipped with five,

wavelength dispersive spectrometers. Operating conditions were a beam energy of 15 keV with 96 97 a 5 nA beam current and 3 micrometer diameter. The low beam current was necessary because 98 of the small beam diameter that was needed to document the composition of the fine grained 99 (<5-20 µm) celestine crystals. Elements were acquired using analyzing crystals LiFH (H for 100 large crystal) for Ba L-alpha and Fe K-alpha, PETH for S K-alpha, PET for Sr L-alpha and Ca K-101 alpha, and TAP for Si K-alpha lines. The counting time were 20 seconds for Ba and Fe, 30 102 seconds for Si, and 50 seconds for Ca, S, and Sr. The standards were UCLA Diopside for Ca 103 and Si, benitoite for Ba, Staunton meteorite troilite for Fe, strontianite for Sr, and a nearly pure 104 celestine for S ka (Table 1). Detection limits the minor elements in celestine were 0.02 wt.% for 105 Si, 0.1 wt.% for Fe, and 0.16 wt.% for Ba based on counting statistics. Analytical precision (at 106 the 99% confidence level) ranged from 0.60 percent relative for S to 2.5 percent relative for Ca 107 based on repeated measurements of standards. Oxygen was calculated by cation stoichiometry and included in the matrix correction. A ZAF matrix correction method (Armstrong, 1988) was 108 109 applied to process the raw data to yield concentration values. Structural formula were calculated for our celestine analyses to demonstrate the near end-member composition of the Kaula 110 111 celestine (>90% celestine component for 13 of 15 analyses) and the high data quality (cation 112 totals of 2.000  $\pm$ 0.035, mostly within  $\pm$ 0.020; Table 1).

113 Whole-rock XRF major and trace element (Ba, Rb, Sr, Y, Zr, Nb, Ba, Zn, Ni, Cr, and V) analyses of four of the five basalts used in this study were originally reported in Garcia et al. 114 (1987). They were reanalyzed for this study along with a new sample, KA-16, in the same lab at 115 116 the University of Massachusetts as previously used but with enhanced detection 117 instrumentation. In addition, the Ka'ula submarine basalts used for comparison with the Kaula 118 Island basalts in this study were analyzed in the same lab a few years earlier. For the XRF 119 procedural methods and analytical precision, see Rhodes and Vollinger (2004). All of the basalt 120 samples were coarsely crushed (1-8 mm) with a tungsten-carbide coated hydraulic press, 121 ultrasonically cleaned in Millipore water, then dried for 24 hours at 40 °C followed by powdering 122 in a tungsten-carbide mill.

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#### RESULTS

# 124 **Petrography**

125 The Ka'ula celestine-bearing basalts are basanites (41-43 wt.% SiO<sub>2</sub> with 3-5 wt.% total

- alkalis; Garcia et al., 2016). They contain abundant olivine 10-15 vol.% in a mostly
- 127 cryptocrystalline matrix with clinopyroxene, magnetite and rare mantle-derived olivine and
- 128 clinopyroxene megacrysts. Many of the vesicles and other voids in the matrix are partially filled

129 with phillipsite (Fig. 2a). Celestine was discovered using backscattered electron imagery (Fig. 2). The distribution of celestine is patchy. It occurs partially filling vesicles (along with earlier 130 formed phillipsite) and in matrix voids of the Ka'ula accidental volcanic blocks (Fig. 2c). 131 132 Celestine was also found to be incipiently replacing the rim of unaltered olivine crystals (Fig. 133 2d). X-ray maps were made of several areas with well-developed celestine (Figs. 3). The maps 134 of Sr and Ba show the complex distribution of both elements in the Ka'ula celestine aggregates 135 (Fig. 2). The brighter areas in the BSE image have higher Ba and lower Sr contents than the 136 darker areas (Fig. 2).

137

### 138 Chemistry

Celestine forms a solid solution with barite, with each mineral typically containing only minor components of the other endmember (e.g., celestine usually contains less than 4 mole% BaSO<sub>4</sub>; Hanor, 1968, 2000). There are, however, reports of celestine with up to 20 wt.% BaO in lamproite deposits (Rukhlov et al., 2013). Celestine normally contains impurities of Ca (up to 2000 ppm) and FeO (up to >1 wt.%), and traces of Si, REE and Pb (Hanor, 2000; Anenburg et al., 2014), although most previous analyses of celestine don't report all of these elements.

