1   **Highlights and Breakthroughs**

2   **First principles molecular dynamics maps out complete mineral surface acidity**

3   **landscape**

4   **Kevin Leung***

5   *Sandia National Laboratories, MS 1415,*

6   *Albuquerque, New Mexico 87185, U.S.A.*

7   ∗kleung@sandia.gov

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11   In "Interfacial structures and acidity constants (pKa) **{{editor, shouldn' the a be a**

12   **subscript?}}** of goethite from first principles molecular dynamics siluations," authors Y. Zang,

13   X. Lui, J. Cheng, and X. Lu (Zhang et al. 2021) apply First Principles molecular dynamics

14   (FPMD, also called Density Functional Theory MD, DFT/MD, or ab initio MD, AIMD) to

15   evaluate the complete set of acidy constants (pKa) of the hydroxyl groups on the most prominent

16   goethite crystal facets. The pKa of these OH and OH+ (Sprik 2000) groups are compared with

17   available data from the multisite complexation (MUSIC) model traditionally used to estimate

18   pKa on mineral surfaces. The authors have presented eloquent rational for the importance and

19   implications of understanding goethite acidity constants in room temperature geochemistry

20   settings. Here I focus on the computational aspects, the strengthes of FPMD, and its possibilities.

21   pK calculations represent a significant triumph of the FPMD free energy formulation. Many

22   FPMD simulations in the literature are conducted in a non-equilibrium mode and are "numerical

23 experiments"; others report equilibrium properties such as average bond lengths and correlation

24 functions which can be directly compared to measurements. In contrast, free energy differences,

25 which govern pK and equilibrium constants, require rigorous thermodynamic integration (TI)

26 techniques coupled to FPMD. Even with modern computers, they are computationally intensive.

27 Sprik reported the first pK calculation in liquid water that uses coordination constraints (Sprik

28 2000). The method has since been significantly refined, and rigorous statistical mechanics

29 constraints are used to model the acidity of water-material interfaces (Cheng et al. 2014).

30 The authors' work (Zhang et al. 2021) examines the protonation and deprotonation pK of all

31 relevant sites on the most prominent goethite facets. This is a welcome development; such

32 predictions have yet to be reported for most minerals (Liu et al. 2013, Gittus 2018). The authors'

33 work allows a systematic comparison of different pK on different facets computed using consistent

34 methods, and avoids uncertainties due to differences in software, reaction coordinates, and other

35 computational details. They find agreement with MUSIC predictions for most hydroxyl groups, but

36 also differences for other OH groups, particularly those on the (021) surface. MUSIC estimates rely

37 on crystal chemical considerations and inputs, and for certain hydroxyl groups two or more pK

38 values are reported, contingent upon variable hydrogen bonding configurations which are statically

39 assigned. FPMD samples water configurations dynamically at finite temperature using atomic

40 forces generated by electronic structure calculations, and is arguably the more rigorous and reliable

41 approach.

42 A systematic FPMD mapping of pK on all relevant surface hydroxyl groups on all relevant

43 surfaces for every common crystalline mineral (and clay edge)—each requiring calculations as

44 extensive as the author's—will lead to the creation of a mineral acidity database that will be

45 extremely valuable for geochemical research. Apart from updating MUSIC pK values, such a

46 database will guide static assignment of protonation states in MD simulations which use far less

47 costly classical force fields that do not permit acid-base reactions. Such a database can also be used

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48   for calibrating FPMD-based machine learning estimates of pK without requiring explicit TI. The

49   issue here is that FPMD TI calculations examine one OH (or OH_2^+) site at a time, and remain

50   computationally costly. For oxides that are amorphous [e.g., silica (Pfeiffer-Laplaud et al. 2015),

51   and alumina in many applications], or have surface defects, enumerating the pK of each chemically

52   distinct hydroxyl group is challenging. As an alternative, the correlation of a large set of known pK

53   values, with descriptors like hydrogen bond strengths and bond lengths associated with them

54   (Sulpizi et al. 2012), can potentially enable neural network estimates of pK. In fact, equilibrium

55   FPMD trajectories have been used as training sets, without directly applying TI on individual OH

56   groups, to study TiO acidity (Calegari et al. 2020). Comparison with explicit FPMD pK predictions

57   would be extremely valuable.

58   The above discussion can be generalized to conditions beyond room temperature. Adapting the

59   authors' approach to high temperatures/pressures, aspects of which have already been

60   demonstrated (Liu et al. 2016, Liu et al. 2015, Zhang et al. 2018), further permits the prediction

61   of pK at non-ambient conditions, including geothermal temperatures where measurements may

62   be difficult and less thermodynamic data are available. The protonation states of mineral surfaces

63   are critical for understanding the reactions and dissolution of minerals at conditions relevant to

64   geothermal energy harvesting and "origin of life" studies.

