**Introduction:** There has been a resurgence in interest in jarosite, (K,Na)Fe$_2$(SO$_4$)$_3$(OH)$_6$, and related minerals since their detection on Mars by the MER rover Opportunity [1]. In this context, the presence of jarosite has been recognised as a likely indicator of water at the surface of Mars in the past and it is hoped that study of their formation mechanisms will provide insight into the environmental history of Mars [2].

Jarosites are also of great importance to a range of mineral processing and research applications. For example: they are used in the removal of iron species from smelting processes; they form detrimentally in biometallurgical systems and they are present in acid mine drainage environments. Jarosites are also of considerable theoretical interest as model compounds for spin frustration in Kagomé-Heisenberg antiferromagnetic materials [3].

Knowledge of the formation mechanisms of jarosites is an indispensable prerequisite for understanding their occurrences, stabilities and potential environmental impacts both on Mars and Earth. We are engaged in a program of research to study the nucleation and crystal growth of jarosites under a variety of conditions. Here we report the results of in situ synchrotron powder diffraction experiments designed to follow the crystallisation and growth kinetics of jarosite minerals in the presence of seed materials.

Figure 1 shows the structure of jarosite. Layers of blue corner sharing Fe octahedra are connected by yellow sulphate tetrahedra. Cations such as potassium or sodium can also be found in these interstitial layers (red). Jarosite is traditionally reported with rhombohedral symmetry [3]. However, we have synthesised monoclinic jarosite under certain preparative conditions [4].

**Experimental method:** Jarosite forms readily by co-precipitation on gentle warming of an appropriate solution. 2.25 g of Fe$_2$(SO$_4$)$_3$.xH$_2$O and 0.70 g of K$_2$SO$_4$ were dissolved in 10 mls of deionized H$_2$O. Seed materials were diamond, hematite and goethite. Hematite and goethite are commonly found in association with natural jarosite deposits. The inclusion of diamond provides a baseline for the effect of an inert seed material. These materials were added to the jarosite starting-solutions to give 5 wt% seed. An additional solution was prepared with no seed material to provide a comparison set of data.

Portions of each slurry were transferred to 1.0 mm diameter quartz capillaries for in situ synchrotron X-ray diffraction experiments. Samples were heated to 120 °C using a hot-air blower. Experiments were conducted on the Powder Diffraction beamline at the Australian Synchrotron. Scattering data were collected contiguously throughout the reactions at 1 minute intervals for approximately 1 hour. An equivalent experimental setup is described in greater detail in [5].

**Results:** For all the experiments except the diamond seeded synthesis, jarosite peaks are apparent within the first few minutes. While the unseeded experiment produced a mixture of monoclinic and rhombohedral jarosite compositions, the seeded datasets are best fit using a single monoclinic structure.

Figure 3 shows the unit cells of the in situ syntheses plotted as pseudo hexagonal axes relative to literature values for pure endmember hydronium and potassium jarosite.  

**Figure 2.** Unit-cell parameters of jarosite produced in each in situ synthesis, represented as pseudo hexagonal unit-cell axes for ease of comparison with literature values for rhombohedral endmember potassium and hydronium jarosite. Diamond seeded synthesis is red, hematite purple, goethite green, unseeded blue and literature values from [6] are crosses joined with a solid line.
All syntheses are initially hydronium rich before transitioning toward a potassium rich composition. The goethite synthesis behaves very similarly to the unseeded synthesis, while the diamond and hematite syntheses follow the same general trend but are offset in unit-cell volume. Diamond seeded jarosite has a smaller unit cell, and hematite larger.

**Kinetics:** Figure 3 shows the relative amount of jarosite produced in each *in situ* synthesis as a function of time. A modified version of the Avrami equation has been fitted to these data to obtain reaction rates and order. The most obvious feature to note is that the diamond-seeded jarosite formation has a substantial induction period, after which the reaction progresses at a similar rate to the other seeded (and indeed unseeded), syntheses.

![Figure 3](image3.png)

Figure 3. Relative amount of jarosite produced in each *in situ* synthesis with time. Diamond seeded synthesis is red, hematite purple, goethite green, unseeded blue.

Initially, the goethite and hematite seeded syntheses progress at a similar rate to the unseeded synthesis and the goethite reaction undergoes a mechanism change at similar point and of a similar reaction order to the unseeded reaction as reported in [7]. The hematite reaction, however, produces less jarosite at a slower rate. This may be due to poor dispersion of the seed material in the initial slurry – see figure 4.

**Morphology:** Figure 4 shows microscope images of the final products taken through the walls of the capillary. The scale is the same on each image. Clearly the different seeds produce morphological differences in the jarosites produced. The diamond seeded crystals are similarly sized to the unseeded jarosite; however, there is some evidence of multiple size distributions which are not seen in the unseeded synthesis [7]. The jarosite crystals in the goethite seeded synthesis are much smaller than in all the other syntheses. This may reflect a well dispersed seed powder in the initial slurry. There is also evidence of clustering around the seed material in the hematite synthesis to support this.

![Figure 4](image4.png)

Figure 4. Microscope images of the final products.

**Summary:**
- Addition of seed material makes a difference to the amount and rate of jarosite production as well as the composition of jarosite formed.
- The effect of the seed is not simply to provide more nucleation sites on which the jarosite forms.
- Reaction mechanisms are different with different seed material. This may reflect the degree of interaction of the seed material with the solution.


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