

## **New kinetic model for the nanocrystalline anatase-to-rutile transformation revealing rate dependence on number of particles**

**HENGZHONG ZHANG\* AND JILLIAN F. BANFIELD**

Department of Geology and Geophysics, University of Wisconsin-Madison, 1215 West Dayton Street,  
Madison, Wisconsin 53706, U.S.A.

### **ABSTRACT**

Existing kinetic models are unable to describe published experimental data for the anatase-to-rutile phase transformation in nanocrystalline samples. A new kinetic model is proposed that combines interface nucleation at certain contact areas between two anatase particles and formation and growth of rutile nuclei. Kinetic equations, incorporating mass-balance considerations, derived for this “interface nucleation and constant growth” model fit the experimental data of Gribb and Banfield (1997) fairly well. Results confirm that the transformation is second order with respect to the number of particles of anatase. Over shorter reaction times, the net transformation rate is determined by the rate of nucleation, which is initiated from rutile-like structural elements in the contact area. The activation energy of  $165.6 \pm 1.1$  kJ/mol for rutile nucleation within nanocrystalline anatase particles is much lower than values previously measured for rutile nucleation in coarse anatase samples ( $>330$  kJ/mol). Nuclei growth proceeds at a constant rate with a very small activation barrier. Over longer reaction times, the net transformation rate is determined both by nucleation and nuclei growth. Results quantitatively explain the origin of the size dependence of phase transformation rates in this system.