

Supplementary information for the Manuscript “Magmatic volatiles (H, C, N, F, S, Cl) in the lunar mantle, crust, and regolith: Abundances, distributions, processes, and reservoirs”

Analytical techniques used for studying lunar magmatic volatiles

A wide range of techniques have been used to analyze volatile elements and volatile-bearing minerals in lunar samples. In fact, many analytical techniques and protocols have been developed and enhanced specifically for the study of lunar samples. We provide a summary of techniques that were used and how they were implemented and/or improved upon for the study of lunar volatiles in an online supplement. We do not cover every technique used to analyze volatiles on the Moon, but we cover those techniques that required specific development for the analysis of volatiles in lunar samples.

Electron probe microanalysis (EPMA)

Fluorine, chlorine, and sulfur have all been analyzed in lunar samples using the electron microprobe. Although somewhat difficult to analyze, carbon and nitrogen can be measured by EPMA, but this has not yet been demonstrated on lunar samples. Sulfur and chlorine are typically measured using a traditional pentaerythritol (PET) crystal. However, to accurately measure the light element fluorine, a synthetic multilayer crystal with a large d-spacing (e.g., LDE-1, OV-60, PC0) is typically preferred over the more classically used and widely available thallium acid phosphate (TAP) crystal because the intensity of the F K α peak using the multilayer crystal is approximately 14 times more intense than with TAP. This enhanced intensity in the F K α line renders the interference from the third order P K α line (and all other third order or greater interferences) on the F K α line insignificant, which was one of the primary

problems with analyzing F in apatite using a TAP crystal (Potts and Tindle, 1989; Raudsepp, 1995; Reed, 2005).

Appropriate standards for F, Cl, and S are also crucial to the overall quality of the data. Sulfides are typically used for S because sulfate has not been verified in any lunar materials and there is a substantial difference in S $K\alpha$ peak position between S^{2-} and S^{6+} . Sodalite, boracites, tugtupite, and scapolite are typically used as reliable chlorine standards because both have more Cl than most lunar apatites, and they are substantially less beam sensitive than chloride salts (e.g., KCl, NaCl) that are commonly used. McCubbin et al. (2011) have shown that SrF_2 is a reliable fluorine standard for the analysis of fluorine in both glasses and apatite. MgF_2 has also been reported as a reliable standard (Goldoff et al., 2012; Webster et al., 2009), although we advise against its use due to possible interference of the F $K\alpha$ line with the second order $L\alpha$ line of Mg. Fluorapatite should also be avoided as an EPMA fluorine standard due to the possibility of variable fluorine X-ray count rates (Stormer et al., 1993), although exceptions to this exist for well characterized and reliable samples (e.g., Ap020 from McCubbin et al., 2012). Amphiboles, micas, and glasses should also be avoided as fluorine standards due to interferences with the F $K\alpha$ line from the first order $L\alpha$ line of Fe and second order $L\alpha$ line of Mg. Moreover, when analyzing unknowns for F in Mg- and Fe-rich matrices, appropriate selection of background positions is also very important (Goldoff et al., 2012; Witter and Kuehner, 2004).

EPMA has been used to analyze sulfides, apatites, and glasses (both volcanic and impact-derived) for F, Cl, and S. All three of these phases are beam-sensitive, and care must be taken in choosing appropriate voltage, current, and spot sizes for accurate quantitative analysis. Detection limits for all three elements are typically in the 100's ppm, which is commonly above the concentration level of these elements in many lunar glasses. Detection limits of volatile elements

in sulfides and apatite are not typically an issue because their respective volatile constituents are essential structural constituents and commonly occur at the 1000's to 100,000's ppm concentration level. Although specific EPMA routines have not been developed for lunar sulfides (Papike et al., 2011), the analysis of lunar apatite posed a technological hurdle to overcome given the typically small grain size, the need to quantify a missing structural component, and the problem of variable fluorine and chlorine X-ray count rates (McCubbin et al., 2010c; Stormer et al., 1993).

In addition to the volatiles F and Cl, apatite also commonly hosts OH as an essential structural constituent. Hydrogen cannot be measured directly by the EPMA technique; however, a missing component in the X-site of the apatite can be calculated on the basis of stoichiometry. If both F and Cl are analyzed with sufficient accuracy, this missing component can be attributed to some combination of the anions OH^- , O^{2-} , CO_3^{2-} , S^{2-} , Br^- , and I^- and/or structural vacancies (Pan and Fleet, 2002) and/or structural H_2O (Mason et al., 2009). The most likely culprit for this missing component in terrestrial igneous systems is OH^- (Piccoli and Candela, 2002), and recent analyses of lunar apatite indicate the same (Boyce et al., 2010; Greenwood et al., 2011; McCubbin et al., 2010b; McCubbin et al., 2010c). However, Boyce et al. (2010) have shown that some S is also present in lunar apatite, although the maximum amount reported by Boyce et al. (2010) was 460 ± 40 ppm (maximum of ~ 0.02 structural formula units (sfu)). Because the stoichiometric determination of a missing component depends on the amount of F and Cl, the uncertainty in quantifying a missing component is directly related to the analytical uncertainty for F and Cl.

