

CALCIUM-SULFUR-CHLORINE-BEARING PHASES WITHIN SUTTER'S MILL SAMPLE SM3 (PRE-RAIN). C. W. Haberle¹, Laurence A. J. Garvie², K. Domanik³, and P. R. Christensen¹; ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, (chaberle@asu.edu), ²Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287-6004, USA. ³Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721.

Introduction: On April 22nd, 2012 the Sutter's Mill meteor entered the atmosphere over the northern Sierra Nevada Mountains, with pieces falling around the towns of Coloma and Lotus in California. As of November 28th, 2012, 90 samples have been recovered, with a cumulative mass ~1 kg [1]. The first three samples recovered (SM1-SM3) were collected on April 24th, before heavy rain fell across the area on the 25th and 26th. This investigation focuses on the pre-rain stone SM3 obtained by Arizona State University's Center for Meteorite Studies (Fig. A).

Materials: SM3 was an almost complete 5.0 g fusion-crusted stone (Fig. A). To allow for scanning electron microscopy, a 3-5 mm chip was embedded in epoxy and polished. Polishing was done dry to prevent contamination of the sample. Petrographic observations show the brecciated nature of the sample, with a heterogeneous distribution of white mineral grains and sulfides embedded in a dark fine-grained matrix (Fig B). Recognizable chondrules are scarce. Powder X-ray diffraction analysis of SM3 [2] show it to be olivine rich, with lesser amounts of enstatite, Fe-sulfides, magnetite, and oldhamite.

Methods: The polished chip was analyzed at the University of Arizona's Michael J. Drake Electron Microprobe lab. This lab is equipped with a CAMECA SX100 electron microprobe, which utilizes five Wavelength Dispersive Spectrometers (WDS), and a Bruker XFlash 5010 Energy Dispersive Spectrometer (EDS). Backscatter electron imaging (BSE), EDS, WDS, and x-ray mapping were conducted to ascertain the chemical and mineralogical nature of the samples. Element maps were acquired for Ca, Fe, Mg, P, Si, Al, Cl, Ni, Na, and S.

Results: BSE images and element maps show the macro- to microscopic brecciation and chemical heterogeneity (Figs. C, D). Mg, S, Si, and Fe element maps show dispersed grains of Fe-Mg silicates and Fe(Ni) sulfides, though in general, these elements are uniformly distributed, attesting to the fine-grained nature of the bulk mineralogy. Similarly, comparison of Ca and S maps shows correlations consistent with oldhamite. However, comparison of x-ray maps for Ca, S, and Cl show some Ca-S grains containing Cl; these grains are randomly distributed across the section (Fig. D). The Cl-rich hotspots contain ~1 to 3 wt% Cl.

One Ca-S-Cl area shows three Cl-bearing grains (Figs. E,F,G): WDS scans show these regions to be free of C. The element maps show that Grain **a** is zoned with an S-rich rim and Cl-rich interior. Grains **b** and **c** are irregularly shaped. BSE images and element maps show these grains to be chemically heterogeneous, and by inference mineralogically complex, at the micron scale. The center of Grain **a** is very beam sensitive with a hole forming after a few seconds of irradiation. Other Ca-S-Cl grains were not so beam sensitive.

The center of Grain **a** is dominated by Ca and O, with a Ca:O ratio of 1:2.4, with 1.5 wt% S and 1.9 wt% Cl. The rim of Grain **a** is dominated by Ca, S, O (with 1:0.6:2.1 ratio), with 1.0 wt% Cl. Low WDS totals may be the result of the extreme beam sensitivity of the area. The identity of the phase at the center of Grain **a** is a mystery. One possibility is Ca(OH)₂, which would likely be beam sensitive. Analysis of multiple Ca-S-Cl regions failed to clearly identify a specific Cl-bearing mineral. A search was conducted for Na in the Cl-rich regions, but none was detected.

Discussion: Sutter's Mill is a carbonaceous chondrite [1], although the powder XRD data for SM3 show an absence of clays and a predominance of olivine. This bulk mineralogy is similar to that measured for the Belgica-like chondrites [3,4], which are thought to be dehydrated CM chondrites that were heated between 700 and 900° C for geologically short periods of time [4].

Sutter's Mill is unique to date amongst the CM chondrites in containing oldhamite, which is normally found in reduced chondrites such as enstatite chondrites. The presence of oldhamite in SM3 likely reflects the high temperature-heating event that dehydrated the putative serpentine to yield the fine-grained matrix olivine [2]. Oldhamite can be formed from CaSO₄ in the presence of C (both of which occur in CM chondrites) viz. $\text{CaSO}_4 + 2\text{C} \rightarrow \text{CaS} + 2\text{CO}_2$

Ashing experiments with coal containing clays, Fe-sulfides, and calcite show that CaS can form ~750°C [5], suggesting that a similar reaction could produce the CaS found in SM3, at the temperatures determined for serpentine dehydration. Several of the Ca-rich regions are O rich but with low S, and could form according to: $3\text{CaSO}_4 + \text{CaS} \rightarrow 4\text{CaO} + 4\text{SO}_2$, and the CaO may further react to give Ca(OH)₂.

The mineral association for the Cl is less clear. No peaks were present in the XRD patterns for "common" chlorides such as NaCl, MgCl₂, or FeCl₃. Aqueous leachates from carbonaceous chondrites show the presence of Cl [6,7], attesting to the presence of soluble salts such as NaCl and MgCl₂. Extractable chlorinated benzoic acids are reported for Murchison [8], suggesting another potential source of Cl. These organic Cl compounds would likely decompose and liberate Cl at the high temperatures associated with serpentine decomposition.

