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

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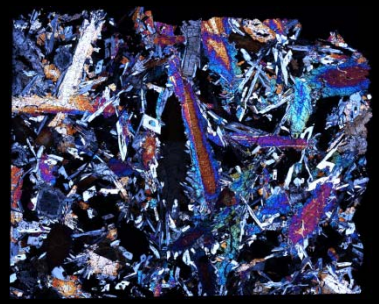
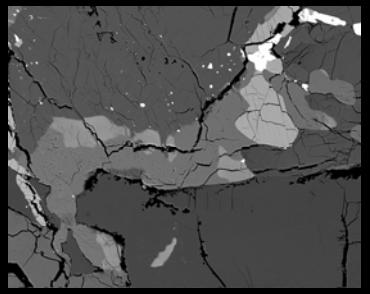
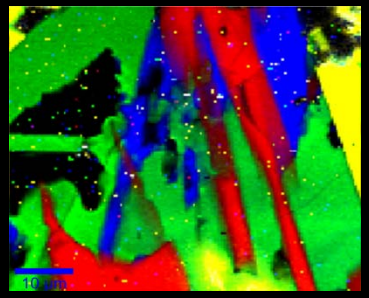
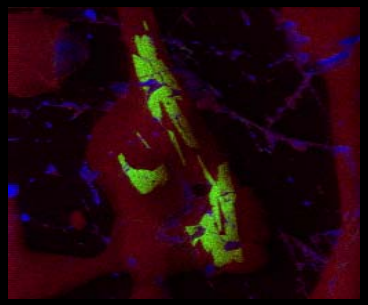
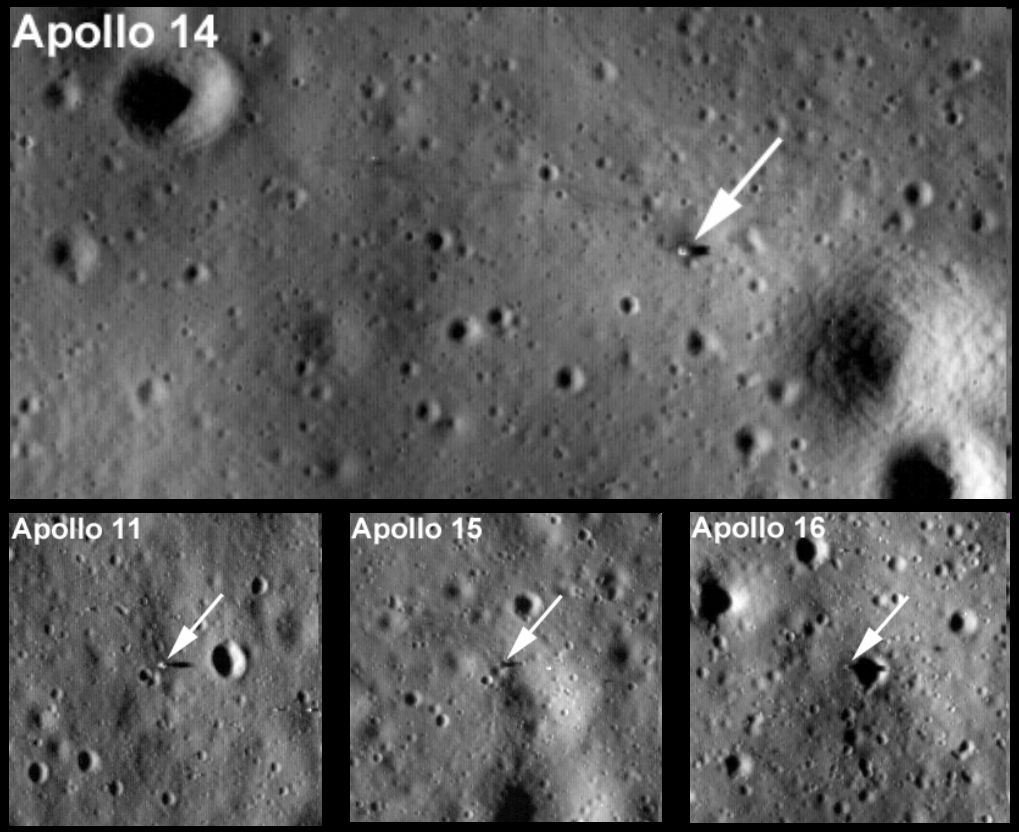








Post Apollo view of lunar water



http://www.nasa.gov/mission_pages/LRO/multimedia/lroimages/apollosites.html

No hydrous minerals

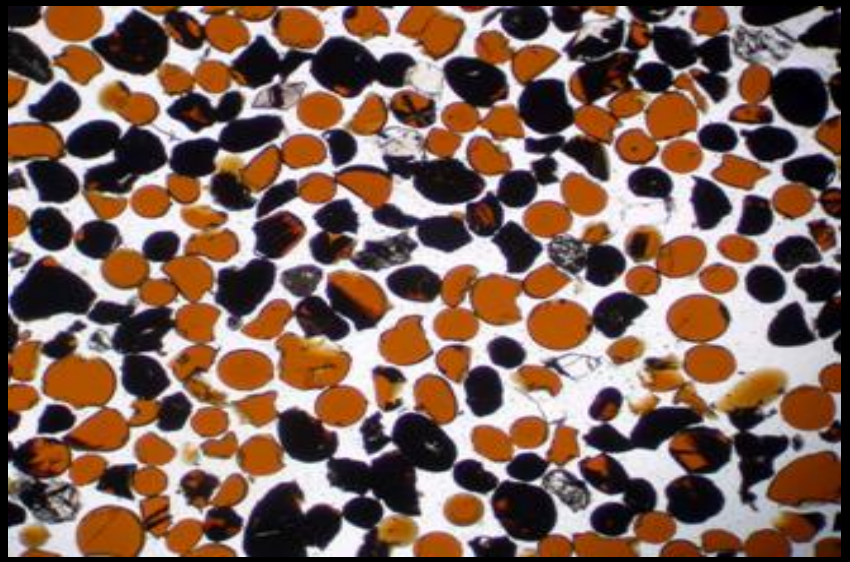
No evidence of aqueous alteration textures