Stormer et al. (1993) documented that fluorine and chlorine X-ray count rates change with time during electron microprobe analysis of apatite as a function of crystallographic

orientation. McCubbin et al. (2011; 2010c) revisited this problem with lunar samples and reported that fluorine count rates were not always constant during the course of an analysis; although the changes in count rate did not appear to correlate with crystallographic orientation (determined on the basis of grain morphology). Chlorine count rates, on the other hand, were found to be constant for all of their analyses and analytical uncertainty was typically <0.01 sfu of Cl. To correct for the fluorine X-ray count variations, McCubbin et al. (2011; 2010c) used a time-dependent intensity (TDI) correction in the PROBE for EPMA software to monitor the time dependence and then project fluorine X-ray count rates to time zero. Apatite grains in the natural lunar samples exhibited a range of time-dependent behavior. However, only those analyses that either exhibit minimal time-dependence behavior (< 25 counts/second² (c/s^2) variation during a given analysis) or linear and positive time-dependence behavior provide accurate enough fluorine values to assess the potential missing structural component in the apatite X-site. Analyses that exhibit other types of time-dependent behavior can result in F+Cl sums that exceed the maximum value of 1.00 sfu and result in large uncertainties on the fluorine value. To determine the uncertainty of each fluorine analysis, a regression line was fitted to time-dependent count data and reported as a 1σ standard deviation of the regression (1σ SDOR). The ability to detect a missing component that can be attributed to OH^- from this technique was approximately 0.08 sfu of missing component in the apatite X-site for fluorine-rich analyses exhibiting minimal or linear time-dependence. This value was calculated based on the average uncertainty of the fluorine values from the apatite grains analyzed in McCubbin et al. (2010c).

Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry is a diverse micro-beam technique that is capable of quantitative analysis of various atomic masses. Consequently, SIMS is capable of determining

both elemental concentrations of certain elements as well as some isotopic ratios provided appropriate standards are available and the mass resolution of the instrument is sufficiently high to avoid unwanted mass interferences. Of the elements of interest to this work (H, C, N, F, S, Cl), all of them have been analyzed in lunar samples. In addition to elemental concentrations, isotopic values for δD , $\delta^{13}C$, $\delta^{15}N$, $\delta^{37}Cl$, and $\delta^{34}S$ have been determined in various lunar materials by SIMS. SIMS has also been used to conduct quantitative and qualitative ion imaging of volatiles.

Elemental concentrations of (H, C, N, F, S, and Cl) in lunar materials.

SIMS has been used to determine the abundances of H, F, S, and Cl in volcanic and agglutinitic glasses, the abundances of H, C, N, F, S, and Cl in some nominally anhydrous phases and the abundances of H, F, S, and Cl in apatite. In some cases, these measurements were facilitated through recent advances in the field. Specifically, the Cameca IMS 6f laboratory at the Department of Terrestrial Magnetism, Carnegie Institution of Washington (DTM-CIW) have pioneered protocols for the microanalysis of trace amounts of H_2O , CO_2 , F, S, and Cl in terrestrial glasses and nominally anhydrous minerals that have demonstrated improved detection limits for the volatiles H_2O (~1-6 ppm), CO_2 (3 ppm), F (100's ppb), S (100's ppb), and Cl (100's ppb) (Aubaud et al., 2004; Hauri et al., 2002; Hauri et al., 2006; Koga et al., 2003). These protocols have since been applied and modified in many other SIMS laboratories. The increase in detection sensitivity is in part due to the low pressure in the ion probe sample chamber of 6×10^{-10} torr during the analyses; however, to achieve the lowest detection limit, especially for H_2O , the samples and standards are mounted in indium, polished flat and to a mirror finish, and placed in the ion probe sample chamber at least 12 h prior to analysis. For the analysis of volatiles, a Cs^+ primary beam is typically used. Detection limits for the volatiles are determined during each

session based on analyses of a dry synthetic forsterite crystal, although other dry crystals can be used for this purpose in place of forsterite. For the analysis of volatiles in glasses and nominally anhydrous minerals, volatile abundances are derived from calibrations calculated using glass and silicate mineral standards with known volatile contents before each analytical session. For the analysis of apatites, natural and/or synthetic apatite crystals with known volatile abundances (Table 1) are used in place of silicates to avoid unwanted matrix effects. Additionally, a self-calibration technique for analyzing phosphates by SIMS has also been developed and successfully implemented (Boyce et al., 2012). Uncertainties are then calculated by propagating the errors in the detection limit, the counting statistics, and the error in slope from the calibration curve. If a sample cannot be mounted in indium and only an epoxy-mounted sample can be analyzed (common for many lunar samples), detection limits are determined by analyzing nominally anhydrous phases that are spatially associated with analysis spots. Furthermore, if C is not expected to occur in the analysis target, maximum contributions of various volatile elements from the thin section epoxy can be computed by analyzing the thin section epoxy and comparing C/volatile count ratios between the epoxy and unknown. Before each analysis on an unknown target, the beam is set to pre-sputter for 3 to 5 minutes to clean the sample surface of contaminants. For analyses on the f-series instruments, a field aperture is inserted during the analysis of the unknown to allow transmission of secondary ions from only the central area of the much larger crater. For the Cameca NanoSIMS 50L ion microprobe, crater edge contamination is eliminated by electronic gating rather than with a physical field aperture. A mass resolving power (MRP) of about 6000 is needed for volatile analysis to resolve $^{16}\text{O}^1\text{H}$ from ^{17}O . Further details on the exact beam conditions that are appropriate for each specific type of analysis can be

found in the literature, but the preceding represents the commonalities among the f-series and NanoSIMS instruments for quantifying volatiles in lunar samples.

Analysis of volatile isotope systems in lunar samples with SIMS.

