

# Combined Chemical, Isotopic and Geochronological Analysis of Accessory Minerals at High Spatial Resolution – Insights into Mantle Sources and Melt Crystallization History

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# Introduction

- LA-(MC)-ICP-MS techniques now make it possible to obtain reliable radiogenic (e.g., Sr, Nd, Pb, Hf) isotope signatures and U-Pb ages on individual mineral grains
- Suitable accessory minerals (e.g., *apatite*, *zircon*, *titanite* *perovskite*) may crystallize early and during a significant period of melt crystallization
- Combined major **& trace element data**, **isotope ratios**, and **ages** yield valuable insights in relation to mantle source region(s) and melt differentiation processes

# Why accessory minerals in carbonatites?

- **Carbonatites** – mantle-derived, igneous rocks (intrusive or extrusive) that contain >50% modal carbonate minerals (e.g., calcite, dolomite)



# Why accessory minerals in carbonatites?

- Although scarce in number (527 occurrences), ***these occur on all continents*** and ***span in age from ~3.0 Ga to present-day*** (Oldoinyo Lengai, Tanzania)
- ***Low viscosity*** and ***unique geochemistry*** with extremely high abundances of Sr, Nd, REEs buffer their inherited mantle isotope signature from possible contamination during ascent and emplacement

# 527 occurrences worldwide

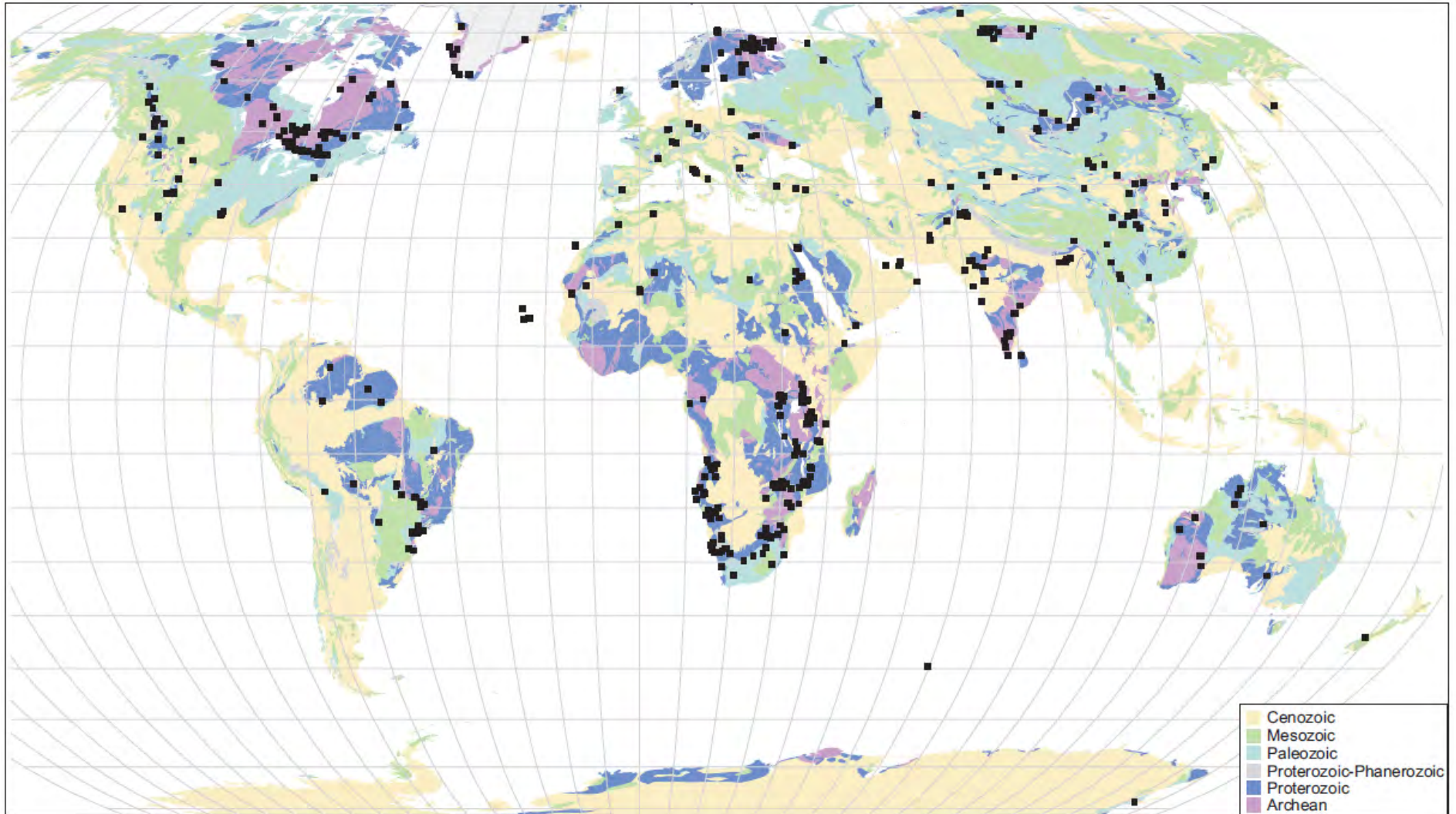


Figure 1. World map showing all known carbonatite localities.

Woolley & Kjargaard (2008)

# Why accessory minerals in carbonatites?

- Important for understanding mantle metasomatic processes
- **Calcite** and a variety of accessory minerals (e.g., **apatite**, **perovskite**, **niocalite**) can be examined for their chemical & isotopic compositions and U-Pb ages at high spatial resolution
