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### **Publication Date**

2016-07-01

### DOI

10.1016/j.geothermics.2016.02.007

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### Geochemical bias in drill cutting samples versus drill core samples returned from the Reykjanes Geothermal System, Iceland

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#### ARTICLE INFO 81

Article history:

Received 4 January 2016

Received in revised form 22 February 2016 10 Accepted 23 February 2016 11

- Available online xxx
- 12
- 13 14 Keywords:
- Drill core 15
- Drill cuttings 16
- 17 Geochemical bias
- 18 Revkianes
- Elemental exchange 19
- Hydrothermal alteration 20

### ABSTRACT

The wholerock major and trace element composition of drill cutting samples are compared to drill core samples from adjacent depths in the seawater recharged Reykjanes geothermal system in Iceland. The first appearance of alteration minerals and lithologies in drill cutting samples is a useful tool for interpreting broad subsurface characteristics. However, use of drill cutting samples for determining igneous affinity and elemental exchanges during hydrothermal alteration is problematic. Samples recovered from immediately above and below the cored intervals in wells RN-17B and RN-30 demonstrate that drillcutting samples are biased towards preservation of least altered primary igneous minerals and more resistant alteration minerals, including albite, quartz, and epidote, with preferential loss of finer-grained and less resistant minerals including chlorite and actinolite. This selective recovery obscures elemental exchanges resulting from hydrothermal alteration processes. For some elements, compositional variations (enrichments and depletions) measured from 9.5 m of core exceeds that observed in ~3000 m of cutting analyses. Concentration ratios of hydrothermally immobile elements including Zr, Nb, V, Y, HREE, Hf, Ta and Th in deep (>2245 m) spot drill core samples record bimodal, trace element-enriched and trace element-depleted precursor compositions similar to subaerial Reykjanes Peninsula basalts. The same elements in nearly 3000 m of drill cutting samples from well RN-17 overwhelmingly reflect the more common trace element-enriched igneous precursor, demonstrating that mixing of drill cutting samples obscures details of their igneous affinity. A new and different drill rig was used to deepen well RN-17 below 2266 m in a sidetrack hole (RN-17ST), which resulted in a change in drilling conditions, accompanied with an increased well deviation angle from  $\sim 0^{\circ}$  to  $\sim 4^{\circ}$ . Wholerock geochemical results for drill cutting samples from RN-17ST are homogenous for virtually every element; suggesting the change in drilling conditions resulted in extreme mixing of the drill cuttings. Anomalously high concentrations of Cu, Ni, Cr and Ta in some drill cutting samples likely reflects contamination of drill cutting samples by metal alloys used in drill bits and drill collars or more resistant spinel and sulfide phases.

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#### 22 1. Introduction

The seawater-recharged Reykjanes Geothermal System is 23Q3 located on the immediate onshore extension of the submarine 24 Reykjanes Ridge in southwest Iceland (Fig. 1). Over 30 geothermal 25 wells have been drilled in the Reykjanes Geothermal System for the 26 production of geothermal electricity, and drill cuttings have been 27 archived from depths exceeding 3000 m. Reykjanes drill cutting 28 samples have proved useful for developing a broad understanding 29 of the stratigraphy, hydrothermal alteration and evolution of the 30 geothermal system at depth (i.e., Björnsson et al., 1972; Tómasson 31

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http://dx.doi.org/10.1016/j.geothermics.2016.02.007 0375-6505/© 2016 Published by Elsevier Ltd.

and Kristmannsdóttir, 1972; Sakai et al., 1980; Lonker et al., 1993; Franzson et al., 2002; Franzson, 2004; Freedman et al., 2009; Pope et al., 2009; Marks et al., 2010). The geological setting and nature of the recharge fluids in the Reykjanes Geothermal System also make it a useful analog for seafloor hydrothermal processes (Bischoff and Dickson, 1975; Elderfield et al., 1977; Mottl and Holland, 1978). Q4 37

Geochemical bias in drill cutting samples may stem from: (1) the loss of clay minerals during sample collection and washing, because grain impacts during ascent preferentially remove less resistant mineral phases, (2) mixing due to the development of cutting beds on the sides of inclined holes, (3) mixing due to collapse and abrasion of material from shallower depths during ascent, (4) mixing during ascent due to cutting size and density differences, (5) mixing due to variations in drilling fluid pumping rate and drilling parameters, and (6) contamination from drilling equipment (Hulen and

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Sibbett, 1981; Bar-Cohen and Zacny, 2009). In contrast, drill core preserves depth relations, alteration mineral interrelations, and alteration mineral phases that are not always preserved in drill cutting samples (Kristmannsdóttir, 1982). Paragenetic alteration mineral relationships (i.e., episodic veining and wall rock interrelationships) are also much better preserved in drill core samples. While previous studies have acknowledged potential geochemical and preservation bias in drill cutting samples relative to drill core samples (Kristmannsdóttir, 1982; Wood, 1996; Solum et al., 2006),

few studies have quantitatively evaluated the significance of this 56 57 bias and the implications for geochemical studies. The Iceland Deep Drilling Project (IDDP) recently collected three 58 spot drill cores (RN-17B, RN-19, and RN-30) from geothermal wells 59 in the Reykjanes geothermal system. The spot cores were recov-60 ered from true vertical depths ranging between ~2245 m and 61  $\sim$ 2570 m and in situ temperatures ranging from  $\sim$ 250 to 345 °C 62 (Friðleifsson et al., 2005; Friðleifsson and Richter, 2010; Friðleifsson 63 et al., 2014; Fowler et al., 2015). The purpose of this study is to com-64 pare wholerock geochemical results from the Reykjanes drill core 65 samples to vertically adjacent drill cutting samples to understand 66 67 the limitations of using drill cutting samples to elucidate subsurface lithology and alteration processes during geothermal energy 68 exploration, and for addressing questions about seawater-crust ele-69 mental exchanges that are of interest to the seafloor hydrothermal 70 research community. 71

