Investigating silicate mineral dissolution with computational tools while crossing scales

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Computational tools are used to cross scales in the investigation of geochemical reactions and mineral surfaces. Density functional theory (DFT) calculations are employed to investigate M–O_{br} (M = Mg^{2+}, Ca^{2+}, and Ni^{2+}) bond breaking and H_2O exchange using a H_2O molecule and molecular sized clusters analogous to sites on silicate mineral surfaces. The barrier heights for the hydrolysis of protonated, neutral, and deprotonated Mg–O_{br}–Si sites on the forsterite surface were determined. These barrier heights were used to calculate the rate constants, and in turn, a rate for the release of Mg^{2+} due to the breaking of the Mg–O_{br} bond.[1] In a second set of calculations, the hydrolysis of protonated M–O_{br}–Si (M = Mg^{2+}, Ca^{2+}, and Ni^{2+}) sites was investigated to determine whether H_2O exchange or bond breaking occurred for Ni^{2+}, Mg^{2+}, and Ca^{2+} silicate molecular clusters. Here again, the barrier heights are used to calculate the rate constants for the release of these metals from protonated sites on silicate surfaces.[2] A comparison with experimental data is given.

Ab initio molecular dynamics (AIMD) simulations enable the use of a unit cell sized system and allow for an investigation of several reaction sites on the mineral surface. The forsterite (100) and (010) surfaces were investigated to determine the most stable structures for these surfaces when initially covered with all H_2O molecules or OH groups. The surfaces yielded similar structures comprised of H_2O, OH, O^-, and O_{br},[3] and a true forsterite surface likely has a distribution of all of these sites.

[1] Morrow, C. P. Kubicki, J. D. Mueller, K. T. Cole, D. R. *J. Phys. Chem. C* **2009**, DOI: 10.1021/jp9057719. [2] Morrow, C. P. Olsen, A. A. Kubicki, J. D. **2010**, in preparation. [3] Morrow, C. P. Kubicki, J. D. unpublished.

Hot shock vs. Cold shock zircon across the Vredefort Dome: A guide for interpreting residua of the LHB?

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Refractory, U-bearing accessory phases such as zircon and monazite are excellent candidates for surviving metamorphism, and recording large-scale melting, produced by a period of Late Heavy Bombardment. Such early planetary residua are likely to be detrital [1], necessitating age and microstructural interpretations out of primary context. To improve our understanding of primary spatial relationships of zircon microstructure and U-Pb isotope response in large craters, we present new microstructural and ID-TIMS data on zircon microcrystals from bedrock across ~65 km radial distance of the deeply eroded collar and central uplift of the 2.020 Ga Vredefort impact basin of South Africa, the largest recognized terrestrial impact basin.

Pre- and syn-impact zircons can generally be categorized as 'cold shock' and 'hot shock' with the latter associated with the central, ~10 km radius zone of intense impact-related heating [2]. The outer 'cold shock' zircon zone is exemplified by populations from the Schurwedraai syenite and Skietkop alkali feldspar granite that exhibit multiple sets of pervasive planar shock microstructures yet do not yield any U-Pb isotopic evidence of the Vredefort event. High degrees of radiogenic Pb-loss and discordance are instead related to far-field tectonism more than 1 Ga after impact, presumably aided by shock-induced increase in effective surface area.

Hot-shock zircons consist of several subcategories. Pre-impact zircons from Archean gneiss can exhibit partly annealed planar features with thin impact-age, unshocked overgrowths. A second category has experienced advanced recrystallization, and penetration of high angle grain boundaries far into planar microstructure domains. Wholly recrystallized zircons occur as xenocrysts in small bodies of impact-generated magma. In all cases significant to complete, impact related Pb loss occurred at the time of the impact event. This spatial variation in preservation of pre-impact vs. impact ages will aid provenance and age interpretations of detrital impact residua on Earth, and possibly guide sampling strategies of extraterrestrial geochronology missions.

[1] Cavosie *et al.* (2010) *GSA Bulletin*, *in press*. [2] Moser (1997) *Geology*, **25**, 7–10