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Concentrations of Volatiles in the Lunar Regolith

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1. Introduction

To set lower and upper limits on the overall amounts and types of volatiles released during heating of polar regolith, we examined the data for equatorial lunar regolith and for the compositions of comets. The purpose, specifically, was to answer these questions from Janine:

1. Upper/Lower limits and 'best guess' for total amount of volatiles (by weight %) released from lunar regolith up to 150ºC
2. Upper/Lower limit and 'best guess' for composition of the volatiles released from the lunar regolith by weight %

We evaluate measurements of lunar volatiles in some detail below. For the bottom line (our best guess for the limits of volatiles), see section 6.

2. Preliminary Considerations

Making estimates of the volatile concentrations in the cold traps based on model data is quite difficult, because we do not know why there are hydrogen concentrations there. The Watson, Murray, Brown (1963) and Arnold (1979) models, in which the volatiles were due to comets or meteoroids, suggested that there could be concentrations due to the condensation of water. If that is the case, to a first approximation, the concentration of other (solar wind) volatiles in the cold traps may be the same as those in the equatorial regions. Other volatiles that might be trapped, particularly CO_2, would be intermediate because of their much higher sublimation rates. If, on the other hand, the cold trap volatiles are there mostly due to a process that preferably retains solar wind gases in the cold traps (Schmitt has argued this), then the retention of other gases may not be affected much because the process that lowers the hydrogen content of the equatorial regolith is dominated by the ease of diffusion of hydrogen from the regolith. (Studies show that in equatorial regions much more hydrogen is delivered to the regolith than is retained.) The easier release of lighter ions (H and He) from the regolith may also be caused by the different depths to which they are implanted compared to heavier ions. The implantation of ions is a direct function of their velocities and masses. The heavier they are, the deeper they are implanted. With all traveling at about the same speed, H and He are in the outer 20 nm or so; the others are deeper. Thus, if hydrogen is retained 10 times as well in the cold traps, heavier atoms probably wouldn't be elevated much, because their diffusion rates are much slower from regolith grains, although helium could be concentrated by similar amounts. On the other hand, during a micrometeorite impact, small amounts of regolith are melted, perhaps releasing all the solar wind volatiles, and allowing their transport to the cold traps.

For the purpose of RESOLVE, the question is whether we are going to assume that we are going to a volatile rich spot or not. If we go into a cold trap where volatiles are believed to be concentrated, perhaps verified by a surface neutron spectrometer, then the questions are: (1) what is the form of hydrogen – water or some other molecular form of hydrogen (H_2, OH) and (2) what else is present? If we make measurements in an area where there is not an elevated

hydrogen content (e.g. a non-shadowed area), we would want to know: (1) what is the hydrogen content? Is it higher than typical regolith elsewhere? These two scenarios lead to different conclusions as to minimum/maximum limits for RESOLVE. In other words, this is a tricky business with great uncertainties and a severe lack of knowledge of what we will find. This is, of course, the reason why we need to land the RESOLVE system in a cold trap!

3. Inferences from Regolith Data

3.1 Element abundances

Total contents of gases and molecules have been measured in lunar regolith, by step-wise heating experiments (e.g., Gibson and Johnson, 1971). We will discuss the total elemental concentrations first, then the form and temperatures at which they should be released. The concentrations of H, C, N, S, and the noble gases are summarized by Haskin and Warren (1991) and Fegley and Swindle (1993). Fegley and Swindle also discuss the complexities of the analyses and discrepancies between different laboratories and techniques. Table 1 is their best guess for the average concentrations in equatorial regolith. We also list the range in abundances for the Apollo 16 site (Haskin and Warren, 1991) because it is mineralogically most similar to what we expect at the polar cold traps; for the other sites, see Table A8.6 (p.472-473) in the *Lunar Sourcebook*. The column labeled "Estimated Concentration in Shadowed Soils at Poles" is a guess based on dividing the mean H concentration (46 μg/g, same as ppmw) into the standard 1000 μg/g, which we have decided on the basis of Lunar Prospector data and an assumption of the fraction of permanently shadowed areas. We assume *all* elements would be enriched by the same amount, but that is far from proven, so remember that is simply a guess. Because H is more mobile than the other elements (lowest mass), the heavier the element, the closer it may be to the equatorial value. We do not really care about the noble gases heavier than Ar, but we list them for completeness. Pay attention to the units in Table 1.

