

Lunar Soil Sample 74221,2 – A Study of Unusual Fines. M. R. Martinez^{1,2}, D. C. Barker³, and J. K. Meen^{2,4},
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Introduction: The regolith that enshrouds the lunar surface has a mode dominated by minerals and rock fragments derived from lunar bedrock by excavation at the sites of major impacts, agglutinates (minerals welded by glasses interpreted to have formed by *in situ* melting resulting from the continual micrometeorite bombardment of a billion years), and volcanic glass [1]. These materials have been modified by impact of atoms (dominantly H and He) in the solar wind and by cosmic rays. The regolith has consequently evolved in chemical and mineralogic composition and the details of its current make-up are important in understanding its evolution and seeing back to the processes by which it formed. We report here a study of one small sample of the fine-grained component of regolith collected by Apollo 17. Small modal proportions of the regolith are of minerals not expected to have formed in the original lunar igneous rocks. The occurrence and chemistry of some of these minerals are documented. Mokhov and co-workers [2], [3] (and references therein) found unusual oxides, bronzes, native elements, alloys, sulfides and an iodide in Luna-16, Luna-20, and Luna-24 samples of regolith. Apparently, regolith contains a wealth of minor phases; there is as yet insufficient data to know how such phases are distributed in the regolith.

Sample Analysis: The subject of this study is approximately 40 mg of the fine fraction of regolith from which glass spherules had previously been removed and studied [4]. A sheet of 5 mm thick polyethylene terephthalate was cut to fit a scanning electron microscope (SEM) stage. X-ray mapping of the pristine sheet showed no peaks other than those for C and O. Regolith was sprinkled on the stage in a layer as near to one grain thick as possible. The sample was coated with 25 nm of carbon to render it electrically conductive. All studies were on a JEOL JSM-6330F SEM with an EDAX Octane Pro EDS and using TEAM software. X-ray maps were obtained on regions of 400 μm by 300 μm with each integrated pixel approximately 5 μm square. Most of each region is dominantly of the abundant rock-forming elements (Si, Al, Fe, Mg, Ca, Na, O) but the presence of high concentrations of other elements in individual pixels was recorded and each area examined at higher magnification. Many grains described here are only a few microns across and some have subgrains (or

compositional heterogeneities) that are significantly smaller. The electron beam that imaged the sample has a diameter much less than that of the excitation volume which generates the x-rays (approximately 1-2 μm). X-rays from surrounding minerals therefore contribute to the spectra of small grains. We x-ray mapped the mineral grains with a pixel size less than 1 μm to produce a map showing the “moving average” of elemental content and which allows one to see the distribution of elements in each grain.

X-ray Maps of Individual Grains:

Sulfides. Areas producing S x-rays exist in each region of the fines. S is not associated with Fe or another transition metal as a major constituent (cf. [5]). The most abundant sulfide is calcium-rich. X-ray maps for one of the larger grains are shown as Figure 1.

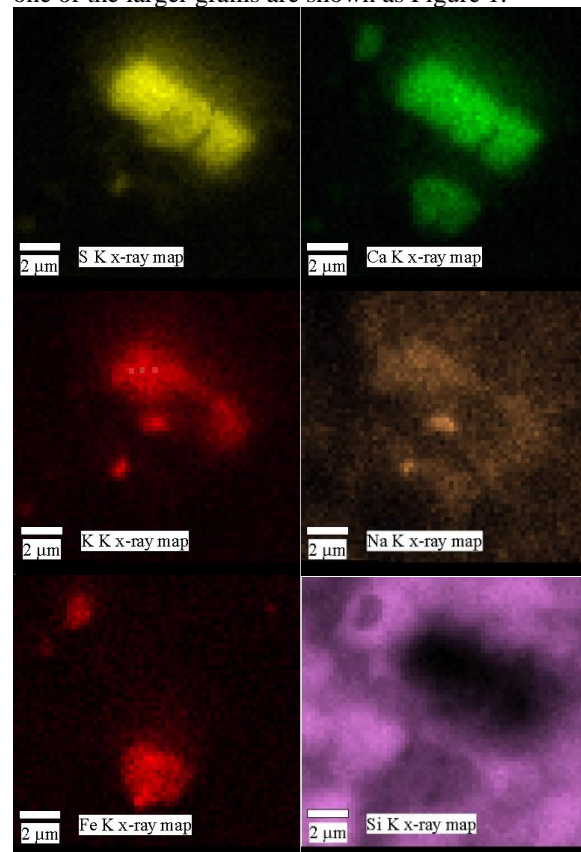


Figure 1. X-ray maps of S, Ca, K, Na, Fe, and Si in one CaS grain and the surrounding phases.

Ca and S x-rays are emitted from all the rectangular grain while those of K and Na have an uneven distribution, suggesting chemical variation. In fact the atomic ratio as measured by EDS Ca:Na:K ranges from 41:5:8 to 19:21:25. In all cases, S has the appropriate content to suggest a mixture of CaS, Na₂S, and K₂S. Fe is concentrated in phases other than the sulfide (those grains are both agglutinates that contain <0.1 wt.% S). It is also clear that Si is abundant in all surrounding phases but absent from the sulfide.

