

FERROSILITE, FAYALITE AND MAGNESIOFERRITE FORMATION BY ISOTHERMAL ANNEALING OF AN IRON-CONTAMINATED Mg-SiO SMOKE.

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Laboratory studies of thermally-annealed vapor condensates will advance the understanding of dust evolution in oxygen-rich protostellar environments. A previous analytical electron microscope (AEM) study of an annealed Mg-SiO smoke showed coarsening of forsterite and enstatite nanocrystals accompanied by equilibration of bulk Mg/Si (at%) ratios as a function of annealing time (2, 4, 8, & 39 hours) *in vacuo* at 1000°K [1]. This AEM study used dispersed, 3-dimensional "bulk" samples [1] in which it was difficult to obtain grain size distributions, and to perform electron diffraction and quantitative chemical analyses of individual nanocrystals. The introduction of serially-sectioned, ultrathin (80-100 nm) sections for AEM analyses of interplanetary dust [2] was the incentive to re-analyse the thermal-annealing history of the Mg-SiO smoke because the individual grains in ultrathin sections are accessible to quantitative chemical, electron diffraction and textural analyses. Traces of an unidentified Fe-bearing contaminant in the "bulk" samples did not react with the Mg-SiO smoke [1]. We exploit the greatly improved sample preparation to look for Fe-silicates that might have formed during annealing. Ultrathin sections of smoke samples annealed for 8, 30 and 167 hours were prepared for AEM analyses using a Jeol 2000FX AEM equipped with a TN-5000 energy dispersive spectrometer [cf. 3]. The samples appear dull-grey to black in white light, but ~40% of the 167h-sample has a yellow tinge that is probably due to ferric iron-bearing phases. We prepared ultrathin sections of the differently-coloured materials.

RESULTS. The annealed samples have an open cluster morphology. Relics of the crude network of interconnected ribbons of the original condensate [1] are still present in the 167h-sample (black fraction). All samples are dominated by equigranular (*i.e.* a narrow size distribution), poorly-crystalline Mg-SiO material with randomly oriented nanocrystals. Distinctly fine-grained (< 20 nm in diameter) polycrystalline materials are in variable proportions associated with coarse-grained material with nanocrystals of ~40-60 nm (8 hours) and ~60-80 nm in diameter (167 hours). The quantity of nanocrystals, and porosity of the Mg-SiO material, gradually increase with annealing time. The fine-grained domains are slightly Mg-richer than coarse-grained polycrystalline materials. The electron diffraction data are consistent with forsterite, enstatite and tridymite. Small amounts of amorphous silica-rich (>95 wt% SiO₂) areas and tridymite crystals (both up to ~200 nm in size) occur throughout the Mg-SiO material in all samples. The coarse-grained Mg-SiO material in each sample contains round to irregularly-shaped, platey single-crystal grains of ~100 nm up to ~500 nm in diameter. In the 167h-sample they tend to form subhedral single-crystal grains. The compositions of the Fe-SiO grains range from ~30-75 wt% FeO (8 hours) and ~30-95 wt% FeO (30 & 167 hours) with two clusters at 35 and 52 wt% FeO of ferrosilite and fayalite grains, and an a third cluster at 70 wt% FeO of hematite, and possibly maghemite, grains. In addition to equigranular Mg-SiO material, the 167h-sample's yellow fraction is characterised by (I) randomly-distributed, euhedral magnesioferrite single-crystals (< 300 nm long; ~18 wt% MgO) and euhedral, single-crystal brucite, Mg(OH)₂, up to 50-100 nm in size and (II) smoke-like domains of subrounded grains that include (a) euhedral periclae (MgO) grains with a Mg-SiO mantle (~16-65 nm in diameter) and (b) core-free Mg-SiO grains (~9-60 nm in diameter).

Fayalite and ferrosilite. In both iron-rich olivine and pyroxene $Fe^{2+}/(Mg+Fe^{2+}) = \sim 0.85 - 1.0$. These silicates generally contain ferric iron, *viz.* Fe³⁺ ions between 0.05 - 0.65 (calculated from stoichiometry), but mostly 0.05-0.10 (~70% of data). The $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratios are 0.6-1.0 (olivine) and $fe = 0.90-1.0$ (pyroxene). In rare pyroxenes all iron is Fe³⁺. We have not yet unambiguously identified laihunite (La) by electron diffraction but rare olivines in the 30h- and 167h-samples fit the structural formula of this 'ferrifayalite' mineral. These olivine are $Fe_{0.75}Fa_0La_{0.25}$ and $Fe_{0.54}Fa_0La_{0.46}$ (30 hours), and $Fe_5Fa_{90}La_5$ and $Fe_1Fa_{69}La_{30}$ (167 hours). We estimate $\log fO_2$ between -15 and -10 atm. at the FMQ and HM buffers.

