A Quick Lunar Material-Mineral Primer for Oxygen Extraction

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Lunar Chemistry and Mineralogy – A Quick Primer

(from The Lunar Sourcebook)

Major rock-forming chemical elements - the Big 8

Oxygen (∼60% of atoms)
Silicon (∼16-17%)
Aluminum (∼10%, highlands, ∼4.5%, mare)
Calcium (∼5%)
Magnesium (∼5%)
Iron (∼2.5%, highlands, ∼6%, mare)
Titanium + Sodium (∼1%)

OR

Oxygen (∼45 wt%)
Silicon (∼21 wt%)
Aluminum (∼13 wt%, highlands, ∼5 wt%, mare)
Calcium (∼10 wt%, highlands, ∼8 wt%, mare)
Iron (∼6 wt%, highlands, ∼15%, mare)
Magnesium (∼5.5 wt%)
Titanium (< 1 wt%, highlands, ∼1-5 wt%, mare)
Sodium (< 1 wt%)

PLUS

Many, many more minor and trace elements to act as irritants to ISRU systems (i.e, sulfur)

Chemical Elements → Minerals → Rocks

Silicate minerals make up over 90% of the Moon - the Big 3

Pyroxene, $(Ca, Fe, Mg)_2Si_2O_6$
Plagioclase Feldspar, $(Ca, Na)(Al, Si)_4O_8$
Olivine, $(Mg, Fe)_2SiO_4$

Oxide minerals are 'next' most abundant (particularly concentrated in mare)

Ilmenite, $(Fe, Mg)TiO_3$
Spinel
- Chromite, $FeCr_2O_4$
- Ulvöspinel, Fe_2TiO_4
- Hercynite, $FeAl_2O_4$
- Spinel, $MgAl_2O_4$

Armalcolite $(Fe, Mg)Ti_2O_5$ (only in Ti-rich mare)

Other minor minerals of note

Native iron, (Fe)
Troilite, FeS (holds most of the sulfur in lunar rocks)

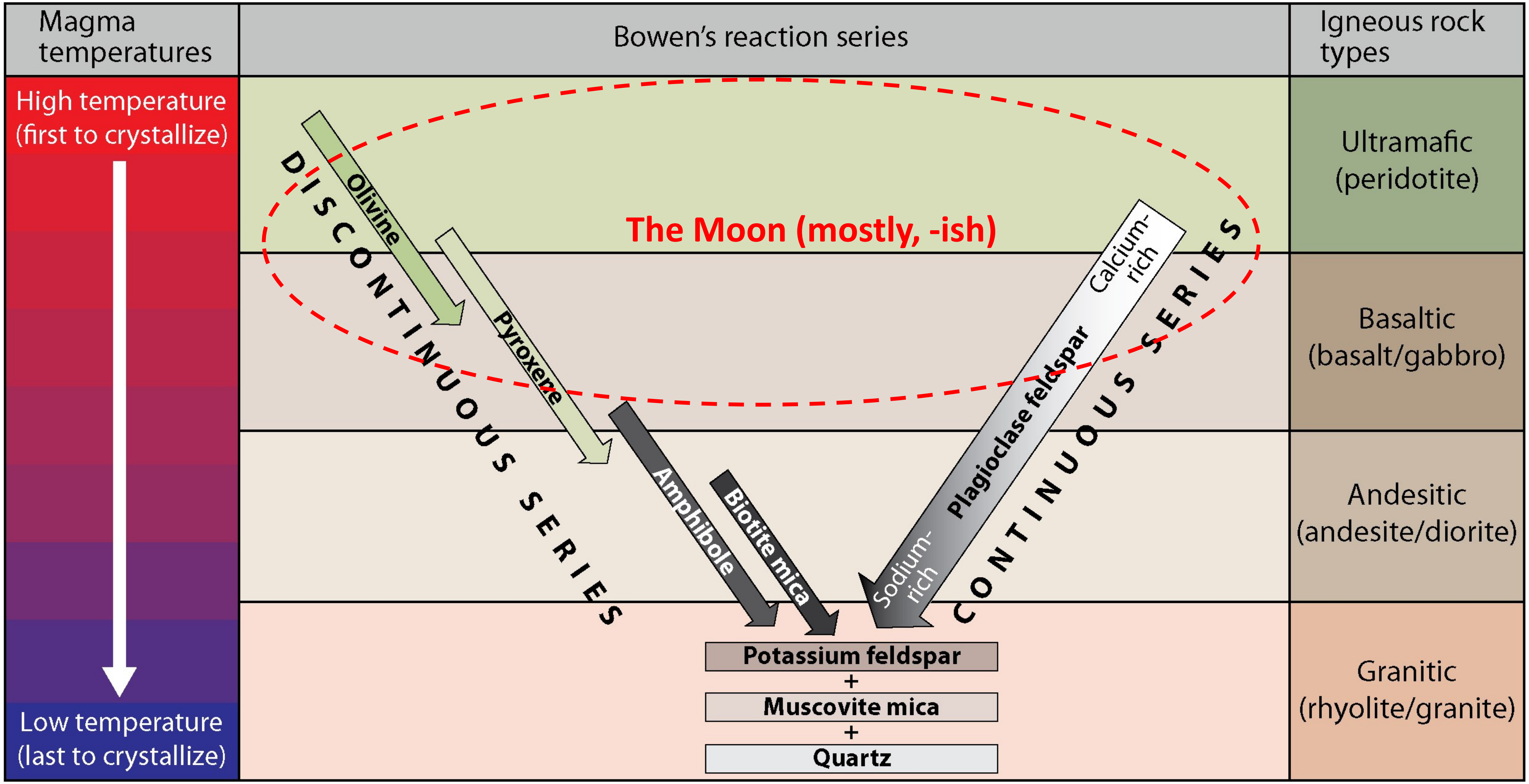
PLUS

Many, many more trace minerals [i.e., apatite, $Ca_5(PO_4)_3(OH, F, Cl)$]

Bowen’s Reaction series

(from www.nps.gov, photo gallery, National Park Service)

Chemical Elements → Minerals → Rocks



Basalt: The most common rock in the inner solar system (the dark areas on the Moon)

(from NASA RELAB Facility at Brown University)

<u>Primary Elements</u>
O, Si, Ca, Al, Mg, Fe

<u>Primary Minerals</u>
Plagioclase Feldspar
Pyroxene
Olivine

<u>Rock Type</u>
Basalt

Bulk chemistry (oxides wt %)	Low-Ti basalt (15071)-52	Medium-Ti basalt (12030)-14	High-Ti basalt (71501)-35
SiO_2	46.07	46.25	31.87
TiO_2	1.89	3.32	9.52
$Al2O_3$	13.87	11.70	11.83
$Cr2O_3$	0.44	0.43	0.43
MgO	10.88	9.42	9.49
CaO	10.52	9.78	10.36
MnO	0.19	0.20	0.22
FeO	13.87	16.27	16.05
Na_2O	0.40	0.46	0.38
K_2O	0.16	0.29	0.09
P_2O_5	0.15	0.25	0.06
SO_2	0.11	0.12	0.19

Source: RELAB

How a geochemist describes basalt

Modal abundance of minerals (wt %)	Low-Ti basalt (15071)-52	Medium-Ti basalt (12030)-14	High-Ti basalt (71501)-35
Ilmenite	1.63	2.93	9.86
Plagioclase	19.10	15.76	18.76
Pyroxene	16.56	23.50	14.60
Olivine	2.86	3.50	3.40
Agglutinitic glass	52.16	48.06	45.40
Volcanic glass	3.90	1.43	6.70
Others	3.76	4.80	1.30

Source: RELAB

How a mineralogist or petrologist describes basalt

This causes confusion!

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O, Si, Ca, Al, Mg, Fe

Primary Minerals
Plagioclase Feldspar
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Rock Type
Basalt

This is where the ISRU community needs to focus

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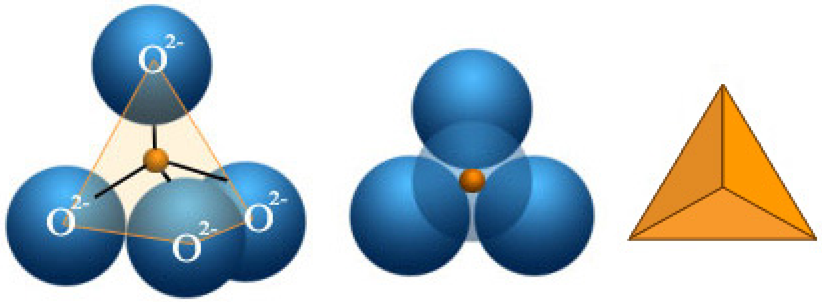
Silicate Minerals

(from Danna Shrewsbury, www.slideplayer.com)



Three ways of drawing the silica tetrahedron:

a) At left, a ball & stick model, showing the silicon cation in orange surrounded by 4 oxygen anions in blue

b) At center, a space filling model

c) At right, a geometric shorthand model. This is the model favoured by geologists because of their simplicity.