SIMS has been used to determine δD in volcanic and agglutinitic glasses, δD , $\delta^{13}C$, and $\delta^{15}N$ in some nominally anhydrous phases, δD and $\delta^{37}Cl$ in lunar apatites, and $\delta^{34}S$ in lunar sulfides. Cameca f-series, 12-series, and NanoSIMS instruments have all been used to make these measurements. A Cs^+ primary beam is typically used to make measurements for all isotopic systems listed above, and the beam is usually (but not always) rastered over an area that typically ranges anywhere from 100 x 100 μm to 10 x 10 μm after a few minutes of pre-sputtering over a larger raster area. The area of data acquisition can be limited to a smaller area by inserting a physical field aperture or by the use of electronic gating. The mass resolution needed to avoid interferences varies with the isotopic system being measured, and is discussed in more detail below. Standards range from basaltic to rhyolitic glass samples to apatite and silicates from numerous locations (Table 1). Isotopic ratios are derived from calibrations calculated using glass and mineral standards with known isotopic ratios before each analytical session to correct for instrumental mass fractionation (IMF).

Liu et al. (2012) have reported the water content and H isotope composition of mineral fragments, glasses and agglutinates from different lunar soil samples. Analyses were carried out using the Cameca IMS 7f-GEO at Caltech. Secondary ions were then collected through the mass sequence ^{12}C , $^{16}O^1H$, ^{18}O , $^{12}C^{16}N$, ^{30}Si , ^{31}P , ^{32}S , and ^{35}Cl at a mass resolution of ~ 5500 (sufficient to resolve $^{16}O^1H$ from ^{17}O). The same spot was analyzed for D and H using a mass resolution of approximately 600. Saal et al. (2013) expanded their previous work on volatile abundances in volcanic glasses and reported their H isotopic composition. Analyses were carried out using the

DTM-CIW NanoSIMS 50L in dynamic SIMS (D-SIMS) mode for glasses and in scanning ion imaging SIMS (SII-SIMS) mode for melt inclusions. Secondary ions of ^1H , D and ^{17}O were simultaneously collected on electron multipliers at a mass resolution of 6000 (sufficient to resolve D from $^1\text{H}_2$ and $^{16}\text{O}^1\text{H}$ from ^{17}O). Basaltic glass ALV519-4-1 (1600 ppm H_2O , $\delta\text{D} = -72 \pm 4 \text{‰}$) and synthetic forsterite (0.4 ppm H_2O) were used for calibration of the H_2O content, D/H ratio, and detection limits.

Hashizume et al. (2000) studied H, C, and N abundances and isotopic compositions in different mineral grains from regolith breccia 79035 and soil 71501. Analyses were performed at Centre de Recherches Pétrographiques et Géochimiques (CRPG, CNRS) in Nancy (France) using the Cameca IMS 1270 ion probe. Analyses of H and C, N, and Si were performed separately. Secondary ions of H^- , CC^- , and CN^- , and their isotopes, were measured sequentially in mono-collection mode, at a mass resolution of >7500 (required to resolve $^{11}\text{B}^{16}\text{O}$ from $^{12}\text{C}^{15}\text{N}$).

The measurement of δD in lunar apatite was pioneered by Greenwood et al. (2011) using the Cameca IMS 1270 instrument, equipped with a SCAPS ion imager, at Hokkaido University (Japan). The SCAPS detector allowed imaging of ^1H distribution, which facilitated identification and analysis of crack-free areas to avoid contamination. Negative secondary ions of ^1H and ^{18}O were first collected sequentially followed by sequential collection of ^1H and ^2D in an electron multiplier at a mass resolution of 2300. Reproducibility of $^1\text{H}/^{18}\text{O}$ ratios measured in the two apatite standards among different sessions were 5 to 17 %.

Barnes et al. (2013) carried out analyses of OH contents and D/H ratios for lunar apatites using the Cameca NanoSIMS 50L instrument at the Open University (UK). Secondary ions of ^1H , D, ^{12}C and ^{18}O were simultaneously collected on electron multipliers at a mass resolution of ~ 4300 (sufficient to resolve D from $^1\text{H}_2$). H_2O detection limits were estimated using the y-axis

intercept of the H_2O vs. $^1\text{H}/^{18}\text{O}$ calibrations curves, and ranged from 9 to 92 ppm H_2O over the different analytical sessions. Tartèse et al. (2013) used the same analytical protocol as described by Barnes et al. (2013) to analyze the water content and its H isotope composition in apatite in several mare basalts. Standard errors on the slopes of the calibration lines used to calculate H_2O contents ranged from 0.5 % to 5 %, with an average value of 1.7 %. The overall reproducibility of the D/H ratios measured on the reference apatites varied between 10 and 51 ‰, with an average of 29 ‰ (2σ standard deviation).

SIMS has also been used to analyze the Cl isotope composition of lunar apatites. Sharp et al. (2010) carried out in-situ ion microprobe analyses using the Cameca IMS 1270 instrument at the University of California, Los Angeles (UCLA). Secondary ions of ^{35}Cl and ^{37}Cl were collected on electron multipliers. Measurements were made at high mass resolution in order to eliminate all isobaric interferences, such as $^{34}\text{S}^1\text{H}$ on ^{35}Cl . Precision of individual spot analyses ranged from 0.4 to 1.2 ‰, depending on Cl concentration.

Shearer et al. (2012) used the Cameca NanoSIMS 50L at Caltech to measure $\delta^{34}\text{S}$ in sulfides from Mg-suite and ferroan anorthosite (FAN) samples 67016,294, 67915,150, and 67016,297. Ion images of ^{32}Si and ^{28}Si were used to target sulfide grains and avoid cracks. Secondary ions of ^{16}O , ^{28}Si , ^{32}S , and ^{34}S were measured simultaneously using electron multipliers at high mass resolution. Instrumental mass fractionation, which is variable between the f-series, 12-series, and NanoSIMS machines owing to their different geometries, was corrected using known fractionation factors.

