

APOLLO 14 HIGH-Ti PICRITIC GLASS: OXIDATION/REDUCTION BY CONDENSATION OF ALKALI METALS. J. W. Delano, Department of Earth and Atmospheric Sciences, University at Albany (SUNY), Albany, NY 12222 jdelano@atmos.albany.edu

Introduction: The role of graphite (C) in oxidation-reduction reactions during the ascent and eruption of picritic magmas on the Moon has been well-documented [e.g., 1-5], especially in the Apollo 17 orange glass (74220). The occurrence of sublimates on the surfaces of picritic glasses is also well-known [e.g., 6-9]. Electron microprobe analyses of the high-Ti (~16 wt% TiO₂), black (microcrystalline) picritic glasses from Apollo 14 show evidence for addition of alkali metals (i.e., Na, K) with associated reduction of FeO to metallic Fe.

Results: Electron microprobe analyses (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, K) were acquired on 45 picritic black spherules in polished thin-sections of regolith breccias, 14301 and 14307. All of these samples were microcrystalline droplets of quenched picritic melt. In several spherules, a metallic Fe (Fe_{0.996}Ni_{0.004}) phase was present (Figure 1).

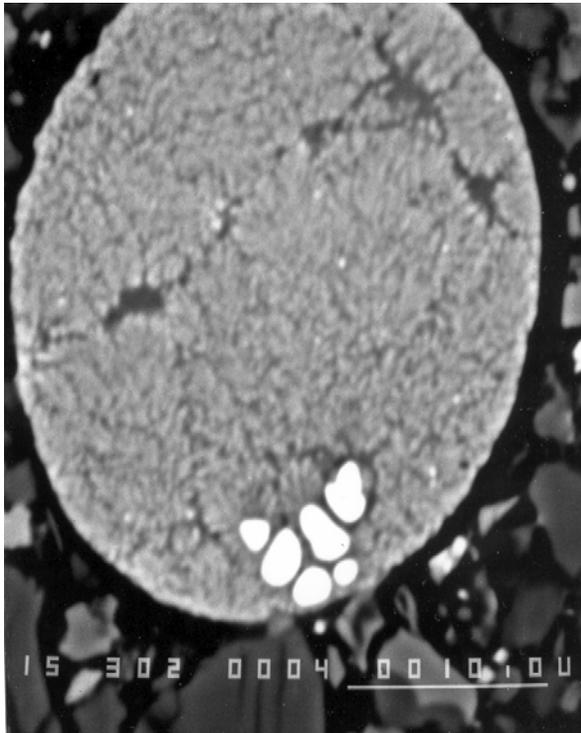


Figure 1: Backscattered electron image of picritic spherule with 16.4 wt% TiO₂ in regolith breccia 14301,17 showing the microcrystalline texture and metallic Fe phase (white portions at lower edge of spherule). The spherule has a horizontal dimension of 26 μ m. The composition of this spherule is FeO=18.3 mole % and (Na₂O + K₂O)= 3.4 mole % (refer to Fig-

ure 3). The scale bar in the lower right corner of the image is 10 μ m.

The principal chemical variations among these 45 samples were in their abundances of Fe, Na, and K. The linear correlation coefficient between Na and K was +0.86, while the correlation coefficient between Fe and each of the alkali metals was -0.85. Analyses of the picritic droplets purposefully avoided the metallic phase in order to determine the composition of the melt phase. Due to the microcrystalline nature of the droplets, multiple analyses were acquired on each spherule and then averaged to obtain an estimate of the melt composition.

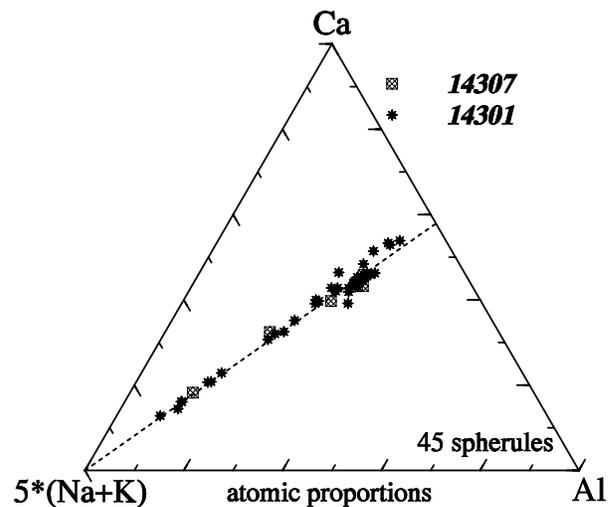


Figure 2: Atomic proportions of refractory lithophile elements, Ca and Al, and volatile alkali metals, Na and K, are plotted for these high-Ti picritic spherules. Note that the Ca/Al shows negligible variation, but significant variations in the relative abundances of the alkali metals.