Since the common rock forming minerals are all silicates it is worthwhile showing how the silicon tetrahedron is formed. The smaller Si^{4+} cation fits almost perfectly in the middle of a tetrahedron formed of larger O^{2-} anions.

Silicates are network covalent solids that are very stable and have high melting points. Within silicate structures are metal cations – so ionic bonds are also found. The more ionic bonds in the structure, the more easily the mineral is broken down through chemical erosional processes.

There are 7 classes of silicate minerals

Nesosilicates – isolated single tetrahedra

Sorosilictaes – isolated double tetrahedra

Cyclosilictaes – rings of tetrahedra

Inosilicates – single or double chains of tetrahedra

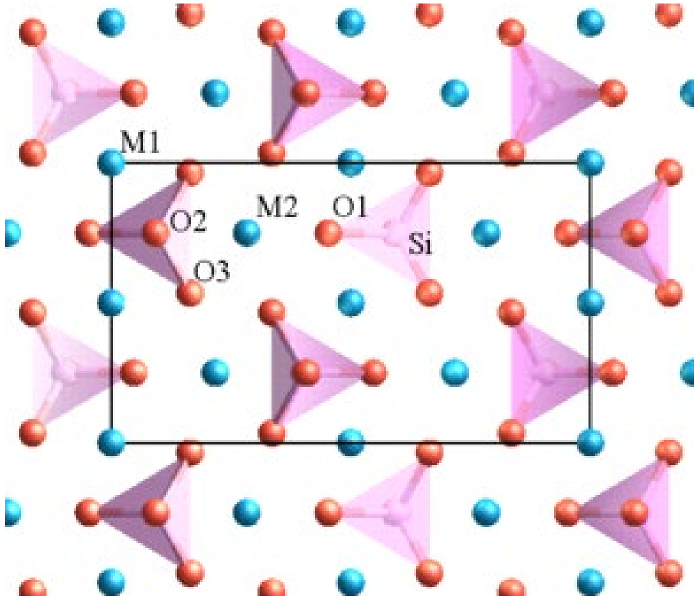
Phyllosilictates – sheets of tetrahedra

Tectosilicates – framework of tetrahedra

The three primary silicate minerals on the Moon

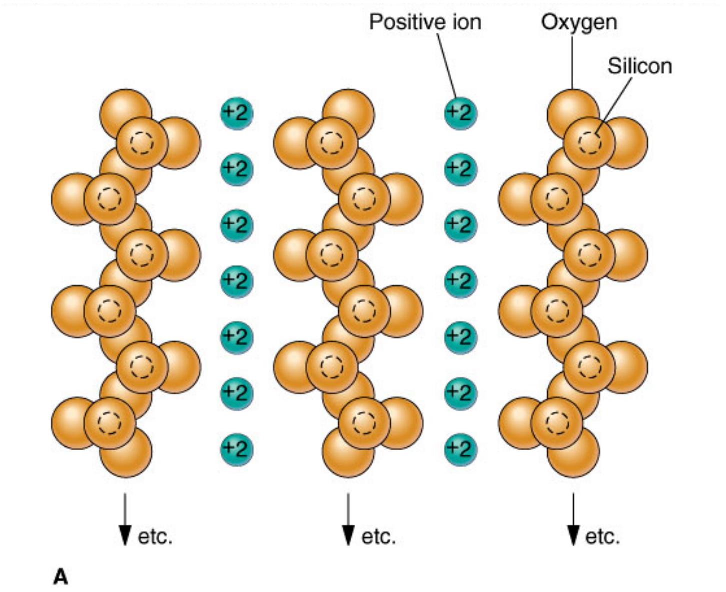
(from Danna Shrewsbury, www.slideplayer.com)

Olivine



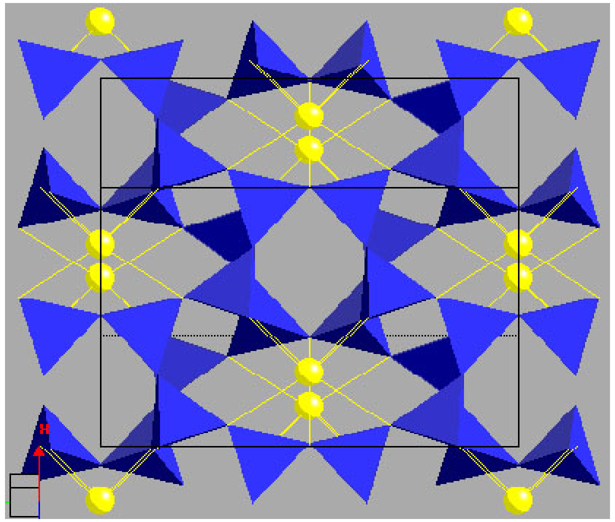
The diagram shows Olivine with isolated silica tetrahedra. As a result the Si:O ratio is 1:4. The blue dots represented by M1 and M2 are the locations of the 2+ cations. Olivines have the structural formula M_2SiO_4. Typically the M cations are Mg^{2+} and Fe^{2+}.

Pyroxene



The diagram shows Pyroxene with single chain silica tetrahedra. As a result the Si:O ratio is 1:3. The blue dots represent the locations of the 2+ cations. Pyroxenes have the structural formula M_2SiO_3. Typically the M cations are Ca^{2+}, Mg^{2+}, and Fe^{2+}.

Feldspar

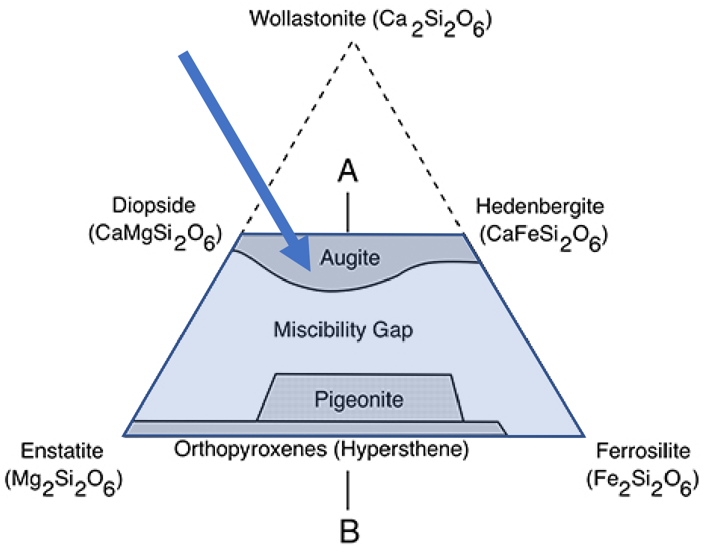


The diagram shows Feldspar as a framework silica tetrahedra. As a result the Si:O ratio is 3:8. The yellow dots represent the locations of the metal cations. Typically the cations are Ca^{2+}, K^{1+}, Na^{1+} and Al^{3+} on the earth. On the Moon, K, and Na rarely exist in the structure.

