NATIVE SILICON AND FE-SILICIDES FROM THE APOLLO 16 LUNAR REGOLITH: EXTREME REDUCTION, METAL-SILICATE IMMISCIBILITY, AND SHOCK MELTING. M. J. Spicuzza[1], J. W. Valley[1], J. Fournelle[1], J.M. Huberty[1], and A. Treiman[2]. [1]Dept of Geoscience, Univ. of Wisconsin, Madison, WI 53706-1692 (spicuzza@geology.wisc.edu), [2]Lunar and Planetary Institute, Houston TX.

Silicon in metallic form – dissolved in Fe-Ni metal, as silicide, or as Si^0 – is rare in solar system materials because its formation requires extremely reducing temperatures or oxidation states or both. Fe-Ni metal in carbonaceous chondrites can contain small proportions of Si [1], as does metal in shocked enstatite chondrites and aubrites [2]. Iron silicides are known from ureilite meteorites [3,4], where extreme reduction and shock heating are both significant. Silicides are also reported from the Stardust mission comet-return samples, both as indigenous phases [5] and as products secondary to dust capture [6]. Iron silicides have recently been reported in fragments of lunar regolith, and are inferred to represent deposits from vapor generated in impact events [7]. These lunar silicides include Fe_3Si (hapkeite), Fe_2Si, and FeSi [7]. Here, we report phases even richer in silicon – native silicon and iron silicides (with Fe:Si ratios ≤ 1) – in anorthositic fragments from the Apollo 16 regolith. Textures suggest that these materials formed as the result of silicate-metal immiscibility driven by high temperature shock melting.

Such silicon-rich phases are known in terrestrial samples, but are extremely rare. The best-documented occurrence is in a fulgurite [8], where extremely reducing conditions arose from the combination of organic carbon (from soil and plant roots) and the intense heating of a lightning strike; Native silicon coexisting with Fe-silicides (FeSi, Fe_3Si_7) was identified. Fe-silicides are found in other fulgurites [9]. Other reports of native silicon include volcanic sublimates [10], inclusions in moissanite from kimberlite [11], inclusions in terrestrial Fe-Ni metal [12] (likely to be silicides) and detrital grains in heavy sands [13] (possibly human artifacts).

Samples and Methods. During a search for zircon in the >20µm fraction of Apollo 16 regolith sample 61501,22, two grains (A6-8 and A6-7) were found to contain native silicon. Chemical analyses for A6-8 were obtained at the University of Wisconsin by electron microprobe (Cameca SX51). SEM, BSE, forescatter and EBSD analyses were obtained using a Hitachi 3400N.

Petrography: Although lunar grain A6-8 is relatively small (~90 µm diameter) it displays great complexity (Fig. 1). An EPMA traverse (A-B) across the major features of this grain (numbered #1-#6 in Fig 1A) is shown in Figure 2. The sample is cut by a Si-rich vein-like feature (#3) that is bright in BSE. In the upper portion of Fig. 1A, the relatively uniform grey phase (#1) cut by a few cracks is a single crystal of anorthite (An 97). The lower portion of the image (#4,6) is comprised primarily of interlocking crystallites of more sodic plagioclase (An 80-84, darker grey) with abundant native silicon and Fe-rich grains. The largest Fe-rich grains have been identified as Fe-silicides, however most were too small to confidently characterize. Semi-quantitative EDS/BSE analyses (9kV) of Fe-silicides suggest different stoichiometries, including ~Fe_3Si_7 ($Fe_{28}Si_{71}$) ~$FeSi_2$ ($Fe_{32}P_{02}Si_{66}$) and ~FeSi ($Fe_{44}Si_{56}$). Variable Ni, Ti, and P contents are also observed. Domains of native silicon (quantitative analysis by EPMA >97% Si, up to 4µm maximum dia.) are slightly less bright in BSE, and commonly found in direct contact with Fe-rich phases.

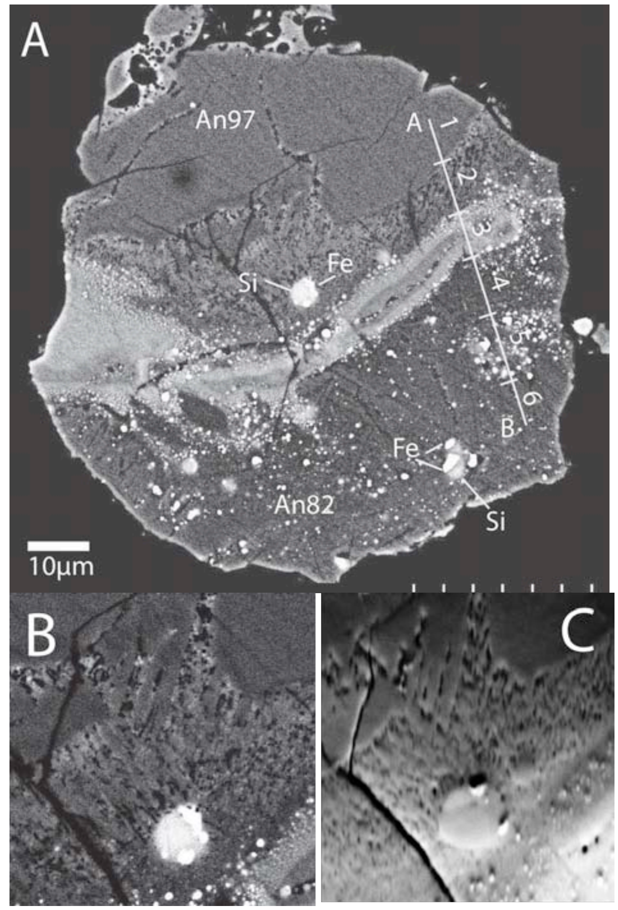

Figure 1: Apollo 16 Lunar grain A6-8. 1A (BSE) shows the entire grain and the locations of the largest native Si grains and associated Fe-silicides [Fe]. [An] is anorthite. Line A-B is analytical traverse in Fig.2. Numbers 1-6 designate discrete zones referred to in the text. 1B is a magnified [BSE] image of central region including Si (4µm across) and associated Fe-silicides. 1C is a forescatter image of the same region.