References: [1] Jenniskens P. et al. (2013) *Science* **338** 1589. [2] Garvie L.A.J. (2013) 44th LPSC. [3] Ivanova M.A. et al. (2010) *MAPS* **45** 1108. [4] Nakato A. et al. (2008) *Earth Planet Sci.* **60** 855. [5] Biggs D.L. and Lindsay C.G. (1986) in *Mineral Matter and Ash in Coal*, ACS Symp. Series, **310**, 128. [6] Fanale F.P. et al. (2001) *JGR* **106** 14595. [7] Izawa M.R.M. et al. (2010) *EPSL* **298** 443. [8] Kuehner S.M. et al. (2007) 70th Ann. Meteor. Soc. Meeting. Abstr#5131.

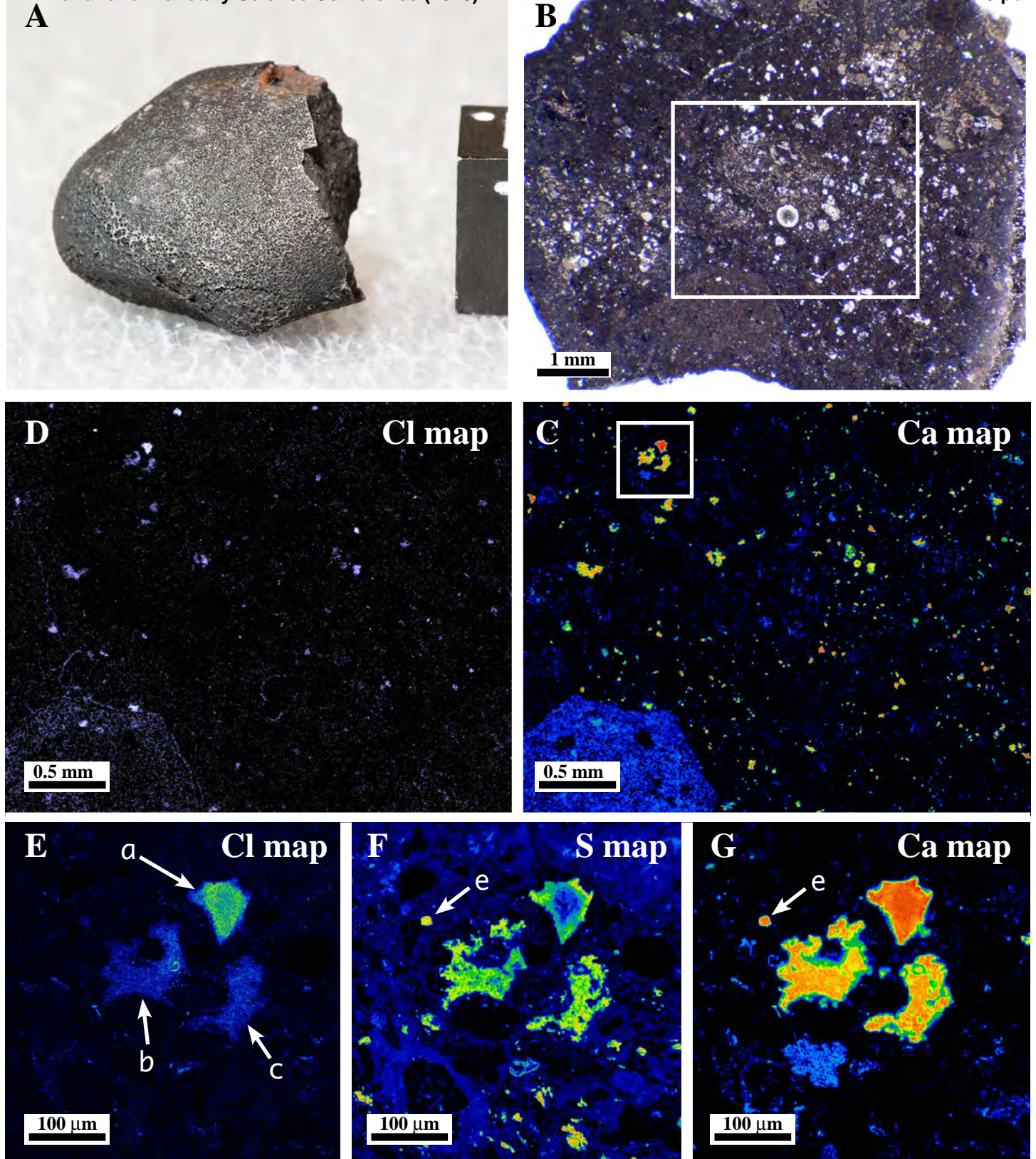


Figure 1. A) Whole, 5.0 g Sutter's Mill stone SM3. Cube at side of image has a 1 cm edge. B) Optical reflected-light image of a polished fragment of SM3. Evident is a 300 μm chondrule at the center, the heterogeneous distribution of mineral grains, and sulfides (golden brown). Near the bottom of the fragment is an angular Ca-rich clast. The white-boxed region is magnified in C. C and D) Ca and Cl element maps. The white-boxed region in (C) is shown at higher magnification in E, F, and G. E, F, and G) Cl, S, and Ca element maps, respectively. The grains labelled a, b, and c are described in the text. The S-rich map shows the fine distribution of S in the matrix, which correlates with the Fe distribution (not shown). Grain e in (F) and (G) contains S and Ca only and is likely an oldhamite grain.