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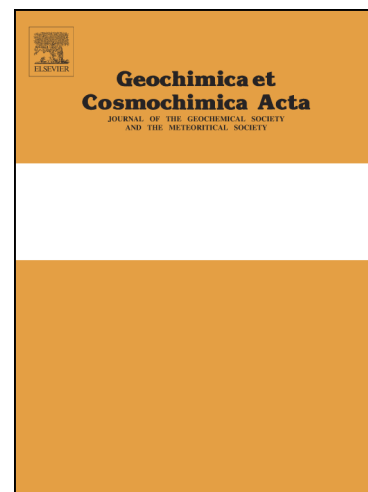
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Main text, references, table, and figure captions

Water in evolved lunar rocks: Evidence for Multiple Reservoirs

1 **Abstract**

2   We have measured the abundance and isotopic composition of water in apatites from

3 several lunar rocks representing Potassium (K), Rare Earth Elements (REE), and Phosphorus (P) -

4 KREEP - rich lithologies, including felsites, quartz monzodiorites (QMDs), a troctolite, and alkali

5 anorthosite. The H-isotope data from apatite provide evidence for multiple reservoirs in the

6 lunar interior. Apatite measurements from some KREEP-rich intrusive rocks display moderately

7 elevated δD signatures, while other samples show δD signatures similar to the range known for

8 the terrestrial upper mantle. Apatite grains in Apollo 15 quartz monzodiorites have the lowest

9 δD values measured from the Moon so far (as low as - 749 ‰), and could potentially represent

10 a D-depleted reservoir in the lunar interior that had not been identified until now. Apatite in all

11 of these intrusive rocks contains < 267 ppm H_2O, which is relatively low compared to apatites

12 from the majority of studied mare basalts (200 to > 6500 ppm H_2O). Complexities in

13 partitioning of volatiles into apatite make this comparison uncertain, but measurements of

14 residual glass in KREEP basalt fragments in breccia 15358 independently show that the KREEP

15 basaltic magmas were low in water. The source of 15358 contained ~ 10 ppm H_2O, about an

16 order of magnitude lower than the source of the Apollo 17 pyroclastic glass beads, suggesting

17 potential variations in the distribution of water in the lunar interior.

18 **1. Introduction.**

19   The detection of water in lunar volcanic glasses, apatites, and melt inclusions has

20 implications for planetary accretion, the source(s) of water in the Earth-Moon system, and the

21 role of water in lunar evolution (Saal et al., 2008; McCubbin et al., 2010; Boyce et al., 2010;

22 Greenwood et al., 2011; Hauri et al., 2011; Tartèse et al., 2013, 2014; Barnes et al., 2013,

23 2014a). (In this paper we use "water" as a shorthand way of referring to all hydrogen species,

24 H_2O, OH, and H_2.   More than one may be present, depending on oxygen fugacity and pressure

25 (e.g., Hirschmann et al., 2012.) Recent work has shown that apatites in mare basalts contain

26 appreciable amounts of water, and are generally enriched in deuterium (^{2}H, or D) with respect

27   to Earth, possibly due to the addition of D-rich material early in the Moon's history (Greenwood

28   et al., 2011) or to the loss of H preferentially over D during magma degassing (e.g. Saal et al.

29   2008; Tartèse and Anand, 2013; Tartèse et al., 2013, Saal et al., 2013). The final fraction of the

30   global lunar magma ocean (LMO) model is considered to be urKREEP, so named for its

31   enrichment in incompatible elements compared to other lunar materials (e.g., Warren and

32   Wasson, 1979). Because water behaves as an incompatible element in major silicate phases

33   that formed during the LMO crystallization (Koga et al., 2003; Aubaud et al., 2004; Grant et al.

34   2007), KREEP-rich rocks are expected to be enriched in water relative to other lunar rocks.

35   Many KREEP-rich lithologies consist of evolved rocks that formed as intrusions, which means

36   that they would have avoided or experienced minimal water loss (unlike the mare basalts), and

37   potential hydrogen isotope fractionation due to magmatic degassing.

38   The mineral apatite $[Ca_5(PO_4)_3(F,Cl,OH)]$ incorporates OH into its crystal structure, making

39   it a potential recorder of the concentration of OH in magma at the time of apatite

40   crystallization. The OH in apatite is resistant to exchanging O or H with adsorbed terrestrial

41   water on thin section surfaces (Greenwood et al., 2011) hence it is useful for H isotopic

42   measurements by secondary ion mass spectrometry (SIMS). The D/H ratio, expressed as δD (‰)

43    $= ([D/H]_{sample}/[D/H]_{standard} - 1)$ x 1000, relative to Vienna Standard Mean Ocean Water (V-

44   SMOW), is important for identifying the source of the Moon's water and the extent of water

45   loss during magmatic processing (e.g., Greenwood et al., 2011; Elkins-Tanton and Grove, 2011;

46   Tartèse et al., 2013).   Previous studies have demonstrated that the water content of lunar

47   apatite varies among different rock types. Apatites in Apollo mare basalts record the highest

48   H_2O contents (up to ~7500 ppm) and δD (+390 to +1100‰) (McCubbin et al., 2010;

49   Greenwoood et al., 2011,; Barnes et al., 2013; Tartèse et al., 2013) , while apatites in more

50   evolved, KREEP-related rocks generally have lower H_2O contents (< 3000 ppm) and δD values (-

51   384 to +791‰, Greenwood et al., 2011; Barnes et al., 2014a; Tartèse et al., 2014; Robinson et

52   al., 2013, Robinson and Taylor, 2014).

53   Though it was initially thought that apatite water contents could be used to infer initial

54   magmatic water abundances (McCubbin et al., 2010, Boyce et al., 2010, Tartèse et al, 2013,

55 2014, Barnes et al. 2014a), Boyce et al. (2014) demonstrated that the F-Cl-OH partitioning into

56 apatite is not well-described by a simple apatite-melt partition coefficient. Apatite water

57 content thus cannot be used to quantitatively determine the amount of water in the co-existing

58 melt, unless the F or Cl content are also known for both melt and apatite, and that it can be

59 confirmed that apatite crystalized in equilibrium with the melt. However, the measured D/H

60 ratios are still useful for gaining insights into processes that might have affected the parental

61 magmas.

62   Rocks formed in an intrusive environment could have experienced minimal D-H

63 fractionation and water loss prior to apatite crystallization because they form at pressures

64 where water is far more soluble in silicate melt than at low pressures near or on the surface

65 (e.g., Dixon et al., 1995). Water solubility in magmas decreases with decreasing pressure, so

66 when a hydrous magma approaches a planetary surface, the melt degasses and water is lost

67 assuming water is present as OH and H_2O. Diffusion modelling of water loss from volcanic lunar

68 pyroclastic glasses indicates that they lost up to 98% of their initial water content upon

69 eruption (Saal et al., 2008). Mare basaltic magmas would also have degassed during eruption

70 onto the lunar surface, but probably less than the 98% loss experienced by pyroclastic glasses.

71 Based on water contents of melt inclusions in olivine from subaerial and submarine Hawaiian

72 lavas (which have little water loss due to the pressure at which they erupted; Hauri 2002), we

73 estimate that lava flows lose up to 90% of their pre-eruptive H_2O. Low-Ti mare magmas could

74 have lost 85 to 99% of their pre-eruptive water contents (Tartèse et al., 2013), but such

75 estimates assume an initial D/H ratio. The degassing of hydrogen from a magma or lava also

76 fractionates lighter H from heavier D, especially if H_2 is lost rather than H_2O (e.g. Richet et al.,

77 1977; Tartèse and Anand 2013; Tartèse et al., 2013). Degassing experiments with apatite

78 suggest that volatile loss occurs rapidly in extrusive magmas, and that apatite, which forms late,

79 will not preserve pre-eruption volatile contents and will instead reflect the post-degassing

80 volatile composition of the magma (Ustunisik et al., 2015). The erupted mare basalts have the

81 highest δD values (up to ~+1100‰) found in lunar rocks so far (Greenwood et al., 2011; Barnes

82 et al., 2013; Tartèse et al., 2013).

4

83   Apatite in intrusive rocks may represent a more pristine sampling of the lunar interior

84   water than the water bound in apatites in the mare basalts, due to their formation at depth at

85   higher pressures (Robinson et al., 2013; Robinson and Taylor, 2014; Barnes et al., 2014a).

86   Reaction relations in symplectitic intergrowths in troctolite 76535 indicate a depth of origin of

87   ~40 km (Gooley et al., 1974; McCallum et al., 2006), corresponding to a pressure of over 1.5 kb.

88   On the other hand, gabbronorite sample 76255 may have formed as shallow as a few

89   kilometers (McCallum et al., 2006), and quartz-monzodiorite 14161,7373 as shallow as 1 km

90   (Jolliff et al., 1999), at a pressure of 50 b. The liquidus temperatures and presence of quartz in

91   highly fractionated lunar felsites (Hess et al., 1975; Hess et al. 1978; Hess et al. 1989; Robinson

92   and Taylor, 2011; Robinson et al., 2015) indicate crystallization at a pressure of at least ~1 kb

93   (Tuttle and Bowen, 1958), corresponding to a depth of over 20 km, assuming a crustal density

94   of 2550 kg/m^3 (Wieczorek et al., 2013). Up to 3 wt. % H_2O is soluble in rhyolitic melts at ~1kb,

95   and even 0.5 wt.% would have been soluble at the 50 b pressure experienced by the parental

96   melt for QMD 14161, 7373 (VolatileCalc, Newman and Lowenstern 2002; Jolliff et al. 1999).

97   Common mineral phases associated with hydrous melts such as amphibole and micas have

98   never been reported in lunar rocks, and no lunar magma has been shown to have contained

99   weight percent levels of water (e.g. Robinson and Taylor, 2014 and references therein). While

100   the concentration of water in the melt would have increased during crystallization, it would

101   have had to reach weight percent levels to degas *before* apatite crystallization began and

102   removed F, Cl, and OH from the melt (Boyce et al., 2014). Assuming that water is completely

103   incompatible in the crystallizing silicates and that a magma had an initial H_2O content of 0.1

104   wt% (similar to A17 melt inclusions, Saal et al., 2013), the H_2O concentration would have only

105   increased to 1 wt.% after 90% crystallization. Apatite forms after 90% crystallization in basaltic

106   systems, and earlier in KREEP-rich melts (Harrison and Watson, 1984; Tartèse and Anand, 2013;

107   Tartèse et al. 2014). Unless they were exceptionally water-rich, water would have remained

108   soluble in the parental melts for all the KREEP-rich intrusive rocks discussed here.

109   While H loss by degassing may not occur in the KREEP-rich intrusive rocks, their H isotopes

110   could be affected by diffusion. Studies of melt inclusions in basalts show that lighter H can

111   escape from melt inclusions by diffusion, therefore enriching heavier D in the melt inclusion

5

112 over time (Gaetani et al., 2012, Bucholz et al., 2013). It is unclear if a similar process affected
113 the H isotopes in apatite from the KREEP-rich intrusive rocks, or if H from country rock
114 surrounding the magma bodies could have been incorporated. However, in order for H to be
115 lost (or gained), it would have to diffuse through either a liquid or solid medium. This would
116 have a less extreme fractionation effect than degassing into vacuum or a low-pressure
117 environment (Bucholz et al., 2013). A magmatic system is more complex than a melt inclusion,
118 and some water loss and H isotope fractionation might occur, but apatite in a rock formed
119 intrusively is generally more likely to have retained the isotopic composition of lunar interior
120 water than rapidly degassed samples such as apatite in mare basalts or glass in pyroclastics.

121   If water was present in the lunar magma ocean, it should be highly concentrated in KREEP-
122 rich materials, assuming no significant loss occurred during magma ocean crystallization and
123 subsequent cumulate overturn (Tartèse et al., 2014).   Anything KREEP-rich or derived from
124 KREEP basaltic magmas should also be enriched in water. However, it is not a simple path from
125 late-stage magma ocean products to KREEP-rich or KREEP-related magmas, which formed
126 either by the assimilation of the urKREEP component by rising Mg-rich diapirs at the base of the
127 lunar crust, or by the partial melting of hybrid mantle sources, formed by sinking urKREEP (and
128 other dense components) mixing with Mg-rich olivine-orthopyroxene cumulates (Shearer and
129 Floss, 1999; Shearer and Papike, 2005; Elardo et al, 2011). Regardless of the formation
130 mechanism, these magmas gave rise to what we now know as the KREEP basalts, and the
131 norites and troctolites of the magnesian (Mg) suite (recently reviewed by Shearer et al., 2015).
132 Fractional crystallization of magmas resembling KREEP basalts is thought to have produced
133 geochemically evolved rocks such as quartz monzodiorites (Ryder, 1976; Ryder and Martinez,
134 1991, Jolliff 1991). Alternatively, silicate liquid immiscibility (SLI) is proposed to have played a
135 role in the formation of the lunar felsites (e.g., Hess et al., 1975, Warner et al., 1978 Snyder et
136 al., 1995; Ryder and Martinez, 1991, Shearer et al., 2015). Most importantly, any petrologic
137 processing took place inside the Moon at pressures high enough to inhibit water loss from
138 magmas or mantle rocks.

