doi:10.1017/S1431927614005212
Microsc. Microanal. 20 (Suppl 3), 2014

Soft X-Ray EPMA Analyses of Extremely Reduced Phases from Apollo 16 Regolith: Problems and Solutions for Sub-Micron Analysis

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Conventional electron probe microanalysis (EPMA) generally uses high electron beam energies (1520 keV) to excite core state electrons for elements up to Z ~34. The goal here being to cause an electron transition that will emit a measurable X-ray. In general these high keV beam energies excite an analytical area, on the order of 2-6 μm in diameter making it impossible to properly analyze most phases under 2-3 μm in size. It is widely recognized that to properly analyze samples under 1μm, it becomes necessary to use low voltage electron beams. However, this has been difficult with traditional tungsten source electron probes. With the development of field-emission source electron probes, it is possible to focus low voltage beams to sizes required for submicron scale features. Doing so introduces many complications such as changes in peak position/shape and intensity of the available X-ray lines (generally L- and M-lines), surface contamination, and high uncertainties of the mass attenuation coefficients (MAC) for low energy (soft) X-rays.

Our research focuses on the analysis of sub-micron Fe-Si blebs, which are extremely reduced phases. These rare phases have been reported in lunar regolith [1,2], in lightning strike fulgurites [3], and in Stardust samples [4], and in core/mantle boundary rocks [5]. The fulgurite samples formed under the necessary reducing conditions because of the presence of organics, which at ultra-high temperatures scavenge the oxygen during the lightning strike [3]. It is possible that carbon, most likely from a carbonaceous impactor, plays a similar role in the formation of lunar Fe-Si. If this is the case one might expect to find trace amounts on carbon in the lunar iron-silicides.

The iron-silicon system is particularly well suited for experimenting with low-voltage analytical techniques. It is a simple binary system, Si Kα can be excited at low voltage allowing us to focus on the problem of the Fe L lines, and a relatively large suite of possible Fe-Si phases exists to conduct analyses on.

Prior soft X-ray analysis of iron has generally involved the Fe La line. Analysis in bulk steels, using the Fe La line, yields erroneously high iron concentrations [6]. The energy for this line (Fe La, 704 eV) lies on the L3 absorption edge. This means that if there is even a slight shift in the peak position, the MAC could be wrong by an order of magnitude, as it increases drastically over a very small energy range [7]. The La line involves an electron transition from the M_5 orbital moving to the L_3 orbital. Since the M_5 orbital is unfilled in the transition metals, this orbital is involved in bonding making it extremely sensitive to its chemical environment. The Lβ line (M_4-L_2 transition) is also affected (though not as strongly as the Lα line) by changes in the bonding environment making it also unacceptable for quantitative analysis (unless a matching Fe-Si standard is used). The Ll line (M_1-L_3) is unaffected by these changes in bonding environment, although the cross section for the production of this line is rather low leading to poor counting statistics [8].

Low-voltage analyses can be strongly affected by surface contamination. Care must be taken to remove any hydrocarbons prior to the sample being loaded into the chamber. Furthermore, for low-voltage EPMA, carbon coatings should be avoided because they tend to be dirty and can ablate under a low voltage electron beam at high currents [8]. Iridium or platinum coatings much improve sample

cleanliness, compared to carbon coating, and allow for easy plasma cleaning of the sample surface prior to analysis. Epoxy mounts are also undesirable, as they are made of hydrocarbons and are beam sensitive, prompting us to explore the use of pressed indium mounting [9].
Combining the knowledge described here, we have been able to successfully analyze phases under 0.5 μm in size for Ni, Fe, P, S, Si, and O. Notably we were able to detect carbon in the iron-silicide blebs. Carbon is absent from the plagioclase and Si metal, and is concentrated in the iron-silicides along with Ni and P [Figure 1].