- **Apatite:**  $\text{Ca}_5(\text{PO}_4)_3\text{F}$
- **Perovskite:**  $\text{CaTiO}_3$
- **Niocalite:**  $(\text{Na}_{0.34}\text{Fe}_{0.06}\text{Mn}_{0.19}\text{Mg}_{0.09}\text{Ca}_{13.40}\text{REE}_{0.15}\text{Ti}_{0.02})_{\text{total}=14.25}\text{Nb}_{2.12}\text{Ta}_{0.06}(\text{Si}_2\text{O}_7)_4\text{O}_{7.65}\text{F}_{2.44}$

Chen et al. (in press, *Can. Mineral.*)



# Why investigate apatite?

- Apatite is also employed in low-temperature thermochronology studies in relation to apatite fission track and apatite (U–Th)/He thermochronometers
- Apatite has also been investigated in high temperature thermochronology studies - U–Pb apatite system has a closure temperature of ca. 450–550 °C (Chamberlain and Bowring, 2000; Schoene and Bowring, 2007).

# In-situ U-Pb dating of accessory minerals by LA-(MC)-ICP-MS method

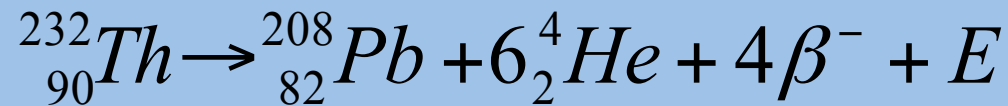
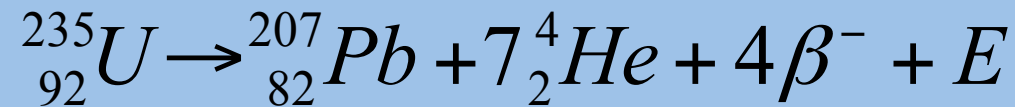
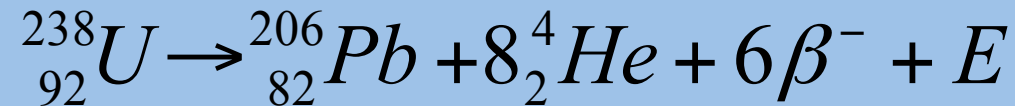
- The advent of U-Pb geochronology by LA-ICPMS offers low-cost, rapid data acquisition and sample throughput compared to the ID-TIMS or ion microprobe U-Pb methods (e.g., Košler and Sylvester, 2003).
- However, few studies demonstrated the applicability of the LA-ICPMS to U-Pb apatite, perovskite, niocalite geochronometry.
- The methodology for apatite was recently validated by the detailed study by the group at Memorial University (Chew et al., 2011, Chem. Geol.) by dating apatite standards of known crystallization age



## **U-Th-Pb apatite, perovskite, niocalite dating by LA-ICP-MS - advantages**

- Accessory minerals that contain both abundant **U** and **Th**, hence there are several independent geochronometers that can be used simultaneously, and serve to cross-validate results

