Thermal evolution of surface silanols and nanopores in silica particles

QUAN WAN*, SHANSHAN LI, ZONGHUA QIN
AND YI XIAO

Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou, 550002, P.R. China
(* Correspondence: wanquan@vip.gyig.ac.cn)

Nanoporous structures have been commonly found in rocks, soils, minerals, and organic matters. It is believed that nanopores are closely related to a range of vital geo-processes and geo-engineering applications, including rock weathering, elemental enrichment and bioavailability, shale gas exploration, carbon cycling and sequestration, etc [1]. Yet knowledge gaps still exist toward understanding fundamental structures and properties of nanopores. Difficulties and inaccuracies in determining nanopore structure and its evolution easily lead to misinterpretation and contradiction of experimental observation [2]. In this study, we used monodisperse, submicron-sized silica particle (synthesized through Stöber process) as our model system, which was subject to dehydration (2hr at 200°C), dehydroxylation (2hr at 400~800 °C) and rehydroxylation (overnight boiling in water). The thermally treated silica particles were subsequently characterized by thermogravimetry (TGA), differential scanning calorimetry (DSC), TGA-IR, pycnometry, elemental analysis and scanning electron microscopy (SEM), etc [3]. Our experimental findings indicated that thermal evolution of surface silanols for Stöber silica (~500nm diameter) accurately fits with the Zhuravlev model for surface chemistry of amorphous silicas [4]. For example, heating at 400°C quantitatively removed all vicinal silanol groups resulting a weight loss (200~1000°C) of ~48.3% ($i.e.$,1.728/3.574 from TGA data), which was nearly identical to the calculated result using theoretical silanol densities ($i.e.$, 4.6, 2.35, and 0.25 groups/nm^2 at 200°C, 400°C and 1000°C, respectively; (2.35-0.25)/(4.6-0.25)=48.3%). Our results also indicated a fully reversible recovery of silanol density through boiling in water and a specific surface area (SSA) of ~550 m^2/g for silica treated ≤400°C. The large SSA apparently supports a nanoporous structure, which was observed to undergo irreversible pore collapse when heating at above 600°C. This nanopore structure evolution is consistent with the results from density measurements.

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Late Triassic adakitic rocks formed by partial melting of ancient mafic lower crust in the North China Craton

CHAO WANG[1] AND SHUGUANG SONG[1]*

[1]School of Earth and Space Sciences, Peking University, Beijing 100871, China
(*correspondence: sgsong@pku.edu.cn)

Adakites were originally defined as partial melts of young subducting oceanic crust [1]. However, based on investigations of adakitic rocks in various settings, several other genetic mechanisms have also been proposed, including partial melting of slab-melt modified mantle wedge [2], assimilation and fractional crystallization of basaltic magmas [3], mixing between felsic and basaltic magmas [4], partial melting of thickened lower crust [5] and partial melting of delaminated lower crust [6].

Here we report the Late Triassic adakitic rocks in the eastern part of the North China Craton. They are granitic gneisses with high SiO_2 (68.87-70.15 %), Sr/Y (118-176) and $(La/Yb)_N$ (54-66) and low MgO (1.30-1.47 %), which are similar to adakitic rocks formed by partial melting of thickened lower crust. In-situ zircon LA-ICP-MS U-Pb dating reveals that they were emplaced in the Late Trassic (218-229 Ma). In-situ Hf isotope data for zircons show that they are characterized by the evolved $\varepsilon_{Hf}(t)$ of -17.4 to -14.6 and T_{DM2} ages of 2.18-2.36 Ga, implying their source materials were extracted from the depleted mantle in the Paleoproterozoic. Trace element modeling suggests that they might be produced by 20-30 % partial melting of the Paleoproterozoic mafic lower crust materials equlibrated with eclogite residues (Grt/Cpx = 30/70).

Based on the above lines of evidence, plus the post-collisional extensional enviroment in the Late Triaasic, we propose that these adakitic rocks in the NCC were produced through melting of the thickened ancient Paleoproterozoic mafic lower crust triggered by upwelling of basaltic magmas. Futhermore, they might be the result of the onset of lithospheric thinning of the NCC initiated in the Late Triassic.

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