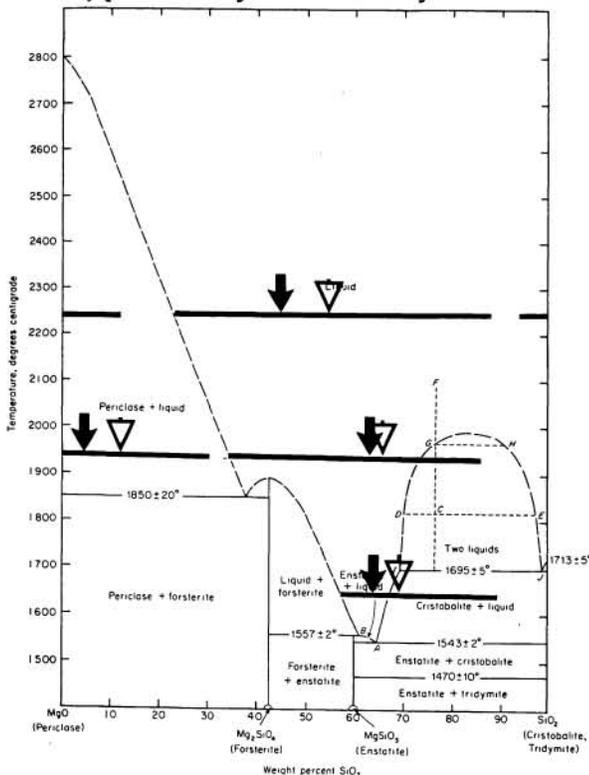


AN ANALYTICAL ELECTRON MICROSCOPE [AEM] STUDY OF HYDROUS ALTERATION IN A SMOKE OF MODAL FORSTERITE COMPOSITION

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Many studies have simulated vapor phase condensation in astrophysical environments such as the solar nebula. They generally investigated simple (Mg,Fe)-SiO vapors that yielded fine-grained amorphous and/or crystalline smokes with pyroxene and olivine compositions. A typical study matched infrared [IR] spectra of these smokes with those of astrophysical dusts but AEM analyses of smokes at the level of their constituents were rarely attempted. These analyses of the condensation event, including autometamorphism [1], and thermal alteration and hydration are necessary to constrain the onset of mineralogical activity in the solar nebula [2-4], in particular the nature of protophyllosilicates. Infrared spectroscopy, X-ray diffraction, scanning electron microscopy and AEM are the most common techniques for smoke characterization. The fact that IR spectroscopy is sensitive to different properties than AEM, for example, is not always appreciated, *e.g.* AEM analyses of hydrated Mg-SiO smokes with distinct IR features for layer silicates [2] showed small amounts of proto-phyllosilicates restricted to domains with the appropriate MgO/SiO₂ ratio [4]. I report the ongoing effort of AEM characterization of experimentally hydrated Mg-SiO smokes with a resolution that allows comparisons with AEM studies of interplanetary dust particles [IDPs] and undifferentiated meteorite matrices. A JEOL 2000FX AEM operating at 200 keV was used to determine the chemistry, and crystalline or amorphous nature, of individual smoke particles. Three samples include the Mg-SiO smoke that was the used for hydration at 423°K (22 hours) and 573°K (74 hours). A small volumes of each sample was embedded in epoxy to prepare ultrathin (80-100 nm) sections for AEM analyses.

OBSERVATIONS. The constituent compositions in the starting material, but for two distinct gaps, range from pure SiO₂ to pure MgO [Figure 1]. As constituents may be smaller than the section thickness individual analyses may be compromised. The ranges of the populations are slightly misleading because the variations in MgO/SiO₂ ratios may in part be an experimental artifact, particularly the texturally distinct end-members.



The hydrated samples do not show the complete range of MgO/SiO₂ ratios which may be due to heterogeneity at a larger scale than the sample volumes selected for ultrathin sectioning. This effect seems most likely for the silica-rich materials, that is a related study of hydrated Mg-SiO smokes showed that silica leached from the original smoke precipitated in distinct location in the sample [4].

FIGURE 1: The binary phase diagram MgO-SiO₂ [reproduced from E.G. Ehlers, *The Interpretation of Geological Phase Diagrams* (1972) W.H. Freeman and Company, San Francisco] showing from top to bottom the MgO wt% ranges of (1) the starting material, (2) the hydrated sample at 423°K, and (3) the hydrated sample at 573°K for 74 hours. The modal (solid arrows) and mean values (open arrowheads) are also indicated.

Hydrous Alteration of Forsterite Smoke: Rietmeijer, F.J.M.

