# Kinetics and mechanisms of silica nanoparticle formation

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Silica polymerisation and the subsequent formation of silica nanoparticles occur in many modern terrestrial environments (e.g. brines, hot springs, deep reservoirs). They also played an important role in ancient geological settings and are believed to have been crucial to the formation of silica-rich deposits that were recently observed on Mars. In the literature, most studies aiming at elucidating the reaction mechanisms and rates of silica polymerisation are based on the time-dependent depletion of monosilicic acid in the polymerizing solution. However, little to no quantitative or time-resolved data on the size of the growing nanoparticles within the solution is available.

Here we present results from an *in situ* time-resolved study that provided quantitative information on the initial steps of silica polymerisation and silica nanoparticle formation from both inorganic and organic solutions. The experiments were carried out in near neutral pH (7 – 8) solutions with silica concentrations ranging form 640 – 1600 ppm $SiO_2$ and ionic strengths (IS) of 0.02 – 0.22 M. These ranges were chosen as they represent those most often found in natural geothermal systems. Furthermore, the presence of specific organics (50 - 300 ppm of either glucose, glutamic acid or xanthan gum, representing microbial cell wall functional groups) on the nucleation and growth process was also examined. The formation of silica nanoparticles (i.e. change in particle size over time) was followed using synchrotron-based Small Angle X-ray Scattering (SAXS) and conventional Dynamic Light Scattering (DLS) combined with conventional or cryo-high-resolution scanning and transmission electron microscopy (SEM/-HR-cryo-TEM). The polymerization reactions were induced either by neutralizing a high pH solution (from pH 12 to 7) or by rapid cooling of a supersaturated hot silica solution (from 230ºC to below 100ºC). The data was used to derive a kinetic model which shows a 3 stage growth process for silica nanoparticles: (1) nucleation of critical nuclei (2 nm in size, regardless of $[SiO_2]$ or IS), (2) particle growth (surface-controlled, following $1^{st}$ order reaction kinetics) and (3) particle coarsening and aggregation via Ostwald ripening. Variations related to the different experimental variables (i.e. $[SiO_2]$, IS or organics) on the kinetic pathways and mechanisms of polymerization will be discussed.

# Non-relationship between slab melting and high-Mg andesite from northwestern Kyushu, SW Japan

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Major and trace elements, and Sr-Nd-Hf-Pb isotopic compositions of mafic volcanic rocks from the northwestern Kyushu, SW Japan, provide insight into the nature of mantle wedge and reflect the magmatic evolution linked with active continental margin. The simultaneous occurrence of chemically diverse magma composition, from alkali basalt through tholeiitic basalt to high-Mg andesite, characterizes the northwestern Kyushu magmatism, ranging age from ca. 10 to 5 Ma. Majority of volcanic rocks consists of the tholeiitic basalts, in contrast, the alkali basalts and the high-Mg andesites are minor. The alkali basalts have trace element pattern similar to oceanic island basalt (OIB). The OIB-like pattern shifts progressively to typical island-arc lava pattern, marketable depletions of HFSE, with increasing degree of silica-saturations from the alkali basalt to the high-Mg andesite. Recently, a seismic tomographic study suggested young Shikoku basin lithosphere has been present around 300 km depth beneath the northern Kyushu [1]. However, advocated process of interaction between mantle wedge and partial melts derived from subducting sediment and altered oceanic crust [e.g. 2, 3], cannot explain the observed geochemical variations. The magmatism seems to be closely liked with active back-arc basin, Okinawa Trough, because the northwestern Kyushu has been located at an extension of northern edge of the Okinawa Trough and its early rifting stage [4] (9-6 Ma) coincided approximately with the initiation of the voluminous magmatism in the northwestern Kyushu. The extensional tectonic environment might have led to intense thinning and detachment of continental lithosphere by asthenospheric upwelling. The additional upwelling would trigger greater degree of partial melting to form the tholeiitic melts and subsequent varying degree of interactions with metasomatized lithospheric mantle having notably depleted in Sr-Nd-Hf isotopic compositions, which would result in producing the simultaneous occurrence of chemical diversity.

[1] Abdelwahed & Zhao (2007) *Phys. Earth Planet. Inter.* **162,** 32-52. [2] Tatsumi & Hanyu (2003) *Geochem. Geophys. Geosyst.* **4**(9) doi, 10. 1029/2003GC000530. [3] Tatsumi (2006) *Annu. Rev. Earth Planet. Sci.* **34,** 467-499. [4] Letouzey & Kimura (1985) *Mar. Pet. Geol.* **2,** 111-130.