THERMODYNAMIC MODELS OF THE CHEMISTRY OF LUNAR VOLCANIC GASES

Bruce Fegley, Jr.[1]

LPI, Houston, TX & MPI f. Chemie, Mainz, Germany

Abstract. Thermodynamic models and mass balance arguments are used to constrain the chemistry of lunar volcanic gases. The results predict that lunar gases were dominated by reduced C and S gases such as CO, COS, CS_2, S_2. The more oxidized gases CO_2 and SO_2 were also important, but only in limited temperature ranges. Gases such as Cl_2, CCl_4, and CF_4 were more abundant than HF and HCl, which were the two major H compounds in the lunar gases. Chlorides and fluorides were important species for transporting many volatile and ore-forming metals, and the implications for fractionating and concentrating metals into lunar "ore-deposits" merit further study.

Introduction

The vesicles and vugs in lunar rock samples [LSPET 1969] provide evidence for lunar volcanic gases. Further evidence is provided by volatile-rich (e.g., S, F, Cl, Br) surface coatings on the Apollo 15 green and Apollo 17 orange glasses [Meyer et al. 1975], which are probably the product of pyroclastic volcanism [Delano 1986]. Careful analytical work indicates that the coatings are probably condensates from a volcanic gas, but relatively little is known about the bulk composition of this phase. In this paper thermodynamic modelling and mass balance arguments are used to constrain the chemistry of lunar volcanic gases. Preliminary results showing that chlorides and fluorides are the major gases for many volatile and ore-forming metals are also presented.

Computational Methods

The calculations were done with a modified version of the TOP20 code, which uses the dual constraints of chemical equilibrium and mass balance to iteratively solve for the molecular speciation of a gas phase having a specified temperature, pressure, and elemental composition [Barshay and Lewis 1978]. At present, ~ 460 gases of 24 elements (H, C, O, N, S, Cl, F, P, Si, Fe, Mg, Al, Ca, Na, Ni, Ti, Cr, Mn, Co, Zn, Cu, V, Br, I) are included in the code. The input thermodynamic data are taken from the JANAF Tables [Chase et al. 1985].

The elemental compositions of lunar volcanic gases are unknown, and any assumed compositions are somewhat arbitrary because no gas samples are available. For several reasons, it was decided to model lunar volcanic gases as modifications of terrestrial volcanic gases. Prior theoretical work [Wellman 1970; Naughton et al. 1972], measurements of oxygen fugacities (f_{O_2}) of lunar samples [Sato 1979], and

analyses of volatiles in lunar rocks [Haskin and Warren 1991; Fegley and Swindle 1991] all suggest that the major differences between lunar and terrestrial volcanic gases are probably caused by two factors. One is the absence of indigenous water (and hence H) on the moon. Careful analytical work [e.g., Epstein and Taylor 1973; Merlivat et al. 1974; Stievenard et al. 1990], shows no evidence for indigenous lunar water and evidence for only very small amounts ($\leq 0.5\mu$moles H_2/g) of lunar H. The second factor is that lunar rocks are ~ 4 orders of magnitude more reduced than terrestrial volcanic rocks [Papike et al. 1991]. By comparison, changes in the ratios of S and the halogens are found to be less important for volcanic gas chemistry. Thus, appropriate modifications, such as H depletion, to the observed compositions of terrestrial volcanic gases are likely to lead to plausible models for lunar volcanic gases.

Table 1 lists the major element abundances in the volcanic gas models used in this work. Model 1 is an "average" terrestrial fumarolic gas [Rubey 1951; White and Waring 1963]. Models 2-4 are successively depleted in H by factors of 10^2, 10^4, and 10^6 times relative to model 1. Steam is the dominant H compound in terrestrial volcanic gases and the H depletion is therefore accompanied by removal of the stoichiometric amount of O. The abundances of all other elements are held constant. In model 5 the volcanic gas is made more reducing by fixing the C/O atomic ratio at 0.8. As a result, CO is the dominant C gas and graphite precipitation occurs. Model 5 was studied because Sato [1979] argues that the orange glasses were derived from a graphite saturated magma, and that CO was the dominant gas over this magma. Model 6 is a variation on model 4 in which F/Cl = 10 is assumed. This model was studied because the average F/Cl ratio is ~ 10 for many lunar basalts [Fegley and Swindle 1991].

