U-Pb dating of carbonate-fluorapatite: a potential chronological tool for ancient marine sediments

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1 BACKGROUND & STRATEGY

Carbonate Fluorapatite (CFA) is a relatively widespread early diagenetic component precipitated in sub-aqueous sediments. Nodules, laminae and shell overgrowths or infills composed of CFA are relatively common features in phosphorites, carbonates and other marine sediments. Sedimentary phosphate typically has very high U-concentrations. CFA U-Pb dating thus has potential application as a chronometer in a wide variety of ancient marine sediments, particularly in those marine sections lacking diagnostic faunal and/or floral assemblages, or well-dated volcanogenic horizons.

We have analysed several samples of phosphorite, or phosphate-bearing sediments in order to characterise CFA for dating by the U/Pb method. These measurements were made by LA-Q-ICPMS at the National Centre for Isotope Geochemistry in University College Dublin. These include samples of Cretaceous phosphatic chalk from southern England, phosphatic nodules from the Cretaceous of western Scotland, and several samples from a laterally extensive Carboniferous phosphorite in western Ireland. These Carboniferous samples are discussed here.

2 Simple Workflow

XRF & Optical characterisation

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BSE & EDX analysis

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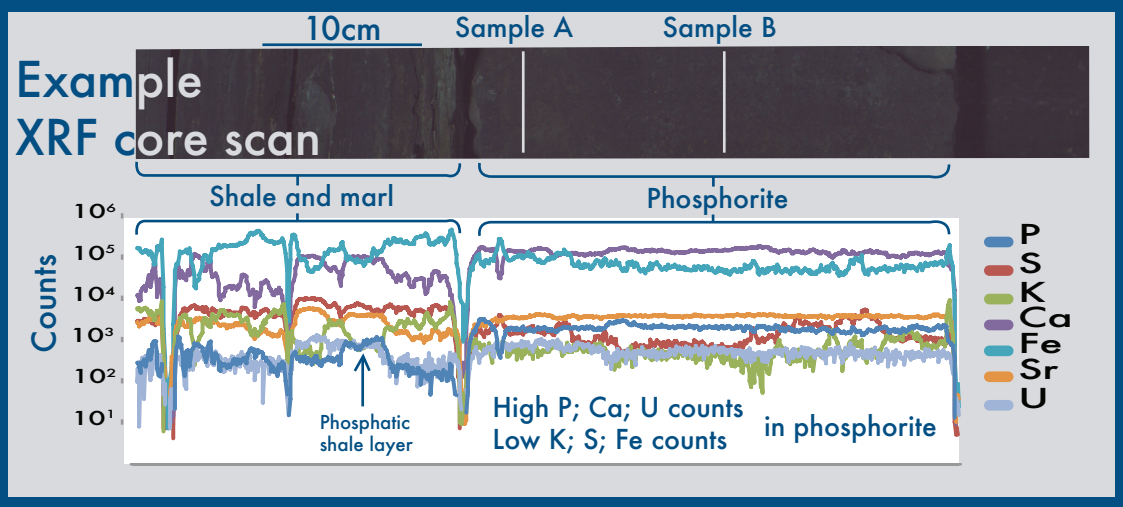
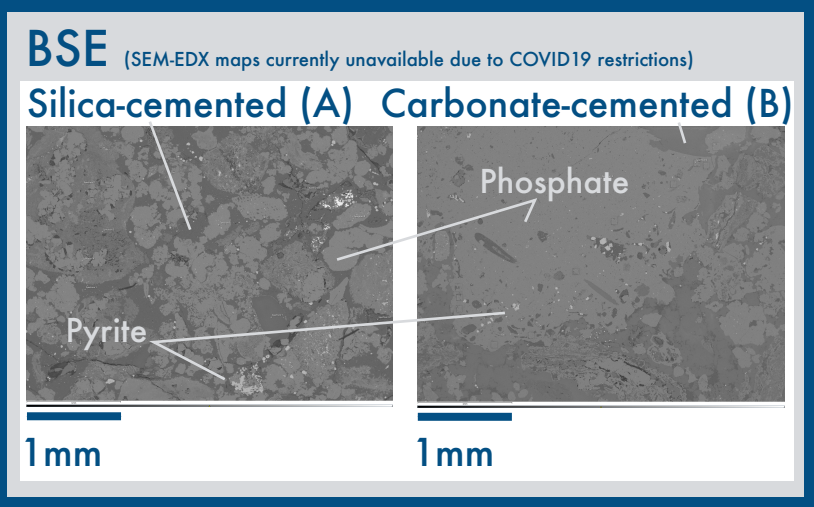
LA-Q-ICPMS anaalysis based upon BSE & SEM maps

