Geophysical Research Abstracts, Vol. 8, 06987, 2006
SRef-ID: 1607-7962/gra/EGU06-A-06987

Amino acids in calcite: a tiny time-capsule for the Quaternary

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Whilst amino acid racemization (AAR) has been applied widely as a dating technique for the Quaternary in Europe, some results have proved controversial and in recent years other geochronological tools have become more routinely used, at the expense of AAR. We have spent four years trying to refine the methodology used on gastropod shells by (i) using multiple amino acid DL ratios, (ii) cross-checking the AAR values of only Free amino acids (released from degraded proteins) against AAR values of the Total amino acid in the mineral, (iii) bleach treating to remove contaminants and the degradable organic matrix and (iv) temperature modelling. Whilst some of these refinements have been reported before, they are here integrated together for the first time.

This approach both ensures the analysis of only the original amino acids, and allows the identification of bacterial contamination and post-depositional recrystallization. Yet despite all these innovations, whilst the gastropod shell values can successfully identify marine isotope stages up to MIS 9, beyond that their level of resolution becomes limited. However, this work has been eclipsed in the last year by results obtained from the analysis of the tiny Bithynia opercula, common fossils in Quaternary freshwater deposits.

The shells are aragonite, but the humble operculum which closes the gastropod valve is calcite. Preliminary results with opercula are spectacular: within a single site multiple opercula yield consistent results and the data from multiple sites fall into discrete

clusters. As a consequence, the extent of protein degradation in opercula can be used to resolve not only stages but sub-stages within the Quaternary. The analyses of over 500 single opercula from 100 northern European sites are reported, with this coherent calcite intra-crystalline system allowing the development of an AAR chronology to at least the Pliocene ($>$ 2.5 Ma).

The utilisation of these robust biominerals has given increased resolution over the last 0.5 Ma and pushed back the range of this technique in Europe far further than expected. Whilst the limits of dating using solely racemization is reached within the Pliocene in the areas studied, the isolation of an intact closed-system of amino acids from Miocene and Eocene opercula opens up a world of other amino acid degradation reactions which can be used for dating.