

Sum Frequency Vibrational Spectroscopy (SFVS) of water and hydroxyls on the corundum (1 $\bar{1}$ 02) surface: Acid-base properties from direct observation of protonation states

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SFVS is a powerful tool for quantitative measurement of protonated functional groups on mineral surfaces, especially when used in a phase-sensitive mode [1]. This is demonstrated for the corundum (1 $\bar{1}$ 02) interface where the orientation and nature of surface hydroxyls on the dry protonated surface can be obtained and compared with models for the surface termination derived from crystal truncation rod (CTR), X-ray reflectivity (XRR) measurements, and with the most likely functional group assignments [2]. Hydroxyl orientations are determined from pole-figure type measurements of the magnitude of the non-linear optical susceptibility for each band, and the polar orientation (up-down with respect to the z-direction) is determined from measurements of the imaginary part of the susceptibility. A scheme for describing the hydrogen bonding among these protonated groups is found to be consistent with surface symmetry and the particular vibrational frequencies observed. The addition of water to the interface alters the hydrogen bonding of the hydroxyls and introduces water-functional group hydrogen bonding [3]. Direct measurement of the SFVS hydroxyl and water band amplitudes as a function of pH can be used to test the expected pKa values for the functional groups, and hence link interfacial acid-base properties to precise molecular surface entities and their protonation states.

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[2] Sung *et al.* (2011) *J. Amer. Chem. Soc.* **133**, 3846-3853.

[3] Sung *et al.* (in review, *J. Amer. Chem. Soc.*)

Evolution of the lower crust from S. Mexico: Constraints from Lu-Hf isotopes and U-Pb ages in zircon

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Unraveling the origin and tectonic evolution of lower continental crust is often complicated by granulite facies metamorphism that obscures petrogenetic features and resets isotopic systems. In order to reconstruct the assemblage of ancient supercontinents (like Rodinia), it is crucial to understand the evolution of individual crustal blocks, its relations, and its position with respect to the cratons. Four isolated lower crustal complexes of mid-Proterozoic (Grenville) age also referred to as "Oaxaquia" [1] are exposed in E and SE Mexico. Oaxaquia was interpreted in terms of arc magmatism, followed by backarc rifting, and migmatization, predating AMCG (anorthosite-mangerite-charnockite-granite) intrusions and granulite facies metamorphism [2].

U-Pb zircon dating by laser ablation MC-ICPMS and single-grain Lu-Hf analysis by solution MC-ICPMS was applied to elucidate crustal growth and igneous history of Oaxaquia. Typical Oaxaquia rocks include AMCG suite rocks as well as arc-type migmatites and orthogneisses, all of which having zircon cores at ~1.2 Ga, additional igneous growth zones migmatite zircons, and granulite facies rims at ~1.0 Ga. Hafnium isotopes of typical Oaxaquia rocks display little variations yielding $T_{DM(Hf)}$ model ages from 1.50 to 1.65 Ga [3]. Significant differences could be observed in zircons from E Mexico orthogneiss (Huiznopala) with $T_{DM(Hf)}$ at ~1.8 Ga [3]. New detailed laser dating of such zircons revealed mostly ~1.4 Ga and older zircon cores, surrounded by ~1.2 Ga igneous zones, indicating melting of crustal precursors different from typical Oaxaquia.

The results lead to a new model in which typical Oaxaquia evolved as juvenile arc in the early mid-Proterozoic. Continental crustal slices, probably from the continental arc of Amazonia, were thrust over or attached to the Oaxaquia oceanic arc, which was then buried and partially melted to produce AMCG rocks prior to the collision with Baltica during the final stage of Rodinia assemblage.

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