Introduction. Although CO$_2$ and H$_2$O are the main reactive components of Mars’ climate system, they are not the only ones. N$_2$, CH$_4$, and SO$_2$ are some of the components that may affect the volatile system at various times and places. Knowledge of how these species interact with the CO$_2$-H$_2$O system has widespread utility in understanding various aspects of the Martian climate system.

Binary pressure (P) – temperature (T) phase diagrams (Figs. 1,2,3) were constructed for the N$_2$–, CH$_4$–, and SO$_2$-H$_2$O systems making use of published triple points, critical points, and limited experimental determination of univariant equilibria (binary reactions) [1,2]. Each of the 3 phase diagrams below compares the equilibria of one of these 3 components plus H$_2$O to the CO$_2$-H$_2$O system [3]. Such comparisons are supported by the topological similarities between the H$_2$S-H$_2$O [4] and CO$_2$-H$_2$O systems [3], which are in turn reflections of the presence of clathrate and the low solubility of the “guest” component in liquid H$_2$O.

Equilibria in the N$_2$–, CH$_4$–, and SO$_2$-H$_2$O systems for which there is experimental data are solid curves; equilibria that are interpolated or inferred are shown as dashed lines. Equilibria in the 3 end-member systems are shown as light gold lines. Equilibria in the pure H$_2$O system are shown as light red lines. In each binary the phases are the same: gas (G), liquid rich in the end member component (L), clathrate hydrate (H), the solid form of the end-member (S), liquid rich in H$_2$O (W), and H$_2$O ice (I). The N$_2$-H$_2$O (N-H) and the CH$_4$-H$_2$O (M-H) systems in Figs. 1 and 2, respectively, have similar topologies that differ from CO$_2$-H$_2$O (C-H) in that their end members have critical points at lower temperatures than the melting curve of pure H$_2$O and also lower than the C-H binary melting curve of ice. This means that the quadruple point {SI} in C-H where clathrate (H - hydrate), 2 liquids (L,W), and gas (G) coexist is not possible because the L and G phases are supercritical and thus are one. The positions of the equilibria involving clathrate and a fluid phase in the N-H and M-H are offset to higher pressures and lower temperatures relative to their equivalents in the C-H systems. This means that N$_2$ and CH$_4$ destabilize clathrate relative to C-H under Martian surface conditions and that N$_2$/CO$_2$ and CH$_4$/CO$_2$ ratios in a CO$_2$-rich fluid will be higher than the same ratios in coexisting clathrate [6]. Thus whatever their roles interacting with other volatile components, significant fractions of the available N$_2$ and CH$_4$ are unlikely to have been stored in clathrates that formed from or exchanged with a greenhouse Martian atmosphere. The SO$_2$-H$_2$O (SH) system is different, however. The triple point of SO$_2$ is at a temperature similar to that of CO$_2$, but lies at a much lower pressure. Moreover, the SO$_2$ critical end point lies at a much higher temperature than the melting point of water. Consequently, the topology of the SH system is similar to that of the CH system, but the equilibria involving clathrate are offset to lower pressure and higher temperature relative to the CH system. This means that not only will clathrates be more likely to form from a SO$_2$-CO$_2$-H$_2$O atmosphere than from a simple CH atmosphere, but also the SO$_2$/CO$_2$ ratio in clathrate will be greater that in coexisting gas, thus there is the potential for significant storage of SO$_2$ in clathrates once it is injected into the atmosphere by volcanic eruption.

None of the 3 volatile species is significant under present Martian conditions. Of these, only N$_2$ plays even a small role: with cooling and CO$_2$ condensation at the poles the atmospheric pressure drops and the N$_2$ (and Ar, Ne, etc.) concentration increases. As Fig. 1 suggests, for every percent increase in N$_2$, the condensation temperature of CO$_2$-rich gas decreases by a degree. This is an interesting but, probably, minor facet of volatile history.

Fig. 1 Comparison of the N$_2$-H$_2$O and CO$_2$-H$_2$O systems. Red curves are the pure CO$_2$ and H$_2$O systems; blue curves are the CO$_2$-H$_2$O system after [3]. Green curves are the N$_2$-H$_2$O system. Solid curves drawn from published data [1,2,3]; dashed curves are inferred.

Fig. 2 Comparison of the CH$_4$-H$_2$O and CO$_2$-H$_2$O systems. Gold curves are the pure CH$_4$ system; orange curves are the CH$_4$-H$_2$O system. Solid curves drawn from published data [1,2,3]; dashed curves are inferred.

Fig. 3 Comparison of the SO$_2$-H$_2$O and CO$_2$-H$_2$O systems. Gold curves are the pure CH$_4$ systems; pink curves are the SO$_2$-H$_2$O system. Data from [1,2,3,5].