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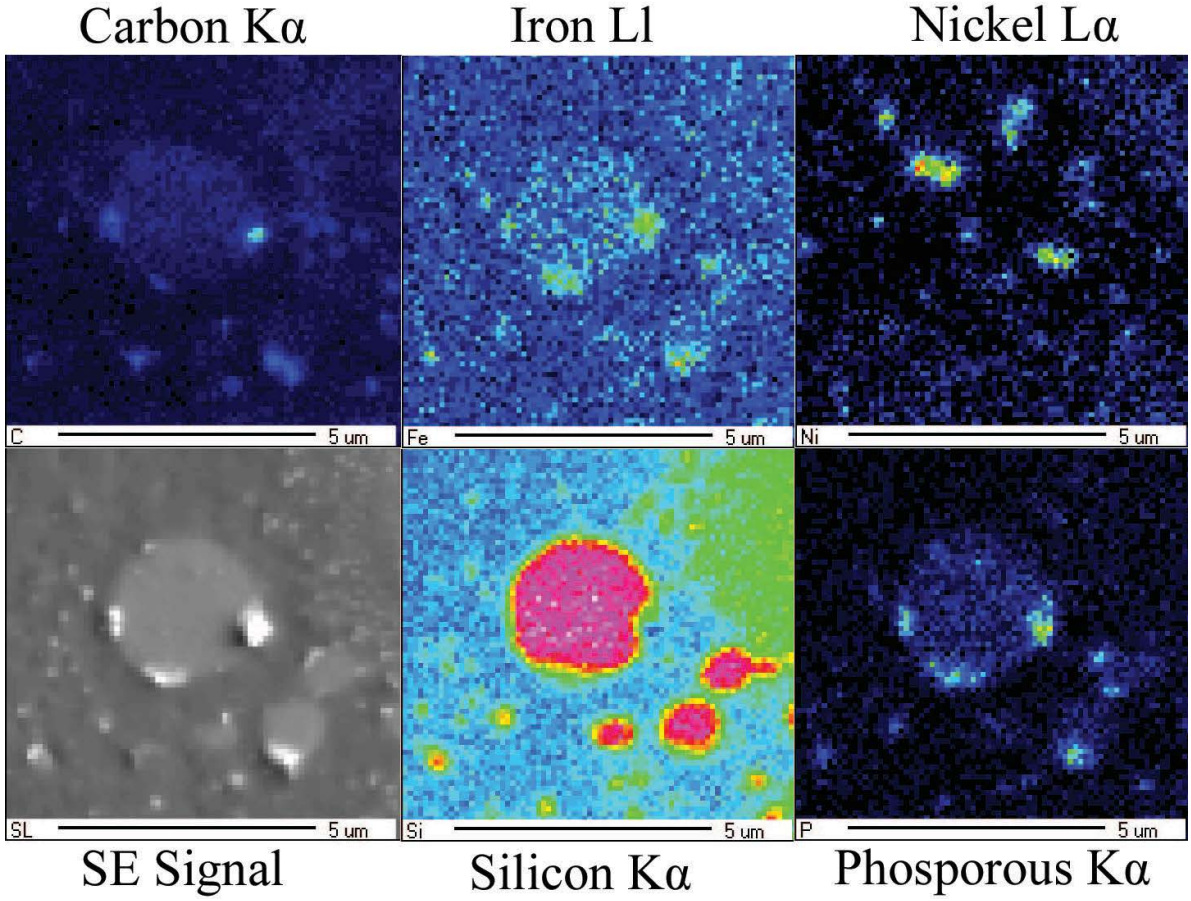

Figure 1: X-ray map of Apollo 16 lunar regolith grain A6-8, scale bar is 5 μm The iron-silicides are the bright phases in the SE image, the darker phases the native silicon, and the dark background is plagioclase (~An80). X-ray map was acquired at 5 keV, 10 nA, 250 ms dwell time, crystals used (C Kα: LDE2H, Fe Ll: LDE1, Ni La: TAP, Si Kα: TAP, PKα: PETH).

https://doi.org/10.1017/S1431927614005212 Published online by Cambridge University Press