

VARIATION OF THE CONDENSATION PATH OF SUPERCOOLED SILICATE MELT. H. Nagahara and K. Ozawa, Dept. Earth Planet Sci., Univ. Tokyo (hiroko@eps.s.u-tokyo.ac.jp; ozawa@eps.s.u-tokyo.ac.jp).

Introduction: Although compositional variation of equilibrium condensation of the solar nebular gas has been well studied since 1960th [e.g., 1-2], the effect of condensation kinetics has not yet been studied so far. It is because due to (1) the lack of kinetic condensation model, (2) the lack of information on kinetic parameters of silicate minerals and melts, particularly condensation coefficients, and (3) it has been implicitly thought that condensation proceeds maintaining equilibrium despite that evaporation is thought to take place under disequilibrium.

Equilibrium condensation model of the solar nebular partly succeeds in explaining the meteoritic components, particularly CAIs [3], although equilibrium condensation and later short time melting is proposed recently [4]. Equilibrium condensation accompanying with fractionation also succeeds in explaining bulk chemical composition of some chondrite groups [5].

Contrary to CAIs, the diversity of chondrule compositions has been attributed to be that of the precursors and/or change due to evaporation. The diversity, however, has been satisfactorily explained neither equilibrium condensation nor evaporation in vacuum.

In the present study, we develop a new kinetic model to describe composition change of a multi-component condensed phase during condensation as well as evaporation under kinetic conditions. It is applied to investigate the path of condensing silicate melt by using parameters available from evaporation experiments. Based on the results, the diversity of chondrule compositions in primitive ordinary chondrites is considered.

Model: The condensation model adopted in this study is an extension of the evaporation model for multi-component systems developed by [6], which is based on the Hertz-Knudsen equation for the kinetic theory of gases. In order to extend the model to condensation reactions, a kinetic model properly describing surface reaction in both undersaturated and supersaturated conditions is required. In the model, the net flux of evaporation or condensation of a component normalized by its free evaporation rate is expressed as a function of ambient pressure of the relevant gas species normalized by its equilibrium vapor pressure. The relationship is constrained by evaporation experiments,

theory, and Monte Carlo simulations on crystal growth and dissolution [7].

For condensation from a completely gaseous state, nucleation and subsequent growth of a spherical condensed phase is supposed to start at certain supercooling, where the saturation temperature is calculated for the given initial conditions according to [8]. The composition of nuclei is determined by relative amount of the net fluxes of components, which is dependent on the nuclei composition. Any open-system behavior (e.g., separation and/or influx of either condensed phase or gas) can be examined with this model and is applicable to any condensed phases if kinetic parameters are available.

The closed-system model is applied to silicate melt in the present study. Crystallization in the silicate melt and condensation of crystalline phases are neglected for simplicity. The calculation was done in the nondimensionalized form, and thus the time-scale is determined if several variables, such as free evaporation rate (or equilibrium vapor pressure), size of melt sphere, and hydrogen pressure, are given.

The system consists of O-Na-Mg-Al-Si-K-Ca-Fe, where hydrogen is not considered. The temperature in the present calculation, thus, is not applicable to estimate the conditions of chondrule formation, but the trends are valid.

Parameters: Kinetic parameters for evaporation, such as activation energy of evaporation and chemical fractionation factors, are optimized for the present model on the basis of free evaporation experiments on silicate melts [9-11], in which the total mass loss data are available. The free evaporation rates are used as references to model composition and temperature dependence of the net flux of each component. The parameters related to condensation, such as degree of supersaturation and condensation coefficients, are unknown and thus regarded as free parameters.

The system is assumed to be closed at a constant volume. Metallic iron is subtracted from the total Fe according to the redox state of ordinary chondrites. The initial values of FeO and (CaO+Al₂O₃) are varied to find the optimal values to model the variation of Type I chondrules. The temperature and composition dependence of molar volume of silicate melt is taken from [12].