Table 1. Volatiles in the lunar regolith. Column 2 values from Haskin and Warren (1991) for Apollo 16 regolith. Column 3 values from Fegley and Swindle (1993) for all sites. Column 4 values are ~20 X those in column 3.

Volatile	Range in Concentration in Apollo 16 Soil	Concentration in Soil (average of all Apollo soils)	Estimated Concentration in Shadowed Soil at Poles
^{3}He	-	4.2±3.4 ng/g	90 ng/g
^{4}He	3–36 μg/g	14±11.3 μg/g	300 μg/g
^{20}Ne	0.4–1.2 μg/g	1.2±0.8 μg/g	26 μg/g
^{36}Ar	0.6–3 μg/g	0.50±0.19 μg/g	11 μg/g
^{84}Kr	.29–2.2 ng/g	0.54±0.22 ng/g	12 ng/g
^{132}Xe	0.2 ng/g	0.14±0.06 ng/g	3 ng/g
H	4–146 μg/g	46±16 μg/g	1000 μg/g
C	312–280 μg/g	124±45 μg/g	2700 μg/g
N	4–209 μg/g	81±37 μg/g	1800 μg/g
S	470–640 μg/g	715±216 μg/g	-

The concentrations in the cold traps for everything except H and He might be greatly overestimated because, as discussed above, their loss rates from equatorial regolith may be much less than that of H. The S contents in the cold trap would be particularly overestimated as it is bound in primary minerals, so we do not list it.

3.2 Gas release patterns

The bulk of the He, Ne, and Ar is released by 700°C; only a small fraction is released at temperatures less than 400 °C (see Fig 1 below, from Fegley and Swindle, 1993). There might be small amounts of loosely-bound He released at lower temperature, or even by agitation, but that is not quantified well. Note that the gases are released in order of their atomic weights, so Ne would presumable lie between He and Ar.
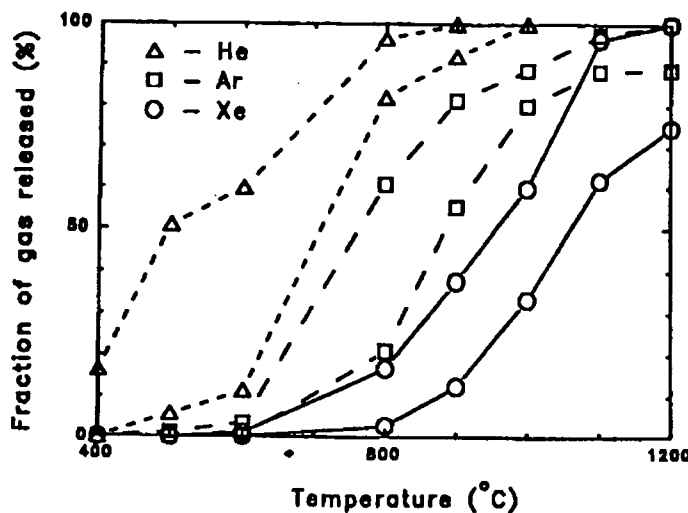

Fig. 1. Gas released vs temperature during stepwise heating. Summary by Fegley and Swindle (1993). Primary sources listed in that paper. The two curves for each element represent lower and upper bounds on the gas release patterns.

Experiments on regolith samples indicate that H is released generally as H_2, with some H_2S coming off at high temperature (Fig. 2). As discussed below, the H_2O is likely terrestrial contamination. C is released as CO_2 and CO, though some investigators reported small amounts of C_2H_2, CH_4, and HCN (see summary in *Lunar Sourcebook* (p.447). N is released as N_2. Typical gas-release patterns are shown in Fig. 2 (Gibson and Johnson, 1971).

Quantities of gases released at low temperatures are not so easy to determine from the plots shown in Fig. 2. The peak heights are roughly proportional to the concentrations measured. Gibson and Johnson (1971), Fig. 2, could not distinguish between CO and N_2, but other studies were able to (e.g., Simoneit et al., 1973). Both CO and N_2 are released in the large peaks labeled "CO, N_2" in Fig. 2. Notice that H_2 comes off at a fairly high temperature (400 °C or more). This means that we might measure water at the poles, but not H, at low temperatures. However, if there are hydrogen concentrations in these cold areas, there must be some process that preferably retains the hydrogen that would be lost at temperatures less than 100oC in the equatorial regions.

Therefore, if you heated the polar regolith to 100°C, some hydrogen should be released at this temperature, and you should be able to measure that fraction of hydrogen that is preferably retained just because the regolith is cold. As suggested above, the loss of hydrogen in the equatorial regolith is due to a balance between input from the solar wind and loss by diffusion, perhaps in part at elevated temperatures associated with micrometeoroid impacts.

