Direct *in situ* Dating of Carbonates by LA-ICP-(MC)-MS and its Applications to Chronostratigraphy*

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Search and Discovery Article #41269 (2014)**
Posted February 11, 2014

*Adapted from oral presentation given at AAPG 2013 Annual Convention and Exhibition, Pittsburgh, Pennsylvania, May 19-22, 2013

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Abstract

A viable method to provide absolute age constraints in carbonate strata has proven elusive. Direct dating of primary carbonate deposits, and/or early marine cements would constrain rates of carbonate platform growth, allowing refinement of models of sea level and climate change that might have influenced the carbonate depositional environment. Absolute age constraints on later diagenetic elements such as meteoric and burial cements and tectonic veins is very important to a wide range of problems in both the hydrocarbon industry (such as burial history and timing of fluid migration) and earth science more generally. U-Pb dating of carbonate has been shown to be viable but so far has been restricted in application due to use of time consuming ID-TIMS methods that involve dissolution and processing of a sample of carbonate. A major hurdle is that there is currently no a priori way to know if a sample has a viable U/Pb ratio, and many carbonates are not datable.

We have successfully adapted LA-ICP-(MC)-MS methods (used routinely in zircon U-Pb dating) by using a well characterized 254+/-6 Ma calcite standard (dated by ID-TIMS at NIGL and Stony Brook) to correct the U/Pb ratio for matrix effects. This approach allows in situ U-Pb dating with uncertainties as little as ±4% at 95% confidence with minimal sample consumption. We have applied this method to the dating of samples with average uranium concentrations (0.4-5 ppm) such as speleothems, paleosols, lacustrine carbonates, tufa, early marine cements (in ammonite chambers), calcite veins from fractures in MORB and marine fossils. The age of dated materials so far ranges from Permian to late Quaternary, as young as 250ky. Laser ablation allows us to quickly assess the U/Pb ratios of the variety of carbonate phases in a sample to determine if the sample has potential for dating. Carbonate components with favorable U/Pb are subjected to in situ dating using textural petrography and SEM/fluorescence imaging to guide the analysis of coherent zones of growth. Examples of these applications will be presented.

The wealth of applications to explore in the future include structural geology and the dating of structural veins, post-depositional cementation, and direct dating of biogenic aragonite (biogenic calcite usually being too low in uranium to be suitable). The future scope of applicability of this method to earth science, sedimentary geology, and hydrocarbon exploration is very exciting.

