

## Deducing marginal marine seawater composition from biogenic carbonate and evaporites

R. FLECKER<sup>1,2</sup>, S. DE VILLIERS<sup>3</sup>, I. SANCHEZ-ALMAZO<sup>3</sup>  
& A. CARUSO<sup>4</sup>

<sup>1</sup>School of Geographical Sciences, University Road, Bristol  
BS8 1SS, UK (r.flecker@bristol.ac.uk)

<sup>2</sup>Scottish Universities Environmental Research Centre, East  
Kilbride, Glasgow G75 0QF, UK

<sup>3</sup>Dept. Earth Sciences, Downing Street, Cambridge CB2 3EQ  
(svil99@esc.cam.ac.uk, isabel00@esc.cam.ac.uk)

<sup>4</sup>Dept Geologia e Geodesia, Palermo Italy (acaruso@unipa.it)

Knowledge of the natural variability of ocean water composition has grown with the number of chemical studies published. While disentangling the controls on chemical composition of biogenic minerals remains poorly constrained, an appreciation of the range of trace element, stable and some radiogenic isotope values typical of ocean water has developed. Values outside these established ranges are commonly discarded on the pretext that they represent diagenetically altered rather than primary signals. Marginal marine settings such as semi-enclosed seas, lagoons and estuaries are subject to much more extreme chemical changes than the open ocean. Discriminating between primary and altered material from marginal marine systems is therefore difficult and controversial.

We present data from a multi-proxy study of the Late Miocene evaporite succession preserved at Eraclea Minoa, Sicily. The succession of alternating foram-bearing marls and gypsum illustrates the strong variability of the water chemistry at the time where salinity fluctuated abruptly between levels able to support a foraminiferal assemblage to those required for gypsum precipitation (130-160 g/L). Careful visual, chemical and LA-ICP-OES screening of samples permits discrimination between primary and secondary mineralisation and allows interpretation of the composition of this anomalous Late Miocene seawater around Sicily. It also reveals chemical characteristics of fluids circulating either during or after deposition. Combined chemical, faunal and sedimentological interpretation of this succession allows a better understanding of the impact of climate and the relative dominance of ocean versus freshwater influx on marginal marine systems.

## Carbonate apatite at high pressure

M. E. FLEET, XIAOYANG LIU AND P. L. KING

Department of Earth Sciences, University of Western Ontario,  
London, Ontario, N6A 5B7, Canada (mfleet@uwo.ca)

There is an increasing awareness of the contribution of carbonated apatite (C-OHAp, C-FAp) to bone and dental enamel, as well as in the *in vivo* remodelling of bone material. However, the structural roles of the carbonate group in apatite remain unclear. In this study, carbonate apatite (CAp) and C-OHAp and C-FAp have been synthesized in an end-loaded piston cylinder apparatus at 2-3 GPa and 1400°C, and investigated by EPMA, FTIR and C *K*-edge XANES spectroscopy and single-crystal structure analysis, to follow structural change with progressive substitution of carbonate. The composition series investigated was  $(9-y)\text{Ca}(\text{PO}_4)_{2/3} + (x+y)\text{CaCO}_3 \pm [\text{CaF}_2, \text{Ca}(\text{OH})_2]$ , where  $x = 1$  for CAp and  $x < 1$  for C-OHAp and C-FAp. Our apatites saturated in the calcite stability field at  $(x + y) \approx 2.0-2.5$ .

In FTIR spectra, asymmetric stretch ( $\nu_3$ ) bands of the carbonate group are present at about 1459 and 1539  $\text{cm}^{-1}$  in A-type CAp ( $x = 1, y = 0$ ); about 1409, 1453, 1504, 1539, and 1563  $\text{cm}^{-1}$  in A,B-type CAp; about 1408, 1455, 1471, and 1546  $\text{cm}^{-1}$  in A,B-type CAp annealed in air at 1000°C; and about 1428, 1456, 1511, 1550, and 1574  $\text{cm}^{-1}$  in B-type C-FAp. C *K*-edge XANES spectra are characterized by a sharp absorption peak at  $\sim 290.2$  eV and a broad peak at  $\sim 301.3$  eV due to transition of C 1s electrons to unoccupied states of  $\pi^*$  and  $\sigma^*$  character, respectively. The area of the  $\pi^*$  peak increases in proportion to the amount of carbonate present.

Different from previous studies, X-ray structures of A,B-type CAp (space group  $P6_3/m$ ) show that the channel (A) carbonate groups are deflected from the vertical plane to avoid a prohibitively short Ca2-O distance (1.74Å in the ideal structure). Also, high-pressure CAp can accommodate more than one channel (A) carbonate group per unit cell. This is possible because one of the oxygens in each group is located at the position of O(H) in OHAp but, even so, minimization of unfavourable O-O interactions results in considerable disruption in the decompressed structure. Partial decarbonation of the excess channel carbonate occurs on annealing A,B-type CAp in air at 1000°C. The B-type carbonate group is oriented close to one of the sloping faces of the vacant  $\text{PO}_4$  tetrahedron, but tilted closer to the horizontal plane. For the full complement of Ca atoms (10 pfu), the ideal partitioning of the carbonate group between A- and B-type sites appears to be  $A = [x + (y/3)]$ ,  $B = [6 - (2/3)(9 - y)]$ . However, the X-ray structures reveal that the amount of channel (A) carbonate is typically in excess of this ideal ratio in CAp because, under high pressure, carbonate is stuffed into the channel (A) sites in preference to available B sites.