Pyroxene: A silicate mineral

Pyroxene – Augite $(Ca,Na)(Mg,Fe,Al)(Al,Si)_2O_6$

Note: Augite can have a wide range of chemical compositions



Pyroxene Quadrilateral, from:
http://www.alexstrekeisen.it/english/pluto/pyroxene.php

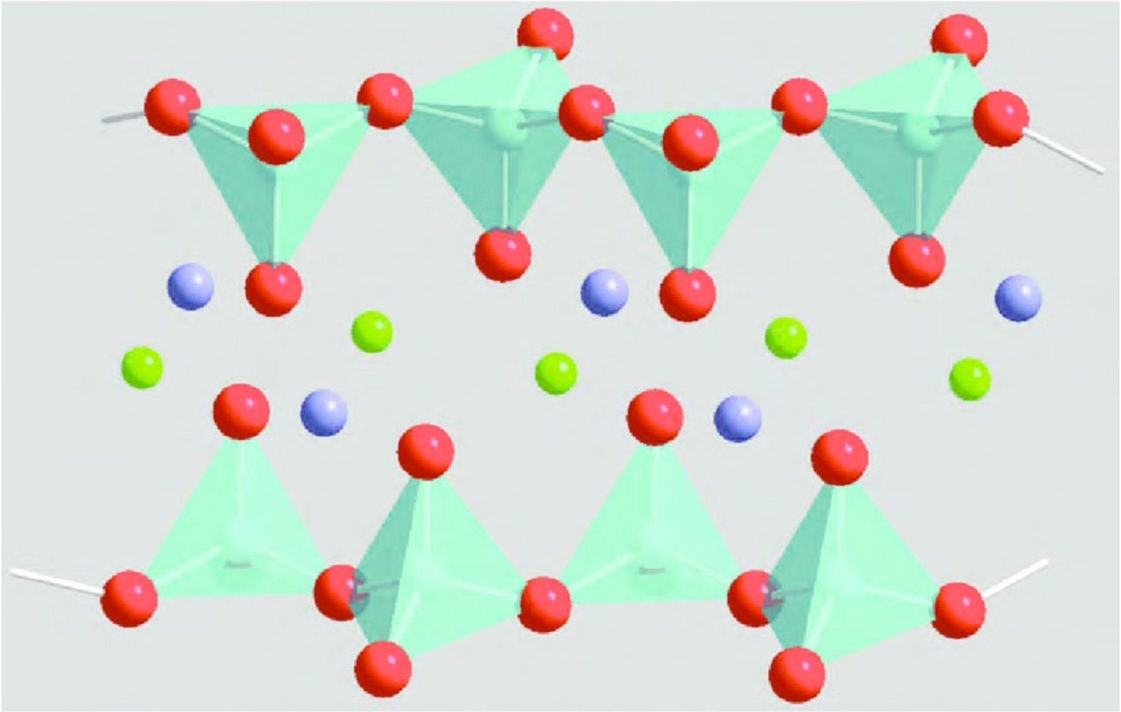


Figure 9. Section of the Augite crystal structure. The gaps within the parallel silicate chains are occupied by the metal ions calcium or iron (blue), magnesium or aluminium (green).

From: https://www.researchgate.net/figure/Abbildung-9-Ausschnitt-der-Kristallstruktur-des-Augits-In-die-Zwischenraeume-der_fig3_275580379

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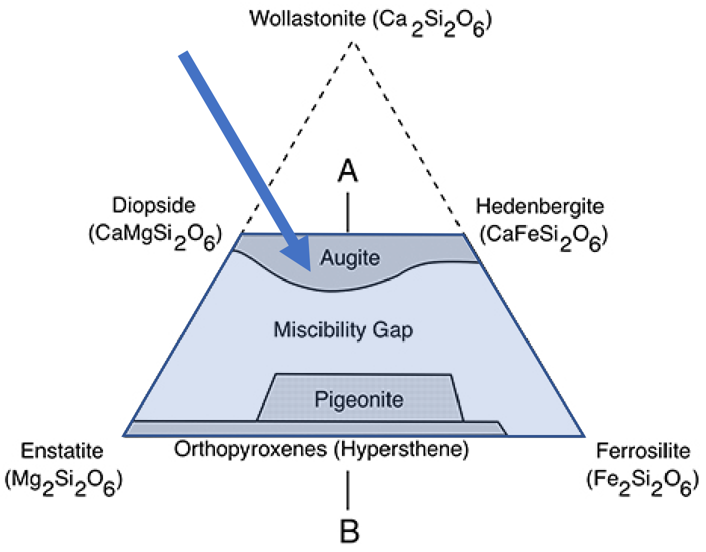

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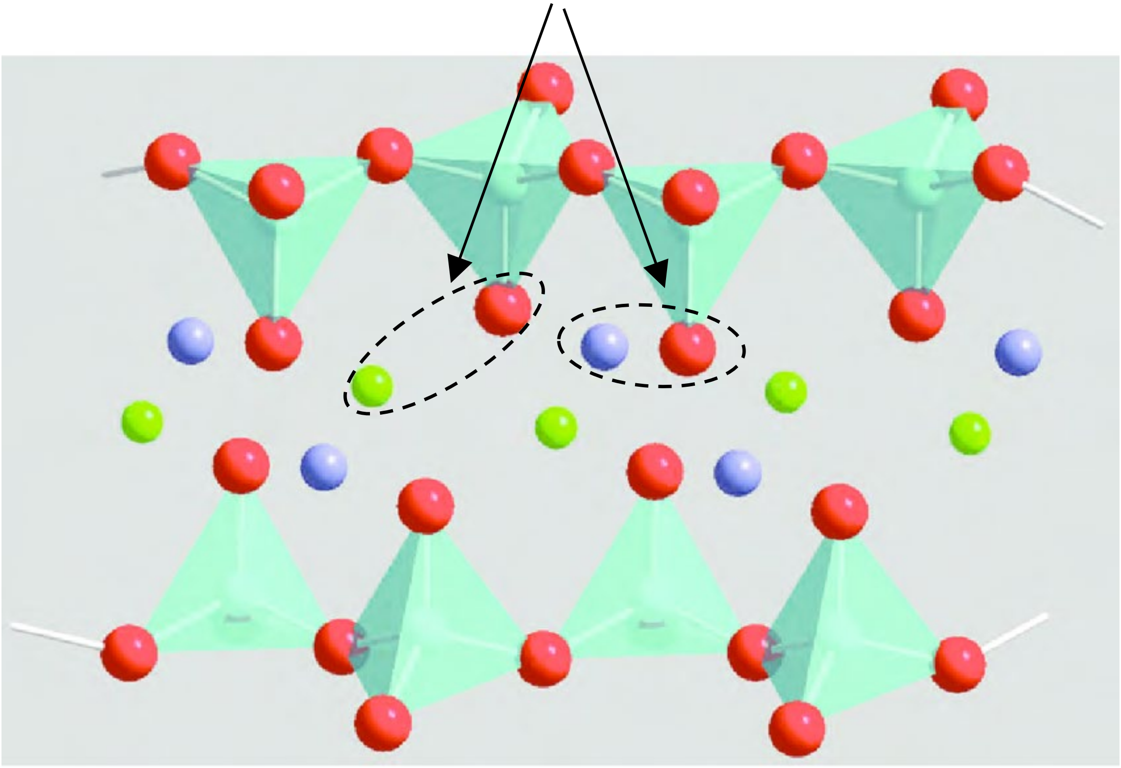
Even if you break these metal-oxygen bonds, the oxygen is <u>still</u> tightly bound in the silica tetrahedra