72 Our results suggest that drill cutting samples significantly intermix material from different depth intervals and are biased toward 73 preservation of more resistant phases including epidote, quartz, 74 and albitized plagioclase, while less resistant hydrous alteration 75 phases such as chlorite, actinolite, and anhydrite are selectively 76 lost. The drill cutting samples investigated also show signs of 77 trace element contamination from metal alloys used in down hole 78 drilling equipment. It is widely acknowledged that drill core pro-79 vides advantages in interpreting geologic relationships down hole, 80 but the advantages need to be weighed against the increased cost of 81 core drilling. Conclusions drawn about primary igneous protolith, 82 alteration mineral interrelationships, and hydrothermal elemental 83 exchanges based on drill cutting samples should be treated with 84 caution, particularly when using drill cuttings from great depth. 85

### 2. Geology of the Reykjanes Peninsula

The Reykjanes Peninsula is a subaerial continuation of the submarine Reykjanes Ridge (Fig. 1). The direction of tectonic extension on the peninsula is highly oblique to the ridge spreading axis (Clifton and Kattenhorn, 2006). The four volcanic systems present on the peninsula (Reykjanes, Krísuvik, Brennisteinsfjöll, and Hengill) each have a distinct magma supply (Sæmundsson, 1979; Einarsson and Sæmundsson, 1987). The peninsula is divided into five neo-volcanic fissure swarms (Reykjanes, Grindavík, Krísuvik, Bláfjöll, and Hengill) characterized by an en echelon arrangement of post-glacial eruption sites, fissures and seismic activity (Jakobsson et al., 1979; Clifton and Kattenhorn, 2006). The 05 97 Reykjanes and Grindavík neo-volcanic fissure swarms are indistinguishable in terms of petrology and major element chemistry (Jakobsson et al., 1979). Several active high-temperature geothermal areas on the peninsula result from a combination of extensional tectonics and active volcanism (Jakobsson et al., 1979; Arnórsson, 1995). The Reykjanes geothermal system occurs on the westernmost tip of the Peninsula, and is recharged by seawater that is subsequently modified by progressive reaction with the basaltic host rock and boiling (Tómasson and Kristmannsdóttir, 1972; Arnórsson, 1978).

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Subaerially exposed basalt flows on the Reykjanes Peninsula west of the Hengill volcanic system span a petrographic range from picritic basalts to tholeiitic basalts (Jakobsson et al., 1979). Less than 2% of exposed basalt on the western Reykjanes Peninsula is picritic (Jakobsson et al., 1979). Highly variable proportions of cumulate phases (olivine, spinel and plagioclase) in the picritic basalts suggest the parental liquid was primitive basalt as opposed to a true picrite (Gee et al., 1998; Revillon et al., 1999). "Picritic" basalts in the Reykjanes volcanic system are defined by high MgO, low trace element concentrations, Nb/Zr ratios <0.7, and are referred to as "trace element depleted (TED)" (Gee et al., 1998; Peate et al., 2009). Tholeiitic basalts make up the preponderance of exposed lavas. Compared to the "picritic basalts, the tholeiitic basalts are more evolved (MgO generally <8%), have high trace element concentrations, have Nb/Zr ratios >0.7, and are referred to as 'trace element enriched (TEE)' (Gee et al., 1998; Kokfelt et al., 2006; Peate et al., 2009).

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taken from two intervals (2792 m and 2796 m) immediately above the RN-17B core, two intervals (2878 m and 2886 m) below the RN-17B core, and three intervals (2400 m, 2450 m, and 2500 m) above the RN-30 core (Fig. 2). Drill core samples analyzed for this study were taken from one interval in the RN-17B core (2800.35 m; an altered crystalline basalt pillow) and two intervals from the RN-30 core (<2510.5-2 and 2512.53; hyaloclastite and coarse basalt, respectively). Skinner et al. (2010) provide specifications for Reykjanes drill coring technology and sampling procedure. We also include wholerock analytical results for drill cuttings sampled at 50 m intervals between 350 m and 3050 m in well RN-17 (Marks et al., 2010). Drill cutting and core samples were provided by IDDP and HS Orka hf.

Drill cuttings from above the RN-17B core in the interval from ~2530 to 2790 m consist entirely of fine- to coarse-crystalline basalt (Helgadóttir et al., 2009; Fig. 2). Drill cuttings in the interval  $\sim$ 8 m above the RN-17B core ( $\sim$ 2790–2798 m) contain fragments of greenish, very altered glassy basalt with abundant quartz, epidote, and actinolite (Helgadóttir et al., 2009). Drill cuttings from below the RN-17B core contain fragments of light green, very altered, fineto medium-grained crystalline basalt with a fair amount of quartz (Helgadóttir et al., 2009). While altered fragments are present in drill cuttings from above and below the RN-17B core, the samples are predominantly composed of largely unaltered crystalline basalt fragments. Drill cuttings above the RN-30 core in the interval from 2308 to 2510 m were derived from hyaloclastite (Fig. 2), composed of glassy basalt and greenish glass fragments that are altered to chlorite, epidote, guartz, prehnite, and moderate amounts of pyrite (Sigurgeirsson et al., 2011). A significant proportion of the cutting samples from above the RN-30 core contain relatively unaltered crystalline basalt fragments.

