**ELECTRON-PROBE MICROANALYSIS OF FE SPHERULES IN LUNAR AGGLUTINATE 76503,7020.** P. K. Carpenter[1] and B. L. Jolliff[1], [1]Dept. Earth and Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University in St. Louis, Campus Box 1169, Saint Louis, MO, 63130 (paulc@levee.wustl.edu).

**Introduction:** Lunar agglutinates are rock and mineral clasts combined with vesicular impact glass formed by micrometeorite impact events and exposure to solar wind processes [1]. TEM imaging of agglutinate grains reveals nanophase $Fe^0$ spherules that form by exposure to energetic particles. Electron energy-loss (EELS) analysis of agglutinate glass fragments establishes the degree of reduction to form $Fe^0$ [2]. As impact processes rework the regolith, nanophase $Fe^0$ and other melt products which include a meteoritic component are redistributed in agglutinate glass. Coalescence of nanophase $Fe^0$ spheres during this reworking may ultimately produce μm-sized Fe spherules. The chemistry of Fe spherules is an indicator of source material and oxygen fugacity, and thus provides insight into agglutinate formation. This study was initiated to evaluate the composition of Fe-rich spherules coupled with efforts to improve the spatial resolution of the analytical volume sampled by electron-probe microanalysis (EPMA).

**Agglutinate Sample 76503,7020:** Agglutinate 76503,7020 consists of vesicular impact glass with pervasive submicron to micron-sized Fe-rich spherules, Ti-rich zoned glass, and clasts of mineral grains and lithic fragments (Fig. 1A and B) [3]. Characterization of this sample has been done using backscattered-electron (BSE) imaging, X-ray mapping, qualitative energy-dispersive (EDS) and quantitative wavelength-dispersive (WDS) analysis. EPMA of Fe spherules reveals variable concentrations of Ni, Co, P, and S. The Fe and Ni X-ray maps in Fig. 1 C and E were collected from a Ti-rich region of glass and illustrate that all μm-sized spherules contain Ni. No pure Fe spherules have been observed with a size greater than approximately 0.25 μm. Presumably, ilmenite was melted to form these Ti-rich zones, but no spherules or inclusions of ilmenite have been observed. The abundance of submicron Fe spherules becomes evident at high probe current using contrast expansion of the BSE image (Fig. 1D).

**Microanalysis Considerations:** In EPMA, the analytical volume is an energy-contoured region defined by electron scattering and X-ray production. Quantitative analysis algorithms treat the region as single phase, but significant errors result from processing data collected on multiphase volumes. EPMA of submicron inclusions in a matrix results in excitation of matrix elements by electron side-scattering through the inclusion. For analysis of Fe-rich spherules, the matrix elements Mg, Al, Si, and Ca are excited in this way. X-rays produced within the spherule can also excite X-rays in the matrix by secondary fluorescence. The Kα X-rays of Ni can efficiently fluoresce Fe, and those of Fe can fluoresce Ti and Ca from matrix glass. A reduction in accelerating voltage improves X-ray spatial resolution especially for Fe, Co, and Ni, which have relatively high excitation energies. Gopon et. al. [4] used low-voltage EPMA at 5 kV to analyze submicron Fe-Si spherules from Apollo 16 soils, but identified significant errors in measurement using the Fe Lα line. We follow an alternative approach due to the need to accurately analyze Fe, Co, and Ni using the Kα lines by using reduced accelerating voltage (e.g., 10 kV), coupled with simulation of electron and X-ray physics using Monte Carlo software to discriminate primary vs. secondary excitation of Fe-rich spherules and glass matrix.

Monte Carlo and EDS spectral simulations using DTSA-II [5] have been made for a model cubic inclusion embedded in a matrix, using a 0.5 μm cube of composition Fe 96.4, Ni 2.3, P 0.43 (wt.% element), and a representative agglutinate glass using EPMA data from 76503,7020. The results are shown in Fig. 2 for simulations at 10 kV vs. 15 kV. At 10 kV the analytical volume for Fe, Ni, and Co is within the 0.5 μm cube, and is a 2X reduction in scattering volume compared to 15 kV. These simulations were run with secondary fluorescence options enabled in order to more accurately match observed measurements. The simulated EDS spectra show a significant reduction in the matrix elements Mg, Al, Si, and Ca at 10 kV, and these elements are sensitive to spherule size as they are excited either by increasing kV or reducing the spherule size. These simulations thus provide an important analytical tool for measurement.

**Fe-rich Spherules in 76503,7020:** EPMA of Fe-rich spherules was performed at 10 kV on micron and submicron spherules using WDS and the mean atomic number (MAN) background calibration to provide consistent sensitivity and accuracy for P, S, and Co. Several areas of glass in the agglutinate with brighter BSE contrast reflect elevated Fe and Ti concentrations apparently due to melting of ilmenite grains. The Fe-rich spherules in these zones contain Ni, P, and Co as shown in Table 1, suggesting that the Fe-rich melt fractionates available siderophile elements when in the molten state. The apparent Al concentration of Fe spherules is a measure of matrix glass sampled during analysis, and inspection of data using a Fe vs. Al plot shows that using Al/Fe < 0.01 is a good screening tool for data selection. The composition of agglutinate glass was also measured to evaluate the average composition and the contribution of submicron spherules to sampling by the electron beam. Table 2 lists data for agglutinate glass

that contains submicron Fe spherules. The Fe content of the glass exhibits a larger standard deviation which is likely due to variable sampling of submicron Fe in the analytical volume.

