High resolution valence band spectra of silicates

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The surface reactivity is a fundamental control on rock weathering. X-ray Photoelectron Spectroscopy is one useful technique for probing fresh and reacted surfaces, from which insight into surface reaction mechanisms may be gained. The technique is routinely used to study conductors and semiconductors but has been much less extensively used to document surfaces of non-conductors such as silicates. Both uniform and differential charging result in shifted and dispersed signals thereby limiting the usefulness of the data collected. Recent advances in the charge compensation allow collection of very narrow (lines almost half of the width of previously collected) core level line width of silicates (Nesbitt et al., 2004). High resolution valence band spectra of silicates now can be collected. The valence bands of olivines: forsterite, $(Mg, Fe)_2SiO_4$, fayalite, Fe_2SiO_4, and quartz have been collected and each is different. The deep valence band of fayalite and forterite are similar, but the outer portions differ substantially. This difference is due to the intensities of two Fe peaks from the Fe 3d t_{2g} and e_g orbitals in M1 and M2 sites.

These valence bands now may be used to monitor reactions and orbital involvement in reactions.

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Kinematics of interlayer reactions

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Growth/dissolution of minerals in aqueous solutions often takes place at monolayer steps on atomically flat terraces. A model to describe this type of reaction can be set up by employing kink-site kinematics and the kinetics of kink-site nucleation. This model provides a good description for the appearance of rough or straight step morphologies. Furthermore, the model can describe the increased advance/retreat rates at unbounded steps as generated by coinciding growth islands or etch pits, and has been applied to the rotation of step-orientation induced by different solution compositions (e.g., Jordan and Rammensee, 1998; Jordan et al., 2001).

Recent advances in in-situ atomic force microscopy at solid-liquid interfaces yield insights into the alteration kinematics within the topmost interlayers of phyllosilicates in aqueous solutions (e.g., Aldushin et al., 2004a,b). In the case of apophyllite in acidic solutions, removal of interlayer cations along with a protonation of the non-bridging tetrahedral oxygens and swelling of the interlayers takes place. This reaction propagates in several successive fronts. The fronts are marked by different degrees of interlayer swelling. Various types and features of fronts were detected such as straight and rough fronts as well as increased propagation rates at unbounded fronts. The orientations of the reaction fronts depend on the crystal structure and the solution composition. Thus, the kinematics of the reaction fronts bears an amazing analogy to kink kinematics but also clearly points out limitations in applying kink kinematical models.

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