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

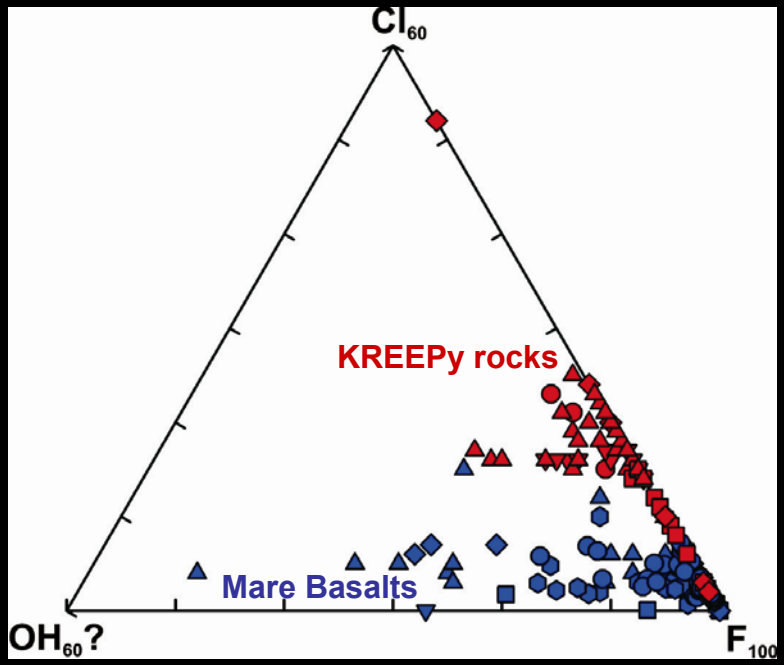
Water was not detected with the best analytical techniques of the day

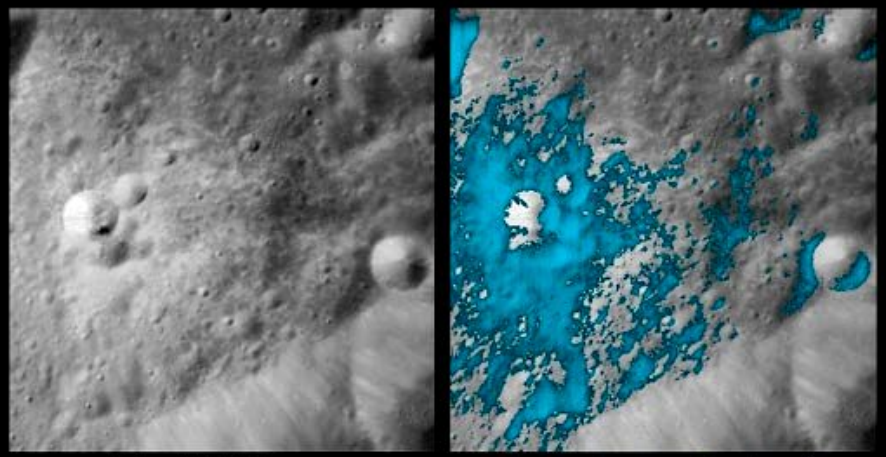
Resulting conclusion: The Moon is "Bone Dry"

Water in and on the Moon



http://www.geol.umd.edu/pages/faculty/WALKER/walker_homepage/meteorites.html





http://www.chandrayaan-i.com/images/chandrayaan-nasa-moon-water.jpg

Up to 46 ppm H_2O in lunar glasses

Saal et al. 2008

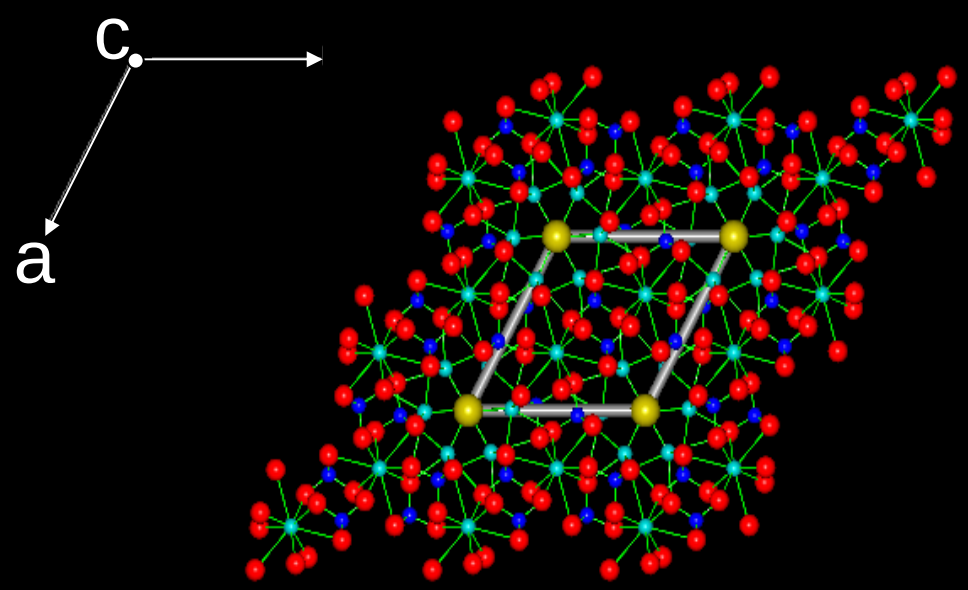
Hydration/hydroxylation process occurs on lunar surface