**Conclusion:** This study establishes a combined method for EPMA of Fe spherules using Monte Carlo simulation to support interpretation of analyses. Fe spherules in 76503,7020 that are µm-sized contain Ni, Co, P, and S. We are currently pursuing EPMA of agglutinate glass containing smaller nm to submicron Fe spherules in order to compare the chemistry of spherules indirectly.

**References:**[1] Lucey, P., (2006) *New Views of the Moon*, pp 83-220, Mineralogical Society of America. [2] Keller et. al., (2001) *Lunar Planet. Sci.* **32**, #2097. [3] Jolliff et. al., (1996) *Met. Planet. Sci.* **31**, 116-145. [4] Gopon et. al., (2013) *Microsc. Microanal.* **19**, 1698-1708. [5] DTSA-II web site: http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html

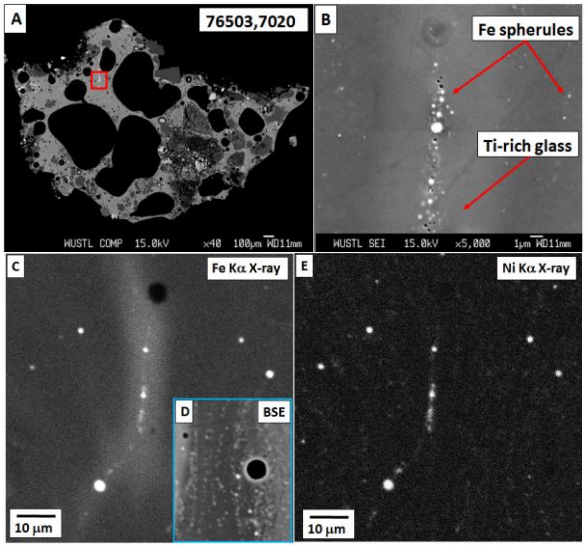


**Figure 1.** Agglutinate 76503,7020. **A.** BSE 40X image showing dark lithic and mineral clasts and light vesicular glass. Red square outlines BSE and X-ray map area. **B.** BSE 5000X image of Fe spherules in Ti-rich agglutinate glass. **C.** and **E.** Stage X-ray maps for Fe and Ni Kα indicating spherules contain Ni and also Co (not shown). **D.** BSE inset showing pervasive submicron Fe-spherules.

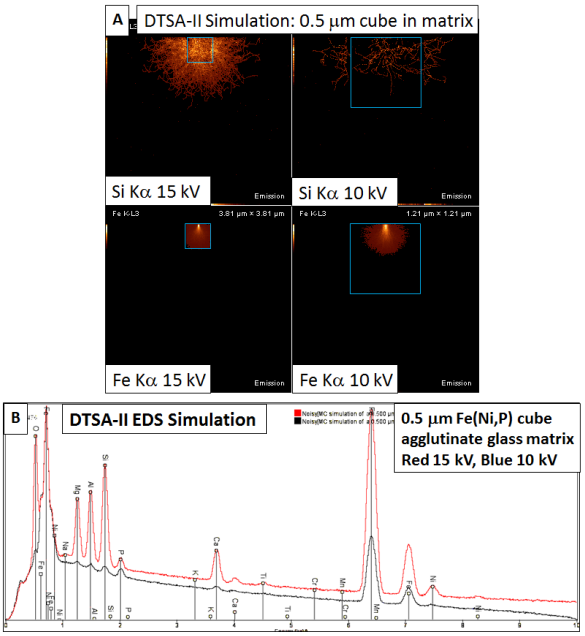


**Figure 2. A.** DTSA-II simulation of 0.5 µm cube (blue outline) in agglutinate glass matrix using EPMA data from 76503,7020. Scale of box is 3.81 µm for 15 kV and 1.21 µm for 10 kV. **B.** DTSA-II simulated EDS spectra. Analysis at 10 kV should excite elements Mg, Al, Si, and Ca only for spherules less than 0.5 µm diameter; these elements are a sensitive indicator of spherule size and depth.

**Table 1. EPMA Data Average, Wt% Element 76503,7020 Fe-rich spherules, n=15, 10 kV**

| Element | Avg | 1 SD |
|---|---|---|
| Fe | 86.0 | 8.2 |
| Ni | 5.0 | 2.7 |
| Co | 0.36 | 0.12 |
| P | 2.2 | 1.8 |
| S | 1.7 | 2.3 |

**Table 2. EPMA Data Average, Wt% Element 76503,7020 Agglutinate glass, n=260, 10 kV**

| Element | Avg | 1 SD | Element | Avg | 1 SD |
|---|---|---|---|---|---|
| Na | 0.19 | 0.02 | Ti | 0.89 | 0.09 |
| Mg | 7.98 | 0.33 | Cr | 0.14 | 0.02 |
| Al | 10.89 | 0.23 | Mn | 0.08 | 0.04 |
| Si | 20.16 | 0.21 | Fe | 6.29 | 0.40 |
| P | 0.02 | 0.01 | Co | BD | |
| S | 0.05 | 0.02 | Ni | BD | |
| K | 0.06 | 0.01 | O | 44.05 | |
| Ca | 8.71 | 0.15 | Total | 99.52 | |

**Table 1.** EPMA data average for Fe-rich spherules.
**Table 2.** EPMA data average for agglutinate glass. 1 SD is actual standard deviation of measured data in wt.% element. Analyses performed at 10 kV, 25 nA on Washington University JEOL JXA-8200.