Chemical Geology 376 (2014) 76–83

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

U–Pb dating of cements in Mesozoic ammonites

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ARTICLE INFO

Article history:
Received 25 September 2013
Received in revised form 26 March 2014
Accepted 31 March 2014
Available online 12 April 2014

Editor: K. Mezger

Keywords:
Mesozoic
Carbonate
Ammonite
Diagenetic
Cement
U-Pb dating

ABSTRACT

Dating sedimentary carbonates using the U-Pb method can help improve the Phanerozoic timescale. Using a novel combination of laser-ablation, multi-collector, inductively-coupled-plasma, mass-spectrometry (LA–MC–ICP–MS) and thermal ionization multi-collector mass spectrometry (TIMS), U-Pb numerical ages were obtained on early-diagenetic calcite cements in Jurassic ammonites in which concentrations of U range from 0.47 to 5.3 ppm.

The calcite cements of two ammonites, IS1 and IS2, from the uppermost *Bifrons* Zone of the Toarcian (179–180 Ma) of the UK, gave TIMS-normalized LA U–Pb dates of 164.9 ± 5.3 Ma and 166.7 ± 4.8 Ma respectively. Normalizing LA–ICP–MC–MS data to an in-house calcite standard gave a more precise date of 165.5 ± 3.3 Ma for IS1 cement. An unzoned ammonite, SS2, of Bajocian age (168–170 Ma) yield a TIMS-normalized LA U–Pb age of 158.8 ± 4.3 Ma for its early-diagenetic cement. Both the combined LA–MC–ICP–MS and TIMS approach, and the use of a calcite laser ablation standard can result in accurate ages of cements with uncertainties of 2–3% (2σ). The later, however, is more efficient and precise. These U-Pb dates of cements are 10 to 20 Myr younger than the numerical ages of the biostratigraphic intervals from which the ammonites derive. The U-Pb dates are taken to represent the time at which the aragonite shell of the ammonite inverted to calcite and released its U to precipitate in a late-diagenetic alteration of early-diagenetic fringing cements.

Concentrations of U and Pb in a range of other pristine biogenic carbonates were found too low (U < 0.01 ppm) for meaningful dating using laser ablation method.

1. Introduction

The feasibility of the Pb-Pb (and so U-Pb) method for dating carbonates was established with apparently meaningful Pb–Pb isochrons for the Archean Mushandike stromatolitic limestone (Moorbath et al., 1987) and the Archean Schmidtsdrif Formation (Jahn et al., 1990) in southern Africa, and with U-Pb dating of coral secondary calcite in Devonian limestones of the Lucas Formation, Ontario (Smith and Farquhar, 1989). Since then U-Pb dating has been applied, with varying robustness, to a range of geological problems through dating of late-diagenetic calcite cements (Smith et al., 1991), early-diagenetic marine carbonate concretions (Israelson et al., 1996), pedogenic calcite (Rasbury et al., 1997), speleothems (Richards et al., 1998), dolomitic hard grounds (Winter and Johnson, 1995), recrystallized biogenic carbonate grainstones (DeWolf and Halliday, 1991), secondary calcite that had inverted from aragonite (Jones et al., 1995; Rasbury et al., 2004), and Pleistocene and Miocene coral aragonite (Getty et al., 2001; Denniston et al., 2008). Reviews by Jahn and Cuvellier (1994) and by Rasbury and Cole (2009) discuss these, and other, examples of such application.

As noted before (e.g. Jones et al., 1995; Israelson et al., 1996), the ability to date sedimentary carbonate rocks using the U–Pb dating method would greatly enhance our ability to calibrate the Phanerozoic timescale. For example, the geological timescale (Gradstein et al., 2012) for the Early and Middle Jurassic Period is calibrated with 19 numerical dates, only one of which derives from Europe where, for this time, the most refined biostratigraphy exists. Direct numerical dating of European sediments would thus improve the tie between numerical and biostratigraphic ages.