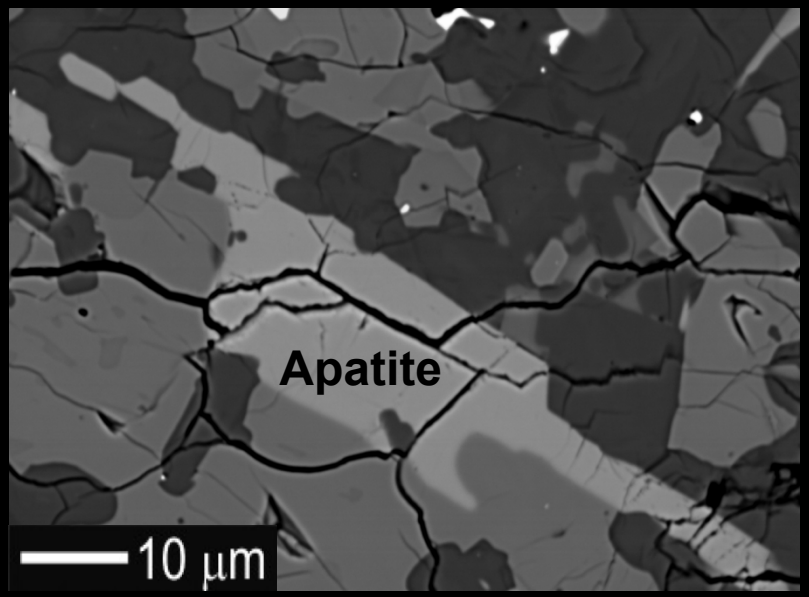
Chandrayaan-1, 2009

Missing structural component in apatite X-site

McCubbin et al. 2008

Apatite

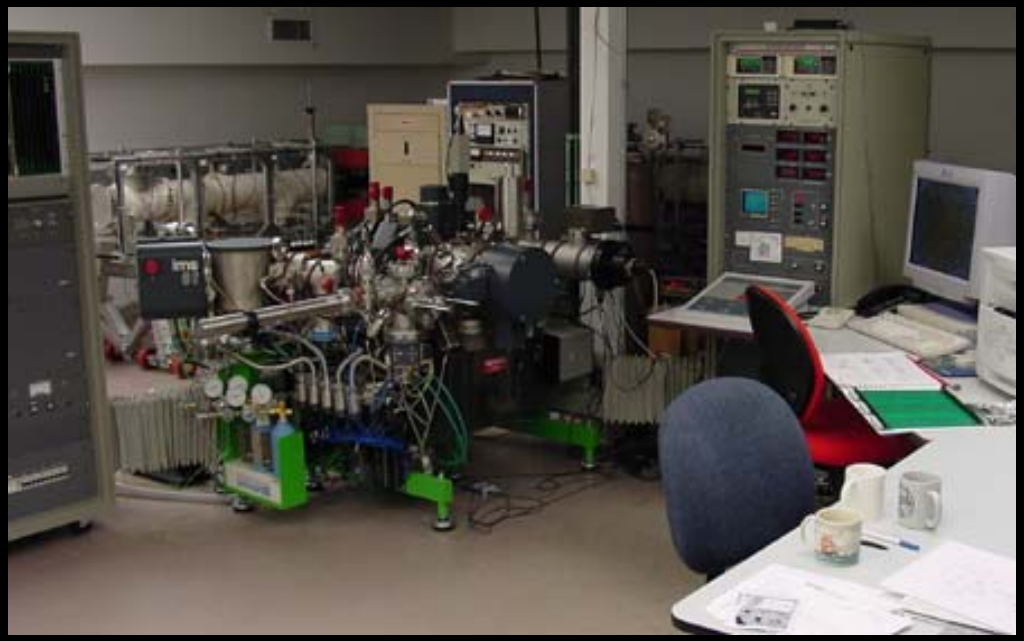




- $(OH)^-$, Br^-, I^-, $(CO_3)^{2-}$, O^{2-}, and S^{2-} can substitute for F and Cl in apatite
- Terrestrial apatites primarily consist of F, Cl, and OH
- Carbonate is more common in apatite from sedimentary rocks or carbonatites

Is there OH in lunar apatite?

Analysis of lunar apatite by SIMS



Other standards

Synthetic Forsterite
(0.000 wt.% H_2O)

Basaltic Glass
(2.43 wt.% H_2O)

2 heterogeneous apatites
(??? wt.% H_2O)

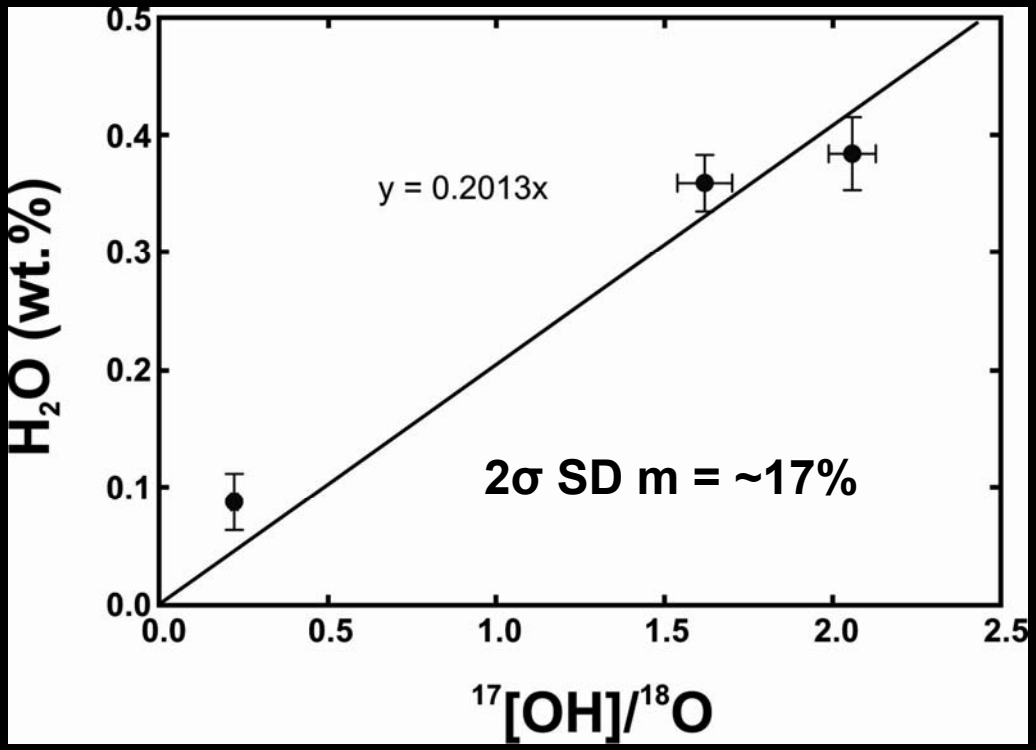
Apatite standards

Durango, Mexico
(0.088 wt.% H_2O)

Crystal lode pegmatite, CO
(0.359 wt.% H_2O)

Unknown, Morocco
(0.384 wt.% H_2O)

Analysis of lunar apatite by SIMS



Regression line forced through origin because synthetic forsterite (blank) yielded 3 ppm H_2O

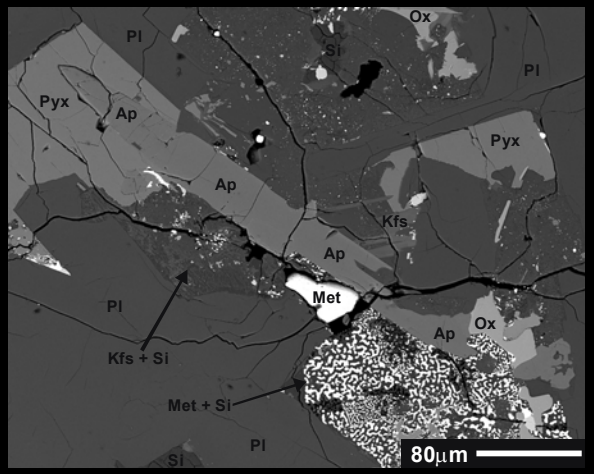
Apatite standards

Durango, Mexico
(0.088 wt.% H_2O)

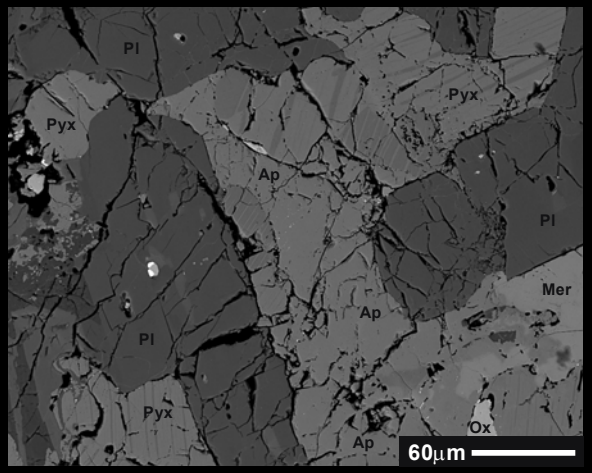
Crystal lode pegmatite, CO
(0.359 wt.% H_2O)