The Jötunn Gardner Denver 700E drill rig (Iceland Drilling, Ltd.) was used to drill RN-17 to ~2266 m in a near vertical hole when the drill pipe broke and a sidetrack hole was necessary to continue drilling (Friðleifsson et al., 2005). The Geysir Drillmec HH-200S drill rig (Iceland Drilling Ltd.) successfully completed the second attempted sidetrack hole (RN-17ST) from 1816 m to 3082.4 m in a  $\sim 4^{\circ}$  deviated sidetrack hole (Friðleifsson et al., 2005). The Týr Drillmec HH-300 drill rig (Iceland Drilling, Ltd.) was used to drill the deviated (SSW; 35° from vertical) RN-17B sidetrack of well RN-17 with a kick off point at approximately 920 m depth (Helgadóttir et al., 2009). The Óðinn Drillmec HH-220 drill rig (Iceland Drilling, Ltd.) was used to drill well RN-30, which was deviated (SE; 35° from vertical) at a kickoff depth of approximately 550 m (Sigurgeirsson et al., 2011). Mud was used as the drilling fluid for the cased interval, and water for the uncased production interval. Mica was introduced to seal zones of lost circulation, when encountered. Drill cutting samples were collected at 2 m intervals using a series of sieves (generally <1 mm mesh, depending on the coarseness of the cuttings). Cuttings were first separated from the drilling fluid using vibrating sieves, and then washed with water for archiving. A small subset of the bulk cuttings sample was thoroughly washed with water and archived separately from the bulk sample.

The 9.3 m RN-17B core was recovered at an in situ temperature of 345 °C, a TVD of ~2560 m (2798.6–2807.9 m down hole depth), and is composed of basalt pillows, hyaloclastite and lithic breccia, and volcanic sandstone (Friðleifsson et al., 2005; Friðleifsson and Richter, 2010; Fowler et al., 2015). RN-30 consists of three sequential cores totaling 22.5 m. The RN-30 cores were recovered at an in situ temperature of 345 °C, a TVD of  $\sim$ 2240 m (2510.3–2532.8 m down hole depth), and are composed of a series of fine and coarse crystalline basalt intrusions with an ophitic texture. Several hyaloclastite slough blocks originating from an unknown depth above the core were recovered overlying the upper most intact drill core.



Fig 2. Drill logs.

#### 3. Samples and analytical methods 124

3.1. Samples 125

All sample names and depths in this study refer to the down hole 126 127 depth as opposed to the corrected true vertical depth (TVD), unless explicitly stated. Drill cuttings samples analyzed for this study were 128

> Please cite this article in press as: Fowler, A.P.G., Zierenberg, R.A., Geochemical bias in drill cutting samples versus drill core samples returned from the Reykjanes Geothermal System, Iceland. Geothermics (2016), http://dx.doi.org/10.1016/j.geothermics.2016.02.007

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Fig. 3. RN-17B cutting BSE images.

<sup>19</sup> The lithology and alteration present in the RN-30 drill cores were
<sup>194</sup> evaluated during sampling.

### 195 3.2. Methods

Mica introduced as a loss circulation prevention agent during 196 drilling was carefully removed from drill cutting samples by hand-197 picking under a binocular microscope. Bulk drill cutting and drill 198 199 core samples were submitted to the Washington State University (WSU) GeoAnalytical Laboratory for major element, trace element, 200 and loss on ignition (LOI) determinations using X-ray fluorescence 201 spectrometry (XRF) and inductively coupled plasma mass spec-202 trometry (ICP-MS). Samples were ground at WSU in a tungsten 203 carbide ring mill prior to analysis. Samples analyzed by XRF were 204 prepared according to the methods outlined in Johnson et al. (1999) 205 and analyzed using a Thermo-ARL AdvantXP instrument. Samples 206 analyzed by ICP-MS were prepared according to the methods out-207 lined in Jenner et al. (1990) and analyzed using an Agilent 4500 208 ICP-MS. Polished thin sections of cuttings and core were exam-209 ined using transmitted and reflected light petrography. A Cameca 210 SX-100 electron microprobe (EMP) at the University of California 211 Davis was used to obtain back-scattered electron (BSE) images and 212 perform mineral identification using the energy dispersive energy 213 (EDS) spectrometer. 214

#### 215 4. Results

BSE images of drill cutting samples from above and below the RN-17B core confirm the cuttings predominantly consist of crystalline basalt, and are largely composed of igneous plagioclase and clinopyroxene, along with fragments containing chlorite, epidote and actinolite veins (Fig. 3A and B). The top of the RN-17B core (2798.64 m) differs from drill cuttings immediately above (2796 m) in that the core consists of hyaloclastite shards pervasively replaced by hydrothermal hornblende and albite while relict igneous plagioclase and clinopyroxene are absent (Fig. 3A and C). A sample from the RN-17B core (2800.35 m) is composed of a hydrothermally altered crystalline interior of a basalt pillow that preserves an igneous texture similar to the cuttings (Fig. 3D). In contrast to the RN-17B cuttings, the RN-17B core is more pervasively altered with albitized igneous plagioclase, actinolite after igneous clinopyroxene, and near complete replacement of the pillow interior to chlorite + hornblende (Fowler et al., 2015). The drill cuttings immediately above the core do include a few fragments of epidote, actinolite, pyrite and titanite veins similar to those common throughout the RN-17B core (Fowler et al., 2015; Fig. 3B and D).