The abundances of each of the other elements in the calculations were set to one part per billion. By doing this, their chemistry can be calculated without affecting the overall mass balance of the gas phase. This approach is justified for several reasons. Studies of terrestrial volcanic gases and sublimates from these gases [Symonds et al. 1987; White and Waring 1963] show that compounds other than those in the H-O-C-N-S-Cl-F system generally have negligible abundances relative to those of the major gases. Furthermore, theoretical models of the vaporization of rock-forming elements (Si, Fe, Mg, Al, Ca, Ti) from silicate magmas show negligible vapor pressures for compounds of these elements [Fegley and Cameron 1987]. Some elements such as Na, K, and Cu are more volatile, but even so their vapor pressures over silicate magmas are expected to be less than those of S, Cl, and F gases.

The calculations discussed in this paper assume ideality and were done from 500-2000 K at a pressure of 1 bar. Calculations done at pressures ranging up to 1000 bars showed that the mole fractions of the important gases are generally independent of the total pressure. The variations that do occur do not alter the major conclusions. Wellman [1970] noted that pressures of 0.01-100 bars were probably appropriate for lunar volcanic gases, depending on their depth of

[1]Present address: Department of Earth & Planetary Sciences, and MacDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130 USA.

Table 1. Elemental composition (%) of average terrestrial fumarolic
gas (1) and lunar volcanic gas models (2–6).

Element	1.	2.	3.	4.	5.	6.
H	63.8	12.1	0.15	15 ppm	20 ppm	16 ppm
O	34.2	50.6	54.4	54.4	36.3	58.6
C	1.4	26.6	32.4	32.4	45.4	34.9
Cl	0.3	5.9	7.2	7.2	10.1	0.1
S	0.2	3.6	4.3	4.3	6.1	4.7
F	0.06	1.1	1.4	1.4	1.9	1.5
N*	90 ppm	0.2	0.2	0.2	0.3	0.2
Br†	7 ppm	125 ppm	160 ppm	160 ppm	230 ppm	3 ppm
I†	0.5 ppm	10 ppm	12 ppm	12 ppm	17 ppm	0.3 ppm
TOTAL	100.0	100.1	100.1	99.9	100.1	100.0

*The reported nitrogen may represent contamination from air.

†CI chondritic Cl/Br and Cl/I ratios were assumed.

origin within the moon. Any errors which may be introduced by the neglect of non-ideality are probably small in comparison to errors arising from uncertainties in volcanic gas bulk compositions.

Major Element Chemistry

The calculated compositions as a function of temperature for the "average" terrestrial fumarolic gas agree well with those of Heald et al. [1963] done on a similar bulk composition in the H-C-O-S system. As illustrated in their paper, the dominant C gas is always CO_2 with CO being much less abundant except at high temperatures which are probably not reached in magmatic systems. By 500 K, CH_4 is becoming important, but the rate of the $CO_2 \rightarrow CH_4$ conversion at these low temperatures is probably insignificant relative to either the cooling (or ascent) rate of the gas. The dominant Cl and F gases are always HCl and HF, and atomic Cl and all other F and Cl gases are much less abundant. Sulfur chemistry is more complex with SO_2 the major gas at high temperatures and H_2S the major gas at lower temperatures. The COS and S_2 abundances are always just a fraction of the total S abundance.

The results for model 2 are qualitatively similar in many respects. One important difference is that the CO/CO_2 ratio is larger than in the terrestrial gas, and another difference is that COS is sub-equal to H_2S over a large temperature range where H_2S is the dominant S gas. However, the situation is markedly different in the more H depleted gases which are probably more relevant to the lunar interior.