Unknown, Morocco
(0.384 wt.% H_2O)

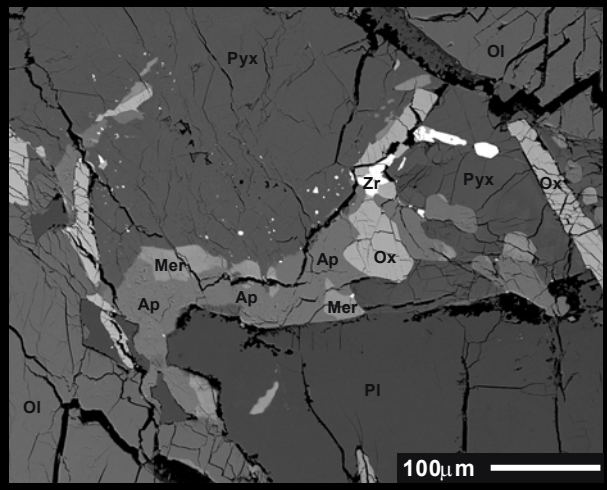
Choices of Samples to Analyze



14053 Apollo 14 sample



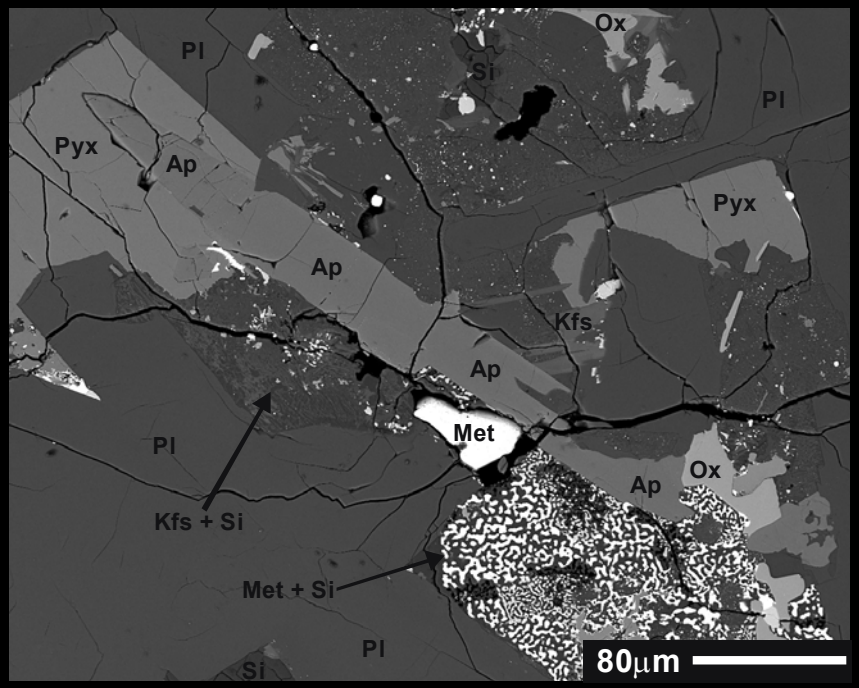
15404 Apollo 15 sample



NWA 2977

- 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

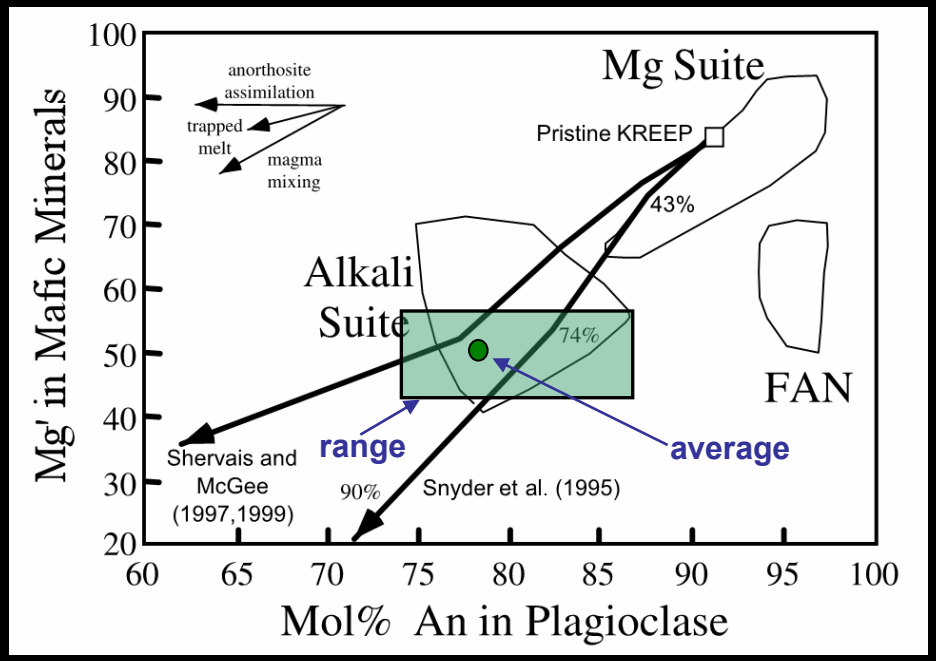
High Al-basalt 14053



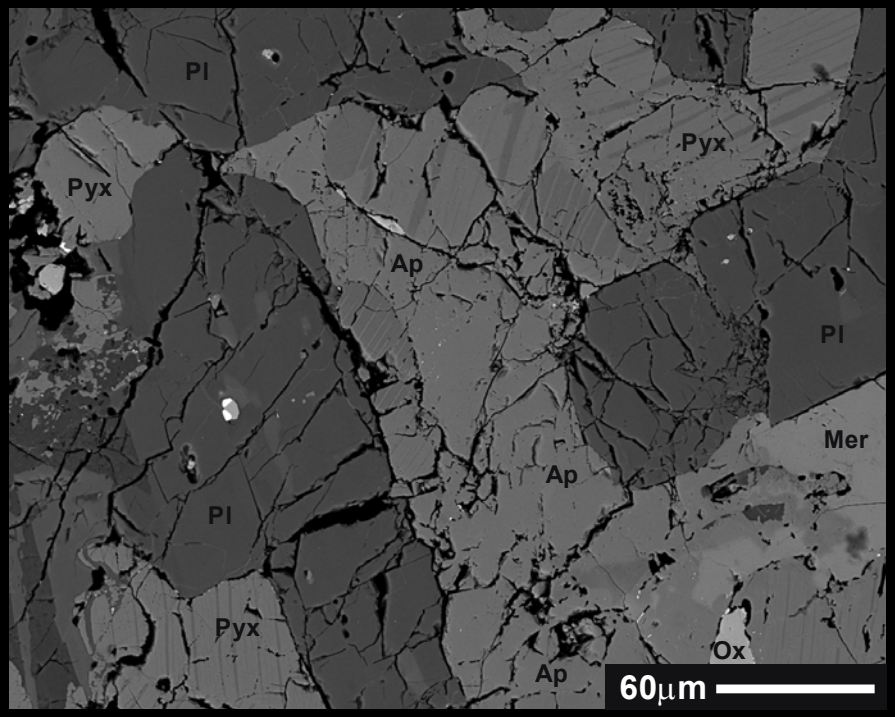
- High-Al basalt consisting primarily of pyroxene and plagioclase with minor phases include fayalitic olivine, fluorapatite, baddeleyite, K-feldspar, Fe-Ti oxides, Fe-metal, silica, troilite, and K-Ba-rich glass