Drill cuttings from 2400 m in well RN-30 are largely composed of crystalline basalt fragments containing igneous clinopyroxene showing incipient alteration to actinolite on the grain edges, and igneous plagioclase with patchy replacement by albite, especially along the grain edges. The sample also includes numerous fragments of hyaloclastite composed of chlorite, quartz, secondary plagioclase, and titanite (Fig. 4A). Cuttings from 2450 m and 2500 m above the RN-30 core are similar to those from 2400 m, but contain a higher proportion of altered hyaloclastite (Fig. 4B and C). The hyaloclastite fragments present in RN-30 drill cuttings have mineralogical similarities to a hyaloclastite slough block recovered with the RN-30 core (Fig. 4D). 219

0.15

JZ/qN 0.10

0.05

0.00

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Fig. 5. Wholerock spider diagrams.

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Enriched

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Nb/Zr = 0.07 (Gee et al., 1998)

•Reykjanes Drill Cores (RN-17B, RN-19, and RN-30)

100

120

Unaltered Surface Basalt

80

Zr

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60

40

0

0.15

JZ/9N 0.10

0.05

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Enriched

Depl

160

140

Nb/Zr = 0.07 (Gee et al., 1998)

100

120

Drill Cuttings (This study)

80

Zr

Drill Cuttings (Marks et al., 2010)

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Table 1

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Sample/Depth (m)	2400	2450	2500	2792	2796	2878	2886	2512.53	<2510.5-2	2800.35
Drill Hole	RN-30	RN-30	RN-30	RN-17B	RN-17B	RN-17B	RN-17B	RN-30	RN-30	RN-17B
Sample Type	Cuttings	Cuttings	Cuttings	Cuttings	Cuttings	Cuttings	Cuttings	Core	Core	Core
Lithology <sup>a,b,c</sup>	Glassy Basalt	Breccia	Glassy Basalt	Basalt	Basalt	Basalt	Basalt	Coarse Basalt	Hyaloclastite	Basalt Pillow
Major Elements by XRF (Wt.%)										
SiO <sub>2</sub>	48 59	50 19	49 11	49.67	49 16	48 50	50.08	49 20	57 15	44 53
TiO2	1.76	1.53	1.10	1.18	1.41	1.28	1.03	1.76	1.07	1.21
Al <sub>2</sub> O <sub>2</sub>	13.09	14.85	14.72	14.05	13.74	13.33	14.41	13.68	9.39	14.92
FeO*	12.39	10.68	10.14	11.51	11.81	11.23	9.74	13.04	8.03	11.54
MgO	6.43	7.72	8.32	7.46	7.28	8.31	8.01	6.87	8.92	10.99
MnO	0.19	0.12	0.17	0.27	0.25	0.22	0.20	0.22	0.12	0.23
CaO	9.91	7.48	10.38	11.11	10.68	13.35	13.09	11.17	4.55	8.69
Na <sub>2</sub> O	3.08	2.30	2.77	3.03	3.11	1.72	1.92	2.58	0.84	2.39
K <sub>2</sub> O	0.10	0.17	0.07	0.06	0.06	0.04	0.05	0.05	0.15	0.06
P <sub>2</sub> O <sub>5</sub>	0.16	0.15	0.10	0.09	0.13	0.09	0.10	0.17	0.18	0.11
LOI (%)	3.15	3.95	3.14	1.26	1.57	1.56	1.20	<1.00	4.89	4.43
TOTAL	98.85	99.14	100.03	99.68	99.20	99.63	99.84	98.74	95.29	99.10
Trace Elements by XRF (ppm)										
V	352	316	312	322	341	333	276	336	198	349
Cr	233	300	205	296	230	360	309	221	121	94
Ni	91	104	65	149	143	113	99	101	70	73
Cu	137	124	53	160	125	105	87	157	424	<7.4
Zn	96	83	29	121	119	106	84	95	96	179
Trace Floments by ICB MS (ppm)										
Sc	44.15	11 16	17 52	45.05	11.96	19 52	45.00	11 59	27.85	12 22
SC Rb	1 / 8	1.60	5 18	45.05	0.45	0.71	43.00	0.27	27.05	45.52
Sr	131.02	112 64	115.88	151.00	146.23	134 78	136.29	152.07	81.07	71.88
v	29.50	29.35	23.92	24.03	26.87	21.92	21.86	28.12	19.85	28.00
7r	95.85	76.15	52.86	53 73	68.87	54 10	56.23	89.65	56.97	57.92
Nb	11.37	8.48	6.03	5.14	7.26	6.69	5.58	9.76	7.09	4.82
Cs	0.08	0.04	2.15	< 0.014	< 0.014	0.02	0.02	< 0.014	0.03	0.02
Ba	36.11	101.98	34.80	19.47	22.24	22.33	25.79	33.36	100.53	20.29
La	8.70	6.92	4.12	3.97	5.66	4.43	4.67	7.66	5.11	6.54
Ce	20.44	16.73	10.11	9.81	13.82	10.79	11.32	18.47	12.76	15.93
Pr	2.87	2.42	1.51	1.53	2.09	1.65	1.72	2.67	1.86	2.38
Nd	13.27	11.78	7.29	7.58	10.19	8.15	8.30	12.52	8.91	11.46
Sm	3.85	3.57	2.49	2.53	3.24	2.58	2.61	3.80	2.58	3.41
Eu	1.47	1.35	1.04	1.02	1.24	1.01	1.02	1.37	0.86	1.41
Gd	4.82	4.65	3.36	3.42	4.09	3.34	3.38	4.55	3.16	4.33
Tb	0.86	0.85	0.64	0.65	0.76	0.62	0.62	0.84	0.56	0.76
Dy	5.61	5.57	4.41	4.45	5.09	4.16	4.16	5.30	3.50	5.08
Но	1.18	1.19	0.97	0.94	1.08	0.89	0.89	1.14	0.74	1.10
Er	3.28	3.29	2.69	2.66	2.96	2.43	2.46	3.17	2.01	3.07
Tm	0.47	0.48	0.39	0.40	0.43	0.36	0.36	0.45	0.30	0.45
Yb	2.91	2.94	2.48	2.49	2.72	2.23	2.20	2.84	1.76	2.87
Lu	0.46	0.47	0.40	0.39	0.43	0.35	0.35	0.44	0.28	0.47
Hf	2.63	2.14	1.52	1.58	1.96	1.58	1.59	2.41	1.53	1.69
Та	0.73	0.55	1.44	0.29	0.42	0.39	0.36	0.68	0.48	0.33
Pb	2.19	1.14	1.30	0.84	0.90	0.69	0.58	<0.204	0.39	0.72
Th	0.73	0.48	0.36	0.26	0.37	0.29	0.31	0.49	0.25	0.34
U	0.26	0.82	0.63	0.09	0.13	0.11	0.11	0.14	0.13	0.12
Nb/Zr	0.12	0.11	0.11	0.10	0.11	0.12	0.10	0.11	0.12	0.08
A Halmadáttin at al. (2000)										

