# An *in situ* SAXS/WAXS study of sulfate- and carbonate-green rust formation

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Green rust (GR) nanoparticles have been shown to reduce and immobilise many toxic metals (e.g., Cr^{6+}) and radionuclides (e.g., U^{6+}). This property makes them potentially important for environmental remediation in such systems as permeable reactive barriers. Their structure consists of Fe^{II}/Fe^{III} octahedral layers that alternate with anionic species (e.g., SO_4^{2-}, CO_3^{2-}) in the interlayer space. The presence of Fe^{2+} within the structure acts as a reducing agent. The formation and stability of GR within the environment are poorly understood. This is because the particles rapidly oxidise in air making them difficult to study using conventional techniques.

The kinetics and mechanisms of GR formation and transformation were studied *in situ* using synchrotron-based time-resolved Small and Wide Angle X-ray Scattering (SAXS/WAXS). GR was formed by the controlled addition of Na_2CO_3 to mixed sulphate Fe^{II}/Fe^{III} solutions (i.e., pH ramp). The effects of Zn and Se on these processes were also studied. The time resolved data (Fig.1) shows the formation of a poorly-ordered Fe^{3+} oxyhydroxide phase at pH < 6.7, followed by the growth of GR-SO$_4$ (pH ≈ 7) and its transformation to GR-CO$_3$ at higher pH (≈ 9.5).
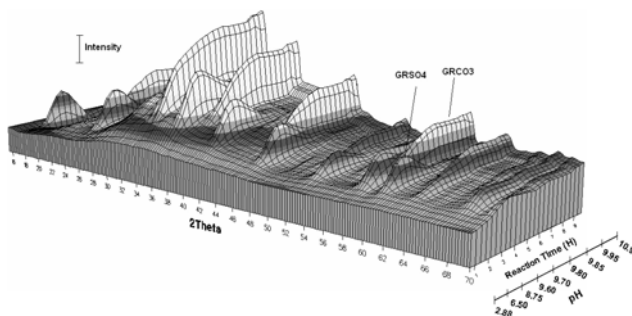
Figure 1: WAXS data illustrating the successive formation of GR-SO$_4$ and GR-CO$_3$ with increasing pH.

Data from the Zn and Se experiments indicate that the Zn is adsorbed to the initial FeOOH phase and becomes structurally incorporated into GR by direct substitution for Fe^{2+}. Se^{6+} is reduced to Se^{4+} and Se^0 during the formation of GR-SO$_4$.

Precise measurements of atmospheric CO_2 trapped in polar ice cores and its application to the West Antarctic Ice Sheet Divide (WAIS Divide) ice core

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How atmospheric CO_2 varies and is controlled is an important question for understanding how the carbon cycle and climate change are linked. CO_2 variations on glacial-interglacial cycles are relatively well studied, but sub-millennial scales are not. The WAIS Divide CO_2 record will be unique – providing the highest resolution, best dated long CO_2 record yet available (http://www.waisdivide.unh.edu/).

To obtain this high temporal resolution, we developed a high-precision method. Occluded air in ice samples weighing 8 ~ 15 g is liberated by crushing at -35°C and trapped at -262°C in stainless steel tubes in a cryogenic cold trap. CO_2 in the extracted air is analyzed using a gas chromatographic method. Replicate measurements for several samples of high quality ice from the Siple Dome and Taylor Dome Antarctic ice cores have pooled standard deviations of better than 1 ppm, comparable to the best results from the average of 4 to 6 replicates in other facilities.

We applied this high-precision technique to the shallow WAIS Divide ice core (<300m, < ~1000 yr) drilled in 2005-2006. The initial results cover the onset of the Little Ice Age (1500 ~ 1700 A.D.) and show atmospheric CO_2 decreased ~10 ppm in less than 100 years at the onset of the Little Ice Age. This drop lags a similar decrease in atmospheric CH_4 by ~ 40 yr. These CO_2 variations confirm previous studies for Law Dome and EDML ice cores. We will continue the CO_2 analysis and the updated results will be presented at the meeting.