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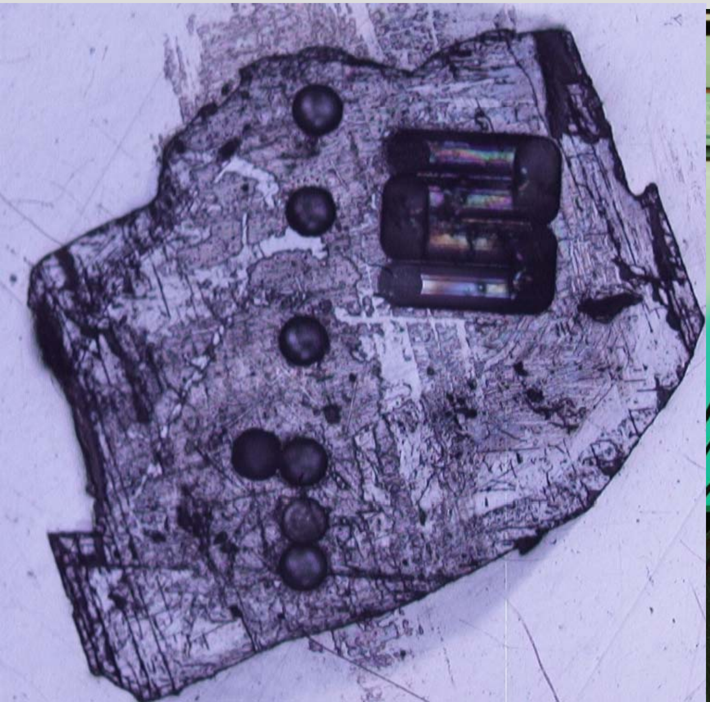
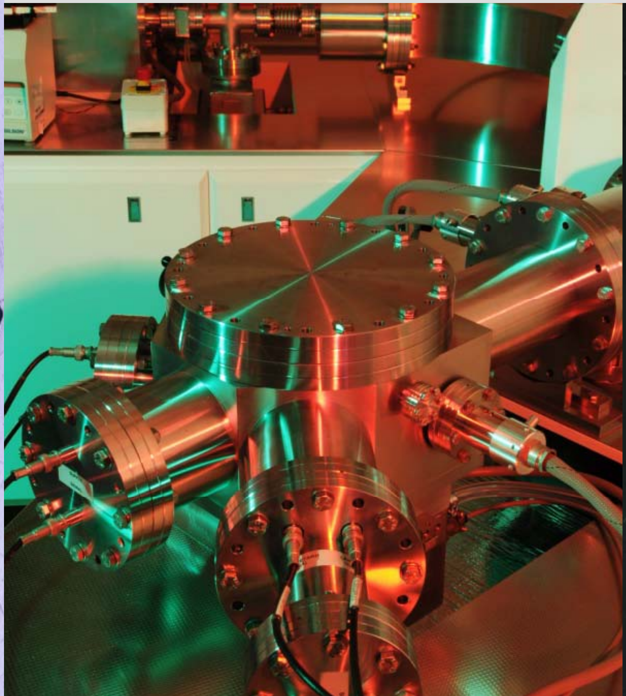
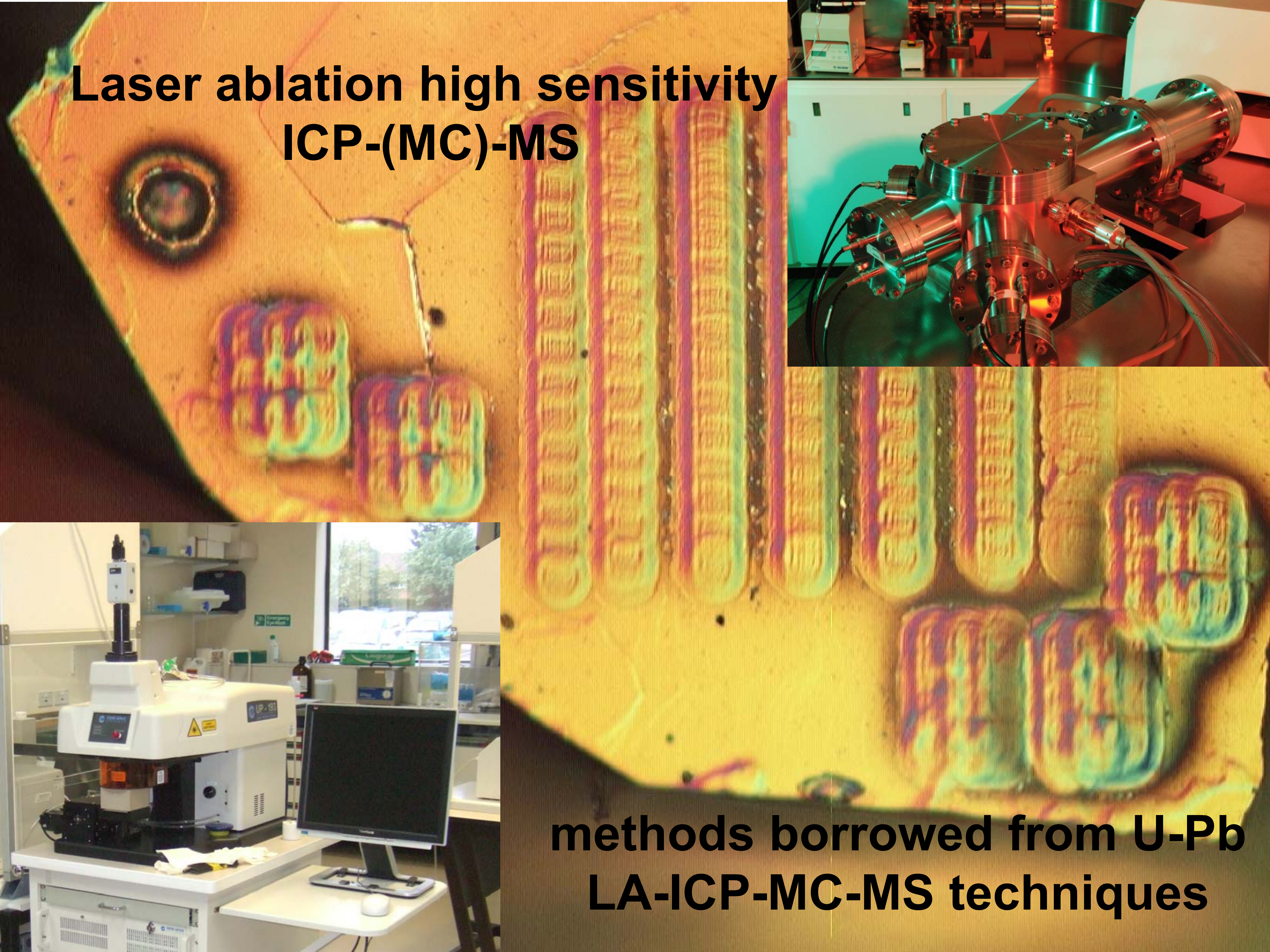




Wouldn't we like to …

- Date calcite cement in carbonate rocks
- Determine when diagenesis took place,
- Directly date fossils and other carbonate deposits, speleothems, paleosols, etc.
- Date calcite in structural settings – tension veins, stretched belemnites, calcite in fault rocks, slickenfibers, etc.

