

Rhino Ruby, Mozambique (22.04 ct),  
ca. 500 million years old

Burma Ruby,  
ca. 30-25 million years old

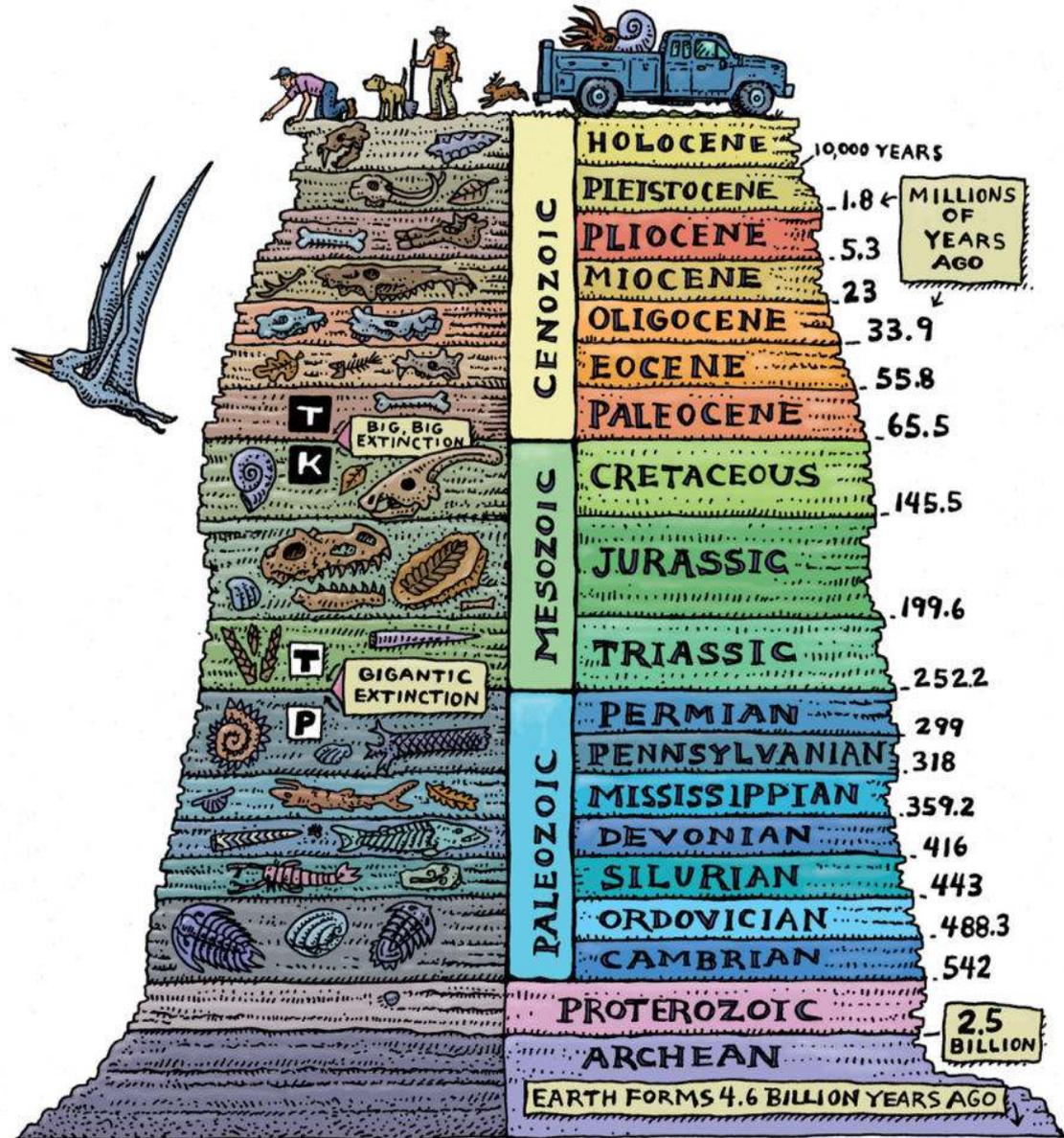
36th IGC Conference | August 2019

# | AGE DATING APPLIED AS A TESTING PROCEDURE TO GEMSTONES AND BIOGENIC MATERIALS

Michael S. Krzemnicki, Hao A.O. Wang, Myint M. Phy

# BASICS

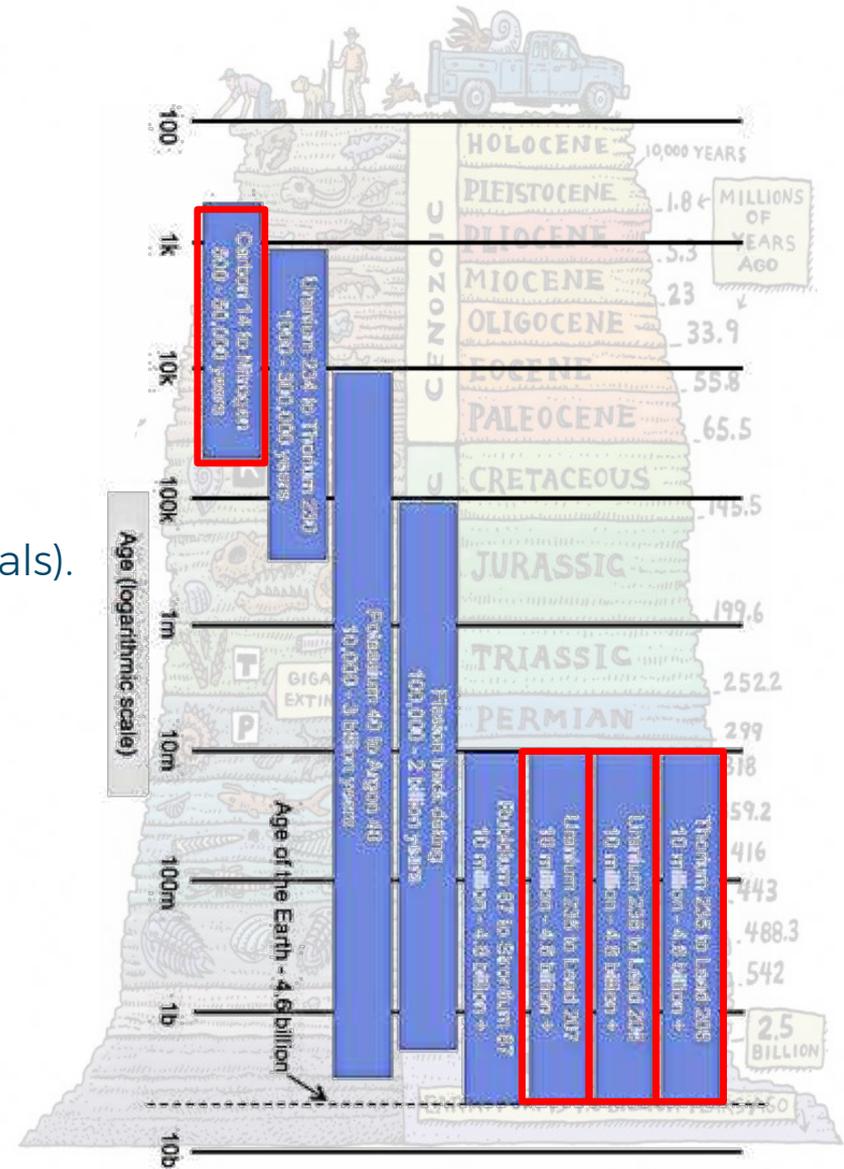
Radiometric age dating is used to date materials such as for example rocks, minerals, or historic artefacts by comparing the abundance of naturally occurring radioactive isotopes and their decay products.



# BASICS

Some of the most commonly used radiometric methods are:

- U-Pb and Th-Pb for geologic samples (e.g. zircon)
- $^{14}\text{C}$  radiocarbon for very young samples (e.g. historic artefacts or biogenic materials).





