Quantification of minor phases in growth kinetics experiments with powder X-ray diffraction

JOHN M. HANCHAR,1,* KATHRYN L. NAGY,2† PAUL FENTER,1 ROBERT J. FINCH,1 DONALD J. BENO,1‡ AND NEIL C. STURCHIO1.§

1Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, U.S.A.
2Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, U.S.A.

ABSTRACT

Minor amounts of clay minerals precipitated from aqueous solution can be rapidly identified and quantified in a mineral mixture with powder X-ray diffraction using a rotating-anode source and a position-sensitive detector. For the case of gibbsite precipitated on a kaolinite powder substrate we demonstrate a simple method having a minimum detection limit of 0.1 wt%, using pure gibbsite as the intensity reference in mechanical mixtures of gibbsite and kaolinite. The amount of gibbsite precipitated onto kaolinite at 80 °C, pH 3 is higher when determined from solution chemistry than from the X-ray method, and the difference in amounts increases with increasing Al concentration in solution. This discrepancy can be explained by assuming that a fraction of the precipitated material is effectively invisible to the X-ray diffraction technique, either due to a small diffracting domain size along the gibbsite [001] direction or formation of an Al-phase that is amorphous to X-rays. This method should be generally useful for a range of mineral mixtures where at least one intense reflection for the phase of interest is not obscured. The ability to identify, characterize, and quantify trace phases by X-ray diffraction, especially when combined with surface analysis by electron or atomic force imaging, is an important complement to the conventional approach of monitoring solution composition in growth kinetics experiments.

INTRODUCTION

Many secondary minerals form by heterogeneous nucleation and growth due to the slight extent of mineral supersaturation common to natural waters and the relatively large energy barrier to homogeneous nucleation. Of paramount importance in attempts to model water-rock interaction is the development of accurate rate laws for dissolution and precipitation reactions. These rate laws should ideally incorporate the effects of solution composition (saturation state and ionic strength) and temperature and be applicable to polymineralic systems. Kinetic data for mineral-fluid systems are typically obtained by reaction of single-phase powders with solutions in various types of reactors. Most kinetic data of this type are for dissolution rather than precipitation reactions. Recently, efforts have been increased to determine precipitation rate laws for a variety of common minerals, with more attention given to the roles of saturation state and substrates for heterogeneous nucleation (e.g., Nagy and Lasaga 1993; Nagy et al. 1999).

Although solution composition can be monitored with ease and accuracy during such powder-reaction experiments, this approach has several shortcomings. Kinetic parameters are generally derived from changes in solution composition. Relating these kinetic parameters to specific mechanisms of crystal nucleation and growth requires accurate characterizations of the surface area of the substrate, the identity of the precipitate, its growth mechanism, and its crystallographic relation to the substrate. It is difficult to characterize the precipitate because the amount of material precipitated is small relative to the amount of substrate. These uncertainties in growth kinetics experiments are being reduced somewhat by the introduction of new surface analytical tools such as atomic force microscopy and electron- and photon-based probes (e.g., Gratz et al. 1993; Charlet and Manceau 1994; Chiarello and Sturchio 1994; Chiarello et al. 1997; Teng et al. 1998; Manceau et al. 1999; Nagy et al. 1999). However, improvements are needed in experimental methods. To address this need, we evaluate the utility of powder X-ray diffraction (XRD) for identifying and quantifying minor amounts of precipitates in growth kinetics experiments performed with powders.

Identification and quantification of minerals in mixtures are two of the most common applications of powder XRD (e.g., Lennox 1957; Copeland and Bragg 1958; Chung et al. 1974a, 1974b; Klug and Alexander 1974; Popovic et al. 1983; Bish and Howard 1988; Snyder and Bish 1989; Batchelder and Cressey 1998; Pratapa et al. 1998). Clay minerals are typically identified by XRD analysis of oriented and treated samples and/