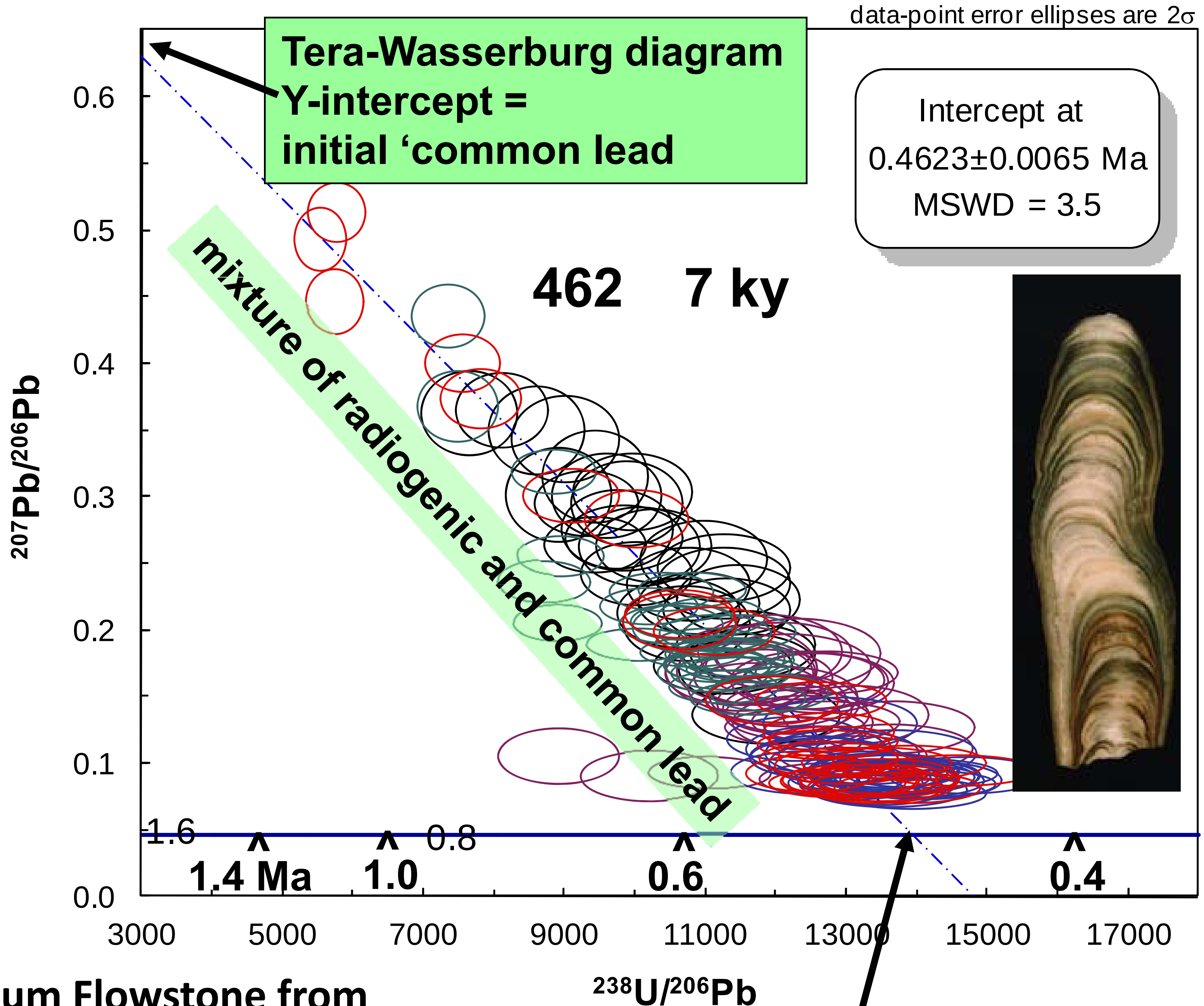
These applications have been nearly intractable, but there is real progress…..


Laser ablation high sensitivity
ICP-(MC)-MS
methods borrowed from U-Pb
LA-ICP-MC-MS techniques

A vital ingredient to an efficient method is … standardisation during analysis – using reference materials that are appropriate

U-Pb calcite standard: about 4ppm U, 251 Ma old

This material is fantastic: almost no initial lead (<1ppb), ~100ppm uranium, and not altered, meaning little if any recrystallisation/ replacement during subsequent precipitation of younger calcite; the age via U-Pb agrees with the U-series (U-Th) date



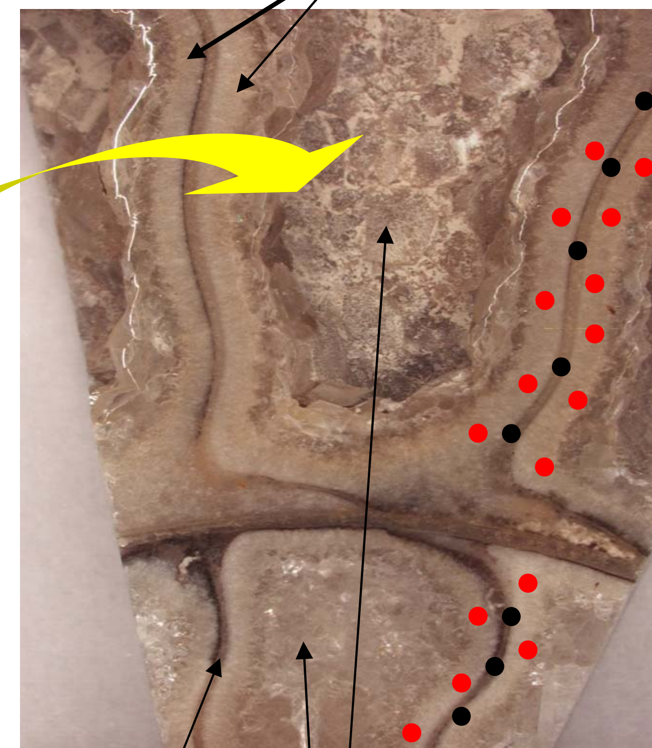
'Concordia' intercept = pure radiogenic lead, ratio a function of age

Data from high uranium Flowstone from Nahanni Park, Yukon Territory
Data courtesy of Chris Smith, University of Bristol 2012

Early diagenetic calcite cements (photos: Q Li, 2011)

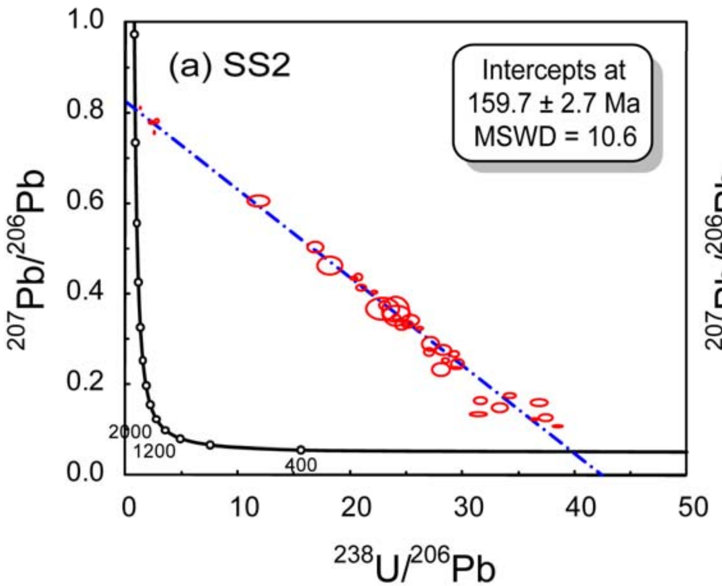
Large amount of calcite cements, less open deposit environment