# PEARLS IN HISTORY

*Pliny, Historia Naturalis*

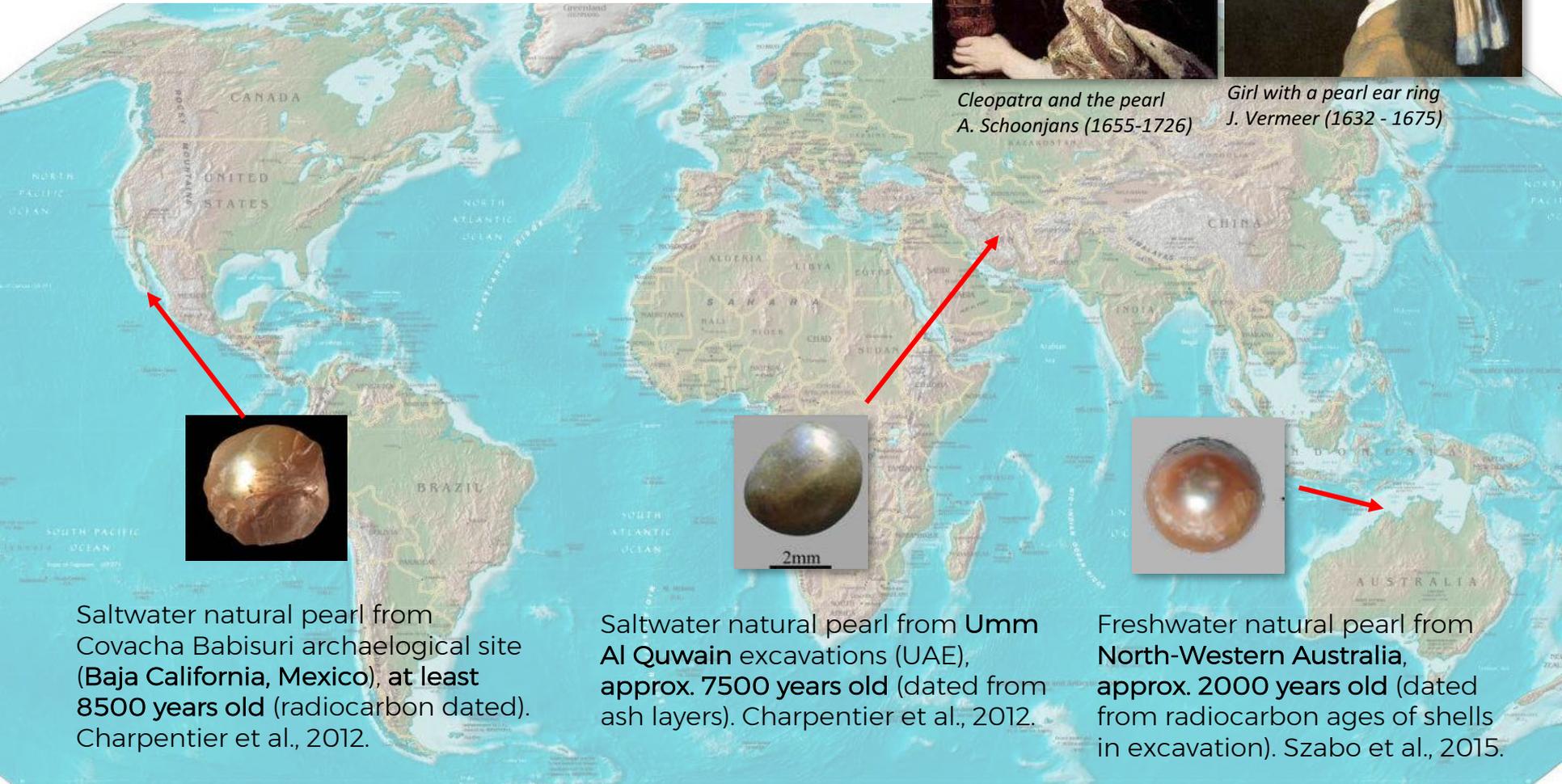
“[Pearls] occupied the first rank...and the very highest position among valuables.”



*Cleopatra and the pearl*  
A. Schoonjans (1655-1726)



*Girl with a pearl ear ring*  
J. Vermeer (1632 - 1675)

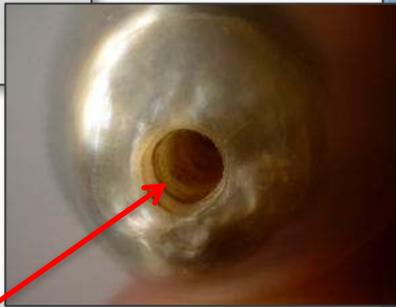


Saltwater natural pearl from Covacha Babisuri archaeological site (Baja California, Mexico), at least 8500 years old (radiocarbon dated). Charpentier et al., 2012.

Saltwater natural pearl from Umm Al Quwain excavations (UAE), approx. 7500 years old (dated from ash layers). Charpentier et al., 2012.

Freshwater natural pearl from North-Western Australia, approx. 2000 years old (dated from radiocarbon ages of shells in excavation). Szabo et al., 2015.

# QUASI NON-DESTRUCTIVE SAMPLING (0.004 g)



A minute amount (less than 0.004 g) of calcium carbonate is taken from inside the drill-hole.

„quasi“ non-destructive testing even for objects of archaeological and cultural heritage.

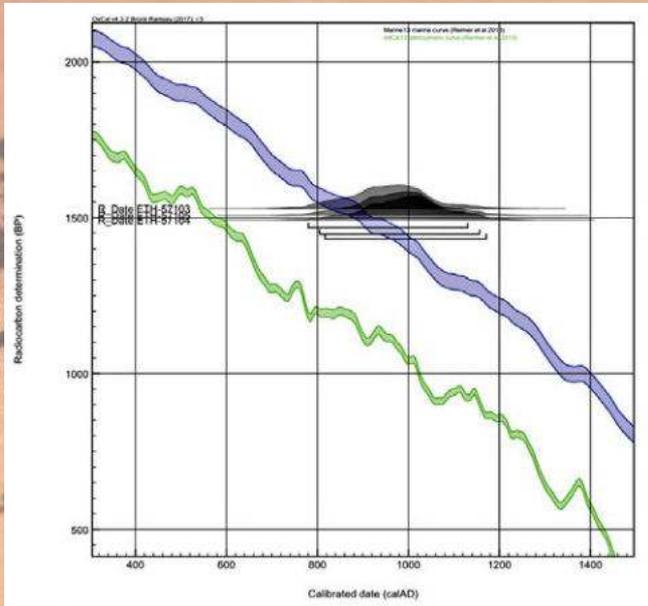


0.02 ct powder of calcium carbonate for age dating.



# PEARLS FROM CIREBON SHIPWRECK

1000 year old pearls from the Cirebon ship-wreck, discovered in 2003 in the Java Sea (Indonesia).



Feature Article

## Radiocarbon Age Dating of 1,000-Year-Old Pearls from the Cirebon Shipwreck (Java, Indonesia)

Michael S. Krzemiński, Laurent E. Cartier and Irka Hajdas

The 10th-century Cirebon shipwreck was discovered in 2003 in Indonesian waters. The excavation yielded an incredible array of archaeological finds, which included pearls and jewellery. Radiocarbon dating of the pearls agrees with the age of the shipwreck, which previously was inferred using recovered coins and ceramics. As such, these are some of the oldest pearls ever to be discovered. Based on this example, the present article shows how radiocarbon age dating can be adapted to the testing of historic pearls. The authors have further developed their sampling method so that radiocarbon age dating can be considered quasi-destructive, which is particularly important for future studies on pearls (and other biogenic gem materials) of significance to archaeology and cultural heritage.

The Journal of Gemmology, 36(5), 2017, pp. 728–736. <http://dx.doi.org/10.1080/00456365.2017.1361878>  
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**Introduction**