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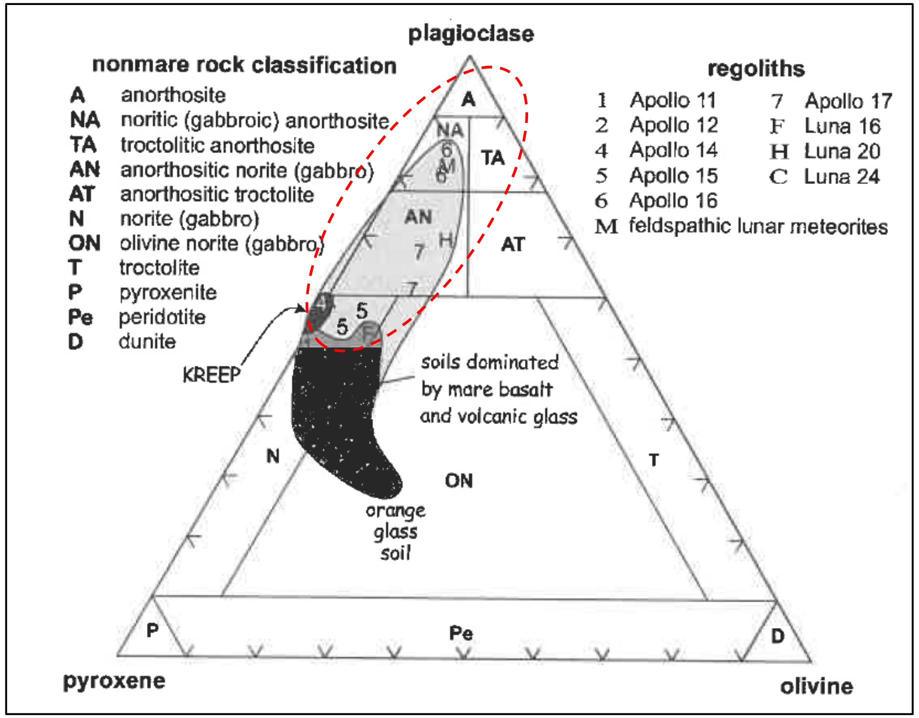
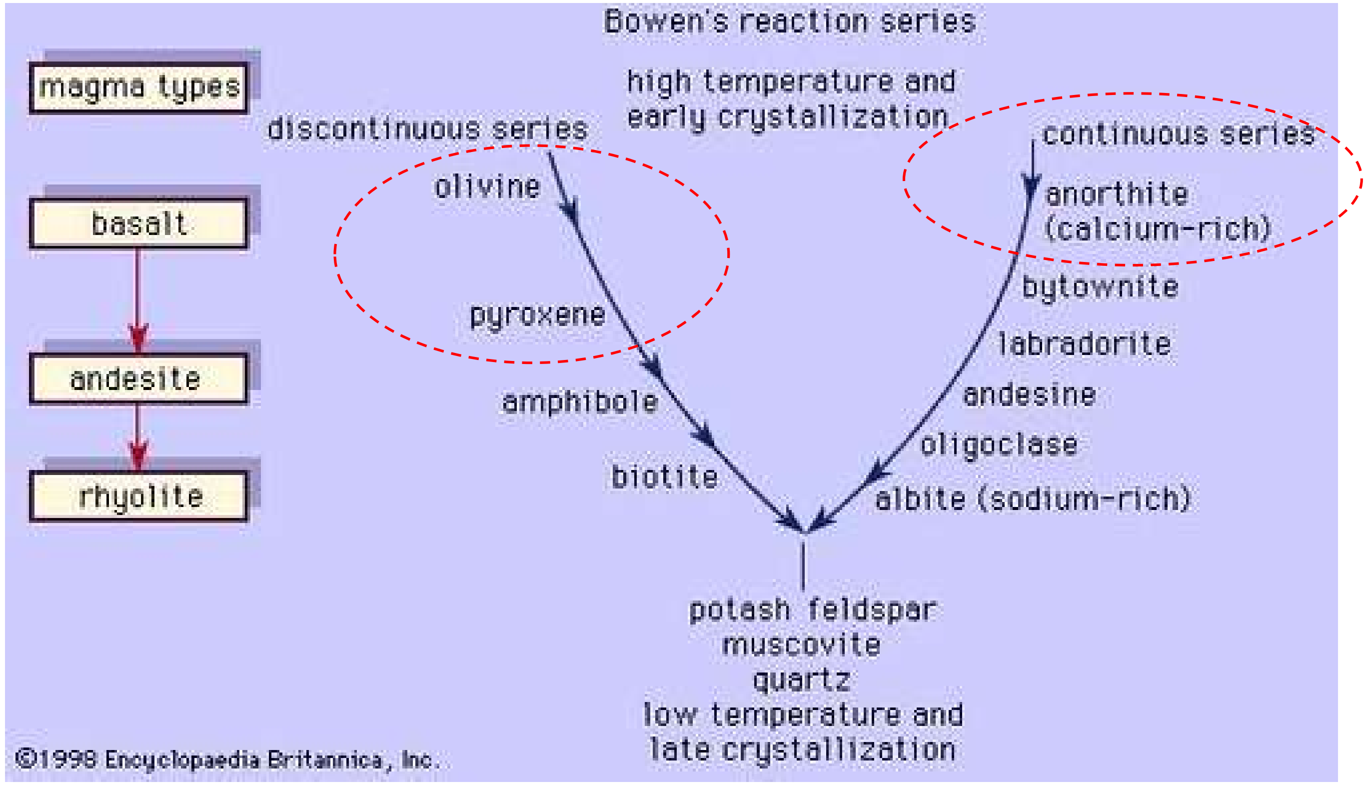
So, what can we expect at the Lunar Poles?



From New Views of the Moon



Primary Elements		Primary Minerals		Primary Rock Types
O, Si, Ca, Al, Mg, Fe	→	Anorthite (Ca-rich plag) Pyroxene Olivine	→	Anorthosite (plag) Norite (plag + pyx) Troctolite (plag + ol)

ISRU processes used at the lunar poles will have to be able to break apart the Si-O tetrahedra

(NOTE: NU-LHT simulant is basically a noritic anorthosite)

Hydrogen Reduction Process using Lunar Highlands Regolith results in <u>much</u> less than 1% O2 production

"The feldspathic lunar meteorites provide the best estimate of the composition of the surface of the Feldspathic Highlands Terrane." (Korotev et al., 2003)

Polar regoliths are FHT

A norm is essentially a set of 'idealized' mineral components that are calculated from a bulk chemical analysis of a rock. It does not include a glass component, which could incorporate the chemical elements as well.

Polar regoliths could contain up to 50% glass.

Using average chemistry of FHT from Korotev et al., and two different CIPW Norm calculators, . . .

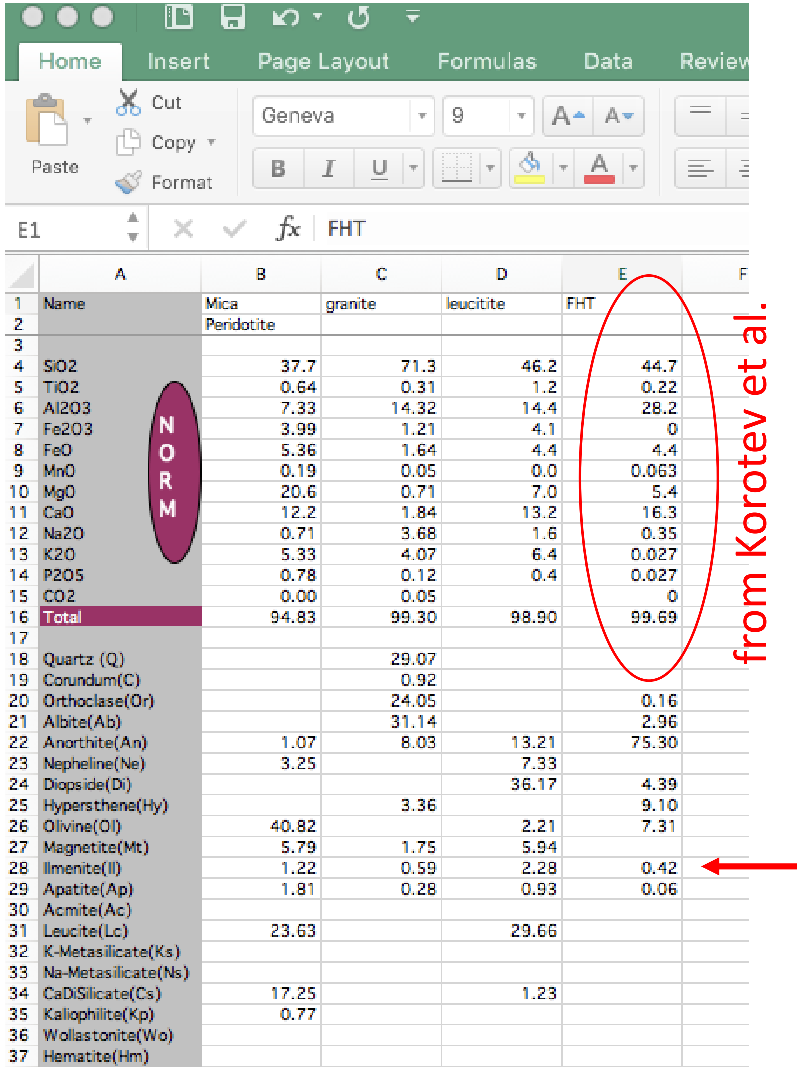
→ 'Best case' Ilmenite wt.% = 0.42

Average lunar ilmenite is $Fe_{0.8}Mg_{0.2}TiO_3$

Using the hydrogen reduction process on 1kg of FHT regolith will result in approximately 0.4 g of O_2, or 0.04 wt.% O_2

