**HETEROGENEOUS NUCLEATION AND GROWTH OF METAL ON SILICATES AND ITS ASTROPHYSICAL IMPLICATION.**

H. Nagahara[1] and K. Ozawa[2], [1]Dept. Earth Planet. Sci., The Univ. Tokyo (7-3-1 Hongo, Tokyo 113-0033, Japan and hiroko@eps.s.u-tokyo.ac.jp), [2]Dept. Earth Planet. Sci., The Univ. Tokyo.

**Introduction:** Magnesium, Si, and Fe are the most abundant metallic elements, which are responsible for astrophysical dusts that causes interstellar extinction and which are in particular important to carry thermal structure of circumstellar discs. Recent astrophysical observation with infrared spectra has revealed that there are abundant silicate dusts around evolved and young stars. They are mostly amorphous [1], but smaller abundance of crystalline silicates has been reported [e.g., 2, 3]. The spectra are well fitted by multiple silicate phases: crystalline forsterite (Fo), crystalline enstataite (En), amorphous olivine, amorphous enstatite, and amorphous silica with size distribution for all phases for discs around T-Tauri stars [4] and Herbig Ae/Be stars [5]. Contrary to silicates, presence of metallic iron is not reported because of absence of vibration or rotation bands in infrared.

**Metal/silicate relationship and grain size distribution**: The occurrence and size distribution of dusts are critical for interpretation of infrared spectra and modeling of thermal structure of discs. Chemical equilibrium is the guide for appearance of phases, but it does neither predict the occurrence of the two phases nor the grain size.

Homogeneous nucleation and growth model developed by [6,7] calculates nucleation delay, which depends on $P_{tot}$ and cooling time ($\tau$) of gas. The effect is larger for metallic iron due to larger surface tension than silicates; for example, silicate delays by ~50° compared to equilibrium, while metal ~100° at $\tau = 10^4$ year [8]. The grain size distribution is estimated to be in a narrow range, but independent nucleation and growth of silicates and metal is implicitly assumed.

**Kinetics of metal condensation:** We have carried out a series of condensation experiments of Fe [9-11], and showed two important results: the condensation coefficient of metallic iron is approximated to be unity in the temperature range of metal condensation in discs around young stars, and Fe metal heterogeneously condenses on alumina oxide with the super saturation ratio ($\sigma=P/P_{eq}$) at least seven. The latter gives us very important view that metal heterogeneously condenses on silicates (or oxides if any) in a cooling gas, which has not been investigated yet. The change of condensation mode and temperature is expected to affect the occurrence of condensing phases and grain size distribution, and therefore the IR spectra. We will investigate the phases and grain size distribution in kinetically condensing system, where heterogeneous nucleation of metal on silicate is taken into consideration.

**Model:** The model consists of two basic equations: (1) the nucleation and growth rate is a function of gas velocity, abundance of the gas species concerned, and condensation coefficient, and (2) net mass conservation, which means that the concentration of gas species concerned decreases with progress of condensation. The model contains two important parameters, $P_{tot}$ and $\tau$, which may not be independent in astrophysical conditions.

Nucleation of forsterite takes place homogeneously, of which timing is defined by the surface tension. Metal nucleates heterogeneously at $\sigma$=7 on forsterite because forsterite condenses always prior to Fe. We have also tested how $\sigma$ affects the consequences. The system consists of H, He, C, O, Mg, Si, and Fe with the solar abundance ratios, $\tau=10^2$ to $10^{12}$ sec (~$3\text{x}10^5$ yrs), and $P_{tot}=10^{-9}$ to $10^{-2}$ bar. The condensation coefficient of Fe is taken to be 1, and those of forsterite and enstatite are assumed to be 0.1, which has not yet to be experimentally determined and which may contain significant error.

In the present calculation, all the phases are assumed to be crystalline, though it is not evident. The abundant presence of amorphous silicates in astrophysical environments may indicate that amorphous silicate are the products of condensation and crystallization took place by certain high energy processes [12]. We did not consider this possibility here, because high-energy process easily breaks down structures of crystalline materials to amorphous, but hardly transform amorphous materials to crystalline due to short time scale of the process. Transformation of solid materials from amorphous to crystalline needs heating for considerable duration. Thus, we assume that crystalline materials astrophysically observed are direct condensates from gas.

**Results:** Figure 1 shows the condensation sequences and number of condensed phases for rapid cooling (left; $\tau=1\text{x}10^4$ sec) and slow cooling (right; $1\text{x}10^{12}$ sec = ~ $3\text{x}10^4$ years) at $P_{tot}=10^{-5}$ bar.

The phase appeared at first at smaller $\tau$ (rapid cooling) is Fo, of which size is very small and the number density is high. A small amount of En also condensed with Fo. They were followed by Fe, which condenses at ~1205K heterogeneously on the previously condensed Fo. Because $\tau$ is small, there still remains Mg in the residual gas, and Fo restarted to condense at ~1180K (secondary Fo) after $\sigma$<7 due to the significan condensation of Fe. The secondary Fo later partly reacts with residual gas to form En. En started to condense as independent grains at ~1175K. The final products in this condition are Fe with Fo core, Fo, En with Fo core, En and Fe on En in the decreasing order of abundance. It is noteworthy that grains with Fo core and Fe mantle are formed, which has not been expected in previous models. There is no isolated metal grain.

