PETROLOGY AND GEOCHEMISTRY OF LUNAR REGOLITH PARTICLE 65903,16-7: EVIDENCE FOR EXTREME REDUCTION AND OXIDATION. R. A. Zeigler B. L. Jolliff, R. L. Korotev, D. T. Kremser and L. A. Haskin, Dept. Earth and Planetary Sciences, Washington Univ., 1 Brookings Drive, Campus Box 1169, St. Louis, MO 63130 (zeigler@levee.wustl.edu).

Introduction: Sample 65903,16-7 is a 16.7 mg rock fragment identified among the 2–4 mm size fraction of Apollo 16 rake sample 65900. In composition the particle resembles the KREEP-bearing impact melt breccias of group 1M [1]. It differs from such breccias, and known lunar samples in general, in several important ways. It contains abnormally high concentrations of alkali and siderophile elements (Table 1), the mafic silicates have unusually low Fe/Mg and Fe/Mn ratios, and there are no phosphates but an abundance of phosphides. In contrast to these indicators of stark reduction, the particle contains secondary carbonate and iron oxyhydroxide in veins and surface deposits. Here, we report on the petrology and geochemistry of the particle as a whole, with an emphasis on the unusual geochemistry and redox history. The reduction of Fe and P, but not Mn, constrains the fO_2 of the sample during reduction to a maximum of ~$10^{-12.5}$. The carbonate and iron oxyhydroxide are described elsewhere [2].

Methods: The chemical analysis reported here (Table 1) was done by instrumental neutron activation analysis (INAA) of the entire rock fragment [3]. Mineral identification and compositions were determined using reflected light microscopy and a JEOL 733 electron microprobe on a polished thick section made from ~1/3 of the neutron-irradiated particle.

Petrography: The sample is a slightly vesicular impact melt breccia composed of anorthite clasts, forsteritic olivine grains, and opaque phases surrounded by a very fine-grained matrix (<30 µm) of plagioclase, augite, and glass (Fig. 1a-c). The matrix has a mode of 60% plagioclase, 24% augite, 16% glass.

Na_2O	0.901	**Cr**	1337	**Zr**	570	**Sm**	18.7	**Hf**	17.1
K_2O	1.4	**Co**	111	**Cs**	1.1	**Eu**	1.54	**Ir**	63.8
CaO	10.6	**Ni**	2740	**Ba**	383	**Tb**	3.68	**Au**	63.0
FeO	7.28	**Rb**	55.0	**La**	41.4	**Yb**	12.5	**Th**	6.45
Sc	10.8	**Sr**	174	**Ce**	109	**Lu**	1.7	**U**	2.41

Table 1: INAA derived chemistry for sample 65903,16-7. Oxides are in wt %, all other elements are in ppm, except Ir and Au (ppb).

The plagioclase clasts range in size from 0.02–0.5 mm, are of typical lunar highlands composition ($An_{96.2}Ab_{3.8}Or_{<0.01}$; Fig. 2a), are rounded, and are rimmed by more sodic plagioclase ($An_{81}Ab_{15}Or_4$), which is slightly less sodic than the matrix plagioclase. One rounded clast (~0.1 mm) of low-Ca pyroxene ($En_{65}Wo_2Fs_{33}$; Fig. 2b) is also observed. The olivine (Fo_{91}; Fig. 2c) typically forms elongated grains (up to 0.5 mm), with matrix plagioclase commonly found as inclusions. The matrix consists of randomly oriented $An_{77}Ab_{18}Or_5$ plagioclase laths, magnesian augite ($En_{63}Wo_{31}Fs_6$), and a glass with approximately ternary (but relatively mafic) feldspar composition. The opaque grains (up to ~0.1 mm) are intergrowths of schreibersite [$(Fe,Ni)_3P$] and Fe,Ni metal grains, with minor amounts of associated troilite (FeS) grains. Modally, opaque grains are ~4% of the sample. The schreibersite:Fe,Ni metal ratio for the bulk sample is abnormally high (~2:1), although the ratio varies among individual metal grains. Calcic siderite [$(Fe_{0.81}Mg_{0.05}Mn_{0.00}Ca_{0.14})\ CO_3$] commonly rimmed by goethite (α-FeOOH) occurs in the sample as grains on the surface of the particle and filling in veins and vesicles within the particle [2].

