LUNAR VOLCANIC GASES: THE PREDICTED PRESENCE OF CHLOROFLUOROCARBON GASES; Bruce Fegley, Jr., Department of Earth & Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130

Introduction. Evidence for lunar volcanic gases is provided by the vesicles and vugs in lunar rock samples and by the volatile-rich (e.g., S, F, Cl, Br) surface coatings on the Apollo 15 green and Apollo 17 orange glasses [1,2]. Although careful analytical work shows that the surface coatings are probably condensates from a lunar volcanic gas, relatively little is known about the chemistry and composition of this phase. Recently, Fegley [3] presented thermodynamic models of lunar volcanic gases which predict that these gases were dominated by reduced C and S species such as CO, COS, CS₂, and S₂. These models also showed that HCl and HF were the major H-bearing species in lunar volcanic gases, but not the major halogen-bearing compounds. Instead, Cl₂, CCl₄, and CF₄ were found to be the dominant Cl- and F-bearing species. This situation arises because the moon is essentially devoid of any water. As a result, the (F + Cl)/H atomic ratio in lunar basalts is generally ≫ 1 and not enough H is present to bond with all the available F and Cl.

The predicted importance of CCl₄ and CF₄ suggested that the chlorofluorocarbon gases may also be stable. The results presented here show that in fact the chlorofluorocarbons (CFCs) are predicted to be present in lunar volcanic gases. This is apparently the only natural environment in which these compounds are formed in significant amounts.

Calculational Methods. The chemical equilibrium calculations were done with the TOP20 code, which iteratively solves for the molecular speciation of a gas phase having a specified temperature, pressure, and elemental composition. The TOP20 code has now been modified to include the chlorofluorocarbons CCl₂F, CCl₃F₂, and CCl₄F. Sulfur chlorides and fluorides have also been included. A total of ~ 460 gases of 25 elements (H, C, O, N, S, Cl, F, P, Si, Fe, Mg, Al, Ca, Na, Ni, Ti, Cr, Mn, Cu, V, K, Br, I) are in the code. The thermodynamic data are mainly from the JANAF Tables [4] and an analogous set of tables issued by the Soviet Academy of Sciences [5]. Ideal gas calculations were done from 2000 K to 500 K at total pressures of 0.01 bars to 100 bars. Wellman [6] first noted that this pressure range is appropriate for lunar volcanic gases, depending on their depth of origin within the moon. Any errors which may be introduced by non-ideality under these conditions are negligible in comparison to the uncertainties in estimating the bulk compositions of the volcanic gases.

As reviewed previously [3], the major differences between terrestrial and lunar volcanic gases are probably the absence of indigenous water (and thus H) on the moon, and the lower oxygen fugacities of gas phases in equilibrium with lunar basalts. These factors led Fegley [3] to model lunar volcanic gases by making appropriate modifications, such as He depletions, to the observed compositions of terrestrial volcanic gases. This approach is also taken in this work. The composition considered here is model 3 of Fegley [3] modified to have O/C = 1.2. The bulk elemental abundances expressed as atomic percent are: 46.0% O, 38.4% C, 8.5% Cl, 5.1% S, 1.7% F, 0.2% N, 0.1% H, 190 ppm Br, and 14 ppm I. This composition was chosen because it has an oxygen fugacity which closely follows the fO₂ for the iron-wüstite (IW) buffer. As illustrated in Fig. 1, this fO₂ closely approximates the upper end of the range of oxygen fugacities measured for lunar rocks.

Discussion and Results. The temperature and pressure dependence of the major species of O, C, S, Cl, F, and H are shown in Figure 1. Nitrogen is essentially inert under these conditions and is present as N₂. CO is the dominant C gas under all temperatures and pressures studied, and CO₂ is the second most abundant. The graphite activity is greater than one over most of this temperature range. However, graphite precipitation was not allowed to occur in these calculations because it may be kinetically inhibited in nature.

Sulfur chemistry is fairly complex. The major S gas at temperatures below ~ 1400 K is COS and S₂ dominates above this temperature. However, a large number of other S gases are also significant. At high temperatures near 2000 K, SF₂ and SO₂ have abundances equal to or exceeding the COS abundance. Other sulfur fluorides and oxides, and elemental sulfur vapor species also have non-negligible abundances at high temperatures. Three sulfur chlorides, SCCl₂ and to a lesser extent SCCl and SCCl₂ are prominent minor gases over a large temperature and pressure range. It is interesting to speculate that the reactive sulfur chlorides may play a role in the formation of the surface coatings on the green and orange glasses.

The most interesting results are the large abundances of the three CFCs. In agreement with the previous results [3], the major Cl gases are Cl₂ (T ≥ 800 K) and CCl₄ (T < 800 K), and the major F gas is CF₄ (T ≤ 1900 K). However, the CFC gases individually make up 0.1-1% by volume of the gas phase and combined make up ~ 10% of the total chlorine and several tens of % of the total fluorine. These are enormously large numbers, especially when one considers that the CFCs are man-made compounds which are not produced by most natural geochemical processes. The abundances of the CFCs are a direct result of the anhydrous and reducing conditions assumed to prevail in the lunar interior. The CFCs are thus chemical probes of the lunar interior, and if any remained trapped in lunar glasses or rocks their abundances may provide important constraints on compositional conditions in the lunar interior at the time that the trapping occurred.
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Figure 1. (a) Top left; The oxygen fugacity for the model is compared to that for the iron–wüstite buffer and to the observed range for lunar rocks. (b) Top right; The effect of assumed total pressure on the abundances of the major C, S, Cl, F gases is illustrated for pressures ranging from 0.01 bars to 100 bars at a constant temperature of 1000 K. (c) Bottom left; The abundances of the major C, Cl, and F gases are plotted as a function of temperature at a constant pressure of one bar. (d) Bottom right; The abundances of the major S gases are plotted as a function of temperature at a constant pressure of one bar.