65   If the relative surface area of each facet exposed is known, obtaining a complete set of FPMD

66   pK values leads to the pH-of-zero-charge (PZC) which can be directly compared to

67   measurements. PZC is relevant to adhesion, aggregation, and adsorption isotherms of molecules

68   and ions on to mineral surfaces. PZC measurements often involve electroytes like NaCl at low

69   concentrations, and pK are known to depend on electrolytes (Azam et al. 2012)·FPMD pK

70   simulations have indeed incorporated simple monovalent cations and anions (Pfeiffer-Laplaud et

71   al. 2016a) which do not chemisorb on to mineral surfaces. However, ionic motion is relatively

72   slow, and enhancing adequate sampling of salt configurations in low concentration electrolytes in

73   FPMD trajectories remains a much needed area of research (Pfeiffer-Laplaud et al. 2016a,

74   2016b; Dellostritto et al. 2016).

75   Indeed, the explicit treatment of physisorbed and chemisorbed ionic species, and of mineral

76   dissolution, is another frontier of FPMD free energy geochemical application. These phenomena

77   are closely linked to mineral surface acidity. As the authors have discussed (Zhang et al. 2021),

78   surface hydroxyl protonation states affect the adsorption equilibrium constants of

79   toxic/radioactive cations and anions. Atomic length-scale ion adsorption studies benefit from using

80   the set of FPMD pK to identify starting configurations for ion binding. Cations/anions

81   preferentially reside near the deprotonated/doubly protonated hydroxyl sites on facets; in addition,

82   oxy-anions like SeO_3^{2-} can can insert on to the surface, replacing one or more surface OH group.

83   Here FPMD ion adsorption predictions would be compared with charge-distribution multisite ion

84   complexation (CD-MUSIC) model (Venema et al. 1996), the Triple Layer Model (Fukushi et al.

85   2007), and related models traditionally used in geochemistry. Some of the ionic complexes, like

86   Cu(II)(H O) and SeO_3^{2-}, themselves undergo acid-base reactions as they adsorb and desorb. As

87   such, these process are highly pH dependent. The desorption pathway of Cu(II) on silica surfaces

88   has been predicted to involve concerted proton transfer via the Grotthuss mechanism (Leung et al.

89   2018); protonation state changes have also been demonstrated to have significant impact on Fe(III)

90   dissolution free energies (Klyukin et al. 2018). Another emerging topic of interest is pH-dependent

91   ion dimerization and polymerization on mineral surfaces, which involve more than a single ion and

92   may mark the onset of heterogeneous nucleation and precipitation. Cu(II) in Cu-dimers on silica

93   nanopores are found to be linked by two hydroxide bridges (Knight et al. 2020). Similar behavior is

94   seen in Al(III) dimers in water (Schenter et al. 2018). The "pK " of these hydroxide bridges are

95   not well-known. So far FPMD simulations of ion dimerization have relied on the intrinsic fast

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96   proton motion in aqueous media. Adaptation of the statistical mechanical constraints used in the

97   authors' calculations may further enhance proton sampling in such systems.

98   Finally, at the risk of making a too-obvious point, the pK techniques used by the authors have

99   been applied to research areas outside geochemistry, including photocatalytic and catalytic water

100   splitting (Calegari et al. 2020; Guo et al. 2020; Jia et al. 2020) lanthanide and actinide chemistry

101   (Liu et al. 2016), organic molecules (Parashar et al. 2018), ion exchange, and other applications.

102   Adapting and quantifying acidity concepts to low humidity environments would be useful for

103   many technologies. Synergistic research relevant to geochemistry and these material science

104   areas, enabled by FPMD free energy calculations, is expected to yield cross-cutting benefits.

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118   References

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120   Azam, M.S., Weeraman, C.N., and Gibbs-Davis, J.M. (2012) Specific Cation Effects on the

121   Bimodal Acid-Base Behavior of the Silica/Water Interface. J. Phys. Chem. Lett., 3,

122   1269-1274.

123   Calegari, M.F., Ko, H.-Y., Zhang, L., Car, R., and Selloni, A. (2020) Free energy of proton

124   transfer at the water-TiO_2 interface from *ab initio* deep potential molecular dynamics.

125   Chem. Sci., 11, 2335-2341

126   Cheng J., Liu, X., VandeVondele, J., Sulpizi, M., and Sprik, M. (2014) Redox potentials and

127   acidity constants from Density Functional Theory based molecular dynamics. Acc.

128   Chem. Res., 47, 3522-3529.

129   Dellostritto, M.J., Kubicki, J.D., and Sofo, J.O. (2016) Effect of ions on H-bond structure and

130   dynamics at the quartz(101)-water interface. Langmuir, 32, 11353-11365.

131   Fukushi, K. and Sverjensky, D.A. (2007) A predictive model (ETLM) for arsenate adsorption

132   and surface speciation on oxides consistent with spectroscopic and theoretical

133   molecular evidence Geochim. Cosmochim. Acta, 71, 3717-3745.