USGS: Volcano Hazards Program

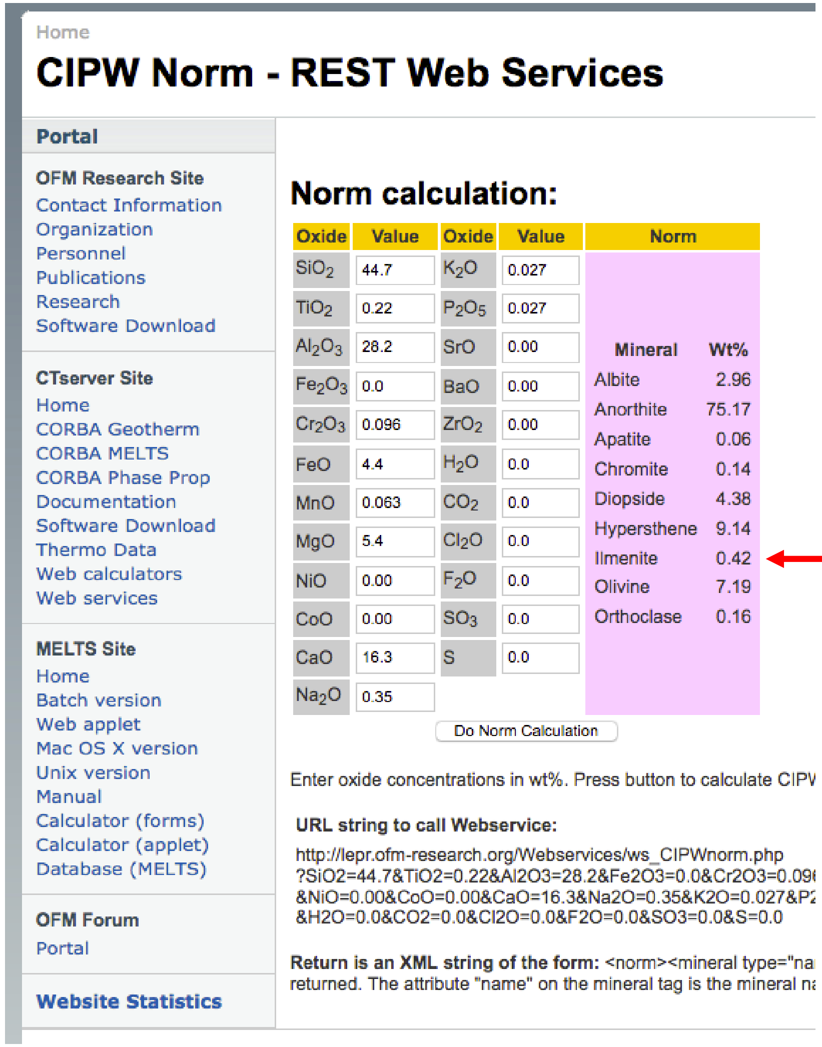
https://volcanoes.usgs.gov/observatories/yvo/jlowenstern/other/NormCalc_JBL.xls



	A	B	C	D	E
1	Name	Mica	granite	leucitite	FHT
2		Peridotite			
3					
4	SiO2	37.7	71.3	46.2	44.7
5	TiO2	0.64	0.31	1.2	0.22
6	Al2O3	7.33	14.32	14.4	28.2
7	Fe2O3	3.99	1.21	4.1	0
8	FeO	5.36	1.64	4.4	4.4
9	MnO	0.19	0.05	0.0	0.063
10	MgO	20.6	0.71	7.0	5.4
11	CaO	12.2	1.84	13.2	16.3
12	Na2O	0.71	3.68	1.6	0.35
13	K2O	5.33	4.07	6.4	0.027
14	P2O5	0.78	0.12	0.4	0.027
15	CO2	0.00	0.05		0
16	Total	94.83	99.30	98.90	99.69
17					
18	Quartz (Q)		29.07		
19	Corundum(C)		0.92		
20	Orthoclase(Or)		24.05		0.16
21	Albite(Ab)		31.14		2.96
22	Anorthite(An)	1.07	8.03	13.21	75.30
23	Nepheline(Ne)	3.25		7.33	
24	Diopside(Di)			36.17	4.39
25	Hypersthene(Hy)		3.36		9.10
26	Olivine(Ol)	40.82		2.21	7.31
27	Magnetite(Mt)	5.79	1.75	5.94	
28	Ilmenite(Il)	1.22	0.59	2.28	0.42
29	Apatite(Ap)	1.81	0.28	0.93	0.06
30	Acmite(Ac)				
31	Leucite(Lc)	23.63		29.66	
32	K-Metasilicate(Ks)				
33	Na-Metasilicate(Ns)				
34	CaDiSilicate(Cs)	17.25		1.23	
35	Kaliophilite(Kp)	0.77			
36	Wollastonite(Wo)				
37	Hematite(Hm)				

Integrated Earth Data Applications (IEDA)

http://lepr.ofm-research.org/WebServices/test_CIPWnorm.php



Oxide	Value	Oxide	Value
SiO_2	44.7	K_2O	0.027
TiO_2	0.22	P_2O_5	0.027
Al_2O_3	28.2	SrO	0.00
Fe_2O_3	0.0	BaO	0.00
Cr_2O_3	0.096	ZrO_2	0.00
FeO	4.4	H_2O	0.0
MnO	0.063	CO_2	0.0
MgO	5.4	Cl_2O	0.0
NiO	0.00	F_2O	0.0
CoO	0.00	SO_3	0.0
CaO	16.3	S	0.0
Na_2O	0.35		

Norm

Mineral	Wt%
Albite	2.96
Anorthite	75.17
Apatite	0.06
Chromite	0.14
Diopside	4.38
Hypersthene	9.14
Ilmenite	0.42
Olivine	7.19
Orthoclase	0.16

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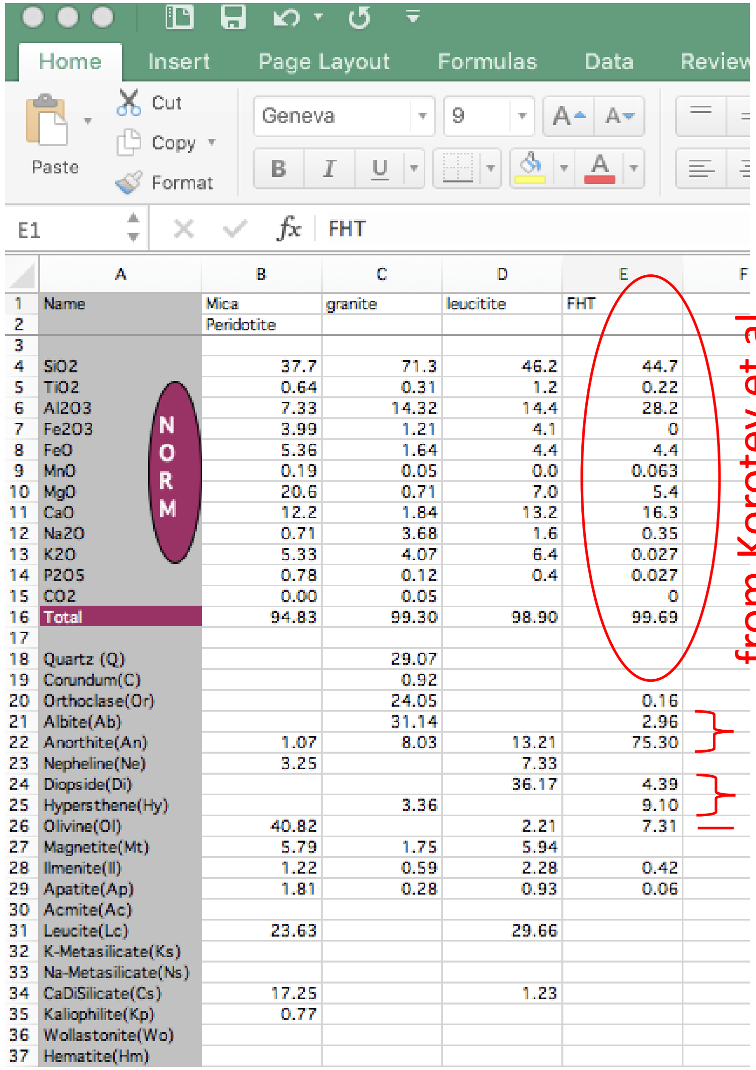

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5	TiO2	0.64	0.31	1.2	0.22	
6	Al2O3	7.33	14.32	14.4	28.2	
7	Fe2O3	3.99	1.21	4.1	0	
8	FeO	5.36	1.64	4.4	4.4	
9	MnO	0.19	0.05	0.0	0.063	
10	MgO	20.6	0.71	7.0	5.4	
11	CaO	12.2	1.84	13.2	16.3	
12	Na2O	0.71	3.68	1.6	0.35	
13	K2O	5.33	4.07	6.4	0.027	
14	P2O5	0.78	0.12	0.4	0.027	
15	CO2	0.00	0.05		0	
16	Total	94.83	99.30	98.90	99.69	
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18	Quartz (Q)		29.07			
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27	Magnetite(Mt)	5.79	1.75	5.94		
28	Ilmenite(Il)	1.22	0.59	2.28	0.42	
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from Korotev et al.