139

6

2. Samples.

The felsites and quartz monzodiorites (QMDs) are both intrusive late-stage fractionates of KREEP-basaltic magmas (Ryder et al., 1975; Ryder and Martinez, 1991). The felsite suite consists of evolved Si-rich (~ 70 wt % SiO_2) rocks with graphic intergrowths of quartz and K-feldspar (Ryder et al., 1975; Warner et al., 1978; Taylor et al., 1980; Warren et al., 1983, 1987; Jolliff 1991; Robinson and Taylor, 2011). Silica-rich compositions can be generated by partial melting, but extensive fractional crystallization also produces silica-rich melt through the process of silicate liquid immiscibility (SLI) (e.g. Rutherford et al., 1974). After 90-98% crystallization of a basaltic magma, the remaining liquid will spontaneously separate into Si-rich and Fe-rich liquids (FeO 12-14 wt. %; Roedder and Weiblen 1971, Hess et al. 1975). The Si-rich end member is called a felsite, while the Fe-rich end member is called a ferrobasalt (Rutherford et al., 1974). Based on felsite texture and the presence of quartz, rather than another silica polymorph, the felsites and their corresponding Fe-rich phases formed in small intrusive bodies through silicate liquid immiscibility of an evolving magma of KREEP-basalt composition (e.g. Warner et al., 1978; Taylor et al., 1980; Warren et al., 1983; Robinson and Taylor 2011).

Felsite sample 14321,1047 is well-known, consisting of clasts of graphically-intergrown quartz and K-feldspar, and resides in clast-rich impact breccia 14321 (Warren et al., 1983; Fig. 1a). Apatite was found enclosed by quartz in Si-rich 14321,1047, suggesting that it was a liquidus phase. Sample 77538,16 is unique in that it preserves both silicate liquid immiscibility end-members in co-existing felsite and ferrobasalt areas (Warner et al. 1978)(Fig. 1b). Apatite was found in both the Si-rich and Fe-rich end members; it is enclosed in clinopyroxene in the Fe-rich regions of 77538 and in K-feldspar in the Si-rich regions of 77538.

The quartz monzodiorites (QMDs) are also evolved rocks. They exhibit a cumulate texture and are probably fractional crystallization products of KREEP basaltic magmas (Ryder and Martinez, 1991; Jolliff 1991), though not quite as extreme fractionates as the felsites. Many contain exsolved pyroxenes, indicating they formed in a slow-cooling, intrusive environment. Both 14161,7069 (Fig. 1d) and -,7373 were classified as QMDs (Jolliff 1991). Section 14161,7373 is particularly notable for its inverted, exsolved pyroxenes and high phosphate

7

168 content, mostly in the form of whitlockite (Jolliff 1991); strictly speaking, this anhydrous

169 phosphate is more properly called merrillite (Hughes et al., 2006; Jolliff et al., 2006; Hughes et

170 al., 2008; McCubbin et al., 2014). Based on An contents of plagioclase some QMDs are

171 probably more accurately described as monzogabbros, but we use monzodiorites here to

172 maintain consistency with the majority of previously published literature on these samples.

173   We studied three QMD clasts from soil sample 15400, (15404,51, 15404,55 and 15403,71)

174 which was likely derived from the top of a large boulder (sampled as 15405) at Station 6A on

175 the Apollo 15 mission. Sample 15403,71 is a single fragment from the 2-4 mm fraction of

176 15400. It consists of roughly 50% impact melt and 50% shocked QMD. The QMD contains large

177 phosphates, including a single > 500 μm apatite grain (Marvin et al., 1991). Sample 15404,51

178 and ,55 come from the 4-10 mm size fraction. Apatite in QMD 15404,51 was studied previously

179 by McCubbin et al. (2010). Sample 15404,55 (Fig. 1c) is also a QMD, from the same chip and

180 lithology as 15404,51. In each of the three thin-sections studied, pyroxene shows fine

181 exsolution lamellae, indicating an intrusive origin. Moreover, the samples' enrichment in rare

182 earth elements (Lindstrom et al., 1992), relative to Apollo 15 KREEP basalts, show they probably

183 formed via fractional crystallization of an Apollo 15 KREEP-like magma, as shown by previous

184 studies (e.g., Ryder and Martinez, 1991; Taylor et al., 2012).

185   Alkali anorthosite clasts were studied in breccia 14305,656 (Fig.1f). The alkali anorthosites

186 are also products of fractional crystallization of a KREEP-rich basaltic magma, thought to have

187 formed as flotation cumulates in intrusive magma bodies (Shervais and McGee, 1999).

188 Merrillite was reported in other alkali anorthosite sections of 14305 (Shervais and McGee,

189 1999), and our thin-section seems to be particularly rich in merrillite. Apatite is intergrown with

190 merrillite in sample 14305,656.

191   Troctolite 76535 is coarse-grained and shows signs of slow subsolidus annealing, leading to

192 the interpretation that it could have formed at depths of tens of kilometers in the crust,

193 significantly inhibiting water loss (Gooley et al., 1974; Dymek et al., 1975; Schwartz and

194 McCallum, 1999). There are also reports that this rock may have been altered by post-

195 crystallization metasomatism, which likely would have altered the magmatic volatile contents

196   of apatite in this rock (Elardo et al., 2012; Barnes et al., 2014a). We measured apatites in two

197   thin-sections, 76535,52 and -,56 (Fig 1e). The troctolite is not directly derived from KREEP

198   basaltic magma like the felsites or QMDs, but it does have a high-KREEP content as revealed by

199   trace element analyses of mineral grains (Shearer and Floss, 1999).

200   We also examined two KREEP basalt fragments in impact melt breccia 15358,6. These

201   KREEP basalts have intersertal to intergranular textures and abundant yellow glass that is

202   interpreted to be the last 11-18 % of a KREEP basaltic melt, which quenched instead of

203   crystallizing (Ryder 1988; Taylor et al. 2012). No evidence for the clasts being impact melt

204   breccias, such as unmelted mineral fragments, is present (Taylor et al., 2012). Apatite large

205   enough for SIMS analysis was not identified in either fragment; instead the D/H ratio and H

206   concentration of the glass was measured. These unique clasts likely represent late-stage break

207   outs from KREEP basalt lava flows (Taylor et al., 2012).

208   **3. Methods**

209   *3.1. Secondary Ion Mass Spectrometry (SIMS).* Two instruments, the Cameca ims-1280 and

210   the NanoSIMS 50L, have both been successfully used to measure H isotopes in extraterrestrial

211   apatite (e.g. Hallis et al., 2012; Robinson et al., 2012; Barnes et al., 2013; Tartèse et al., 2013;

212   2014). The ims-1280 has higher analytical precision, but a large analysis size. The 50L

213   NanoSIMS has a smaller analysis size, allowing the measurement of apatites that are too small

214   or cracked to be analyzed with the ims-1280. This paper reports data from both instruments,

215   and the respective protocols are described below.

216   *3.1.1. University of Hawaii (UH).* The protocol for measuring H isotopes in apatite at UH

217   was developed for use with both Martian and lunar materials. A detailed description of this

218   protocol can be found in Hallis et al. (2012). Lunar apatites were analyzed *in-situ* with the ims

219   1280 secondary-ion mass spectrometer during four separate analytical sessions (May and

220   November 2011, August 2012, and July 2014). We used a 2 nA Cs^{+} primary beam (4 nA in

221   August 2012 and July 2014). The secondary-ion mass spectrometer was operated at 10 keV

222   (giving a 20 keV impact energy) with a 50 eV energy window. The mass resolving power was

223 ~1900 (defined as peak width at 10% of peak height), sufficient to separate any interfering

224 molecular ions. A normal-incidence electron flood gun was used for charge compensation of

225 the analyzed area.

226   Using a rastered beam, a 25 × 25 μm^2 area was sputtered for 300 s to remove the carbon

227 coat and any surface contaminants before the actual measurement took place. During the pre-

228 sputtering, we monitored the H ion image to identify and then avoid any possible terrestrial

229 contamination. In the H ion image, H-rich material such as epoxy or small cracks appears very

230 bright. The beam was repositioned (when possible), in order to avoid H-rich areas. The

231 measurement was aborted if no "clean" area could be identified. $^1H^-$, $^2D^-$, and $^{18}O^-$ were then

232 measured sequentially on an electron multiplier in monocollection mode from a reduced

233 rastered area of 15 x 15 μm^2. For glass measurements, ions of $^{30}Si^-$, instead of $^{18}O^-$ were

234 collected. An electronic gate was used to exclude counts from all but the inner ~8 x 8 μm^2 of

235 this area to avoid the edges of the sputtered pit and H creep across the sample surface. If

236 contamination appeared (as a very bright signal on the H image and/or a sudden large spike in

237 the H count rate) during the course of a measurement, the affected cycles were eliminated

238 during data reduction.

239   Each measurement consisted of 40 cycles. ^1H was counted for 3 s, D for 40 s, and ^{18}O (or

240 ^{30}Si for glasses) for 2 s in each cycle. The primary beam was blanked for the first 10 and final 5

241 cycles in order to measure background H and D signals (mainly contributed by the electron

242 gun). The background counts were subtracted from the measured isotope signal, which was

243 collected between cycles 11 and 35 while the beam was positioned on the sample. We made

244 appropriate corrections in data analysis to account for the electronic gate and deadtime of the

245 electron multiplier (c.f. Hallis et al., 2012). Hydrogen isotopes of KREEP basalt glasses were

246 measured on the same instrument in March 2012 using the same analytical conditions.

247   The SIMS measurements were calibrated prior to lunar apatite measurements using 3

248 natural terrestrial apatite standards (Ap003 Durango, Ap018 Russia, and Ap005 Crystal Lode),

249 mounted in epoxy, that were characterized previously by McCubbin et al. (2012). Ap018 and

250 Ap005 were also used for instrumental mass fractionation corrections of measured D/H ratios.

251   The H_2O content of lunar apatite was determined from their measured $^1H/^{18}O$ ratios and a

252   calibration curve of H_2O (wt.%) vs. $^1H/^{18}O$ determined using the 3 apatite standards with

253   different H_2O abundances (Fig. 2a). The curve was forced through the origin.

254   For the KREEP glass measurements, we used two basaltic glass standards (D52-5 and D51-

255   3) with published D/H ratios (Hauri et al., 2002). The H_2O contents of these two standards were

256   determined by Rhea Workman using FTIR at Caltech. The H_2O content of KREEP glass was

257   calculated using a calibration curve (Fig. 2b) for H_2O (wt.%) vs. $^1H/^{30}Si$. That curve was also

258   forced through the origin. The reported errors on water contents and δD values include both

259   the internal precision of an individual analysis and the external reproducibility (standard

260   deviation) for standard measurements during a given analytical session.

261   The detection limit for H_2O content was estimated by measuring nominally anhydrous

262   minerals, such as olivine and pyroxene present in the same thin-sections, and a San Carlos

263   olivine standard in a separate, epoxy-free standard mount. Samples were stored in a 60 °C

264   vacuum oven to minimize the adsorption of water on section surfaces. As shown in Table 1,

265   measurements with 2 nA primary beam resulted in a detection limit of ~ 100 ppm. The

266   detection limit was later significantly improved by up to 10x by using a 4 nA primary beam.   At

267   least two things conspire to produce this improvement. First, a higher beam current increases

268   the signal from the species that make up the sample, while the H from the vacuum system and

269   that creeping along the sample surface remains approximately constant. Second, a higher

270   beam current could more-efficiently remove surface H creeping in to the measurement area,

271   thereby reducing the contaminant steady-state value. Yurimoto et al. (1989) and Stéphant and

272   Robert (2014) also reported that use of higher primary beam current efficiently improves the

273   detection limit of hydrogen measurement.

