

Effect of amino acids on energy barriers to silica nucleation and polymerization

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The processes by which silicifying marine organisms synthesize amorphous silica into skeletal structures are receiving considerable attention in the biomineralization community. Previous studies propose that charged macromolecules (specialized proteins and polyamines) found at sites of silicification lower the energy barrier to facilitate silica polymerization. This idea emerged from studies of zeolite minerals but was untested by experiment. Findings from a recent *in situ* study of silica nucleation onto charged biosubstrates has challenged this explanation by showing that carboxyl and carboxyl/amine surfaces promote nucleation through increases in kinetic factors while having no measurable effect on thermodynamic barriers to nucleation [1].

In this experimental study, we determined the effect of acidic, basic, and uncharged polar amino acids on the induction time and kinetics of silica polymerization from monomeric silicic acid solutions. Using 0.1 M NaCl solutions as the control condition; measurements were compared to solutions that also contained 0.1 M of each amino acid. All experiments were conducted at 20°C. The data show that both NaCl and biomolecules reduce the induction time to polymerization. Analysis of these data show that biomolecules: 1) do not affect the energy barrier to nucleation; 2) lower the kinetic energy barrier to growth; and 3) decrease the energy barrier to growth in proportion to their electrophoretic mobility (combination of size and charge). These measurements for aqueous silica polymerization support findings for silica nucleation onto model biotemplates [1] and reiterate the need to revisit nucleation theory in light of increasing evidence for the critical roles of kinetic barriers.

[1] Wallace, A.F. *et al.* (2009) *JACS*, **131**, 5244-5250.

Genesis of the Huize zinc-lead deposit from an infrared microthermometric study of fluid inclusions in sphalerite, Yunnan, China

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Infrared microthermometric technique is an efficient method to study fluid inclusions in opaque-translucent minerals, using the equipments which are composed of infrared microscope and heating-freezing stage. The Huize surper-large scale carbonate-hosted Zn-Pb-(Ag-Ge) deposits is located in Northeast Yunnan District, with the characteristics of high Zn-Pb grade, rich Ag and dispersed elements, large scale and huge economic value. Sphalerite (main ore mineral) has rich color from dark grey-brown to light yellow, and different crystal forms from the euhedral crystal to the anhedral, which has reflected the special ore-forming fluid and unique ore-forming environment.

Five types of fluid inclusions can be observed in sphalerite, pure gaseous inclusions, pure liquid inclusions, gas-liquid inclusions with rich liquid, gas-liquid inclusions with rich gas and three-phase inclusions containing a daughter. The homogenization temperature of fluid inclusions in sphalerite ranges from 100.2°C to 344.5°C, which have two change temperature sectors obviously, 150°C~200°C and 250°C~350°C. Salinity of fluid inclusions in sphalerite is similar to homogenization temperature, which ranges from 1.06 wt%NaCl_{eq} to 18.04 wt%NaCl_{eq}, and have two change sectors, 1~13 wt%NaCl_{eq} and 13~20 wt%NaCl_{eq}. For calcite, fluid inclusions dominated by liquid and pure liquid types, homogenization temperature ranges from 164°C to 221°C and salinity ranges from 6.6 wt%NaCl_{eq} to 12 wt%NaCl_{eq}.

Compare with gangue mineral, fluid inclusions in sphalerite contains more information of ore-forming fluid, and the infrared microthermometric technique has provided an ideal method to study the ore-forming fluid of Zn-Pb deposits in Northeast Yunnan.

Granted jointly by the Funds for Program for NSF (40863002), NCET (NCET-04-917), the project of State Crisis Mine (20089943) and the Distinguishing Discipline of KUST (2008).