Time-resolved SAXS study of nucleation and growth of iron(III) oxyhydroxides

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Introduction.The process of hydrolysis and polymerization of Fe(III) oxyhydroxides plays an important role in the chemistry of natural waters. However, these transformations are rapid and occur over timescales that are much smaller than those typically studied. Time-resolved SAXS studies provide the capacity to investigate nucleation and the evolution of particle size distribution on a sub-second timescale. Different mechanisms of particle production have previously been identified, for example, a nucleation burst followed by monomer addition [1] and, nucleation followed by aggregation [2]. In this study we use TR-SAXS to examine polymerization of Fe(III) oxyhydroxides following rapid mixing, such that mixing times are less than reaction times. In this initial study, at [Fe] = 1 mM, required to produce sufficient scattering intensity, reaction times were sufficiently long only at pH 3 and 4. Investigation of higher pHs will require the optimization of a micro-fluidic device.

Results and Conclusions. The SAXS curves were analysed, both directly and by fitting a pair distance function, to produce values for the invariant Q, zero-angle scattering intensity $I(0)$, and radius of gyration R_g. Q is a measure of the total scattering mass while $I(0)$ is sensitive to particle size and number. At pH 3, with $[NO_3]$ = 6 mM, R_g stabilized at ~25 nm after only 30 s while both Q and $I(0)$ continued to increase till ~300 s. At times >300 s, Q was relatively stable while $I(0)$ decreased. In the same system at pH 4, R_g followed the same pattern as for pH 3, however maximum values for Q and $I(0)$ were attained after ~77 s, and decreased thereafter. These results show that at early times, small but increasing numbers of maximum sized particles coexisted with monomers or oligomers that were too small to scatter significantly in the q-range used to calculate Q. Such a system evolution implies that slow nucleation and relatively rapid particle growth proceeded concurrently until the maximum scattering mass was achieved. Particle growth appears to have occurred via a monomer addition mechanism (‘monomers’ here may be oligomers) since the stable R_g implies that significant aggregation is not occurring. The more rapid development of the maximum scattering mass at pH 4, compared to pH 3, is consistent with a higher rate of polymerisation of Fe(III) hydrolysis species and therefore more rapid production of stable nuclei. Whether the observed decreases of Q and $I(0)$ following attainment of maximum values are due to sedimentation or further transformation via dissolution and reprecipitation remains unclear and will be the subject of further investigation.

[1] Liu *et al.* (2010) *Langmuir* **26**, 17405-17412. [2] Polte *et al.* (2010) *ACS Nano* **4**, 1076-1082.

Determining garnet crystallization kinetics from growth zoning and Mn-calibrated Sm-Nd ages at Townshend Dam, VT

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Introduction

Essential to an understanding of metamorphic rocks are the rates at which a metamorphic reaction can occur. Kinetics of porphyroblast crystallization includes rates of both growth and nucleation. Though some studies have been able to quantify growth rates, direct measurements of nucleation rates have remained enigmatic. We present a method to indirectly measure nucleation as well as growth rates of chemically zoned porphyroblasts by linking chemical and age data.

This project examined a garnet + muscovite + paragonite + biotite + chlorite + quartz + plagioclase schist from the Pinney Hollow formation at Townshend Dam, VT. Biotite-quartz-rich layers alternate with muscovite-paragonite-rich layers on a millimeter scale and define the foliation. Garnets are sub- to euhedral, vary in size from 5 to 30 mm in diameter, and display curved quartz inclusion trails continuous with foliation at the rims.

Method

The specimen was imaged in 3D using high-resolution X-ray computed tomography. Garnet porphyroblasts were extracted and portions of them with quantified Mn content underwent Sm-Nd geochronology methods to produce a Mn-age curve for the rock [1]. A subvolume from the interior of the specimen was separated and disaggregated, allowing extraction of 62 garnets. Morphological centers of each were exposed, polished, and chemically mapped (via SEM-EDS). The EDS characterization facilitated location of peak-Mn regions, from which core-rim linescans were performed via EPMA for quantitative zoning determination. Mn data were converted to ages via reference to the Mn-age curve [1], allowing determination of nucleation and growth kinetics.

Results

Townshend Dam garnets show concentric, smooth Mn zoning curves. Microprobe analyses yield central garnet MnO content ranging from 2.3 to 11 wt%, depending on the size of the garnet. Rims of garnets are Mn-poor with ca. 0.1 to 0.2 wt% MnO. Data collection is ongoing, but preliminary EPMA results indicate that among the analyzed garnets, the range of core X(Mn) is 0.047-0.249, corresponding (via the curve in [1]) to an age range of 384.8-378.1 Ma. Given this duration of nucleation (6.7 m.y.), the number of garnets (62), and the subvolume size (1210 mm^3), we calculate a nucleation rate of approximately 0.0076 nuclei per m.y. per mm^3.

[1] Gatewood et al. (2011) AGU Fall Mtg., Abstract #V13G-05.