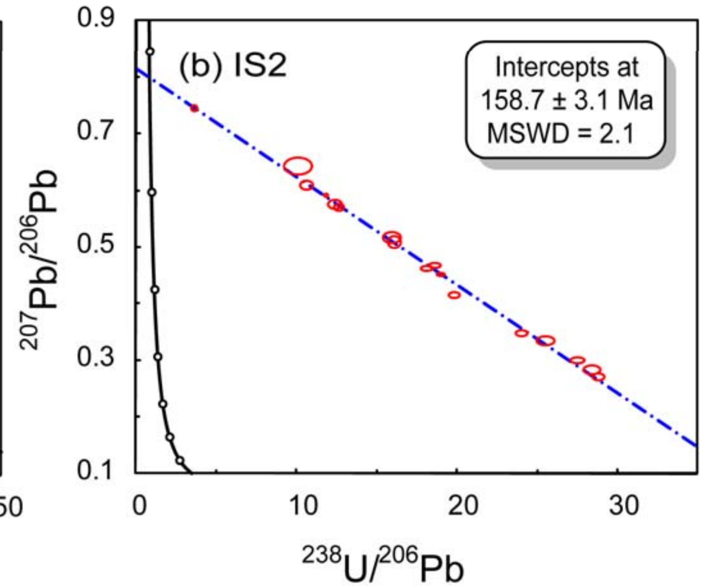
Hildoceras spp 1.
Somerset, Bifrons Zone