134   Gittus, O.R., von Rudorff, G.F., Rosso, K.M., and Blumberger, J. (2018) Acidity constants of

135   the hematite-liquid water interface from ab Initio molecular dynamics. J. Phys. Chem.

136   Lett., 9, 5574-5582.

137   Guo, Z., Ambrosio, F., and Pasquarello, A. (2020) Evaluation of photocatalysts for water

138   split- ting through combined analysis of surface coverage and energy-level alignment.

139   ACS Catal., 10, 13185-13195.

140   Jia, M., Zhang, C., Cox, S.J., Sprik, M., and Cheng, J. (2020) Computing surface acidity

141   constants of proton hopping groups from Density Functional Theory-based molecular

142   dynamics: application to the $SnO_2(110)/H_2O$ interface. J. Chem. Theory Comput., 16,

143   6520-6527.

144   Klyukin, K., Rosso, K.M., and Alexandrov, V. (2018) Iron dissolution from goethite (α-

145   FeOOH) surfaces in water by ab initio enhanced free-energy simulations. J. Phys.

146   Chem. C, 122, 16086- 16091.

147   Knight, A.W., Ilani-Kashkouli, P., Harvey, J.A., Greathouse, J.A., Ho, T.A., Kabengi, N., and

148   Ilgen, A.G. (2020) Interfacial reactions of Cu(II) adsorption and hydrolysis driven by

149   nano-scale confinement. Environmental Science: Nano, 7,68-80.

150   Leung, K., Criscenti, L.J., Knight, A.W., Ilgen, A.G., Ho, T.A., and Greathouse, J.A. (2018)

151   Concerted metal cation desorption and proton transfer on deprotonated silica surfaces.

152   J. Phys. Chem. Lett., 9,5379-5385.

153   Liu, X., Cheng, J., Sprik, M., Lu, X., and Wang, R. (2013) Understanding surface acidity of

154   gibbsite with first principles molecular dynamics simulations. Geochim. Cosmochim.

155   Acta, 120, 487-495.

156   Liu, X.D., Cheng, J., He, M.J., Lu, X.C., and Wang, R.C. (2016) Acidity constants and redox

157   potentials of uranyl ions in hydrothermal solutions. Phys. Chem. Chem. Phys., 18, 26040-

158   26048.

159   Liu, X.D., Xu, L., Cheng, J., Sprik, M., and Wang, R.C. (2015) Temperature dependence of

160   interfacial structures and acidity of clay edge surfaces. Geochim. Cosmochim. Acta,

161   160, 91-99.

162   Parashar,S., Lesnicki, D., and Sulpizi, M. (2018) Increased acid dissociateion at the

163   quartz/water interface. J. Phys. Chem. Lett., 9, 2186-2189.

164   Pfeiffer-Laplaud, M., Costa, D., Tielens, F., Gaigeot, M.-P., and Sulpizi, M. (2015) Bimodal

165   acidity at the amorphous silica/water interface. J. Phys Chem. C, 119, 27354-27362.

166   Sulpizi, M., Gaigeot, M.-P., and Sprik, M. (2012) The silica-water interface: how the silanols

167   determine the surface acidity and modulate the water properties. J. Chem. Theor.

168   Comput., 8, 1037-1047.

169   Pfeiffer-Laplaud, M., Gaigeot, M.-P., and Sulpizi, M. (2016) Pk(a) at quartz/electrolyte inter-

170   faces. J. Phys Chem. Lett., 7,3229-3234.

171   Pfeiffer-Laplaud M. and Gaigeot, M.-P. (2016) Electrolytes at the hydroxylated (0001) α-

172   quartz/water interface: location and structural effects on interfacial silanols by DFT-

173   based MD. J. Phys Chem. C,120, 14034-14047.

174   Pfeiffer-Laplaud, M. and Gaigeot, M.-P. (2016) Adsorption of singly charged ions at the hy-

1

175   droxylated (0001) α-quartz/water interface. J. Phys Chem. C, 120, 4866-4880.

176   Schenter, G.K., Pearce, C.L., and Clark, A.E. (2018) Pairing as new challenges of

177   elucidating prenucleation aluminum speciation. J. Phys. Chem. B, 122, 7394-7402.

178   Sprik M. (2000) Computation of the pK of liquid water using coordination constraints.

179   Chem. Phys., 258, 139-150.

180   Venema, P., Hiemstra, T., and van Riemsdijk, W.H. (1996) Multisite adsorption of

181   cadmium on goethite. J. Coll. Interface Sci., *183*, 515-527.

182   Zhang, C., Liu, X.D., Lu, X.C., and He, M.J. (2018) Complexation of heavy metal cations

183   on clay edges at elevated temperatures. Chem. Geology, 479, 36-46.

184   Zhang, V., Lui, X., Cheng, J., and Lu, X. (2021) Interfacial structures and acidity constants

185   (pK_a) of goethite from first principles molecular dynamics simulations. Amer. Miner.

186