

Avanavero Large Igneous Province: a short-lived and widespread Paleoproterozoic mafic event in the Guiana Shield, Amazonian Craton: U-Pb geochronological, geochemical and paleomagnetic evidence

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The Avanavero Large Igneous Province (LIP) constitutes the most important Paleoproterozoic mafic magmatic event in the Guiana Shield, northern Amazonian craton. It comprises voluminous tholeiitic dykes and sills, the latter intrusive into regional sedimentary cover sequences such as Roraima Supergroup and Urupi Formation. Geochemical evidence suggests variable influence and modification by continental lithosphere, similar in many respects to chemically equivalent Karoo and Columbia River continental flood basalts of the Phanerozoic.

We present new U-Pb (ID-TIMS) baddeleyite ages of 1795 ± 2 Ma and 1793 ± 1 Ma from the Pedra Preta and Quarenta Ilhas gabbroic sills occurring in the Pakaraima and Urupi Blocks, respectively, at the north and south extremes of the Guiana Shield, north of the Phanerozoic Amazon basin. Combined with a single earlier ID-TIMS U-Pb age of 1794 ± 4 Ma for a mafic dyke [1], these ages confirm a broad suspicion from earlier isotopic studies (Rb-Sr, K-Ar, U-Pb SHRIMP) for the existence of a major ca. 1.78-1.80 Ga Avanavero magmatic event spanning eastern Venezuela-Guyana-Suriname-northern Brazil. The new results, however, potentially collapse the duration of intrusive activity to only a few Myr. Moreover, coeval gabbroic magmatism (Crepuri sill) in the Central Brazil Shield suggests the Avanavero LIP originally extended across Brazil, south of the Amazon basin, towards the opposite side of Amazonia.

A synoptic summary is provided regarding the interpreted geometry of this expansive magmatic province, and we explore possible links between the dominant suite of sills and potential feeder dyke swarms. Available reliable paleomagnetic data favour a Laurentia/Baltica/Amazonia link at 1.78 Ga, and this large landmass may have represented the core of a hypothesized Columbia (Nuna) supercontinent during Paleo- and Mesoproterozoic times.

[1] Norcross et al. (2000) *Precamb. Res.* **102**, 69-86.

Kinetics and thermodynamics of calcite nucleation on self-assembled monolayers

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Sites of biogenic calcification are comprised of a complex macromolecular assemblage that is implicated in regulating the onset of mineralization. Previous studies have qualitatively investigated the influence of functional group chemistry on calcium carbonate (CaCO₃) formation using self-assembled monolayers (SAMs) as proxies for the macromolecules associated with biominerals. While these efforts have demonstrated that chemical functionality influences calcium carbonate phase, morphology, and nucleating face, they cannot provide insights into the kinetics of nucleation or the energy barrier associated with mineralization.

This study tests the hypothesis that specific chemical functional groups regulate the kinetics and thermodynamics of CaCO₃ formation by using SAMs with different termini (-COOH, -PO₄, and -SH) as substrates for calcite nucleation. We measured nucleation rates on each substrate at a variety of chemical driving forces both above and below the reported solubility of amorphous calcium carbonate (ACC), although ACC formation was not observed in these systems. Using classical nucleation theory to interpret the kinetic data, we calculated calcite-substrate interfacial energies and estimated substrate-specific effects on the thermodynamic barrier to nucleation. Calcite – substrate interaction forces were quantified with independent dynamic force microscopy measurements. A second part of the study investigated the effect of magnesium on calcite nucleation rates and barriers for selected substrates.

The kinetic measurements show a strong dependence of calcite nucleation rate on functional group chemistry. Interfacial free energies for 16-C alkanethiols terminated by -COOH and -SH were reduced to 82 and 91 mJ/m², respectively, from approximately 110 mJ/m² reported for calcite in solution. The kinetic behaviour is accurately described with classical models of nucleation, and calcite-substrate interaction force is positively correlated with the reduction in interfacial free energy. Rate measurements from solutions containing progressive amounts of magnesium demonstrate reductions in calcite nucleation rate without affecting the thermodynamic barrier to nucleation.