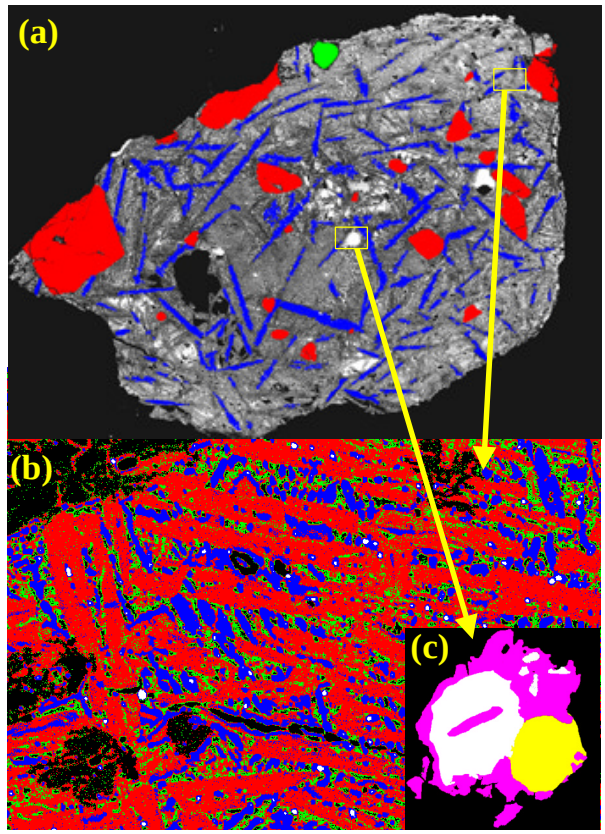

Figure 1: (a) False color back-scattered electron image (FCBSE) of sample 65903,16-7. Field of view is ~2 mm. Red = plagioclase clasts, blue = olivine, green = low-Ca pyroxene clast, white = opaques, and gray = matrix. **(b)** FCBSE of matrix. Field of view is ~0.1 mm. Red = plagioclase, blue = augite, green = glass, white = opaques, black = olivine. **(c)** FCBSE of an opaque grain. Field of view is ~70 µm. Pink = schreibersite, white = metal, yellow = troilite.

Geochemistry: The major-element composition of the bulk particle was determined by modal recombination and mixing-model analysis using average mineral compositions (Table 2). The resulting bulk chemistry closely matches the INAA values, with the exception of Na and K which are underestimated by a factor of 1.2 and 3.3 respectively. Overall, the particle is exceptionally magnesian, with a bulk Mg' of 83, and silicate Mg' of 92 (Mg' = molar Mg/(Fe + Mg)*100).

Incompatible trace-element (ITE) concentrations have KREEP-like interelement ratios, but absolute con-

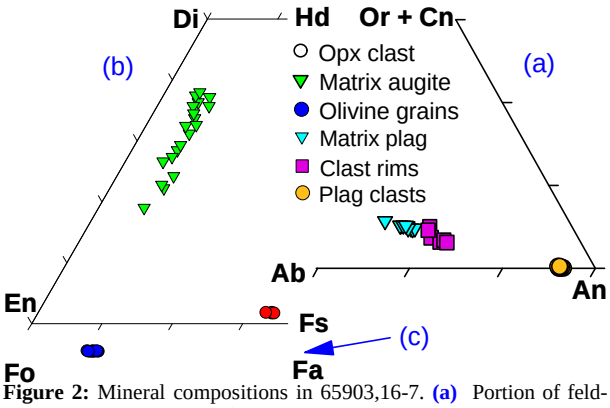

Figure 2: Mineral compositions in 65903,16-7. **(a)** Portion of feldspar ternary. **(b)** Portion of pyroxene quadrilateral. **(c)** Olivine compositions. Each tick = 10 units.

centrations about 1/3 those of high-K KREEP [4]. Notably, U is enriched by a factor of 1.4 in the bulk particle relative to other ITE, and the particle has high concentrations of alkali elements (but not Ba), particularly Rb, which is enriched by a factor of 5 when compared to average group-1M IMB composition. To a first approximation the composition, the particle corresponds to a mixture of 81% average group 1M IMB [1], 15% ferroan anorthosite [5], and 4% average 65903,16-7 metal (Table 2). Because of its small size, the particle may be an unrepresentative sample of a group 1M IMB; high U/ITE ratios and high alkali element ratios have not previously been reported in small subsamples of group 1M IMB, however [1].

Oxidation: The presence of siderite and goethite indicates that the sample has been in contact with an oxidizing fluid after (and unrelated to) the earlier reducing event. In sample 65903,16-7 alkali-rich feldspar can not account for all of the excess alkali elements observed. Trace amounts of K-feldspar in the matrix might account for the excess K, Rb, and Cs; we note, however, that Ba is not similarly enriched. Other alkali rich components on the Moon (e.g., felsite, granite) have distinctive ITE patterns not observed in the sample [6]. The excess alkalis may be a result of deposition of soluble alkali minerals by the same fluid that formed the siderite. Excess U may also be associated with secondary enrichment because, unlike most ITE, U is easily oxidized from U^{4+} to more soluble U^{6+}. Excess U could be present as an undetected nanophase uranium mineral or as a trace constituent in other fluid deposited minerals, particularly goethite, which contains trace amounts of Pb (~0.2 wt % as PbO).

Reduction: Based on modal recombination, the sample has approximately 0.5 wt % P expressed as P_2O_5. Assuming that P behaves like the other ITE, then the silicate portion of the sample should have a minimum of 0.3 wt % P_2O_5 (~1/3 the P concentration in hi K-KREEP). Over 98% of the P is concentrated in the schreibersite, however. Furthermore, the polished section contained only one ~4 µm whitlockite grain, suggesting that phosphate has been reduced to by the event that produced the impact melt.