Here is reported an attempt to improve the numerical calibration of the geological timescale for Toarcian and Bajocian time by using U-Pb methods to date early diagenetic cements in ammonites of known age. Such ammonites commonly occur well-preserved inside carbonate concretions from Cretaceous and Jurassic mudstones of the UK (Taylor, 1995; Simms et al., 2004). Because they are uncompressed, the ammonites must have been encased in concretionary calcite during very early burial in sediment — probably at depths of no more than a few meters (Marshall, 1981; Raiswell, 1987, 1988; Curtis et al., 2000). The ammonite chambers contain several generations of calcite cements (Marshall, 1981; Curtis et al., 2000) formed under sub-oxic to anoxic

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http://dx.doi.org/10.1016/j.chemgeo.2014.03.020
0009-2541/

conditions, including an earliest fringing cement that precipitated directly onto the internal walls and septa of the ammonite chambers either before, or immediately on, burial; and a late sparry calcite cement (Fig. 1). It is this early fringing cement that we attempted to date. The original aragonite shell of the ammonites could not be used to date the time of original calcification as it had inverted to calcite after burial.

2. Samples

Measurements of U and Pb concentrations in a range of Mesozoic belemnites, inoceramids, bivalves, ammonites, and diagenetic calcite, showed that only the calcite cements from three ammonite specimens dated here had U–Pb values amenable to dating. For reference, the range of U and Pb concentrations are given in Table 1, while more details of samples are in Appendix 1.

Of the three ammonite specimens suitable for dating, two, IS1 and IS2, were *Hildoceras semipolitum* Buckman (Fig. 1) collected as field finds next to the Hurcott Lane Cutting, near Ilminster, Dorset UK. They derived from the mid-Toarcian Beacon Limestone Formation (p94 of Simms et al., 2004; Boomer et al., 2009) and correlate to the *semipolitum* Horizon of the Submediterranean biostratigraphic scheme of Page (2003). This Horizon correlates to the uppermost subdivision of the *Bifrons* Zone (or Chronozone) of the UK Toarcian (Boomer et al., 2009) and is dated at 178 to 179 Ma (Gradstein et al., 2012). A third ammonite SS2, used for method development because of its excellent quality, was obtained from the collection of the British Geological Survey. The given age was Bajocian (168–170 Ma; Gradstein et al., 2012), but no further details of age or provenance are available.