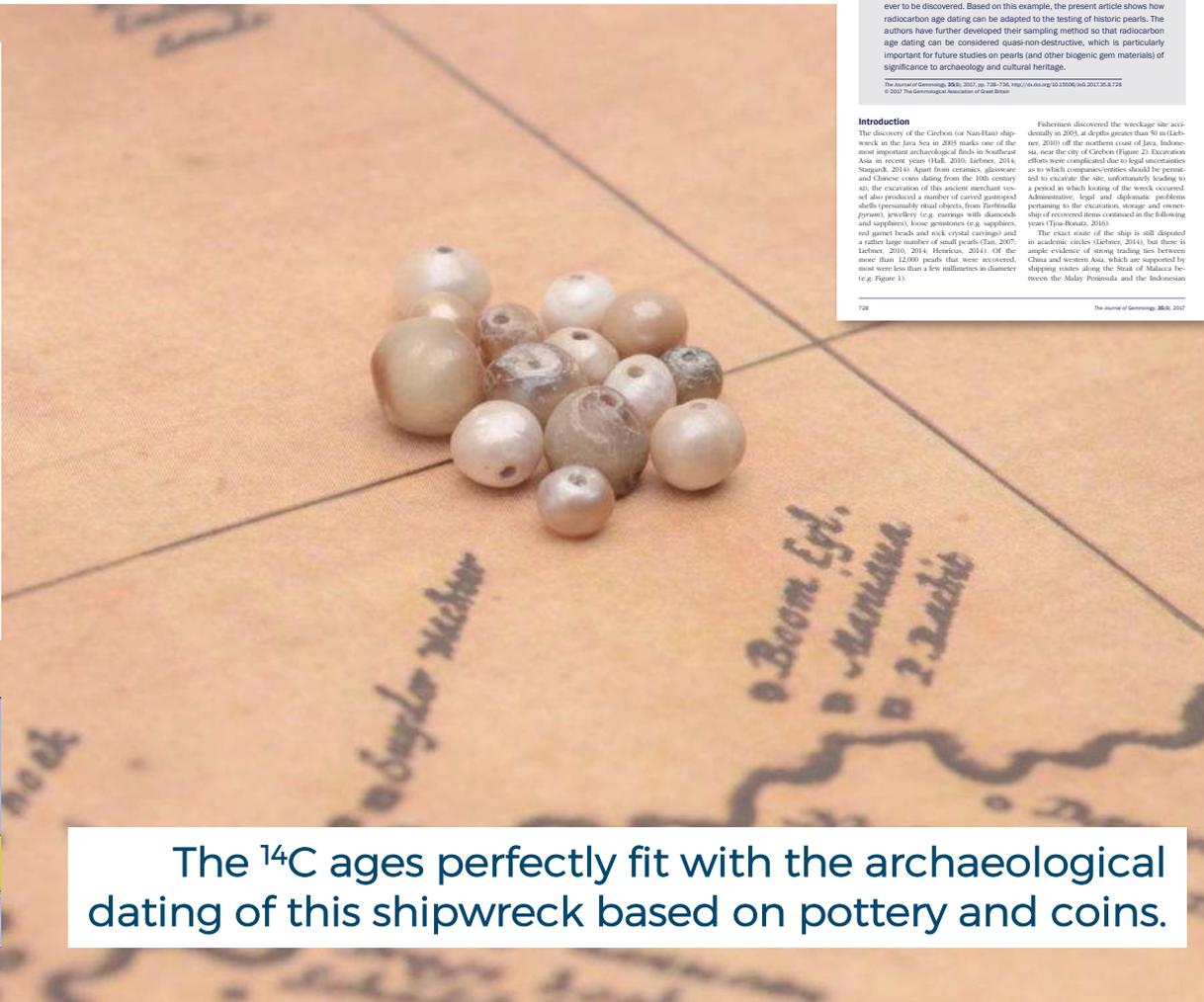
Fishermen discovered the wreck-keel site accidentally in 2003, at depths greater than 50 m (Lichner, 2010) off the northern coast of Java, Indonesia, near the city of Cirebon (Figure 2). Excavation efforts were complicated due to legal uncertainties as to which competences should be permitted to excavate the site, unfortunately leading to a period in which looting of the wreck occurred. Administrative, legal and diplomatic problems pertaining to the excavation, storage and ownership of recovered items continued in the following years (Prua-Bonatz, 2016).

The exact route of the ship is still disputed in academic circles (Lichner, 2014), but there is ample evidence of strong trading ties between China and western Asia, which are supported by shipping routes along the Strait of Malacca between the Malay Peninsula and the Indonesian

The discovery of the Cirebon (or Nan-Han) shipwreck in the Java Sea in 2003 marks one of the most important archaeological finds in Southeast Asia in recent years (Hall, 2010; Lichner, 2014; Stangor, 2014). Apart from ceramics, glassware and Chinese coins dating from the 10th century AD, the excavation of this ancient merchant vessel also produced a number of carved gemstone shells (presumably ritual objects from Partholinda pyramids), jewellery (e.g. earrings with diamonds and sapphires), loose gemstones (e.g. sapphires, red garnet beads and rock crystal carvings) and a rather large number of small pearls (Tan, 2007; Lichner, 2010, 2014; Henricus, 2014). Of the more than 12,000 pearls that were recovered, most were less than a few millimetres in diameter (e.g. Figure 1).

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The Journal of Gemmology, 36(5), 2017



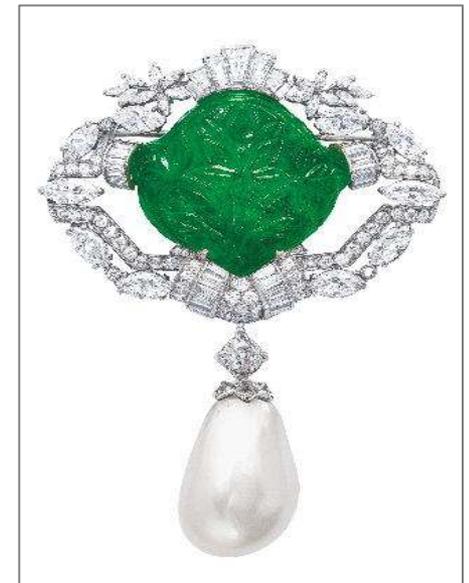
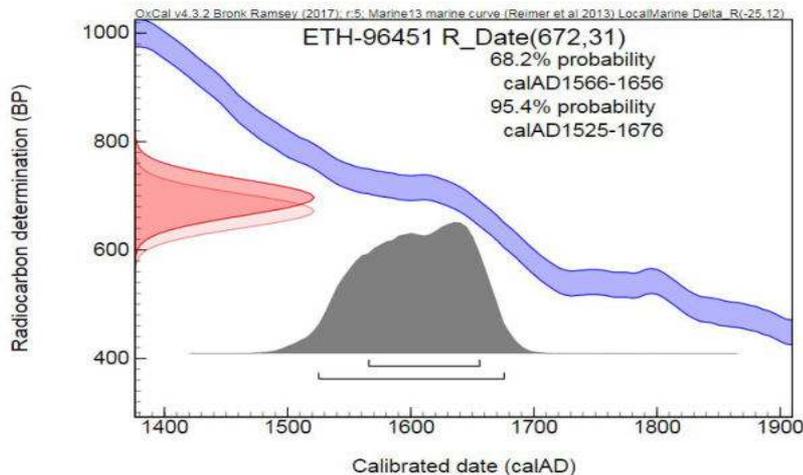
The <sup>14</sup>C ages perfectly fit with the archaeological dating of this shipwreck based on pottery and coins.

# ANA MARIA PEARL

Documented since mid 19th century:

Originally belonging to Ana María de Sevilla (1828-1861); probably fished during Hernán Cortéz' conquest of the Aztec empire in the 16<sup>th</sup> century .

The radiocarbon analyses (carried out by ETH Zurich) date this pearl to the **16<sup>th</sup> – 17<sup>th</sup> century**, thus perfectly matching the documented provenance of this pearl.

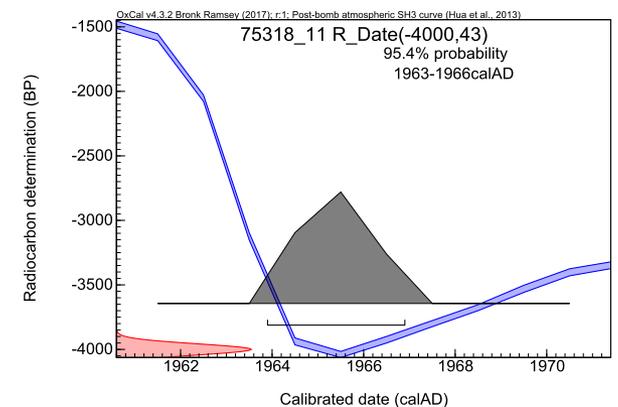
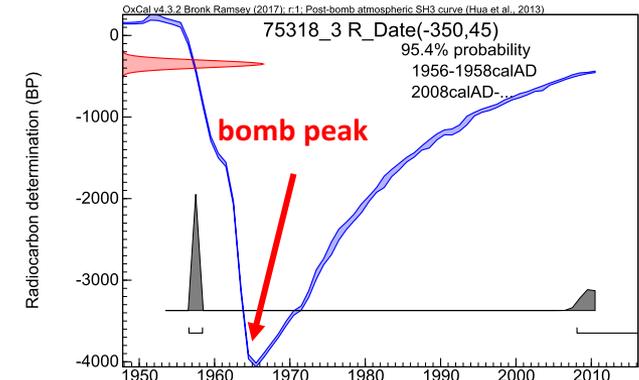


# Recent pearl formation

Cultured pearls formed around the “bomb” peak (1966, southern hemisphere). Early production from Kuri Bay, Australia’s first pearl farm (first production in 1958). The cultured pearls are presumably from the 1960’s.

