

USING THE SULFIDE REPLACEMENT TEXTURES IN LUNAR BRECCIA 67915 TO CONSTRUCT A THERMODYNAMIC MODEL OF H-S-O-C FLUIDS IN THE LUNAR CRUST

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Introduction: Post-magmatic sulfide replacement textures present in lunar breccia 67915 suggest that some clasts contained within these breccias have interacted with a sulfur-bearing volatile phase [1, 2, 3]. Previous studies have recognized that these replacement textures represent an important mineralogical record of sulfur-bearing, circulating fluid in the lunar crust. In this study, we have investigated the possible origin and compositions of the metasomatic fluids that are suggested to have been responsible for the formation of sulfide replacement textures in Mg-Suite lithologies of lunar samples 67915. The primary goal of this work was to construct a thermodynamic model of the composition of the metasomatic S-bearing fluid. This quantitative model has been constructed using fO_2 , fS_2 , and temperature constraints that were derived from a thermodynamic analysis of the metasomatic fluid-mineral reactions and the measured compositions of the phases present in the sulfide assemblages.

Calculating Temperature, fO_2 , and fS_2 from Mineral-Volatile Equilibria: The chemistries of the minerals present in the sulfidation-replacement assemblages contain important information about the composition and temperature of the causative volatile phase. The sulfide replacement textures typically consist of secondary silicate, sulfide and oxide phases, pseudomorphically replacing primary igneous olivine (Figure 1a & b). The most prominent feature of the

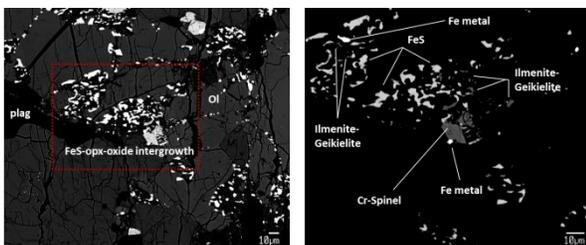


Figure 1. 1a contains a backscatter electron image (BSEI) of the sulfide replacement texture in an olivine phenocryst. The outlined area is shown at higher magnification in 1b. The BSEI in 1b was acquired at extremely high contrast to highlight the relationships among the oxide and sulfide phases. This image shows the apparent breakdown of Cr spinel to Mg-rich ilmenite that is disseminated among the troilite. The image also shows the how Fe metal is distributed throughout the replacement assemblage.

replacement textures is the presence of “myrmekite-like” intergrowths of low Ca pyroxene and troilite. Textural observations suggest orthopyroxene, troilite, geikielite-rich (MgTiO₃) ilmenite, and iron metal are produced at the expense of magmatic olivine and Cr-spinel. Three divariant, equilibria describe the

relationships among all of the mineral components observed in the sulfide replacement assemblages. These equilibria are given as:



The coexistence of metallic Fe and FeS in the alteration assemblages indicates that the equilibrium fS_2 of the fluid phase is defined by the metallic iron troilite buffer reaction. With this constraint, and the compositions of the mineral components, the mineral fluid equilibria above can be rearranged and solved to determine the equilibrium temperature and fO_2 of the mineral fluid equilibria. The results of these calculations are presented in Figure 2.

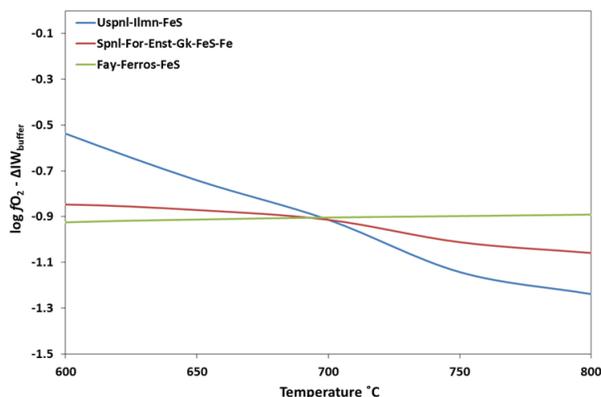


Figure 2. The fO_2 values calculated as a function of temperature for each of the three mineral fluid equilibria listed in the previous section. Note the fO_2 values have been listed relative to the IW buffer. The point of intersection suggests an equilibrium temperature of approximately 700°C at an oxygen fugacity of IW-0.9.

Modeling the Composition Fluid Phase: Using the temperature, fO_2 , and fS_2 constraints derived from the thermodynamic modeling of the mineral fluid equilibria in the previous section, we have modeled the composition of the fluid phase that was in equilibrium with the sulfidation assemblages. For C-O-H-S fluids at fixed T and P, the composition of the fluid phase is fully defined and invariant if the fugacities of three of the four system components are specified. As graphite is not present in the phase assemblage, the activity of carbon is not constrained for the system. Therefore, in order to explore the effects of this variable, we have calculated the equilibrium composition of the fluid phase using a range of graphite activities. Pressure is another poorly constrained variable in the system, so in a similar way,

we have also explored the effects of pressure on the fluid composition (to accomplish this goal, the activity