Oldhamite, CaS, is known from terrestrial pyrometamorphic coals and surrounding sediments and anthropogenic blast furnace slag and from meteorites. It generally contains moderate amounts of Mg. We have not determined the symmetry of the sulfide grains in 74221,2 and note that centers of grains give Mg contents <0.5% and that some (but not all) grains contain significant amounts of Na, K, or both (which is not typical of oldhamite). We do not know whether the sulfide is oldhamite or has a different crystal structure.

Chlorides. Some maps show regions of high Cl content. At higher magnification these are resolved as grains or groups of grains with cubic habit. They have spectra dominated by x-rays of Na, K, and Cl. The largest cluster of grains found so far is 8 μm across with the largest cube having a 4 μm side. X-ray analysis is Na_{0.56}K_{0.44}Cl. Given the grains cubic habit, they are believed to be solid solutions between halite and sylvite. There is essentially no solubility of K in NaCl or vice versa below 200 °C [6]; the solvus has closure at 505 °C. As the chloride grain has a composition near the solvus maximum (59% Na), these grains presumably formed at temperatures above 500 °C. K has a boiling point of 759 °C and Na one of 883 °C. Alkali and chloride gases could have reacted to form a (Na,K)Cl liquid that crystallized the cubes. (The eutectic at 657 °C is to 51% Na solid solution.)

Others. Some areas of native antimony were located. These are of multiple grains in close proximity and no grain has a maximum dimension of more than 1.5 μm. One area was near CaS grains and to a TiO₂ grain. Figure 2 is the x-ray maps of Sb, S, Ca, and Ti in this area which appear to be on the same agglutinate glass and to be attached to that glass. The mineral grains are all thin and all x-ray maps include photons derived from the glass (suggesting grains are <1 μm thick).

Some grains that generate high Ca x-ray intensity have only background levels of x-rays produced from any elements other than C and O. These may have been grains of CaO (or native Ca) when collected but they have reacted with the terrestrial environment since to form Ca(OH)₂ or CaCO₃. Their highly anhedral habits are, therefore, not representative of the original ones. Grains are typically on the order of 5 μm across.

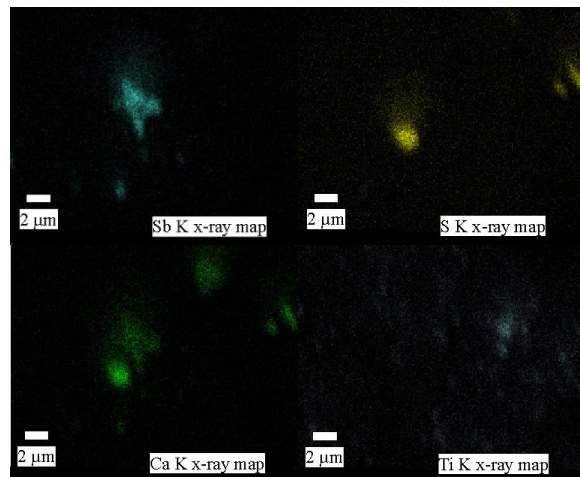


Figure 2. X-ray maps of micron and sub-micron grains of CaS, native Sb, and TiO₂ all on a background dominated by agglutinate glass. The Sb map shows a region of sub-micron grains in the center of the field with a few more grains below it. The S and Ca maps show one central grain of CaS and two small grains to the right. (The apparent Ca concentration coincident with Sb reflects a Sb x-ray interference on the Ca K α peak.) The TiO₂ grain is to the right.

Conclusions: Any meteorite impact on the Moon is likely to volatilize S or Cl in impacted materials. Relatively low temperatures volatilize alkali metals and reactions between alkalis and Cl in the vapor phase can produce an alkali chloride liquid that crystallizes (Na,K)Cl grains. Antimony has a higher boiling point (1635 °C) but one readily attained at impact sites. Native Sb and S therefore also potentially result from vapor deposition. Calcium has a reasonably low boiling point (1484 °C) but CaO is difficult to reduce and is notoriously refractory (melts at 2613 °C) so Ca is likely to occur in the vapor phase only at the highest impact temperatures. Ca, Na, and K in a cooling vapor can amalgamate and the multi-metal liquid react with S, O, or any other anion encountered to produce small grains found in the regolith. These grains will be incorporated into agglutinate glasses if heated by a later impact.

References: [1] McKay, D.S. *et al.*, (1991) Chapter 7 In “Lunar sourcebook: a user’s guide to the Moon”, (Heiken, G.H. *et al.* editors), Cambridge University Press, p. 285-356; [2] Bogatkov, O.A. *et al.*, (2004), *Dokl. Earth Sci.* 395, 448-452; [3] Mokhov, A.V. *et al.*, (2008), *Dokl. Earth Sci.* 421A, 923-925; [4] Barker, D.C. and Snow, J.E., (2012), *LPS XLIII*, Abstract #2926; [5] Frondel, J.W. (1975), *Lunar Mineralogy*, Wiley New York; [6] Scheil E. and Stadelmaier H. (1964), *Phase Diagrams for Ceramists*, ACeramS, Columbus OH.