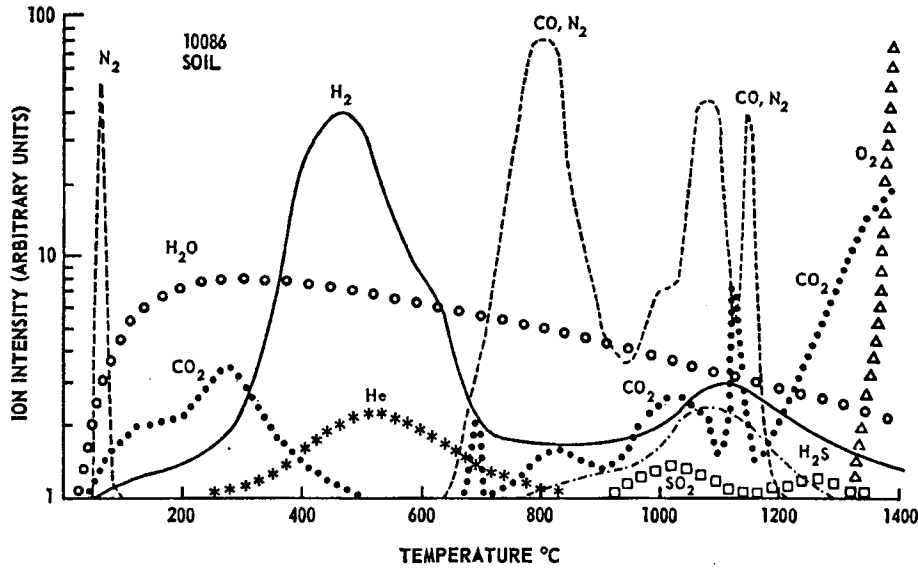1354   EVERETT K. GIBSON, JR. and SUZANNE M. JOHNSON

Fig. 1. Gas release pattern for Apollo 11 soil 10086,16. Sample weight 242.94 mg.
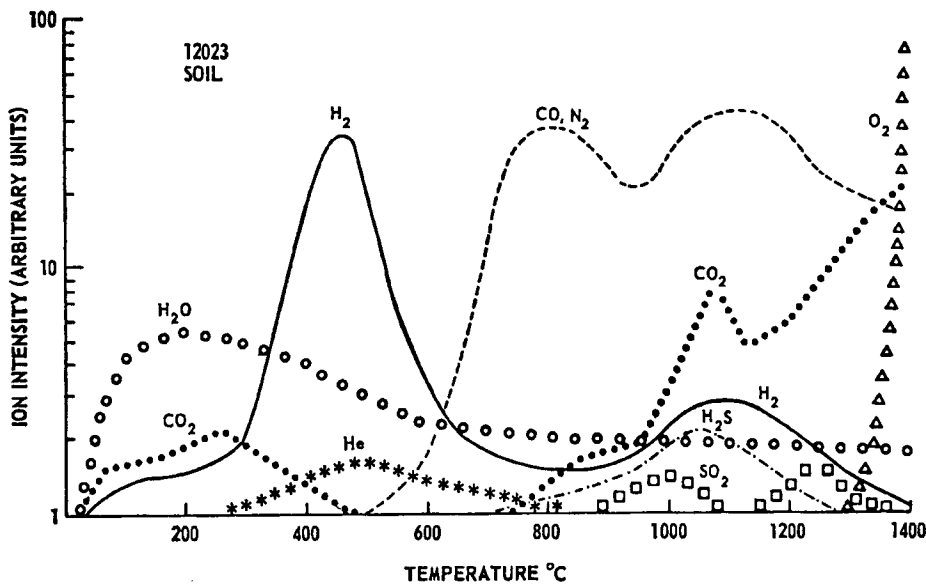Heating rate 4°C/minute.

Fig. 2. Gas release pattern for Apollo 12 soil 12023,9. Sample weight 208.50 mg.
Heating rate 4°C/minute.

Figure 2. See their caption in the figure (from Gibson and Johnson, 1971).

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3.3 Was water detected in the Apollo samples?

