



# Lunar Soil Sample 74221, 2 – A Study of Unusual Fines

M. R. Martinez<sup>1, 2</sup>; J. K. Meen<sup>2, 3</sup>; D. C. Barker<sup>4</sup>



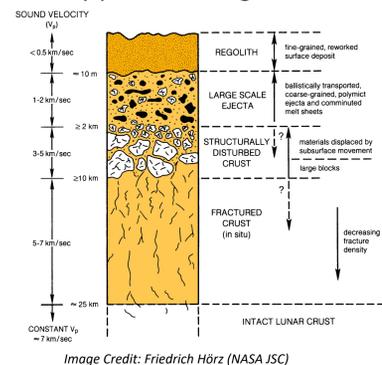
<sup>1</sup>Department of Mechanical Engineering, University of Houston; <sup>2</sup>Texas Center for Superconductivity, University of Houston; <sup>3</sup>Department of Chemistry, University of Houston; <sup>4</sup>Department of Earth and Atmospheric Sciences, University of Houston

## Background.

The protolith of the lunar regolith is the product of meteorite impact on both lunar mare (dominantly basaltic) and highlands (dominantly anorthositic and gabbroic). The regolith is between 5 and 10 meters thick and overlies fractured rock.

Micrometeorites continually impact the lunar surface, melt it, and overturn its contents – a process referred to as impact gardening. Solar wind and cosmic rays impact the surface materials. The mineral content of the regolith is derived from its precursor rocks, and agglutinate glasses dominantly consist of material derived from the minerals; as discussed in “Lunar Sourcebook: A User’s Guide to the Moon.”

Examination of the regolith fines reveals the presence of various phases that did not originate within the precursor materials and potentially provides insight into the regolith gardening process.



The dominant components of the regolith are pieces of rock, pyroxene, feldspars, olivine, ilmenite, volcanic glasses, and agglutinates. The last of these are particles bonded together by glass. The density of the regolith is ~1.5 g/cc with ~50% pore content.

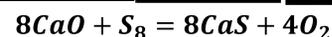
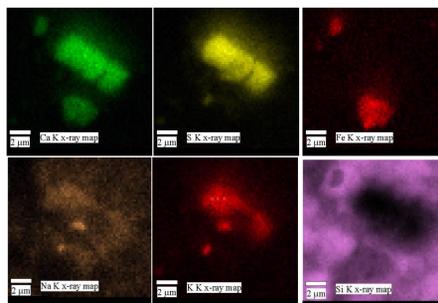
## Sample Analysis.

A sample of approximately 40 mg of fine-grained regolith collected by Apollo 17, from which glass spherules were removed, was sprinkled on mylar in a layer as near to one grain thick as possible.

X-ray mapping was employed in a JEOL JSM-6330F Scanning Electron Microscope (SEM) with an EDAX Octane Pro EDS and TEAM software.

## Species Not in Igneous Rock.

### • Sulfides - CaS:



$\text{xt} \rightarrow \text{xt} \Delta G = 84.0 \text{ kJ/mol (CaO)@ 2000 K}$   
 $\text{liq} \rightarrow \text{liq} \Delta G = 78.3 \text{ kJ/mol (CaO)@ 3000 K}$   
 $\text{gas} \rightarrow \text{gas} \Delta G = 6.6 \text{ kJ/mol (CaO)@ 4000 K}$

$$\Delta G = \Delta G^\circ + RT \ln K$$

$$\ln K = \ln \frac{a_{\text{CaS}}^8 \cdot P_{\text{O}_2}^4}{a_{\text{CaO}}^8 \cdot P_{\text{S}_8}} = \ln \frac{P_{\text{O}_2}^4}{P_{\text{S}_8}}, \text{ assuming pure CaS and CaO, and}$$

$$P_{\text{O}_2} = 10^{-15} \text{ bar}$$

$$\Delta G = \Delta G^\circ + \left( 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) * (4000\text{K}) * 4 * \ln\left(\frac{10^{-15}}{P_{\text{S}_8}}\right)$$

$$\Delta G = \Delta G^\circ - 4594 * \ln\left(\frac{1}{P_{\text{S}_8}}\right) \frac{\text{kJ}}{\text{mol}}$$

### • Other CaS with Unusual Grain Structure

The grain appears to be attached to an agglutinate. The structure it displays suggests it grew rapidly from a fluid.

Oldhamite, CaS, is known from meteorites, anthropomorphic blast furnace slag, and terrestrial pyrometamorphic coals and their surrounding sediments. Generally, it contains Mg in moderate amounts.

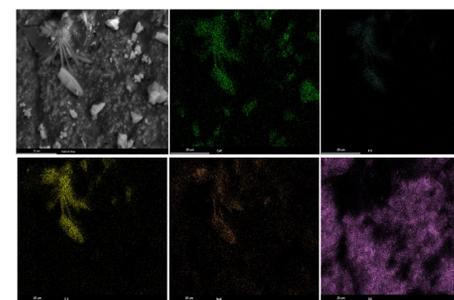
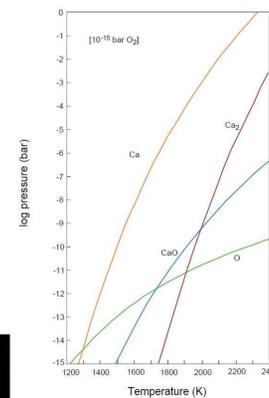
However, in the CaS grains found, the Mg content present is <math><0.5\%</math>. Some also display significant amounts of Na and K, which is not typical of oldhamite. Additionally, the symmetry and structure of the sulfide grains have yet to be determined.