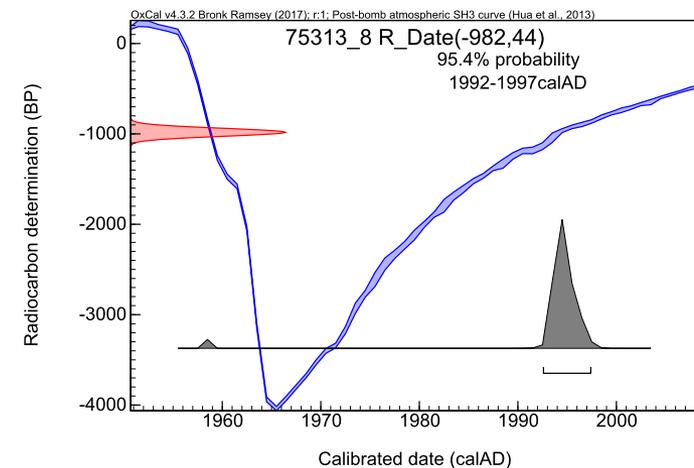
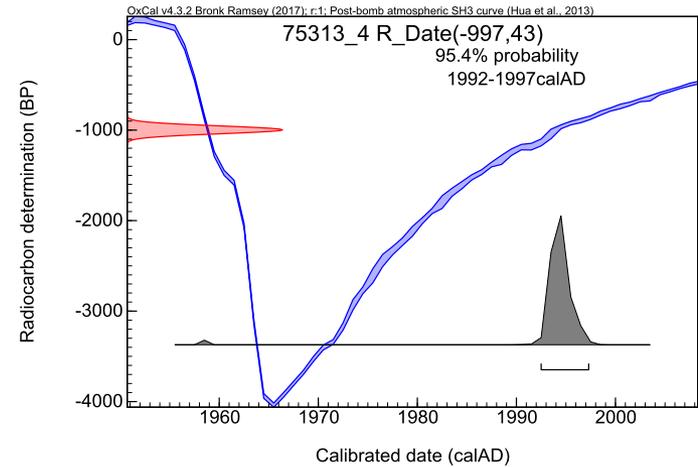
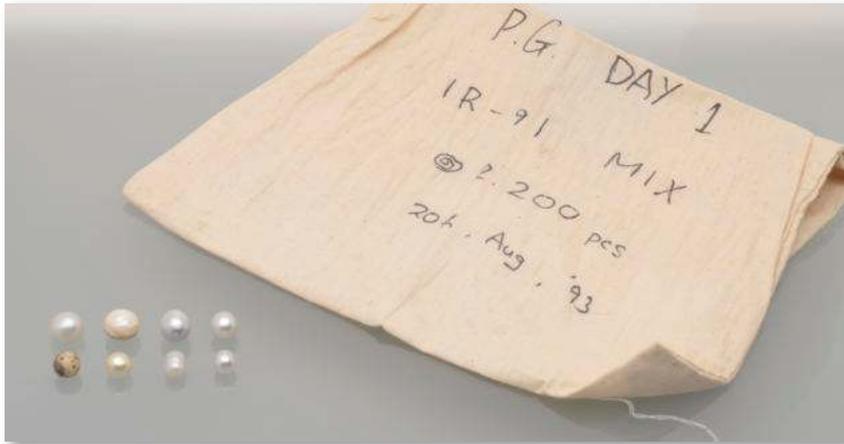


In the Paspaley pearl office in Darwin with Peter Bracher



# Recent pearl formation

Cultured pearls from a test run by Paspaley: Seed grafting in 1991 and harvest in 1993.

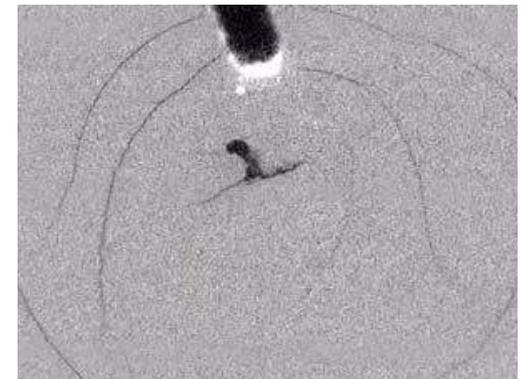


# NP / CP separation

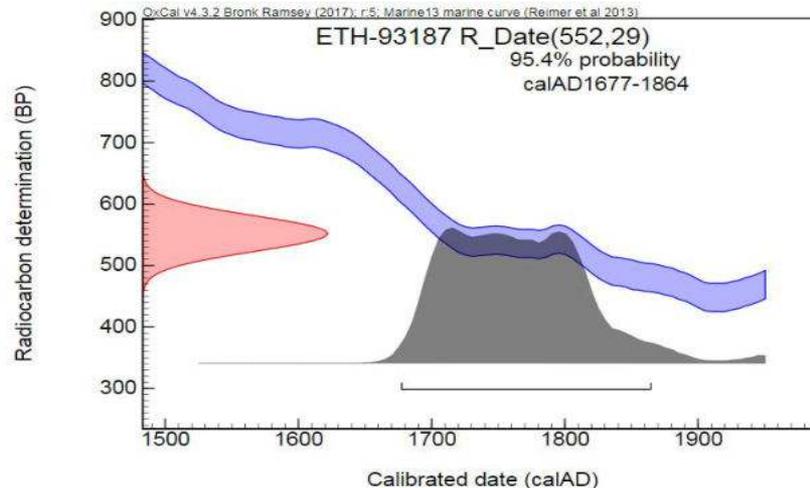
## Supporting evidence due to radiocarbon age dating

This saltwater pearl shows internal structures which are also known in beadless cultured pearls (Krzemnicki et al. 2010, Sturman 2009).

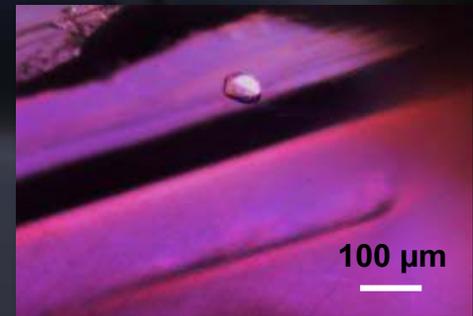
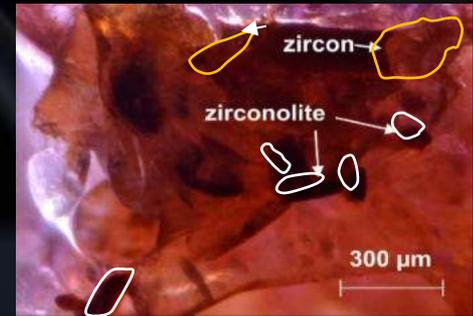
The radiocarbon analyses (carried out by ETH Zurich) date this pearl to the **17<sup>th</sup> – 18<sup>th</sup> century**, distinctly pre-dating any pearl farming. The radiocarbon age thus supports the conclusion of natural pearl.



Micro X-ray tomographical section of pearl centre.



# AGE DATING OF GEMS



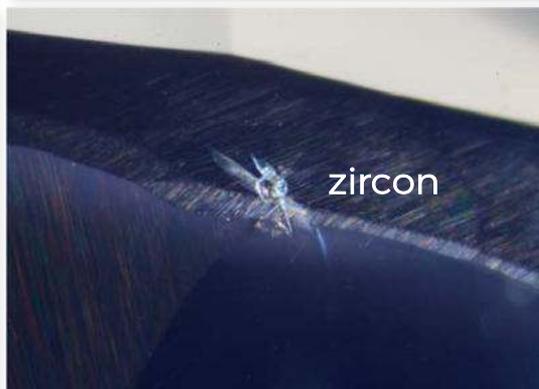
Microphotos: M.M. Phyo, 2019

- LA-ICP-Time Of Flight-Mass Spectrometry (LA-ICP-TOF-MS)
  - Full mass spectrum (simultaneous  $m = 7 - 238$ )
  - Laser spot size-  $35\mu\text{m}$
- LA-ICP-Sector Field-Mass Spectrometry (LA-ICP-SF-MS)
  - High sensitivity (measured isotopes 202, 204, 206, 207, 208, 232, 235, 238)
  - Laser spot size-  $13\mu\text{m}$  &  $19\mu\text{m}$

