

**X-ray diffraction studies of hydrous carbonates - Alistair Lennie (a.lennie@dl.ac.uk),
Chiu Tang (c.c.tang@dl.ac.uk) & Steve Thompson (s.p.thompson@dl.ac.uk)**

Work supported by the EPSRC

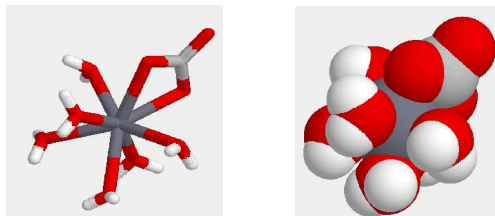
Changes in carbon dioxide in the atmosphere over geological time are interconnected with organic and mineral carbon reservoirs. The predominant carbonate mineral calcite (CaCO_3) acts as a buffer for long-term cycling of carbon dioxide between the atmosphere, oceans and solid Earth. However, calcite is not the only calcium carbonate mineral, and there are still discoveries to be made in this complex and fascinating mineral system. In 1963, a then little-known calcium carbonate phase was reported as a new mineral, ikaite, in unusual underwater formations at Ikka Fjord, Greenland.

Although ikaite was first discovered as a mineral in 1963, it had been reported from laboratory studies made during the 19th century. Ikaite plays a role in the carbon cycle, sequestering carbon dioxide produced by bacterial oxidation of organic matter in cold marine sediments. How important this role is in the total carbon dioxide budget of the Earth's oceans has not yet been established.

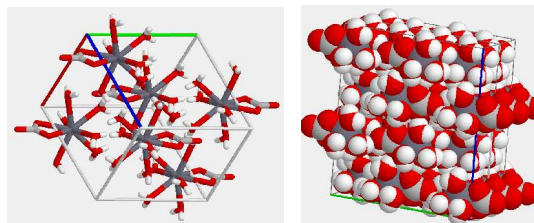
Ikaite, although metastable at low pressures, will form below about 278 K if there is sufficient dissolved calcium and carbonate available. This explains its presence in sediments in Bransfield Strait, Antarctica, and in the Zaire deep sea fan, as well as its occurrence at Ikka Fjord. This mineral thus provides a sink for carbon dioxide in Arctic, Antarctic and deep-sea marine sediments.

Using synchrotron radiation, we are measuring properties of this mineral at low temperature and at high pressure, and are following processes of decomposition as temperature is increased. Our studies investigating the behaviour of this unusual mineral are helping us to understand the role of ikaite in the Earth's CO_2 cycle.

The crystal structure of ikaite consists of repeating units of six water molecules, a carbonate anion and a calcium ion. Oxygens from six water molecules, and two oxygens from carbonate, coordinate calcium to form calcium carbonate hexahydrate units ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$). This description of the structure becomes clearer when viewing the structure in three dimensions, possible with the aid of CrystalWeb, the Chemical Database on-line facility for crystallographic display.



In ikaite, hydrogen atoms belonging to water molecules link with nearby oxygens to form hydrogen bonds. These weak bonds join individual units together to form the crystal with similarities to the formation of ice which consists of a network of hydrogen-bonded water molecules.



We synthesised crystals of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ and examined these at the SRS, Daresbury. The data collected has shown us how, as the crystal cools, weak hydrogen bonds in the structure undergo greatest change. When we compare ikaite with ice (H_2O) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), we observe that ikaite thermal behaviour lies in-between these minerals.

Here again, the databases of CDS provide invaluable reference data from which we can build up a picture of comparative behaviour. Gypsum has significantly less hydrogen bonding within its structure than ikaite, while ice has more, with water molecules linked by hydrogen bonds only. These structural differences are reflected in their crystallographic behaviour.

When ikaite is warmed to room temperature, it breaks down into calcite (CaCO_3) and vaterite (CaCO_3), another rare calcium carbonate phase, with water of crystallisation being released. We are now following the formation of these new phases using X-rays to track down structural features in common, and to understand mechanisms of formation and transformation. Again, the databases are of great help here, allowing easy visualisation of crystal structural relationships.

An unusual feature of this icy carbonate is that the molar volume is 21% smaller than that occupied by calcite + 6 H_2O liquid phase. Under high water pressure therefore, ikaite becomes a stable phase, and we are using high-pressure studies to find out how this structure is stabilised. Again, we can compare this with other high-pressure phases recorded in ICSD.

Hopefully in the future we will be able to contribute to the database of structures from which we are at present drawing by providing new structural information to add to the present database.