There still seems to be a lot of dispute about whether the H_2O released (not doubt about that) is lunar or terrestrial. If lunar, the idea is that it forms by chemical reaction of solar wind H with oxygen in the ilmenite and other oxide minerals, like ulvöspinel. The abundance of water is on the order of 20% of the amount of H (rough estimate based on peak heights and area under the curves). The question of whether water is lunar or terrestrial was addressed by Epstein and Taylor (1974); this is a different Taylor from the two scholars known and loved by the RESOLVE team. They give a bunch of reasons why they think the water is terrestrial contamination. Here is an abbreviated list:

1. Almost all the H_2O escapes more readily (lower temperature) than do the solar wind gases, suggesting it is adsorbed.
2. D/H ratios are consistent with terrestrial water, not solar wind (see below).
3. Radiation and other regolith processes produce chemically active surfaces that can readily adsorb water molecules from the air.

Gibson and Johnson (1971) analyzed crushed rock (basalt) samples. One chip was from the outside surface of a lunar rock, the other from the interior. Both samples had been crushed to < 60 mesh size (< 250 microns). They measured the gases released from these samples (see Fig. 3), finding a sharp peak in H_2O for the surface sample and a broad release pattern for H_2O for the interior sample (similar to the release from the regolith). Because lunar basalts do not contain any hydrous phases, it seems likely that the water was adsorbed from the terrestrial atmosphere. The crushing of the samples and allowing them to be exposed to air for a long time (they had been used in a study published in 1970, so for about a year), may have promoted water adsorption. In short, the basalt analysis is consistent with the idea that water is a terrestrial contaminant, not the product of reaction of solar wind H with oxygen in regolith grains. On the other hand, adsorbed water should have been evolved at low temperatures, not all the way up to 1200°C. Perhaps this experiment is flawed in some way. The gas release profile from lunar soils (Fig. 2) indicates that H_2O was released continuously to 1200°C, though it peaks at 200°C. This argues that some of the water released from the regolith samples is lunar in origin.

There is more to the story. Epstein and Taylor (1974) measured D/H and oxygen isotopes in regolith samples. The solar wind, like the Sun, is highly depleted in D because of nuclear reactions inside the Sun. Solar wind D/H is 20 x 10^{-6} (weight), compared to 150 x 10^{-6} for mean ocean water (and the bulk Earth). Standard Mean Ocean Water is abbreviated SMOW. The H_2O released by heating the regolith is depleted in deuterium, but is not inconsistent with terrestrial atmosphere in mid-latitudes. This is shown by the two graphs below (Figs. 4 and 5). The D/H plateaus at about -100 δ (Fig. 4), in the range of air samples in Pasadena (Fig. 5), where Epstein and Taylor worked (Caltech). You calculate δD from $\delta D = [(D/H)_{sample}-(D/H)_{SMOW})]/(D/H)_{SMOW}$. It is expressed in parts per thousand.

The bottom line is that the isotopic composition (δD) for the water released from lunar regolith samples suggests that the water is terrestrial. On the other hand, the release shows how adsorbed (frozen onto) water might be released from regolith in permanently shadowed regions at the poles, though it does not say much about the amount released. It is also interesting that the H_2O is released over the entire temperature range (Fig. 2), not just at the low-temperatures expected for adsorbed water. The may indicate that not all the H_2O released is adsorbed terrestrial water. Furthermore, in the experiments Larry Taylor did with heating small chips of

Apollo12 regolith breccia in sealed silica to 800°C, he constantly got water mist from reduction, whereas the basalts did not give this mist.