# AGE DATING OF GEMS

The following inclusions have been used so far for radiometric age dating of gemstones at SSEF:

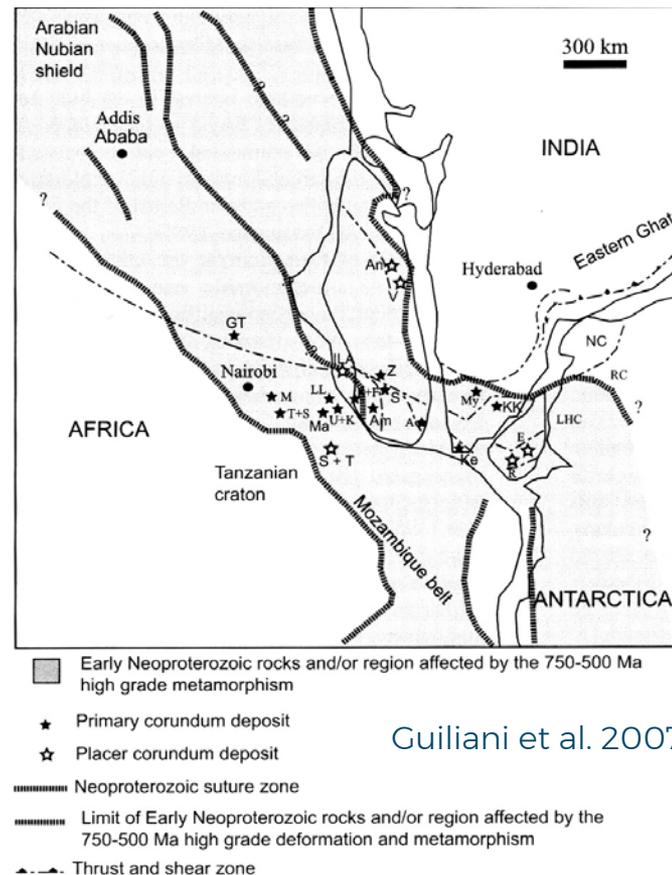
- Zircon
- Zirconolite
- Baddeleyite
- Titanite
- Apatite
- Xenotime
- Monazite
- Rutile



# AGE DATING OF GEMS

Three main global geological frameworks in which many gemstone deposits are found:

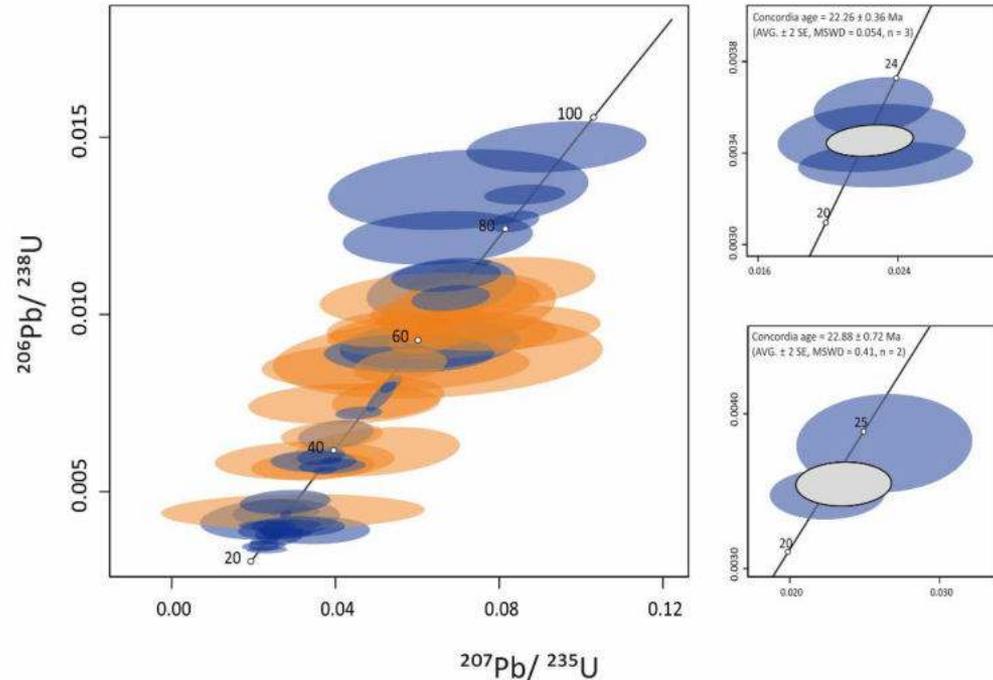
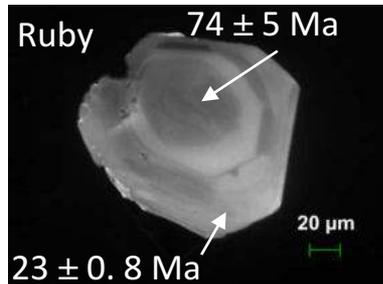
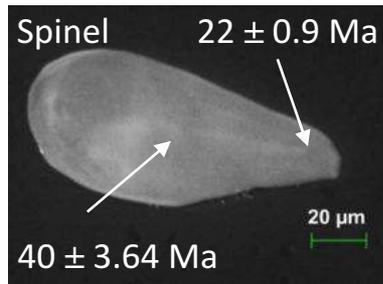
- Deposits connected to Pan-African tectono-metamorphic events by the collision of eastern and western Gondwana about **750-450 ma ago**.
- Deposits connected to tectono-metamorphic events due to the collision of the Indian plate with the Eurasian plate (Himalayan orogeny), about **40-10 ma ago**.
- Volcanic activity (alkali-basalts), often linked to extensional tectonics (rift valley in East-Africa, Southeast-Asia...), mostly about **4 ma ago and younger**.



Uluguru mountains, Tanzania. © Michael S. Krzemnicki

# AGE DATING OF GEMS

Zircon in Gemstones from Mogok (Himalayan orogeny)



$22.88 \pm 0.72$  Ma (Spinel)

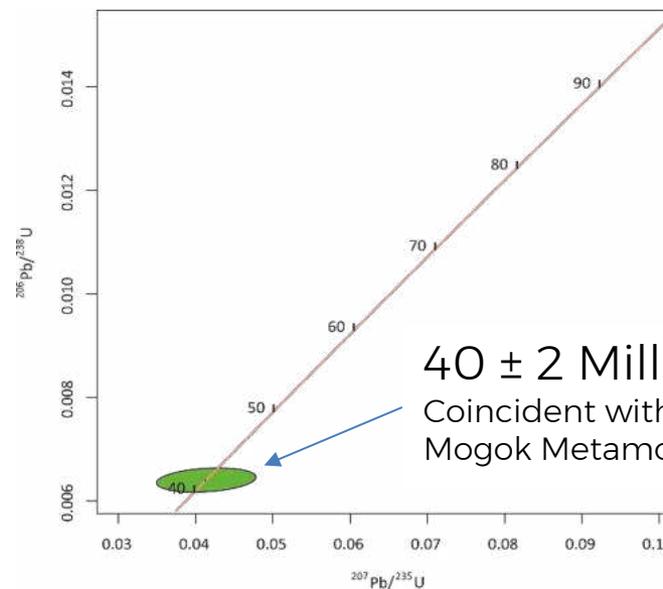
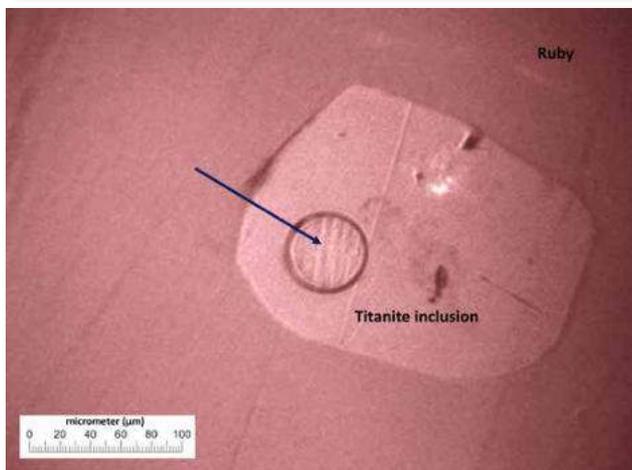
$22.26 \pm 0.36$  Ma (Ruby)

● LA-ICP-SF-MS  
● LA-ICP-TOF-MS

Data and figures from Myat Myint Phyo, (unpublished PhD thesis, University Basel)

