

WHAT DO TITRATIONS TELL US ABOUT SILICATE SURFACE CHEMISTRY?

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Much of what is known, or believed to be known of silicate surface chemistry is the result of potentiometric titrations of protons onto these surfaces. Such titrations suggest a pH of zero net proton charge (PZNPC)¹ that is near neutral for alumino-silicate minerals such as albite or at basic pH for many divalent metal silicates such as olivine (c.f. Sverjensky and Sahai, 1996). Such titrations allegedly determine the amount of protons adsorbed to the mineral surface from the difference between the quantities of protons titrated into an aqueous solution-mineral powder slurry and that measured in the solution using a pH electrode. In contrast, the isoelectric point (IEP)¹ of these surfaces as determined by zeta potential yields very different values of the pH. The zeta potential measures the direction and mobility of small grains of solid in an aqueous solution-mineral powder slurry when it is exposed to an electric current. Zeta potential measurements of these minerals indicate that multi-oxide silicates have a zero surface charge at pH ~3, similar to that of pure SiO₂. These observations on multi-oxide silicates contrast dramatically with those of simple oxides (e.g. quartz), which indicate that the IEP corresponds closely to the PZNPC (Jara et al., 2005).

To explore the origin of these different pH of 'zero surface charge' determinations, the total mass of each element liberated to aqueous solution during potentiometric titrations of several minerals including diopside, forsterite, enstatite, and albite was measured. Results indicate that proton consumption during potentiometric titrations stem from 1) consumption by dissolution reactions, 2) consumption by metal-proton exchange reactions involving monovalent, divalent and trivalent cations from the near surface, 3) adsorption of protons onto internal surface sites formed by the metal for proton exchange reactions and 4) adsorption on the metal depleted, Si-rich mineral surface. It is only this last process that is sampled by Zeta potential measurements. This last process tends to be the smallest or second smallest

consumer of protons during potentiometric titrations. Mass balance calculations taking account of all proton consumption processes demonstrate the consistency between zeta potential measurements and potentiometric titrations after taking full account of all proton consuming processes.

CONSEQUENCES OF THESE OBSERVATIONS INCLUDE:

- 1) The surfaces of multi-oxide silicates are dynamic; their composition depends on pH which controls the degree to which near-surface mono, di and trivalent cations are removed from the surface. As such the number and type of surface sites depends on the aqueous solution chemistry. This observation questions the applicability of many popular mineral surface chemistry models to describe the surface chemistry of multi-oxide silicates.
- 2) Potentiometric titrations of multi-oxide minerals measure the sum of protons consumed by 4 distinct processes; the quantity of protons adsorbed to the surface can only be deduced if one accounts accurately for each of these processes.
- 3) At acidic pH, the surface properties of multi-oxide silicate minerals is similar to that of pure SiO₂.
- 4) Metal-proton exchange reactions dominate proton consumption at multi-oxide mineral surfaces. This observation underscored the role of these reactions on the reactivity of these surfaces, including, for example, their dissolution mechanisms (e.g. Oelkers, 2001).

REFERENCES

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¹ There is much confusion of the language used to describe the zero point of charge of surfaces in the literature. In this study, the zero net proton charge (PZNPC) is that generated from potentiometric titration data whereas isoelectric point (IEP) refers to that generated from zeta potential measurements