# U-Th-Pb geochronometers



However, in almost all instances,  ${}^{207}\text{Pb}/{}^{235}\text{U}$  ratios (ages) are not measured but rather calculated.

$${}^{207}\text{Pb}/{}^{235}\text{U} = {}^{207}\text{Pb}/{}^{206}\text{Pb}_{\text{meas}} \times {}^{206}\text{Pb}/{}^{238}\text{U}_{\text{meas}} \times {}^{238}\text{U}/{}^{235}\text{U}(137.88)$$

# U-Th-Pb dating by LA-ICP-MS - problems

- However, precise and accurate U–Pb and Th–Pb apatite age determinations are commonly hindered by low U, Th and Pb concentrations and **high common Pb contents**, which requires a common Pb correction.
- Since apatite, perovskite, niocalite can accommodate a significant amount of initial Pb into its crystal structure, this places limitations on the accuracy and precision of age determinations.

# U-Th-Pb dating by LA-ICP-MS - problems

Thus, strategies to curtail or address the common Pb issue include:

- 1) Define concordia or isochron plots on a suite of cogenetic apatite grains with a large spread in common Pb/radiogenic Pb ratio; or
- 2) to undertake a Pb correction based on an appropriate choice of initial Pb isotopic composition.

# U-Th-Pb dating by LA-ICP-MS – possible solutions

- A variety of methods do not require an estimate of the initial Pb isotope composition
- These require several analyses of a suite of cogenetic apatite grains with a significant variation in common Pb/radiogenic Pb ratios, which in turn define a well-constrained linear array on a Concordia diagram or isochron.
- E.g., Total-Pb/U isochron, a three-dimensional  $^{238}\text{U}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$  vs.  $^{204}\text{Pb}/^{206}\text{Pb}$  plot (Ludwig, 1998)

# U-Th-Pb dating by LA-ICP-MS – possible solutions

- An alternative approach often employed in the LA-ICP-MS U–Pb dating of high common Pb phases, such as perovskite (Cox and Wilton 2006; Simonetti et al. 2008) and titanite (Simonetti et al. 2006; 2008) involves projecting an intercept through the uncorrected data on a ***Tera–Wasserburg Concordia*** to determine the common Pb-component (y-intercept) on the  $^{207}\text{Pb}/^{206}\text{Pb}$  axis.
- The  $^{238}\text{U}/^{206}\text{Pb}$  age can then be calculated as either a lower intercept age on the  $^{238}\text{U}/^{206}\text{Pb}$  axis (x-intercept) or as a weighted average of  $^{207}\text{Pb}$ -corrected ages (see below) using the Concordia  $^{207}\text{Pb}/^{206}\text{Pb}$  intercept as an estimate of the initial Pb isotopic composition.
- This approach also assumes that the U–Pb\* data are concordant and equivalent.

