

Clathrate Type II Hydrate Formation *in vacuo* under Astrophysical ConditionsBlake, D.F.,<sup>1</sup> Allamandola, L.J.,<sup>2</sup> Sandford, S.,<sup>2</sup> and Freund, F.<sup>3</sup><sup>1</sup>Planetary Biology Branch, MS 239-4 and<sup>2</sup>Astrophysics Branch, MS 245-6

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Numerous authors have called on the properties of clathrate hydrates to explain the complex and poorly understood physical processes taking place within cometary nuclei and other icy solar system bodies.<sup>1-3</sup> However, suitable mechanisms for clathrate hydrate formation in the outer solar nebula, on the surfaces of planetesimals or in other low-pressure environments have not been identified. Recently the formation of clathrate type II hydrates was reported from vapor-deposited amorphous mixed molecular ices which were warmed in the high vacuum of an electron microscope.<sup>4,5</sup> There may be a variety of reasons why earlier published experiments apparently did not yield clathrate hydrates. Most importantly, most or all of the experiments previously conducted used starting compositions which would yield clathrate type I hydrates. The main criterion for type I vs. type II clathrate hydrate formation is the size of the guest molecule, which for clathrate type I is  $< 5.8 \text{ \AA}$  (dynamical diameter), and for type II,  $> 5.8 \text{ \AA}$ .<sup>3</sup> The stoichiometry of the two structure types is quite different. A fully occupied clathrate contains  $\sim 6$  mole % guest molecules for type II and  $\sim 17$  mole % guest molecules for type I. In addition, the larger molecules which would form type II clathrate hydrates typically have lower vapor pressures. The result of these considerations is that at the temperatures where we have identified clathrate formation (120-130 K), it is more likely that type II clathrate hydrates will form.

We have also formed clathrate II hydrates of methanol by direct vapor deposition in the temperature range 125-135 K. This surprising result suggests that there may be other conditions, quite common in the Solar System, under which type II clathrates form. For example, if ices are vaporized by an impact, their recondensation may result in clathrates if the temperature regime is appropriate. Lastly, although clathrate type II hydrates can be formed only by relatively large molecules, there are two sites in the type II structure which may be filled by small molecules for each large site. Thus, small molecules can be passively incorporated into the smaller unoccupied cages of the type II structure either as it forms or at a later time.

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## A POSSIBLE ORIGIN OF EII CHONDRITES FROM A HIGH TEMPERATURE-HIGH PRESSURE SOLAR GAS

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Calculations of condensates from a gas of "solar" composition were made to investigate the origins of EII chondrites using a unique free energy minimization computer program with a data base for the thermodynamic properties of multicomponent molten silicates as well as for solids, solid solutions and gaseous species. Because of the relatively high volatility of silicon and silica, the high silicon content of metal (2.6 mole percent) can only be produced at pressures greater than  $10^{-2}$  atm at temperatures greater than 1475 K. At very high pressures (100-500 atm), a liquid silicate phase crystallizes at a temperature where the silicon content of the metal, the ferrosilite content of the enstatite and the albite concentration in the plagioclase are close to measured values. Thus, one attractive mode for freezing in the compositions of these three phases is the disappearance of the fluxing liquid. If the plagioclase can continue to react with the nebula without a liquid phase, then lower pressures of e.g.  $10^{-1}$  to 1 atm might be possible. We are exploring the possibility that these assemblages might have condensed at lower pressures from gases of non-solar compositions.