Results: Several calculation results are shown in Fig.1 with equilibrium and vacuum evaporation paths in a closed system. Kinetically controlled condensation paths are not so largely different from the equilibrium path, however, the nonlinearity is larger as compared with the equilibrium paths, that is, curvature of the path is steeper. It is in particular obvious in Mg-Si-Fe and Mg-Si-(Al+Ca) diagrams. A large degree of disequilibrium condenses silicate melt with large Mg/Si fractionation during cooling. It is worth noting that the nonlinearity increases with increasing degree of disequilibrium: large cooling rate and large degree of supersaturation at the initial condition generate more fractionated composition.

The gas coexisting with the condensing melt has composition rich in SiO₂ and FeO. The trajectory of gas composition is closer to linear compared to the gas, which becomes more linear at large cooling rate or supersaturation. Although the degree of disequilibrium does not affect gas composition significantly, the effect is fairly large for the gas coexisting with refractory melt.

Discussion: The composition of chondrules in least metamorphosed chondrites is characterized by (1) almost constant refractory component with the Al/Ca ratio equal to that of the solar system, (2) highly variable Mg/Si ratio, and (3) almost constant FeO content in FeO-poor chondrules and variable FeO in FeO-rich chondrules, and variation ranges from more refractory to less refractory compositions. [3] discussed that equilibrium condensation fails to produce a chondrule composition with Al-poor and Mg-rich compositions.

Kinetic condensation can produce Al-poor and Mg-rich chondrule compositions, which is closer to the distribution of natural chondrules. It is, however, still not satisfactory. Very rapid cooling or large degree of supersaturation produces Al-poor and Mg-rich composition, but it fails to produce Al-poor and Si-rich compositions.

In order to produce whole range of composition of common chondrules, we have changed the initial composition of the gas and found that the depletion of refractory component by about 30% and the FeO content by 20 to 50% of the CI abundances is necessary.

Conclusions: Rapid cooling of the gas produces silicate melt with composition more fractionated than equilibrium condensation. It is, however, still not enough to explain the whole range of chondrule compositions. The whole range of the diversity requires

the initial depletion of refractory component and FeO by several tens of %, indicating chemical fractionation in the earlier stage of the solar nebula before chondrule formation.

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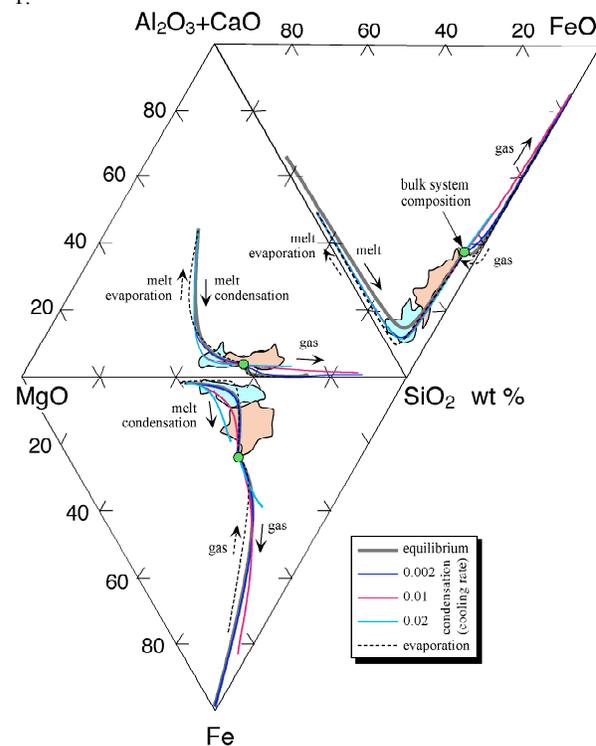


Fig. 1: Kinetic condensation (solid colored curves), vacuum evaporation (dashed curve), and equilibrium (solid gray curve) paths for multi-component silicate melt and gas in a closed system (SiO₂-MgO-CaO-Al₂O₃-FeO-Na₂O-K₂O) with bulk composition shown as the green circle. The fields for compositions of Type I (blue) and Type II (pink) chondrules after [13] also shown. Arrows indicate direction of compositional change during condensation or evaporation. Used parameters: supercooling $\Delta T = \sim 15\text{K}$, the ratio of evaporation and condensation coefficients = 1.0 (linear pressure – flux relation), initial temperature = 1673K, linear cooling, kinetic fractionation factors = proportional to the square root of the inverse of mass of gas species.