## **HIGHLIGHTS AND BREAKTHROUGHS**

# First-principles Molecular Dynamics maps out complete mineral surface acidity landscape

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In "Interfacial structures and acidity constants (pKa) of goethite from first-principles Molecular Dynamics simulations," authors Y. Zhang, X. Liu, J. Cheng, and X. Lu (Zhang et al. 2021, this issue) apply first-principles Molecular Dynamics (FPMD, also called Density Functional Theory MD, DFT/MD, or ab initio MD, AIMD) to evaluate the complete set of acidy constants (pKa) of the hydroxyl groups on the most prominent goethite crystal facets. The pKa of these OH and OH<sup>+</sup><sub>2</sub> groups are compared with available data from the multisite complexation (MUSIC) model traditionally used to estimate pKa on mineral surfaces. The authors have presented eloquent rationale for the importance and implications of understanding goethite acidity constants in room-temperature geochemistry settings. Here I focus on the computational aspects, the strengths of FPMD, and its possibilities.

These pK calculations represent a significant triumph of the FPMD free energy formulation. Many FPMD simulations in the literature are conducted in a non-equilibrium mode and are "numerical experiments"; others report equilibrium properties such as average bond lengths and correlation functions that can be directly compared to measurements. In contrast, free energy differences, which govern pKa and equilibrium constants, require rigorous thermodynamic integration (TI) techniques coupled to FPMD. Even with modern computers, they are computationally intensive. Sprik reported the first pKa calculation in liquid water that uses coordination constraints (Sprik 2000). The method has since been significantly refined, and rigorous statistical mechanics constraints are used to model the acidity of water-material interfaces (Cheng et al. 2014).

The work by Zhang et al. (2021) examines the protonation and deprotonation pKa of all relevant sites on the most prominent goethite facets. This is a welcome development; such predictions have yet to be reported for most minerals (Liu et al. 2013; Gittus et al. 2018). This study allows a systematic comparison of different pKa on different facets computed using consistent methods, and avoids uncertainties due to differences in software, reaction coordinates, and other computational details. They find agreement with multisite ion complexation (MUSIC) predictions for most hydroxyl groups, but also differences for other OH groups, particularly those on the (021) surface. MUSIC estimates rely on crystal chemical considerations and inputs, and for certain hydroxyl groups two or more pKa values are reported, contingent upon variable hydrogen bonding configurations that are statically assigned. FPMD samples water configurations dynamically at finite temperature using atomic forces generated by electronic structure calculations, and is arguably the more rigorous and reliable approach.

A systematic FPMD mapping of pKa on all relevant surface hydroxyl groups on all relevant surfaces for every common crystalline mineral (and clay edge)-each requiring calculations as extensive as in Zhang et al. (2021)-will lead to the creation of a mineral acidity database that will be extremely valuable for geochemical research. Apart from updating MUSIC pKa values, such a database will guide static assignment of protonation states in MD simulations that use far less costly classical force fields, which do not permit acid-base reactions. Such a database can also be used for calibrating FPMD-based machine learning estimates of pKa without requiring explicit TI. The issue here is that FPMD TI calculations examine one OH (or OH<sup>+</sup>) site at a time, and remain computationally costly. For oxides that are amorphous [e.g., silica (Pfeiffer-Laplaud et al. 2015) and alumina in many applications], or have surface defects, enumerating the pKa of each chemically distinct hydroxyl group is challenging. As an alternative, the correlation of a large set of known pKa values, with descriptors like hydrogen bond strengths and bond lengths associated with them (Sulpizi et al. 2012), can potentially enable neural network estimates of pKa. In fact, equilibrium FPMD trajectories have been used as training sets, without directly applying TI on individual OH groups, to study TiO acidity (Calegari et al. 2020). Comparison with explicit FPMD pKa predictions there would be extremely valuable.

