

Computational studies of hydrolysis reactions of CO₂ and actinides

DAVID A. DIXON,* K. SAHAN THANTHIRIWATTE, JOSHUA MOON, JESSICA DUKE AND VIRGIL E. JACKSON

Department of Chemistry, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa AL 35487-0336.

*(correspondence: dadixon@bama.ua.edu)

Advances in theory, algorithms, software, and computer architectures have made it possible to begin to calculate reliably the thermodynamics for geochemical processes in solution. The sequestration of CO₂ in geological formations can be used to mitigate global warming. A substantial amount of fundamental chemistry knowledge is still needed to ensure that the CO₂ does not have additional environmental impacts and that it remains in the subsurface. The supercritical CO₂ that is pumped into the ground will interact with H₂O and with various minerals. The properties and reactions of H₂O-CO₂ nanoclusters have been calculated at high levels of electronic structure theory and will be discussed. Issues with the electronic structure methods will be described. A surprising result is that CO₂ clusters can impact the hydrogen bonding in small H₂O clusters, which may impact reactivity. The important role of Lewis acid-base interactions in determining the structure of the clusters will be discussed. The hydrolysis of CO₂ in the presence of geochemically relevant metal ions in aqueous solution will be discussed. The metal cations can reduce the reaction barriers in part by changing the thermodynamics of the relevant reactions. The reactions of UO₂²⁺ with phosphates is of importance for extraction processes and for environmental remediation. The difficulties in predicting reliable properties for such systems will be discussed, especially for the solvation energetics. An important result is the critical role of CN 5 in the equatorial plane for these compounds. We find that there is both monodentate and bidentate binding depending on the nature of the PO₄H_x^{y-} and the number of water molecules in the first solvation shell. These studies have been performed at the density functional theory and correlated molecular orbital theory levels with a self consistent reaction field to model the continuum solvent.

This work is supported by the U.S. DOE Office of Sciences (BES).

Geochemical evidence for multiple gold mineralisation events in the Witwatersrand Basin

ROGER D. DIXON¹

¹Department of Geology, University of Pretoria, Pretoria, South Africa (roger.dixon@up.ac.za)

There are currently a number of competing hypotheses for the origin of the gold in the conglomeratic reefs in the Witwatersrand Basin, from hydrothermal to alluvial and variations between the two extremes. Though it has long been theorised that the gold deposits of the Witwatersrand Basin are at least partially hydrothermal in origin, there has been insufficient trace element analysis of gold and associated minerals from around the basin to evaluate this hypothesis, mainly due to inadequacies of routine analytical techniques.

A basin-wide study looking at the composition of gold produced in the different gold fields in the Witwatersrand Basin, and the composition of individual gold grains from different reefs, has been conducted utilising ICP-OES and LA-ICP-MS, and shows that the gold produced in each goldfield is compositionally distinct and that sediment source area is the main factor in determining the trace element distribution.

Results of the analysis of large gold grains from the Vaal Reef and gold associated with carbon derived from microbial mats in the Carbon Leader Reef, reveals the presence of at least three distinct types of gold.

The first type consists of alluvial gold which has been transported from source area and deposited in the calm conditions of the braided stream depositional environment.

The second type consists of very fine particles of colloidal gold precipitated from suspension during deposition of the sediments. At the same time that the gold was being precipitated from suspension, other elements in colloidal suspension were also being precipitated, such as uranium, thorium, silver, aluminium and iron.

Subsequent to deposition, one or more hydrothermal events remobilised much of the colloidal gold and this was redeposited as a third type of gold with distinct elemental and isotopic trace element signatures. Where carbon was present this redeposition took place almost in-situ, and where carbon was absent gold was redeposited from solution at some distance, in higher reefs and associated with cross-cutting quartz veins.