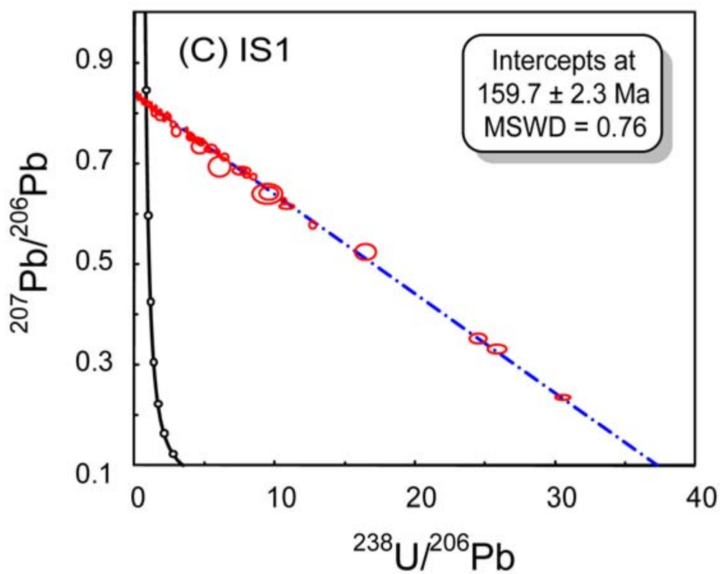


Regions <100µm can be targeted and dated to ± 2-3% in calcite

LA-ICP-MC-MS U-Pb data on early diagenetic cements

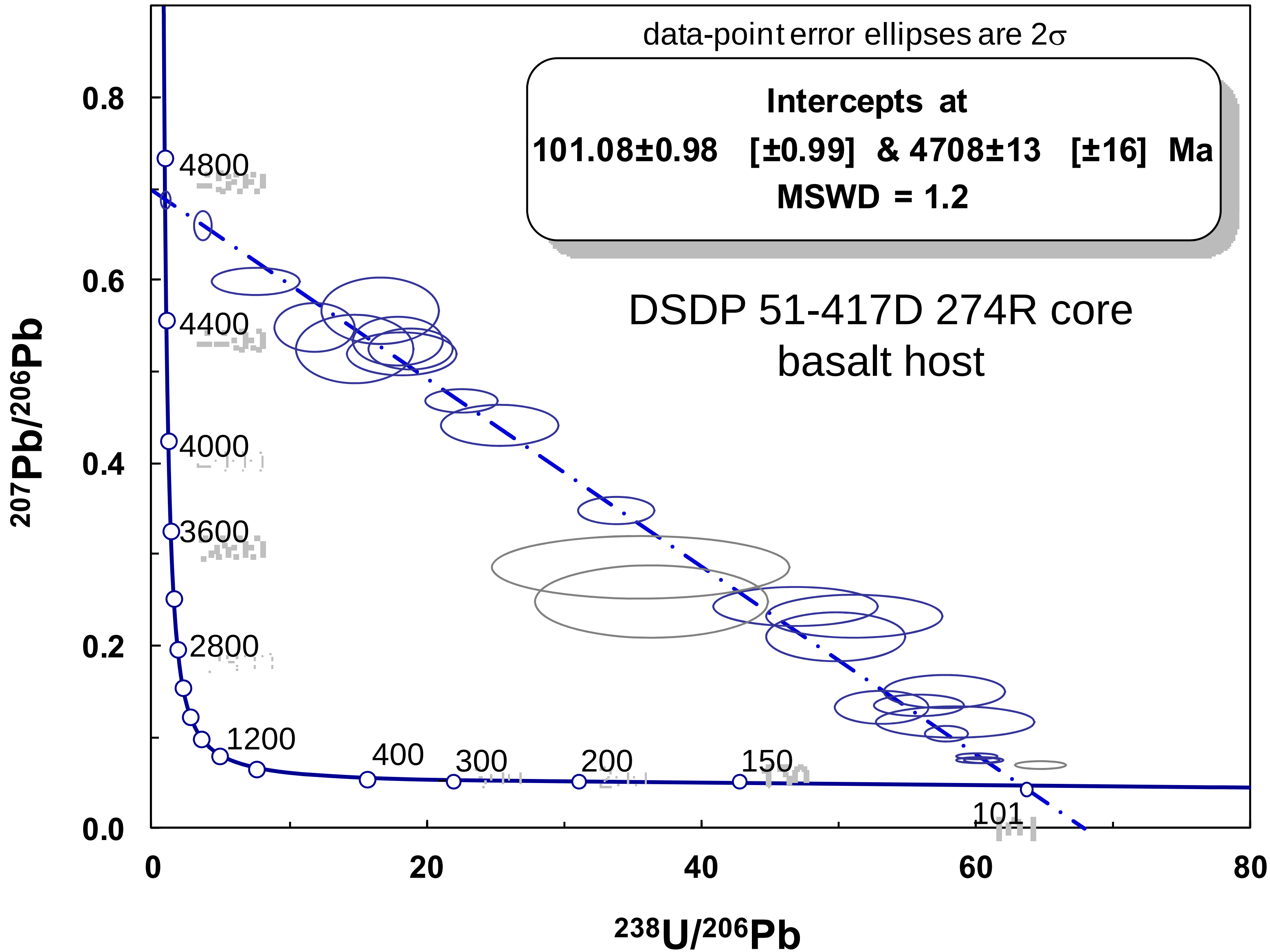






Ages of earliest cements are 10-15 Ma younger than chronostratigraphic ages

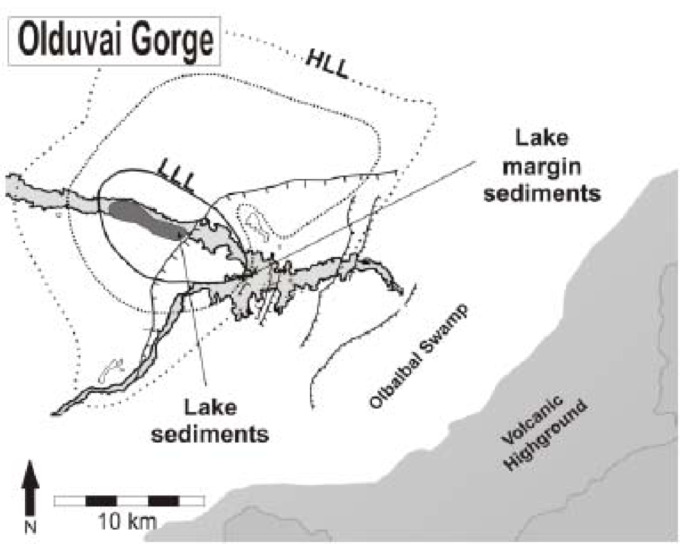
