1   **New evidence for lunar basalt metasomatism by underlying regolith.**

2   John F. Pernet-Fisher*

3   School of Earth, Atmospheric, and Environmental Sciences, University of Manchester,
4   Manchester, M13 2PL, UK

5   *john.pernet-fisher@manchester.ac.uk

6

7   **Abstract:** Earth-like δD values reported from lunar mare-basalt apatites have typically been

8   interpreted to reflect the intrinsic isotopic composition of lunar-mantle water. New data

9   indicates that some of these basalts are also characterized by having experienced a slow

10   cooling history after their emplacement onto the lunar surface. This suggests that these

11   basalts may have experienced metasomatism by fluxes generated during the degassing of the

12   lunar regolith induced by the long-duration high-temperature residence times of overlying

13   basalts.

14   **Keywords:** lunar volatiles, basalt metasomatism, lunar petrology, hydrogen isotopes.

15

16   The volatile elements affect a wide range of important physical properties of

17   geological materials, playing a fundamental role during the mass transport of melt from the

18   mantle to the crust. Relative to the Earth, the Moon is generally considered to be volatile-

19   element depleted (e.g., Wolf and Anders, 1980; Canup et al., 2015), with the exception of

20   water (Saal et al., 2008). One of the major volatile-bearing basaltic mineral phases, apatite

21   $(Ca_5(PO_4)_3(OH,F,Cl)$, has shown that lunar magmatism is potentially not entirely anhydrous

22   (Boyce et al., 2010; Greenwood et al., 2011; Barnes et al., 2013; Tartèse et al., 2013). Since

23   the direct measurement of water (OH) within a diverse range of lunar materials (apatite,

24   olivine, plagioclase, basaltic glass), allowing for the interpretation of how water is distributed

25   on the Moon on a global scale. In particular, a key question that is currently debated is what

26   is the origin of this water (e.g., primordial, cometary sources, asteroid sources, solar wind): to

27   date this issue has been primarily been addressed using H-isotope systematics (expressed as

28   δD, relative to Standard Mean Ocean Water; SMOW).

29   Based on a recent review of lunar apatite OH-δD systematics (McCubbin et al., 2015),

30   mare basalts have been noted to fall within two broad groups: 1) a relatively isotopically

31   heavy δD suite, which lies above the terrestrial range (> +200 ‰ δD), and 2) an isotopically

32   lighter, Earth-like, suite (~ 0 to ~250 ‰ δD). Within individual mare suites, several

33   processes such as volatile degassing (which acts to increase δD; Tartèse and Anand, 2013), or

34   spallogenic production from cosmic-ray exposure (which will to decrease δD; Füri and

35   Deloule, 2016), can modify δD compositions from their inherited melt signature. However,

36   recent reports of δD values that extend to compositions below the terrestrial range (+100 to -

37   500‰) from a range of lunar lithologies, including incompatible element rich KREEP basalts

38   and evolved highland lithologies (such as quartz monzodiorites), have been argued to reflect

39   a primordial, isotopically distinct, lunar mantle reservoir (Barnes et al., 2014; Robinson et al.,

40   2014). Such a reservoir has recently gained support by the occurrence of similar δD

41   compositions from basalts associated with the Icelandic mantle plume, which are interpreted

42   to reflect deep 'primordial' signatures (Hallis et al., 2015); together providing some for the

43   strongest evidence for a primordial origin for water in the Earth–Moon system (Barnes et al.,

44   2014).

45   In this issue Treiman et al. (2016) presents an alternative case accounting for the

46   relatively isotopically light apatite δD signatures, based on the mineral texture of the host

47   basalts. The petrological context of apatite, and other OH-bearing phases, have been often

48   overlooked within the literature, however, can provide important clues for putting water

49   abundance and H-isotope systematics into context (Pernet-Fisher et al., 2014). In their

50   model, Treiman et al. (2016) highlight that basalt samples with the lowest apatite δD values

51   also display the least amount of zoning within olivine and pyroxene phenocrysts. This

52   suggests that these samples have been held at high temperatures for long periods relative to

53   other basaltic samples that display large mineral zonational gradients. As a result of such a

54   protracted thermal history, Treiman et al. (2016) propose a model whereby that these basalts

55   incorporated an additional source of H during the emplacement of lavas flows onto the lunar

56   regolith. The regolith, as the result of a long history of solar-wind and cosmic-ray

57   implantation, is thought to be characterized by very isotopically light δD values (< -400‰

58   δD; Epstein and Taylor, 1973); thus, 'metasomatism' by regolith induced heating during lava

59   flow emplacement, could act to lower the δD value of the overlying molten basaltic lava.

60   Models of lunar regolith heating and degassing with hot lava interaction (Rumpf et al., 2013),

61   and melt assimilation are not new, having been used to account for variable trace-element

62   systematics for some high-Al Apollo 14 basalts (Hui et al., 2011) and for some xenocrystic

63   spinel within some Apollo 12 basalts (Dungan and Brown, 1977). However, the extent to

64   which the volatile element systematics will modify basalts through this process has to date

65   not fully considered. Overall, Treiman et al. (2016) reinforces how important it is to consider

66   the extent to which mixing with the underlying lunar regolith may modify mare basalts

67   during their emplacement, particular for the most mobile and volatile elements.