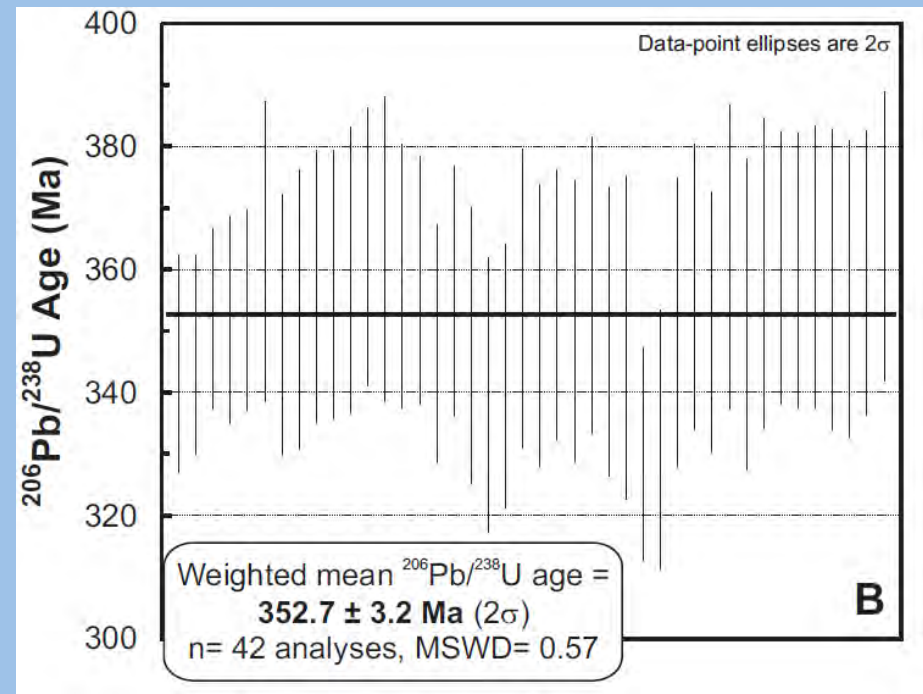
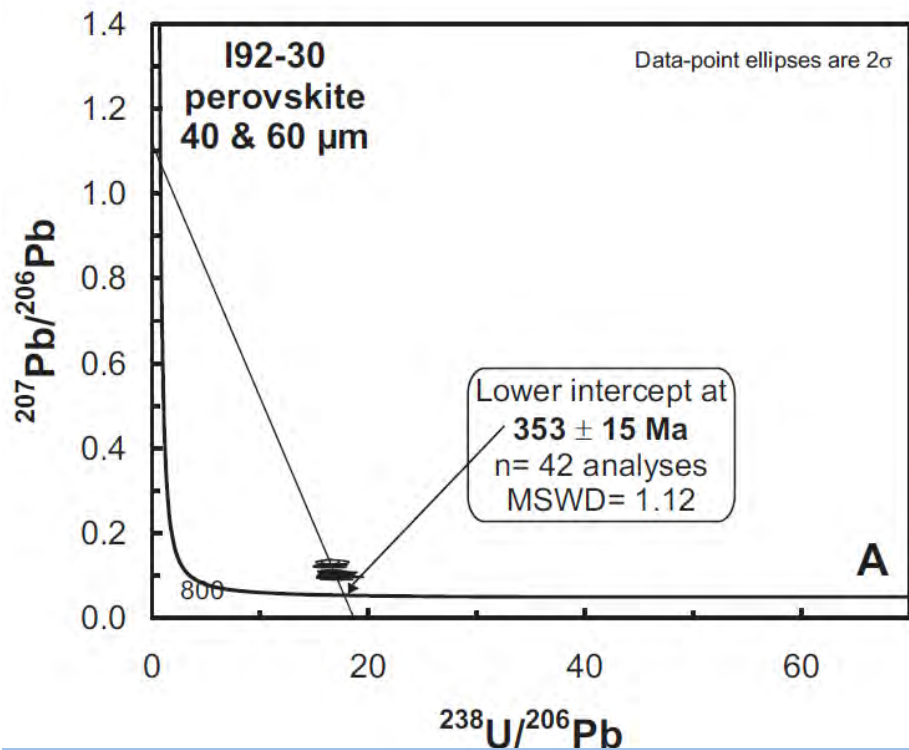
# Common Pb correction schemes- $^{207}\text{Pb}$ method

$$f = \frac{\left( ^{207}\text{Pb}/^{206}\text{Pb}_{\text{measured}} - ^{207}\text{Pb}/^{206}\text{Pb}_{\text{radiogenic}} \right)}{\left( ^{207}\text{Pb}/^{206}\text{Pb}_{\text{common}} - ^{207}\text{Pb}/^{206}\text{Pb}_{\text{radiogenic}} \right)}$$

f = proportion of common Pb



# Common Pb correction schemes- $^{207}\text{Pb}$ method



From Simonetti et al. (2008)

# Common Pb correction schemes- correction for initial $Pb_{common}$

- Estimates of initial Pb isotopic compositions are typically derived from Pb evolution models (e.g., Stacey and Kramers, 1975) or by analyzing a low-U co-magmatic phase (e.g., K-feldspar or plagioclase), which exhibits negligible ingrowth of radiogenic Pb.

# Common Pb correction schemes- <sup>204</sup>Pb correction method

- This method relies on the *measurement of the low abundance non-radiogenic <sup>204</sup>Pb isotope.*
- Measured Pb isotopic signals are corrected using the assumed <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb ratios of the common Pb to extract net signal intensities of the radiogenic daughter <sup>206</sup>Pb\*, <sup>207</sup>Pb\* and <sup>208</sup>Pb\* isotopes.