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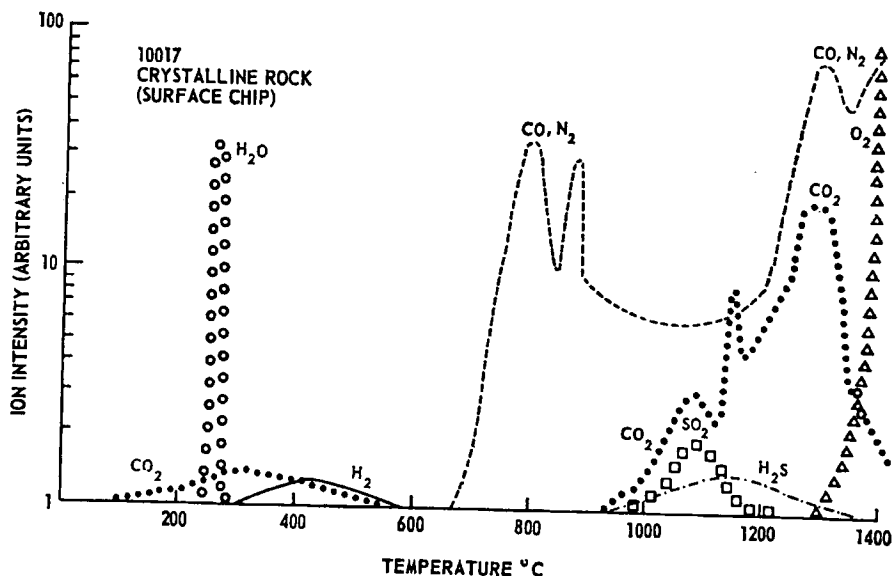
Fig. 3. Gas release pattern for a surface chip of Apollo 11 crystalline rock 10017,57. Sample weight 400.45 mg. Heating rate 4°C/minute.
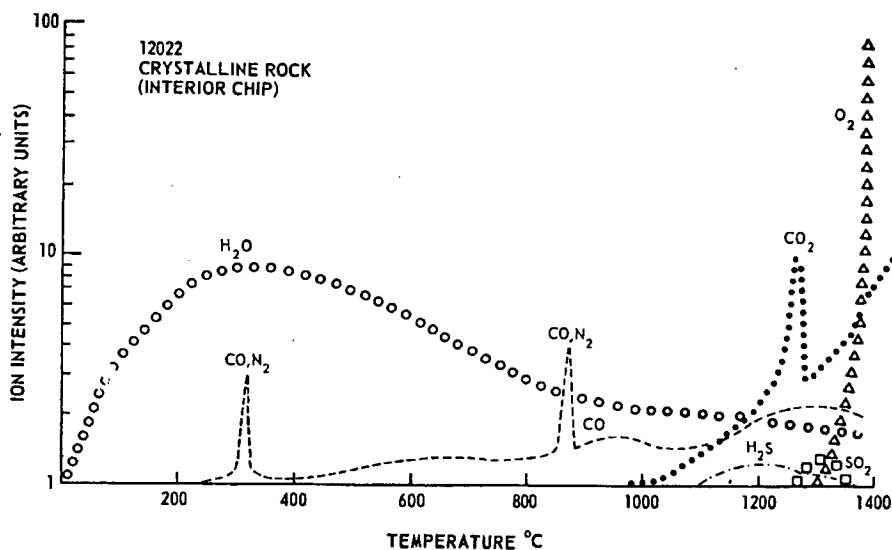
Fig. 4. Gas release pattern for an interior piece of Apollo 12 crystalline rock 12022,38. Sample weight 500.65 mg. Heating rate 4°C/minute.

Figure 3. See captions from the paper (Gibson and Johnson, 1971). This experiment might be flawed. Adsorbed water should have been released at low-T only.
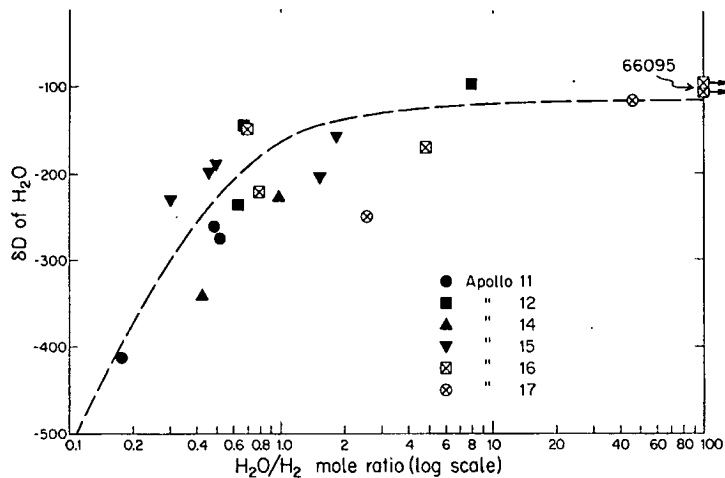
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Fig. 3. Modification of Fig. 2 of Epstein and Taylor (1973) showing all of our isotopic data on lunar samples, with the addition of data points on 66095 (this work) and on some other lunar samples (S. Epstein and H. P. Taylor, unpublished data). The data points for 66095 lie well off to the right of the diagram; the lower point represents the average H_2O evolved at 25°C and the upper point represents the average H_2O evolved in the interval 25–700°C.