The starting material is a porous smoke with pure silica particles and coagulated particles with MgO between the mean and modal values. The smoke includes (1) amorphous particles, SiO₂ > 65 wt%, with a well-defined grain boundary (ϕ = 30-60 nm) and rare ordered domains of tridymite or cristobalite, and (2) ragged (coagulated) particles (up to ~200 nm in size), MgO > 35 wt%, with scattered (sub)circular electron-opaque domains (ϕ \approx 6 nm). The domains are single-crystal forsterite that invariably occur in particles of mean MgO content, and higher. Particles of both morphological types contribute to the population with 12-78 wt% MgO. Forsterite, and possibly periclase (MgO), domains occur in particles with MgO > 90 wt%, while those in coagulated grains, MgO \approx 37 wt%, may also include enstatite.

During hydration the porous smoke has collapsed into a dense amorphous material with 14.5 - 65 wt% MgO with patches showing 0.7 nm lattice fringes (cristobalite?) (423/22) and MgO = 12 - 42 wt% in the 573/74-sample. This material is dominated by tangled networks and sinuous protophyllosilicate grains that are typically two to three basal layers thick. They are most abundant when the Mg-contents is close to the mean MgO value. The density of these protophyllosilicates, that may show turbostratic stacking, is much higher in the 573/74-sample compared to the sample hydrated at 423°K. The former also contains spikey (1-2 basal layers thick) and large (up to 600 x 100 nm) protophyllosilicate grains. In both samples the lattice fringe spacings and chemistry support the talc hydrate, kerolite, (d_{002} = 0.99 nm; d_{001} = 1.9-2.1 nm) and smectite with an average basal spacing of 1.6 nm (range: 1.3-1.9 nm).

The 423/22-sample has many tabular pure-Mg grains (< 60 nm thick). A protophyllosilicate that is two 1.7 nm basal layers thick covers the planar surfaces of the pure-Mg grains. The grain interior shows a mottled chessboard texture of domains with a 2.6 nm fringe spacing. The electron diffraction data support brucite, Mg(OH)₂, but with incipient damage caused by the incident electron beam. Some diffraction maxima fit both brucite and periclase (MgO) and are probably an experimental artifact. A few relic forsterite domains remain.

DISCUSSION. The collapsed condensate texture and formation of distinct end-member domains indicate that leaching was the rate limiting step in the mineralogical development of hydrated samples [cf.4]. The mean and modal MgO values of the starting material are close to the forsterite composition. The Ostwald Step Rule thus favors metastable growth of this olivine during autoannealing of the quenched Mg-SiO melt and possibly also MgO. Hydration of the Mg-SiO matrix yielded the saponite: $4 \text{Mg}_2\text{SiO}_4 + 4 \text{H}_2\text{O} \cdot \text{SiO}_2 + n\text{H}_2\text{O} = \text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O} + 2 \text{Mg}(\text{OH})_2$, and kerolite, viz. $4 \text{Mg}_2\text{SiO}_4 + 4 \text{H}_2\text{O} \cdot \text{SiO}_2 + 2 \text{H}_2\text{O} = \text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot 2\text{H}_2\text{O} + 2 \text{Mg}(\text{OH})_2$. Silica saturation during hydration is shown by formation of these metastable protophyllosilicates matching the mean and modal MgO matrix contents instead of serpentine, Mg₆Si₄O₁₀(OH)₈. The kinetically controlled co-precipitation of saponite and kerolite reflects the variable availability of water during these hydration experiments. The temperatures in both hydration experiments were high enough that diffusion was not a limiting factor for growth of these protophyllosilicates and brucite from nanometer sized forsterite. Brucite or MgO were not found in AEM analyses of carbonaceous chondrite matrix. A porous mass of periclase occurs in one Mg-rich, saponite dominated, IDP [5]. From this work it appears that formation of MgO or Mg(OH)₂, saponite and talc, or kerolite, is restricted to the pure MgO-SiO₂ system. Trace amounts of impurities, e.g. Al, may affect the product phases of hydration. Hence, MgO or brucite are probably rare minerals in meteorite matrix and IDPs.

CONCLUSIONS. Hydration of an Mg-SiO condensate under silica-saturated conditions favors protophyllosilicates with high Si/Mg ratios instead of serpentine. The resulting saponite and talc hydrate, or kerolite, reflect kinetically favored growth controlled by the availability of water for hydration. The results support that serpentine-rich chondritic IDPs are rare among the most primitive, hydrated solar system materials.

REFERENCES. [1] Rietmeijer FJM & Nuth JA (1991) Proc. Lunar Planet. Sci. 21, 591-599; [2] Nelson R et al. (1987) JGR, 92 (B4), E657-E662; [3] Rietmeijer FJM et al. (1986) Icarus 66, 211-222; [4] Rietmeijer FJM (1995) LPS XXVI, 1163-1164; [5] Zolensky ME & Lindstrom DJ (1992) Proc. Lunar Planet. Sci. 22, 161-169. The samples were provided by J.A Nuth (NASA-GSFC). This work was supported by NASA Grant NAGW-3646.