<sup>a</sup> Helgadóttir et al. (2009).

<sup>b</sup> Sigurgeirsson et al. (2011).

<sup>c</sup> Fowler et al. (2015).

Results for wholerock analyses of drill cutting samples from 248 above and below the Reykjanes drill cores, along with select inter-249 2508 vals in the drill cores are provided in Table 1. Immobile element concentrations and ratios in drill cutting samples from wells RN-251 17 (Marks et al., 2010), RN-17B, and RN-30 overwhelmingly reflect 252 a TEE protolith (Fig. 5A–D). A higher proportion of TED protolith 253 compositions are present in drill core samples from wells RN-17B, 254 RN-19 and RN-30, compared to what would be expected based 255 on the abundance of TED surface flows in the Reykjanes Volcanic 256 System. 257

The down hole wholerock geochemical variation of drill cutting samples from well RN-17 and RN-17ST (Marks et al., 2010) are compared to samples from the adjacent RN-17B sidetrack drill core (Fig. 6). Cuttings from depths <2250 m generally have elevated LOI, K<sub>2</sub>O, Rb, Cs, Ba, Pb, Th and U, especially intervals identified as dominated by clastic lithologies (breccia, hyaloclastite, pillow basalt breccia) (Fig. 6). Below 2250 m (corresponding to the horizontal dashed line on Fig. 6), the concentrations of most elements in RN-17ST drill cutting samples are essentially invariable. In contrast, the 9.8 m long RN-17B core from this same interval reflects geochemical heterogeneity comparable to, or even exceeding, that observed from the entire ~3000 m of RN-17 drill cuttings (Fig. 6). For example, Si, Na, and Ca concentrations in RN-17B drill core samples show both enrichments and depletions that exceed the range in the overlying ~3000 m of analyzed cutting samples.

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### 273 5. Discussion

### 274 5.1. Mixing of drill cuttings

Mixing and homogenization of drill cuttings during transport 275 from the subsurface to the surface sampling location is influenced 276 by gravity, viscous drag, buoyancy, impact from other cuttings, and 277 sidewall friction (Bar-Cohen and Zachny, 2009). These factors are 278 in turn controlled by drill bit type, rotation speed, weight-on-bit, 279 and density and circulation rate of drilling fluid (Hulen and Sibbett, 280 1981). In non-vertical holes, cutting beds develop on the "hanging 281 wall" of the borehole, and impacts to the beds from other cuttings 282 result in increased disaggregation (Bar-Cohen and Zachny, 2009). 283 Mixing and homogenization of the drill cutting samples included 284 in this study is evidenced by nearly ~3000 m of drill cuttings sam-285 ples from well RN-17 (along with cuttings from more limited depth 286 ranges in RN-17B and RN-30) only reflecting a TEE basalt lithology. 287 This is in stark contrast to the three Reykjanes spot drill cores; RN-288 17B and RN-30 preserve both TEE and TED protoliths and RN-19 289 (Ottolini et al., 2012) only preserves a TED protolith (Fig. 5A-D). 290 Mixing of only a small amount of the TEE lithology, which has 291 292 higher immobile element concentrations, has likely obscured any TED affinity beyond recognition in the cutting samples. 293

Drill cutting mixing and homogenization is more extreme at depths below 2266 m in well RN-17. Concentrations of virtually all elements in bulk cutting samples below this depth are essentially invariable (Fig. 6). This interval coincides with the depth from which the 9.8 m long RN-17B core was recovered. The geochemical variability of samples from the RN-17B core is comparable to, or exceeds, that of nearly 3000 m of drill cuttings from well RN-17, suggesting that cutting samples from below 2250 m in well RN-17 are not representative of the true nature of the subsurface at these depths. The zone of homogenized drill cuttings below ~2250 m in well RN-17 an increase in well deviation from ~vertical to ~4°, a change in down-hole drilling assembly, and most notably changes in drilling parameters including a four-fold increase in torque and near doubling of the total weight-on-bit (Friðleifsson et al., 2005).