Ion imaging of volatiles in lunar samples with SIMS.

McCubbin et al. (2010c) used time-of-flight secondary ion mass spectrometry (TOF-SIMS) to identify the presence of F, Cl, and OH in lunar apatite. Their TOF-SIMS analyses were

performed using a TOF-SIMS IV instrument from Ion-TOF GmbH housed in the Department of Mineral Sciences at the Smithsonian Institution in Washington, D.C. TOF-SIMS is a surface-sensitive analytical method capable of parts per million level detection sensitivity, and provides information from depths corresponding to one to three atomic monolayers. Surface contamination on the sample was thoroughly removed prior to analysis by pre-sputtering for ~2 min on $300 \times 300 \mu\text{m}$ areas using an Ar^+ ion-beam. For acquisition of ion images, an intermittent Bi^+ primary ion beam with a 1 ns pulse length was used. Spectra were collected in negative and positive ion mode. Mass calibration was performed from these spectra using the system reference masses at ^1H , ^{12}C , $^{12}\text{C}^1\text{H}$, $^{12}\text{C}^1\text{H}_2$, $^{12}\text{C}^1\text{H}_3$ for negative ions and $^{12}\text{C}^1\text{H}_3$, $^{12}\text{C}_2^1\text{H}_5$, and $^{12}\text{C}_3^1\text{H}_7$ for positive ions. These high-resolution spectra were collected so the correct masses could be assigned to each peak before collecting high spatial resolution (low mass resolution) ion images. The same target areas were reanalyzed using a pulse length of ~100 ns, which was necessary to obtain high lateral-resolution ion images. Each measurement consisted of ~50-150 scans, dependent on total ion yield, which corresponded to total measurement times of ~10-20 min.

Hauri et al. (2011) conducted quantitative ion imaging on olivine-hosted melt inclusions from high-Ti orange glass beads. Data were acquired using the DTM-CIW SIMS 50L using a slightly modified protocol compared to the one described in Saal et al. (2008). The primary Cs^+ ion beam was rastered over $30 \times 30 \mu\text{m}$ or $10 \times 10 \mu\text{m}$ areas, and negatively charged secondary ions of $^{16}\text{O}^1\text{H}$, ^{19}F , ^{30}Si , ^{32}S and ^{35}Cl were measured simultaneously on 5 electron multipliers using a MRP of ~6000. Each analysis was preceded by 2 min pre-sputtering over a $30 \times 30 \mu\text{m}$ area using a 10 nA primary beam, before switching to a 1 nA primary beam for data acquisition. Data were acquired using the scanning ion imaging mode (SII-SIMS) of the NanoSIMS ion probe. The sputtered crater was divided into 256×256 pixels and no electronic gating was used.

The data were recorded as ion images obtained simultaneously for each mass with the total analysis consisting of the acquisition of 10 single frames, each of them taking ~ 16 s, resulting in a ~ 3 min analysis. The data were then processed using the L'Image software package developed by Larry Nittler (DTM-CIW). After correction for system dead time, the last 9 frames were summed (first image used as a pre-sputter), scanning isotope ratio images of $^{16}\text{O}^1\text{H}/^{30}\text{Si}$, $^{19}\text{F}/^{30}\text{Si}$, $^{32}\text{S}/^{30}\text{Si}$ and $^{35}\text{Cl}/^{30}\text{Si}$ were calculated, and data were extracted from specific user-defined regions of interest (ROIs), allowing to extract information from the melt inclusions only, without overlapping host olivine or areas containing surface contamination of volatiles. Calibrations of the volatile abundances in melt inclusions were derived from the isotope ratio images obtained in the same way on glass standards and synthetic forsterite.

Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique for detecting molecular groups as opposed to individual elements. Consequently, Raman is typically used to identify mineral phases or molecular groups in glass phases rather than to quantify concentrations of specific elements in lunar materials. Raman spectroscopy has been used to identify a number of volatile-bearing phases in lunar samples including sulfides, graphite, akaganéite, carbonates, apatite, and macromolecular organic carbon (McCubbin et al., 2010c; Shearer et al., 2014; Steele et al., 2010; Thomas-Keprta et al., 2014; Zeigler et al., 2001). Although not typically a quantitative tool for volatile-bearing lunar materials, the benefit of using Raman spectroscopy over other techniques to determine mineralogy in lunar samples includes the non-destructive nature of the analysis, the high spatial resolution that can be obtained during both single spectrum acquisition as well as spectral imaging ($0.3\mu\text{m} \times 0.3\mu\text{m} \times 1\mu\text{m}$ per pixel), and the ability to analyze phases below a sample surface provided the sample is translucent in

transmitted light and the instrument has a confocal geometry capability. Lastly, Raman spectroscopy is an excellent tool for identifying organic compounds with high spatial resolution (Steele et al., 2007; Steele et al., 2012a; Steele et al., 2012b), and this was recently demonstrated for the first time on a lunar sample (Thomas-Keprta et al., 2014).