- Apatites are typically subhedral to anhedral, and they range in size from ~2 μm to larger than 200 μm.

Clast in impact melt 15404

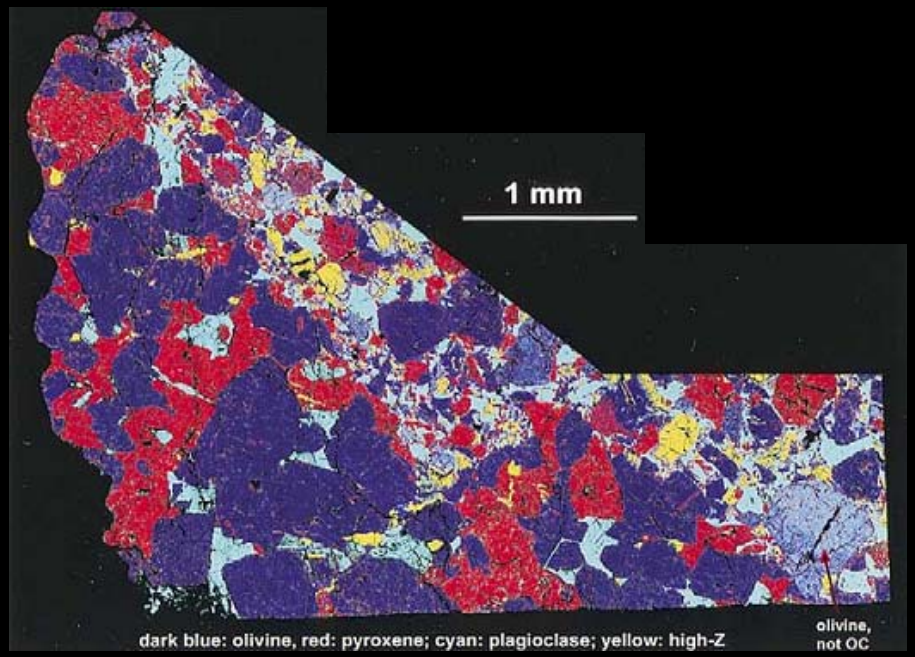


Shearer and Papike 2005

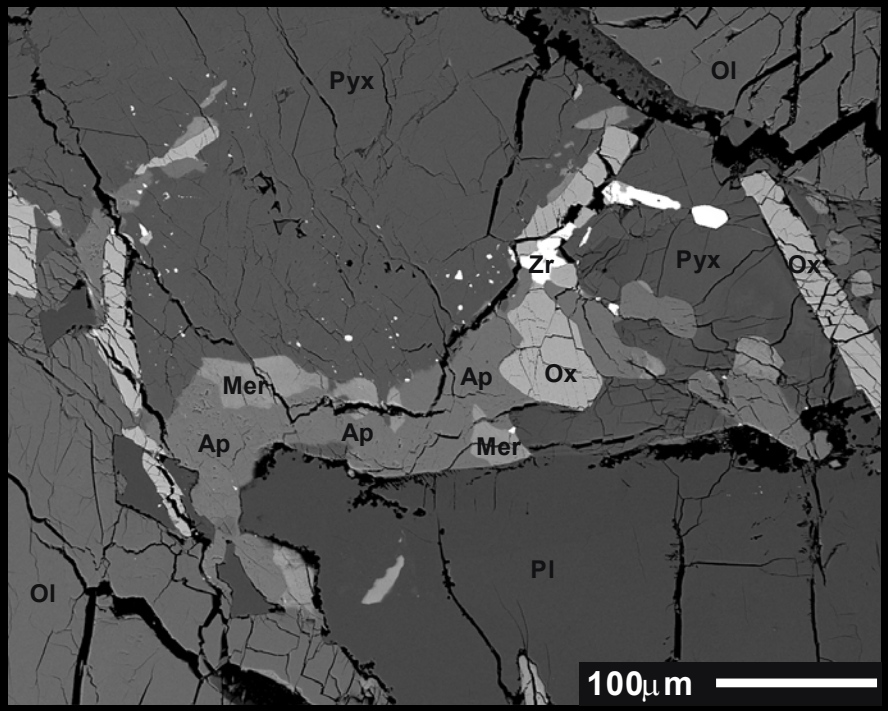


- Apollo sample 15404 is a soil grain from the 4-10 mm sieve fraction, and it consists of an impact melt breccia with a lithic clast
- The lithic clast primarily contains pyroxene and plagioclase with a significant amount of K-rich feldspar and minor silica, fluorapatite, merrillite, Cr-rich spinel, and Fe-Ti oxides
- Apatites are typically anhedral, and they range in size from ~10 μm to ~100 μm.

VLT-basalt NWA 2977

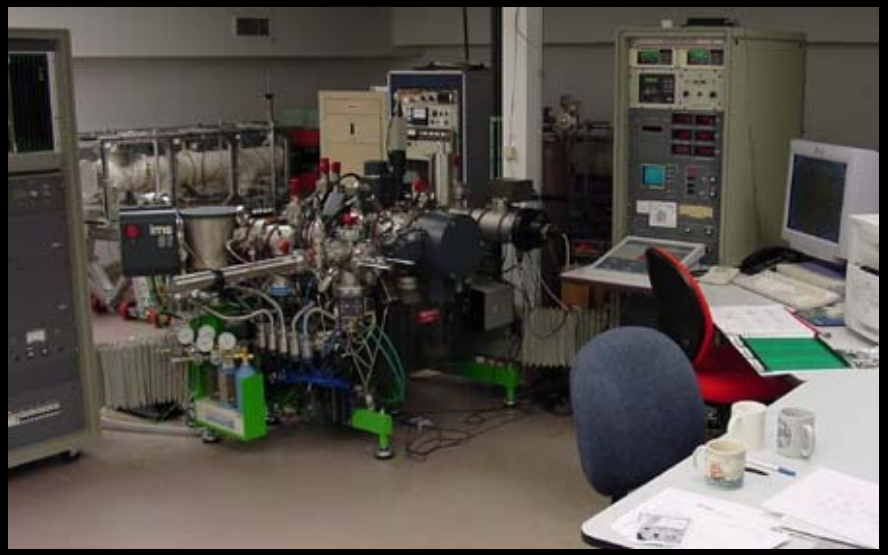


NWA 773 Jolliff et al. 2003



- 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.