274   *3.1.2 The Open University (OU).* The Cameca NanoSIMS 50L was used for determining the

275   H_2O contents and H isotopic composition of apatites following the protocol described in details

276   in Barnes et al. (2013, 2014a) and Tartèse et al. (2013). Polished samples were gold-coated for

277   NanoSIMS analysis. A Cs+ primary beam of ~ 260 pA current was used and negative secondary

278   ions of ^1H, D, ^{12}C, and ^{18}O were collected simultaneously on electron multipliers. Electronic

11

279 gating was used to restrict counting secondary ions to the innermost 25 % of the sputtered

280 area. Before analysis, pre-sputtering was performed over a 20 μm x 20 μm area using a ~ 600

281 pA primary beam for 1 minute to clean the sample surface and to locate the apatite using real

282 time imaging (RTI), then further pre-sputtering was performed at a reduced area (analysis area)

283 using the same beam conditions. An electron gun was used to provide charge compensation.

284 Because of the variation in apatite grain size within and between samples, and the need to

285 avoid cracks or inclusions, the analysis areas varied from 8 μm x 8 μm to 5 μm x 5 μm. The

286 vacuum in the analysis chamber during analyses was ~ 6.0 x 10^{-10} Torr.

287 RTI was also carried out during the pre-sputtering to monitor ^{1}H and ^{12}C in order to identify

288 cracks and hotspots. Occasionally, during an analysis a crack or hotspot appeared; in such a

289 case, only the signal corresponding to analysis of the pristine sample was considered. This

290 signal was isolated using the NanoSIMS DataEditor, software developed by Frank Gyngard

291 (Washington University). Data inclusion was based on the ^{12}C signal, which is very low in lunar

292 apatites but is several orders of magnitude higher for material filling the cracks (c.f. Barnes et

293 al., 2014a; Tartèse et al., 2014).

294 Three terrestrial apatite standards (Ap003, Ap004, and Ap018 described in McCubbin et al.,

295 2012) pressed in indium were used for calibration along with a "dry" San Carlos olivine crystal.

296 This dry olivine was used to monitor instrumental background, which ranged between 13 and

297 24 ppm H_2O for the different analytical sessions. To ensure that this measure is adequate for

298 epoxy-mounted samples, analyses were also carried out under routine analytical conditions in

299 two plagioclase crystals in sample 15404. Two analyses of plagioclase yielded between 19 and

300 33 ppm H_2O, which is considered background H_2O assuming that the crystals are indeed dry.

301 Overall, the calculated background H_2O contents for indium-pressed dry olivine and epoxy-

302 mounted nominally anhydrous plagioclase were similar. Background H_2O was then subtracted

303 from the measured values of the unknown apatites.

304 *3.2. Galactic Cosmic Ray Exposure.*

12

305 Exposure to cosmic rays on the surface of the Moon can produce D and H *in situ*, which can

306 alter the indigenous D/H ratio of lunar materials. Saal et al. (2013), Barnes et al. (2014a), and

307 Robinson and Taylor (2014) demonstrated the importance of correcting for spallogenic D,

308 especially in materials with low H_2O content. Spallation-produced D will have a proportionally

309 larger effect on the D/H ratio in samples with low water content than in samples with high

310 water content (Saal et al. 2013) and for samples with long cosmic ray exposure ages. Since the

311 apatites and glasses analyzed in this study have very low water contents (< 300 ppm H_2O), this

312 correction is important.

313   The measured data were corrected following the procedure of Saal et al. (2013), by

314 determining the amount of spallation-produced D using the D production rate (4.6×10^{-11}

315 mol/100 Myr, Merlivat et al., 1976) and the cosmic ray exposure (CRE) age of each sample, and

316 then that contribution was subtracted from the measured D abundance for recalculating the

317 D/H ratio. The reported uncertainty includes the uncertainty in the D production rate and the

318 2σ analytical uncertainties. The large uncertainty in the D production rate dominates the error

319 of the corrected δD values (~ 50 %, Saal et al. 2013). Unlike Saal et al. (2013), spallogenically

320 produced H is not taken into account, because correcting for H has little effect on the overall

321 D/H ratio. For example, the typical spallation correction for H expressed as H_2O is only ~1 ppm

322 (Saal et al., 2013).

323   Cosmic ray exposure age data were available for samples 14321 (23.8 Ma, Lugmair and

324 Marti, 1972; and 24 Ma, Burnett et al., 1972), 14161 (363 Ma, Kirsten et al., 1972), 76535 (195

325 Ma, Bogard et al., 1975; 211 Ma, Crozaz et al., 1974; 233 Ma, Lugmair et al., 1976). When

326 multiple ages were available, we averaged the ages. Since the error associated with the

327 correction for cosmogenic D is dominated by the large uncertainty on the D production rate, we

328 did not factor errors on the cosmic ray exposure ages into the total uncertainty of the corrected

329 values. As the cosmic ray exposure (CRE) age of sample 15403/15404 has not been

330 determined, the CRE age of 11 ± 1.1 Ma for sample 15405 was used. Soil sample 15400 was

331 collected from on top of 15405, and is classified as an immature soil.

13

332   Two samples, 77538 and 15358, have no CRE ages available. Sample 77538 was

333   collected at Station 7 as a rake sample with lunar soil that was designated mature (Meyer,

334   2015). According to Morris (1978), it takes 100 Ma of exposure time to develop a mature soil.

335   Therefore, we take 100 Ma as the exposure age of 77538 for the purposes of spallogenic D

336   correction, but this is only meant to be a rough estimate. Likewise, 15358 was collected as a

337   rake sample from the rim of Spur Crater. Another KREEP basalt from the same rake sample,

338   15382, has been CRE dated to 230 Ma (Stettler et al., 1973) and 240 Ma (Turner et al., 1973).

339   We use the average of these two dates as an estimate for the CRE age of 15358.

340

341   **4. Results**

342   Although we measure H, we report its concentration as H_2O equivalent. In the lunar

343   literature, "water" has been used to describe the presence of H, OH, or H_2O collectively. As

344   explained by Robinson and Taylor (2014), in magma "water" is present largely as OH until the

345   total concentration reaches ~3.5 wt.%, at which point H_2O becomes the dominant molecular

346   species (Dixon et al., 1995). No lunar magmatic water concentrations reach such high levels,

347   implying that it is present dominantly as OH. However, under the reducing conditions (e.g., IW-

348   1) prevailing in lunar magmas, "water" probably consists of a combination of OH and H, with

349   the proportion of H rising with increasing P and decreasing fO_2 (Elkins-Tanton and Grove, 2011;

350   Hirschman et al., 2012, Sharp et al., 2013). To avoid confusion because of the uncertainty in

351   how much of each species is present, we report our results as H_2O equivalent. This approach is

352   similar to reporting total Fe as FeO in electron microprobe analyses.

353   We performed analyses with the UH ims-1280 on a total of 18 points among 11 apatite

354   grains from eight thin sections of intrusive rocks to determine their D/H ratios and water

355   contents. We also made four measurements of residual glass in two KREEP basalt clasts in

356   sample 15358,6 using the same instrument. Many apatite grains are too small (<30μm) or too

357   cracked to be measured with the ims-1280, so they were analyzed with the NanoSIMS 50L ion

358   microprobe at the Open University. A total of 19 points among 13 apatite grains from three

359   thin sections were measured using the NanoSIMS. All of the δD values, water contents, and

14

360   their associated uncertainties are listed in Table 1. Apatite data are plotted on Fig. 3 and

361   compared with literature apatite data in Fig. 4. Some of the data obtained with the ims-1280

362   was first reported in Robinson et al. (2012, 2013) and Robinson and Taylor (2014).

363   The low H_2O contents measured in KREEP-related materials (ranging from 23-267 ppm) is

364   in stark contrast to apatite in most mare basalts, which contain ~1000-7500 ppm H_2O (Fig. 4).

365   One apatite in felsite 14321,1047 and two apatites in QMD 14161,7373 had H_2O content below

366   our detection limits. The KREEP basalt residual glass was similarly found to be water-poor,

367   containing 58-95 ppm H_2O with elevated δD value of +610 to +830 ‰ (Table 1).

368   The range in δD values for apatite in intrusive samples measured here is astoundingly large,

369   varying from ultralow (-749 ‰) to quite elevated (+973 ‰). There are substantial uncertainties

370   on the NanoSIMS measurements (2σ from 317-650‰) due to poor counting statistics when

371   using relatively low probe currents, which are a result of low water abundances in the apatite,

372   but these data are consistent with more precise measurements of apatite in the same sample

373   (14321,1047 apt1) made with the ims-1280. Correction for spallogenic D decreases the δD

374   value by up to 184‰, yet many lunar apatites with detectable water show δD values higher

375   than in the Earth's mantle, -218 to +60‰ (Boettcher et al., 1980; Michael 1998; Ahrens 1989;

376   Deloule et al., 1991; Bell and Rossman 1992; Thompson 1992; Graham et al., 1994; Jambon

377   1994; Wagner et al., 1996; Xia et al., 2002, Hallis et al., 2015). The δD values of other apatites

378   fall near or somewhat below the terrestrial range. However, the δD of apatite in 15403,71 (as

379   low as -749 ± 56‰) is by far the lightest δD value yet reported from the Moon, indicating that

380   there could be a low D source in the lunar interior.

381   **5. Discussion.**

382   The data reported here and those previously published suggest that hydrogen isotopic

383   compositions and possibly water concentrations vary widely in the lunar interior. Here we

384   evaluate the extent of these apparent heterogeneities and the important implications these can

385   have with regards to lunar formation and differentiation, and the accretion of volatiles to the

386   lunar interior.

387 **5.1 Hydrogen isotopic composition: Multiple Reservoirs**

388   Apatites in this sample suite vary widely in δD value (Table 1, Fig. 3, 4), ranging from -754 ±

389 57 ‰ to +934 ± 514 ‰ (spallation corrected) . The δD values of apatites in individual samples

390 (measured in this study and also in the literature) can also vary by 100s ‰ (Fig. 4). To evaluate

391 broad variations among δD values and H_2O content of many samples, we made a histogram of

392 the lowest D apatite analyses from each sample (Fig. 6). If degassing affected the H isotopic

393 composition of a given sample, the lowest δD value will represent the least degassed δD for

394 that sample.   The data seem to cluster into groups with similar δD values. These clusters could

395 represent different reservoirs in the lunar interior, which we evaluate below (Fig. 6).

396 *5.1.1. Earth-like reservoir.*

397   The range in δD value of Earth's present day upper mantle is estimated to be between -

398 -218 and + 60 ‰ (Boettcher et al. 1980; Michael 1998; Ahrens 1989; Deloule et al. 1991; Bell

399 and Rossman 1992; Thompson 1992; Graham et al. 1994; Jambon 1994; Wagner et al. 1996; Xia

400 et al. 2002; Hallis et al., 2015), shown by a line on Fig. 6. Several samples, including two KREEP

401 basalts, five KREEP-rich intrusive rocks, and a mare basalt, fall in or near to this range in δD

402 values. As explained above, these KREEP-rich intrusive rocks formed at depth and pressure, so

403 are less likely to have degassed and fractionated D from H prior to apatite crystallization. The

404 rocks could thus retain their original (or close to their original) D/H ratios, which are essentially

405 Earth-like (Barnes et al., 2014a). All of this evidence indicates that there is at least one

406 reservoir in the lunar interior that has a δD value like the terrestrial mantle.

407   Despite the elevated δD values observed in mare basalt apatites, the mare basalt source may

408 also be similar to the Earth-like δD reservoir. Calculations by Tartèse and Anand (2013) and

409 Tartèse et al. (2013) showed that the entire range of elevated δD values observed in mare

410 basalt apatite could be produced by degassing of 85-99% of the hydrogen from a melt with

411 CI/CM-like chondritic δD signature of ~ +100 ‰, (Alexander et al. 2012). While the water

412 content of the mare basalts appears to be greater than the KREEPy intrusive rocks, they all

413 could have had similar initial δD values, which are in or near the range of the terrestrial mantle.

16

414 Saal et al. (2013) and Füri et al. (2014) show that δD values of the pyroclastic glasses can be

415 reconciled (after accounting for degassing) with being derived from a source region in the lunar

416 interior with a δD value in the range of terrestrial rocks and carbonaceous chondrites. This is

417 consistent with the isotopic compositions of olivine-hosted melt inclusions trapped within glass

418 beads(Saal et al., 2013)

419 *5.1.2. Moderately elevated D reservoir.*

420 Another cluster of analyses on Fig. 6 appears between ~150-350 ‰. Three of these samples

421 are alkali suite rocks, formed intrusively though extensive fractional crystallization of KREEP

422 basaltic magmas (Snyder et al., 1995). The alkali and Mg-suite rocks, however, formed

423 intrusively and thus did not degas, or degassed little compared to eruptive samples. They could

424 represent a reservoir inside the Moon with an inherent moderately elevated δD signature. It is

425 also possible that these samples represent the high part of a range that begins with the

426 terrestrial values, similar to those (δD +187 to +327 ‰) measured in melt inclusions by Saal et

427 al., (2013), and so may not actually be resolvable from the Earth-like reservoir.