Micro Fourier transform infrared spectroscopy (micro-FTIR)

Fourier transform infrared spectroscopy is also a vibrational spectroscopic technique for detecting molecular groups as opposed to individual elements. This technique has primarily been used to quantify the concentrations of molecular H-species (OH and H₂O) in lunar minerals and glasses through application of the Beer-Lambert law (1),

$$A_{band} = \frac{C_x \times d \times \rho \times \epsilon_{band}}{m_x} \quad (1)$$

where A_{band} is absorbance of a specific band in the spectrum, C_x is the weight fraction of a molecular species x , d is the thickness of the sample, ρ is the density of the material being measured, ϵ_{band} is the linear molar absorptivity or molecular absorption coefficient for that material and corresponding spectral band position, and m_x is the molar mass of the molecular species x . The Beer-Lambert law is only applicable to isotropic materials and for the principal optical directions in anisotropic materials (Libowitzky and Rossman, 1996). Furthermore, it is a standardless technique that requires having accurate molecular absorption coefficients, which have been determined for quantifying H₂O in most silicates, some glass compositions, and apatite (Hauri et al., 2002; King et al., 2002; Libowitzky and Rossman, 1997; Mandeville et al., 2002; Wang et al., 2011). The detection limit for OH abundances is approximately 100's ppb to 10000's ppb H₂O depending on the sample (Fogel and Rutherford, 1995; Libowitzky and Rossman, 1997). The primary limitation for applying this technique to a broad range of lunar samples is the need for obtaining doubly polished thin wafers of sample for quantitative analysis

with high detection sensitivity, and for anisotropic mineral samples, doubly polished thin wafers oriented perpendicular to each of the principal optical directions. Micro-reflectance FTIR techniques have been developed for quantifying volatile abundances in glasses from a single polished surface like that of a thin section (King and Larsen, 2013), however detection limits are substantially higher (~ 1000 's ppm) than with transmittance analyses. This technique has also been used to search for various dissolved C-species within lunar volcanic and impact glasses, but the C-species were below detection (50-100 ppm) in all analyses (Fogel and Rutherford, 1995).

Stepped Heating Mass Spectrometry and Gas Chromatography Techniques

Various heat extraction techniques have been applied to the study of lunar volatiles since the Apollo era with periodic improvements to procedures and instrumentation to permit the analysis of smaller sample sizes. The different forms of this technique, as described below, have been used for analyzing both crystalline rocks and soil (bulk and separated fractions) primarily for various C-species. However, all such analyses are based on the same basic principle; a sample is heated incrementally, and volatiles are released from the sample as gases at each temperature step. These gases are then transferred to a mass spectrometer for isotopic analysis (Epstein and Taylor, 1970b; Furi et al., 2012; Norris et al., 1983a). Nevertheless, samples can be heated in a number of ways. The most widely-applied method utilizes a furnace, although there are some variations in furnace design (e.g., Assonov et al., 2002; Burnett et al., 1975; Epstein and Taylor, 1970a; b; Epstein and Taylor, 1971; 1972; 1973; Epstein and Taylor, 1974; Epstein and Taylor, 1975; Friedman et al., 1970a; Friedman et al., 1970b; Kaplan and Smith, 1970; Kaplan et al., 1970; Merlivat et al., 1974a; Merlivat et al., 1974b). However, several recent studies targeting single grains in lunar soil samples for example, have made use of infrared lasers as a heat source (e.g., Wieler et al., 1999). Two main variations of the stepped heating technique

exist: pyrolysis or combustion. Pyrolysis involves the sample being heated under vacuum, without the presence of any oxidizing agent (e.g., Epstein and Taylor, 1974; Simoneit et al., 1973). Thus, carbon-bearing volatiles released from the sample are measured in the mass spectrometer as CO, CO₂, and CH₄ (Des Marais et al., 1973; Pillinger, 1979), preserving original speciation. On the other hand, in combustion analyses, the sample is heated in the presence of oxygen, facilitating combustion of all C-bearing species to CO₂ (e.g., Norris et al., 1983a; Norris et al., 1983b). In combustion analyses, all other volatiles (apart from carbon) are released by pyrolysis; only C compounds are combusted.

In several studies, the first, low temperature step is a combustion step, included to remove terrestrial organic contaminants. Subsequent temperature steps usually utilize pyrolysis to release volatiles (Mathew and Marti, 2001). It has been shown that isotopic values collected for the same samples using both pyrolysis and combustion methods separately give similar results (Becker, 1980; Epstein and Taylor, 1971; Friedman et al., 1970a; Friedman et al., 1974; Friedman et al., 1971; Friedman et al., 1970b; Kaplan and Petrowski, 1971; Kerridge et al., 1975), permitting the comparison of isotopic data collected using these different techniques.

One major difference between various groups using this type of technique is the number and temperature of heating steps chosen for specific analyses. These factors may be pre-determined by sample volatile yields and the detection limits of the instrumentation used, or by the release temperatures of components of interest (Burnett et al., 1975; Epstein and Taylor, 1973). An example of this is the temperature chosen for the first measurement step; below ~ 500 to 600 °C, releases are dominated by terrestrial contamination, and so data from temperatures lower than this step are often discarded, if collected at all (Norris et al., 1983a; Norris et al., 1983b; Thiemens and Clayton, 1980). However, the use of varying heating pathways can make

comparison of data collected by different groups problematic. Alternatively, samples can be heated directly to a final high-temperature (Moore et al., 1970; Smith and Kaplan, 1970), with the final volatile abundances and isotopic values representing a mixture of all of the volatile components released up to the final temperature. Such stepped (sometimes known as ‘stepwise’) heating procedures are similar to the thermal gas analyses carried out by Gibson and co-workers in the 1970s (Gibson and Johnson, 1971; Gibson and Moore, 1972; Gibson and Moore, 1973a; Gibson and Moore, 1973b), although in these analyses, a ramped heating regime was chosen, not stepped heating. Again coupled with a mass spectrometer to record the volatile species released, samples were heated at a rate of either 4 °C or 6 °C per minute, giving ‘smooth’ volatile release profiles across the whole temperature range up to 1400 °C. However, in these studies, no isotopic data were collected alongside abundance measurements.