# AGE DATING OF GEMS

Age dating of ruby set in iconic Harry Winston necklace

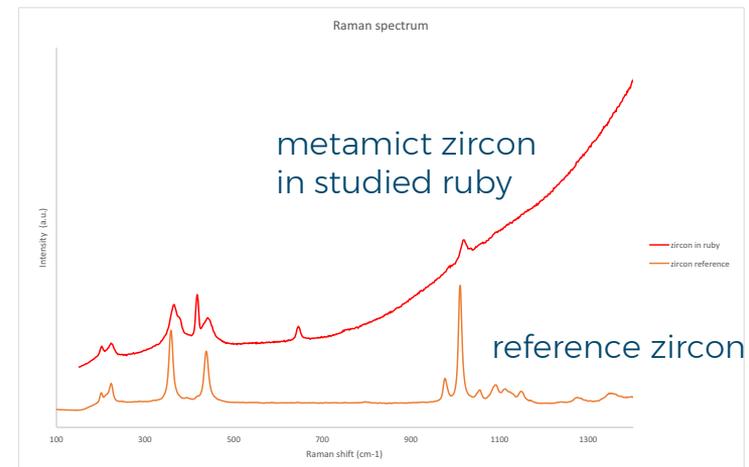
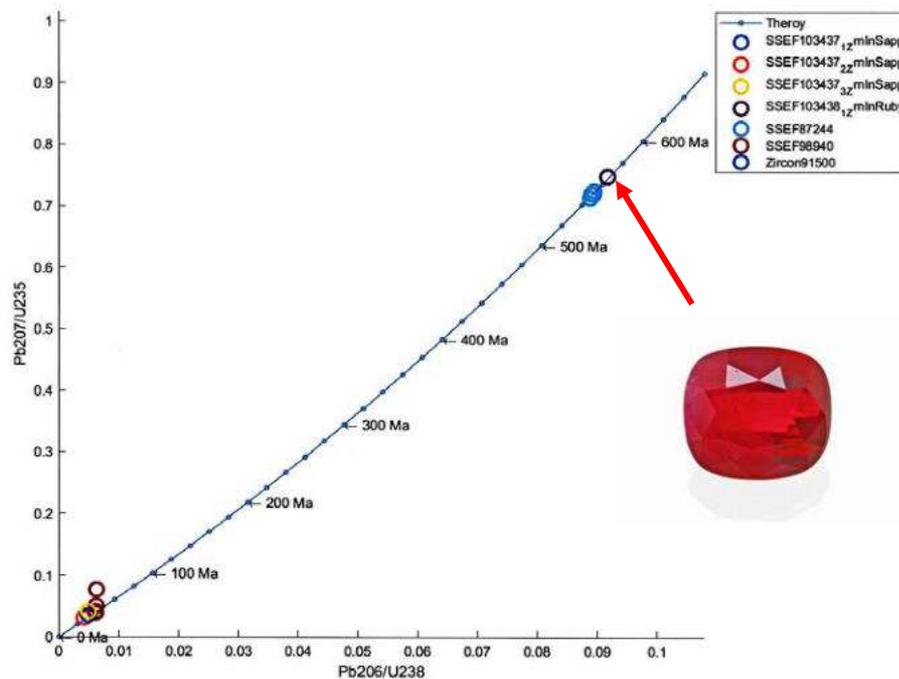
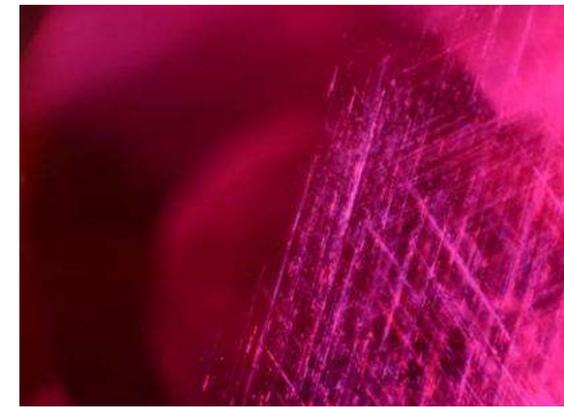


40 ± 2 Million Years  
Coincident with  
Mogok Metamorphic Event

U-Pb dating on titanite inclusion (40 ± 2 Ma) supports a Burmese origin of this 12 ct ruby.

# ORIGIN DETERMINATION CASES

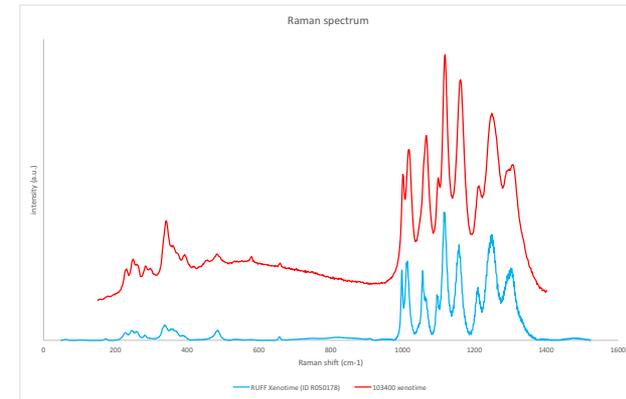
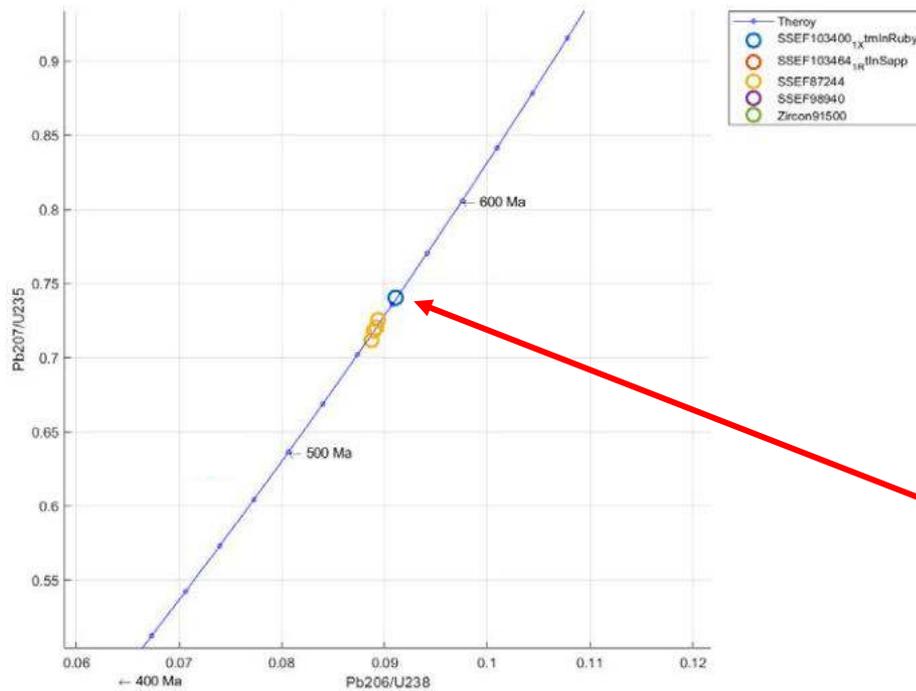
Marble-type ruby of 5.1 ct.  
Doubtful origin based on “classical” analytical methods.



U-Pb dating on zircon inclusion (approx. 565 Ma) supports an East-African origin of this ruby.

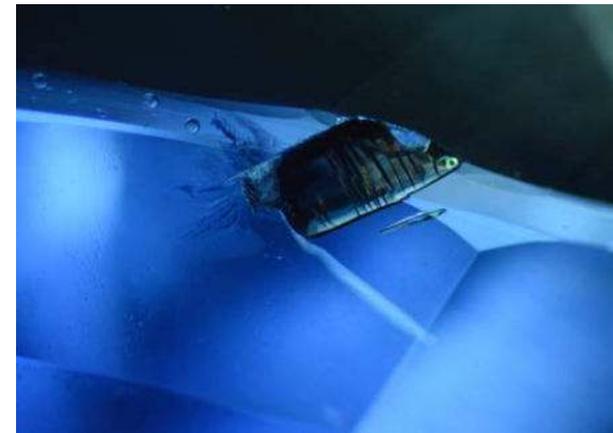
# ORIGIN DETERMINATION CASES

Marble-type ruby cabochon of 76 ct.  
Doubtful origin based on “classical” analytical methods.