Data courtesy of Qiong Li, 2011

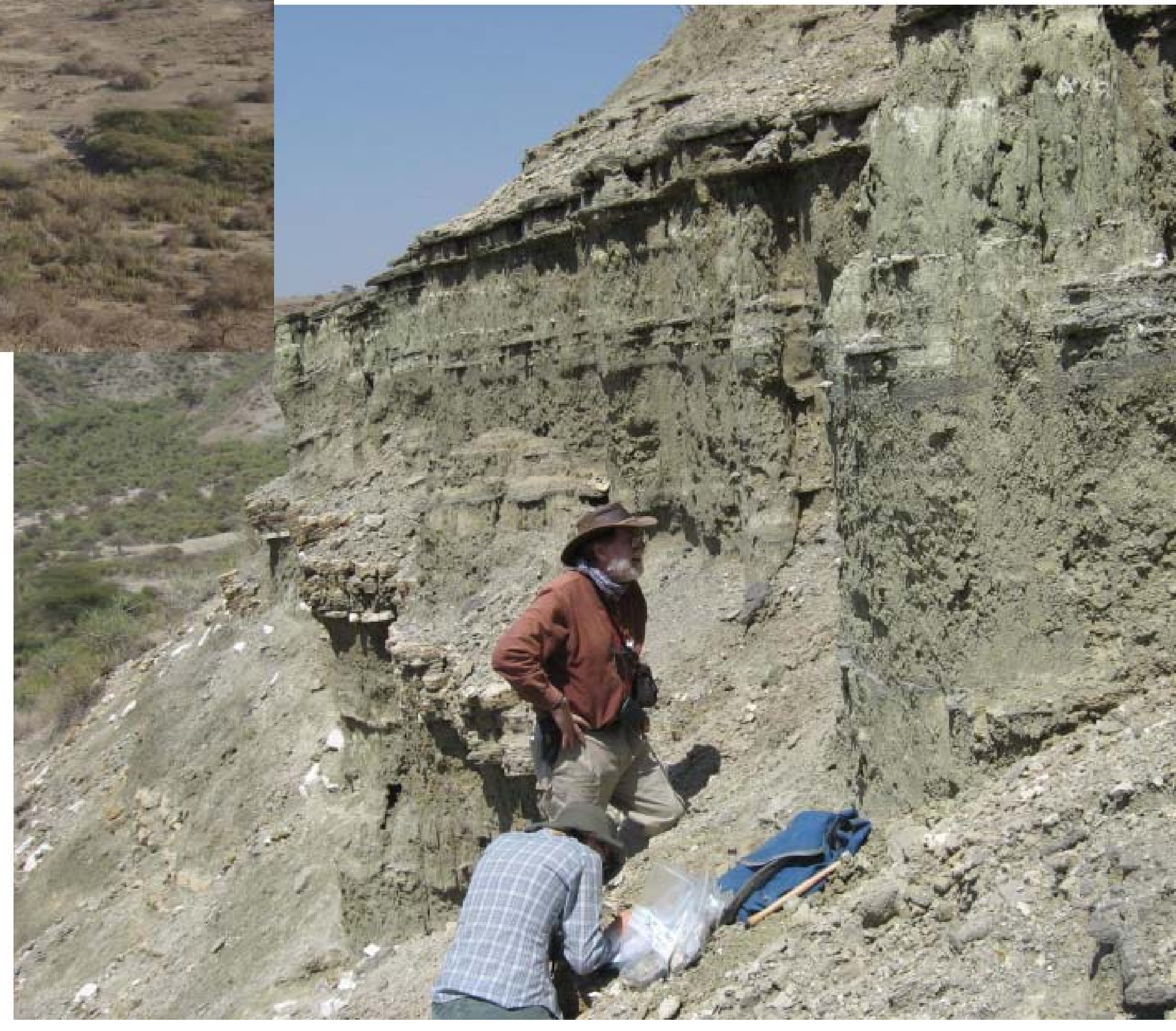


Fragments of calcite in vein hosted MORB, oceanic crust known to be ~115 Ma old; this data demonstrates hydrothermal deposition of calcite off the ridge axis for millions of years following generation of oceanic crust