A final variation of the stepped heating technique involves the use of a gas chromatograph alongside the same sample extraction apparatus used for mass spectrometric measurements. At each temperature step, a mixture of volatiles may be co-released; the inclusion of a gas chromatography element to the analysis allows these individual volatiles to be separated out as they travel along the chromatography column, prior to measurement. For example, the use of gas chromatography coupled with pyrolysis extraction procedures, enabled Des Marais et al. (1973; 1974) to separate out C species from total C releases, and measure CH₄ abundances alongside total C abundances in lunar soils. Alternatively, Moore et al. (1970; 1972; 1974; 1973 and ; 1971) used a gas chromatographic analyzer to detect CO₂ produced after combustion of C-bearing volatiles in lunar soils and rocks, to derive total C abundance for individual samples.

Remote Sensing Techniques for Detecting Hydrogen, Hydroxyl and Water

Several techniques have been used from orbit to search for water on the lunar surface. These include mapping neutron flux to detect elemental hydrogen, measuring ultraviolet through near-infrared reflected light to detect emissions of H_2 and absorption caused by OH^- and H_2O , and mapping radar return to search for a signature of ice in the regolith. As orbital remote sensing techniques, each of these provides different information about the lateral and vertical extent of H and H-bearing volatiles in the regolith.

Neutron Spectroscopy.

Planetary neutron spectroscopy is a standard technique that has been used to remotely measure the hydrogen concentration at the lunar poles (Feldman et al., 1998). Neutrons having a range of energies (<0.5 eV to >10 MeV) are created by nuclear spallation reactions when high-energy cosmic rays strike the airless lunar surface. Hydrogen has a unique ability to moderate neutrons because hydrogen atoms and neutrons have the same mass, which allows a highly efficient momentum transfer between the two. This efficient momentum transfer causes the number of medium energy neutrons (0.5 eV to 0.5 MeV) to be strongly depressed so that they are highly sensitive to the presence of hydrogen in the top tens of centimeters of lunar soil. The first measurements of hydrogen concentrations at the lunar poles were made using data from the Lunar Prospector Neutron Spectrometer (LP-NS) (Feldman et al., 1998). These data measured the hydrogen concentration with a spatial resolution on order of 45 km with a sensitivity of 10s of ppm H (Lawrence et al., 2006). Spatial reconstruction analyses have provided information about polar hydrogen concentrations at smaller spatial scales than nominal LP-NS data (e.g., Teodoro et al., 2010). Neutron measurements from the Lunar Exploration Neutron Detector (LEND) on board the Lunar Reconnaissance Orbiter (LRO) mission have reported hydrogen concentrations with a spatial resolution roughly a factor of four better than those obtained by LP-

NS (e.g., Boynton et al., 2012; Mitrofanov et al., 2012; Mitrofanov et al., 2011; Mitrofanov et al., 2010).

Ultraviolet Spectroscopy.

Ultraviolet (UV) spectroscopy can be used to search for water ice, as it has a strong, diagnostic absorption edge at 165 nm (Wagner et al., 1987). The Lyman Alpha Mapping Project (LAMP) far-ultraviolet spectrograph was flown on the LRO to search for hydroxyl/water on the lunar surface and in the lunar exosphere (Hendrix et al., 2012). Because it operates in the UV, LAMP can obtain sufficient signal using reflected starlight and lyman-alpha sky glow to image within the permanently shadowed craters (Gladstone et al., 2010). In addition to surface absorptions indicative of ice, the UV wavelengths measured by LAMP can, with sufficient integration time and atmospheric density, reveal atmospheric emissions of species including H (121.6 nm), H₂ (146.2 nm), C (165.7 nm), CO (151.0 nm), N (113.4 nm), and S (147.4 nm) (Gladstone et al., 2010). Since it operates in the UV, LAMP is sensitive only to the upper ~1 μm of the lunar regolith. The spatial footprint of each LAMP observation is 260 m x 5.2 km when the spacecraft is in a 50 km orbit (Gladstone et al., 2010).

Near-Infrared Spectroscopy.

Vibrations of OH⁻ and H₂O molecules in the near-infrared (NIR) can be directly detected by remote instruments, including flight spectrometers and Earth-based telescopes. The fundamental O-H stretching modes between ~2.8-3.6 μm are the same vibrations typically analyzed when using micro-FTIR spectroscopy to quantify water in the laboratory. However, remote measurements are made in reflectance rather than transmission, and are thus complicated by scattering effects within the regolith. Since even relatively high spatial resolution instruments still measure light reflected from spatial footprints that range in surface area from 100's of m² to

10's of km², both linear and nonlinear mixtures with other minerals must be considered in order to extract quantitative abundances. When a surface is hydrated, vibrational overtones that occur near 1.9 μm , 1.47 μm , and 1.2 μm may also be measured from orbit. Near-infrared spectroscopy is sensitive to the top $\sim 10\text{-}100$'s μm of the exposed surface.