Water Analysis by SIMS at DTM



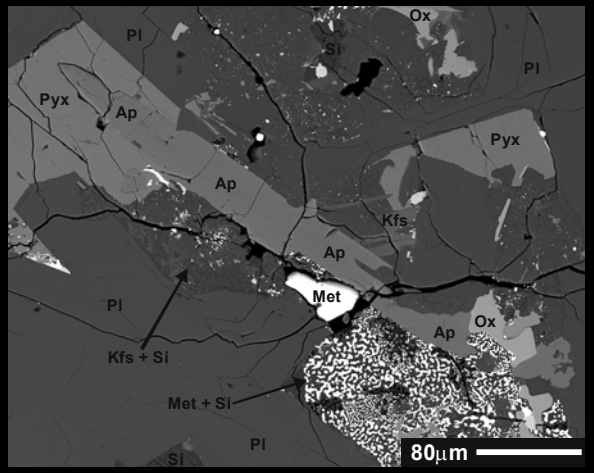
http://www.dtm.ciw.edu/content/view/86/93/

We analyzed multiple apatite Grains from each sample

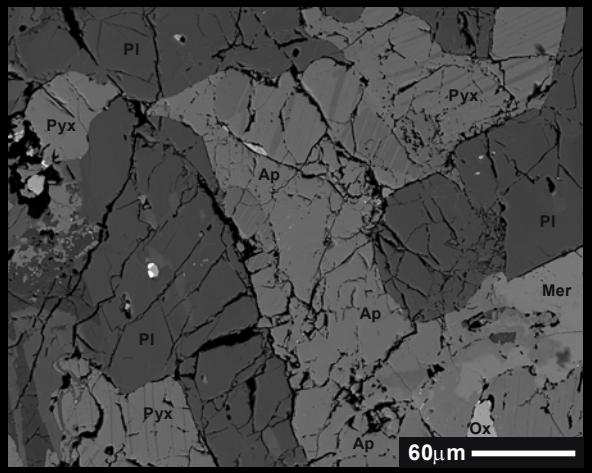
	15404_{min}	15404_{max}	14053_{min}	14053_{max}	$NWA2977_{min}$	$NWA2977_{max}$
H_2O_{ppm}	120±20	600±100	700±100	1400±200	2100±400	3700±600
$F_{wt.\%}$	2.54	2.47	2.87	2.48	2.73	2.70
$Cl_{wt.\%}$	1.07	1.16	0.173	0.466	0.033	0.212

→ **Is this lunar water?**

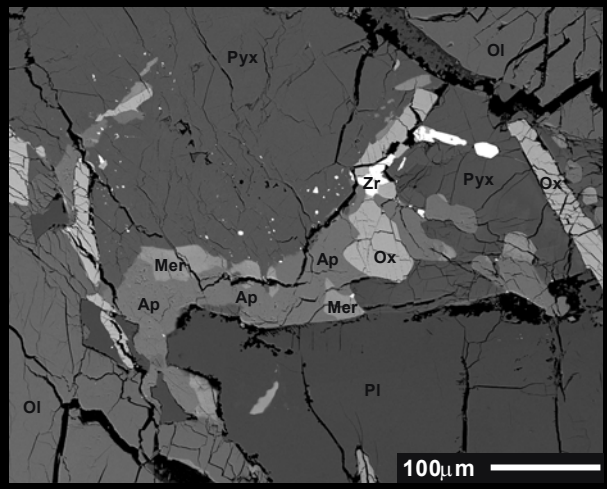
Analytical artifacts?



14053 Apollo 14 sample
No



15404 Apollo 15 sample
No

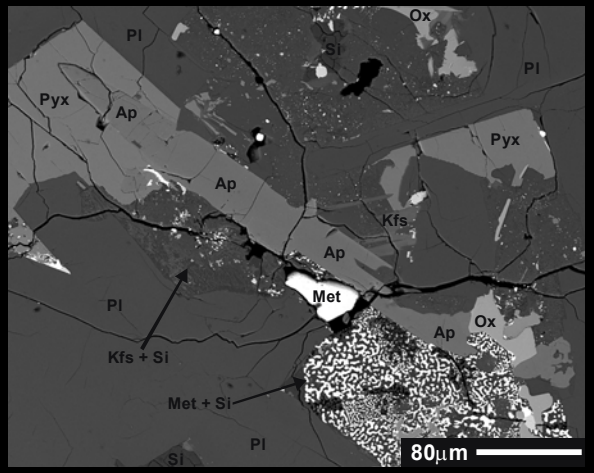


NWA 2977 desert meteorite
No

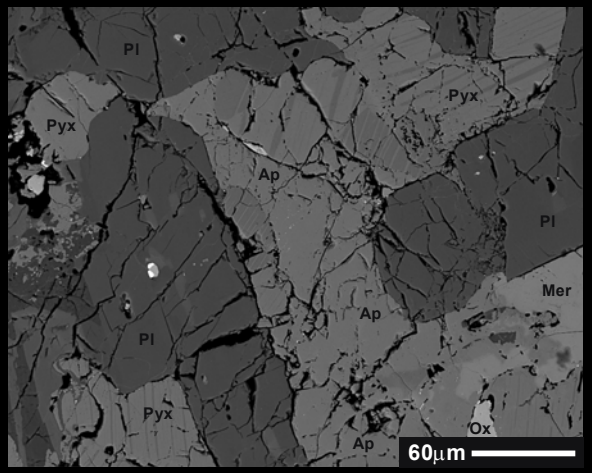
Silicates adjacent to the apatite grains in the epoxy mounted lunar samples were analyzed, and the 3 ppm H_2O detection limit was verified

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.

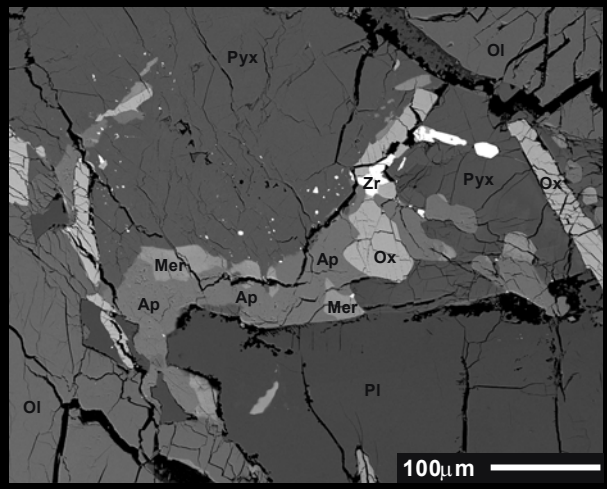
Terrestrial contamination?



