EVIDENCE FOR A "WET" EARLY MOON. Hejiu Hui[1], Anne H. Peslier[2], Youxue Zhang[3] and Clive R. Neal[1], [1]Department of Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, IN 46556, [2]Jacobs Technology, ESCG, Mail Code JE23, Houston, TX 77058, and ARES, NASA-Johnson Space Center, Mail Code KR, Houston, TX 77058, [3]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109.

Introduction: The Moon was thought to have lost its volatiles during impact(s) of a Mars-size planetesimal with the proto Earth [1] and during degassing of an early planet-wide magma ocean [2]. This view of an anhydrous Moon, however, has been challenged by recent discoveries of water on its surface [3-5] and in lunar volcanics [6-10] and regoliths [11]. Indigenous water is suggested to be heterogeneously distributed in the lunar interior and some parts of lunar mantle may contain as much water as Earth's upper mantle [6,10]. This water is thought to have been brought in part through solar wind implantation [3-5,8,11] and meteorite/cometary impacts [3,4,8,12] after the formation of the primary crust.

Here we measured water in primary products of the Lunar Magma Ocean (LMO) thereby by-passing the processes of later addition of water to the Moon through impact events or during mantle overturn as suggested by previous studies (e.g., [8,12]). So far, ferroan anorthosite (FAN) is the only available lithology that is believed to be a primary product of the LMO [2]. It is generally accepted that plagioclase, after crystallization, floated in the LMO and formed FAN as the original crust [2]. Therefore, any indigenous water preserved in FAN was partitioned from the LMO. These data can be used to estimate the water content of the magma ocean at the time of plagioclase crystallization, as well as that of the mare magma source regions.

FTIR Analyses: Fourier transform infrared spectroscopy (FTIR) was used to measure water contents in plagioclases of FANs 15415,238 and 60015,787. Both samples have >98 vol.% of plagioclase with anorthite contents >96%. The olivines and plagioclases in troctolite 76535,164 were also analyzed using FTIR to assess the water inventory in the lunar highland upper crust. This troctolite was derived from melts of LMO crystallization products is an olivine-rich end member of the Mg-suite that composes about half of the highland upper crust (e.g., [13]).

The mineral grains allocated for this study are from the interior portion of each individual rock. Therefore, potential hydrogen implanted by solar wind [11] was avoided because direct solar implantation is limited to 0.2 μm depth from the sample surfaces [14], and even though micrometeorite gardening and melting can transfer OH to some depth based on a recent study of lunar agglutinitic glasses [11], such OH is in impact glasses, not within pristine minerals. Each mineral grain was embedded in crystal bond and a doubly polished section was prepared manually using sandpaper and alumina powder (down to 1 μm) for FTIR analyses. Tens to a few hundred μm layers on both sides of each grain were removed in the sample preparation, which further assured the removal of any layer affected by solar implantation. The polished grains were cleaned with acetone, ethanol, deionized water and CH_2Cl_2 in an ultrasonic bath.

Results and Discussion: Infrared spectra of plagioclase from FAN 15415,238 and 60015,787 are characterized by a small wide absorption band in the O-H region (Fig. 1) that resembles those observed in terrestrial plagioclases [15]. This broad band (~3700 to ~3100 cm^{-1}) is interpreted as absorption by structural O-H bond vibrations in plagioclase for two reasons. (1) One of our doubly polished grains of 15415 was heated to 1000°C for 24 h in a high-purity N_2 atmosphere and then cleaned with the same procedure. The band is strongly diminished in the heated sample demonstrating that dehydration occurred. (2) The anisotropy of the O-H absorption band height or absorbance area during rotation of the infrared polarizer relative to the plagioclase crystals, and the 90° interval between maximum and minimum. Furthermore, O-H absorbance area does not seem related to the degree of plagioclase fracturing that was likely produced during impact. This band (Fig. 1) cannot be caused by water in minute melt or fluid inclusions or by contamination during sample preparation. Total integrated absorption areas of the OH bands (A_{tot} in cm^{-2}) along three mutually perpendicular directions were converted to water contents (C_{H2O} in ppm by weight of H_2O) using the Beer-Lambert law in the form $C_{H2O} = A_{tot}/I'$, where I' is 15.3±0.7 ppm^{-1}cm^{-2} for feldspars [15]. The water contents in plagioclases are ≥5.0 ppm (grain Pl3) for 15415,238 and 6.4 ppm for 60015,787. Intrinsic water was also detected in plagioclase of troctolite 76535,164 (Fig. 1). The minimum water contents vary from 0.8 to 2.7 ppm (Pl1 of 76535,164). No O-H absorption band has been observed in olivine (Fig. 1), implying an H_2O content of <1 ppm. The minimum whole-rock water content of troctolite 76535 is ~ 2 ppm based on its mineral modal abundance, which is