This situation is exemplified by model 3, which is illustrated in Figure 1. In this case, the H abundance is only 0.01% of that originally present in the average terrestrial fumarolic gas. In fact, the H abundance is so low that Cl, S, and F are more abundant than H. As a result, the dominant S gases are SO_2 at high temperatures, S_2 at lower temperatures, and COS at the lowest temperatures. Carbon disulfide, which had an abundance below 0.1 ppb in model 1, is about 4% of total S at low temperatures. Hydrogen sulfide is totally negligible because of the extremely low H abundance and the large thermodynamic stability of HCl and HF. These two gases are the dominant H-bearing gases in this model. However, HCl and HF are no longer the dominant halogen gases because the H abundance is too small to combine with all the available Cl and F. Instead, CF_4 is the dominant F gas over the entire temperature range considered and the major Cl gas shifts from atomic Cl at the highest temperatures, to Cl_2 at lower temperatures, and then to CCl_4 at the lowest temperatures.
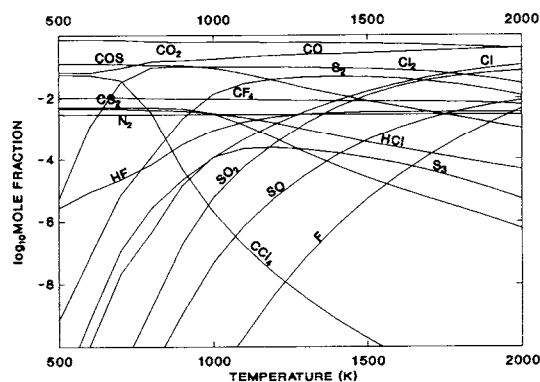

Fig. 1. A simplified representation of the chemistry for model 3 in Table 1. The abundances of the major gases of the elements C, H, N, S, Cl, and F are plotted as a function of temperature. Some less abundant species of interest are also included. In this H-depleted composition, the major H gases are HCl and HF while H_2O is totally negligible with an abundance below 0.1 ppb.

The results for models 4–6, which have even less H, are qualitatively similar to those illustrated for model 3. The major differences are in model 5, which is illustrated in Figure 2. In this case, CS_2 is the dominant S gas from 2000 K to 1200 K. Below this temperature the dominant S gas is COS. At 500 K, S_8 is nearly as abundant as COS, and S condensation occurs. Interestingly, Butler and Meyer [1976] showed that S is the major constituent of the coatings on the green and orange glasses. This model also gives the best agreement between the calculated f_{O_2} for the volcanic gas and the observed f_{O_2} of lunar rocks (Figure 3). However, model 5 and variants on it have not been studied in sufficient detail to tell whether or not they are a reasonable explanation for the S-rich coatings.

The calculations also show that three qualitatively different types of halogen chemistry may occur. Lunar volcanic gases with the bulk abundance ratio $H/(F+Cl) > 1$ will have HF and HCl as the dominant halogen gases, as in terrestrial volcanic gases. However, lunar gases with $H/(F+Cl) < 1$ will have HF and HCl as the dominant H gases but not as the dominant halogen gases. Finally, lunar gases with $H/(F+Cl) = 1$ will display more complex chemistry involving HF, HCl, and other halogen gases.

The amount of indigenous (i.e., non-spallogenic) H_2 in lunar basalts is probably 0.5 μmoles/g or less [Stievenard
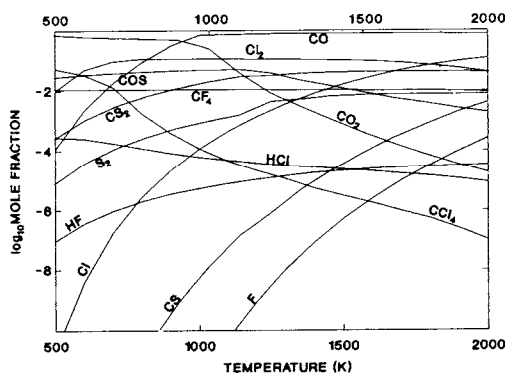
Fig. 2. A simplified representation of the chemistry for model 5 in Table 1. Sulfur condenses just above 500 K and S_8 (not graphed) is a major S gas at 500 K.