The Moon Mineralogy Mapper (M³) spectrometer was a guest instrument on Chandrayaan-1, the Indian Space Research Organization's (ISRO) first mission to the Moon (Goswami and Annadurai, 2008). Although the primary goal of M³ was to map the mafic mineralogy of the Moon, the spectral range was extended to 3 μm to enable detection of OH⁻ and H₂O vibrational absorption features. The M³ was designed to operate in two modes, global and targeted, to obtain high spatial and spectral resolution coverage of the entire lunar surface. Full spatial resolution (600 cross-track pixels at 70 m/pixel) and full-spectral resolution (260 bands at 10 nm spectral sampling from ~ 0.4 to 3 μm) targeted data were only obtained for a limited number of locations on the Moon, largely because of the early end of the mission (Green et al., 2011). However, almost the entire lunar surface was imaged at the reduced-resolution global mode (140 m/pixel from a 100 km orbit, 280 m/pixel from a 200-km orbit and 85 spectral bands). The binning of the global data results in a 40 nm spectral sampling near 3 μm .

Near-infrared spectra of the Moon were also obtained for calibration purposes by instruments onboard the Deep Impact and Cassini spacecrafts. The Deep Impact High-Resolution Instrument-infrared spectrometer (HRI-IR) measures the spectral range of 1.05-4.8 μm (Hampton et al., 2005), and obtained coarsely resolved measurements of the Moon during two flybys in 2007 and 2009 (Sunshine et al., 2009). The Visual and Infrared Mapping Spectrometer (VIMS) covers a spectral range of 0.35 to 5 μm and obtained several image cubes of the Moon during a flyby in 1999. The spatial resolution of the VIMS data is roughly 175 km/pixel.

Radar

Radar has long been used as a technique for exploring planetary surfaces. Typical transmission wavelengths for planetary exploration range from cm to m, and thus penetrate deeply enough to provide information about the scattering properties and dielectric constants of the materials within the upper centimeter to tens of meters depth within a planet's regolith. Unlike the orbital techniques already outlined, radar measurements rely on an active source. This means that the radar source and receiver must both be located on the orbital spacecraft, unless a signal can be transmitted or received by Earth or another spacecraft. The latter case of bistatic radar measurements, where the geometry between the transmitter and receiver is not fixed, is more favorable for distinguishing scattering due to surface roughness that are caused by accumulation of water ice or other volatiles.

Bistatic measurements of several locations on the Moon were obtained in 1994 when the orbital spacecraft Clementine transmitted an unmodulated S-band (13.19 cm wavelength) signal, which was received by the Deep Space Network on Earth (Nozette et al., 1996). A synthetic aperture radar instrument, Mini-SAR was flown on the Chandrayaan-1 mission. This instrument transmitted an S-band (12.6 cm wavelength) signal and had a spatial resolution of ~75 m/pixel (Spudis et al., 2009). A similar instrument, Mini-RF, was flown on the LRO spacecraft, with both S (12.6 cm wavelength) and X (4.2 cm wavelength) band transmission modes (Nozette et al., 2010). Since the LRO and Chandrayaan-1 missions were contemporaneous, there were hopes that bistatic observations using the two instruments might be possible (Nozette et al., 2010). This was prevented by the early loss of communication with the Chandrayaan-1 spacecraft. However, bistatic measurements using the Arecibo observatory on Earth to transmit a signal and the Mini-RF instrument to measure the radar return are underway (Bussey et al., 2014).

Unconfirmed volatile-bearing lunar minerals

Amphibole

Amphiboles $[A_{0-1}M(4)_2M(1-3)_5T_8O_{22}O(3)_2]$ are double-chain silicate minerals with the essential volatile constituents OH, F, and Cl. On Earth, amphibole is commonly considered an indicator of hydrous magmatic or metamorphic conditions (Ridolfi et al., 2010); however, F and Cl can also stabilize amphibole in relatively dry systems. Similar to apatite, amphibole incorporates F, Cl, and OH into a distinct crystallographic site (O(3) site). However, amphibole also readily incorporates O^{2-} into the O(3) site as a primary magmatic feature (Hawthorne and Oberti, 2007; Popp et al., 1995), making quantification of structurally bound OH in amphibole difficult without direct OH-analysis. In addition to terrestrial rocks, amphiboles are present in martian meteorites (Johnson et al., 1991; McCubbin et al., 2013; McCubbin et al., 2010a; McCubbin et al., 2009; Monkawa et al., 2006; Nekvasil et al., 2007; Sautter et al., 2006; Treiman, 1985; Watson et al., 1994) and in several types of asteroidal materials, both achondrites and chondrites (Floss et al., 2007; Gross et al., 2013; McCanta et al., 2008; Rubin, 2008; 2010).

Amphiboles are absent from, or very rare in, lunar materials (Papike et al., 1991). There have been several published reports of amphibole in lunar samples, some of which appear to be credible, *prima facie*, and others of which could reasonably represent extra-lunar material, either terrestrial contamination or meteoritic infall. To our knowledge, none of the following reports have been confirmed independently as being amphibole and being lunar.

Agrell et al. (1970) and Gay et al. (1970a; b) reported a single amphibole grain extracted from a vug in lunar basalt 10058, and provide optical data, a partial EPMA analysis (lacking Cl, Table S6), and unit cell parameters from X-ray diffraction. This grain is clearly an amphibole, but its chemical composition (in relation to those of other lunar materials) suggests that it is a

contaminant. The amphibole is highly magnesian, Mg# of 70, in a rock where late-stage mafic silicates (such as would occur next to a vug) have exceedingly low Mg#s. Furthermore, the amphibole is alkali-rich, with 8.5 % Na₂O and 1.5 % K₂O, which implies that its 'A' site is entirely filled with Na+K. Such an alkali-rich amphibole seems unlikely from an alkali-poor planet with a crust dominated by calcic plagioclase. The amphibole composition would be unusual among terrestrial rocks, but it is far more likely to be terrestrial than lunar.