# Common Pb correction schemes- <sup>204</sup>Pb correction method

$$f_{206} = {}^{206}\text{Pb}_{\text{common}} / {}^{206}\text{Pb}_{\text{total}}$$

$$f_{206} = \left( {}^{206}\text{Pb} / {}^{204}\text{Pb}_{\text{common}} \right) / \left( {}^{206}\text{Pb} / {}^{204}\text{Pb}_{\text{measured}} \right)$$

$${}^{206}\text{Pb}^* / {}^{238}\text{U} = (1 - f) \left( {}^{206}\text{Pb} / {}^{238}\text{U}_{\text{measured}} \right)$$

# Common Pb correction schemes- $^{208}\text{Pb}$ correction method

- Assumes that the ratio of  $^{232}\text{Th}$  to the parent U isotope in the analyzed sample has not been disturbed (concordant)
- Any excess  $^{208}\text{Pb}$  (e.g.,  $^{208}\text{Pb}_{\text{measured}} - 208\text{Pb}^*$ ) can be attributed to the assumed common Pb component.

# Common Pb correction schemes- <sup>208</sup>Pb correction method

- The proportion of common <sup>206</sup>Pb in this case can be calculated as:

$$f_{206} = \frac{\left( \frac{{}^{208}\text{Pb}}{{}^{206}\text{Pb}}_{\text{measured}} - \frac{{}^{208}\text{Pb}^*}{{}^{206}\text{Pb}^*} \right)}{\left( \frac{{}^{208}\text{Pb}}{{}^{206}\text{Pb}}_{\text{common}} - \frac{{}^{208}\text{Pb}^*}{{}^{206}\text{Pb}^*} \right)}$$

$$\frac{{}^{208}\text{Pb}^*}{{}^{206}\text{Pb}^*} = \left( \frac{{}^{232}\text{Th}}{{}^{238}\text{U}} \right) \left[ \frac{\left( e^{\lambda_{232}t} - 1 \right)}{\left( e^{\lambda_{238}t} - 1 \right)} \right]$$

This formulation works particularly well for targets with very low <sup>232</sup>Th/<sup>238</sup>U (b0.5), but is not suitable for high Th/U targets

# Common Pb correction schemes- <sup>208</sup>Pb correction method

$$f_{208} = {}^{208}\text{Pb}_{\text{common}} / {}^{208}\text{Pb}_{\text{total}}$$

$$f_{208} = f_{206} \left( {}^{208}\text{Pb} / {}^{206}\text{Pb}_{\text{common}} \right) / \left( {}^{208}\text{Pb} / {}^{206}\text{Pb}_{\text{measured}} \right)$$



# In-situ U-Pb dating by LA-ICP-MS method

- In addition to the incorporation of common Pb into the apatite crystal lattice, U–Th–Pb dating of apatite by LA-ICPMS also presents the problem of **laser-induced U–Th–Pb fractionation**.
- A ***matrix-matched standard*** is usually required for external calibration of down-hole fractionation of Pb, Th and U in LA-ICPMS dating of accessory minerals since different minerals (e.g., apatite, titanite, perovskite, and zircon) typically show different time-resolved Pb/U and Pb/Th spectra during lasering (e.g., Gregory et al., 2007).