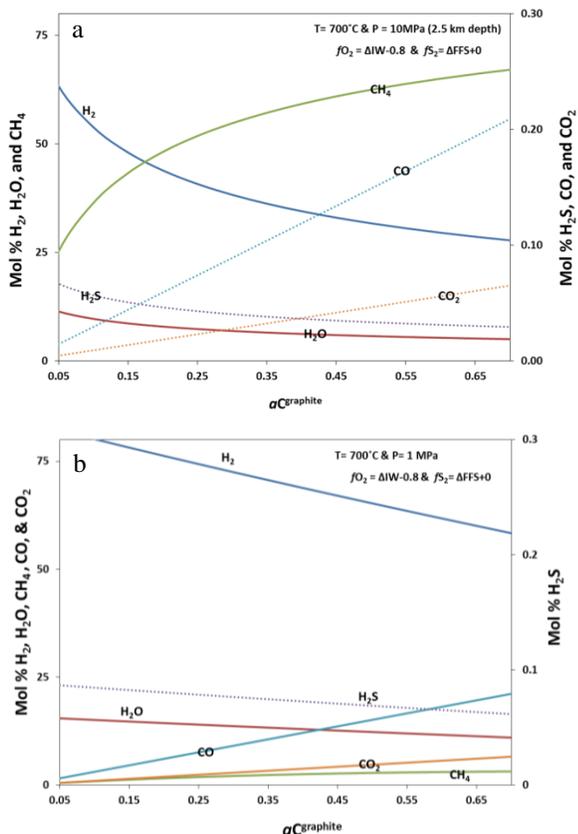


Figure 3. Figures 3a and 3b are plots of the molar abundances of the components of the fluid as a function of the graphite activity of the fluid-mineral system. The curves represented by solid lines have been plotted with respect to the lefthand y-axis, whereas the curves represented by the dashed lines have been plotted with respect to the righthand y-axis. The temperature, pressure, fO_2 , and fS_2 that were used to produce model plots are shown in the upper right corner of each graph. Note that the fO_2 and fS_2 values used in the calculation of these curves are derived directly from the mineral assemblages, and therefore represent the equilibrium composition of the fluid.

coefficients for each fluid component have been calculated with a MRK equation of state). We have included the following nine species in our gas composition modeling: H_2 , H_2O , H_2S , CH_4 , CO , CO_2 , COS , CS_2 , and CS . The last three species- COS , CS_2 , and CS - were specifically included in our model in order to explore the relationship between the calculated fluid composition and the origin of the sulfur isotope signature of the FeS . The results of some of these calculations have been presented in Figure 3a and 3b. The results of the fluid modeling can be summarized with a few salient points:

- I. The composition of the fluid in nearly all cases is dominated by either H_2 or CH_4 , or a combination of both species.
- II. H_2O is present in the equilibrium fluid, albeit at relatively minor abundances.

- III. H_2S is the dominant S species in the fluid phase by multiple orders of magnitude. The mole % H_2S in all calculations ranges from ~800 ppm to ~200 ppm.
- IV. At moderately high graphite activities, CO may be present in limited quantities (although, $aC^{graphite}$ must be less than one as no carbon is present in the phase assemblage).
- V. COS , CS_2 and CS abundances are negligible; in all cases their abundance is less than 1ppm.

Conclusions: The thermodynamic modeling presented above provides important quantitative constraints on the composition of the fluid phase. It is important to note, however, that the calculated fluid composition only represents a single snapshot of the fluid's bulk composition as it existed after its interaction with the magmatic mineral assemblage. This point is of considerable importance as it places the calculated fluid compositions in a meaningful context with respect to the fluid's source. In this way, the modeled fluid compositions provide a unique opportunity to evaluate the hypothesis that the fluids responsible for the sulfidation textures have a magmatic origin.

To develop this argument, we will assume that the fluid source is a carbon-free mare basalt, emplaced at a lithostatic pressure of 10 MPa (depth equivalent of 2.5 km), 1200°C, and an fO_2 of $\Delta IW-1.5$. Using molecular H_2 and H_2O solubility models [4,5] we have calculated the bulk H_2 content (i.e. $H_2 + H_2O$) of the melt in equilibrium with a simple binary O-H fluid at 10 MPa. Lunar mare basalt saturated with an O-H fluid at $IW-1.5$ would contain ~100ppm as H_2O , and 65 ppm H_2 for a "bulk" hydrogen content of ~190 ppm. The calculated H_2 value falls easily within the range of many existing estimates for the late-stage water concentrations of fractionated lunar basalts [6, 7].

These calculations suggest that "garden variety" mare basalts may be capable of exsolving O-H-S-($\pm C$?) fluids late in the shallow lunar crust. Furthermore, the composition of these fluids may be significantly modified by a combination of ascent decompression as well as reaction with existing crustal lithologies. Additionally, magmatic systems that have low bulk H_2 contents can only exsolve a fluid phase at low lithostatic pressure. Therefore, based on these calculations, alteration assemblages related to magmatic degassing must be restricted to crustal depths less than 5 km.

References: [1] Haskin and Warren (1991) Lunar Source Book, 357-474 [2] Norman et al. (1995) GCA, 59, 831-847 [3] Shearer et al. (2012) GCA, 83,138-158 [4] Moore et al. (1998) Am. Min., 83, 36-42 [5] Hirschmann et al. (2012) EPSL, 345-348, 38-48 [6] McCubbin et al. (2010) PNAS, 107, 11223-11228 [7] Saal et al. (2008) Nature, 454, 192-196