428 *5.1.3. Low D reservoir.*

429 A distinct reservoir, with very low δD signature, is represented by apatites from samples

430 15404,51, and -,55, and 15403,71. Apatite in these samples has an average δD value of - 630

431 ‰, which is far below the range of the terrestrial mantle and of other δD values for apatites

432 reported from the Moon (Fig. 4). REE abundances in 15404,36 (the parent chip of 15404,51 and

433 -,55) are elevated with respect to those of Apollo 15 KREEP basalt (Lindstrom et al., 1992),

434 which is consistent with formation from a KREEP basaltic magma, and its texture (exsolved

435 pyroxene) indicates that it formed intrusively, thus avoiding H fractionation due to degassing.

436 Even if the source of these Apollo 15 QMDs had degassed, degassing elevates δD values, which

437 means that their source would have had an even lower initial δD value.

438 Solar wind is also extremely depleted in D (< - 998‰; Huss et al., 2012) and the range in δD

439 values of agglutinate glasses affected by solar wind from the regolith (Liu et al. 2012) is

440 strikingly similar to the range seen in apatites from the Apollo 15 QMDs. However, there is no

17

441 clear mechanism for introducing solar wind H into fragments of intrusive rocks residing inside

442 an impact melt. The Apollo 15 QMDs are considered to have formed at depth, in a shallow

443 intrusion in the lunar crust (Ryder and Martinez, 1991), much deeper than D-depleted solar

444 wind could have penetrated. Rock 15405, on which the 15403/4 regolith developed, is an

445 impact melt breccia deposited at the site ca. 1.3 Ga ago. This boulder was probably formed and

446 thrown to the Apollo 15 site by the impact event that formed Aristillus crater (Ryder 1976;

447 Ryder and Martinez, 1991; Ryder et al., 1991; Taylor et al., 2012). It was subsequently buried

448 and brought to the lunar surface at the Apollo 15 site only 11 Ma ago, based on its cosmic ray

449 exposure age (Drozd et al., 1976). Direct implantation of solar wind H into these apatite grains

450 is unlikely, as solar wind has been demonstrated to penetrate < 1 μm depth into the surface of

451 a grain. Even if an apatite crystal was exposed directly on the surface the ambient lunar surface

452 temperatures (~100° C) are too low to allow significant diffusion of H into the crystal. Using

453 data from Cherniak (2010) and the interdiffusion coefficient for OH, F, and Cl, the total diffusion

454 distance is only ~10^{-5} microns at 100° C in 11 Ma.

455   In order for apatite in the Apollo 15 QMDs to be contaminated with solar wind, H from solar

456 wind would have had to have been incorporated into their source impact melt breccia and

457 subsequently diffused into the apatite grains. As discussed above, these samples were

458 collected from on top of a three-meter boulder, sampled as 15405 (Meyer, 2015).   Drozd et al.

459 (1976) measured Ne, Kr, and Xe isotopes in 15405 and Bernatowicz et al. (1978) measured Ar

460 isotopes in 15405 (matrix and a QMD clast) as part of their Ar-Ar dating. Both papers state that

461 the rock contains no measurable solar wind component. Nevertheless, it is worth investigating

462 whether enough regolith could be incorporated into the 15405 impact melt to impart a low δD

463 signature on the clasts in the rock.

464 Is it possible that the 15405 impact melt was contaminated with solar wind during its formation

465 by the Aristillus impact? The pre-Aristillus regolith could have been a few meters thick, having

466 formed between 3.8 Ga (the age of Imbrium) and 1.27 Ga (the age of Aristillus). We use 10 m

467 for these calculations. How much of that 10 m layer would then be incorporated into the melt

468 formed during the impact that produced Aristillus crater? Using equations 7.10.2 in Melosh

469   (1989) for a 55 km crater and assuming an impact velocity of 17 km/sec, a vertical impact angle,

470   impactor density of 3000 kg/m^3, and target density of 2500 kg/m^3, we estimate that the

471   projectile would have a radius of 1 km. The fraction of the impact melt derived from regolith is

472   the regolith volume intersected by the footprint of the impacting projectile (1 km). Therefore,

473   the regolith constitutes a disk 10 meters thick and 1 km in radius, equivalent to a volume of

474   0.031 km^3. Dividing this by the total volume of the melt produced, 500 km^3 (using projectile size

475   and velocity noted above, after Grieve and Cintala 1992), gives a regolith fraction of 0.0063%. If

476   the regolith contained 100 ppm H (close to the upper limit measured on Apollo regolith

477   samples, Haskin and Warren, 1991), then the impact melt (assuming uniform mixing) would

478   acquire 0.0063 ppm H. If all of the solar wind H was incorporated into apatite and the apatite

479   abundance was 1% (the amount of normative apatite in KREEP basalt), then the apatite would

480   contain a maximum of 0.6 ppm of solar wind derived H from the regolith atop the Aristillus

481   target. This is equivalent to 5.4 ppm H_2O, which is only ~4% of the average water content of

482   apatite in 15403, 71. Moreover, any solar wind H incorporated from the regolith would have

483   then had to diffuse through the very rapidly cooling impact melt (Onorato et al., 1976) and rock

484   fragments to eventually reach the apatite. We conclude that the low δD signature is not derived

485   from solar wind contamination, but instead reflects the nature of the KREEP-rich rocks in the

486   Aristillus target materials. This is supported by δD data from relict apatite grains in the impact

487   melt of 15405 (Barnes et al., 2014b) that have preserved low δD values similar to those

488   measured in 15403 and 15404 in this study.

489   The presence of a very low D reservoir in the lunar interior has interesting implications for

490   potentially degassed samples with low δD values (≈ -100 ‰), such as the two basalts (NWA 773

491   and 14053) that have δD signatures in the terrestrial range. Both of these samples have had

492   their low δD values explained by lack of degassing (NWA 773, average δD ≈ -29 ‰, Tartèse et

493   al., 2014) or incorporation of low D solar wind during impact heating (14053, average δD ≈ -190

494   ‰, Greenwood et al., 2011). However, if a very low D reservoir existed in the Moon perhaps

495   these samples owe their low δD signatures to a mantle source that was depleted in D. We

496   calculate that if they had started with δD value of – 500 ‰, similar to the average δD value of

497   15404,55, the average δD values of apatite in both 14053 and NWA 773 could be obtained with

19

498 > 85 % H_2 loss. This did not necessarily occur for these samples, but it is an intriguing

499 possibility.

500 **5.2 Heterogeneous water distribution in the lunar interior?**

501 The low H_2O content (< 500 ppm) measured in the majority of KREEP-related materials

502 is in stark contrast to the higher H_2O contents (~1000-7500 ppm) of apatites in most mare

503 basalts (Figs. 3, 4). Important exceptions are norites 77215 and 78235, and a granite clast in

504 14303 (Barnes et al., 2014a). Despite attempts to calculate magmatic water contents from

505 apatite data (McCubbin et al., 2010, Boyce et al., 2010, Barnes et al., 2013, Tartèse et al. 2013,

506 2014, Robinson et al., 2013), Boyce et al. (2014) have shown that partitioning of OH, F, and Cl

507 into apatite is complicated and depends on the relative and total abundances of these species,

508 the timing of apatite crystallization, and the extent to which equilibrium was maintained during

509 apatite crystallization of the melt. Estimating water content is further complicated by

510 formation of late-stage melt pockets during crystallization in a lava flow (Pernet-Fisher et al.,

511 2014).

512 While estimating the water content of a magma from apatite H_2O might not be possible,

513 the H_2O concentration of residual glass in KREEP basalts in rock 15358 can be used to estimate

514 the initial concentration in the magma before crystallization and loss occurred. The glass

515 contains between 58 and 95 ppm H_2O (Table 1) and represents the last ~20 % of melt

516 remaining, as determined by modal analyses (Taylor et al., 2012). Because water is

517 incompatible in all lunar minerals except apatite, its initial concentration in the magma would

518 have increased as plagioclase and pyroxene crystallized. Thus, if no loss of H_2O occurred, the

519 parent magma would have contained 20% of the amount we measured in the glass, 12–19 ppm

520 H_2O. The relatively high δD value (average of +560 ‰, corrected for spallation) of the glass

521 suggests that the magma might have lost water, as expected for a lava flow. To assess the initial

522 water content, we calculated the amount of water loss by assuming that the initial δD value

523 was -100 (earthlike) that loss was dominated by H_2, and that the final δD is what we observe in

524 the KREEP basalt clasts (+560 ‰), following the method used by Tartèse et al. (2013). The

525 results are shown in Fig. 5. An initial δD value of -100 ‰ requires an initial H_2O concentration of

20

526 115 ppm to produce the mean δD value of +560 ‰ and 85% loss of initial H. A lower initial δD

527 value would require a higher initial water content, but also a greater loss of H. Initial δD

528 equivalent to VSMOW implies an initial H_2O content of 80 ppm, requiring 80 % loss of the initial

529 water to obtain a δD of 560 ‰. An initial δD signature of -500 ‰ (at the top of the range for

530 the Apollo 15 QMDs), requires > 99.9 % water loss, which is unreasonable considering that the

531 pyroclastic glasses lost only about 98% (Saal et al., 2008).

532 These estimates lead us to conclude that the lava in which the KREEP basalt clasts in

533 15358 formed could have had an Earth-like initial δD signature (~0 ‰) and ~100 ppm H_2O. For

534 comparison, melt inclusions in olivine in Apollo 17 orange glass beads (Hauri et al., 2011; Saal et

535 al., 2013) contain 270–1200 ppm. Assuming that lower values reflect H loss from the inclusions,

536 we infer that the orange glass magma contained ~1000 ppm H_2O, about an order of magnitude

537 larger than we estimate for the KREEP basalts in 15358. Saal et al. (2008) calculated from

538 diffusion profiles of H, Cl, F, and S that the pre-eruption magma for the VLT glass contained

539 260–745 ppm H_2O, consistent with melt inclusion measurements in the orange glass. Assuming

540 10% partial melting, the mantle sources for the orange glass, green glass, and KREEP basalt

541 magmas would have contained 100 ppm, 75 ppm, and 10 ppm H_2O, respectively, suggesting a

542 range in mantle H_2O contents. Clearly, more work on KREEP basalts and KREEP-rich glasses is

543 needed in order to fully understand the relationship between glass/melt inclusion H_2O content

544 and source region water content.

545

546 *5.3 Implications for the lunar interior.*

547 The primary goal of all measurements of water in volcanic glasses, melt inclusions, and

548 apatites is to determine the bulk water content and sources of water in the Moon. The

549 observed heterogeneities in water abundance and δD values in the lunar interior present a

550 major problem, as it is unclear which samples, if any, are the most representative of the Moon

551 as a whole. The most reliable H_2O abundance measurements for determining pre-eruptive

552 water content of lunar magmas come from the melt inclusions in olivine in pyroclastic glass

21

553 beads, which indicates that at least one part of the lunar interior contains as much water as the

554 source regions of MORBs (Hauri et al., 2011). These melt inclusions did not lose much water

555 when they formed, which means their δD values are minimally fractionated (Saal et al., 2013).

556 After correction for spallation, the δD values of the A17 melt inclusions range from +187 to

557 +327 ‰ (Saal et al., 2013). To the extent that H loss did happen, the original δD would have

558 been lower. This is near the Earth range, but it is also near the range of the moderately-

559 enriched δD value reservoir discussed above, which primarily consists of KREEP-rich, intrusive

560 rocks. This may also indicate that the moderately enriched reservoir could be related to the

561 Earthlike reservoir.

562   Füri et al., (2014) reported data suggesting that the source of the Apollo 17 orange glass

563 (74002) had an initial δD value of – 100 ‰, which is within the range of the terrestrial mantle.

564 Does this suggest a common source of water in the terrestrial mantle and some portions of the

565 lunar interior? Füri et al., (2014) point out that a δD value of -100 ‰ is within the range of

566 carbonaceous chondrites, and could indicate the delivery of at least some water to the Earth-

567 Moon system by late accretion (e.g., Saal et al., 2013; Tartèse and Anand 2013; Tartèse et al.,

568 2013; Tartèse et al., 2014). However, if this water was not added after lunar formation to the

569 Earth-Moon system, then it could be conceived that water was retained during the Giant

570 Impact event allowing for some regions to contain substantial water, with Earth-like δD

571 signature (Saal et al., 2013; Barnes et al., 2014a; Füri et al., 2014).