# Laser Ablation U-Pb dating Analysis – Brief Outline

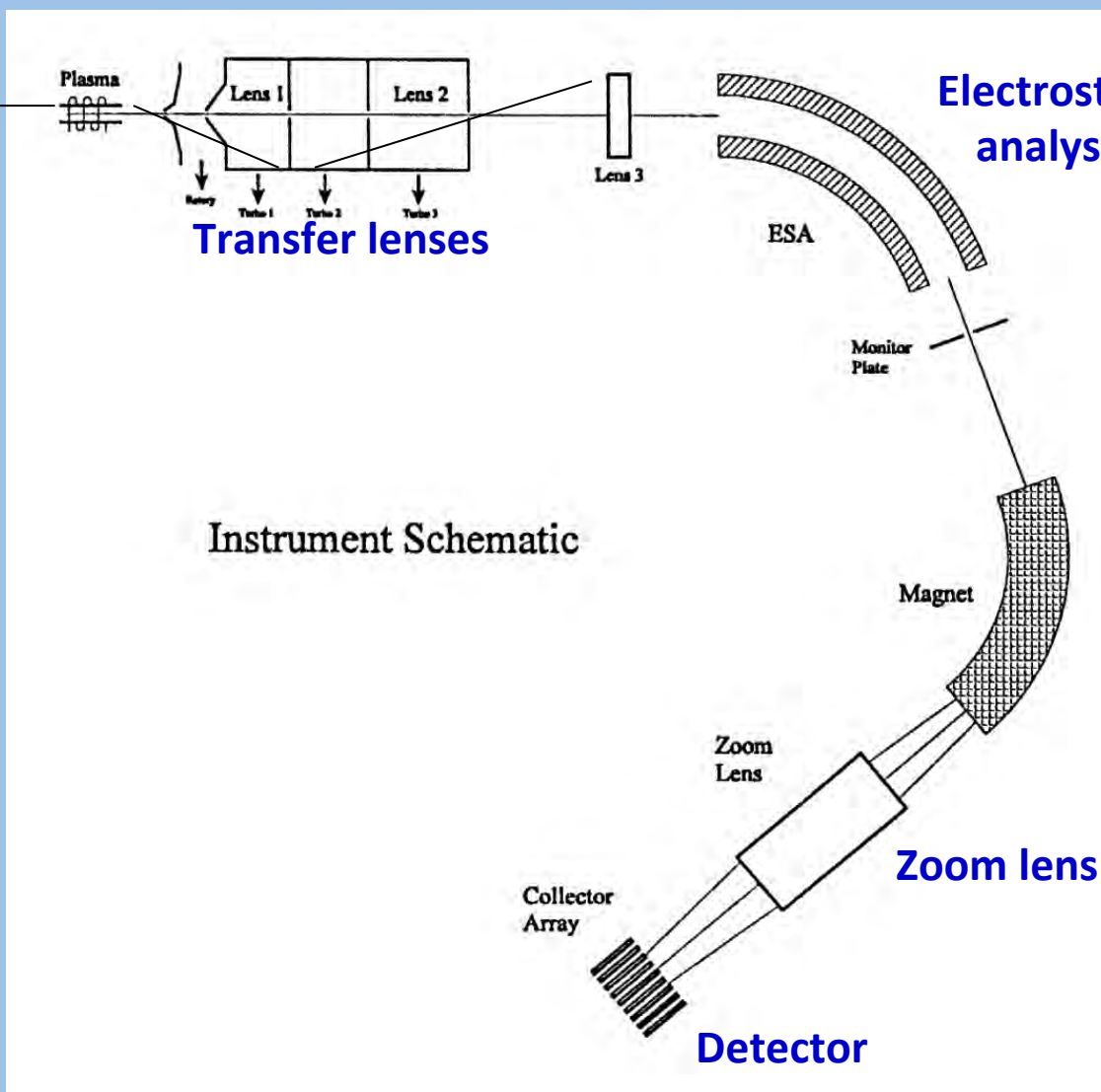
- Analytical protocol is detailed in Simonetti & Neal (2010, *EPSL*);
- UP213 laser ablation system coupled to an Thermo Scientific Element2 HR-ICP-MS
- Apatite crystals were ablated using a 55 micron spot size (stationary mode), fluence of 3-4 J/cm<sup>2</sup>, repetition rate of 4Hz
- Madagascar apatite standard was used for external calibration purposes (i.e. monitoring of instrumental drift and Pb-U laser induced elemental fractionation) with a 'standard-sample bracketing' technique
- Data Reduction- <sup>207</sup>Pb- and <sup>208</sup>Pb common Pb correction was performed (e.g., Simonetti et al., 2006; Chew et al., 2011, Chem. Geo.)

# NuPlasmail -2<sup>nd</sup> Generation



# NuPlasma II Instrument Outline – “Double-focusing” mass spectrometer

Plasma & Introduction system



# Nu Plasma II – MC-ICP-MS

- Equipped with **21 collectors** in total
  - 16 Faraday cups
  - 5 ion counters (discrete dynode SEMs)



