

PLANETARY ATMOSPHERES DURING ACCRETION: THE EFFECT OF C-O-H-S EQUILIBRIA; John R. Holloway, Depts. of Chemistry and Geology, Arizona State University, Tempe, AZ 85287

In a series of papers, Abe and Matsui (1) have proposed that thick atmospheres develop during the accretion of terrestrial planets, and that the thermal blanketing caused by the atmosphere results in the formation of hydrous magma oceans for much of the accretionary period. However their model assumes that H₂O is the only volatile released from impacting planetesimals. However, any probable planetesimal composition that includes significant amounts of H₂O will also contain similar amounts of carbon so that devolatilization will produce gases in the carbon - oxygen - hydrogen system. The effect of chemical equilibria in such complex gas mixtures on the nature and composition of early atmospheres is examined in this paper.

Table 1	
	mole ratio
C	1.0
H ₂ O	0.5
FeS	6.0
FeO	11
Fe ^o	16
From (2)	

For illustrative purposes an unequilibrated ordinary chondrite bulk composition was chosen with very modest amounts of hydrogen and carbon (Table 1), equivalent to 0.22 wt% C and 0.5 wt% H₂O. Homogeneous accretion was assumed. The amount of degassing as a function of planet mass (or radius) was taken from Tyburczy et al. (3), and, following those authors, it was assumed that C and H initially volatilize in the ratio found in the impactor. Equilibrium calculations were done by total free-energy minimization as described in (4). Species considered were all of the thermodynamically important C-O-H gases, H₂S, SO₂, COS, FeS(l), FeS, Fe, graphite, and FeO component in olivine. Calculations were done over a range of total pressure from 1 to 300 bars and from 25° to 1200°C. Real gas thermodynamic properties were used following (5). Under these conditions of relatively low pressure and it is reasonable to assume ideal mixing in the fluid (gas) phase. Typical results are shown in Fig. 1 for the bulk composition and in Fig. 2 for the fluid phase.

An important feature of Fig. 2 is that the proportions of H₂O and CO₂ are very low over the entire temperature range (and this result holds for all pressures investigated). This means that hydrous or

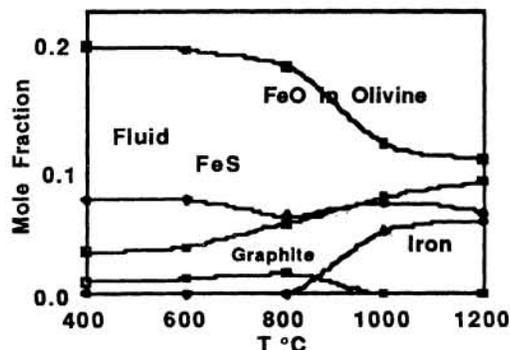


Figure 1. Equilibrium results at 50 bars for the bulk composition.

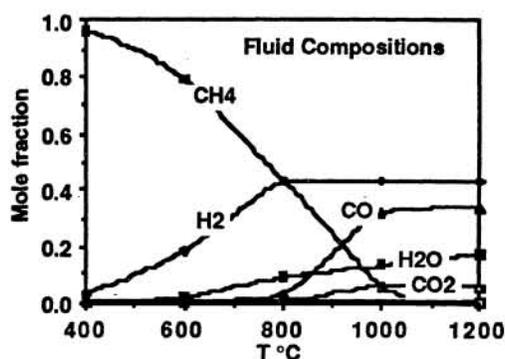
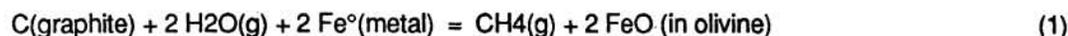


Figure 2. Equilibrium results at 50 bars for the atmospheric gas composition.

carbonated minerals will not be stable, even at low T, and so gases released by impact devolatilization will remain in the atmosphere and not be re-incorporated in the crust or regolith. The reaction important at low T is:



In this low T region, the resulting phase assemblage is governed by the critical molar ratios C:2H₂O:2Fe^o in the impactor. If C:H₂O > 1:2 then there will be residual graphite, and if molar H₂O:Fe^o < 1:1 then there will be residual metallic iron. Given the ratios shown in Table 1, the above reaction results in consumption of all metallic iron until the temperature exceeds about 800°C. At higher temperatures

methane becomes thermally unstable, liberating C and H₂. At temperatures above 900°C the equilibria are dominated by the reaction:



This reaction consumes graphite and produces metallic iron, which for the Table 1 composition results in replacement of graphite by iron in the residual solid assemblage.

The accretion scenario considered here follows (3) so that no devolatilization occurs at $R/R^{\circ} < 0.4$

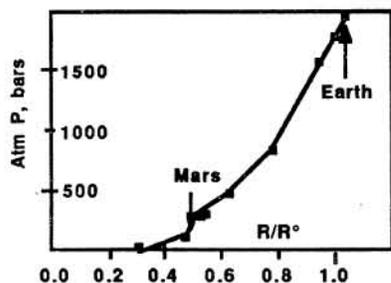


Figure 3. Atmospheric pressure as a function of planet radius.

and devolatilization is total for $R/R^{\circ} > 0.4$. When devolatilization becomes significant all of the hydrogen in the impactor is released (as CH₄, H₂, and H₂O) but a portion of the carbon is retained as graphite at $T < 900^{\circ}\text{C}$. Hydrogen can therefore be used to calculate the mass of the atmosphere by mass balance and the atmospheric pressure calculated as a function of R/R° as shown in Fig.3. These calculations assume no loss of H or other gases by hydrodynamic or Jeans escape. Such escape will be more or less important depending on the time scale of accretion. Because of the uncertainty in accretion timescales these results should be considered an "end-member" for a rapid accretion case. The results in Fig. 3 imply that an optically thick atmosphere will build-up rapidly after R/R° exceeds 0.4, which is the same conclusion reached by Abe & Matsui (1).

However, this atmosphere will have a low H₂O content. This low H₂O content of about 5-10 mole% is independent of total pressure,

temperature, and oxygen partial pressure over a wide range of conditions.

The optically thick atmosphere should result in the formation of a magma ocean as proposed by Abe & Matsui (1), but the low proportion of H₂O will cause differences in the amount of H₂O dissolved in the magma ocean. The amount of H₂O dissolved in the magma at the atmosphere-surface interface can be calculated from the Burnham model (6) from a knowledge of the atmospheric pressure and the mole fraction of H₂O in the atmosphere. Under equilibrium conditions the H₂O content will follow an equipotential curve as shown in Fig. 4. These curves probably give minimum values because convective stirring will tend to mix the higher, interface H₂O contents into deeper parts of the magma ocean.

The results discussed here support the possibility of the formation of optically thick atmospheres, and hence magma oceans, once accreting planets reach about 40% of Earth's radius. The atmosphere's composition will be a mixture of several C-O-H gases, and graphite will be an important solid phase at temperatures below 800°-900°C.

References:

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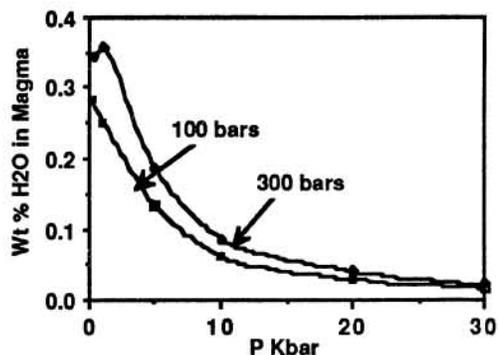


Figure 4. Equipotential curves for H₂O in basaltic magma in surface equilibrium with atmospheres containing a mole fraction of H₂O = 0.05. Curves for atmospheric pressures of 100 and 300 bars shown.