

## XAFS spectroscopy and molecular dynamics: Aqueous ions and ion pairs under non-ideal conditions

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The combination of x-ray absorption fine structure (XAFS) spectroscopy with molecular dynamics (MD) simulation provides a powerful method to probe ion hydration and ion pairing in aqueous system including the extremely non-ideal conditions encountered in brines, acids and at high temperatures. XAFS probes the partial radial distribution of atoms about only the ion of interest. Further, the method can be used to resolve the fine details of first-shell structure by applying both photoelectron multiple scattering and multiple absorption-edge symmetry analyses [1].

An XAFS spectrum can be generated from an ensemble of molecular configurations that are the output from an MD simulation [2]. This MD-XAFS spectrum can then be directly compared to the experimental spectrum. The advantage of MD-XAFS is that all details of the local ion-water structure inherent in the simulations are captured in the MD-XAFS spectrum including first-shell coordination symmetry and any second solvation shell contributions.

Classical intermolecular potentials used in MD simulations faithfully reproduce most of the aqueous structure of the alkali, alkaline earth and halide ions. An accurate description of transition metal cations and of contact ion pair structure is much more challenging problem. Ab initio-based molecular dynamics simulations have moved the quality of simulated structures to a new level. Using these methods we evaluate the hydration structure of various metal cations including Ag<sup>+</sup>, Zn<sup>2+</sup> and Ca<sup>2+</sup>. Further we discuss experimental results for structure of contact ion pairs for H<sub>3</sub>O<sup>+</sup>/Cl<sup>-</sup> and Ca<sup>2+</sup>/Cl<sup>-</sup>, Li<sup>+</sup>/Cl<sup>-</sup>, in brines, acids and at high temperatures.

[1] Fulton, Kathmann, Schenter & Balasubramanian (2009) *J. Phys. Chem. A*, **113**, 13976–13984. [2] Dang, Schenter, Glezakou & Fulton (2006) *J. Phys. Chem. B* **110**, 23644.

## Petrological and tectonic evolution of the Palaeoarchean Barberton Greenstone Belt, South Africa

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The Palaeoarchean Onverwacht Suite of the Barberton Greenstone Belt (BGB) comprises seven separate complexes of komatiite to dacitic volcanic and intrusive rocks, but with basalt as the predominant type. The complexes have tectonic contacts, are tectonically stacked with a total tectonostratigraphic thickness of ~15 km and have an age range of ~120 million years [1]. Some of the complexes have ophiolite-like lithological associations, whereas others are more akin to island-arc assemblages [1]. Detailed logging of the volcanic stratigraphy of the tectonostratigraphically upper Hooggenoeg (HC) and Kromberg Complexes (KC), show a dominance of non- to slightly-vesicular pillow lavas erupted beneath water 2000-4000 m deep [2]. The geochemical characteristics of the volcanic rocks of these two complexes show that the KC is composed entirely of low-MgO tholeiitic basalt, whereas the HC consists of tholeiitic to transitional basalt, as well as komatiitic lava. The basalts of the KC are depleted- to normal-MORB. Some of the HC lavas have boninitic affinities, and consistently elevated contents of Cs, Pb, Ba and Th in all the HC and KC lavas, give evidence of subduction. A compilation of all available geochemical data for mafic extrusive and intrusive rocks from the other complexes of the BGB show a large compositional spread. Elevated TiO<sub>2</sub> at a given Al<sub>2</sub>O<sub>3</sub> in komatiites from the Komati and Mendon Complexes, compared to the MgO-rich HC lavas, suggest that they may be generated from less-depleted sources. Two of the complexes are dominated by dacitic intrusives and subaerial extrusives. The juxtaposed complexes of the Onverwacht Suite were probably generated in subduction-influenced oceanic spreading environments and island arcs.

[1] de Wit *et al.* Precambrian Research (submitted). [2] Furnes *et al.* Precambrian Research (submitted).