Storage of CO_2 in the upper mantle: a solid solution model for Ca-Mg-Fe carbonates

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At convergent plate boundaries, volatiles are transported into the interior of the Earth affecting the chemical evolution of our planet. H_2O and CO_2 are the most important volatile compounds affecting phase stabilities during subduction. The high pressure stability of carbonates, e.g. the occurrence of coesite and diamond inclusions in dolomite and magnesite, is evidence for retention of CO_2 in carbonates during subduction to > 6 GPa. The fate of carbonates is then controlling the residence time of C in the mantle, affecting the global geochemical C-cycle, and contributing to the chemical and, in carbonate rich sediments, also mechanical properties of subducted crust. Nevertheless, the phase diagram of $CaCO_3$-$MgCO_3$-$FeCO_3$ was unknown at high pressure and is now investigated.

Piston-cylinder experiments have been performed at 35 kbar and temperatures between 900°C and 1100°C to constraint subsolidus relations of carbonates. Two miscibility gaps have been observed at 900°C: a narrower miscibility gap between dolomite and calcite, which closes with decreasing X_{Mg} at an X_{Mg} near 0.7, and a broader miscibility gap between the two completely soluble solid solution dolomite-ankerite and siderite-magnesite. Increasing the temperature the two miscibility gaps became narrower until the dolomite-calcite solvus on the Ca rich side of the diagram disappears completely between 1000°C and 1100°C.

Combining our data with data available in the literature, an empirical solid solution model for the system $CaCO_3$-$MgCO_3$-$FeCO_3$ has been fitted to calculate the stability field of carbonates as a function of pressure and temperature in the upper mantle.

Fluorescent imaging of radionuclide chemical transformation through permeable reactive barriers

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Oxidative dissolution of uranium deposits leads to the formation of the soluble and mobile uranyl species (UO_2^{2+}). The corrosion products of zero-valent iron (ZVI) are known to adsorb U(VI) under reducing conditions [1]. The main aim of this part of the project is to monitor the changes of U(VI) when in contact with ZVI. These chemical changes are imaged using ultra-violet light and the fluorescence signal emitted will be processed using imaging software.

A bench scale 2-D physical model, incorporating an aquifer flow system with a zone of ZVI placed across the flow field, has been established. Ottawa sand is used to create an unconsolidated aquifer with limited heterogeniety and recycled iron filings act as a reductant. Environmental conditions can be simulated using a uranyl solution and the luminescent characteristics of U(VI) are used to observe the lowering of fluorescence intensity as UO_2^{2+} is immobilised within iron oxy(hydroxides).

A fluorescent indicator, $Ru(phen)_3Cl_2$, has been used to noninvasively image the changes in dissolved oxygen concentrations within the flow cell. An oxygen saturated solution and indicator is pumped through the flow cell. The fluorescence is quenched by dissolved oxygen and we have observed that as the dissolved oxygen is consumed by corrosion processes within the barrier, the fluorescent signal increases. By quantifying the signal, dissolved oxygen concentrations can be mapped across the flow cell. Under these anaerobic conditions, it is thermodynamically favourable for U(VI) to be reduced by ZVI. Wet chemical analysis, electron microscopy and non destructive analytical techniques can be used to characterise the corrosion products involved in absorption and co-precipitation of U(VI). These techniques will indicate the preferred method of immobilisation within the flow cell.

[1] Hsi & Langmuir (1985) *Geochimica et Cosmochimica Acta* **49**, 1931-1941