Quantitative SIMS analysis of OH in lunar apatite: Implications for water in the lunar interior

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Post Apollo view of lunar water

No hydrous minerals

No evidence of aqueous alteration textures

Metal grains were all pristine, and ferric iron was nearly absent

Water was not detected with the best analytical techniques of the day

Resulting conclusion: The Moon is “Bone Dry”
Water in and on the Moon

Up to 46 ppm H$_2$O in lunar glasses
Saal et al. 2008

Hydration/hydroxylation process occurs on lunar surface
Chandrayaan-1, 2009

Missing structural component in apatite X-site
McCubbin et al. 2008
Apatite can substitute for F and Cl in apatite

- Terrestrial apatites primarily consist of F, Cl, and OH
- Carbonate is more common in apatite from sedimentary rocks or carbonatites

Is there OH in lunar apatite?
Analysis of lunar apatite by SIMS

Apatite standards
- Durango, Mexico (0.088 wt.% H₂O)
- Crystal lode pegmatite, CO (0.359 wt.% H₂O)
- Unknown, Morocco (0.384 wt.% H₂O)

Other standards
- Synthetic Forsterite (0.000 wt.% H₂O)
- Basaltic Glass (2.43 wt.% H₂O)
- 2 heterogeneous apatites (??? wt.% H₂O)
Analysis of lunar apatite by SIMS

Regression line forced through origin because synthetic forsterite (blank) yielded 3 ppm H₂O

Apatite standards
- Durango, Mexico (0.088 wt.% H₂O)
- Crystal lode pegmatite, CO (0.359 wt.% H₂O)
- Unknown, Morocco (0.384 wt.% H₂O)
Choices of Samples to Analyze

Of the samples that we obtained, only five were on 1” round slides (required to fit in the SIMS instrument)

Of the five samples, three of them had apatite that were large enough to analyze by SIMS (spot size ~30μm in diameter with 5μm field aperture)

Analyzed high Al-basalt 14053, soil grain from Apollo 15 (15404,51), lunar meteorite NWA 2977
High-Al basalt consisting primarily of pyroxene and plagioclase with minor phases include fayalitic olivine, fluorapatite, baddeleyite, K-feldspar, Fe-Ti oxides, Fe-metal, silica, troilite, and K-Ba-rich glass.

Apatites are typically subhedral to anhedral, and they range in size from ~2 μm to larger than 200 μm.
Apollo sample 15404 is a soil grain from the 4-10 mm sieve fraction, and it consists of an impact melt breccia with a lithic clast.

The lithic clast primarily contains pyroxene and plagioclase with a significant amount of K-rich feldspar and minor silica, fluorapatite, merrillite, Cr-rich spinel, and Fe-Ti oxides.

Apatites are typically anhedral, and they range in size from ~10 μm to ~100 μm.
NWA 2977 is similar in texture and composition to a clast type in paired lunar meteorite NWA 773. This clast was described as an olivine cumulate with VLT-basalt major element characteristics.

Consists primarily of olivine, pyroxene, and plagioclase with minor merrillite, fluorapatite, baddeleyite, K-feldspar, Fe-Ti oxides, Fe-Ni metal, troilite, and pentlandite.

Apatites are typically subhedral to anhedral, and they range in size from ~5 μm to larger than 100 μm.
We analyzed multipleapatite Grains from each sample

http://www.dtm.ciw.edu/content/view/86/93/

<table>
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<tr>
<th></th>
<th>15404$_{\text{min}}$</th>
<th>15404$_{\text{max}}$</th>
<th>14053$_{\text{min}}$</th>
<th>14053$_{\text{max}}$</th>
<th>NWA2977$_{\text{min}}$</th>
<th>NWA2977$_{\text{max}}$</th>
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<tr>
<td>H$<em>2$O$</em>{\text{ppm}}$</td>
<td>120±20</td>
<td>600±100</td>
<td>700±100</td>
<td>1400±200</td>
<td>2100±400</td>
<td>3700±600</td>
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<td>F$_{\text{wt.%}}$</td>
<td>2.54</td>
<td>2.47</td>
<td>2.87</td>
<td>2.48</td>
<td>2.73</td>
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<tr>
<td>Cl$_{\text{wt.%}}$</td>
<td>1.07</td>
<td>1.16</td>
<td>0.173</td>
<td>0.466</td>
<td>0.033</td>
<td>0.212</td>
</tr>
</tbody>
</table>

Is this lunar water?
Analytical artifacts?

Silicates adjacent to the apatite grains in the epoxy mounted lunar samples were analyzed, and the 3 ppm H$_2$O detection limit was verified.

Epoxy was measured for each sample to obtain a C/OH ratio, and epoxy could only account for <5% of the OH measured in apatite.
Apollo samples were carefully collected and stored, and there is minimal chance of contamination.

Hot desert meteorites do experience terrestrial contamination, however the Fe-rich Fe-Ni metal grains are pristine, which would not be the case if sufficient alteration occurred to hydrate the apatite.
Alteration on the Moon?

14053, Apollo 14 sample  
Yes

15404, Apollo 15 sample  
Minimal, apatite OK

NWA 2977, desert meteorite  
Minimal, apatite OK

The apatite in 15404 were not texturally associated with the impact melt lithology.

NWA 2977 is shocked, but this process is not known to affect apatite chemistry in martian meteorites.

14053,16 is from the portion of the rock that experienced an impact induced reduction process in which H is converted into H$_2$O (Taylor, 2004), and this process has been shown to affect the REE’s in the apatite.
Magmatic water contents at the time of apatite crystallization

Apatite/Basalt partition coefficients

\[ D_x^{\text{apat/Basalt}} \]

\[ D_F^{\text{apat/melt}} = 3.4 \]
\[ D_{\text{Cl}}^{\text{apat/melt}} = 0.8 \]
\[ D_{\text{H}_2\text{O}}^{\text{apat/melt}} = 0.25^* \]

Mathez & Webster 2005

* Calculated based on data in M & W 2005

What does this imply about the parental magmatic water contents?
Assuming apatite enters after about 99% crystallization and...

- Magmatic degassing has not affected the water content
- Water was not added after separation from the source region

15404 parent melt 2-28 ppm H₂O

NWA 2977 parent melt 70-170 ppm H₂O

Can we use this to determine water contents in the magmatic source regions?
Although much higher than previous estimates of water in the lunar interior, these values are orders of magnitude drier than magmatic source regions on Earth and Mars.
Concluding Remarks on lunar water

Apatites from lunar rocks do contain OH, therefore, at least some of the missing structural component detected by EPMA consists of OH.

Water contents of lunar apatite from the samples we investigated range from ~100 ppm to ~3700 ppm.

Lunar magmas from which the apatite crystallized had some amount of dissolved water (potentially greater than the amount of water in the apatite by about a factor of 4).

Magmatic source region water contents are bracketed by apatite from 10’s of ppb, and possibly as high as about 17 ppm. These values are consistent with the last 40 years of lunar sample observations.

http://www.pnas.org/content/early/recent