The addition of Na and K was not associated with any correlated effect on the abundances of either plagioclase-associated elements, specifically Ca and Al (Figure 2) or KREEP-associated elements (e.g., P), as might be expected if assimilation of crustal components had occurred during magmatic ascent [10]. Figure 3 shows an inverse relationship between alkali addition and FeO reduction. Figure 3 also shows that the majority of the spherules with low alkali abundances (mole% Na₂O+K₂O \leq 0.5%) vary in FeO abundances from 20-22 mole %. No metallic phase was

observed in backscattered electron images within any of those low-alkali spherules.

Interpretation: The microcrystalline texture of these picritic spherules indicates that they had a history of being suspended in the hot volcanic plume that resulted in their actual cooling rate being less than the critical cooling rate [11,12]. During this prolonged suspension in a hot, vapor plume, the molten droplets exchanged volatiles to-and-from the vapor [10]. Figure 3 suggests that the volatile alkalis, which presumably had been exsolved from the melt as Na_2O and K_2O , had undergone reduction in the plume, and were subsequently recondensed onto some spherules in the metallic form. These recondensed alkali metals caused reduction of FeO (to metallic Fe) in the silicate melt droplets (Figures 1, 3) and oxidation of the alkali metals (to Na_2O and K_2O). The dashed lines in Figure 3 show the expected trend in abundances caused by this redox reaction, which is observed in the smallest spherules only ($<30\mu\text{m}$ diameter spherules). These smaller spherules apparently remained suspended in the hot volcanic plume for times sufficient to cause a uniform distribution of alkalis within the spherules and for the metallic Fe to nucleate into blobs $\sim 5\mu\text{m}$ in diameter (Figure 1). The apparent correlation of this redox reaction with the size of the spherules suggests that the smallest spherules remained suspended in the hot volcanic plume for longer times than the larger spherules.

The range of FeO abundances among the low alkali spherules (Figure 3) suggests that these portions of the high-Ti picritic magma had undergone reduction of $\leq 10\%$ of the total FeO to metallic Fe . Since this metallic Fe is not visible in backscattered electron images of the low-alkali spherules analyzed in this study, this redox reaction may have occurred by graphite oxidation prior to eruption, and the metallic Fe phase removed from that portion of the magma represented by the spherules contained in regolith breccias 14301 and 14307. If correct, this redox reaction is similar to that documented in other varieties of lunar picritic magma [1-5].

Summary: Two redox reactions occurred during the formation of the Apollo 14, high-Ti picritic magma. The first involved oxidation of C (graphite) and reduction of FeO prior to eruption. The second occurred while melt droplets were suspended in the hot volcanic plume (i.e., volatilization of alkali oxides, reduction of alkalis in plume, and subsequent recondensation of alkali metals onto a portion of the high-Ti picritic spherules).

References: [1] Sato M. (1979) *PLPSC 10th*, 311-325. [2] Fogel R. A. and Rutherford M. J. (1995) *GCA*, 59, 201-215. [3] Weitz C. M. et al. (1997) *GCA*, 61, 2765-2775. [4] Nicholis M. G. and Rutherford M. J. (2004) *LPI Contrib. 1203*, 48. [5] Shearer C. A. and Papike J. J. (2004) *LPI Contrib. 1203*, 58. [6] Meyer C., Jr. et al. (1979) *PLPSC 10th*, 327-340. [7] Chou C.-L. et al. (1975) *PLSC 6th*, 1701-1727. [8] Cirlin E. H. and Housley R. M. (1979) *PLPSC 10th*, 341-354. [9] Wasson J. T. et al. (1976) *PLSC 7th*, 1583-1595. [10] Shearer C. K. et al. (1990) *GCA*, 54, 851-867. [11] Arndt J. and von Engelhardt W. (1987) *PLPSC 17th*, E372-E376. [12] Heiken G. and McKay D. S. (1977) *PLPSC 8th*, 3243-3255.

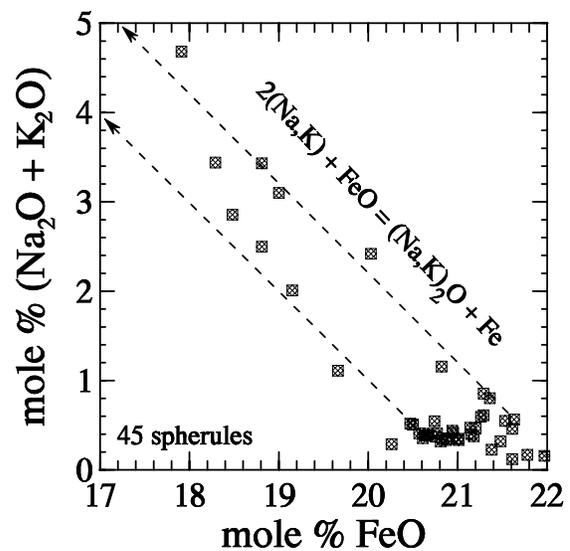


Figure 3: The molar abundance of the alkali metal oxides, Na_2O and K_2O , varies inversely with the abundance of molar FeO in the melt. The dashed lines show the expected variation caused by the oxidation-reduction reaction involving the addition of alkalis in metallic form to the melt with subsequent reduction of FeO .