Lunar Fe:Mn ratios for whole rock compositions are commonly ~75 [6]. Although the Fe:Mn ratio of 65903, 16-7 is 64, the average Fe:Mn ratios in the mafic silicates are these: 30 (olivine), 37 (low-Ca pyroxene), and 14 (augite). These values are considerably lower than typical Fe:Mn ratios of lunar pyroxene and olivine, which are 45-75 and 75-120, respectively [6]. These differences are consistent with reduction of Fe^{2+} to Fe^0 during the impact-melting event.

The low Fe:Mn ratios of the olivine and augite suggest that Fe^{2+} was reduced to Fe^0 without Mn^{2+} being reduced to Mn^0. The almost complete lack of phosphate coupled with the abundance of phosphide suggests that P^{5+} was extensively reduced to P^{3-}. The fO_2 ranges associated with reduction of Fe and P at 1150–1200°C are ~$10^{11.5–12.8}$ and ~$10^{-12.5–13.6}$ respectively (the fO_2 for the reduction of Mn is ~10^{20} [7,8]). Because Fe^{2+} is not completely reduced, the fO_2 during crystallization was probably not far below the level required for P reduction The nearly constant Fe:Mn ratio in the olivine and augite and the nearly complete lack of phosphate indicate that the reduction occurred while the particle was still molten from the impact event. Furthermore, rapid cooling indicated by the fine-grained matrix, precludes later reduction and diffusion of P and Fe.

References: [1] Korotev R.L. (1994) *GCA, 58,* 3931-3969. [2] Zeigler R.A. et al. (2001) *LPS XXXII.* [3] Korotev R.L. et al. (1997) *LPS XXVII,* 753-754. [4] Warren P.H. (1989) *LPI Tech. Rep. 89-03* 149-153. [5] Korotev R.L. (2000) *JGR 105,* 4317-4345. [6] Papike J.J. et al. (1998) *Planetary Materials,* 5:1-5:235 [7] Friel J.J. and Goldstein J.I. (1976) *PLPSC 7,* 791-806. [8] Huebner S.J, (1969) *Am. Min. 54,* 457-481.

Acknowledgments: This work was sponsored by NASA grant NAG5-4172 (LAH). We would like to thank Jeff Gillis for his help with the image analysis.

	Met	Shr	Plm	Aug	Gls	Mat	Oli	Plc	BC	INAA
(n)	6	5	10	14	8	NA	8	9	NA	NA
SiO_2	n.a.	n.a.	51.6	50.6	66.1	53.7	41.0	43.8	46.8	n.a.
TiO_2	n.a.	n.a.	0.10	2.41	2.13	0.98	0.08	bdl	0.57	n.a.
Al_2O_3	n.a.	n.a.	30.4	6.2	16.1	22.3	0.1	36.3	17.6	n.a.
Cr_2O_3	n.a.	n.a.	n.a.	1.36	0.17	0.36	n.a.	n.a.	0.20	0.195
FeO*	96.0	75.8	0.4	3.3	1.7	1.3	8.4	0.2	7.3	7.28
MnO	n.a.	n.a.	bdl	0.24	0.05	0.07	0.28	bdl	0.12	n.a.
MgO	n.a.	n.a.	0.6	18.4	3.8	5.4	49.6	0.1	15.9	n.a.
CaO	n.a.	n.a.	15.0	17.8	6.0	14.2	0.2	19.3	10.7	10.6
Na_2O	n.a.	n.a.	1.89	0.14	0.75	1.29	n.a.	0.41	0.8	0.90
K_2O	n.a.	n.a.	0.78	0.00	1.87	0.77	n.a.	bdl	0.43	1.40
P_2O_5*	0.25	15.0	n.a.	0.11	0.14	0.05	n.a.	n.a.	0.51	n.a.
Ni	3.24	8.23	n.a.	n.a.	n.a.	n.a.	bdl	n.a.	0.273	0.274
Co	0.44	0.19	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.011	0.011
Sum	99.9	99.1	100.8	100.5	98.8	100.4	99.6	100.1	100.1	NA
%	1.3	2.8	33.5	13.5	8.8	55.8	25.9	14.2	100	NA
Mg'	NA	NA	72.1	90.9	79.6	77.9	93.2	46.9	83.4	NA
Fe:Mn	NA	NA	NA	13.8	36.3	21.4	30.1	NA	62.2	NA

Table 2: Average mineral and bulk particle major element compositions. Met = Fe,Ni metal, Shr = Schreibersite, Plm = matrix plagioclase, Aug = augite, Gls = glass, Mat = combined matrix, Oli = olivine, Plc = plagioclase clasts, BC = bulk composition, (n) = number of analyses averaged, % = modal percentage, Fe:Mn = ratio of Fe:Mn, n.a. = not analyzed, NA = not applicable, bdl = below detection limit. *FeO and P_2O_5 are reported as Fe and P for metal and schreibersite.