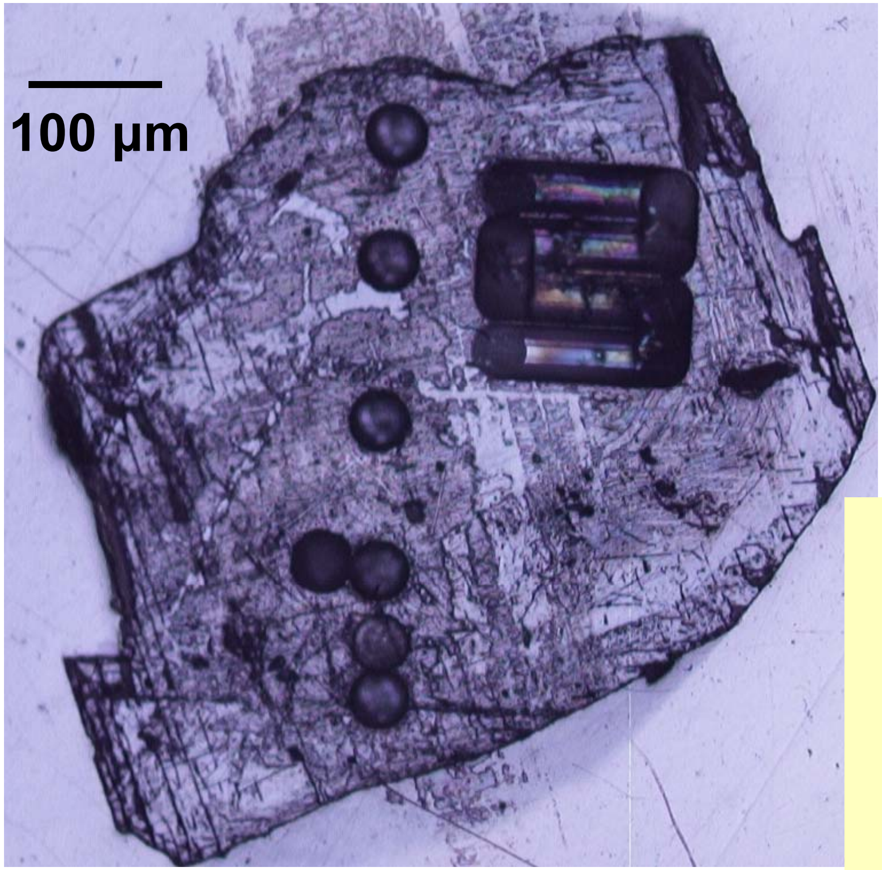
Data: L Coogan U of Victoria 2012

Pilot study
Palaeolake Olduvai
calcite crystals





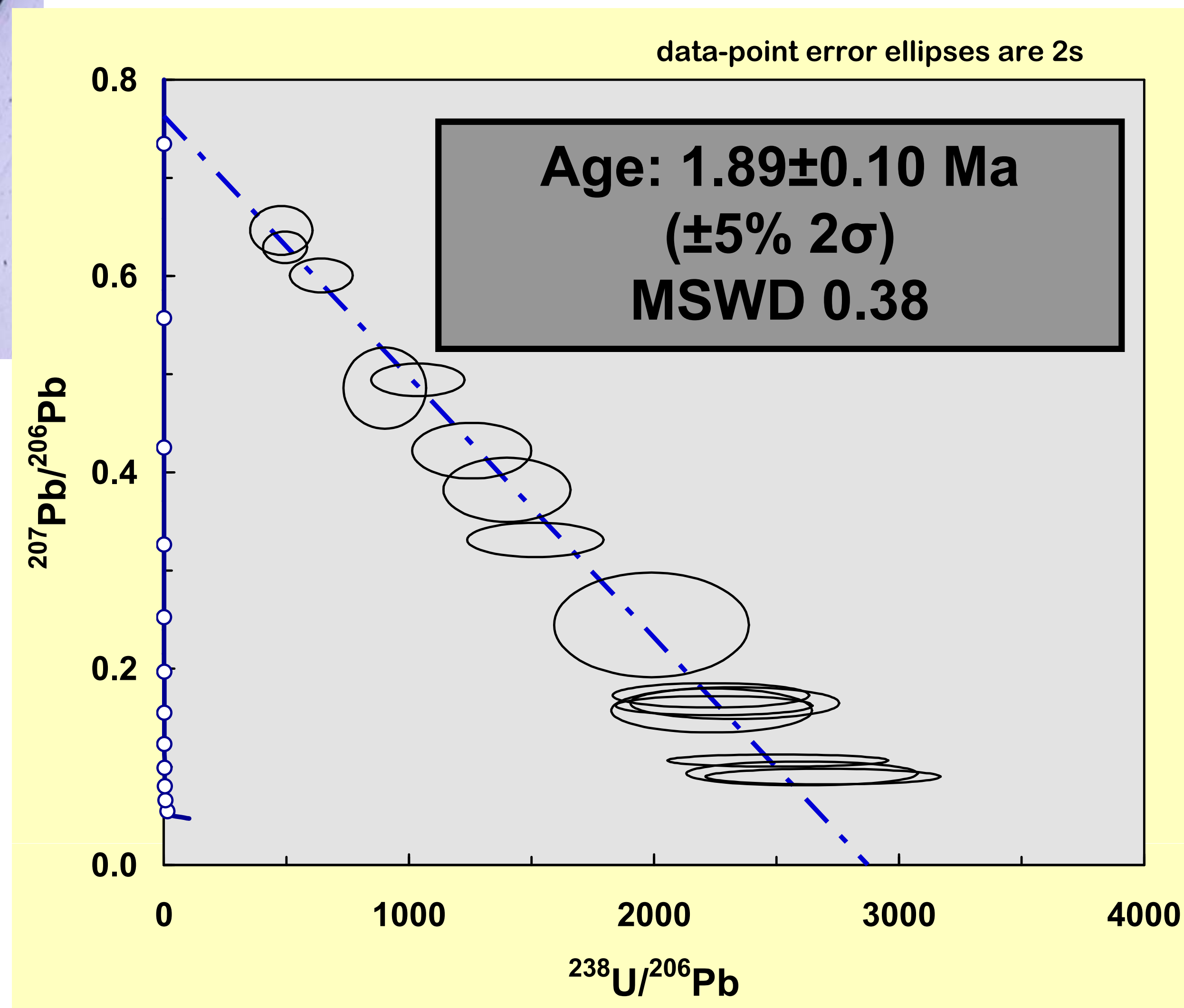
Lake carbonates



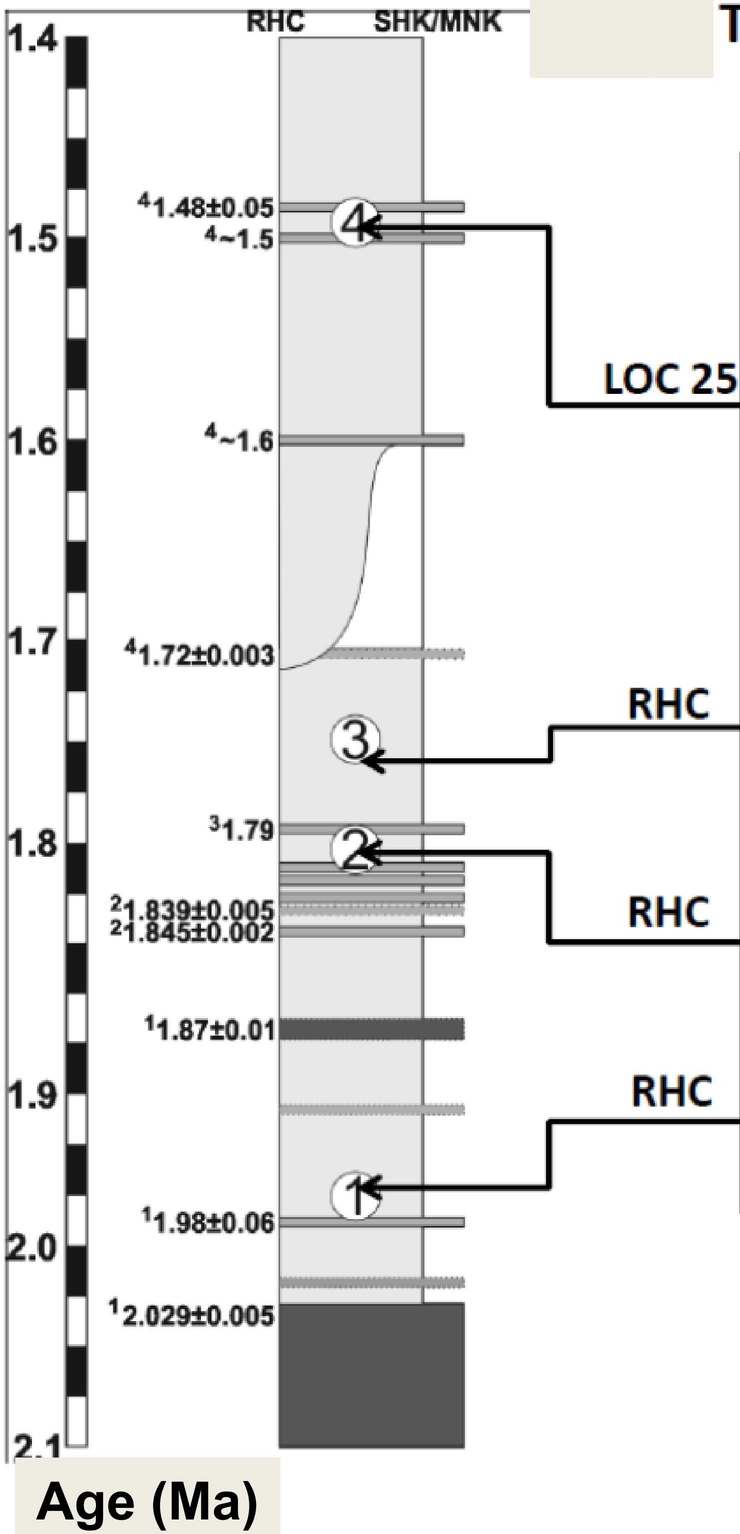
Detrital nodular calcite in lacustrine-derived sediments, Olduvai Gorge, E Africa