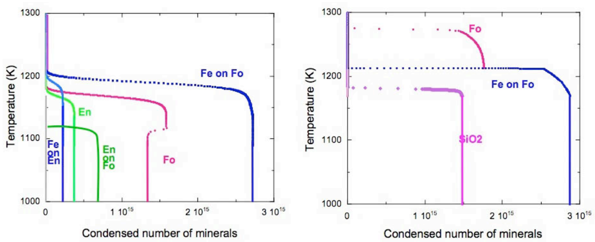


Fig. 1 Condensation sequence of phases at $P_{tot}$=$10^{-5}$ bar for rapid cooling (left; $\tau$=1x$10^4$ sec) and slow cooling (right; $\tau$=1x$10^{12}$ sec or ~ 3x$10^4$ years). Fo:forsterite, En: enstatite, SiO2: silica, Fe: Fe metal.

The condensed phases at large $\tau$ (slow cooling) are Fo, which is totally covered by Fe at ~1215K, and SiO2 appears at ~1185K from the residual gas. The final products in this condition are Fe with Fo core and SiO2. The difference between rapid and slow cooling is whether there remains Mg in residual gas when Fe started to condense, which corresponds to the time when $\sigma_{Fe}$ gets 7, the critical super saturation ratio for heterogeneous condensation.

The assemblage of final products is divided into two cases in the $P_{tot}$ and $\tau$ space; (1) secondary Fo and Fe with Fo core (±En and SiO2), and (2) Fe with Fo core and SiO2. The boundary between the two cases is shown in Fig. 2. The figure suggests that Fe with Fo core grains and SiO2 grains are dominant grains in most conditions of discs around young stars ($P_{tot}$ ~ $10^{-4}$ - $10^{-5}$ bar, $\tau$> ~$10^3$ year). The assemblage of secondary Fo grains and metal with Fo core grains are formed in large $\tau$ such as rapid cooling accompanied by shocks, which corresponds to chondrule formation.

The grain size distribution is also obtained in the above calculations. The average (or typical) size increases with increasing $\tau$, and the size distribution is generally narrow, which is less than an order. The grain size increases drastically with increasing $\tau$; typical size for $\tau$= ~$10^4$ sec and $P_{tot}$ ~ $10^{-5}$ bar (left panel of Fig. 1) is about nm in order for all the phases, 10-100 µm in order for En and mm in order for metal with silicate core at $\tau$= ~$10^{12}$ sec. The size is systematically larger at larger $P_{tot}$.

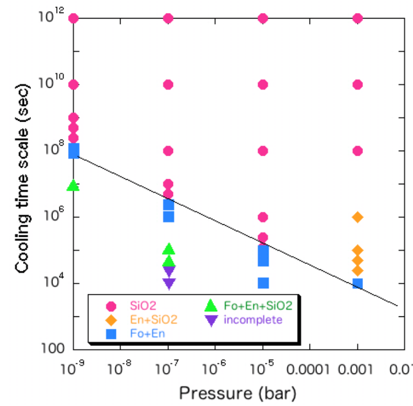


Fig. 2 Final products of kinetic condensation with heterogeneous nucleation of Fe on silicates.

**Discussions:** The present work shows an important result that forsterite that always condenses prior to Fe due to smaller surface tension in astrophysical conditions including solar nebula is covered by Fe, which prevents the reaction between forsterite and gas that is expected in an "equilibrium" model. This finally results in condensation of SiO2. It is easily expected that reactions actually take place in nature are somewhere between two extremes, equilibrium and totally kinetic, and the phases formed in young discs will be a mixture of the products in these two environments, that is, Fo, En, SiO2, Fe on Fo, and Fe on En. This explains the infrared spectra that are well fitted by mixtures of several phases with size distributions [2-5]. The abundant formation of grains with Fo core and Fe mantle may explain the spectra of some discs that show solely PAH [5], where most silicate components are coated by thick metal to show no silicate feature.

The grain size can constrain the dust formation conditions. Io order to satisfy the observed grain size, the cooling time of the gas that condensed silicate was $10^9$ – $10^{11}$ sec at $P_{tot}$=$10^{-5}$ bar and $10^7$ – $10^9$ sec at $P_{tot}$=$10^{-3}$ bar, which are fairly rapid for general nebula evolution time scale.

**References:** [1] Kemper F. et al. (2005) 2004, *ApJ.* 609, 826. [2] Waters L. B. F. M. et al. (1996) *A&A 315*, L361. [3] Waelkens C. et al. (1996) *A&A 315*, L245. [4] Honda M. et al. (2003) *ApJ.* 535 L59. [5] van Boekel R. et al. (2005) A&A, *437,* 189. [6] Yamamoto T. and Hasegawa H. (1977) *Prog. Thoer. Phys. 58*, 816. [7] Draine B. T. and Salpater E. E. (1977) *J. Chem. Phys,* 67, 2230. [8] Kozasa T. and Hasegawa T. (1987) *Prog. Theor. Phys*. 77, 1402. [9] Tatsumi K. et al. (2004) LPSC XXXV, #2013. [10] Ikeda Y. et al. (2007) LPSC XXXIII, # 2403. [11] Nomura R. et al. (2008) LPSC XXXIX.