MC-HR-SIMS oxygen isotope analysis of ferropericlase inclusions in diamond

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Ferropericlase (Mg, Fe)O is an important terrestrial mineral. While relatively rare in the crust, it constitutes approximately 17% by volume of the lower mantle, from ~660km to ~2900km. Importantly, the assemblage of ferropericlase and perovskite (which together are diagnostic of a lower mantle origin) are rarely found together as inclusions in diamond and provide our only solid samples of a region that occupies over 50% of Earths volume [1].

Studies of these ultra-deep diamond inclusions have shown that the periclase inclusions can have a variable Mg#, and have demonstrated the presence of Eu anomalies in coexisting perovskite [2-3]. This has led some workers to suggest that the ultra-deep mineral assemblages trapped in the diamond formed from subducted crust that has passed through the transition zone and into the lower mantle [3]. If verified, this would provide an important geochemical verification of whole mantle convection.

Oxygen isotope ratios of crustal rocks can be distinctly different those of the mantle ($\delta^{18}O_{VSMOW}$ values of ca. 5.5‰) and can therefore provide a crucial test of the crustal or mantle heritage of ferropericlase inclusions. Diamond inclusions of ferropericlase are <100μm in size and therefore best analyzed by microbeam methods. We have performed preliminary experiments on the $^{18}O/^{16}O$ measurement of synthetic and natural crustal periclase on the newly installed Cameca IMS1280 multicollector secondary ion mass spectrometer (MC-SIMS) at CCIM,. The SIMS analytical methods largely follow established procedures, using Cs^- primary ions, normal incidence electron gun, and multi-collection on faraday cups. Synthetic and natural RM's are being characterized by laser fluorination. Preliminary analysis shows that internal spot errors of <0.1‰ (1σ) for $^{18}O/^{16}O$ are readily achieved. Spot-to-spot reproducibility and potential matrix effects due to varying Mg#s will be examined.

[1] Ringwood (1991) *EPSL* **55**, 2083–2110. [2] Harte *et al.* (1999) *Geochem. Soc. Spec. Pub.* **6**, 125–153. [3] Stachel *et al.* (2000) *CMP* **140**, 16–27.

Equation Chapter 1 Section 1 Spectroscopic, structural and electronic properties of acid dissociation intermediates in water

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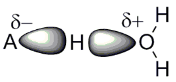
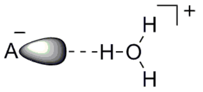
Consider the prototypical acid dissociation reaction:

$$AH(aq) + H_2O \Leftrightarrow A^-(aq) + H_3O^+$$

Although the reactant and product species involved in such dissociation equilibria are well understood, little is known about the chemical nature of intermediate forms. We utilize ab initio molecular dynamics with on-the-fly maximally-localized orbitals [1], computational IR spectrum decomposition into molecular contributions [2] and first-principles molecular polarizability calculations [3] to investigate proton-shared (left) and contact ion pair forms (right) whose structures are depicted below:





We will review the evidence which led us to conclude that: 1) Proton-shared forms exist [4, 5] in aqueous solutions of hydrofluoric acid; 2) These forms can be distinguished [6] from the covalent forms AH (aq) by the appearance of an extremely wide and structureless absorption below 1700 cm^{-1} 3) As illustrated above, the ionization process in water should be conceived as an electron transfer from water to the sigma antibonding orbital of the AH molecule [3] rather than a heterolytic rupture of the A–H bond.

The results concerning contact ion pairs were obtained using aqueous solutions of trifluoroacetic acid. We will show computational evidence indicating that upon formation of contact ion pairs, the carbonyl C=O absorption band at 1700 cm^{-1} from F_3C–COOH disappears, and two absorption bands, corresponding to the asymmetric and symmetric carboxyl vibration modes appear at 1600 and 1400 cm^{-1}.

[1] Iftimie, Thomas & Tuckerman (2004) *J. Chem. Phys.* **120**, 2169–2181. [2] Iftimie & Tuckerman (2005) *J. Chem. Phys.* **122**, 214508. [3] Buin & Iftimie (2009) *J. Chem. Phys.* **131**, 234507. [4] Iftimie, Thomas, Marchand, Plessis & Ayotte (2008) *J. Am. Chem. Soc.* **130**, 5901–5907. [5] Thomas & Iftimie (2009) *J. Phys. Chem. B* **113**, 4152–4160. [6] Iftimie & Tuckerman (2006) *Angew. Chem. Int. Ed.* **45**, 1144–1147.