Ab initio vibrational properties of silica species in aqueous fluids

G. Spiekermann[1*], M. Steele-MacInnis[2], C. Schmidt[1],
P. M. Kowalski[1] and S. Jahn[1]

[1]GFZ German Research Centre for Geosciences, Section 3.3,
Telegrafenberg, 14473 Potsdam, Germany, spiek@gfz-potsdam.de
(* presenting author)
[2]Department of Geosciences, Virginia Tech, Blacksburg VA 24061, USA,
mjmaci@vt.edu

The solubility of minerals in aqueous fluids is an important property to understand the chemical transport of elements. On the atomic-scale the solubility is related to the solute speciation in the fluid. Vibrational spectroscopy is especially useful for probing solute speciation in aqueous fluids because vibrational frequencies depend on molecular structure. Assignment of spectroscopic features to specific structural units can be challenging, but atomic-scale modeling may provide support [1, 2].

We investigate the vibrational properties of silica species in aqueous solution at high pressures and temperatures. The investigated species include H_4SiO_4 and $H_3SiO_4^-$ monomers, $H_6Si_2O_7$ and $H_5Si_2O_7^-$ dimers, three and fourfold silica rings and higher polymers [3]. Simulations are performed at the level of density-functional theory with the PBE exchange-correlation functional. We use periodic boundary conditions and a system of 25-27 H_2O molecules at 300 K and 1000 K, at a fluid density around 1 g/cm^3.

In our approach to analyze the vibrational properties, we exploit the two facts that (1) observed Raman frequencies are equal to the real vibrational frequencies, and (2) the spectroscopically important silica vibrations are quasi-localized normal-mode-like vibrations. The concept of mode-projected velocity autocorrelation (VACF) and its Fourier transform [4] is applied to yield normal-mode-like vibrational subspectra of the vibrational density of states, e.g. from tetrahedral subunits (T_d), Si-O-Si units of bridging oxygens (C_{2v}), the dimer (C_{3d}/C_{3h}), the SiOH bending, and "breathing" of silica rings.

Our results give a comprehensive picture of the vibrational behaviour of small silica species such as monomers and dimers. New insight is given into the polymerization-driven frequency shift. Our studies help to clarify vibrational contributions of Q^1 tetrahedra, the silica dimer, Q^2 tetrahedra, and the SiOH bending motions. We demonstrate that the mode-projection technique is a powerful tool for investigation of vibrational properties of isolated and network-forming species in their environment at elevated temperatures and pressures.

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Lunar Lu-Hf and Sm-Nd systematics – effects of neutron capture reactions

P. Sprung[1*], T. Kleine[2], and E.E. Scherer[3]

[1]Institute for Geochemistry and Petrology, ETH Zürich, Switzerland,
sprung@erdw.ethz.ch (* presenting author)
[2]Institut für Planetologie, Westfälische Wilhelms-Universität
Münster, Germany, thorsten.kleine@uni-muenster.de
[3]Institut für Mineralogie, Westfälische Wilhelms-Universität
Münster, Germany, escherer@uni-muenster.de

The silicate differentiation history of planetary objects including the Moon can be constrained by combined Lu-Hf and Sm-Nd studies [1]. Previous Lu-Hf studies on lunar basalts [2-6] yielded results broadly consistent with a magma ocean history for the Moon as constrained by Sm-Nd systematics, but some inconsistencies persist: Most KREEP-rich bulk rocks have initial ^{176}Hf/^{177}Hf that are too radiogenic, overlapping the composition of chondrites at the same time, and are inconsistent with the unradiogenic initial ^{143}Nd/^{144}Nd of KREEP. This disparity in the Lu-Hf and Sm-Nd systems may reflect a non-chondritic composition of the Moon [7] but could also be due to capture of (epi)thermal neutrons (NC) during cosmic-ray exposure of the lunar surface [8]. NC reactions can induce positive shifts in measured ^{176}Hf/^{177}Hf [8] and negative shifts in measured ^{143}Nd/^{144}Nd [9]. However, none of the previous Lu-Hf studies of lunar samples accounted for NC effects. To assess the significance of NC effects on the lunar Lu-Hf and Sm-Nd systematics we obtained Lu-Hf, Sm-Nd, and Hf and Sm isotope data for a suite of lunar samples (KREEP-rich rocks and mare basalts).

The KREEP-rich samples display no NC-induced Hf or Sm anomalies and yield the lowest initial ^{176}Hf/^{177}Hf yet reported for any KREEP-rich rock. In contrast, most mare basalts exhibit well-resolved, NC-induced anomalies in Hf and Sm. Low-Ti mare basalts show the strongest NC effects, with ^{180}Hf/^{177}Hf and ^{149}Sm/^{152}Sm as low as ≈820 ppm and ≈72 ε-units below those of terrestrial samples, respectively. NC-induced ^{180}Hf and ^{149}Sm anomalies are well correlated, yielding distinct slopes for low- and high-Ti mare basalts. The errors in measured ^{176}Hf/^{177}Hf and ^{143}Nd/^{144}Nd induced by NC reactions are up to +12 and -0.7 ε-units, respectively.

The well-defined, distinct correlations between ^{149}Sm and ^{180}Hf anomalies in low- and high-Ti mare basalts imply almost constant neutron energy spectra for chemically similar samples. Using the respective neutron energy spectra and published ^{149}Sm data [e.g., 9], we estimate that the ^{176}Hf/^{177}Hf$_{now}$ previously reported for low- and high-Ti mare basalts are too high by up to 7 and 1.7 ε-units, respectively. Published ^{149}Sm data suggest that previously reported data for KREEP-rich rocks are biased by NC reactions too, thus yielding more radiogenic initial ^{176}Hf/^{177}Hf values than expected for KREEP. Interpreting lunar Lu-Hf and Sm-Nd systematics without accounting for NC effects may thus yield erroneous conclusions.

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