The Ka'ula celestines range from 84-100% endmember celestine (SrSO<sub>4</sub>; Cs), although 14 145 146 of 15 analyses have >90% Cs (Table 1). These values span nearly the entire range reported in the Hanor (2000) synthesis on celestine and barite (74-100% Cs), although only two of these 147 148 earlier analyses have <84% Cs. BaO content in the Ka'ula celestines is highly variable (0.1-7.5 wt.%) even within localized areas (e.g., single vesicle; Fig. 3; Table 1). Compositional diversity 149 150 was initially detected in BSE images with darker and lighter patches within celestine aggregates. The darker patches contain less Ba than the lighter patches (0.9- 2.4 vs. up to 7.5 wt.% BaO; 151 152 Table 1, Fig. 3). Iron contents are low (<0.1-0.6 wt.% FeO), as is  $SiO_2$  (<0.1-0.9 wt.% but mostly 153 <0.3 wt.%). CaO is somewhat more abundant (0.6-2.5 wt.%). None of these oxides show any 154 correlation with Ba content in the Ka'ula celestine (Table 1). These new analyses (Table 1) are 155 the some of the first high precision analyses of celestine reported in the peer-reviewed literature 156 based on the sum of the oxide totals (13 of 15 analyses are 99.0-100.5 wt.% and cation totals of 157 2.000 ± 0.020; Table 1). Many previously reported celestine analyses were based on EDS 158 methods (Anenburg et al., 2014; Garcia et al., 2016), although some WDS analyses are available for non-basalt hosted samples (e.g., Xu et al., 2010 and Burtseva et al., 2013 for a 159 160 carbonatite occurrences; Nakamura et al., 2010, for a eclogite sample). However, the analytical

161 methods described in these papers are incomplete, some of the oxide totals are not good and 162 no structural formula are given.

163 The new XRF analyses using more precise methods than we previously reported (Garcia et 164 al., 1986) yielded somewhat different major and trace element compositions. In general, the new analyses (Table 2) have somewhat higher Ba and Zr contents and lower Rb. The 165 166 differences in these analyses are also affected by the heterogeneous nature of these basalts, 167 which contain a patchy distribution of secondary minerals. LOI values for these new analyses range from 0.2-4.7 wt.% (Table 2), indicating mild to moderate levels of alteration. This is 168 consistent with the petrographic observations that show common secondary mineral formation 169 170 but also fresh olivine in areas not affected by secondary mineralization (Fig. 2).

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# DISCUSSION

# 173 Hydrothermal Alteration of Ka'ula Accidental Blocks

The concentration of Sr in some Ka'ula rocks is 2-4 times greater than previously observed in any Hawaiian rejuvenated lavas of similar composition or predicted based on the abundance of other similarly incompatible elements (e.g., Zr and Ti) and even highly incompatible elements (e.g., Ba and Nb; Garcia et al., 2016). To evaluate the cause of the high Sr concentration in the Ka'ula Island accidental blocks, we examined them petrographically and compared their incompatible elements concentrations with unaltered Ka'ula submarine basanitic pillow basalts.

180 Petrographically, the basanitic blocks from Ka'ula Island have undergone weak to moderate 181 levels of alteration. The blocks appear relatively unaltered in hand specimen and thin section 182 except for the partial filling of some vesicles with phillipsite. Another indication of their alteration level is their low to moderate loss-on-ignition (LOI) values of 0.4-2.8 wt.% (Table 2). Sample KA-183 184 19 has the most Sr (6400 ppm; previous value was 5384 ppm; Garcia et al., 1997) and highest 185 LOI (2.8 wt.%). There is a positive correlation of LOI with Sr content in these island blocks (Table 2). Comparing them with unaltered submarine Ka'ula pillow basalts (LOI values average 186 187 0.35 wt.%) with similar SiO<sub>2</sub> (41.7 wt.%) and MgO (12 wt%) contents reveals some significant 188 geochemical differences between the altered island and fresh submarine basalts (Table 2; Fig. 189 4). Two trends are evident in this comparison. The sample with the highest Sr content (KA-19), shows depletion in incompatible elements (Rb, Ba, and Nb) with little or no change in Zr, Ti and 190 191 Y (Fig. 4). Thus, the water soluble elements (K, Rb) are depleted in the most altered island 192 basalt. The other samples show a mild enrichment in Ba, that is probably related to the

