

## Empirical determination of goethite surface acidity constants for individual proton-active groups

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Surface acidity is one of the essential characteristics of variable charge minerals such as goethite, and one which influences considerably their behavior towards adsorption of ions. Theoretical determination of surface pKa values for individual proton-reactive site types, through either molecular [1] or surface complexation modelling (SCM) [2-4], so far has not produced reliable pKa values for describing thermodynamic adsorption behavior at the mineral/water interface. Therefore, the pKa values of all proton-active sites present at mineral surfaces in MUSIC SCM are typically equated to the experimental value of the overall point of zero net proton charge of the mineral.

In this work we propose an empirical approach that yields a unique set of individual (and distinct) pKa values and electrolyte binding constants for each proton-active surface group on goethite, i.e., for singly- and doubly-coordinated oxygen sites. This was accomplished by constraining the potential sets of values that are capable of describing proton surface charge curves of any individual goethite, by using two goethite preparations with widely different crystal face distributions, and thus, with considerably different site density values of both proton-active sites. A face distribution-site density model proposed previously for goethite [5] was modified with independent measurements of face contributions through high-resolution TEM images [6]. With these observed contributions the corresponding surface site density values for each site type were calculated using theoretical crystallographic data for each crystal face present, and subsequently used for MUSIC SCM.

[1] Aquino et al. (2008) *Geochim. Cosmochim. Acta* **72**, 3587-3602 [2] Van Riemsdijk & Hiemstra (2006) *Interface Sci. Technol.* **11**, 251-268 [3] Venema et al. (1998) *J. Colloid Interface Sci.* **198**, 282-295 [4] Ghose et al. (2010) *Geochim. Cosmochim. Acta* **74**, 1943-1953 [5] Camacho & Villalobos (2010) *Geochim. Cosmochim. Acta* **74**, 2257-2280 [6] Livi et al. (2014) *Goldschmidt Abstracts*, 1500