# In-situ common Pb – LA-MC-ICP-MS low abundance ( $\leq 1\text{-}2$ ppm) samples- Multiple ion counter configuration

Analysis Mass table - C:\Nu Plasma II\Analyses\In\_situ\_U\_Pb\_v1.nrf

	(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	Integ. Time
	H9	H8	H7	H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	L5	L6	ICD	IC1	IC2	IC3	IC4	
Zero 1	227.90	----	----	222.90	----	----	----	----	----	215.90	----	----	----	----	----	----	208.90	207.90	206.90	204.90	202.90	20
Cycle 1	227.90	----	----	222.90	----	----	----	----	----	215.90	----	----	----	----	----	----	208.90	207.90	206.90	204.90	202.90	10

$^{238}\text{U}$                        $^{232}\text{Th}$

208Pb      207Pb      206Pb      204Pb, 204Hg      202Hg

**Mass Separation : 1.**

Settings:

Measurements per block:

Number of blocks:

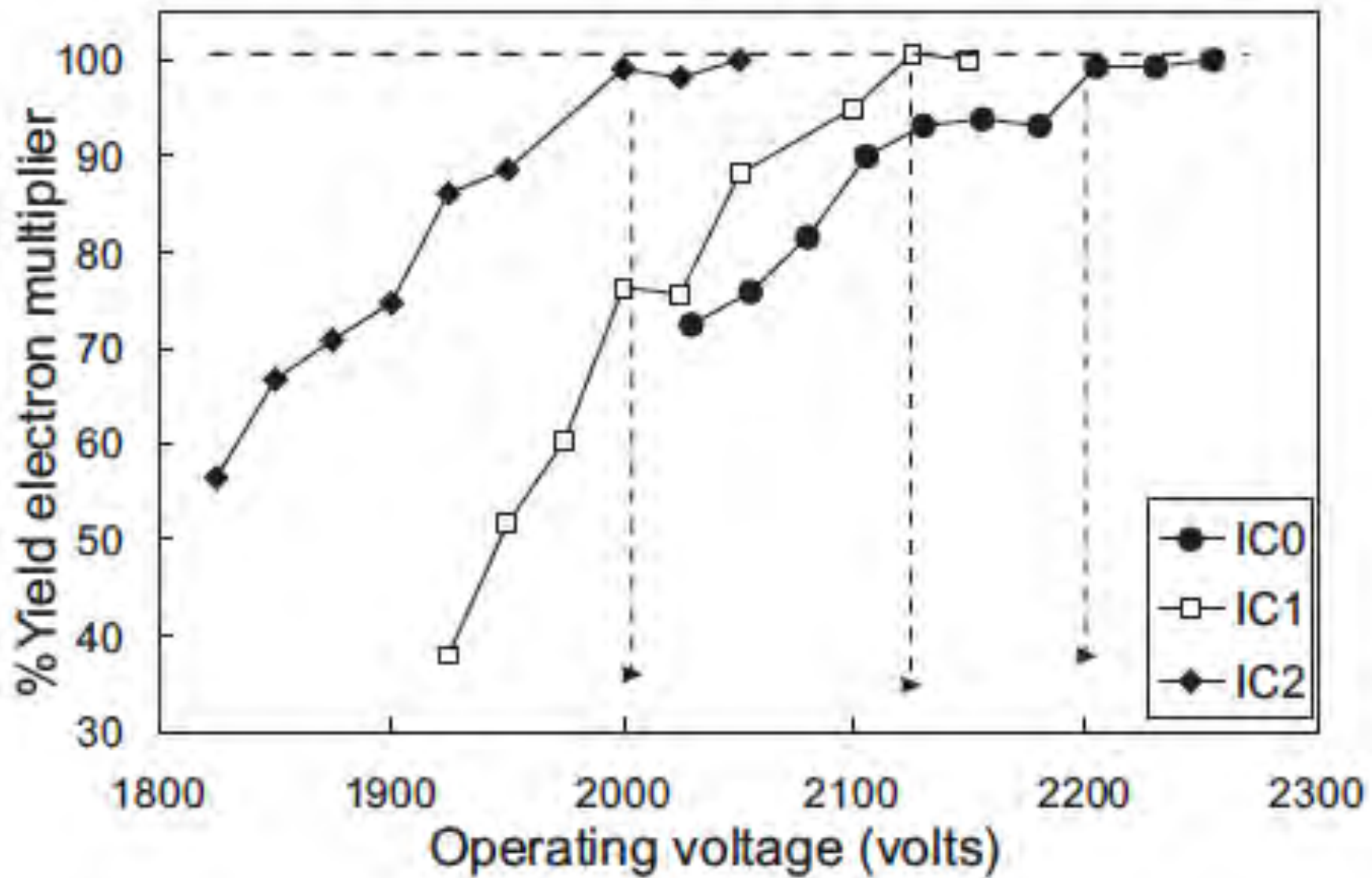
Magnet delay time (s):