Between the single crystal of An 97 (#1) and the crosscutting feature (#3) is a 5-10 µm wide domain (#2) that appears mottled in BSE images. The silicate portion of this domain is amorphous by EBSD and contains less Ca and Al and more Si (and Na) than the adjacent anorthite crystal. A 4µm grain of native silicon in this domain has Fe-silicide grains along its margin (Fig. 1B and 1C).

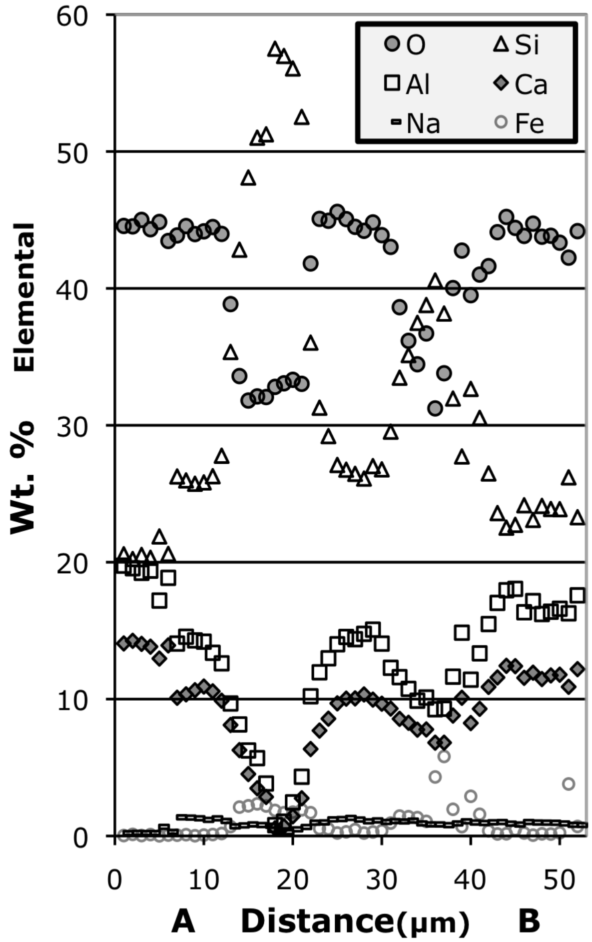

Figure 2: EPMA elemental analyses in traverse of A6-8 (A to B, Fig. 1). Steps are 1µm.

The crosscutting feature (#3) is clearly zoned in the BSE image (Fig. 1a) and Fe-rich grains are concentrated and decorate the margin on both sides. The EPMA data for the center of this feature are rich in silicon (~55wt%) and low in oxygen (33wt%), with less than 6 wt% Ca and Al. If crystalline, as minerals, these data could be represented by a small percentage of anorthite and subequal proportions of SiO_2 and native silicon. This region is too fine-grained to identify the phases using the techniques we have employed to date (SEM, EBSD, EPMA), but we infer that this region likely consists of a mixture or sub-micron intergrowth of phases which include native silicon.

A separate silicon-rich domain (#5) occurs within the interlocking crystallites of An 82 plagioclase (#4,6). Fine-grained native silicon and abundant, small Fe-rich grains are present in this domain.

A second ~60 µm regolith grain (A6-7) contains native silicon grains (up to 3µm) and submicron Fe-rich grains; these phases yield EDS spectra and EBSD patterns consistent with native silicon and Fe-silicides. Quantitative analyses (EPMA) were not performed for this sample.

Discussion. Examples of native silicon in planetary materials (rocks and meteorites) are rare. In particular, high temperatures and extremely low fO_2 conditions on the Si-SiO_2 buffer were proposed for the genesis of native silicon and Fe-silicides in fulgurite [8].

Shock melting experiments (in vacuum) [14] demonstrate metal-silicate immiscibility can be induced in basaltic compositions (1400-1700°C, up to 6 GPa). These experiments produced both a Fe-poor silicate glass, and metallic silicon and iron globules. The fO_2 conditions inferred from these experiments approached 10^{-17} bar, and the proposed reduction mechanism was the production and loss of O_2 gas.

We interpret the presence of native silicon associated with Fe-silicides in the lunar regolith sample A6-8 as the result of shock melting on the Moon. The identification of native silicon is verified by EPMA and EBSD of crystals up to 4 µm dia. BSE imaging and EPMA analyses indicate at least two distinct Fe-silicide phases are present in A6-8. In addition, we suggest that the crystallites of slightly more sodic plagioclase that host silicon and Fe-rich phases (#4-6 in Fig. 1A) are direct evidence for silicate-metal immiscibility, as is the amorphous domain (#2) above the high-Si cross-cutting feature (#3). The phases present in the high-Si crosscutting feature have not been identified yet, but the chemical composition indicates they are related to the shock-melting event and suggests elemental mobility.

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