

VOLCANIC COATINGS ON PICRITIC APOLLO 17 GLASSES: SUBMICROMETER-DEPOSITS OF FE-, CR-METAL. D. S. McKay¹, S. J. Wentworth², K. L. Thomas-Keprta², K. Ross², and S. J. Clemett², ¹NASA Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058 (David.S.McKay@nasa.gov), ²ESC Group, Mail Code JE23, NASA/JSC, 2101 NASA Pkwy, Houston, TX, 77058.

Introduction: The purposes of our ongoing investigations of Apollo 15 green [1] and Apollo 17 orange and black volcanic glasses are threefold: first, to increase our understanding of the volcanic origin of the glasses; second, to determine the nature of the coating materials deposited on the glasses during their cooling in the volcanic environment; and, third, to help determine the nature of the gases involved in the volcanic fire-fountaining that occurred at ~3.5 Ga on the moon. We are continuing studies of coatings on volcanic glasses using analytical techniques not available when these glasses were originally studied [2, 3]; these include high-resolution FE-TEM and X-ray mapping, along with other highly detailed methods including TEM electron diffraction analysis.

Initial studies of Apollo 15 green volcanic glasses using the techniques described above [1] revealed for the first time the presence of areas containing distinct layering of volcanic surface deposits. S was associated with some of the inner layer of metallic Fe but was absent from the outer layer. Zn was associated with S in some places in the inner layer.

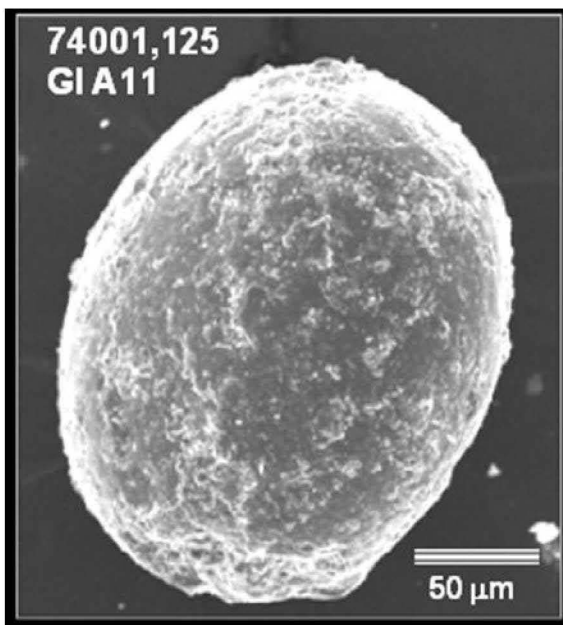


Figure 1: SEM image of typical Ap17 black volcanic bead; coatings evident on surface at this low resolution; lack of exposure at lunar surface precludes space weathering origin for coatings.

An example of a typical spherule used for this study is shown in Fig. 1. It is a black (quench-crystallized)

bead from near the bottom of the 74001/2 double drive tube; black beads such as this one are essentially identical in composition to the orange (uncrystallized) beads of the 74001/2 core.

Results: The most distinctive feature identified in ultramicrotome sections of the 74001,125 bead is the presence of thin patches of Fe-Cr metal deposited directly onto the exterior surface of the bead (Figs. 2a, 2b). The EDS spectrum in Fig. 2c demonstrates the lack of O in the deposit. The height of the Cr peak is consistent with the presence of a few weight percent of Cr within the metal. The electron diffraction pattern and crystallographic data given in Fig. 2d confirm the identification of the deposits as Fe-Cr metal. The X-ray maps in Fig. 2e show that the metal was deposited directly on the spherule surface (note: the Al layer is the conductive coating added to the bead for a previous SEM study of volcanic glass coatings [5]).

Fe metal containing Cr found on lunar or other extraterrestrial samples is typically considered to be stainless steel contamination added during sample handling; such contaminants are commonly found as large (relative to the current study) fragments smeared along sharp edges or onto freshly fractured surfaces during sample preparation.

Conclusions: To the best of our knowledge, the Cr-bearing metallic Fe deposits described here are the first ever found in natural geological samples. According to [4], Cr is the most easily oxidized element present in stainless steel alloys; i.e., it is stable at the lowest oxygen partial pressures (i.e., $f_{O_2} \approx -27$ for the reaction $\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$ at 800 °C). [4] also states that oxygen partial pressures can be controlled by adjusting proportions of CO and H₂ relative to more oxidizing gases. These two reducing gases, perhaps accompanied by others, were probably important components of the vapors driving the fire fountain eruptions that produced the Ap17 orange/black glasses. It is plausible that local micro-environments could have developed that allowed precipitation of Fe-Cr metal onto spherule surfaces during cooling of the volcanic plume.

References: [1] Wentworth S. J. *et al.* (2008) *LPS XXXIX*, Abs. # 2529. [2] Clanton U. S. *et al.* (1978) *Proc. LPSC 9th*, 1945. [3] McKay D. S. *et al.* (1973) *Proc. LSC 5th*, 225. [4] <http://www.tubenet.org.uk/technical/linde.shtml>. [5] McKay D. S. and Wentworth S. J. (1993) *LPS XXIV*, 961.