et al. 1990]. The F abundances in lunar basalts are generally between 10–100 μg/g ($\sim$ 0.5–5 μmoles/g), and the Cl abundances are generally between 1–100 μg/g ($\sim$ 0.03–3 μmoles/g) [Fegley and Swindle 1991; Haskin and Warren 1991]. The corresponding F/H and Cl/H atomic ratios are 1 to 5, and 0.06 to 6, respectively. Large F abundances of up to several hundred μg/g are observed on the surfaces of the Apollo 17 orange glasses [Goldberg et al. 1976]. Thus, it appears likely that the lunar interior is so depleted in H that HF and HCl are the dominant H-bearing compounds, but not the dominant halogen-bearing compounds in lunar volcanic gases.

Although these conclusions appear straightforward, they have not been appreciated by previous workers. For example, Chou et al. [1975] and Wasson et al. [1976] assumed fugacities of 1000 bars for H_2O, 100 bars for H_2S, and 10 bars for HCl in lunar volcanic gases responsible for producing the coatings on the green and orange glasses. However, their assumptions appear incompatible with any plausible model for lunar volcanic gases.

Trace Element Chemistry

The chemistry of Br and I is fairly simple. In the "average" terrestrial fumarolic gas their chemistry is dominated by HBr, I (at high temperatures) and HI. However, in the more H depleted models 3–6, the major species at high temperatures are Br and I and are Br_2 and I_2 at low temperatures.

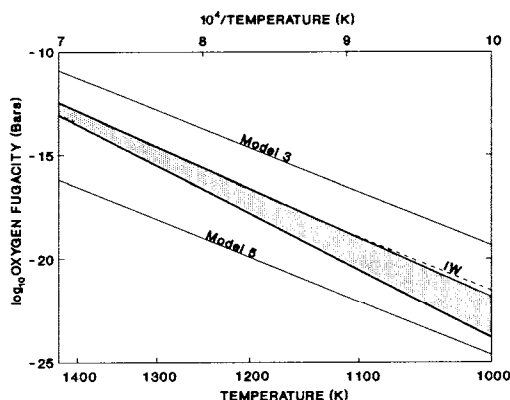Phosphorus chemistry is also fairly simple. The major

Fig. 3. The f_{O_2} values in models 3 and 5 are compared with those measured for lunar samples (shaded region). The f_{O_2} for the iron–wüstite (IW) buffer is also shown as a dashed line. After Papike et al. [1991].

species in model 1 are PO_2 (high temperatures) and P_4O_6 (low temperatures). Some other gases such as PO also occur at the $\sim$1% level, but are never dominant. In the H depleted models (3–6) the only two important gases are PF_5 and PF_3. The former is much more important and is the major gas at all temperatures in models 3–4,6 and at temperatures below 1400 K in model 5. In model 2 the major P gases are PO_2 at high temperatures, PS (briefly at lower temperatures), PF_3 over a wide range at still lower temperatures, and PF_5 just above 500 K. However, this model is probably not relevant to the moon.

The two alkalis included in this study are Na and K. They display similar behavior. At temperatures above $\sim$ 1500 K, Na^+ and K^+ are the dominant gases. As the temperature drops, the monochlorides become dominant, and remain so down to $\sim$ 500 K, where the dimers Na_2Cl_2 and K_2Cl_2 become dominant. Model 6 displays an exception to this behavior in that the fluorides are also important at high temperatures and are comparable to the ionized monatomic species.

Copper displays complex behavior, but its chemistry is still dominated by chlorides and fluorides. In all models considered, CuCl is the dominant gas over a wide temperature range. However, dimers and trimers of CuCl are important below 1000 K. The two fluorides CuF and CuF_2 are important at high temperatures in model 6.