572   Greenwood et al. (2011) were the first to measure δD signatures of apatite in lunar samples,

573 and they showed that apatite in mare basalts were characterized by elevated δD values (> 800

574 ‰). They suggested that the Moon accreted dry (constrained by Moon-formation-evolution

575 models available at the time), and water was added later from a source, such as comets,

576 already characterized by water with high δD values. This seems unlikely. The mare basalts

577 almost certainly lost water when erupted, so their δD values are elevated by the process of

578 magmatic degassing of H_2 which preferentially fractionates H over D isotopes (as discussed in

579 the previous sections). Tartèse and Anand (2013) calculated that pre-eruptive mare basalt

580 magmas could have been characterized by δD values of ~ 100 ‰, but lost 85-99 % of their

581   water, which consequently elevated the δD value of the water. Thus, there is no compelling

582   need for a source with high δD values in the lunar interior. It is possible that late-delivered

583   volatiles could have been added after the mantle cumulates were formed but prior to the

584   formation of a significantly thick crust (e.g., Hauri et al., 2015).

585   The apparently dry regions of the lunar interior vary in δD values from moderately

586   enriched to extremely depleted. The regions that are moderately enriched compared to Earth

587   may reflect fractionation in the proto-lunar disk after the Moon-forming impact (Desch and

588   Taylor, 2012; Hauri et al., 2015). Fractionation of D from H (preferential loss of lighter H) is

589   consistent with the presence of heavy Zn isotopic signatures in lunar samples (Paniello et al.,

590   2012). H loss from the disk needs to be modelled thoroughly, but if H loss was high (~ 90 %)

591   during lunar formation, D/H fractionation could have been sufficient to change the δD value

592   from – 218 ‰ (the lower range of terrestrial mantle values) to the range shown by the

593   moderately enriched lunar reservoir (+200 to +400 ‰). Alternatively, the potentially dry

594   regions of the lunar interior with δD values in the terrestrial range might reflect Moon-forming

595   materials that lost water, but did not fractionate D from H. The regions with Earth-like δD

596   signatures could also have formed by extensive fractionation of H from D during lunar

597   formation, but began with a low δD values like those observed in Apollo 15 QMD apatites. This

598   implies that the primitive Earth could have had a much lower δD signature than is currently

599   considered for the present-day upper mantle. In fact, primitive mantle sources have been

600   identified and at least some contain low δD values, as low as – 218 ± 34 ‰ (Hallis et al., 2015).

601   Halliday (2013) explains the Earth's low δD as a mixture of chondritic and solar components.

602   Our study has contributed to the growing dataset for water and H-isotopes from lunar

603   apatites, and has targeted mostly intrusive rocks of the lunar highlands (felsites and QMDs).

604   The data presented are in agreement with previous work advocating for the heterogeneous

605   distribution of water in the lunar interior (e.g., Anand, 2010; McCubbin et al., 2011; Robinson

606   and Taylor, 2014). The apatites in Apollo 15 QMDs record a water reservoir in the lunar interior

607   that is characterized by an anomalously low D/H ratio (~ -600 ‰), the lowest yet recorded for

608   the lunar interior. This is distinct from the majority of lunar samples, which range in δD values

23

609 of -200 to +100 ‰ compatible with results from lunar highlands cumulates, mare and KREEP

610 basalts, and picritic glasses (Saal et al., 2013; Füri et al., 2014; Barnes et al., 2014a; Tartèse et

611 al., 2014), though some samples have δD values as high as +600 to +700 ‰. The origin or

612 source of this uniquely D-depleted reservoir is ambiguous but could be an isotopic signature

613 resulting from Moon formation through fractionation of H isotopes in the protolunar disk, the

614 incorporation of a primitive Solar component to the lunar interior, or a signature inherited from

615 a depleted reservoir in the proto-Earth.

616 **Summary and Conclusions.**

617   The measurements of KREEP-rich intrusive samples presented here, along with

618 literature data, show that apatite in the KREEP-rich intrusive rocks is low in H_2O. Though

619 apatite cannot be used to calculate pre-eruptive magmatic water content, our measurements

620 of residual glass in KREEP basalt fragments in 15358 suggest that the KREEP-basaltic parent

621 magmas to the felsites and QMDs was very dry, with the mantle source of 15358 containing

622 ~10 ppm H_2O, about ten times less than the mantle source of the A17 pyroclastic glasses. This

623 suggests at least two different reservoirs for water in the lunar mantle; one "wet" and one

624 "dry", which complicates determining the bulk water content of the Moon.

625   In addition to the water content of apatite in these KREEP-rich intrusive rocks, we have

626 also measured their H isotope compositions and compared them with literature data. Lunar

627 apatites show an astonishingly large range in δD and may fall into a number of reservoirs.

628 Many lunar rocks, including the mare basalts, seem to have had initial δD similar to that of

629 Earth's mantle, while the drier KREEP-rich rocks studied here are moderately elevated in D with

630 respect to Earth. The most surprising results came from apatite in Apollo 15 QMDs 15404, 51,

631 15404,55, and 15403, 71, which have the lowest δD measured in lunar apatite so far, as low as -

632 754 ‰. These QMDs may represent another reservoir in the lunar mantle that could preserve a

633 primitive, D-depleted component within the Moon, perhaps inherited from the proto-Earth.

634   Our data indicate that water is heterogeneously distributed in the Moon, varying in both

635 concentration and hydrogen isotopic composition. How these distinctive reservoirs formed is

24

636 unclear, but likely reflect a combination of lunar formation and differentiation. Bulk lunar water

637 concentration is difficult to constrain, but the variability in water content and D/H may be much

638 more informative about lunar origin than is the total amount of water in the Moon.

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652

653 **References.**

654 Ahrens, T. J. (1989) Water storage in the upper mantle. *Nature* **342**, 122–123.

655 Alexander, C. M. O'D. et al. (2012) The provenances of asteroids, and their contributions to the
656   volatile inventories of the terrestrial planets, *Science* **337**, 721-723, doi:
657   10.1126/science.1223474.

658 Anand M. (2010) Lunar water: a brief review. Earth Moon Planet. **107**, 65–73.

659 Aubaud C., Hauri E. H., and Hirshmann M. M. (2004) Water partitioning coefficients between
660   nominally anhydrous minerals and basaltic melts. *Geophys. Res. Lett.* **31**, doi
661   10.1029/2004GRL021341.

662 Barnes J.J., Franchi I.A., Anand M., Tartèse R., Starkey N.A., Koike M., Sano Y., Russell S.S. (2013)
663   Accurate and precise measurements of the D/H ratio and hydroxyl content in lunar apatites
664   using NanoSIMS. *Chem. Geo.* **337-338,** 48-55.

665 Barnes J.J., Tartèse R.**,** Anand M., McCubbin F.M., Franchi I.A., Starkey N.A., and Russell S.S.
666   (2014a) The origin of water in the primitive Moon as revealed by the lunar highlands
667   samples. *Earth Planet. Sci. Lett.* **390**, 244-252.

668 Barnes J.J., Tartèse R.**,** Anand M., McCubbin F.M., Franchi I.A., Starkey N.A., and Russell S.S.
669   (2014b) The hydrogen isotopic composition of apatites in lunar impact-melt breccias. *Lunar*
670   *Planet. Sci. XLV.* Lunar Planet. Inst., Houston. #1978 (abstr.).
671
672 Bell, D. R. & Rossman, G. R. (1992) Water in Earth's mantle: the role of nominally anhydrous
673   minerals. *Science* **255**, 1391–1396.

674 Bernatowicz T.J., Hohenberg C.M., Hudson B., Kennedy B.M. and Podosek F. (1978) Argon ages
675   for lunar breccias 14064 and 15405. *Proc. 9th Lunar Planet. Sci. Conf.*, 905-919.
676
677 Boettcher A. L. and O'Neil J. R. (1980) Stable isotope, chemical and petrographic studies of high
678   pressure amphiboles and micas: evidence for metasomatism in the mantle source regions
679   of alkali basalts sand kimberlites. *Am. J. Sci.* **280A**, 594–621.

680 Bogard D.D., Nyquist L.E., Bansal B.M., Wiesmann H. and Shih C.-Y. (1975) 76535: An old lunar
681   rock. *Earth Planet.Sci. Lett.* **26**, 69-80.
682
683 Boyce J. W., Tomlinson S. M., McCubbin F. M., Greenwood J. P., and Treiman A. H. (2014) The
684   lunar apatite paradox. *Science Express* 20 March 2014 *10.1126/science.1250398*

685 Boyce J.W., Liu Y., Rossman G.R., Guan Y., Eiler J.M., Stolper E.M., and Taylor L.A. (2010) Lunar
686   apatite with terrestrial volatile abundances. *Nature* **466**, 466-469.

687 Bucholz C. E., Gaetani G.A., Behn M.D., and Shimizu N. (2013) Post-entrapment modification of
688   volatiles and oxygen fugacity in olivine-hosted melt inclusions. *Earth Planet. Sci. Lett.* **374**,
689   145-155.

690 Burnett D.S., Huneke J.C., Podosek F.A., Russ G.P., Turner G. and Wasserburg G.J. (1972) The
691   irradiation history of lunar samples. *Lunar Sci.III.*, Lunar Inst., Houston, 105-107 (abstr.)
692
693 Cherniak D.J. (2010) Diffusion in accessory minerals: zircon, titanite, apatite, monazite and
694   xenotime. *Rev. Mineral. Geochem.*, **72,** *827-869.*
695
696 Crozaz G., Drozd R., Hohenberg C., Morgan C., Ralston C., Walker R. and Yuhas D. (1974) Lunar
697   surface dynamics: Some general conclusions and new results from Apollo 16 and 17. *Proc.*
698   *5th Lunar Sci. Conf.,* 2475-2499.
699
700 Deloule E., Albarède F. and Sheppard S. M. F. (1991) Hydrogen isotope heterogeneities in the
701   mantle from ion probe analysis of amphiboles from ultramafic rocks. Earth. Planet. Sci.
702   Lett. **105**, 543–553.

703

704 Desch S.J. and Taylor G. J. (2012) Volatile depletion from the protolunar disk. *Euro. Planet. Sci.*
705   *Cong. 7*, Abst.# 272.

706 Dixon J.E., Stolper E. M., and Holloway J.R. (1995) An experimental study of water and carbon
707   dioxide solublities in mid-ocean ridge basaltic liquids: I. Calibration and solubility models.
708   *Jour. Petrology* **36**, 1607-1631.

709 Drozd R.J., Kennedy B.M., Morgan C.J., Podosek F.A. and Taylor G.J. (1976) The excess fission
710   Xenon problem in lunar samples. *Proc. 7th Lunar Sci. Conf.,* 599-623.

711

712 Dymek R. F., Albee A. L. and Chodos A. A. (1975) Comparative petrology of lunar cumulate rocks
713   of possible primary origin: Dunite 72415, troctolite 76535, norite 78235,and anorthosite
714   62237. *Proc. 6th Lunar Sci. Conf*. 301-341.

715 Elardo S. M., McCubbin F. M. and Shearer C. K. Jr. (2012) Chromite symplectites in Mg-suite
716   troctolite 76535 as evidence for infiltration metasomatism of a lunar layered intrusion.
717   *Geochim. Cosmochim. Acta* **87,** 154-17.

718 Elardo S. M., Draper D. S. and Shearer C. K. Jr. (2011) Lunar Magma Ocean crystallization
719   revisited: Bulk composition, early cumulate mineralogy, and the source regions of the
720   highlands Mg-suite. *Geochim. Cosmochim. Acta* **75**, 3024-3045.

721 Elkins-Tanton L. T. and Grove T.L. (2011) Water (hydrogen) in the lunar mantle: Results from
722   petrology and magma ocean modelling. *Earth Planet. Sci. Lett.* **307,** 173-179.

723 Füri E., Deloule E., Gurenko A. and Marty B. (2014) New evidence for chondritic lunar water
724   from combined D/H and noble gas analyses of single Apollo 17 volcanic glasses. *Icarus* **229**,
725   109-120.

726 Gaetani G.A., O'Leary J.A., Shimizu N., Bucholz C.E. and Newville M., (2012) Rapid re-
727   equilibration of water and oxygen fugacity in olivine-hosted melt inclusions. Geology **40**,
728   915–918.