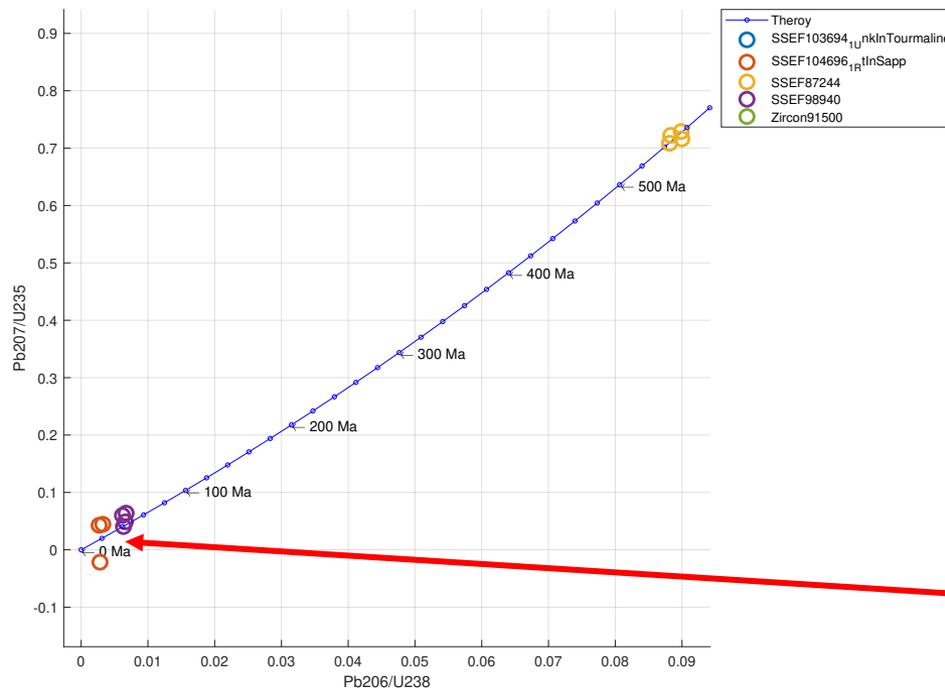


U-Pb dating on **xenotime inclusion** (approx. 560 Ma) supports an East-African origin of this ruby.

# ORIGIN DETERMINATION CASES



Metamorphic sapphire of 14 ct.  
Doubtful origin based on “classical” analytical methods.



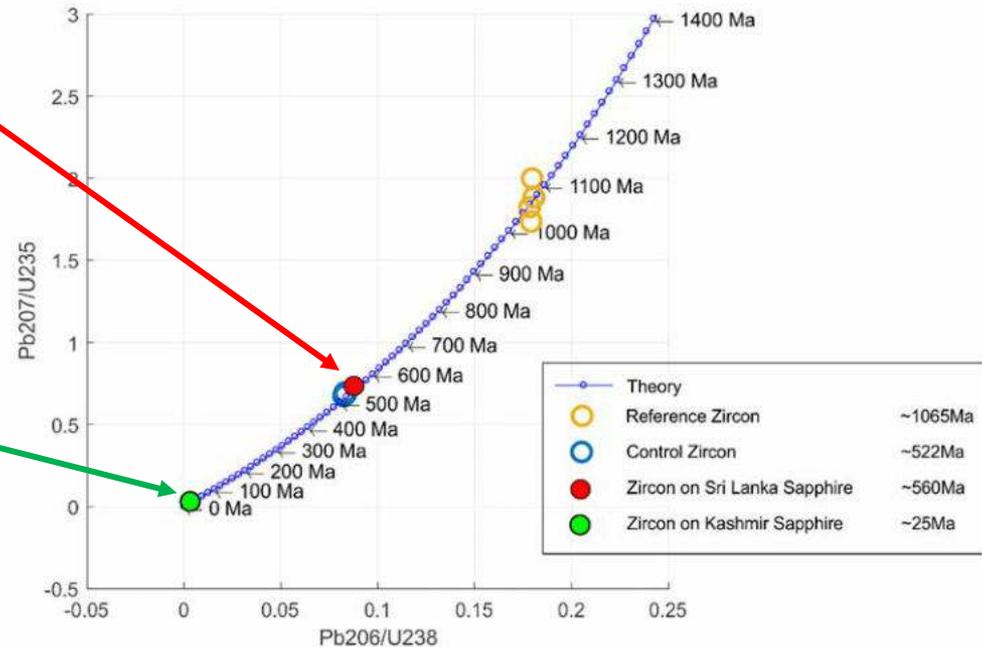
U-Pb dating on **rutile inclusion** (approx. 20 Ma) supports a Burmese origin of this sapphire.

# ORIGIN DETERMINATION CASES

Two metamorphic sapphires with velvety blue “Kashmir-like” visual appearance...



### GemTOF Age Dating on Zircon Inclusions

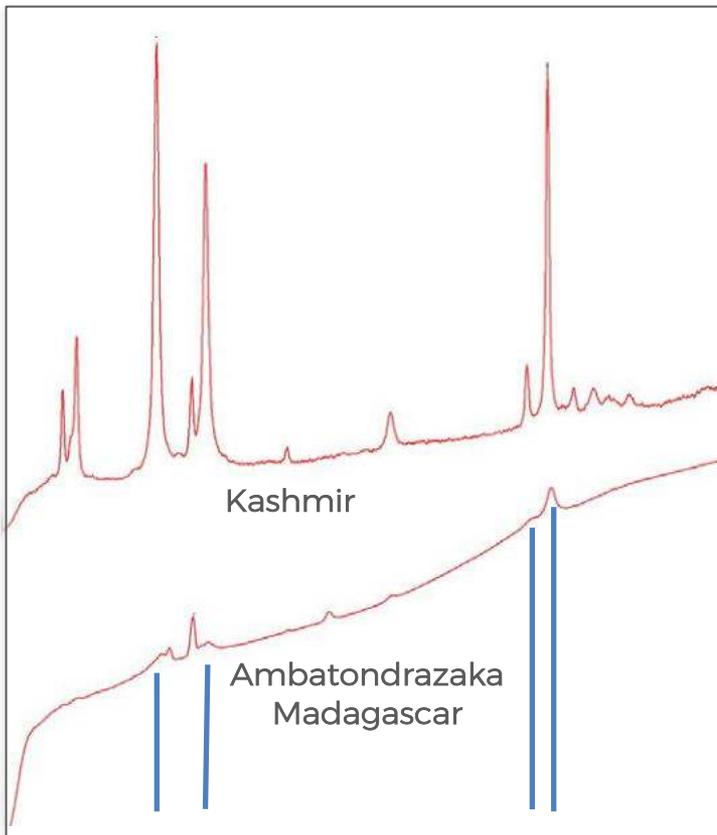


U-Pb dating on **zircon inclusions** allows clear separation, supporting a Kashmir (a) and a Sri Lankan origin of these two sapphires.

# INDIRECT “AGE DATING” USING RAMAN

‘Kashmir-like’ sapphires of excellent quality from new deposit near Ambatondrazaka, Madagascar.

Raman spectra of zircon inclusions



non-metamict zircon inclusion

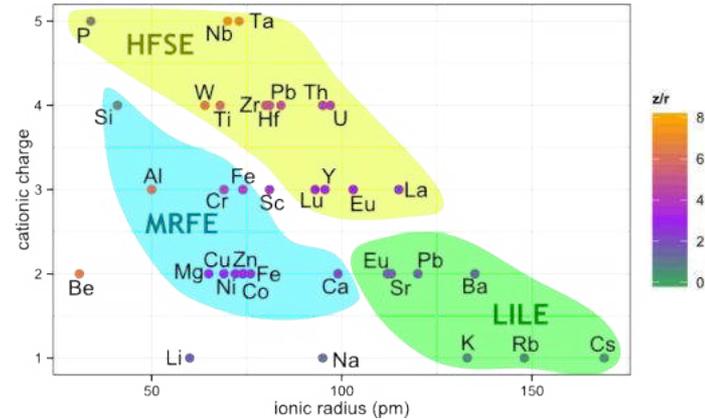
metamict zircon inclusion

**Krzemnicki M.S., 2017.** Trade alert: ‘Kashmir-like’ sapphires from Madagascar are entering the gem trade in large sizes and quantities. *SSEF Press release, 28th March 2017.*