Figure 4. From Epstein and Taylor (1974). Solar wind would plot at -800 δD. Rock 66095 is "Rusty Rock," a breccia chuck full of terrestrial water from oxyhydration of lawrencite (FeCl2).
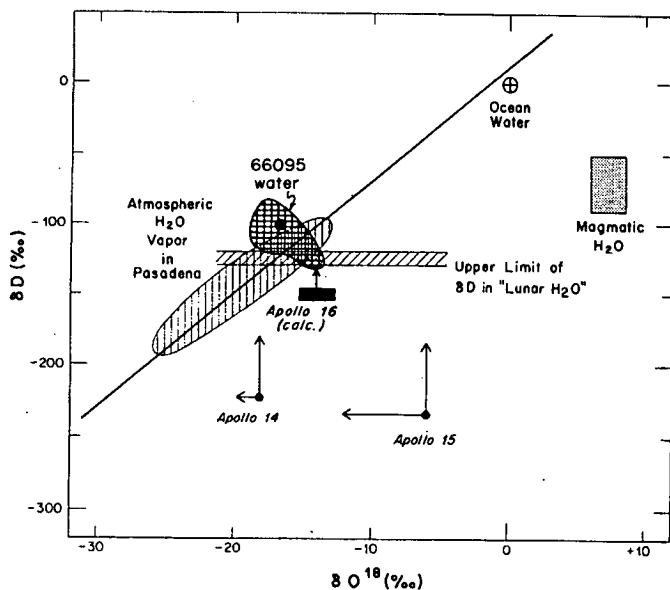
Fig. 4. Modification of Fig. 3 of Epstein and Taylor (1973) with the addition of the field obtained for sample 66095 from Fig. 2 of the present paper. The upper limit of δD in "lunar H_2O" is defined by the "plateau" in Fig. 3. The arrows indicate the directions in which the isotopic compositions of the other lunar H_2O samples should be corrected to take into account certain isotopic fractionations that accompany the laboratory extraction procedures (see text). The positions of the terrestrial meteoric water line, typical magmatic water, and ocean water are also shown for comparison.

Fig. 5. From Epstein and Taylor (1974). Solar wind would plot at -800 δD.

3.4 Preliminary Recommendations

If none of the water released was lunar, can we expect any water from solar wind hydrogen to be at the poles? (Cometary sources are discussed below.) As summarized by Crider and Vondrak (2002), solar wind H can react with surface materials to form H_2 or OH. Further proton bombardment can form H_2O by chemical sputtering. So, some amount of H_2O may be produced (perhaps indicated by the high-temperature release of much of the water, Fig. 2). This would migrate to the poles. How much is estimated by Crider and Vondrak, but that is a model, not based on any measurement of the lunar regolith. Through a series of arguments they conclude that the amount of OH is 0.1 the amount of H; the amount of H_2O should be about 0.02 the amount of H. On the other hand, H is also directly implanted at the poles, so it is difficult to determine the relative amounts of H_2O, OH, and H_2.

We suggest that using the observed H_2O in regolith analyses (Fig. 2) might be a useful lower limit, even though at least some of it is likely to be terrestrial. It was adsorbed onto soil grains, giving a rough idea of how much water is released from a saturated surface. It is possible that the actual amount will be less than this, but a RESOLVE measurement would at least be able to place an upper limit on the concentration. From Fig. 2, the amount of water would be roughly 20% of the amount of H_2. If H_2 abundance is 500 μg/g (half of the H value we assume from Lunar Prospector modeling), then we could expect about 900 μg/g of H_2O [500 x 0.2 x (18/2)], recognizing that it could be substantially less. This corresponds to 5×10^{-2} moles of water in a 1-kg regolith sample. Hydrogen would also be released. The 900 μg/g of H_2O would tie up 100 μg/g of H_2, leaving an additional 400 μg/g of H_2 to be released. Based on the average concentrations in Table 1 (column 4), and assuming all C is released as CO and N as N_2, an additional 6200 μg/g of CO and 900 μg/g of N_2 could be released. However, this assumes that C and N are as enriched in cold traps as is hydrogen. If they are in concentrations like those at Apollo sites, then reasonable lower limits are 285 μg/g of CO and 40 μg/g of N_2.

4. Inferences from Comet Compositions

The most commonly assumed major source of H_2O is from the impact of comets. This can happen continuously as small comets hit the Moon (even micron to millimeter comets) or in the form of occasional large impacts. The latter probably deliver the most water by mass. The basis for estimating the composition of ice formed from comet impacts is the abundances of assorted volatiles in comets. Three have been measured well, Halley, Hale Bopp, and Hyakutake. Because of the great uncertainties of how much of each gas will be retained and how much fractionation would take place during deposition, we give a broad average of data (Table 2). Primary sources are Crovisier and Brokelee-Morvan (1999), Altwegg and Balsiger (1999), and Eberhardt (1999). All are in an issue of *Space Science Reviews* (vol. 90, number 1).