193 presence of Ba-bearing zeolites in these samples (Garcia et al., 2016). Sr enrichment 194 progressively increased with Ba enrichment (except for the sample KA-19) and with Rb 195 depletion. The increase in Sr in these more weakly altered rocks may be related to phillipsite 196 formation, which contains up to 3.3 wt.% SrO (Garcia et al., 2016). Thus, the alteration of the 197 Ka'ula island blocks may have involved two stages of alteration. During the first stage, Ba- and 198 Sr-bearing phillipsite formed occupying most vesicles in the Ka'ula Island samples. The second 199 stage involved the enrichment in Sr and depletion in Ba as celestine filled voids in the matrix 200 and some vesicles, overprinting the earlier increase in Ba from phillipsite crystallization.

201 The absence of barite in the Ka'ula basalts is anomalous compared to other submarine 202 areas that contain sulfate minerals (e.g., Davis et al., 2003; Eickmann et al., 2003). Normally, 203 barite is present with minor or no celestine (Hanor, 2000; Singer et al., 2016). Celestine is 204 normally undersaturated in hydrothermal solutions, suggesting its presence at Ka'ula may not 205 be the result of only thermodynamically controlled precipitation (e.g., Singer et al., 2016). 206 Typically, Ba is preferentially removed from a hydrothermal solution resulting in a Sr-poor solid 207 phase (e.g., barite or anhydrite). Continued precipitation in a closed system may result in a 208 solution enriched in Sr and subsequent precipitation of a more Sr-rich phase, especially if the solution temperature increased because of the retrograde solubility of celestine (Hanor, 2000). 209 210 However, there are occurrences in altered continental igneous rocks of celestine with no barite 211 (basalts and carbonatites; Anenburg et al., 2014; Nickschick et al., 2014), although the two sulfate minerals commonly occur together (e.g., Nickschick et al., 2014). Celestine formation in 212 213 the basalt was related to hydrothermal activity from a dike intruding carbonaceous sediments, 214 which were the source of the Sr. In a zoned carbonatite complex, celestine formation was 215 related to metasomatism by a sulfate-rich fluid from late stage magmatic activity (Enkhbayar et 216 al., 2016).

217 The source of the very high Sr concentrations in some Ka'ula island basalts that contain 218 celestine was most likely the host lava, similar to carbonatite example noted above (Enkhbayar 219 et al., 2016). There is no other source for excess Sr is known at this location. For example, no 220 carbonate material has been recovered from the tephra or known on the volcanic ediface. 221 Ka'ula island is located near the summit of Ka'ula shield volcano (Fig. 1). Thus, it is a prime site for hydrothermal activity. The most likely scenario for celestine formation in the island basalts is 222 223 hydrothermal S-rich acidic solutions related to the eruption that formed the island. These 224 solutions probably leached Sr from the strongly silica undersaturated basalts with elevated Sr 225 contents (~1200 ppm). Subsequently, celestine was precipitated in the voids of these Ka'ula 226 island basalts during or after the eruption that formed the island. Additionally or alternatively, the 227 early formation of Ba-rich phillipsite (Garcia et al., 2016) may have enriched the hydrothermal 228 solutions in Sr. 229 The unusually high Sr abundance in strongly silica understaturated Ka'ula rocks compared 230 to mid-ocean ridge basalts (100-150 ppm; Hemond et al., 2006) vs. 1200 ppm (Garcia et al., 231 2016) may have led to the preferential formation of celestine over barite. Thus, the high Sr 232 abundance in fresh rejuvenated Ka'ula basalts may have led to this unusual and possibly 233 unique occurrence of celestine in the modern ocean basins. 234 IMPLICATIONS 235 236 The presence of celestine and absence of barite in the Ka'ula Island accidental basalt 237 blocks represents a novel discovery in modern oceanic basalts. Barite is normally observed and 238 is thermodynamically favored in most hydrothermal solutions (Hanor, 2000). Future studies of 239 hydrothermally altered basalts from active volcanoes on oceanic islands, especially for basalts 240 with elevated Sr contents (>1000 ppm), should be aware of the possible presence of celestine 241 in moderately altered lavas. 242 243 **ACKNOWLEDGEMENTS** 244 We thank Michael Vollinger for expert XRF analyses of the Ka'ula rocks, David Grooms for 245 collecting these basalts from Ka'ula Island (an active U.S. military bombing target), and the 246 anonymous reviewers of this manuscript. Funding for this study was provided by U.S. National 247 Science Foundation grant, OCE-1737284 to M.G. This paper is SOEST contribution number 248 XXXXX.

