Dating carbonates with in situ U-Pb geochronology

Brief History

Traditional bulk dissolution method
- Pb-Pb in Anhilite and opal - Richards et al., 1987
- Pb-Pb in coralline algal - Valade et al., 1988
- Pb-Pb in opal - Teen et al., 1990
- Pb-Pb in planktonic - Smith et al., 1991

Pb-Pb in coralline algal - Smith et al., 1989

Slickenfibres concretion dated - et al., 1987

Sedimentary carbonates
- dating of cements in Mesozoic
- Paleosol (deposition) and cone

Nicholson & Drake 115

Breccia cement

Thin sections (ideally >100 μm thick)

- Chips in epoxy resin

- Polished blocks

2.5 cm

The LA-ICP-MS Method

Laser ablation for sampling of 5-150 μm diameter spots

Single age determined from >5 to 10s of spots per sample

Normalisation to a carbonate reference material

- WCL 254 ± 7 Ma (x)

- Sample data are limited by this ~2.5% uncertainty

Measurement can use Q, SC or MC - ICP-MS instrumentation

Sample requirements

- Thin sections (ideally >100μm thick)

- Polished blocks

- Chips in epoxy resin

Applications (1)

Since 2014, the LA-ICP-MS method has been applied to a range of different carbonate types and settings.

Most applications have been limited to calcite, but dolomite and other forms of carbonate have been successfully dated too.

As the method progresses, more reference materials comprising different matrices will be required.

- Sickenfibres
- Fracture-filling veins
- hydrothermal
- Breccia cement
- Dolomite
- Diagenetic cement
- Spalekothems
- Authigenic limestone

see LA-CARB.COM

Published dates range from the Quaternary to the Precambrian boundary, with variable precision:

Applications (2)

Neptunian Faults at Solvacks Bay, UK

Dates from the main breccia cement within the damage zone of the ‘Frontal Faults’ exposed at Flamborough Head, UK. From Roberts et al., in review, Sald Earth

Vagly calcite from deep mines in Sweden. Individual crystals grew over a protracted period from ~55 to 12 Ma. (Ellipses on the BSE images show location of spots and are coloured according to their age). From Drake et al., in prep.

Individual calcite crystals with SIMS C-O isotope measurements (yellow ellipses) and U-Pb spots (dashed ellipses). The method of SIMS C-O isotope analysis has shown remarkable variation within single crystals, here related to microbially induced anaerobic oxidation of methane (AOM), and methanogenesis (see Drake et al., 2017, 2019). Diagram shows model for AOM in deep granite-hosted fractures, whereby extreme depletion in δ18O of calcite occurs during oxidation of biogenic methane (Drake et al., 2015). From Ivanesson et al., in prep.

Ding carbonate within basement fractures of the Rona Ridge. The calcite mineralisation opened up the fractures, which were capped by sediments, allowing hydrocarbon migration possibly enhanced by seismic activity (graded bedding shows sediment influx within deep fractures (1-2 km). From Holdsworth et al., 2018.

Dting of hydrocarbon charge in the Nambu Basin, Angola, via bituminoous calcite and dolomite. The Santonian age of the calcite overlaps that of nearby volcanism, indicating a link between magmatism, hydrocarbon migration and possible maturation. From Rochelle-Bates et al., in prep.

Limitations (1)

Low Uranium

Uranium is typically very low in most carbonates (< 1 ppm), but can be high (1-2 ppm) in a variety of settings. The LA-ICP-MS method can be successful at 10 s of ppb.

High initial Pb

Incorporation of Pb during crystallisation/formation of carbonates is the biggest hurdle, initial Pb is typically much higher than the Pb derived from decay of U.

Predicting high U/Pb in carbonates is not easy, and as such, a study will often involve screening of many samples to find those most suitable.

Limitations (2)

Initial disequilibrium

A limitation for accurate dating of young (i.e. <10 Ma) carbonates, is initial disequilibrium in the U-Pb decay chain, such as excess 234U.

We are still learning and accumulating data on the scale of this problem for different settings.

Regarding geochronology, speleothem research is the only field where this has been discussed in any detail.

234U is typically in excess in groundwater (rather than in secular equilibrium), a correction is used to calculate accurate 238U/234U ages.

If the excess 234U is not known or measurable (as is the case for samples beyond the range of 1/2U), then it has to be estimated, limiting the confidence of U-Pb ages.

References

Sedimentary carbonates

From the very young, to the very old...

Spalekothem from cave in Yemen. Base is dated at 1.04 Ma from Nicholson et al., 2020, GSR.

Spherulite deposition and cone-in-cone (fluid overpressure) phases of calcareous concretion dated from upper Ediacaran sediments of Finmark, From Meinhold et al., in review, Geological Magazine.

Micritic limestone, Hubei, China. North China Craton. From Lin et al., in review.