14053 Apollo 14 sample
No



15404 Apollo 15 sample
No

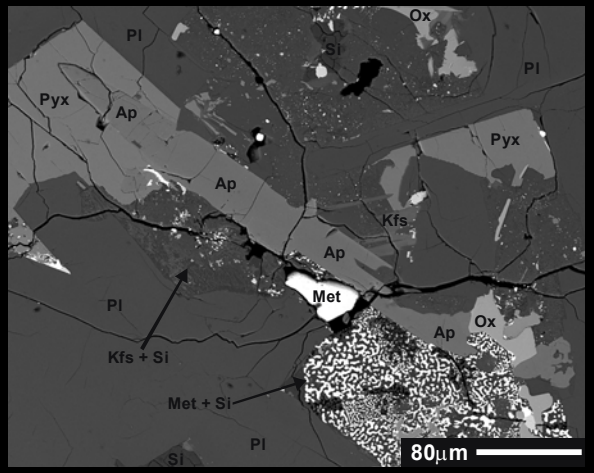


NWA 2977 desert meteorite
Minimal, apatite OK

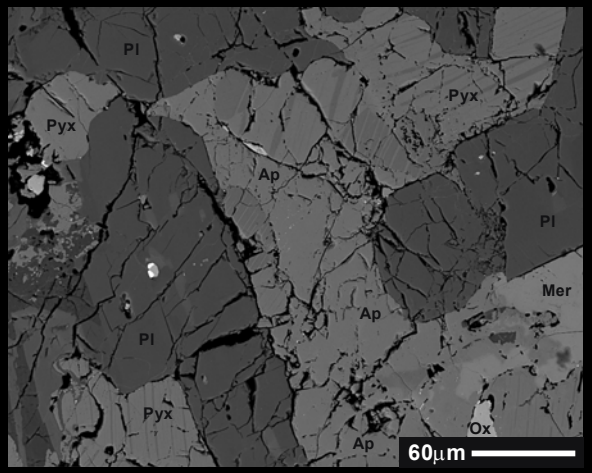
Apollo samples were carefully collected and stored, and there is minimal chance of contamination

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

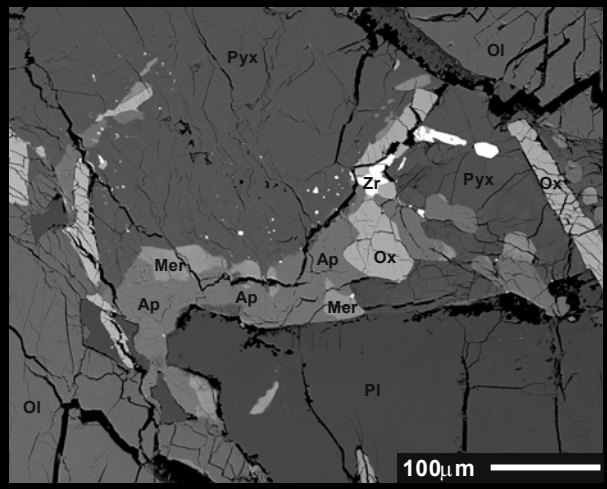
Alteration on the Moon?



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_2O (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

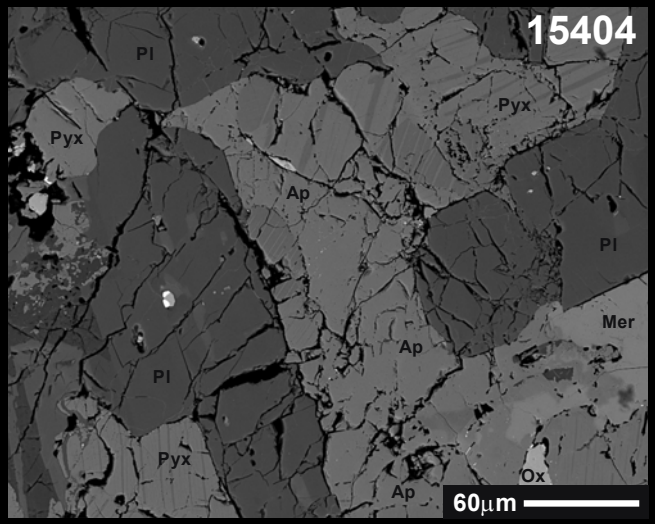
Apatite/Basalt partition coefficients

$D_x^{apat/Basalt}$

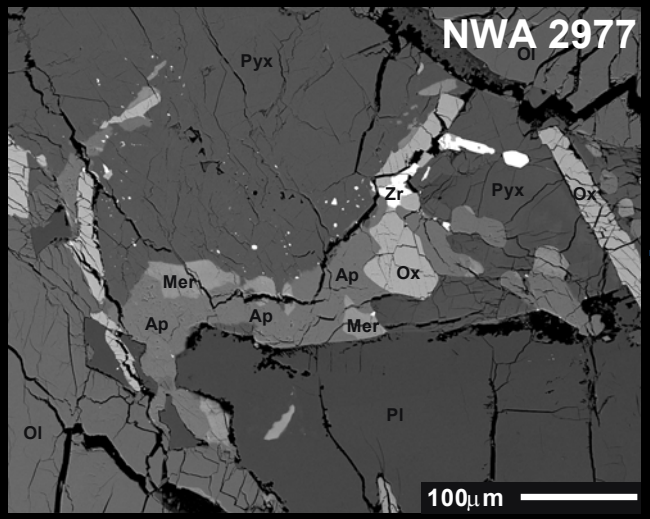
$D_F^{apat/melt}$	3.4
$D_{Cl}^{apat/melt}$	0.8
$D_{H_2O}^{apat/melt}$	0.25*