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# 328 FIGURE CAPTIONS

- 1. Map of northern Hawaiian Islands (Kaua'i, Ni'ihau and Ka'ula shown in green). Ka'ula Island
- is a tuff cone remnant (small green patch on the south side of Ka'ula shield volcano) capping
- a small, independent Hawaiian shield volcano (Garcia et al., 1986; 2016).
- 2. Backscattered electron images of celestine (bright areas) in Ka'ula basalt KA-19. (a and b)
- Vesicles partially to completely filled with celestine (Cs, bright) and the zeolite (zeo)
- phillipsite. Boxed area in image b was X-ray mapped (Fig. 3). (c) Microporosity surrounding
- the vesicles also filled with celestine (upper central area in image 2a. (d) Fresh olivine etched
- by percolating fluids adjacent to celestine-rich area (bright patches). Olivine crystals away
- from celestine patches are devoid of such wedge-shaped etchings. Cpx; clinopyroxene-rich
- matrix was apparently unaffected by celestine-bearing solution.
- 339 3. Backscattered electron image (BSE) and X-ray maps for Ba and Sr in a celestine aggregate
   shown in boxed area on Fig. 2c. Ba enrichments (brighter areas) in parallel bands suggest
   crystallographic control of these areas during celestine growth.
- 342 4. Trace element variation diagram for Ka'ula Island accidental basalts. The abundance of the 343 trace elements is normalized to an average, unaltered submarine Ka'ula basalts of similar 344 composition to the island basalt (see Table 2). Elements are plotted in order of decreasing 345 degree of incompatibility in Hawaiian magmas from left to right. Analytical error is smaller 346 than the symbol size. Samples are listed in the legend from least altered at the bottom and in cooler colors (light blue and green) to most altered in warmer colors (yellow-orange-red) 347 348 based on LOI values (Table 2). The samples with lower and intermediate LOI values (0.2 to 349 2.1 wt.%) show mild Ba enrichments reflecting presence of Ba-rich zeolites. All of the 350 samples except the least altered one (KA-16) show Rb loss relative to the unaltered 351 submarine sample. The sample with the highest LOI (KA-19 with 4.7 wt.%) has the highest 352 Sr and lowest Ba contents. Paradoxically, this sample also has the lowest Nb and Y contents 353 but nearly the same Ti and Zr contents as the other samples.

 Table 1. Representative analyses of celestine in Kaula accidental block KA-19 with cations assuming 4 oxygens

Grain	SiO <sub>2</sub>	SrO	BaO	FeO*	CaO	$SO_3$	Total	Si	Sr	Ba	Fe	Ca	S	Total
1-2	0.01	55.3	0.11	0.39	0.75	42.7	99.2	0.000	0.992	0.001	0.010	0.025	0.990	2.018
2-3	0.03	53.6	0.58	0.27	1.08	44.9	100.5	0.001	0.929	0.007	0.007	0.035	1.007	1.985
2-4	0.29	51.4	1.90	0.51	2.51	42.7	99.3	0.009	0.915	0.023	0.013	0.083	0.983	2.017
2-5	0.52	52.6	1.65	0.57	1.22	42.4	99.0	0.016	0.943	0.020	0.015	0.040	0.983	2.001
3-3	0.10	54.1	0.59	0.20	0.75	44.9	100.6	0.003	0.938	0.007	0.005	0.024	1.007	1.981
3-3	0.15	52.8	0.35	0.30	0.62	44.8	99.0	0.005	0.922	0.004	0.007	0.020	1.012	1.965
5-3	0.37	52.0	2.26	0.06	1.80	43.6	100.1	0.011	0.914	0.027	0.002	0.059	0.992	1.994
11-1	0.23	53.0	1.25	0.47	1.39	43.2	99.6	0.007	0.939	0.015	0.012	0.046	0.992	2.004
13-1	0.05	53.5	2.37	0.46	0.97	43.2	100.5	0.001	0.949	0.028	0.012	0.032	0.992	2.013
13-2	0.00	50.3	4.84	0.34	1.35	43.0	99.9	0.000	0.901	0.059	0.009	0.045	0.995	2.009
13-3	0.06	52.5	1.98	0.34	1.38	42.9	99.2	0.002	0.937	0.024	0.009	0.046	0.993	2.009
13-4	0.02	53.7	0.91	0.44	1.71	43.3	100.1	0.001	0.948	0.011	0.011	0.056	0.991	2.017
13 dark	0.11	51.0	2.43	0.37	1.98	42.9	98.8	0.004	0.911	0.029	0.010	0.066	0.992	2.008
13 bright	0.94	47.0	7.50	0.36	1.35	42.9	100.1	0.029	0.837	0.090	0.009	0.044	0.987	1.967
14-1	0.07	50.7	4.08	0.43	1.16	43.1	99.6	0.002	0.906	0.049	0.011	0.038	0.997	2.001
celestine std. ave.	0.04	56.4	0.08	0.00	0.00	43.7	100.1	0.001	0.997	0.001	0.000	0.000	1.000	1.998
celestine std. given	0.00	56.4	0.10	0.00	0.00	43.6	100.1	0.001	1.000	0.001	0.000	0.000	1.000	2.001
*EoO as total iron														