## 5.2. Implications of drill cutting preservation bias for inferring chemical exchanges

The impression gained from examination of the drill cutting samples is that the drilled section is dominantly unaltered basalt. The variation in LOI, Si, Na, Mg, and Ca, for example, would be consistent with minimal fluid/rock alteration under low water/rock or



Please cite this article in press as: Fowler, A.P.G., Zierenberg, R.A., Geochemical bias in drill cutting samples versus drill core samples returned from the Reykjanes Geothermal System, Iceland. Geothermics (2016), http://dx.doi.org/10.1016/j.geothermics.2016.02.007

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rock-dominated conditions. One would also infer that the degree
of alteration and chemical exchange decreases down hole, with
a significant decline below 2250 m. In stark contrast, the RN-17B
core shows pervasive alteration and includes zones of significant
metasomatic addition and hydrolytic depletion of Si, Na, Mg, and
Ca.

We used the method of Humphris et al. (1998) to visualize bulk 321 elemental differences between drill cutting and drill core samples 322 (Fig. 7, upper diagram). A value equivalent to half the detection limit 323 was used for non-detect data. Data normalized using this method 324 fits the equation of a circle, and points plot along an arc of radius 325 one. The concentration of each component in the drill cutting sam-326 ple and the selected drill core sample is squared, the squares are 327 summed, and the square root of the summed value is normalized 328 to one. Elements with similar concentrations in drill core and drill 329 cuttings samples cluster about a point along the arc, while ele-330 ments that are gained or lost in the drill cutting samples relative 331 to the drill core sample plot at increasing distance from the cluster 332 along the arc. While this technique is useful for rapidly visualizing 333 compositional differences between two samples, a drawback is that 334 small differences in elements with very low concentrations result in 335 large shifts on the diagram. To evaluate the magnitude of absolute 336 337 concentration differences, we plotted elemental data on radar diagrams (Fig. 7; middle and lower diagrams). A benefit of visualizing 338

compositional data on radar diagrams is that concentration changes due to dilution (or enrichment) of a major constituent are readily apparent. Grouping of elements in order of increased, decreased, or invariable concentrations allows quick evaluation of the effect of choosing different protoliths for normalization. The ordering of elements on the radar diagrams is informed by the results of the Humphris et al. (1998) diagrams.

A large source of error in any approach to quantify geochemical bias in drill cutting samples stems from the choice of protolith composition used for normalization. Because drill cutting samples consist of mixtures of lithologies recovered over several meters at minimum (i.e., Kristmannsdóttir, 1982; Fig. 4), there is no unique protolith. In the case of Reykjanes drill cutting samples; the mixtures potentially include TEE basalts. TED basalts, crvstalline material, and originally glassy material. Immobile element concentrations and ratios in the Reykjanes drill cutting samples suggest that the influence of TED lithologies is very minor (Fig. 5). Because the RN-30 cutting samples we analyzed contain a mixture of material derived from crystalline basalt and hyaloclastite, we chose to normalize the drill cutting to both a crystalline protolith (2512.53 m) and a hyaloclastite protolith (<2510.5-2) in an attempt to understand the geochemical exchanges recorded by these cuttings. Wholerock analytical data for drill core samples used for comparison to drill cutting samples are presented in Table 1.

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When normalized to the crystalline protolith sample, RN-30 drill cuttings appear to have gained MgO, K<sub>2</sub>O, Rb, Cs, Pb and U, and have elevated LOI (Fig. 7A). Alkalis, MgO, Pb and U (and elevated LOI) are characteristically gained from seawater by alteration of glassy basaltic protolith in seafloor hydrothermal recharge zones (Thompson, 1973; Humphris and Thompson, 1978a,b; Hart and Staudigel, 1982; Chen et al., 1986; Staudigel et al., 1996; Alt, 1995; Alt et al., 1996; Bach et al., 2001, 2003). In contrast, these same elements have been depleted from RN-30 basalts that were cored directly below the interval from which the cuttings were sampled (Table 1). The apparent gain of alkalis, MgO, Pb and U (and elevated LOI) in RN-30 drill cutting samples calculated assuming a crystalline basalt precursor suggest the hyaloclastite drill core sample may be a more appropriate choice of protolith for the cuttings overlying the drill core. This is consistent with the interpretation that the interval overlying the drill core is a hyaloclastite unit, based on elevated proportion of originally glassy protolith material, which is evident in BSE images of RN-30 drill cutting samples analyzed (Fig. 4).

We therefore normalized RN-30 drill cutting samples to a hyaloclastite sample recovered with the drill core (<2510.5–2) from RN-30, as shown on Fig. 7B. This choice of protolith produces apparent elemental biases for RN-30 drill cutting samples that are more consistent with what we observe for RN-17B drill cutting samples normalized to a crystalline protolith (Fig. 7C). We normalized RN-17B drill cutting samples to a pillow basalt sample from the RN-17B core (2800.35 m), as there was little evidence of glassy protolith material in the cuttings overlying that cored interval (Fig. 3). Our protolith choices are supported by: 1) consistent results for the three RN-30 cutting samples, despite different proportions of crystalline and hyaloclastite lithologies in each of the samples; and 2) agreement of results for elemental bias in RN-17B and RN-30 cuttings, despite very different samples being used for normalization in each case. Our results suggest that Na<sub>2</sub>O, CaO, and Cr are generally gained, while MgO, and Zn are generally lost from both RN-17B and RN-30 drill cutting samples (Fig. 7B and C). The cuttings also have lower LOI compared to the core samples, again suggesting bias in cutting samples towards material with lower degrees of alteration. SiO<sub>2</sub>, Cu and Ni are gained in RN-17B cuttings, while U, Th, and Pb are generally gained, and SiO<sub>2</sub> and Cu are lost, from RN-30 drill cuttings (Fig. 7B and C).