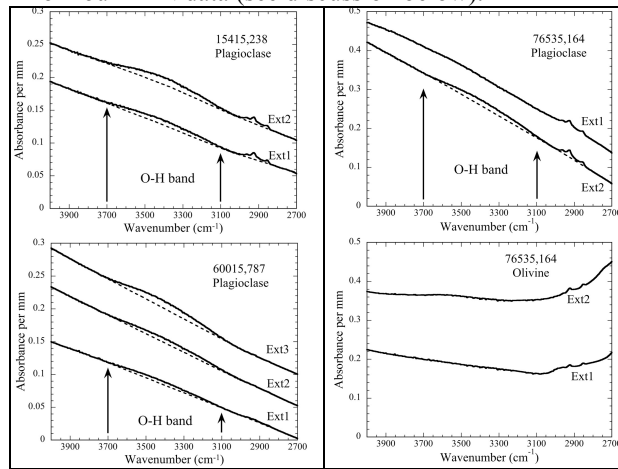lower than that calculated for the initial magma ocean from our FAN data (see discussion below).

Fig. 1. Representative polarized FTIR spectra for FANs 15415,238 and 60015,787 and troctolite 76535,164 at mutually perpendicular orientations (Ext1, Ext2 and Ext3) are normalized to 1 mm and shifted vertically for comparison. The dashed line indicates the baseline position used for water content estimations. The narrow peaks (3000 - 2800 cm^{-1}) most likely come from organic contamination on the mineral surface during sample preparation.

Using a partition coefficient of 0.004 between plagioclase and silicate melt [16], the water content of a melt in equilibrium with 60015 plagioclase is ~1600 ppm. At that point, approximately 80 vol.% of the LMO is thought to have been solidified [2]. Using this degree of crystallization, the water content of the initial magma ocean, is inferred to be ~320 ppm (Fig. 2). The first crystallized olivine cumulate in the LMO could have ~ 0.6 ppm of water using a partition coefficient of 0.002 between olivine and silicate melt [17]. As crystallization of the LMO continued, volatiles and other incompatible trace elements became enriched in the magma ocean residuum. The final 2 vol.% of the magma ocean residuum (urKREEP) that may be the source of the KREEP-rich lithologies unique to the Moon [2], potentially could have had as much as ~1.4 wt.% of water. This is an order of magnitude higher than the thousands of ppm maximum suggested previously [12], and also 1.5 orders of magnitude higher than 850-1100 ppm in Earth's primitive mantle [18]. Thus the LMO crystallization products could have spanned a wide range of water contents, from <1 ppm to ~1.4 wt.% (Fig. 2). After the LMO solidification, these materials are thought to have undergone gravitational overturn driven by density gradients [19]. Overturned lunar cumulate mantle provided the source regions for mare basalts [2,19]. Even assuming 20% of partial melting of the source regions of mare basalts in which water was detected [6-10], calculated water contents of their source regions are still well within the range of those we calculated for the primary LMO products inferred from water content in plagioclase from FANs (Fig. 2).
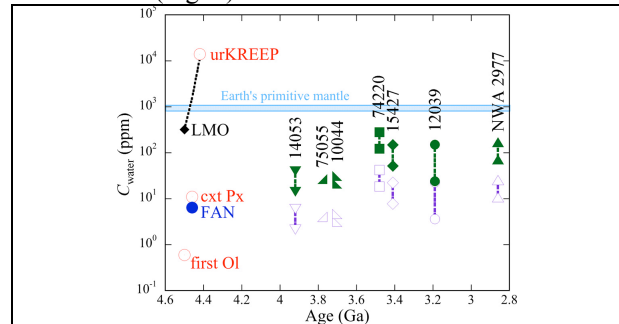

Fig. 2. Water contents in lunar magma ocean products and mantle sources of basalts through time. The black dashed line shows the water content evolution in magma ocean residua. The water contents of mantle sources with isochron ages <4.0 Ga were calculated assuming 20% (green) or 3% partial melting (purple).

The presence of water in FAN and troctolite suggests that the highland upper crust is not anhydrous. Considering the distributions of two major lithologies (FAN and Mg-suite) in the highland upper crust [13] and assuming the results for 60015 (~6 ppm) and 76535 (~2 ppm) are representative of FANs and the Mg-suite, respectively, the upper crust may contain ~4 ppm of indigenous water. Incidentally, trace amounts of water/hydroxyl have been detected in the lunar highlands surface by various spacecraft [4]. The results presented here imply that the water measured in lunar highland lithologies may contribute a significant portion of the water detected by spacecraft.

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