Plagioclase

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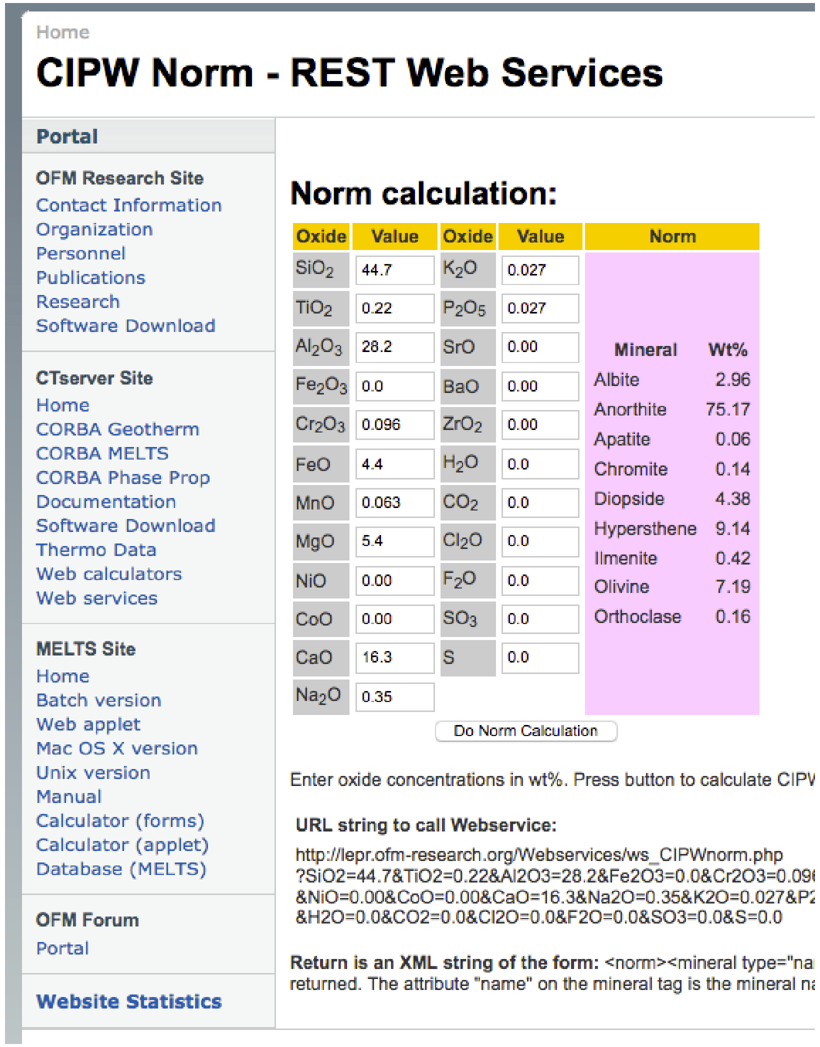

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MgO	5.4	Cl_2O	0.0
NiO	0.00	F_2O	0.0
CoO	0.00	SO_3	0.0
CaO	16.3	S	0.0
Na_2O	0.35		

Norm

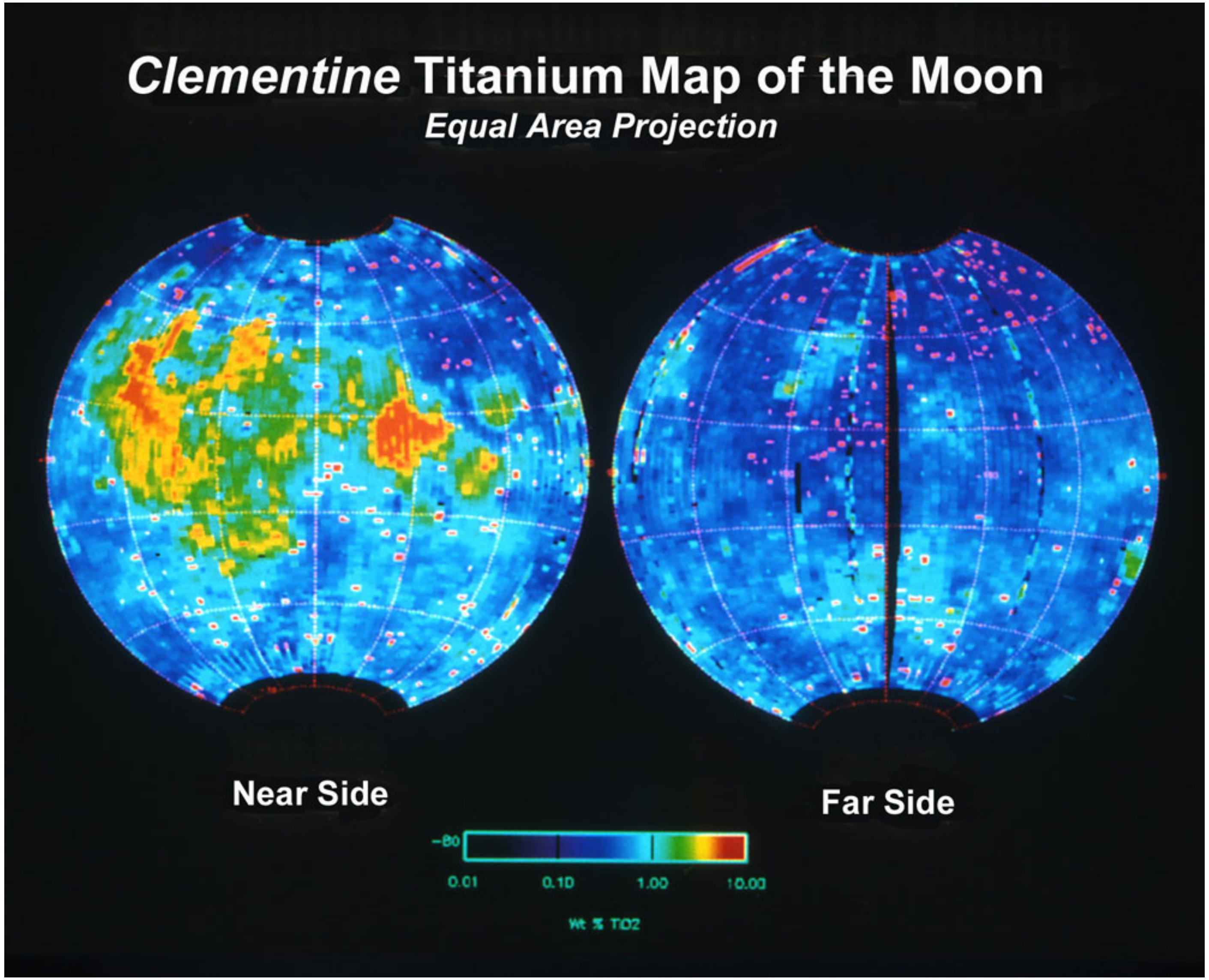
Mineral	Wt%
Albite	2.96
Anorthite	75.17
Apatite	0.06
Chromite	0.14
Diopside	4.38
Hypersthene	9.14
Ilmenite	0.42
Olivine	7.19
Orthoclase	0.16

Lunar locations compatible with the hydrogen reduction oxygen production process.

This chart has been around for a while, and mostly focuses on mare basalts. (Clementine flew to the Moon in 1994). The ‘classic’ feedstock for hydrogen reduction was/is mare basalt high in ilmenite (generally, $FeTiO_3$) content.