Drill cuttings concentrate more resistant alteration mineral phases, which more readily survive grain impacts and more rigorous drilling parameters (Hulen and Sibbett, 1981).

Albitized plagioclase, or plagioclase with albitized rims is ubiquitous in the Reykjanes cuttings samples studied (Figs. 3 and 4), 386

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A.P.G. Fowler, R.A. Zierenberg / Geothermics xxx (2016) xxx-xxx B A С Gained in Gained in Gained in Cutti Cutti ti Rescaled Concentration (RN-30 Cuttings 2500 m) 0.7 0.7 0.7 0.7 (RN-17B Cuttings 2796 m) 700 0.7 800 **Rescaled Concentration Rescaled Concentration** MgO,SiO<sub>2</sub>,LR Cu 0.0 0.2 0.4 0.6 0.8 0.0 0.2 0.4 0.6 0.8 0.0 0.2 0.4 0.6 0.8 **Rescaled Concentration Rescaled Concentration Rescaled** Concentration (RN-17B Core 2800.35 m) (RN-30 Core 2512.53 m) (RN-30 Core <2510.5-2) LOI LOI (% TiO. LOL(% TiO TiO. A1,0, Al<sub>2</sub>O<sub>3</sub> P.0 P.0 AI,O, FeO FeO K.( K FeO K 1gC 4nO (nO Gained in Gained in Pł cutting cuttings Gained in cuttings Та Generall Zn Cu Та Genera Lu Lost in Rb Lost in conserved cutting Th cuttings Generally Ho Cs Lost in conserved Dŷ cuttings TB Gá Eu Sm Pr RN-17B Core (2800.35) Nd -RN-30 Core (<2510.5-2) ----- RN-17B Cuttings (2792) -RN-30 Core (2512.53) -- RN-30 Cuttings (2400) RN-17B Cuttings (2796) -- RN-30 Cuttings (2400) ...RN-30 Cuttings (2450) --- RN-17B Cuttings (2878) .....RN-30 Cuttings (2450) --- RN-30 Cuttings (2500) - - RN-17B Cuttings (2886) ---RN-30 Cuttings (2500) Fig. 7. Drill cutting chemical bias plots. Ni/Zr Cu/Zr Ta/Zr 10 0.0 0 5 2.5 5.0 0.00 0.02 0.04 2350 2790 P П 2810 2400 0 Depth (m) Depth (m) 2830 2450 С 2850 2500 0 2870 П 2890 2550 □ RN-17B Cuttings RN-17B Core (TED) RN-17B Core (TEE) ● RN-30 Hyaloclastite (core) ○ RN-30 Cuttings RN-30 Dolerite (core)

Fig 8. Drill cutting contamination plots.

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and preferential preservation of this phase provides a mechanism 409 to increase both Na and Ca in drill cuttings. Elevated CaO is also 410 potentially hosted in epidote, which is common in cuttings from 411 the intervals studied (Helgadóttir et al., 2009; Sigurgeirsson et al., 412 2011). In the case of RN-17B, elevated  $SiO_2$  likely reflects the high 413 proportion of quartz logged in the cutting samples (Helgadóttir 414 415 et al., 2009), in contrast to the RN-17B core samples where quartz is entirely absent (Fowler et al., 2015). 416

Less resistant alteration minerals are easily disaggregated and lost from cuttings during sample washing and collection (Hulen and Sibbett, 1981). Loss of MgO, Zn and LOI from all drill cuttings is consistent with loss of fine-grained chlorite and or actinolite during sieving and collection of drill cutting samples at the surface. Chlorite  $[(Mg_5Al)(AlSi_3O_{10})(OH)_8]$  and actinolite  $[Ca_2(MgFe)_5(Si_8O_{22})(OH)_2]$  in the Reykjanes geothermal system both host Mg (Lonker et al., 1993), and significantly contribute to

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LOI due to the structural hydroxyls. While there are no available 425 analyses of Zn in Reykjanes chlorite or actinolite, Zn is known to 426 rarely substitute into the chlorite and actinolite structures (Deer 427 et al., 1992). 428

U, Pb and Th are typically enriched in lithologies erupted on the 429 seafloor that are present in the hydrothermal recharge zone (Alt, 430 1995). Gain of these elements in the RN-30 drill cutting samples 431 is a reflection of the abundance of hyaloclastite fragments in these 432 samples. Elevated concentrations of these elements in RN-30 drill 433 cutting samples potentially reflect preferential preservation of a 434 resistant phase hosting these elements, possibly apatite. 435

Offset of clustering elements from unity (dashed line) in the cut-436 ting samples from RN-30 (Fig. 7A), is a reflection of the high SiO<sub>2</sub> 437 content resulting from numerous quartz veins present in the hyalo-438 clastite sample used for normalization. The offset of the clustering 439 elements from unity is an artifact of the closed nature of com-440 positional data (i.e., sum to 100% or 10<sup>6</sup> ppm restriction), where 441 addition of a large proportion of a particular element or oxide, in 442 this case silica, necessarily reduces the concentration of other ele-443 ments by dilution, even though they may not have been removed 444 from the rock. Dilution (or addition) shifts clustering elements 445 446 away from unity, and is apparent in drill cutting samples from RN-30 (Fig. 7). In RN-30 cutting samples, this is due to an unusually 447 high concentration of quartz veins in sample <2510.5-2. The high 448 concentration of SiO<sub>2</sub> veins in the core sample chosen for normal-449 ization (2512.53) therefore yields apparent depletion in SiO<sub>2</sub> in the 450 RN-30 cuttings samples (particularly the sample from 2400 m), and 451 a shift of the clustering elements towards false enrichment in the 452 cuttings samples (Fig. 7). 453