DISCUSSION. Autoannealing describes post-condensation solid-state transformations that occur in a vapor-condensed smoke [4]. It will be difficult to identify nanocrystals as part of the condensation history or of later thermal annealing. For example, fine-grained Mg-silicates in poorly-crystalline material of the 8h-sample might be due to autoannealing. Otherwise the increased grain size and quantities of nanocrystals, and the formation and growth of Fe-silicates, are consistent with prolonged heating. Contrary to the earlier findings [1], an Fe-contaminant in the present allocations did react with the Mg-SiO smoke during isothermal annealing. The Fe-silicates might have formed by reaction of Fe-vapor with Mg-silicates or via solid-state reactions. Considering the boiling points of metallic iron and of various Fe-oxides and the thermal annealing conditions, we presently favour the latter explanation. The Fe-contaminant was probably steel from the collector plate. We propose that enstatite reacted to form fayalite and ferrosilite, *viz.* (a) $\text{MgSiO}_3 + 2\text{Fe} + 1/2\text{O}_2 = \text{Fe}_2\text{SiO}_4 + \text{Mg(g)}$, (b) $2\text{MgSiO}_3 + 2\text{Fe} = \text{Fe}_2\text{SiO}_4 + 2\text{Mg(g)} + \text{SiO(g)} + 1/2\text{O}_2$, and (c) $\text{MgSiO}_3 + 3\text{Fe} + 2\text{O}_2 = \text{FeSiO}_3 + \text{MgFe}_2\text{O}_4$, whilst forsterite formed Fe-silicates according to (d) $2\text{Mg}_2\text{SiO}_4 + 2\text{Fe} = 2\text{FeSiO}_3 + 4\text{Mg(g)} + \text{O}_2$, and (e) $\text{Mg}_2\text{SiO}_4 + 2\text{Fe} = \text{Fe}_2\text{SiO}_4 + 2\text{Mg(g)}$.

The reactions *a, b, d, & e* produce a metallic-Mg vapor consistent with earlier evidence [1] for evaporative Mg-loss during annealing. Reaction *b* also produces SiO vapor. The Mg-bearing vapor condensed into euhedral MgO crystals possible as the result of the vapore reacting with liberated 2O_2 . The euhedral MgO crystals indicate 3-dimensional growth at (local) high supersaturation ratio. They provided nuclei for Mg,Si-O deposition. Rare magnesioferrite spinel formed by reaction *c*. Magnesioferrite occurs naturally as a result of extreme and highly transient temperature gradients that yield disequilibrium mineral assemblages at a bulk scale but with domains of full thermodynamic phase equilibrium [5]. This type of environment is also conducive to laihunite formation via oxidation of fayalite wherein synthetic laihunite uniquely coexists with hematite and silica under atmospheric oxidation conditions [6,7]. Kinetically-controlled mineral formation rather than thermodynamic equilibrium for ultrafine assemblages also occurs during atmospheric entry flash-heating of micrometeorites wherein laihunite has also been observed [8,9]. The data support chaotic disequilibrium during isothermal annealing of an Fe-bearing, Mg-SiO smoke. After prolonged isothermal annealing, Fe^{3+} is no longer accommodated in the silicates which induces the formation of nonstoichiometric Fe-silicates, such as laihunite, and there is evidence for partial evaporation and condensation to produce the distinctly fine-grained Mg(Si-O) smoke. Brucite is probably a post-annealing artifact due to reaction of MgO with atmospheric moisture.

CONCLUSIONS. We exploit the inadvertent contamination of an Mg-SiO smoke with Fe-metal grains. Fayalite and ferrosilite with variable fe-ratios, rare laihunite and magnesioferrite occur alongside existing forsterite, enstatite and tridymite. The Fe-minerals form from their Mg-counterparts as a function of annealing time at 1000°K with (partial) evaporation and condensation of a metallic-Mg vapor after prolonged annealing. When thermal annealing of dust in protostellar regions is an important process, it follows that this dust may contain variable proportions of Mg-rich and Fe-rich olivines and pyroxenes and accompanying MgO and Mg,Fe-oxide minerals. In addition to metamorphism of the dust, partial evaporation and condensation events could occur. The opacity of silicate dust in the near-IR region depends on their $\text{Fe}^{2+}/(\text{Fe}^0 + \text{Fe}^{2+} + \text{Fe}^{3+})$ ratio. This ratio might provide an important constraint on the aging of astrophysical dust [10]. We have shown that thermal annealing of Mg-silicates in the presence of an "Fe-donor phase" tends to produce high *fe*-ratios in a small fraction of the silicate grains. This type of AEM analyses of astrophysical dust analogs may help elucidate the details of dust evolution in environments such as the primitive solar nebula.

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