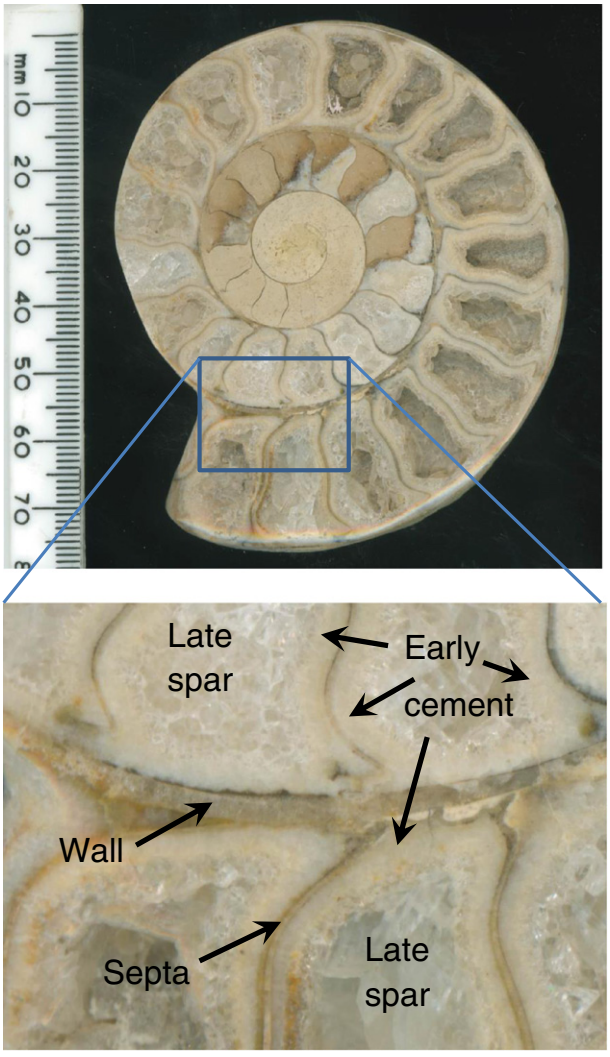

Fig. 1. Specimen IS1 and detail of septa, wall, late spar, and early diagenetic fringing cement that was overprinted during late diagenesis. For explanation, see text. Scale ruler shows unit in millimeters.

Table 1
Summary of U and Pb concentration ranges in various Mesozoic carbonate samples obtained by LA–MC–ICP–MS. Standard zircon 91500 and NIST 614 glass were used as monitors for approximate quantification.

Carbonate sample category	^{238}U ppm	^{206}Pb ppm
Biogenic aragonite	1–8	0.5–19
Belemnite alveolar cement	0.1–0.6	0.3–5.5
Marine concretion cement	0.1	2–10
Biogenic calcite (non-belemnite)	0.02–2.8	0.4
Pristine belemnite calcite	<0.01	<0.04
Altered belemnite calcite	~0.2	~0.02
Ammonite early cement (clean)	0.1–11	0.03–18

Note: there was no attempt to quantify the uncertainty of these rapid screening analyses. These estimates of concentration are indicative only as no calcite standard was available at the time. The detection limit of ^{238}U and ^{206}Pb, was c. 1 ppb.

The fringing cements that have been analyzed by LA–MC–ICP–MS and TIMS are shown in photomicrographs of thin sections in Fig. 2, both in plane-polarized light and with crossed polars. Details of the laser ablation pits and their relation to the cement samples analyzed are shown in Fig. 3.

3. U–Pb methodology

3.1. TIMS analyses

Microsamples of early fringing cements from ammonites (Fig. 1) were obtained using a New Wave Research micromill. The ultrasonically-cleaned sample pieces were completely dissolved in ultrapure 4 N HNO_3 before being spiked with a mixed ^{205}Pb–^{233}U–^{235}U tracer. Following sample-to-spike equilibration, organic matter in samples was destroyed by addition and evaporation of 0.5 ml of concentrated HNO_3 and 0.5 ml H_2O_2. The precipitate was then re-dissolved in 1 ml 1 N HBr for anion exchange chemistry. Eichrom® anion exchange resin (equivalent to BioRad AG 1 - ×8) was used to separate and purify Pb. Uranium was purified using Eichrom UTEVA resin in nitric acid. The purified U and Pb were taken up in 1.2 ml 2% HNO_3 for TIMS analysis. The chemistry blanks were <10 pg for U and <20 pg for Pb.

The U and Pb separates were loaded separately with silica gel and H_3PO_4 onto single outgassed rhenium filaments and analyzed using a Thermo Scientific Triton mass spectrometer fitted with an axial MasCom secondary electron multiplier (SEM) at the NERC Isotope Geosciences Laboratory (NIGL) British Geological Survey, Keyworth, UK. Data were obtained in dynamic single-collector mode on the SEM with Pb and U typically run to exhaustion. Pb and U standards SRM 981 and U500 were analyzed to monitor mass spectrometer performance, ensuring that the SEM linearity, accuracy and reproducibility were better than ±0.1%.

Data reduction, error propagation and plotting were carried out using customized EARTHTIME data reduction spreadsheet following standard parametric statistical methods (Schmitz and Schoene, 2007) and Isoplot version 3.00 (Ludwig, 2003). The decay constants and U isotope composition used were those proposed by Jaffey et al. (1971), as recommended by Steiger and Jager (1977).

3.2. Laser ablation measurements

Laser ablation (LA) analyses were performed using a Nu Plasma HR MC–ICP–MS coupled to a New Wave Research UP193FX (193 nm) excimer laser ablation system. Detection used both Faraday cups and