729 Geiss J. and Gloecker G. (1998) Abundances of Deuterium and Helium-3 in the protosolar cloud.
730   *Space Sci. Rev.* **84**, 239-250.

731 Gooley R.C., Brett R., Warner J.L. and Smyth J.R. (1974) A lunar rock of deep crustal origin:
732   Sample 76535. *Geochim.Cosmochim. Acta* **38**, 1329-1339.

733 Grant K. J., Kohn S. C., and Brooker R. A. (2007) The partitioning of water between olivine,
734   orthopyroxene and melt synthesized in the system albite-forsterite-H_2O. *Earth Planet. Sci.*
735   *Lett.* **260**, 227-241.

736 Graham C., Kinny P., Harte B. and Valley J. (1994) The nature and scale of stable isotope
737   disequilibrium in the mantle: ion and laser microprobe evidence. *Mineral. Mag.* **58A**, 345–
738   346.

739 Greenwood J. P., Itoh S., Sakamoto N., Warren P., Taylor L. and Yurimoto H. (2011) Hydrogen
740   isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. *Nature*
741   *Geosci.* **4,** 79-82.

742 Grieve R. A. F. and Cintala M. J. (1992) An analysis of differential impact melt-crater scaling and
743   implications for the terrestrial impact record. *Meteoritics* **27**, 526-538.
744

745 Halliday A. N. (2013) The origins of volatiles in the terrestrial planets. *Geochim. Cosmochim.*
746   *Acta* **105**, 146-171.

747 Hallis L. J., Huss G. R., Nagashima K., Taylor G. J., Halldórsson S. A., Hilton D.R., Mottl M. J. and
748   Meech K. J. (2015) Evidence for primordial water in Earth's deep mantle. *Science* **350**, 795-
749   797.

750 Hallis L. J., Taylor G. J., Nagashima K. and Huss G. R. (2012) Magmatic water in the martian
751   meteorite Nakhla. *Earth Planet. Sci. Lett*. **359-360**, 84-92.

752 Harrison T.M., and Watson E.B. (1984) The behavior of apatite during crustal anatexis: Equilib-
753   rium and kinetic considerations: Geochim. Cosmochim. Acta **48**, 1467-1477.

754 Haskin L. and Warren P. (1991) Lunar chemistry. In *Lunar Sourcebook: a user's guide to the*
755   *Moon*, eds. G. H. Heiken, D. T. Vaniman, and B. M. French. Cambridge University Press, pp.
756   357-474.

757 Hauri E. (2002) SIMS analysis of volatiles in silicate glasses, 2: isotopes and abundances in
758   Hawaiian melt inclusions. *Chem. Geol.* **183**, 115-141.

759 Hauri E. H., Weinreich T., Saal A. E., Rutherford M. C. and Van Orman J. A. (2011) High pre-
760   eruptive water contents preserved in lunar melt inclusions. *Science* **333,** 213-215.

761 Hauri E., Wang J., Dixon J.E., King P.L., Mandeville C. and Newman S. (2002). SIMS analysis of
762   volatiles in silicate glasses 1. Calibration, matrix effects and comparisons with FTIR. *Chem.*
763   *Geol*. **183**, 99-114.

764 Hauri, E., Saal, A. E., Rutherford, M. J. and Van Orman, J. A. (2015) Water in the Moon's interior:
765   Truth and consequences. *Earth Planet. Sci. Lett.* **409**, 252-264.

766 Hess P. C., Rutherford M. J., Guillemette R. N., Ryerson F. J. and Tuchfeld H. A. (1975) Residual
767   products of fractional crystallization of lunar magmas: An experimental study. *Proc. 6*[th]
768   *Lunar Sci. Conf*., 895-909.

769 Hess P.C., Rutherford M.J. and Campbell H.W. (1978) Ilmenite crystallization in nonmare basalt:
770   Genesis of KREEP and high-Ti mare basalt. *Proc.9th Lunar Sci. Conf.* 705-724.

771 Hess P.C., Horezmpa P. and Rutherford M. J. (1989) Fractionation of Apollo 15 KREEP basalts.
772   *20th Lunar Planet. Sci.*, Lunar Planet Inst., Houston, #1209 (abstr.).

773 Hirschmann M. M., Wirthers A. C., Ardia P. and Foley (2012) N. T. Solubility of molecular
774   hydrogen in silicate melts and consequences for volatile evolution of terrestrial planets.
775   *Earth Planet. Sci. Lett.* **345-348**, 38-48.

776 Hughes J. M., Jolliff B. L. and Rakovan J. (2008) The crystal chemistry of whitlockite and
777   merrillite and the dehydrogenation of whitlockite to merrillite. *Amer. Mineral.* **93**, 1300-
778   1305.

779 Huss G. R., Nagashima K., Burnett D. S., Jurewicz A. J. G. and Olinger C. T. (2012) A new upper
780   limit on the D/H ratio in the solar wind. *Lunar Planet. Sci. XLIII*, Lunar Planet. Inst.,
781   Houston, #1709 (abstr.).

782 Jambon, A. (1994) Earth degassing and large-scale geochemical cycling of volatile elements. In
783   *Volatiles in Magmas* (eds. M. R. Carroll and J. R. Holloway), *Rev. Mineralogy* **30**
784   Mineralogical Society of America. pp. 479–517.

785 Jolliff B.L. (1991) Fragments of quartz monzodiorite and felsite in Apollo 14 soil particles. *Proc.
786   21st Lunar Planet. Sci. Conf.*, 101-118.

787 Jolliff B. L., Floss C., McCallum I. S. and Schwartz J. M. (1999) Geochemistry, petrology, and
788 cooling history of 14161,7373: A plutonic lunar sample with textural evidence of granitic-
789 fraction separation by silicate-liquid immiscibility. *Amer. Mineral.* **84**, 821-837.

790 Jolliff B. L., Hughes, J.M., Freeman, J. J. and Zeigler R. A. (2006) Crystal chemistry of lunar
791   merrillite and comparison to other meteoritic and planetary suites of whitlockite and
792   merrillite. *Am. Min.*, **91***,* 1583-1595.
793
794 Kirsten T., Deubner J., Horn P., Kaneoka I., Kiko J., Schaeffer O.A. and Thio S.K. (1972) The rare
795   gas record of Apollo 14 and 15 samples. *Proc. 3rd Lunar Sci. Conf.*,1865-1889.
796
797 Koga K., Hauri E., Hirshmann M. and Bell D. (2003) Hydrogen concentration analyses using SIMS
798   and FTIR: comparison and calibration for nominally anhydrous minerals. *Geochem.
799   Geophys. Geosys.* **4**, 1019, doi: 10.1029/2002GC000378.

800 Lindstrom M. M., Mittlefehldt D.W., and Martinez R.R. (1992) Geochemical studies of Apennine
801   Front coarse-fines particles. *23rd Lunar Planet Sci.*, Lunar Planet. Inst., Houston, #1388
802   (abstr).

803 Liu Y., Guan Y., Zhang Y., Rossman G. R., Eiler J. M. and Taylor L.A. (2012) Direct measurement
804   of hydroxyl in the lunar regolith and the origin of lunar surface water. *Nature Geosci.* **5**:
805   779-782.

806 Lugmair G. W. and Marti K. (1972) Exposure ages and neutron capture record in lunar samples
807   from Fra Mauro. *Proc. 3rd Lunar Sci. Conf.*, 1891-1897.
808
809 Lugmair G. W., Marti K., Kurtz J. P. and Scheinin N. B. (1976) History and genesis of lunar
810   troctolite 76535 or: How old is old? *Proc. 7th Lunar Sci. Conf.* 2009-2033.

811 Marvin U. B., Lindstrom M. M., Holmberg B. B. and Martinez R. R. (1991) New observations on
812   the quartz monzodiorite-granite suite. *Proc. 21st Lunar Planet. Sci. Conf.,* 119-135.

813 McCallum, I. S., Domeneghetti, M. C., Schwartz, J. M., Mullen, E. K., Zema, M., Cámara, F.,
814   McCammon, C. and Ganguly, J. (2006) Cooling history of lunar Mg-suite gabbronorite
815   76255, troctolite 76535 and Stillwater pyroxenite SC-936: The recored in exsolution and
816   ordering in pyroxenes. *Geochim. Cosmochim. Acta* **70**, 6068-6078.

817 McCubbin F. M., Steele A., Hauri E. H., Nekvasil H., Yamashita S. and Hemley R. J. (2010)
818   Nominally hydrous magmatism on the Moon. *Proc. Natl. Acad. Sci. USA* **107,** 11223-11228.

819 McCubbin F. M., Jolliff B. J., Nekvasil H., Carpenter P. K., Zeigler R. A., Steele A., Elardo S. M. and
820   Lindsley D. H. (2011) Fluorine and chlorine abundances in lunar apatite: Implications for
821   heterogeneous distributions of magmatic volatiles in the lunar interior. *Geochim.*
822   *Cosmochim. Acta* **75**, 5073–5093.

823 McCubbin F. M**.,** Hauri E. H., Elardo S. M., Vander Kaaden K. E., Wang, J. and Shearer C. K.,
824   (2012). Hydrous melting of the martian mantle produced both depleted and enriched
825   shergottites. *Geology* **40**, 683-686.
826
827 McCubbin, F. M., Shearer, C. K., Burger, P. V., Hauri, E. H., Wang, J., Elardo, S. M., & Papike, J. J.
828   (2014). Volatile abundances of coexisting merrillite and apatite in the martian meteorite
829   Shergotty: Implications for merrillite in hydrous magmas. *Amer. Mineral*. **99**, 1347-1354.
830
831 Melosh H. J. (1989) *Impact Cratering: A Geologic Process*. Oxford University Press, New York.
832   245 pp.
833
834 Merlivat, L., Leiu, M., Neif, G. and Roth, E. (1976) Spallation deuterium in rock 70215. *Proc.*
835   *Lunar Sci. Conf. 7th*, 649-658.
836
837 Meyer C. (2015) The Lunar Sample Compendium. http://curator.jsc.nasa.gov/lunar/lsc/
838
839 Michael P. J. (1988) The concentration, behavior and strorage of H2O in the suboceanic upper
840   mantle: implications for mantle metasomatism. *Geochim. Cosmochim. Acta* **52**, 555–566.
841

842 Morris R.V. (1978) The surface exposure (maturity) of lunar soils; some concepts and I_s/FeO
843   compilation. *Proc. 9th Lunar Planet. Sci.* 2287-2297.

844 Newman S. and Lowenstern J.B. (2002) VolatileCalc: a silicate melt-H_2O-CO_2 solution model
845   written in Visual Basic for Excel. *Comp. and Geosci.* **28**, 597-604).

846 Onorato P. I. K., Uhlmann D. R., and Simonds C. H. (1976) Heat flow in impact melts: Apollo 17
847   station 6 boulder and some applications to other breccias and xenolith laden melts. *Proc.*
848   *Lunar Sci. Conf. 7th*, 2429-2467.

849 Paniello R. C., Day J. M. D. and Moynier F. (2012) Zinc isotopic evidence for the origin of the
850   Moon. *Nature* **490,** 376-379.

851 Pernet-Fisher J. F., Howarth G. H., Liu Y., Chen Y. and Taylor L. A. (2014) Estimating the lunar
852   mantle water budget from phosphates: Complications associated with silicate-liquid-
853   immiscibility. *Geochim. Cosmochim. Acta* **144**, 326-341.

854 Robinson K. L. and Taylor G. J. (2011) Intrusive and extrusive lunar felsites. *42nd Lunar Planet*
855   *Sci.,* Lunar Planet Inst., Houston, #1257 (abstr).

856 Robinson K. L. and Taylor G. J. (2014) Heterogeneous distribution of water in the Moon. *Nature*
857   *Geosci.* **7**, 401-408.

858 Robinson K. L., Hellebrand E. and Taylor G. J. (2015) The physical setting for felsite formation.
859   *46th Lunar Planet Sci.*, Lunar Planet. Inst., Houston, #1623 (abstr.).

860 Robinson K. L., Taylor G. J. and Nagashima K. (2013) D/H of intrusive moon rocks: Implications
861   for lunar origin. *Lunar Planet Sci. XLIV,* Lunar Planet. Inst., Houston, #1327 (abstr.).

862 Robinson K. L., Taylor G. J., Hellebrand E. and Nagashima K. (2012) Water in evolved lunar rocks:
863   Implications for water distribution in the lunar mantle. *Lunar Planet Sci. XLIII,* Lunar Planet.
864   Inst., Houston, #1727 (abstr.).