#### 5.3. Contamination by drilling equipment 454

Elevated Cr in all of the drill cutting samples is potentially hosted 455 in more resistant titanomagnetite or a spinel phase, however drill 456 logs do not suggest elevated concentrations of these minerals. 457 An alternate Cr source is potential contamination by Cr-rich steel 458 alloys, which are commonly used in drill bits, stabilizers, and drill 459 collars (Hulen and Sibbett, 1981). 460

Ni and Cu are elevated in cuttings immediately above and below 461 the RN-17B core beyond concentrations of these elements in any of 462 the TEE drill core lithologies, while Ta in the RN-30 sample from 463 2500 m is elevated and Nb is elevated in sample RN-17B 2796 464 (Fig. 7B and C). We normalized Ni and Cu in RN-17B cuttings and Ta 465 in RN-30 drill cutting samples to the immobile element Zr in each 466 sample to avoid the influence of sample dilution (or enrichment) by 467 any single element due to the closed nature of compositional data 468 (Fig. 8). An explanation for these anomalous concentrations is con-469 tamination from down hole drilling equipment. Non-magnetic drill 470 collars used to apply weight on bit are manufactured from Ni-Cu 471 alloys (Hulen and Sibbett, 1981). Ta and Nb contamination poten-472 tially results from grinding samples in a tungsten carbide ring mill 473 (Hickson and Juras, 1986). However Ta and Nb contamination is not 474 observed in any of the drill core samples (Fowler and Zierenberg, in 475 prep), suggesting the contamination may be from worn drill bits, 476 which are also composed of tungsten carbide (Hulen and Sibbett, 477 1981). 478

It is unlikely that the elevated alkali concentrations result from 479 contamination by lost circulation prevention agents (Mica; K, Rb, 480 Cs), because extreme care was taken to thoroughly wash and hand 481 pick mica from cutting samples submitted for analysis (Marks et al., 482 2010). Elevated concentrations of K, Rb, Cs, Ba and Pb in RN-17 483 drill cutting samples at shallow intervals (<500 m) and associated 484 with clastic lithologies (Fig. 5) are consistent with enrichments 485 of the same elements observed in hydrothermally altered drill 486 487 core and dredged samples from shallow oceanic basement rocks (Thompson, 1973; Humphris and Thompson, 1978a,b; Hart and 488

Staudigel, 1982; Chen et al., 1986; Staudigel et al., 1996; Alt, 1995; Alt et al., 1996; Bach et al., 2001, 2003). In seafloor hydrothermal systems, these elements are sequestered in the upper oceanic crust in alteration minerals formed during low temperature seawater circulation. These same elements are subsequently depleted from basaltic rocks at depth that have undergone higher temperature alteration in hydrothermal upflow zones (Alt, 1995). Clastic lithologies present at depth in the Reykjanes system were originally emplaced on the seafloor and have subsided over time to the current depths (Björnsson et al., 1972; Friðleifsson and Richter, 2010).

### 6. Conclusions

Drill cutting samples from well RN-17 preserve element enrichments on the scale of 10's to 100's of meters as evidenced by elevated alkalis, Ba, U, and Pb in shallow drill cutting samples collected at 50 m intervals associated with lithologies emplaced on the seafloor. The same drill cutting samples homogenize basalt so that affinities to the groups TEE and TED are not discernable in the cuttings, but are preserved in Reykjanes drill core samples. Greater depth, slight drill hole inclination, increased weight on bit and torque homogenize drill cutting samples on scales >50m, as evidenced from drill cuttings below 2266 m in RN-17. Drill cutting samples normalized to drill core samples suggest that chlorite and actinolite have disaggregated and been lost during sampling of drill cuttings, while more resistant phases including quartz, plagioclase and epidote have been preferentially retained. Contamination of drill cuttings samples by alloys used in down hole drilling equipment is apparent from elevated Cu, Ni, Ta and Nb in drill cutting samples. The first appearance of alteration minerals and lithologies in drill cutting samples is a useful tool for interpreting broad subsurface characteristics. However, use of drill cutting samples for determining igneous affinity and elemental exchanges during hydrothermal alteration is problematic. While problems of cutting homogenization are difficult to avoid, the bias in selective retainment of the more resistant, coarse-grained minerals can in part be addressed by sampling and analyzing the fine-grained cuttings fraction.

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### Acknowledgements

We thank Guðmundur Ómar Friðleifsson, Wilfred Elders and the Iceland Deep Drilling Project for providing access to the drill core samples. Funding from NSF's Continental Dynamics Program **Q10**533 helped support the cost of core drilling. The research described herein was supported by National Science Foundation grant EAR 0507518. REE analysis was supported by Department of Energy GrantEE00006748.

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Please cite this article in press as: Fowler, A.P.G., Zierenberg, R.A., Geochemical bias in drill cutting samples versus drill core samples returned from the Reykjanes Geothermal System, Iceland. Geothermics (2016), http://dx.doi.org/10.1016/j.geothermics.2016.02.007

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