Mathez & Webster 2005

*** Calculated based on data in M & W 2005**

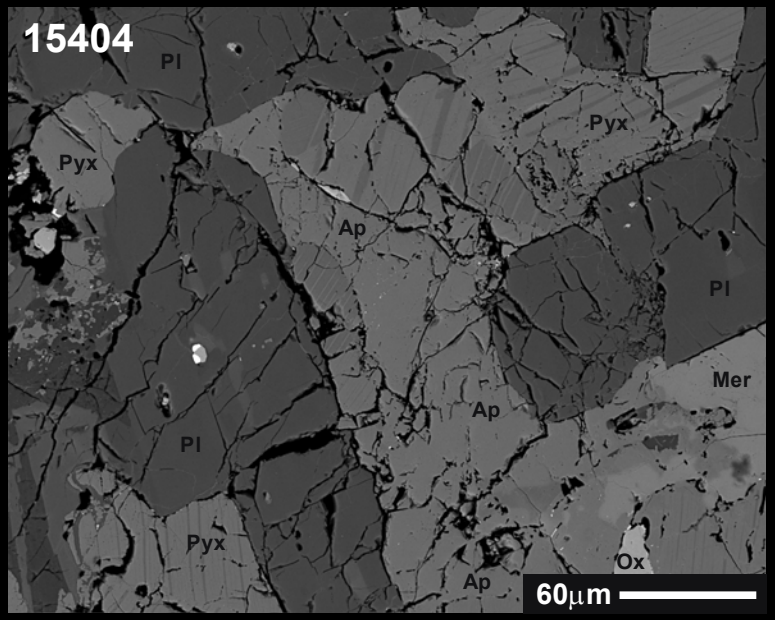


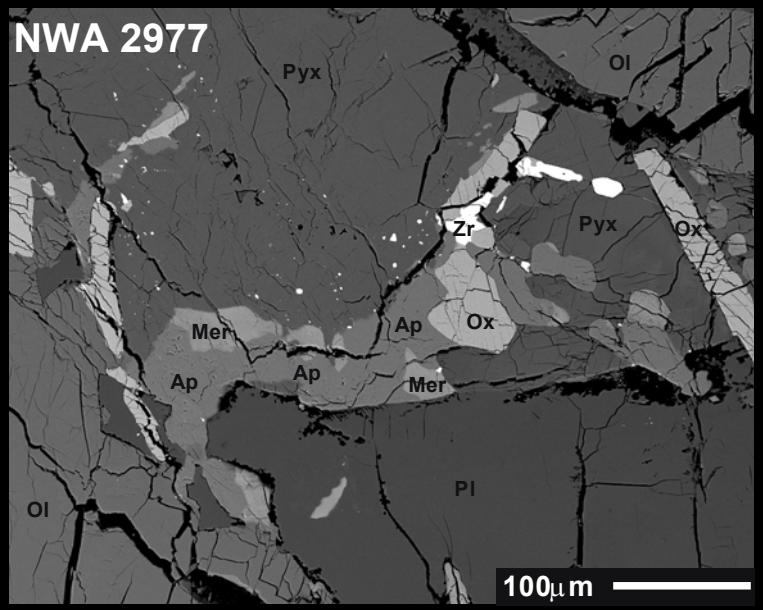
200-2800 ppm H_2O



7000-17000 ppm H_2O

What does this imply about the parental magmatic water contents?





Assuming apatite enters after about 99% crystallization and…

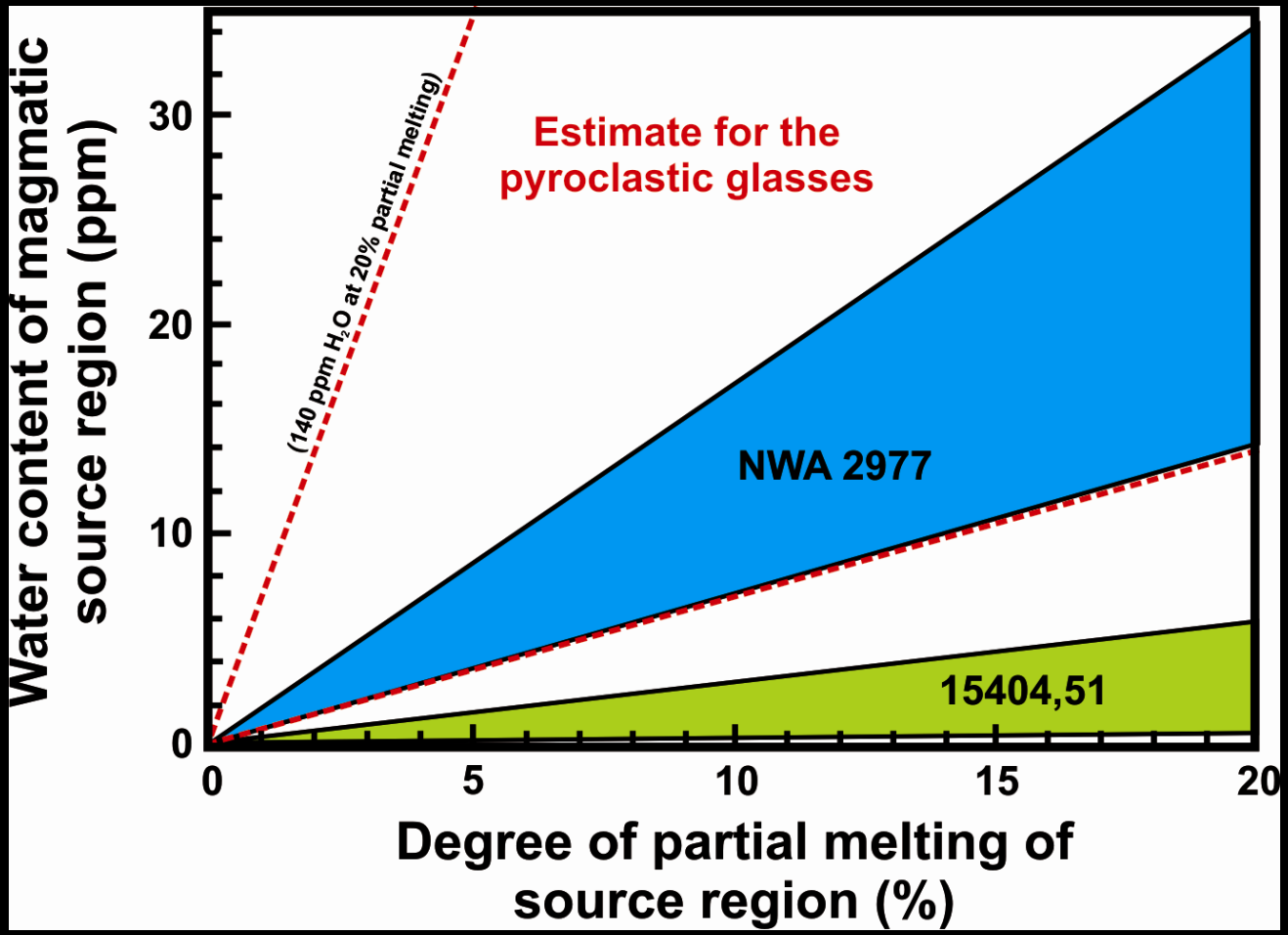
- Magmatic degassing has not affected the water content
- Water was not added after separation from the source region

15404 parent melt 2-28 ppm H_2O

NWA 2977 parent melt 70-170 ppm H_2O

- Can we use this to determine water contents in the magmatic source regions?

Water contents in the magmatic source regions



Pyroclastic Glass
2 ppm – 70 ppm H_2O

NWA2977 source
2 ppm – 17 ppm H_2O

15404 source
64 ppb – 3 ppm H_2O

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