3 Results: Clare Shales Phosphate member, Co. Clare, Ireland

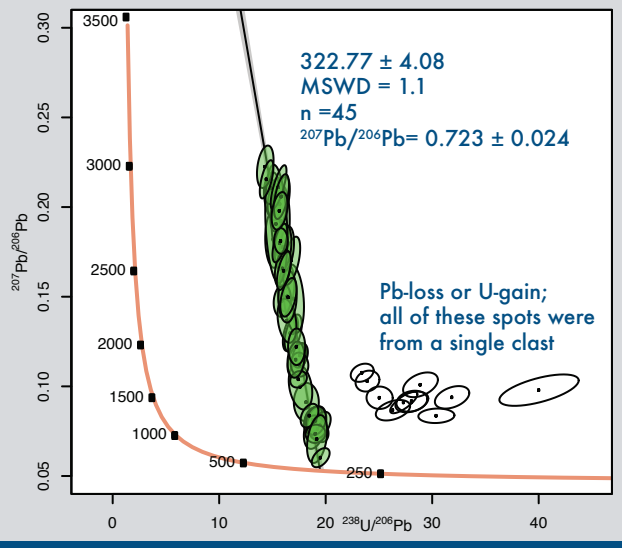
Stratigraphic age is between 330 - 323 Ma based upon conodont and goniatite biostratigraphy (Barham et al., 2015)





U-Pb geochronology

Silica-cemented (A)



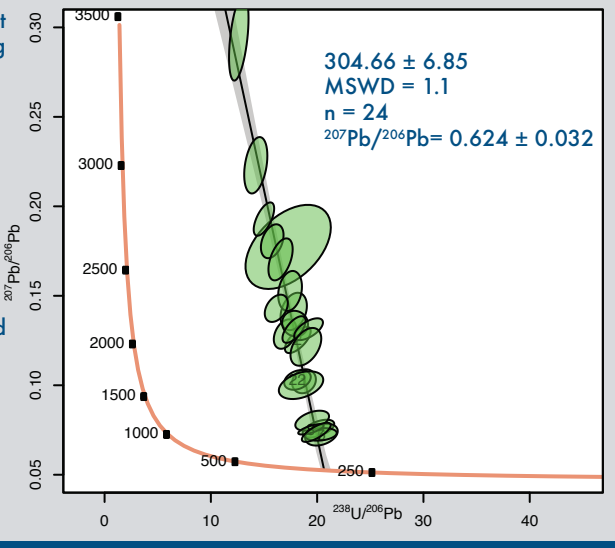
For both samples ages are $^{207}Pb/^{235}U$ / $^{206}Pb/^{238}U$ ages, but are plotted on Tera Wasserburg diagrams.

A sample of silica-cemented phosphate reproduces the biostratigraphic 'age' of the Clare Phosphate member (Barham et al. 2015)

MSWD is improved by analysing ^{235}U; U isotopes are heterogeneous and fractionated in sedimentary phosphate

U contents are extremely high, up to several hundred ppm. Another sample of Clare phosphorite phosphate yielded U-contents over 1,000 ppm

Carbonate-cemented (B)



The carbonate-cemented sample yields an age corresponding to Varsican orogenesis

Ireland is located far from the core of the Variscan orogeny, but jointing and faulting in the Burren limestones, immediately underlying the Clare Shales Phosphate member (c. 4 m below these samples) has been attributed to far-field tectonic effects of the Variscan (Walsh et al., 2019)

Carbonate precipitation appears to be linked to age-resetting of sedimentary apatite in this sample, taken approximately 15 cm away from sample A. Pyrite textures are cubic in sample B, but retain much more frambiodal textures in sample A (see BSE).

Sedimentary phosphate can thus retain stratigraphic age information, but is vulnerable to fluid-overprinting; potentially rendering it a viable low-temperature thermochronological or fluid ingress tracing tool.

4 Further information, further required work

For both samples, precision on acquired ages could be increased by analysis of co-genetic Pb-bearing phases (e.g. pyrite). For sample A, the current precision of the "stratigraphic" U-Pb age using a quadrupole instrument is 1.25%. For a hypothetical 60 Ma sample this would yield an error of ± 0.75 Ma - without **any** analytical improvements, use of multiple collector ICPMS etc.

U-Pb ages were acquired using fluorapatite U-Pb reference materials (Madagascar; Durango; and McClure Mountain apatite). Further characterisation of CFA may be required to assess whether there are differences in ablation behaviour between fluorapatite standards and carbonate-fluorapatite.

We are always looking for other interesting samples to calibrate this emerging method. If you are interested in analysing sedimentary phosphate with us please contact the corresponding author!
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