Multiple heating events recorded in CAI melilite

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Melilite in CAIs covers nearly the entire solid solution range from gehlenite to åkermanite. As part of ongoing petrologic and isotopic studies of several large CAIs from CV chondrites, as well as experimentally grown synthetic analog compositions, quantitative maps of the chemical composition of melilite were collected by SEM-EDX. Each quantative map contains ~50,000 spot analyses and a number of such maps were made for several CAIs and many run products. Comparison of melilite composition histograms in CAIs and run products reveal interesting features that appear to be related to thermal histories.

Melilite compositions have been measured in two types of experiments: compositions along the melilite binary have been heated above the liquidus, cooled slowly and quenched to investigate the phase diagram [1]; and CAI compositions have been heated to near or above the liquidus, cooled at various rates and quenched to investigate crystallization histories of CAIs [2]. Histograms of melilite for both types of run products share common features: (1) a peak at the Ge-rich end, corresponding to the initially crystallizing melilite for that particular bulk composition and temperature; (2) a tail to the right, with the most Åk-rich composition depending on the quench temperature; and (3), for experiments quenched above the solidus, a peak at the Åk-rich end.

Melilite histograms of seven CAIs from CV chondrites are more complicated than the run products and show two to seven peaks. All have a tail from the most Ge-rich peak to nearly pure gehlenite, reflecting a late-stage evaporation event that postdated CAI crystallization. The most Åk-rich melilite in all CAIs is $Åk_{80-82}$, clearly beyond the eutectic in the melilite binary phase diagram. Multiple peaks in histograms may represent partial melting episodes: once the maximum temperature in such an event has been reached and the CAI cools, some degree of undercooling results in melilite nucleation and rapid growth, giving a peak. The number of peaks in melilite histograms may represent the minimum number of reheating events. The current champion is Leoville 3535-1, with seven peaks, representing heating events that all occurred over a time span of <40,000 years, based on very well-behaved ²⁶Al-²⁶Mg systematics [3].

[1] Mendybaev *et al.* (2006) *LPS* **37**, #2268. [2] Mendybaev *et al.* (2006) *GCA* **70**, 2622–2642. [3] Kita *et al.* (2008) *GCA* **72**, A477.

Experimental supercrictical CO₂ and water interactions with Carboniferous coal, Germany

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The three main options for geological storage of CO₂ are depleted oil and gas fields, coal seams and deep saline formations. CO2 is stored in coal mainly as adsorbed molecules on micropore surfaces that allow higher densities at same depths than in conventional oil and gas reservoirs and saline formations. Injected CO2 will also dissolve in formation water and the resulting acid will react with minerals in the coal seam (solution and mineral trapping) which further reduces the risk of CO₂ leakage. In the current study we simulated CO₂ injection into deep coal seams using batch experiments conducted at 40°C and 90 bar for 72 hrs, to evaluate physical and chemical changes caused by exposure of coal to a mixture of water and supercritical CO₂. Within a purpose built batch reactor, two sister coal cubes (15 mm to a side) were separately immersed in a mixture of supercritical CO2 and RO water (SCO₂-H₂O), and a third sister cube was immersed in RO water (H₂O) only. The Carboniferous coal analysed was thinly interbanded, with a vitrinite reflectance of 0.93%. The three sister cubes were cut immediately adjacent to each other from the same horizontal interval of a larger coal block, sourced from an underground coal mine in Germany.

The leachate chemistry from the SCO₂-H₂O experiments indicates significant mobilisation of metals which we attribuite to dissolution of cleat and matrix mineral matter and displacement of cation exchangeable metals from the coal. Visible quantities of fine particles were also produced by the experiments. Coal density is much less affected by exposure to H₂O alone and little mineral matter is mobilised compared with the SCO₂-H₂O experiments. SEM images also provide evidence of dissolution/alteration of cleat and matrix minerals. Demineralisation reactions with SCO2-H2O are evident from sample weight loss (after accounting for fines produced) and an increase in LP CO₂ adsorption (as shown from experiments with coal powders). Thus, any reduction in permeability due to CO₂ induced coal swelling may be at least partly countered by dissolution and mobilisation of mineral matter in the coal seam near the injection well.