With very few exceptions, the chlorides and fluorides are the major species for the other elements included in the calculations. This is true for models 3–6; chemistry in the more H-rich models is somewhat more complex, but is not of interest for lunar geochemistry. The major Si gas is always SiF_4. Similarly, AlF_3 is always the major Al gas in these models, except at temperatures <1000 K, where it is unlikely that any Al remains in the gas phase. Calcium is present as CaF_2 at high temperatures and $CaCl_2$ at lower temperatures. Titanium displays similar behavior with TiF_4 being important down to $\sim$900 K and $TiCl_4$ becoming important thereafter. However, it is doubtful whether any Ti remains in the gas at such low temperatures. Magnesium chemistry is more complex and involves several species. To a first approximation, Mg is present primarily as MgF_2 at high temperatures, but MgClF and $MgCl_2$ may also be important. At lower temperatures, $MgCl_2$ is the major gas. This transition point is highly variable and occurs at $\sim$ 1200 K in model 4 and at $\sim$ 1800 K in model 5. Iron is present primarily as FeF_3 at high temperatures and $FeCl_3$ at low temperatures. Other species such as $FeCl_2$ and FeF_2 can also have significant abundances. Cobalt chemistry is dominated by CoF_2 at high temperatures, $CoCl_2$ at lower temperatures, and $CoCl_3$ at 600 K and below. The major V gases are VF_5 and VCl_4; the latter is the major V gas at all temperatures in model 5. Finally, although other elements (e.g., Ni, Cr, Zn, Mn) are included in the calculations, thermodynamic data are only available for a small number of compounds of each element, so discussing their chemistry seems premature without attempting to expand the thermodynamic data base.

Summary

Appropriate modifications (e.g., H depletion) to the composition of an "average" terrestrial volcanic gas were used to generate plausible compositional models for lunar volcanic gases. Thermodynamic calculations based on these models were used to predict the probable molecular speciation of lunar volcanic gases. The chemistry of some trace elements which may be transported by lunar volcanic gases was also modelled.

This preliminary study predicts that the anhydrous lunar volcanic gases were dominated by reduced C and S species such as CO, COS, CS_2, and S_2. More oxidized species such as CO_2 and SO_2 were also important, but were probably not dominant except in limited temperature ranges or in compositions slightly more oxidizing than those appropriate for the lunar interior. Halogen gases such as Cl_2, CCl_4, and CF_4 are predicted to be more abundant than HF and HCl. However, the latter two species are predicted to be the two major H compounds in lunar volcanic gases. The results also show that chlorides and fluorides are the major species for many other elements (e.g., P, Na, K, Cu, Si, Al, Ca, Ti, Mg, Fe, Co, V).

Finally, this study also points out several areas where further research may be profitable. One such area is a more detailed study of the relative volatilites of many volatile and ore-forming metals in plausible lunar volcanic gases. Depending on the efficiency with which the gaseous chlorides and fluorides can fractionate and concentrate metals such as Cu, Fe, etc., the formation of lunar ore-deposits may have been possible, despite the absence of water on the moon.

References

Barshay, S.S. and Lewis, J.S., Chemical structure of the deep atmosphere of Jupiter, *Icarus* **33**, 593-611, 1978.

Butler, P., Jr. and Meyer, C., Jr., Sulfur prevails in coatings on glass droplets: Apollo 15 green and brown glasses and Apollo 17 orange and black (devitrified) glasses, *Proc. Lunar Sci. Conf. 7th*, pp. 1561-1581, 1976.

Chase, M.W., Jr., Davies, C.A., Downey, J.R., Jr., Frurip, D.J., McDonald, R.A., and Syverud, A.N., *JANAF Thermochemical Tables*, Amer. Chem. Soc. and Amer. Inst. of Phys., 1985.

Chou, C.L., Boynton, W.V., Sundberg, L.L., and Wasson, J.T., Volatiles on the surface of Apollo 15 green glass and trace element distributions among Apollo 15 soils, *Proc. Lunar Sci. Conf. 6th*, pp. 1701-1727, 1975.

Delano, J.W., Pristine lunar glasses: Criteria, data, and implications, *Proc. 16th Lunar Planet. Sci. Conf. J. Geophys. Res.* **91**, D201-D213, 1986.

Epstein, S. and Taylor, H.P., Jr., The isotopic composition and concentration of water, hydrogen, and carbon in some Apollo 15 and 16 soils and in the Apollo 17 orange soil, *Proc. 4th Lunar Sci. Conf.*, 1559-1575, 1973.