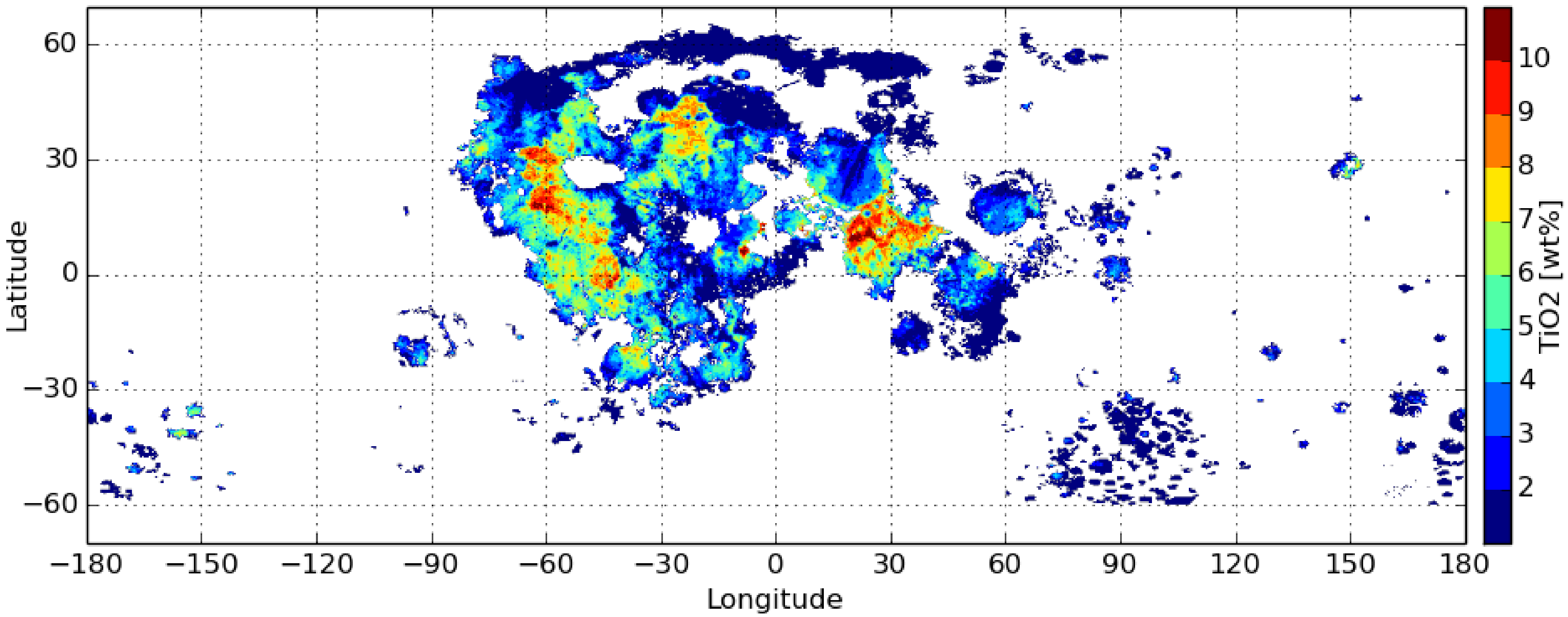
Some question the numerical values (Gillis et al., 2003; Elphic et al. 1998, 2002), so concentrate more on the colors as where to go, and not on the wt.% TiO_2 numbers as a means to predict oxygen yield.

Basically, you want to go to the hot (red) and warm (yellow-orange) regions. Mare Tranquilitatis in the east, Oceanus Procellarum in the west.



Lunar locations compatible with the hydrogen reduction oxygen production process.

Go to this website for more cool stuff: http://lroc.sese.asu.edu/posts/986



This is a newer map based on LROC WAC data (Sato et al., 2017). It basically shows the same thing as the previous slide, but at a higher spatial resolution.

It only shows the mare regions, but that is where the ‘pay dirt’ is anyway for hydrogen reduction.

Again, land in the ‘hot’ colors.

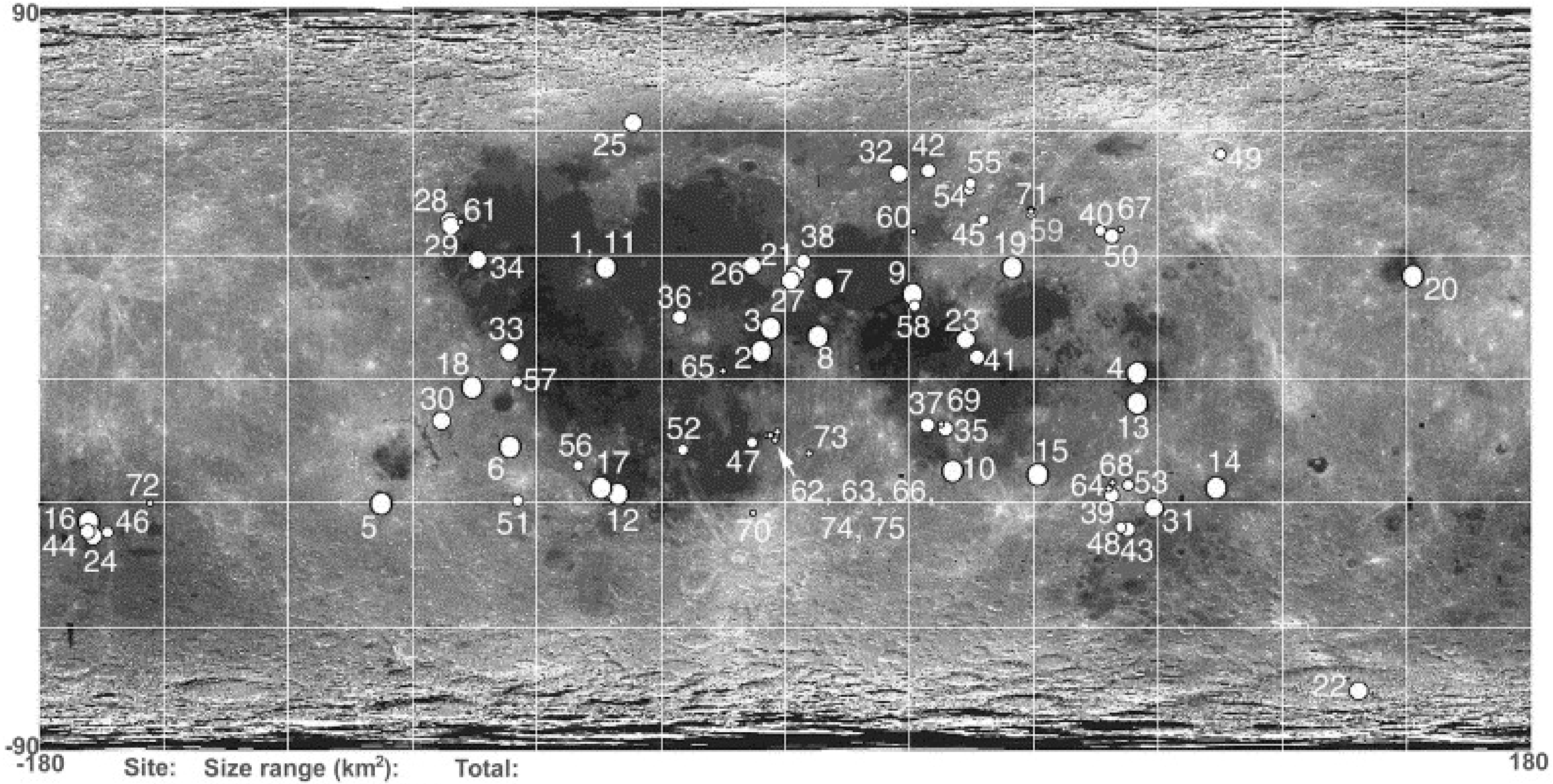
Lunar locations compatible with the hydrogen reduction oxygen production process.

This chart comes from Gattis et al., 2003, Compositional analyses of lunar pyroclastic deposits, Icarus.

Notice most pyroclastic deposits are associated with mare basalts, but some are associated with crypto-mare (i.e., buried basalts), and most all deposits are located in the mid-latitudes.

Spot 22 is the isolated, localized volcanic vent in Schrodinger basin, the highest latitude pyroclastic deposit that is known.

There are no pyroclastic deposits at the lunar poles.