Some observations: Water is clearly the most abundant volatile in comets, though CO and CO_2 are also present in relatively large amounts. Note that although D/H is much higher in cometary water (300×10^{-6}) than in the solar wind (20×10^{-6}) (see Meier and Owen, 1999); the ratio is small and probably would not affect our analysis of H_2. Besides, the deuterium would evolve as D_2, easily distinguished from H_2, though not from [4]He. On the other hand, there is a lot more [4]He than D.

Table 2. Relative abundances of major
gases in comets.

Molecule	Abundance
H_2O	100
D/H in H_2O	3×10^{-4}
CO	15
CO_2	5
H_2CO	2
CH_3OH	1.5
NH_3	0.7
CH_4	0.5

The transport of the volatiles to the poles, their deposition, and their sublimation rates affect how much we can expect to observe. All are more volatile than H_2O and probably would be lost more readily. Thus, their abundance relative to water would be less than the relative abundances listed in Table 2. In addition, trapping in amorphous ice (the only effective way to preserve the volatiles other than water) can fractionate the gases as a function of deposition temperature. Experiments by Bar-Nun et al. (1988) show that at 24-35 K, all gases are trapped equally well. At higher temperatures, however, they are trapped differentially, with efficiency in the order CH_4 > CO > N_2 > Ar. Thus, because deposition temperatures are typically 50–80 K, there will be some significant fractionation. However, since these gases, other than CO, are not very abundant, we probably do not have to worry about this effect.

Preliminary Recommendations

Water will dominate the gas composition, with significant amounts of CO and lesser amounts of other volatiles. Water will come off at a low temperature, and assuming it was deposited as amorphous ice, the gases will come off with the H_2O. Their abundances will almost certainly be less than in comets and will not contribute much to the total volume of evolved gas. But how much water will be evolved? See next section.

5. Inferences from Lunar Prospector

Another way of looking at this is to estimate the distribution of water in permanently shadowed areas in the regolith, from Lunar Prospector data and from statistical analysis. The lower limit is still that given above for solar-wind-derived water. The absolute upper limit is a slab of ice deposited by a comet. The slab is unlikely to be preserved on the surface, but could be buried beneath ejecta from small craters. In this case, no matter how we designed the system, there would be much too much water to analyze. Fortunately, we would probably know this from the CHAMP-Raman observations of the core and could choose not to analyze such a sample,or only a small portion of the core so as not to swamp the system.

The more likely situation is that layers of comet-derived ice would be broken up the way rocks are in the regolith. They would end up as ice chips with a range of sizes from centimeters to fractions of a millimeter. Their abundance would probably vary from place to place inside a permanently-shadowed crater, and would likely be normally distributed. We do not know anything about the normal distribution, but can perhaps make some good guesses. The mean value is unlikely to be larger than the mean estimated by Feldman et al. (2001), making

assumptions about the amount of dark area and their measurement of mean H content. In fact, this mean may be lower: using 1000 μg/g H converts to 1.8 wt.% H_2O. (Reevaluation of the data by Dave Lawrence, Feldman et al, last year, gave a value of ~1600 μg/g for H in the cold traps. We do not know how reliable this is. Like the 1000 μg/g estimate, it is model-dependent.) Let's assume that the standard deviation of the population inside the shadowed areas is 0.9 (the value needed to make 2-sigma be 1.8, equal to the mean). This means that there is only a 5% chance that that we would detect no water. Thus, the lower limit is what we estimated above, about 20% of the H abundance. However, there is a 66% chance that the water content will be between 0.9 and 2.7 wt.% (plus or minus one sigma of the 1.8 wt.% mean). And there is a 33% chance that there will be 3.6 wt% water or more, and a 33% chance that there will be 0.9 wt.% or less.

What is the uncertainty of the mean? It is unlikely to be too much more than a factor of 3 too low. If we take the mean to be 5.4 wt.% (three times higher than 1.8 wt.%), and assume that one sigma is only 1 wt%, then the likely upper limit is 2-sigma higher, or 7.4 wt%. The lower limit is the limiting solar wind case.