Fegley, B., Jr. and Cameron, A.G.W., A vaporization model for iron/silicate fractionation in the Mercury protoplanet, *Earth Planet. Sci. Lett.* **82**, 207-222, 1987.

Fegley, B., Jr. and Swindle, T., Volatile element chemistry of the moon, in *Resources of Near Earth Space*, ed. J.S. Lewis and M.S. Matthews, Univ. of Arizona Press, in press, 1991.

Goldberg, R.H., Tombrello, T.A., and Burnett, D.S., Fluorine as a constituent in lunar magmatic gases, *Proc. Lunar Sci. Conf. 7th*, pp. 1597-1613, 1976.

Haskin, L. and Warren, P., Lunar chemistry, in *Lunar Sourcebook*, eds. G. Heiken, D. Vaniman, and B.M. French, Cambridge Univ. Press, pp. 357-447, 1991.

Heald, E.F., Naughton, J.J., and Barnes, I.L., Jr., The chemistry of volcanic gases 2. Use of equilibrium calculations in the interpretation of volcanic gas samples, *J. Geophys. Res.* **68**, 545-557, 1963.

LSPET (Lunar Sample Preliminary Examination Team), Preliminary examination of lunar samples from Apollo 11, *Science* **165**, 1211-1227, 1969.

Merlivat, L., Lelu, M., Nief, G., and Roth, E., Deuterium, hydrogen, and water content of lunar material, *Proc. 5th Lunar Sci. Conf.* **2**, pp. 1885-1895, 1974.

Meyer, C., Jr., McKay, D.S., Anderson, D.H., and Butler, P., Jr., The source of sublimates on the Apollo 15 green and Apollo 17 orange glass samples, *Proc. Lunar Sci. Conf. 6th, pp. 1673-1699, 1975*.

Naughton, J.J., Hammond, D.A., Margolis, S.V., and Meunow, D.W., The nature and effect of the volatile cloud produced by volcanic and impact events on the moon as derived from a terrestrial volcanic model, *Proc. 3rd Lunar Sci. Conf.*, **2**, pp. 2015-2024, 1972.

Papike, J., Taylor, L., and Simon, S., Lunar minerals, in *Lunar Sourcebook*, eds. G. Heiken, D. Vaniman, and B.M. French, Cambridge Univ. Press, pp. 121-181, 1991.

Rubey, W.W., Geologic history of seawater, An attempt to state the problem, *Bull. Geol. Soc. Amer.* **62**, 1111-1147, 1951.

Sato, M., The driving mechanism of lunar pyroclastic eruptions inferred from the oxygen fugacity behavior of Apollo 17 orange glass, *Proc. Lunar Planet. Sci. Conf. 10th*, pp. 311-325, 1979.

Stievenard, M., Jouzel, J., and Robert, F., The isotopic signature of hydrogen in lunar basalts: Spallogenic or primordial?, *Lunar Planet. Sci.* **XXI**, 1204-1205, 1990.

Symonds, R.B., Rose, W.I., Reed, M.H., Lichte, F.E., and Finnegan, D.L., Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia, *Geochim. Cosmochim. Acta* **51**, 2083-2101, 1987.

Wasson, J.T., Boynton, W.V., Kallemeyn, G.W., Sundberg, L.L., and Wai, C.M., Volatile compounds released during lunar lava fountaining, *Proc. Lunar Sci. Conf. 7th*, pp. 1583-1595, 1976.

Wellman, T.R., Gaseous species in equilibrium with the Apollo 11 holocrystalline rocks during their crystallization, *Nature* **225**, 716-717, 1970.

White, D.E. and Waring, G.A., Volcanic emanations, in *Data of Geochemistry*, ed. M. Fleischer, 6th ed., U.S. GPO, pp. K1-K27, 1963.

B. Fegley, Jr., Lunar & Planetary Institute, 3303 NASA Road One, Houston, TX, 77058 USA and Abt. Kosmochemie, Max Planck Institut für Chemie, D6500 Mainz, Germany.