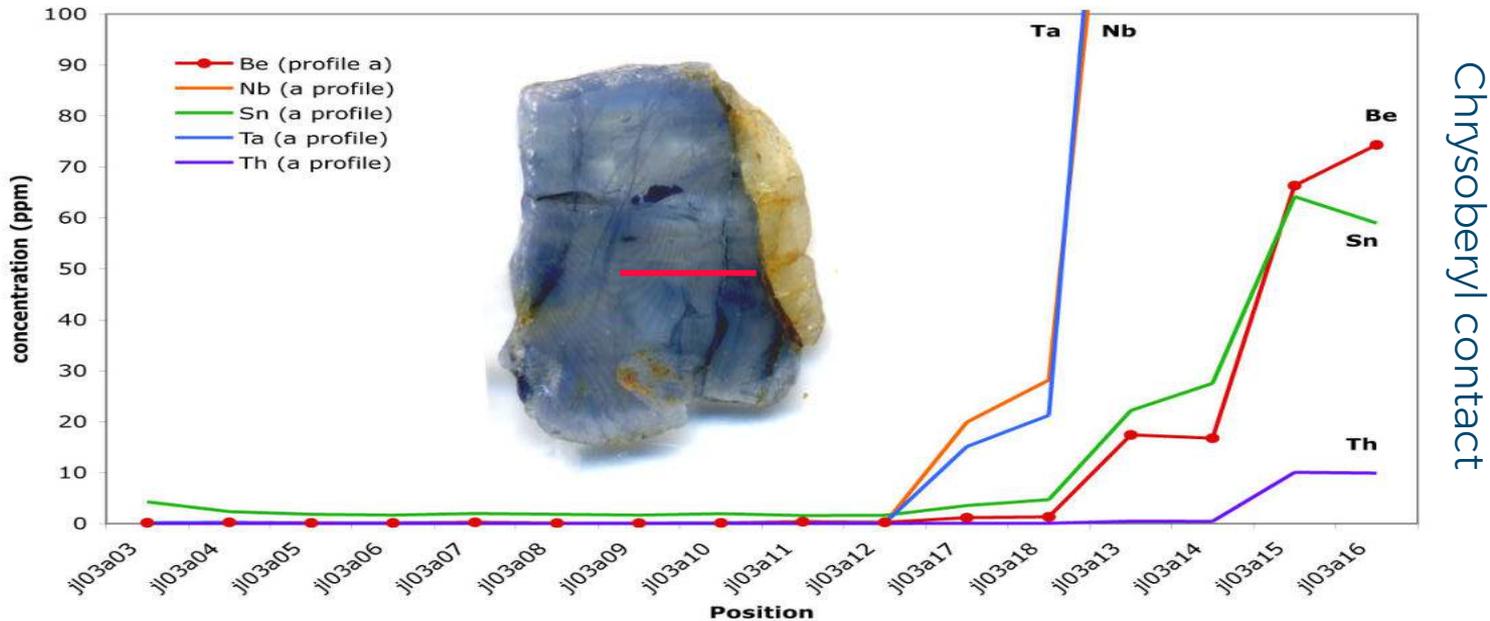
**Krzemnicki M.S., Cartier L.E., Wang H.A.O., Zhou W., Lefèvre P., 2017.** Sapphires from a new deposit at Bemainty near Ambatondrazaka in Madagascar. *InColor Magazine, No. 35, 44-47.*

# DIRECT AGE DATING OF SAPPHIRES

High-Field Strength Elements (HFSE) are occasionally present in metamorphic and basaltic sapphires (commonly linked to sub-microscopic inclusions resulting in “cloudy” appearance, Shen et al. 2007 and 2009)



LA ICP MS data



Chrysoberyl-Sapphire (basaltic) intergrowth. See M.S. Krzemnicki, 2008 (IGC Moscow)

# DIRECT AGE DATING OF SAPPHIRES

Occurrence frequency of incompatible elements (HFSE)

	Be	Zr	Nb	La	Ce	Hf	Th		
Median Conc. [ppm]	Kashmir	<LOD							
	Madagascar	<LOD							
Occ. Freq. [%]	Kashmir	3.7	1.7	4.3	4.3	6.6	2.9	6.0	
	Madagascar	17	42	46	14	18	35	31	

Zr, Nb, Hf, Th more often in Madagascar than Kashmir

Direct  $^{232}\text{Th} / ^{208}\text{Pb}$  age dating of sapphire:

96393

100 ct sapphire with slight turbidity and inclusions possible for Madagascar, Sri Lanka or Kashmir.

Estimated age 400 - 600 Ma, thus excluding a Kashmir origin.



# AGE DATING OF PARAIBA PEGMATITE FORMATION

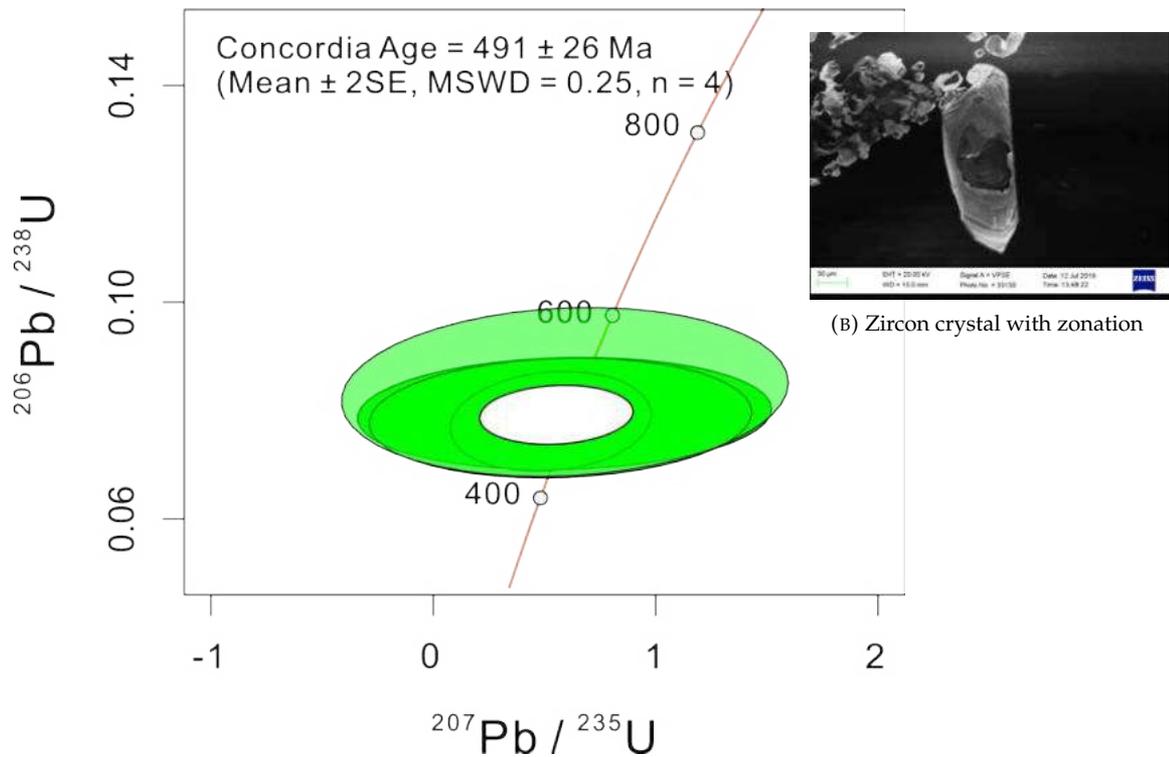


FIGURE 4.9: Age Dating plot (done with isoplotR (Vermeesch, 2018))



(A) The Boqueirão granitic pegmatite: Zoning and coarsening towards the core (Picture from SSEF fieldtrip, 2018)

Our calculated U-Pb age of  $491 \pm 26$  Ma is in good agreement with Strmic & Palinkas et al. 2019, dating the Boqueirao pegmatite using  $^{40}\text{Ar}/^{39}\text{Ar}$  at  $502.1 \pm 5.8$  Ma years.

Figures © S. Degen, 2019. Unpublished Bachelor thesis 2019, University Basel

# CONCLUSIONS

Radiocarbon age dating in principle can be carried out on any pearl (or any other biogenic material) containing carbon.

U-Pb and Th-Pb age dating in most cases requires certain inclusion minerals present at the surface of a cut gemstone.

In specific cases, direct age dating of sapphires (containing Th, Pb traces) is possible.

In lab testing, age dating may provide additional supporting evidence in cases of:

- Pearls of historic provenance
- Separation of natural and cultured pearls
- Origin determination of coloured gemstones



Bottles of wine in the cellars of the Chateau Lafite-Rothschild. © F. Poincet