\*FeO as total iron

Table 2. New XRF analyses of Kaula lithic basaltic blocks with comparison to basanitic Kaula submari

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	$AI_2O_3$	Fe <sub>2</sub> O <sub>3</sub> *	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	$P_2O_5$	Total	LOI	Nb	Ва	Rb
Accidental island blocks															
KA-15	42.18	2.73	11.53	14.32	0.22	13.38	10.44	3.31	1.16	0.70	99.95	0.42	52.8	663	28.1
KA-31	40.97	2.83	12.03	14.20	0.23	12.83	10.85	3.74	1.23	0.86	99.77	0.53	48.9	757	29.9
KA-28	42.42	2.83	12.55	14.60	0.22	10.44	10.67	3.75	1.49	0.74	99.72	0.65	55.7	825	33.0
KA-34	40.89	2.83	11.91	14.74	0.33	11.87	12.62	2.52	1.35	0.87	99.92	2.13	51.4	860	24.9
KA-17	41.49	2.62	11.94	14.23	0.25	12.41	11.41	3.35	1.22	1.13	100.04	1.78	55.2	947	19.6
KA-19	42.79	2.73	12.12	13.97	0.20	12.71	11.53	1.75	1.27	0.69	99.76	2.82	40.2	494	20.7
Submarine pillow basalts^															
J2-304-21	41.63	2.59	12.69	13.82	0.22	11.56	11.29	3.89	1.46	0.77	99.92	0.27	50.4	705	32.5
J2-304-22	41.77	2.55	12.30	13.94	0.25	12.14	11.18	3.72	1.41	0.74	100.00	0.32	48.5	646	31.5
J2-304-23	41.76	2.59	12.67	13.65	0.22	11.63	11.41	3.86	1.43	0.77	99.99	0.45	50.0	688	31.0
average	41.72	2.58	12.55	13.80	0.23	11.78	11.29	<u>3.8</u> 2	1.43	0.76	99.97	0.35	49.6	680	31.7
*Total iron	*Total iron: ^data from Garcia et al. (2016)														

\*Total iron; ^data from Garcia et al. (2016)

ne basalts											
Sr	Y	Zr	Zn	Ni	Cr	V					
1247	20.0	143	108	429	457	290					
1376	22.0	161	118	360	477	293					
1969	21.0	215	126	228	277	270					
2274	21.0	151	114	294	366	281					
2380	24.0	180	115	295	412	279					
6404	18.0	106	106	311	428	286					
1210	21.7	169	116	264	345	259					
1154	21.9	169	116	261	352	262					
1204	22.0	167	113	267	369	256					
1189	21.9	168	115	264	355	259					





This is a preprint, the final version is subject to change, of the American Mineralogist (MSA) Cite as Authors (Year) Title. American Mineralogist, in press. DOI: https://doi.org/10.2138/am-2020-6995



# Figure 3 Garcia and Hellebrand

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Fig. 4 Garcia and Hellebrand