The above discussion can be generalized to conditions beyond room temperature. Adapting the approach of Zhang et al. to high temperatures and high pressures, aspects of which have already been demonstrated (Liu et al. 2015, 2016; Zhang et al. 2018), further permits the prediction of p*K*a at non-ambient conditions, including geothermal temperatures where measurements may be difficult and less thermodynamic data are available. The protonation states of mineral surfaces are critical for understanding the reactions and dissolution of minerals at conditions relevant to geothermal energy harvesting and "origin of life" studies.

If the relative surface area of each facet exposed is known, obtaining a complete set of FPMD pKa values leads to the pH-of-zero-charge (PZC) that can be directly compared to measurements. PZC is relevant to adhesion, aggregation, and adsorption isotherms of molecules and ions onto mineral surfaces. PZC measurements often involve electrolytes like NaCl at low concentrations, and pKa values are known to depend on electrolytes (Azam et al. 2012). FPMD pKa simulations have indeed incorporated simple monovalent cations and anions (Pfeiffer-Laplaud et al. 2016a) that do not chemisorb onto mineral surfaces. However, ionic motion is relatively slow, and enhancing adequate sampling of salt configurations in low-concentration electrolytes in FPMD trajectories remains a much needed area of research (Pfeiffer-

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Laplaud et al. 2016a, 2016b; DelloStritto et al. 2016).

Indeed, the explicit treatment of physisorbed and chemisorbed ionic species, and of mineral dissolution, is another frontier of FPMD free energy geochemical application. These phenomena are closely linked to mineral surface acidity. As the authors have discussed (Zhang et al. 2021), surface hydroxyl protonation states affect the adsorption equilibrium constants of toxic/radioactive cations and anions. Atomic length-scale ion adsorption studies benefit from using the set of FPMD pKa to identify starting configurations for ion binding. Cations/anions preferentially reside near the deprotonated/doubly protonated hydroxyl sites on facets; in addition, oxy-anions like SeO<sub>3</sub><sup>2–</sup> can insert on to the surface, replacing one or more surface OH group.

Here FPMD ion adsorption predictions would be compared with charge-distribution multisite ion complexation (CD-MUSIC) model (Venema et al. 1996), the Triple Layer Model (Fukushi and Sverjensky 2007), and related models traditionally used in geochemistry. Some of the ionic complexes, like Cu(II)(H<sub>2</sub>O)<sub>n</sub> and SeO<sub>3</sub><sup>2-</sup>, themselves undergo acid-base reactions as they adsorb and desorb. As such, these process are highly pH dependent. The desorption pathway of Cu(II) on silica surfaces has been predicted to involve concerted proton transfer via the Grotthuss mechanism (Leung et al. 2018); protonation state changes have also been demonstrated to have significant impact on Fe(III) dissolution free energies (Klyukin et al. 2018). Another emerging topic of interest is pH-dependent ion dimerization and polymerization on mineral surfaces, which involve more than a single ion and may mark the onset of heterogeneous nucleation and precipitation. Cu(II) in Cu-dimers on silica nanopores are found to be linked by two hydroxide bridges (Knight et al. 2020). Similar behavior is seen in Al(III) dimers in water (Schenter et al. 2018). The "pKa" of these hydroxide bridges are not well-known. So far FPMD simulations of ion dimerization have relied on the intrinsic fast proton motion in aqueous media. Adaptation of the statistical mechanical constraints used in the authors' calculations may further enhance proton sampling in such systems.

Finally, at the risk of making a too-obvious point, the pKa techniques used by the authors have been applied to research areas outside geochemistry, including photocatalytic and catalytic water splitting (Calegari et al. 2020; Guo et al. 2020; Jia et al. 2020), lanthanide and actinide chemistry (Liu et al. 2016), organic molecules (Parashar et al. 2018), ion exchange, and other applications. Adapting and quantifying acidity concepts to low humidity environments would be useful for many technologies. Synergistic research relevant to geochemistry and these material science areas, enabled by FPMD free energy calculations, is expected to yield cross-cutting benefits.

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