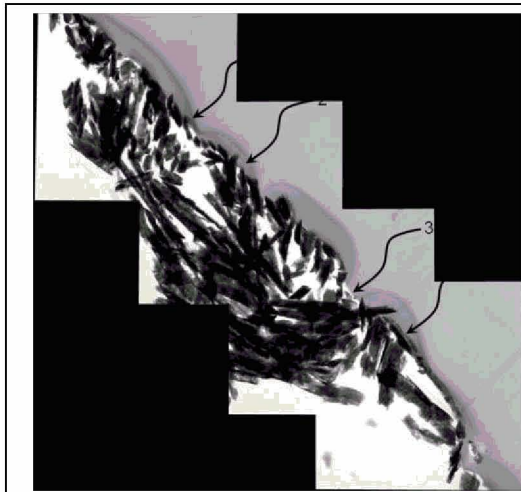


Figure 2a: Composite TEM micrograph showing four areas with Fe-Cr metal deposits. Black = shards of glass/crystals; gray (right) = epoxy; light areas (left) = plucked.

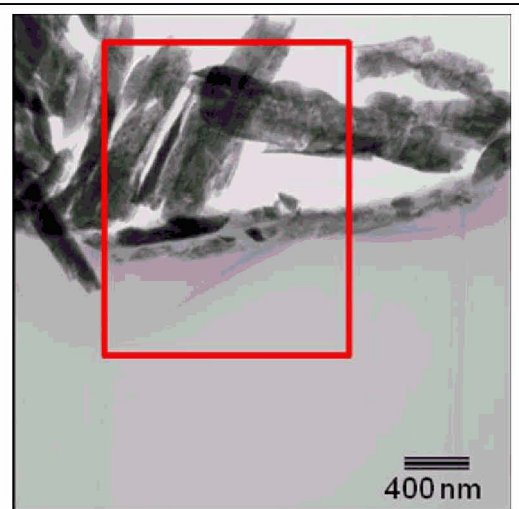


Figure 2b: TEM image of Region 4 (Fig. 2a) but with orientation $\sim +90$ degrees; lower portion = epoxy; red box shows area of X-ray maps, Fig. 2e.

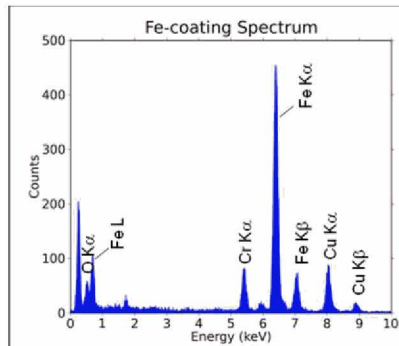
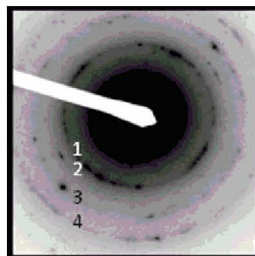


Fig. 2c: TEM-EDS of metal in Region 4; Cu is background from TEM grid.



Fe, Cr metal*	Fe, Cr metal*	74001,125
d(nm)	hkl	d(nm)
0.202	110	1. 0.21
0.166	111	2. 0.17
0.143	200	3. 0.15
0.117	211	4. 0.12

*PDF411466

Fig. 2d: Left: Electron diffraction pattern of Region 4 metal; right: d-spacings as measured and with comparison to published values.

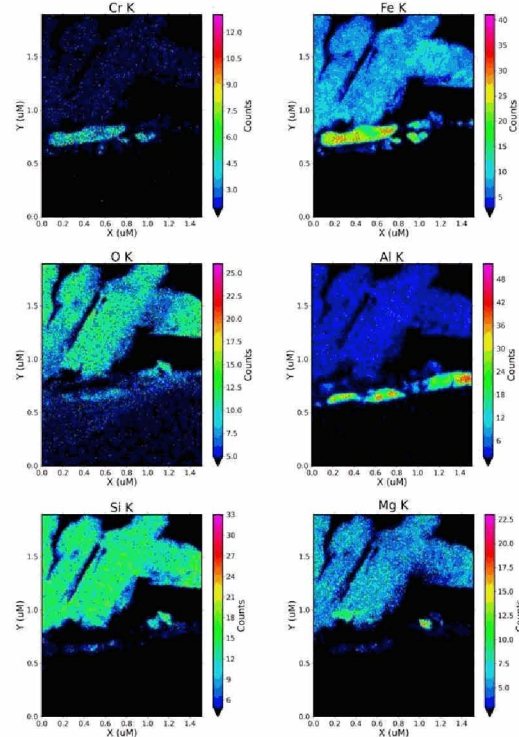


Fig 2e: FE-TEM X-ray maps of Region 4; scale not same as shown in Fig. 2b; clearly, deposit is Fe-Cr metal; Al is conductive SEM coating.