865 Roedder E. and Weiblen P. W. (1971) Petrology of silicate melt inclusions, Apollo 11 and Apollo
866   12 and terrestrial equivalents. *Proc. 2nd Lunar Sci. Conf.,* 507-528.

867 Rutherford M. J., Hess P. C. and Daniel G. H. (1974) Experimental liquid line of descent and
868   liquid immiscibility for basalt 70017. *Proc. 5th Lunar Sci. Conf.*, 569-583.

869 Ryder G. (1976) Lunar sample 15405: Remnant of a KREEP basalt-granite differentiated pluton.
870   *Earth Planet. Sci. Lett.* **29**,255–268.

871 Ryder G. (1988) Quenching and disruption of lunar KREEP lava flows by impacts. Nature **336**,
872   751–754.

873 Ryder G. and Martinez R. R. (1991) Evolved hypabyssal rocks from station 7, Apennine Front,
874   Apollo 15. *Proc. 21st Lunar Planet. Sci. Conf.*, 137-150.

875 Ryder G., Bogard D. and Garrison D. (1991) Probable age of Autolycus and calibration of lunar
876   stratigraphy. *Geology* **19**, 143–146.

877 Ryder G., Stoeser D. B., Marvin U. B. and Bower J. F. (1975) Lunar granites with unique ternary
878   feldspars. *Proc.6th Lunar Planet. Sci. Conf.,* 435-449.

879 Saal A. E., Hauri E. H., Lo Cascio M., Van Orman J. A., Rutherford M. C. and Cooper R.F. (2008)
880   Volatile content of lunar volcanic glasses and the presence of water in the Moon's interior.
881   *Nature* **454,** 192-195.

882 Saal A. E., Hauri E. H., Van Orman J. A. and Rutherford M. J. (2013) Hydrogen isotopes in lunar
883   volcanic glasses and melt inclusions reveal a carbonaceous chondrite heritage. *Science*
884   **340**, 1317-1320.

885 Schwartz J. M. and McCallum I. S. (1999) Inferred depths of formation of spinel cataclasites and
886   troctolitic granulite,76535 using new thermodynamic data for Cr-spinel. *Lunar Planet.*
887   *Sci.XXX*, Lunar Planetary Institute, Houston, #1308 (abstr.).

888 Sharp Z. D., McCubbin F. M. and Shearer C. K. (2013) A hydrogen-based oxidation mechanism
889   relevant to planetary formation. *Earth Planet. Sci. Lett.* **380**, 88-97.

890 Shaw A. M., Hauri E.H., Behn M.D., Hilton D.R., Macpherson C.G. and Sinton J.M. (2012) Long-
891   term preservation of slab signatures in the mantle inferred from hydrogen isotopes. *Nature*
892   *Geosci*. **5,** 224-228.

893 Shearer C. K. and Floss C. (1999) Evolution of the Moon's mantle and crust as reflected in trace-
894   element microbeam studies of lunar magmatism. In Origin of the Earth and Moon (R.
895   Canup and K. Righter, eds.), Univ. of Arizona Press, Tucson, pp 339-359.

896 Shearer C. K. and Papike J. J. (2005) Early crustal building processes on the moon: Models for
897   the petrogenesis of the magnesian suite. *Geochim. Cosmochim. Acta* **69**, 3445-3461.

898 Shearer, C. K., Elardo, S. M., Petro, N. E., Borg, L. E. and McCubbin, F. M. (2015) Origin of the
899   lunar highlands Mg-suite plutonic rocks. An integrated petrology, geochemistry,
900   chronology, and remote sensing perspective. *Amer. Mineral.,* **100**, 294–325.

901 Shervais J. W. and McGee J. J. (1999) KREEP cumulates in the western lunar highlands: Ion and
902   electron microprobe study of alkali-suite anorthosites and norites from Apollo 12 and 14.
903   *Amer. Mineral.* **84**, 806-820.

904 Snyder G. A., Taylor L. A. and Halliday A. N. (1995). Chronology and petrogenesis of the lunar
905   highlands alkali suite: Cumulates from KREEP basalt crystallization. *Geochim. Cosmochim.*
906   *Acta* **59**, 1185–1203.

907 Stéphant A. and Robert F. The negligible chondritic contribution in the lunar soils water. (2014)
908   *Proc. Natl. Acad. Sci. USA* **111**, 15007-15012.

909 Stettler A., Eberhardt P., Geiss J., Grogler N. and Maurer P. (1973) Ar^{39}-Ar^{40} ages and Ar^{37}-Ar^{38}
910   exposure ages of lunar rocks. *Proc. 4th Lunar Sci. Conf*. 1865-1888.

911 Tartèse R. and Anand M. (2013) Late delivery of chondritic hydrogen into the lunar mantle:
912   Insights from mare basalts. *Earth Planet. Sci. Lett.* **361**, 480-486.

913 Tartèse R., Anand M., Barnes J. J., Starkey N. A., Franchi I. A., and Sano Y. (2013) The
914   abundance, distribution, and isotopic composition of Hydrogen in the Moon as revealed by
915   basaltic lunar samples: Implications for the volatile inventory of the Moon. *Geochim.*
916   *Cosmochim. Acta* **122**, 58-74.

917 Tartèse R., Anand M., McCubbin F.M., Elardo S.M., Shearer C.K., and Franchi I.A. (2014). Apatites
918   in lunar KREEP basalts: The missing link to understanding the H isotope systematics of the
919   Moon. *Geology* **42**, 363-366.

920 Taylor G.J., Warner R.D., Keil K., Ma M-.S., and Schmitt R.A. (1980) Silicate liquid immiscibility,
921   evolved lunar rocks, and the formation of KREEP. *Proc. Conf. Lunar Highlands Crust*, 339-
922   352.

923 Taylor G. J., Martel L. M. V, and Spudis P. D. (2012) The Hadley-Apennine KREEP Basalt Igneous
924   Province. *Meteor. Planet. Sci.* **47,** 861-879.

925 Thompson A. B. (1992) Water in the Earth's upper mantle. *Nature* **358**, 295–302.

926 Turner G., Cadogan P. H., and Yonge C. J. (1973) Argon selenochronology. *Proc. 4th Lunar Sci.*
927 *Conf.,* 1889-1914.

928 Tuttle O. F. and Bowen N. L. (1958) *Origin of granite in the light of experimental studies in the*
929   *system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O*, Geol. Soc. Am. Mem. **74**, 151 pp.

930 Ustunisik G., Nekvasil H., Lindsley D. H., and McCubbin F. M. (2015) Degassing pathways of Cl-,
931   F-, H-, and S-bearing magmas near the lunar surface: Implications for the composition and
932   Cl isotopic values of lunar apatite. *Amer. Min.* **100,** 1717-1727.

933 Wagner C., Deloule E.and Mokhtari A. (1996) Richterite-bearing peridotites and MARID-type
934   inclusions in lavas from North Eastern Morocco: mineralogy and D/H isotopic studies. *Cont.*
935   *Min. Petrol.* **124**, 406–421.

936 Warner R. D., Taylor G. J., Mansker W. L., and Keil K. (1978) Clast assemblages of possible deep-
937   seated (77517) and immiscible-melt (77538) origins in Apollo 17 breccias. *Proc. 9th Lunar*
938   *Planet. Sci. Conf.,* 941-958.

939 Warren P. H., and Wasson J. T. (1979) The origin of KREEP. *Rev. Geophys.* **17**, 73-88.

940 Warren P. H., Taylor G. J, Keil K., Shirley D. N. and Wasson J. T. (1983) Petrology and chemistry
941   of two "large" granite clasts from the Moon. *Earth Planet. Sci. Lett.* **64**, 175-185.

942 Warren P. H., Jerde E. A. and Kallemeyn G. W. (1987) Pristine moon rocks: a "large" felsite and a
943   metal-rich ferroan anorthosite. *Proc. 18th Lunar Planet. Sci. Conf.*, E303-E313.

944 Wieczorek M. A., Neumann G. A., Nimmo F., Kiefer W. S., Taylor G. J., Melosh H. J., Phillips R. J.,
945   Solomon S. C., Andrews-Hanna J. C., Asmar S. W., Konopliv A. S., Lemoine F. G., Smith D. E.,
946   Watkins M. M., Williams J. G. and Zuber M. T. (2013) The crust of the Moon as seen by
947   GRAIL. *Science*, **339**, 671-675.

948 Yurimoto H., Kurosawa M. and Sueno S. A. (1989) Hydrogen analysis in quartz crystals and
949   quartz glasses by secondary ion mass spectrometry. *Geochim. Cosmochim. Acta* **53**, 751-
950   755.

951 Xia, Q-K., Deloule, E., Wu, Y-B., Chen, D-G. and Cheng, H. (2002) Anomalously high δD values in
952   the mantle. *Geophys. Res. Lett.* **29**, 2008.

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967 **Table**

Sample		ppm H₂O	ppm H₂O 2σ	δD ‰	δD 2σ	Corrected δD ‰	δD 2σ	detect. limit (ppm H₂O)	Instrument
14305, 656	apt1	23	1	799	650	735	652	13	NanoSIMS
	apt3 #2	136	4	491	320	481	320	13	NanoSIMS
	apt3 #3	41	1	-28	528	-65	528	13	NanoSIMS
	apt3 #4	37	1	973	513	934	514	13	NanoSIMS
	apt4	49	2	-76	458	-107	459	13	NanoSIMS
	apt5	54	2	-6	481	-34	481	13	NanoSIMS
	apt6	36	1	649	417	608	418	13	NanoSIMS
	apt7	53	2	-139	420	-168	420	13	NanoSIMS
14321, 1047	*apt1 #1*	*<100*		*n.d.*		*n.d.*		*100*	ims-1280
	apt1 #2	*<100*		*n.d.*		*n.d.*		*100*	ims-1280
	apt1 #3	82	2	247	415	231	415	24	NanoSIMS
	apt2 #1	*<24*		*n.d.*		*n.d.*		*24*	NanoSIMS
	apt2 #2	137	3	-108	364	-118	364	24	NanoSIMS
	apt4	93	2	-313	439	-327	439	24	NanoSIMS
	apt5	*<24*		*n.d.*		*n.d.*		*24*	NanoSIMS
	apt6 #1	66	2	943	356	925	356	24	NanoSIMS
	apt6 #2	76	2	806	317	790	317	24	NanoSIMS
14161, 7069	triapt #1	162	49	231	55	114	66	110	ims-1280
	triapt #2	189	57	265	56	165	62	110	ims-1280
14161, 7373	apt3	174	52	432	56	323	70	110	ims-1280
	apt2	*<110*		*n.d.*		*n.d.*		*110*	ims-1280
	apt1	*<110*		*n.d.*		*n.d.*		*110*	ims-1280
15403,71	apt1 #1	77	9	-589	78	-597	79	6	ims-1280
	apt1 #2	181	20	-721	48	-724	48	6	ims-1280
	apt1 #3	129	14	-749	56	-754	57	6	ims-1280
15404,51	apt6 #1	58	6	-428	135	-438	138	6	ims-1280
	apt6 #2	46	6	-640	80	-653	82	6	ims-1280
15404, 55	apt1 #1	134	4	-587	432	-592	432	13	NanoSIMS
	apt 1#2	267	9	-344	319	-346	319	13	NanoSIMS
	apt2 #1	76	2	-344	492	-352	492	13	NanoSIMS
	apt2 #2	99	3	-683	491	-689	491	13	NanoSIMS
	apt2 #3	99	3	-541	491	-547	491	13	NanoSIMS
	apt2 #4	69	2	-505	523	-514	523	13	NanoSIMS
15358,6	gls c4 #1	95	11	698	71	566*	88	10	ims-1280
	gls c4 #2	95	11	610	71	477*	86	10	ims-1280
	gls c1 #1	58	7	789	84	572*	124	10	ims-1280
	gls c1 #2	64	8	830	83	634*	117	10	ims-1280
76535, 52	apt1	75	7	791	66	639	93	22	ims-1280
76535,56	bigapt #1	62	6	572	79	388	106	22	ims-1280
	bigapt#2	86	8	475	110	342	103	22	ims-1280
	bigapt #3	*<22*		*n.d.*		*n.d.*		22	ims-1280
77538,16	apt1	175	55	335	74	304*	74	100	ims-1280
	apt2	188	55	411	74	383*	74	100	ims-1280

968   Table 1. Measured H_2O abundances and δD values of lunar apatites and glasses*. Multiple
969   measurements on the same grain are indicated by a #. Italic font denotes measurements below
970   our detection limit. *n.d.* - not detected. Analytical errors are 2σ. Corrected δD values are those
971   after correcting for the contribution of spallation-produced D, and uncertainty on the corrected
972   δD values is dominated by large uncertainty in the D production rate.
973   *Exposure ages have not been determined for these samples. The CRE age estimates used
974   here are described in section 3.2.
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977 **Figure Captions**

978 Fig. 1. Representative backscattered electron (BSE) images of samples described in this work.

979 Where visible, apatites are denoted by arrows. (a) Graphic intergrowth of quartz (dark gray)

980 and K-feldspar (light gray) in 14321, 1047. (b) Felsite-ferrobasalt silicate liquid immiscibility pair

981 in 77538, 16. The darker intergrowth is quartz and K-feldspar, while the bright areas are Fe-rich

982 olivine, pyroxene, and amorphous silica. Fe-Ni metal and ilmenite are also present. (c) Portion

983 of quartz monzogabbro 15404, 55. (d) Portion of quartz monzodiorite 14161, 7373. The

984 exsolved phase is inverted pigeonite, while the brightest phase is merrilite (Jolliff et al. 1999).