Dence et al. (1971) characterized isolated grains of amphibole from lunar basalt 12021,21, although amphibole was not observed in thin sections of 12021. They provide a chemical analysis and unit cell parameters from X-ray diffraction, and the grain is consistent with a Ca-Al amphibole with little alkalis (Table S6) such as might conceivably crystallize from a lunar basalt. In contrast, its composition would not be unusual for a terrestrial amphibole or some meteoritic amphiboles (McCanta et al., 2008), so its origin remains inconclusive.

Mason et al. (1972) reported amphibole in the Apollo 14 regolith sample 14163 and provided a partial chemical analysis by EPMA (lacking F and Cl, Table S6). The analysis is consistent with a kaersutitic or tschermakitic amphibole, such as occurs in martian and terrestrial basalts. Mason et al. (1972) report similar grains in regolith sample 14003, and Wilshire and Jackson (1972) report a similar grain in the lunar breccia 14308. Given the abundance of KREEP component (with its elevated alkalis, F, and Cl) in Apollo 14 samples, these reports could be valid. However, Mason et al. (1972) caution that glasses in the breccia resemble the amphibole, and it is possible that a glass could be found that has a composition comparable to that of an amphibole, so structural analysis of these grains would be required to verify their authenticity.

Finally, Lazko et al. (1980) reported rare amphibole grains in a fragment of plutonic rock from Luna 24 core 24182. Chemically, the amphibole is tschermakitic and magnesian, with Mg#

of 77 (Table S6). The association of amphibole with abundant magnesian olivine and magnetite suggested that rock fragment was from an ‘olivine achondrite’ and possibly not lunar.

There is little information on the possible stability fields of amphiboles in systems relevant to the Moon, although water-rich amphibole requires significant pressures of water vapor (Charles et al., 1971; McCanta et al., 2008; Merzbacher and Eggler, 1984). Fluorine-rich amphiboles, including kaersutitic amphibole, can be stable at low confining pressure provided enough fluorine is available (Floss et al., 2007; McCubbin et al., 2006; Rubin, 2010). Kaersutitic amphibole (Mason et al., 1972) is unstable at low pressures with respect to mineral assemblages containing rhönite, which is present in at least one lunar rock (Treiman, 2008).

Biotite

Biotites $K_2(Mg,Fe)_6(Al_2Si_6O_{20})(F,OH,Cl)_4$ are a sheet-silicate mineral with the essential volatile constituents OH, F, and Cl. This mineral is common in many volatile-rich terrestrial igneous and metamorphic rocks (Cesare et al., 2008; Eugster and Wones, 1962; Wones and Eugster, 1965), and it has also been found in the martian meteorite Chassigny (Johnson et al., 1991; McCubbin et al., 2013; Righter et al., 2002; Watson et al., 1994) and in an R chondrite (McCanta et al., 2008). There has been only one report of biotite in lunar samples that included analysis of volatiles, and that was from an Apollo fines sample 10084 (Gay et al., 1970a). A chemical analysis of the biotite is provided in Table S6. Given that this is the only occurrence of biotite being reported in a lunar sample, it has been speculated that this grain represents contamination (Fron del, 1975; Gay et al., 1970a). There are additional reports of micaceous or mica-like grains in Apollo samples within the first few years of their return (Arrhenius et al., 1970; Brown et al., 1970; Drever et al., 1970), but none of these were analyzed in detail or verified to be indigenous to the samples (i.e., samples 10084,30, 10017, and 10058,23).

Consequently, the presence of indigenous mica on the Moon and in Apollo samples is not supported by any reliable data.

Carbonates

As with other volatile rich minerals, reports of lunar carbonates are extremely rare and texturally ambiguous. Carbonates have been found in the form of unspecified particles (Dikov et al., 2002; Dikov et al., 1998) and calcium carbonate (Gotze et al., 2011) in lunar samples. Dikov et al. (1998) analyzed the fines portion of Luna 16 regolith drill core 1635 using X-ray photoelectron spectroscopy in combination with Ar etching and found a zone in the middle of the drill core, approximately 320 nanometers thick, that was strongly enriched in carbon (8.3-61.9 atom%). The layer is enriched in both graphite- and diamond-like phases, and carbon enrichment was also found on some particle surfaces. After careful analysis of this unit, the authors concluded the carbon is most likely the result of a single impact event of a comet or carbonaceous chondrite onto the lunar surface in which the cooling rate of the gas medium was very high (Dikov et al., 2002; Dikov et al., 1998). Calcium carbonate in the form of calcite (CaCO_3) was also found as small inclusions in a clast of granitic rock from the lunar regolith returned by Luna 20 (Gotze et al., 2011). After analysis by high-resolution cathodoluminescence microscopy and spectroscopy, SEM-EDS, micro-Raman spectroscopy, and elemental analysis by NanoSIMS, the inclusions of calcite were found to be in quartz grains that were intergrown with potassium-rich feldspar. Gotze et al. (2011) interpreted this carbonate to be magmatic in origin where the carbonate inclusion is a residue of an immiscible CO_2 -rich part of the fractionated KREEP-rich melt from which the granite crystallized. This formation mechanism requires highly oxidizing conditions in comparison to typical lunar magmatic systems (Holloway, 1984; Sato, 1979; Saxena and Fei, 1987; Wadhwa, 2008), which calls into question the validity of the claims

that this carbonate is magmatic. Consequently, the presence of the calcium carbonate in this sample is not questioned, but the origin is yet unclear. Although there have not been many occurrences of carbonates in lunar samples, the general consensus is that carbonates are either terrestrial contamination or from extra-lunar materials (i.e., comets and/or carbonaceous chondrites; Miura, 2007).

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