**How is CaS formed?** Reaction between CaO and S is strongly disfavored by thermodynamics, and even more so if Ca is in feldspar or pyroxene. However, if the  $P_{\text{O}_2}$  is very low and  $P_{\text{S}_8}$  is high, the free energy can be overcome.

In the case of sulfur reacting with condensed phases, rather than with other gases, it would still be unexpected to find CaS instead of FeS, NiS, or any other transition metal sulfide. In the basalts with plenty of Ca and S, oldhamite does not form, troilite does (as described by Frondel). Oldhamite is only known to form in Ca-rich, S-rich, O-poor environments.

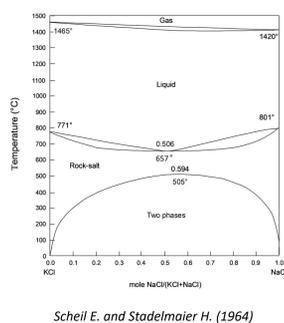
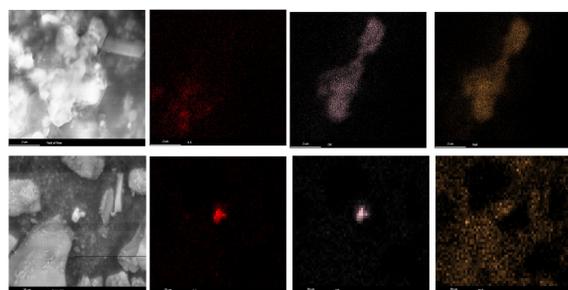
### Why a reaction in the gas phase?

At low  $P_{\text{O}_2}$ , the dominant vapor generated by the volatilization of CaO is Ca;  $P_{\text{Ca}}$  exceeds  $P_{\text{CaO}}$  by ~5 orders of magnitude at all temperatures. In fact,  $P_{\text{Ca}_2}$  exceeds  $P_{\text{CaO}}$ .



## Species Not in Igneous Rock

### • Chlorides – (Na, K)Cl:

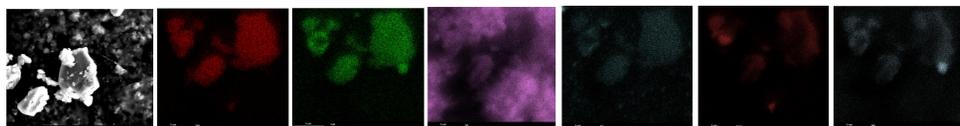


There is no solubility of K in NaCl, or vice versa, below 200 °C; the solvus has closure at 505 °C. The chloride grains have a composition near the solvus maximum (59% Na), indicating they presumably formed at temperatures above 500 °C. **Terrestrial chlorides precipitate from water so there would be no mixture present in crystals.**

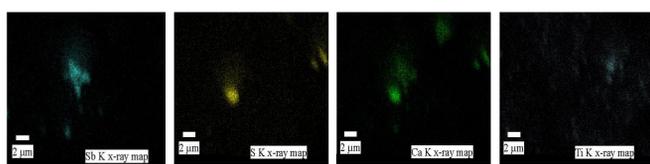
With the boiling points of K and Na being 759 °C and 883 °C, respectively, alkali and chloride gases could have reacted to form a (Na,K)Cl liquid; which then crystallized the grains with a cubic habit.

### • Oxides – TiO<sub>2</sub>, CaO:

- It is probable that lunar CaO has been replaced by Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> since being stored in, and reacting with, the terrestrial environment.
- The presence of TiO<sub>2</sub> speaks to the abundance of ilmenite in the regolith.



### • Elemental Sb:



This Sb grain is near other CaS and TiO<sub>2</sub> grains. They appear to be on, or attached to, the same agglutinate glass.

The mineral grains are thin and all x-ray maps include photons derived from the glass, suggesting a <math><1 \mu\text{m}</math> thickness.

The apparent Ca concentration coincident with Sb reflects a Sb x-ray interference on the Ca K $\alpha$  peak.

The occurrence and chemistry of some of these minerals have been documented previously. Bogatkov *et al.* and Mokhov *et al.* found unusual oxides, bronzes, native elements, alloys, sulfides, and an iodide in regolith samples from Luna-16, Luna-20, and Luna-24.

## Conclusions.

Any meteorite impact on the lunar surface has the potential of volatilizing S or Cl from impacted materials.

- Ca has a boiling point of 1484 °C but CaO is difficult to reduce and is highly refractory (with a melting point of 2613 °C), so Ca is most likely to occur in the vapor phase at the highest impact temperatures.
- Relatively low temperatures volatilize alkali metals; reactions between alkalis and Cl in the vapor phase can produce an alkali metal and chloride liquid, which crystallizes (Na,K)Cl grains.
- Sb has a boiling point of 1635 °C, but it can be easily reached upon impact nonetheless. Native Sb and S therefore also potentially result from vapor deposition.

Ca, Na, and K in a cooling vapor can amalgamate and the multi-metal liquid may react with anions – like S, Cl or O – to produce small grains found throughout the regolith. These will be incorporated into agglutinate glasses when heated by a following impact.

## References.

- Bogatkov, O. A. *et al.* (2004), *Dokl. Earth Sci.* 395, 448-452.
- Frondel, J. W. (1975), *Lunar Mineralogy*, Wiley New York.
- McKay, D. S. *et al.*, (1991) “Lunar Sourcebook: A User’s Guide to the Moon”, (Heiken, G. H. *et al.* editors), Cambridge University Press.
- Mokhov, A. V. *et al.*, (2008), *Dokl. Earth Sci.* 421A, 923-925.
- Scheil E. and Stadelmaier H. (1964), *Phase Diagrams for Ceramists*, ACeramS, Columbus, OH.