

## Standard states for the equilibrium constants of surface adsorption reactions: Practical implications

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A standard state commonly used for the thermodynamic activities of surface sites and surface species is the hypothetical 1.0 molar standard state, which is implied by the use of molarity-based equilibrium constants. An undesirable practical consequence is that the magnitudes of such equilibrium constants are directly dependent on properties of the solid sorbent such as the site density and surface area. For reactions forming binuclear complexes, the magnitudes of the equilibrium constants even depend on the amount of solid. Although widely used, such equilibrium constants cannot be directly compared with each other without correction for differences in the properties or the amount of the solid. In the present study, new more general and useful standard states independent of surface area, site density, and the amount of solid are presented. The analytical relationships between the old and the new standard states permit conversion of equilibrium constants from one standard state to the other. These results have implications for several different types of surface complexation studies. For example, studies which correlate and compare equilibrium adsorption constants for different solids can be refined by taking account of differences caused solely by site density and surface area. Sensitivity-analysis studies of the fitting of surface charge data as functions of pH and ionic strength will be simplified because of the new analytical relationship between equilibrium constants referenced to the hypothetical 1.0 Molar standard state and site densities. Finally, in studies employing correlations involving aqueous logK values for the purpose of predicting equilibrium constants for surface reactions, the predicted surface equilibrium constants will refer to the site density and surface area associated with the specific samples used for calibration.

## Fission-track dating of zircon by laser ablation ICPMS

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Fission-track (FT) dating of accessory minerals such as zircon, titanite and apatite is a useful tool for determining ages of a variety of geological processes including exhumation and cooling of metamorphic and igneous rocks, and for sedimentary provenance studies.

The FT ages are derived from counted number of spontaneous fission tracks present in the mineral lattice, known decay constant for the spontaneous fission and from measured concentration (number of atoms per analysed volume) of <sup>238</sup>U. The concentration of uranium is usually obtained from the proportion of induced fission tracks after irradiation of samples with thermal neutrons. The uncertainty on resulting ages in a conventional FT analysis with sample irradiation is typically 5-10% (2 sigma) and it arises from errors in the track counting and from the uncertainty in neutron flux in the reactor. Alternatively, the concentration of U can be obtained by laser ablation ICPMS measurements. This technique offers the advantage of a higher sample throughput and hence lower cost of the analysis. In addition, laser ablation ICPMS can measure U concentrations in accessory minerals directly using external calibration against matrix-matched standards or NIST silicate glass with uncertainty between 2-5%. This procedure thus eliminates errors associated with counting the induced tracks and measuring the neutron flux and it has the potential of providing more precise age data.

Here we present results of FT laser ablation ICPMS dating of zircons from high-grade metamorphic rocks and associated granites from the Moldanubian Zone in the Bohemian Massif. The data are in a good agreement with the previously determined conventional FT ages that range between 215-240 Ma. The method used to convert the measured U concentration to the number of U atoms per analysed volume of zircon includes measurement of external Fish Canyon zircon standard (27.9 Ma; Hurford and Hammerschmidt 1985) and calculation of a proportionality constant between number of tracks and number of <sup>238</sup>U atoms that was applied to the unknown samples (Cox *et al.* 2000). While the use of laser ablation ICPMS for U determination in FT dating improves the precision and simplifies the experimental procedure, the method is still limited by low track density in young and U-poor samples and track overlaps in the old and U-rich zircons.

Cox R., Kosler J., Sylvester P. And Hodych J. (2000): *Journal of Conference Abstracts* 5, 322.

Hurford A.J. and Hammerschmidt K. (1985): *Chemical Geology* 38, 23-32.