

Coherency of surface protonation data - implication from modelling of dissolution experiments

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Comparison of seven surface titration curves obtained at 25°C reveals strong discrepancies, both in the shape of the curves and in the pH of the point of zero net proton charge (pH_{PZNPC}). We suggest that the observed differences in the pH_{PZNPC} are mostly artifacts of the differences in points of reference used for the measurements of the titration. At the pH range of 3 to 9, the non-permanent surface charge of kaolinite is dominated by the surface charge of the edges, i.e., by the difference between the amount of protonated Al edges ($>AlOH_2^+$) and the amount of diprotonated Si edges ($>SiO^-$). As all the reported values of pH_{PZNPC} of kaolinite ranged from 3 to 7.5, only the edge contributes to the charge at the pH_{PZNPC} of kaolinite. Therefore, changes in the surface area ratio of the edge to that of the basal plain would not affect the pH_{PZNPC} . Hence, at equilibrium, different kaolinite samples are expected to have similar pH_{PZNPC} , although small differences in pH_{PZNPC} may result from differences in the density of ion substitution and defects on the edge surfaces. Therefore, the different titration curves may be shifted so they would have the same pH_{PZNPC} . An agreement between most of the titration curves was observed following this correction.

A prediction of the molar fraction of protonated sites was retrieved from modelling of kaolinite dissolution reaction and was compared to the protonation data obtained from surface titration. This prediction strongly agrees with the adsorption isotherm of Huertas et al. (1998), which was chosen to represent the other curves. A by-product of this comparison is that it predicts that the proton surface density on the major protonated surface site is $8 \cdot 10^{-7}$ mol m^{-2} (≈ 0.5 sites nm^{-2}). The excellent fitting of the surface charge prediction of our proposed model to surface charge measurements and the reasonable obtained value of the surface density strengthen both the model proposed by Cama et al. (2001) and the corrected surface protonation data.

References:

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Study on the mechanism of metallogenesis of the dispersed elements Ge, Se, Cd and Tl

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The data pertaining to the scale and grade of the selected dispersed element deposits are presented in the table:

Ore deposit	Grade ($\cdot 10^{-6}$)	Scale
Niujiatong Cd deposit	Average: 5366	Large
Lincang Ge deposit	Average: 779	Superlarge
Lanmuchang Tl deposit	2000-2800	Large
Yutangba Se deposit	1258-5037	Small

It can be seen from the table that the four dispersed elements can be so abnormally enriched under certain geological conditions as to form relatively large-scale ore deposits.

Most dispersed element deposits are distributed in the southwest of China.

Their metallogenesis are discussed from the following respects.

(1) Most dispersed element deposits are formed under low temperature ($< 200^\circ\text{C}$) conditions. For example, homogenization temperatures (HT) of calcite, dolomite and sphalerite inclusions associated with sphalerite for Niujiatong deposit is $104\sim 131^\circ\text{C}$; Lincang, HT of quartz inclusions in siliceous rocks contemporaneously precipitated with Ge is $85\sim 88^\circ\text{C}$; Lanmuchang, HT of barite coexisting with lorandite and cinnabar is $107\sim 194^\circ\text{C}$.

(2) It is found that many dispersed elements are concentrated as ores in the certain horizons of the strata.

(3) Ore-forming materials of the dispersed elements came from adjacent rocks of ore-host wall rocks.

(4) The nature of ore-forming fluids for the selected Cd, Ge, Tl and Se deposits are of reducibility (e.g. the ore-forming fluids responsible for the Niujiatong deposit have Eh values ranging from -0.7 to -6.3) and weakly alkaline to weakly acidic (e.g. the ore-forming fluids for the Lincang deposit have pH values ranging from 6.50-8.00).

(5) Metallogenic ages mostly dated at Cretaceous and Tertiary.

References

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