New results from metamorphic nucleation experiments

DAVID M. HIRSCH[1*], CRAIG E. MANNING[2]

[1]Western Washington University, Bellingham, WA USA,
hirschd@geol.wwu.edu (* presenting author)
[2]University of California Los Angeles, Los Angeles, CA USA,
manning@ess.ucla.edu

Introduction

The rates and mechanisms of metamorphic crystallization remain poorly understood despite decades of study. In particular, nucleation processes such as the relationship of nucleation rate to driving force have proven difficult to quantify. Nucleation theory predicts that the nucleation rate can be expressed as:

$$\frac{dN}{dt} = C_1 \exp\left(\frac{-C_2}{T\Delta G_{rxn}^2}\right) \qquad (1)$$

where N is the number of nuclei per unit volume, T is the absolute temperature, ΔG_{rxn} is the Gibbs free energy of the chemical reaction, and C_1 and C_2 are constants, which can be related to other, less well-constrained properties of the system [1]. However, this theory has not been adquately tested against geological data.

Experimental Method

We have undertaken a experimental pilot project to model nucleation, focusing on the reaction An + Wo = Grs + Qtz from an initial assemblage An+Wo+Qtz. This reaction is simple enough to make the experiments tractable, yet retains key basic features of reactions studied by others working on crystallization kinetics: aluminous garnet is the nucleating phase and the reaction involves multiple reactants and products. In order to remove temperature as a variable, all experiments are performed at constant temperature (1100 °C), and nucleation is initiated by a change in pressure only (1.41-1.90 GPa). Stereological methods were used to determine 3D nucleation counts.

Results

The experiments successfully nucleated grossular in runs within its stability field. Nucleation rates are generally replicable from run to run. Our preliminary results show that there is a systematic relationship between nucleation rate and driving force. By fitting equation (1) to the data, values for the constants are estimated at $C_1 = 8.9 \times 10^6$ and $C_2 = 2.0 \times 10^4$ (Fig. 1). The results support the theoretical prediction of a sharp increase in nucleation rate with driving force.
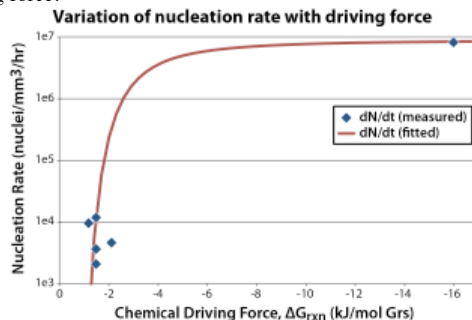
Figure 1: Nucleation rate as a function of thermodynamic driving force.

[1] Kelton, Greer, Thompson (1973) *J Chem. Phys.* **79**, 6261-6276.

Magma ocean influence on early atmosphere composition and mass

MARC M. HIRSCHMANN[1*], HONGLUO ZHANG[1]

[1]Dept. Earth Sci. U. Minneosta Minneapolis, MN USA
mmh@umn.edu (*presenting author)

The composition and mass of the atmosphere overlying early terrestrial magma oceans (MOs) likely had a key influence on Earth's early thermal and dynamical evolution, its geochemical differentiation, its path to an equable climate, and development of prebiotic chemistry. It also set the initial conditions for development of deep Earth volatile cycles. Key questions are how MO processes partitions volatiles between the atmosphere, mantle, and core and how reaction between the the MO and overlying vapor influences the composition of the nascent atmosphere.

The availability of Fe alloy in a MO creates reducing conditions, and the expectation that overlying atmospheres consist chiefly of H_2 and CO, but this may be incorrect if the mean depth of alloy-silicate equilibration is deep, if convection in the MO homogenizes Fe^{3+}/Fe^T throughout the magma column, and if the effect of decreased pressure on the chemical potentials of Fe^{2+} and Fe^{3+} in the magma increases relative f_{O2}. Low pressure data [1,2] suggest the opposite – decreases in Δf_{O2} on isochemical decompression – but Mössbauer spectroscopy of andesite glasses quenched from 1-6 GPa provisionally indicate that this relationship reverses at high pressure. Consequently, it is likely that the overlying atmosphere consisted chiefly of H_2O+CO_2, whilst reducing (~IW-1.5) conditions prevailed deep in the MO.

Owing to low solubility of C-species in reduced magma, virtually all of the available C in the MO and the atmosphere may be partitioned into alloy, leaving a virtually C- free mantle and exosphere. However, it is likely that the MO equilibrates with only a small fraction of metal (<5% [3] and possibly <1%). As the alloy cannot absorb ~ 8 wt.% C, excess reduced C may saturate as diamond. This too will greatly limit the partial pressure of CO_2 in the overlying atmosphere. Floatation of diamond in the MO [4] and could create the principle initial reservoir of C in the BSE.

Following or coinciding with segregation of metal (but not diamond) to the core, the Moon-forming impact resets the volatile distribution in the BSE: virtually all that did not escape ends up in a superheated atmosphere. On cooling, much of the remaining H_2O and some of the CO_2 redissolves in the MO. Upon MO crystallization, much of the H_2O and possibly nearly all the the C returns atmosphere. However, homogenization of Fe^{3+}/Fe^T in the MO should again produce a vertical f_{O2} gradient in the MO and the solubility of CO_2 diminishes by >10X on cooling from a MO adiabat to the peridotite solidus. Thus, precipitation of a C-rich phase (diamond, carbide, or alloy) during crystallization of this final MO is likely, setting up conditions for a MO carbon pump [5] that draws down much of the CO_2 in the atmosphere and deposits much of the BSE C in the mantle rather than the exosphere. This speculative, but plausible, scenario may produce a mantle with a high H/C ratio compared to the exosphere, as remains true at present [6].

[1] Kress&Carmichael (1991) *Contrib. Mineral. Petrol.* **108**, 82-92. [2] O'Neill et al. (2006) *Am. Mineral* **91**, 404-412.[3] Dahl & Stevenson (2010) *EPSL* **295** 177-186. [4] Suzuki et al. (1995) *Science* **269** 216-281. [5] Hirschmann (2011) *42nd LPSC Abstracts* #2321. [5] Hirschmann&Dasgupta (2009) *Chem. Geol.* **262** 4-16.