985 The bleb near the center of the image is intergrown silica and K-feldspar formed through

986 immiscibility. Bright squares are ion microprobe analysis pits. (e) Apatite-merrilite intergrowth

987 surrounded by plagioclase in troctolite 76535 56. The darkest phase is olivine. Round dark

988 marks in the apatite are pits from previous analyses. Note the large grain size. (f) Apatite-

989 merrillite intergrowth in an alkali anorthosite clast in breccia 14305, 656. The bright gray is

990 merrillite, the darker intergrowths are apatite (indicated by arrow). Darkest gray is plagioclase.

991

992 Fig. 2. Sample calibration curves for ims-1280 analysis. (a) $^1H/^{18}O$ calibration curve for H_2O in

993 apatite and (b) $^1H/^{30}Si$ calibration curve for H_2O in basaltic glass. Similar calibration curves were

994 used to calibrate NanoSIMS data.

995

996 Fig. 3. Apatite data for KREEP-rich intrusive samples, with 2σ error bars. The spallation

997 correction can lower the δD of apatite by > 100 ‰ in samples with long cosmic ray exposure

998 ages.

999

1000 Fig. 4. Plot showing δD value versus ppm H_2O content of apatite in this study (colored points)

1001 compared with literature apatite data (grayscale points, Greenwood et al. 2011; Tartèse et al.

1002 2013, 2014, Barnes et al. 2013, 2014a). Note the log scale on the x-axis.

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1005 Fig. 5(a)(b) BSE images of KREEP basalt fragments containing quenched residual glass in

1006 15358,6. Dark, straight-sided phase is plagioclase, medium gray is pyroxene, and the bright

1007 areas are Fe-rich yellow glass. Silica (darkest gray) and ilmenite (white needles) are also

1008 present. White squares indicate ion microprobe analysis pits. (c) Calculation of the increase in

1009 δD value due to hydrogen loss, constrained by the δD value measured in 15358 KREEP basalt

1010 glass (corrected for crystallization). To reach the observed δD in 15358 requires loss of 85% of

1011 an initial H_2O concentration of 115 ppm.

1012

1013 Fig. 6. Histogram of the lowest apatite δD measurement in lunar samples by rock type,

1014 including literature data from Greenwood et al. (2011); Tartèse et al. (2013, 2014), and Barnes

1015 et al. (2013, 2014a). The lowest δD apatite should represent the δD value least affected by

1016 degassing, if degassing occurred. The range in δD value of Earth's mantle and CI and CM

1017 chondrites is also shown (Boettcher et al., 1980; Michael 1998; Ahrens 1989; Deloule et al.,

1018 1991; Bell and Rossman 1992; Thompson 1992; Graham et al., 1994; Jambon 1994; Wagner et

1019 al., 1996; Xia et al., 2002; Alexander et al., 2012; Hallis et al., 2015). The protosolar δD value of

1020 ~ -865 ± 32 ‰ is from Geiss and Gloecker (1998). There appear to be at least three H reservoirs

1021 in the lunar interior: an Earth-like reservoir, a moderately elevated reservoir, and a very low D

1022 reservoir. The mare basalts would have had an initial undegassed δD signature compatible with

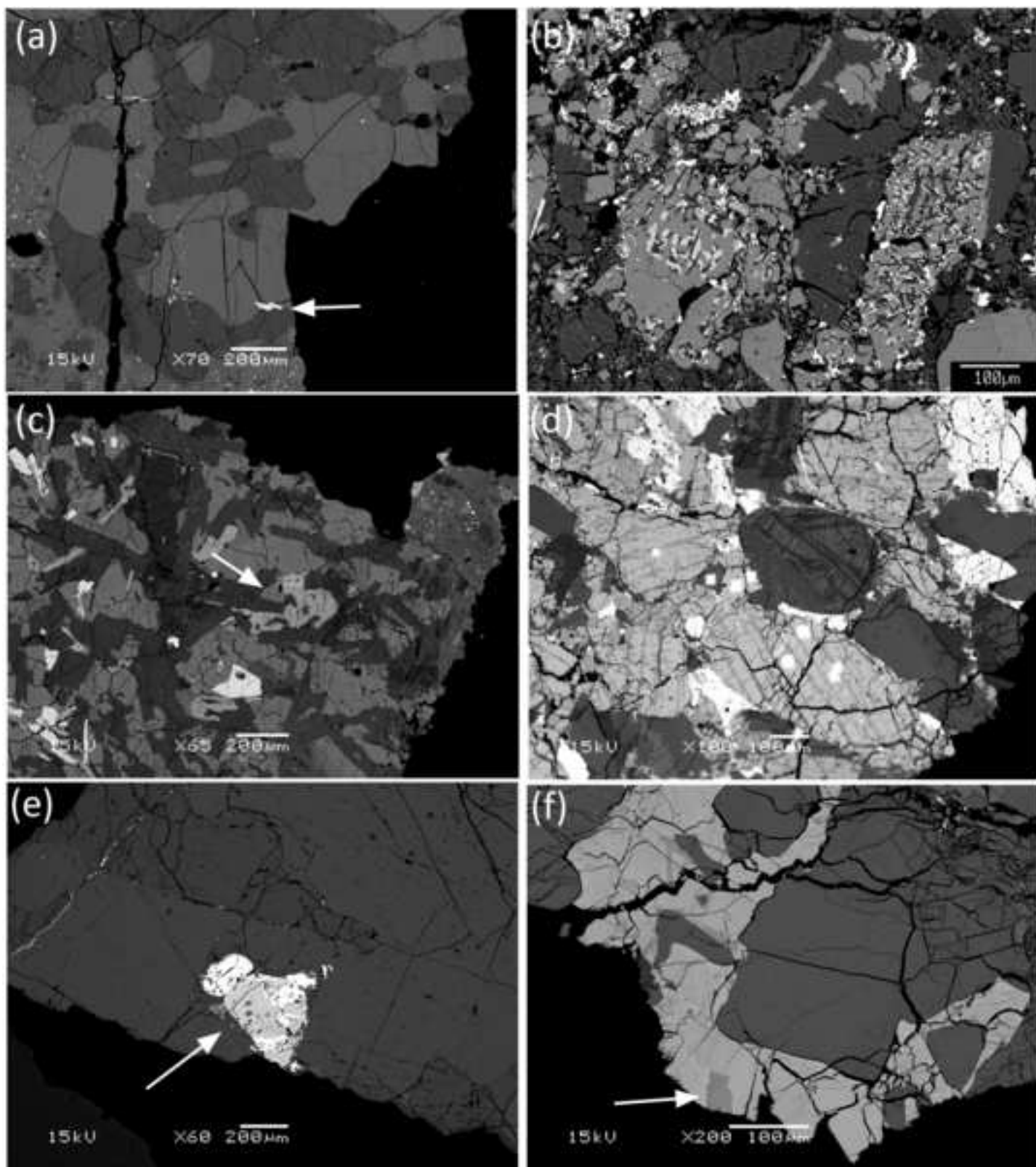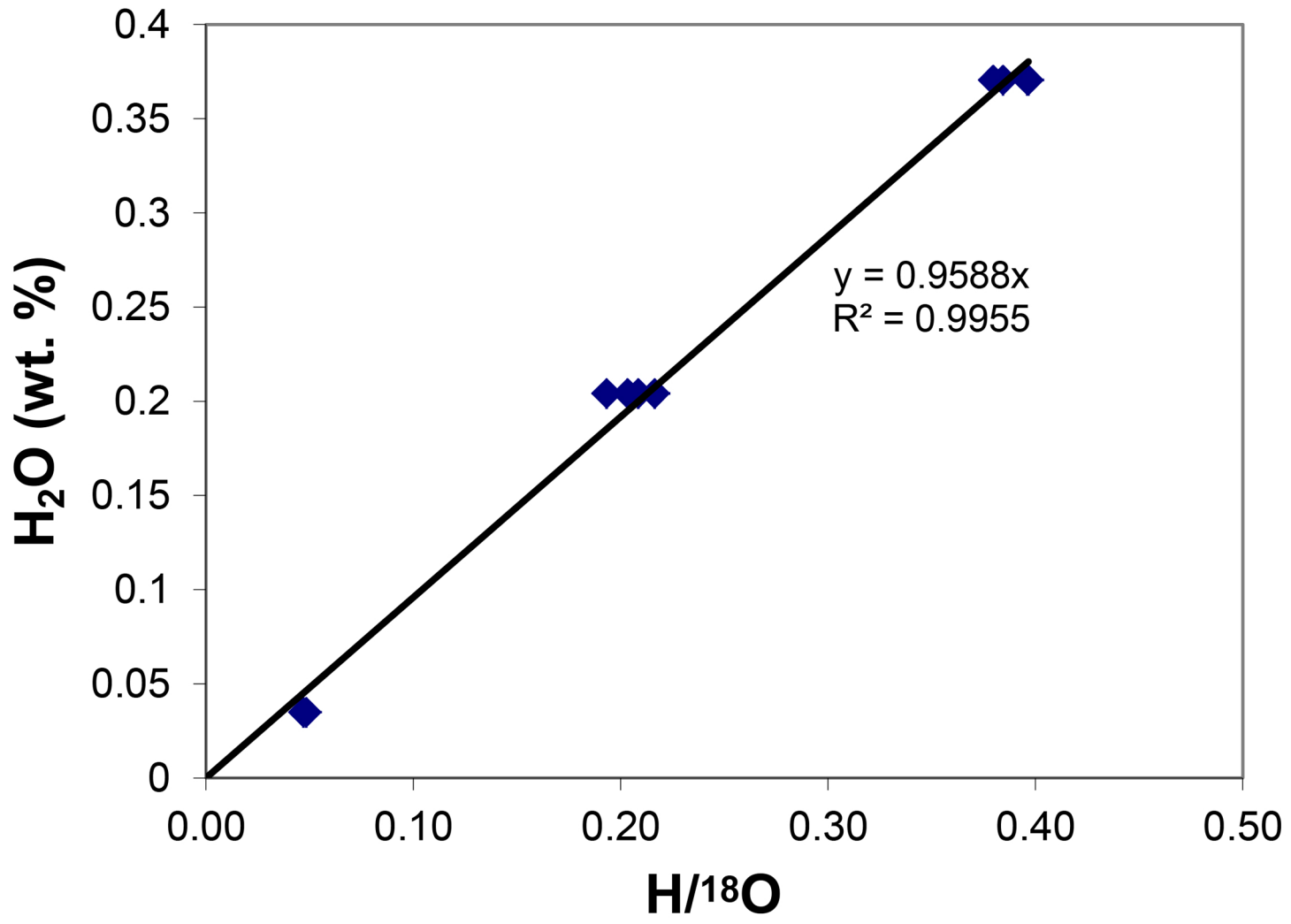1023 the Earth range, ~100‰ (Tartèse and Anand 2013).

1024

Figure 1

Figure 2

(a) H/^{18}O calibration

$y = 0.9588x$
$R^2 = 0.9955$

(b) H/^{30}Si calibration

$y = 0.7008x$
$R^2 = 0.9794$

Figure 3

Figure 3

Figure 4

Figure 5ab

Figure 5c

Initial magma with 115 ppm and δD of -100 requires loss of 85% of the initial H_2O.

15358 KREEP Basalt Clasts

85% loss

0% loss

δD in Magma

H_2O (ppm) in Initial Magma

Figure 6

Figure 6