69   **References cited**

70   Barnes, J. J., Franchi, I. A., Anand, M., Tartèse, R., Starkey, N. A., Koike, M., & Russell, S.
71   S. (2013). Accurate and precise measurements of the D/H ratio and hydroxyl content in lunar
72   apatites using NanoSIMS. Chemical Geology, 337, 48-55.

73

74   Barnes, J. J., Tartèse, R., Anand, M., McCubbin, F. M., Franchi, I. A., Starkey, N. A., &
75   Russell, S. S. (2014). The origin of water in the primitive Moon as revealed by the lunar
76   highlands samples. Earth and Planetary Science Letters, 390, 244-252.

77

78   Boyce, J. W., Liu, Y., Rossman, G. R., Guan, Y., Eiler, J. M., Stolper, E. M., & Taylor, L. A.
79   (2010). Lunar apatite with terrestrial volatile abundances. Nature, 466, 466-469.

80

81   Canup, R. M., Visscher, C., Salmon, J., & Fegley Jr, B. (2015). Lunar volatile depletion due
82   to incomplete accretion within an impact-generated disk. Nature Geoscience, 8, 918-921.

83

84   Dungan, M. A., & Brown, R. W. (1977). The petrology of the Apollo 12 ilmenite basalt suite.
85   In Lunar and Planetary Science Conference Proceedings (Vol. 8, pp. 1339-1381).

86

87   Epstein, S., & Taylor Jr, H. P. (1973). The isotopic composition and concentration of water,
88   hydrogen, and carbon in some Apollo 15 and 16 soils and in the Apollo 17 orange soil. In
89   Lunar and Planetary Science Conference Proceedings (Vol. 4, p. 1559).

90

91   Füri, E., & Deloule, E. (2016, March). New Constraints on the Production Rate of
92   Cosmogenic Deuterium at the Moon's Surface. In Lunar and Planetary Science Conference
93   (Vol. 47, p. 1351).

94

95   Greenwood, J. P., Itoh, S., Sakamoto, N., Warren, P., Taylor, L., & Yurimoto, H. (2011).
96   Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon.
97   Nature Geoscience, 4, 79-82.

98

99   Hallis, L. J., Huss, G. R., Nagashima, K., Taylor, G. J., Halldórsson, S. A., Hilton, D. R., &
100   Meech, K. J. (2015). Evidence for primordial water in Earth's deep mantle. Science, 350,
101   795-797.

102

103   Hui, H., Oshrin, J. G., & Neal, C. R. (2011). Investigation into the petrogenesis of Apollo 14
104   high-Al basaltic melts through crystal stratigraphy of plagioclase. Geochimica et
105   Cosmochimica Acta, 75, 6439-6460.

106

107 McCubbin, F. M., Kaaden, K. E. V., Tartèse, R., Boyce, J. W., Mikhail, S., Whitson, E. S., &
108 Hauri, E. H. (2015). Experimental investigation of F, Cl, and OH partitioning between apatite
109 and Fe-rich basaltic melt at 1.0–1.2 GPa and 950–1000 C. American Mineralogist, 100, 1790-
110 1802.

111

112 Pernet-Fisher, J. F., Howarth, G. H., Liu, Y., Chen, Y., & Taylor, L. A. (2014). Estimating
113 the lunar mantle water budget from phosphates: Complications associated with silicate-
114 liquid-immiscibility. Geochimica et Cosmochimica Acta, 144, 326-341.

115

116 Robinson, K. L., Barnes, J. J., Tartèse, R., Nagashima, K., Hallis, L. J., Franchi, I. A., &
117 Taylor, G. J. (2014, March). Primitive Lunar Water in Evolved Rocks?. In Lunar and
118 Planetary Science Conference (Vol. 45, p. 1607).

119

120 Rumpf M. E. Fagents S. A., Crawford I. A., and Joy K. H. (2013) Numerical modelling of
121 lava-regolith heat transfer on the Moon and implications for the preservation of implanted
122 volatiles. Journal of Geophysical Research. Vol. 118. pp. 382-397.

123

124 Tartèse, R., Anand, M., Barnes, J. J., Starkey, N. A., Franchi, I. A., & Sano, Y. (2013). The
125 abundance, distribution, and isotopic composition of Hydrogen in the Moon as revealed by
126 basaltic lunar samples: Implications for the volatile inventory of the Moon. Geochimica et
127 Cosmochimica Acta, 122, 58-74.

128

129 Tartèse, R., & Anand, M. (2013). Late delivery of chondritic hydrogen into the lunar mantle:
130 Insights from mare basalts. Earth and Planetary Science Letters, 361, 480-486.

131

132 Treiman, A. H., Boyce, J. W., Greenwood, J. P., Eiler, J. M., Gross, J., Guan, Y., Ma, C.,
133 Stolper, E. M., (2016) D-poor hydrogen in lunar mare basalts assimilated from lunar regolith.
134 American Mineralogist, this issue.

135

136 Wolf, R., Anders, E. (1980) Moon and Earth: compositional differences inferred from

137 siderophiles, volatiles and alkalis in basalts. Geochimica et Cosmochimica Acta, 44, 2111–
138 2124.