Site:	Size range (km^2):	Total:
○	1001 - 49000 (vlarge)	20
○	401 - 1000 (large)	15
○	201 - 400 (medium)	9
○	101 - 200 (small)	17
○	1 - 100 (vsmall)	14
		75

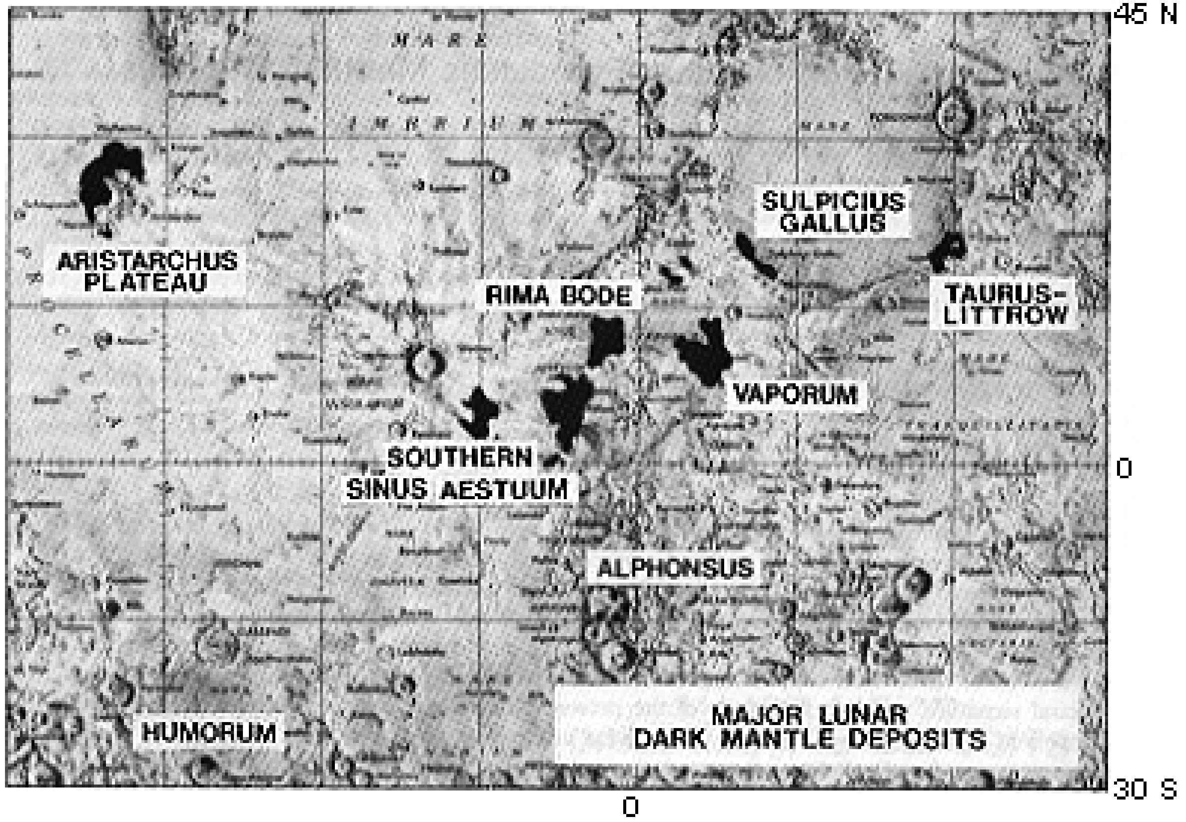
Distribution of Lunar Pyroclastic Deposits

Lunar locations compatible with the hydrogen reduction oxygen production process.

Another oldie, but a goodie. This chart shows the large, regional pyroclastic (aka dark mantle) deposits.

Pyroclastic deposits are produced by explosive, gas-rich, Hawaiian-style fire-fountaining volcanic eruptions that spread particles far and wide.

Allen et al. (1994, 1996) successfully conducted oxygen extraction from iron-rich pyroclastic glass in the lab.



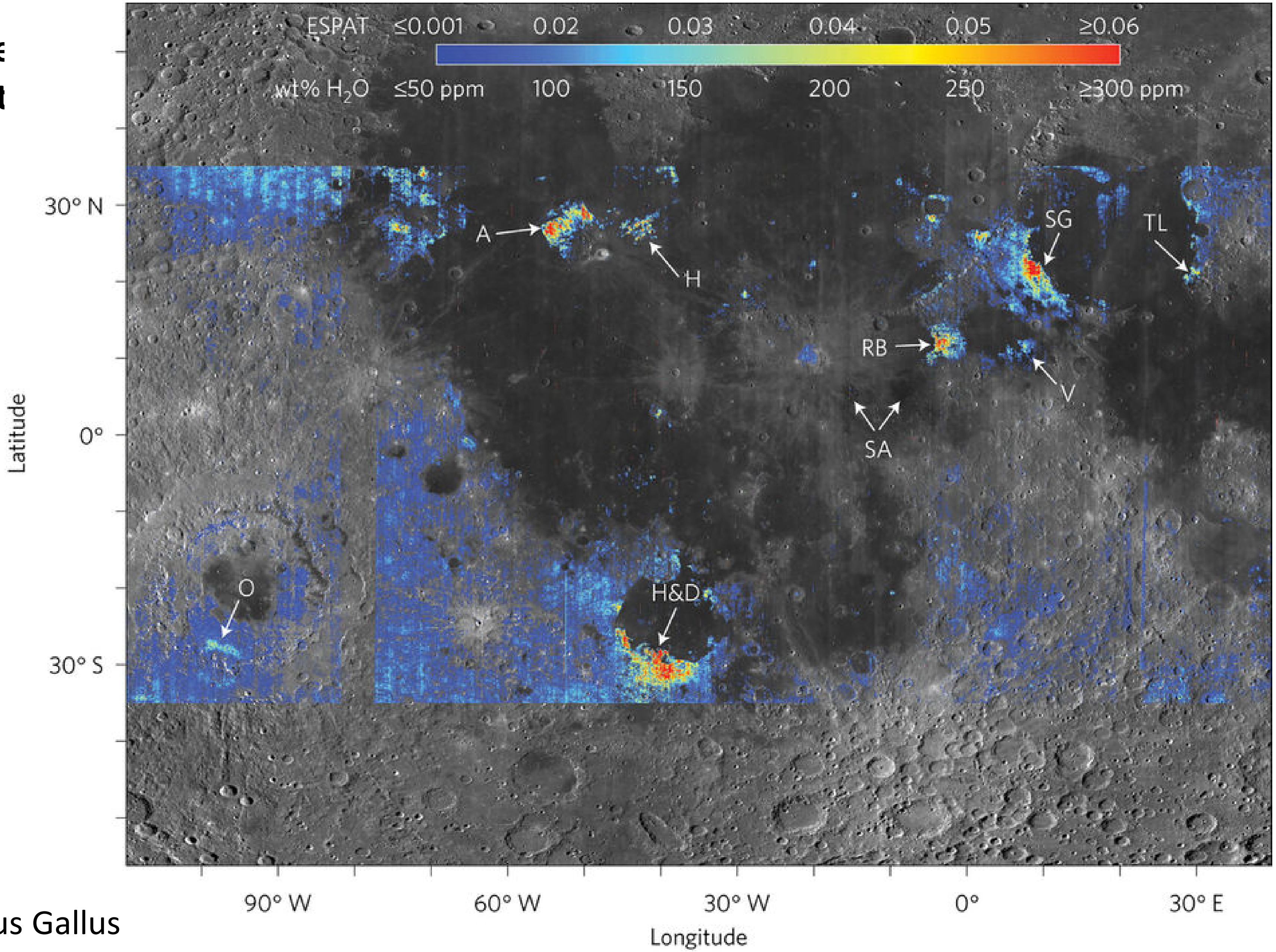
(Map from J. W. Head, 1974, Lunar Dark Mantle Deposits: Possible Clues to the Distribution of Early Mare Deposits, Proc. LPSC 5th, p. 207-222.)

Lunar locations compatible with the hydrogen reduction oxygen product process.

Icing on the cake!

This image comes from Milliken and Li (2017), and shows that some of the regional pyroclastic deposits are hydrated, likely OH, but possibly H2O.

So, if you are using the hydrogen reduction process to get oxygen out of pyroclastic glass, you will also get a small amount of water (up to 300 ppm) as a bonus.



A = Aristarchus Plateau
H = Harbinger
H&D = Humorum & Dopplemayer
O = Orientale
RB = Rima Bode
SA = Sinus Aestuum
SG = Sulpicius Gallus
TL = Taurus-Littrow
V = Vaporum

Lunar locations compatible with the hydrogen reduction oxygen production process.

Work by Gibson, et al. (1974) conducted evolved gas analyses on Apollo soils.

This is the gas release data for the Apollo 17 ‘orange soil’ that contains orange pyroclastic glass beads.

Notice water comes off at low temperatures (100-500 °C), compared to the higher temperatures that will be used for hydrogen reduction.

A challenge with pyroclastic glass will be the sulfur content, that is released as SO2. This will have to be separated from the water vapor.