

Probing the aqueous nucleation and growth of TiO₂ with high time-resolution small-angle and wide-angle X-ray scattering

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Titanium oxide nanoparticles have been widely studied due to the sequence of metastable phases commonly observed during their precipitation in aqueous settings [1]. We have monitored the homogeneous crystallization of TiO₂ phases from aqueous TiCl₄ solutions between 100 and 200 °C using both time-resolved small-angle X-ray scattering (SAXS) and time-resolved wide-angle X-ray scattering (WAXS). The WAXS data reveal that the metastable anatase phase is always the first phase to crystallize, but begins transforming to either brookite or rutile (the stable phase) within the first hour of reaction [2]. Scherrer analysis of peak widths reveals that anatase particles nucleate rapidly and grow to an average size near 7 nm on a time scale of minutes, after which their size remains static. Rutile particles grow quickly from 3 nm to ~10 nm, and then continue growing slowly over many hours.

Using a novel sample cell modified to withstand higher temperatures and pressures, we collected *in situ* SAXS data under the same conditions as the WAXS experiments. Fourier analysis of the SAXS images revealed the rapid emergence of a particle population with a broad, Gaussian-type size distribution. The distribution had a range from 1 to ~15 nm and a mean near 7 nm, in excellent agreement with the WAXS data. Size distributions slowly developed tails at larger particle sizes, representing the continued growth of primary rutile nanoparticles observed in the WAXS patterns. Some experiments also showed multimodal size distributions, which we attribute to the previously reported oriented aggregation of anatase crystallites [3].

[1] Navrotsky (2004) *PNAS*. **101**, 12096-12101. [2] Hummer *et al.* (2009) *J. Phys. Chem. C* **113**, 4240-4245. [3] Penn and Banfield (1999) *Geochem. Cosmochem. Acta*. **63**, 1549-1557.

Noble gases in the natural gas of western New York and north-central Pennsylvania: Natural analogs for evaluating possible impacts of carbon sequestration and horizontal drilling

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Noble gases in the natural gas produced from western New York and north-central Pennsylvania provide a powerful tool for evaluating potential pitfalls associated with geological sequestration of carbon dioxide and for anticipating possible problems during horizontal well drilling and completion. The natural gas produced from unconventional Ordovician, Silurian and Devonian reservoirs in the Northern Appalachian Basin are mixed thermogenic hydrocarbon accumulations. Noble gas data in conjunction with carbon isotopic data from the hydrocarbons supports the existence of two separate gas sources. One type of gas was generated *in situ* and is characterized by isotopically light methane with a noble gas composition dominated by atmospheric isotopes. The second type of gas consists of isotopically heavy methane with a distinct noble gas composition characterized by radiogenic/nucleogenic noble gases. The second post-mature gas migrated upward from an Upper Ordovician Utica/Point Pleasant Shale source as a fluid into the Lower Silurian Medina and Tuscarora sandstones as well as into the Devonian Marcellus and Dunkirk shales. Whereas the Ordovician/Silurian reservoirs preserve the key isotopic signatures of the post-mature gas, the Devonian reservoirs contain a mixture of an *in situ* generated gas and a component from deeper sources. The noble gas compositions of the Devonian reservoirs (thermogenic shale-gas) are representative of a fractionation process that involves multistage equilibration with shallow, air-saturated groundwater. This fractionation pattern indicates that the system is periodically open to the influx of fluids to the reservoir and that at times a hydrological connection exists between local groundwater systems and the reservoir.