6. The Bottom Line

Based on all the discussion above, we suggest:

- The quantities of gases released changes greatly with temperature; and the amounts of loosely-bound H (which would be released at low temperature) and adsorbed H_2O (also released at low temperature) are unknown.
- The lower limit for the amount of water evolved when regolith is heated is 900 μg/g of H_2O, corresponding to 5×10^{-2} moles of water in a 1-kg regolith sample. It would be accompanied by about 400 μg/g of H_2. The concentration of water may be much lower, but we suggest this limit as a useful lower detection limit for RESOLVE. An additional 6200 μg/g of CO and 900 μg/g of N_2 might be released, but a reasonable lower limit is based on the mean Apollo values, 285 μg/g of CO and 40 μg/g of N_2.
- The upper limit for the amount of water evolved when regolith is heated is 7.4 wt% (75,000 μg/g), corresponding to 3.6 moles in a 1-kg regolith sample. (This would be associated with a total hydrogen content of ~7000 μg/g). If there is independent evidence that suggests the water content in a given sample is higher, the RESOLVE analysis could be bypassed or performed on a smaller amount of sample (take shorter cores sections).
- The most likely value is water from a regolith with 1.8 wt.% H_2O, corresponding to 0.8 moles in a 1-kg regolith sample.
- The only significant gases to evolve at <150°C is H_2O and trapped cometary gases if present. H_2 evolves at >400 °C in the Apollo soils, but significant quantities may evolve at lower temperatures if the hydrogen concentration is 7000 μg/g and the concentrations are high because of a special low-temperature retention process.

7. Is there a problem with Sulfur?

Sulfur gases may have deleterious effects on RESOLVE hardware and analytical capabilities. Using the values in Table 1 and the gas release profiles in Fig. 2, we can estimate roughly how much sulfur gases could be released. According to Figure 2, H_2S and SO_2 come off

starting at about 800°C, but their abundance is much less than CO and N_2. Let's assume conservatively that the S concentration is 1000 $\mu g/g$ (Table 1) and that the S is partitioned between H_2S and SO_2 in a 3:1 proportion (rough estimate of the areas under the curves in Fig. 2). This means that there are roughly 750 $\mu g/g$ of S in H_2S and 250 in SO_2, hence 797 $\mu g/g$ of H_2S and 500 $\mu g/g$ of SO_2 released. This is equivalent to 0.02 moles of H_2S per kg of regolith and 0.008 moles of SO_2 per kilogram of regolith.

Referenes

Atlwegg, K. Balsiger, H., and Geiss, J. (1999) Composition of the volatile material in Halley's coma from in site measurements. *Space Sci. Rev.* **90**, 3–18.

Bar-Nun, A., Kleinfeld, I., and Kochavi, E. (1988) Trapping of gas mixtures by amorphous water ice. *Phys. Rev. B* **38**, 7749–7754.

Crovisier, J. and Bockelee-Morvan, D. (1999) Remote observations of the composition of cometary volatiles. *Space Sci. Rev.* **90**, 19–32.

Crider, D. and Vondrak, R. (2002) Hydrogen migration to the lunar poles by solar wind bombardment of the Moon. *Adv. Space Res.* **30**, 1869-1874.

Eberhardt, P. (1999) Comet Halley's gas composition and extend sources: Results from the neutral mass spectrometer on Giotto. *Space Sci. Rev.* **90**, 45–52.

Epstein, S. and Taylor, H. P. (1974) D/H and $^{18}O/^{16}O$ ratios of H_2O in the "rusty" breccia 66095 and the origin of "lunar water." *Proc. Fifth Lunar Sci. Conf.*, 1839–1854.

Fegley, B. and Swindle, T. (1993) Lunar volatiles: Implications for lunar resource utilization. In *Resources of Near-Earth Space* (J. Lewis et al., eds), p. 367-426. Univ. of Arizona Press.

Feldman, W. C. et al. (2001), Evidence for Water Ice Near the Lunar Poles, *J. Geophys. Res., Planets* **106**, #E10, 23232 - 23252.

Gibson, E. K. and Johnson, S. M. (1971) Thermal analysis-inorganic gas release studies of lunar samples. *Proc. Second Lunar Sci. Conf.*, 1351–1366.

Haskin, L. A., and Warren, P. H. (1991) Lunar Chemistry. In *Lunar Sourcebook.* See especially chapter 8, pp. 436-448 and appendix table A8.6.

Meier, R. and Owen, T. C. (1999) Cometary deuterium. *Space Sci. Rev.* **90**, 33–43.

Simoneit, B. R., Christiansen, P. C., and Burlingame, A. L. (1973) Volatile element chemistry of selected lunar, meteoritic, and terrestrial samples. *Proc. Fourth Lunar Sci. Conf.* 1635–1650.