A15 GREEN GLASS VOLATILES AND OXIDATION STATE  M.J. Rutherford, Dept. of
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Introduction:  A15 green glasses are widely accepted as products of lunar fire-fountain
volcanism because they are phenocryst-free, more primitive than known low-Ti lunar basalts, and
because they are variously coated with what appears to be volcanic gas condensates including S,
Cl, F, and various volatile metals [1, 2, 3, 4]. The origin of the picritic green glass melts is still not
well known, however [5], and the driving force for the fire-fountaining is still in question [6,7]. This
paper primarily deals with the eruption process because this is the last process to effect the
texture and composition of the green glass with the possible exception of post-depositional
modifications [7] which can be readily identified. In this project we have studied the green glass
samples with a view toward identifying the composition and abundance of the gas present during
the fire-fountaining event and the oxidation state of the magma before and after the eruption.
The approach used is a combination of microprobe analyses and thermodynamic and diffusion
profile analysis. No relics of S diffusion-out profiles are present in the green glass in contrast to
what is predicted by the diffusion data and cooling rates, but there are significant S composition
variations; these are attributed to differences that existed at fragmentation. Ni-rich metal grains in
the outer margins of glass spherules fix the log fO2 of the melt at -11.05 at 1350 °C.

In assessing the previous work on A15 green glass, we note the following well
documented and potentially important results: (1) glass particles range from ~10 µm to about 1
mm and are well rounded, usually spherical, but ellipsoid, rod, dumbbell and rain-drop shapes are
also present; fragments are common [8]. (2) Smaller grains averaging 0.094 mm in diameter are
predominantly vitric, larger particles (average diameter = 0.22 mm) are generally partially devitrified
with dendritic lattice olivine [9]. Based on experiments, these devitrification textures are
interpreted to indicate a 1400 to 1000 °C cooling rate of 1 to possibly 10 °C/sec [9]. (3)
Individual glass particles are homogenous in terms of major and trace elements [2, 5] but different
compositional groups have been identified and are interpreted to represent batches of magma
[10]. (4) The gas phase which drove the eruptions and fragmentation of the A15 green glass
magma is considered to have included C, O, S, Cl and F based on the surface coatings, but
thermodynamic calculations [11] indicate that CO is the only volumetrically important species.

In order to determine what gas phase was present in the A15 lunar green glass fire
fountains, we have obtained high precision composition profiles across different types of glass
particles for the volatile elements. Composition profiles have also been determined across and
away from Fe-Ni metal grains found in some spherules. These profiles are compared to those
which would theoretically have been produced in different eruption environments.

Methods and Results:

S and Cl theoretical:  Calculations using the latest diffusion data for CO3±, S and Cl [7]
show that 0.400 mm diameter green glass spherules cooling at 1 to 10 °C/sec as indicated by
devitrification textures [9] should still have significant fractions (~ 0.9) of the original S
concentration remaining in the core of the spherule, but will have essentially lost all CO3± and Cl
by diffusion.

S and Cl measured:  Electron microprobe traverses across green glass spherules were
done using 300 sec counting times, 15 K and 30 na. The results show that the S content of
individual grains ranges from 80 to 250 ±10 ppm, and is somewhat variable within a particle, but
no remnants of a core to rim diffusion gradient are detectable. A similar situation was observed for
Cl (Fig. 1), although the concentrations are generally much lower (0 to 150 ppm). In many of the
spherules analyzed there were statistically real variations in the S content (50 ppm), however; and in
one spherule studied in detail, there is a 20-40 mm wide annular ring of low S contents (90 vs.150
ppm S) which extends more than one-quarter way around the spherule (Fig. 1). This annular low
in S is not the intersection of diffusion-in and diffusion-out profiles as shown by the remainder of
the concentration profile. None of the major elements reflect this variation in the glass S content.

Ni-Fe metal grains in the green glass:  One of the ten green glass spherules separated
from 15427,42 for sectioning and FTIR analysis and fifteen spherules exposed in 1.7 cm² PTS's
of 15426, and 15427, have been observed to contain small (1-10 µm) grains of metal. These
metal grains and the surrounding glass have been analysed for major elements and Ni. Only two
of the grains were big enough for quantitative analysis of the metal (Ni = 68 wt %, Fe = 31.5 wt %, and Co = 0.5 wt %), but traverses across the grains indicate all are Ni-rich. A few also contain chlorine (<1 wt %) possibly indicating some NiCl. Electron microprobe analyses of the glass in traverses away from the metal grains show a low in the Ni abundance around the metal grain (Fig. 2) indicating that the metal formed at least in part by in-situ reduction of the green glass melt.

Discussion and Conclusions:
The latest diffusion data for S in green glass melts suggests that there should be some remnant of the original (time of fragmentation) S content remaining in the core of 400 mm diameter spherules even for the slow (1°C/sec) cooling rates indicated by dendritic olivine nucleation and growth (9). However, there is no sign of any elevated S content in the cores of the many different spherules analyzed, even though the S content of the spherules is significantly above detectability. The variation in S content within individual spherules suggests that these variations may derive from variations that were present as the spherule formed by fragmentation of the green glass magma. Loss of S by diffusion after fragmentation could not have been significant unless resulting profiles were destroyed by flow within the spherule. It is concluded that at the time of fragmentation this magma was essentially a foam with very thin bubble walls which were broken to form the very fine (<1 mm) spherules. The absence of further S loss could be explained if fragmentation was very near surface (at low pressure) and further loss was not required to maintain the gas phase composition. The main component of the gas phase had to be CO, however, if the thermodynamic calculations [11] are correct.

The other new observation relative to this eruption process is the presence of small (1 to 10 μm) Ni-Fe metal grains, primarily near the outer margins of some spherules. The low Ni content of the glass immediately around these metal grains indicates that they formed in-situ probably by a reduction process. The Ni-rich iron metal is exactly the phase which would form first as the green glass melt spherules undergo reduction. The reduction may be the result of oxidation of the last remnants of C in the green glass melt [6]. Whatever the origin, the formation of the metal yields an important indication of the oxidation state of the green glass melt. Using the data of [12] for the composition of coexisting silicate melt and metal, the log fO2 of the melt is calculated to be -11.05 at 1350°C, about 0.9 log units below IW, in good agreement with our recent conclusions [7].

Fig. 1 Microprobe traverses (at 90°) for S and Cl across a typical green glass spherule. Note low in S content along one side of this grain.

Fig. 2. Ni content in green glass along a microprobe traverse away from a grain of Ni-rich (68%) Fe-metal.

References:

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