(E Rushworth 2010 data)

In favourable samples, calcite is datable by U-Pb LA-ICP-MS; here, linear arrays of data allow a precise date with very small uncertainties



Test the potential resolution by dating crystals in older and younger parts of the sequence

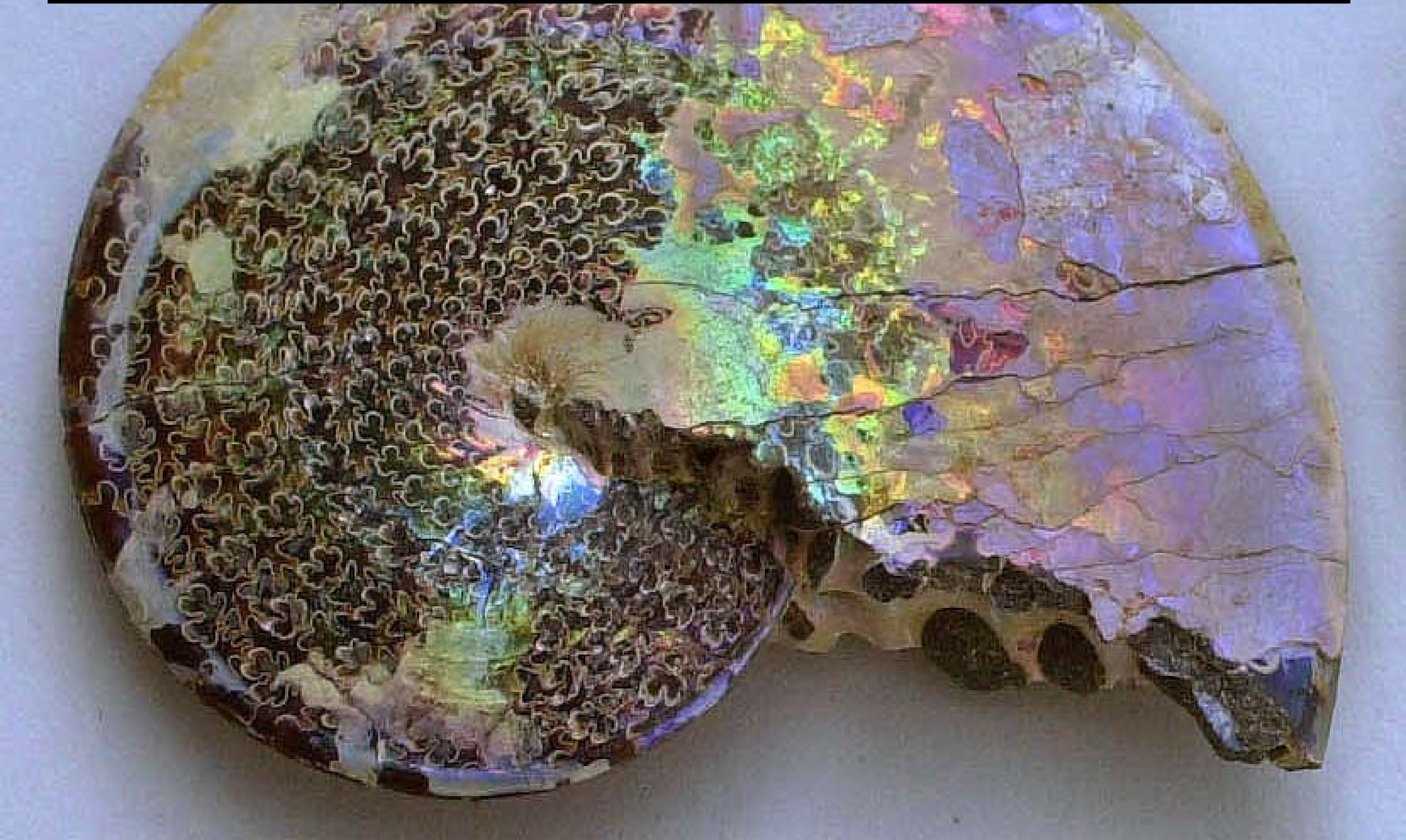


$^{40}Ar/^{39}Ar$ ages*	Calcite crystal ages
~1.5 – 1.48 ± 0.05	1.623±0.033
1.79* – 1.72 ± 0.003	1.89 ± 0.10 1.873 ± 0.086 1.85 ± 0.11 1.89 ± 0.12
1.839 ± 0.005 – 1.79	1.917±0.037 1.900±0.059
1.98 ± 0.06 – 1.87 ± 0.01	2.022±0.033

Mean deviation of 0.103Ma with a 2-6% uncertainty

'excess' age attributable to high initial Uranium activity;
This excess activity is common in terrestrial waters

Primary aragonite and some calcite suitable for $^{87}Sr/^{86}Sr$ may be datable for U-Pb, depending upon degree of alteration, common Pb content, and initial uranium content.



How widely applicable is this method?

- **Calcite cement in ammonite/fossil chambers**
- **Calcite in veins in basalt, ophiolites**
- **Carbonate lake sediments, and oolite-like concretionary grains**
- **Speleothems and flowstones 0.26->4 Ma**
- **Fracture-filled veins**
- **Tufas and paleosols, crusts on boulders**
- **The above have been demonstrated**

However, it is early days of exploiting this method and its application to sedimentary geology and chronostratigraphic applications

Structural Geology applications

Other Applications ….

- Structural veins in foldbelts and thrusting
- Stretched belemnites and other extensional structural features
- Chronology and timescales of porosity occlusion in carbonate reservoir rocks
- Better chronology in strata with non-diagnostic biostratigraphy
- Molar tooth structure in Precambrian
- Applications to strata of unknown age, in Precambrian (potentially)

Thank you for your interest in this work

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