Options:

Centre each Block

Zero each cycle

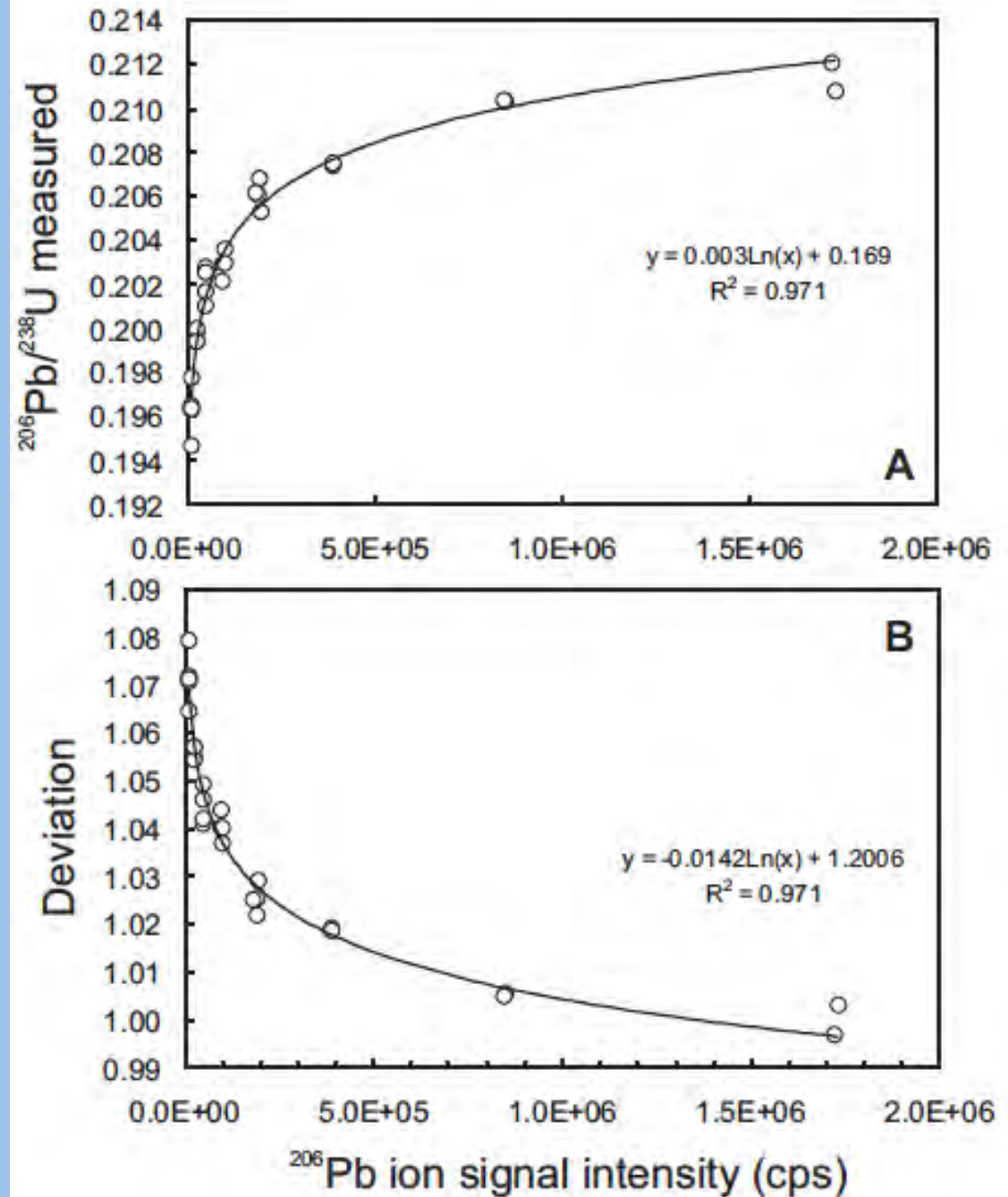
Sit on set (Delta M)



Simonetti et al. (2008)

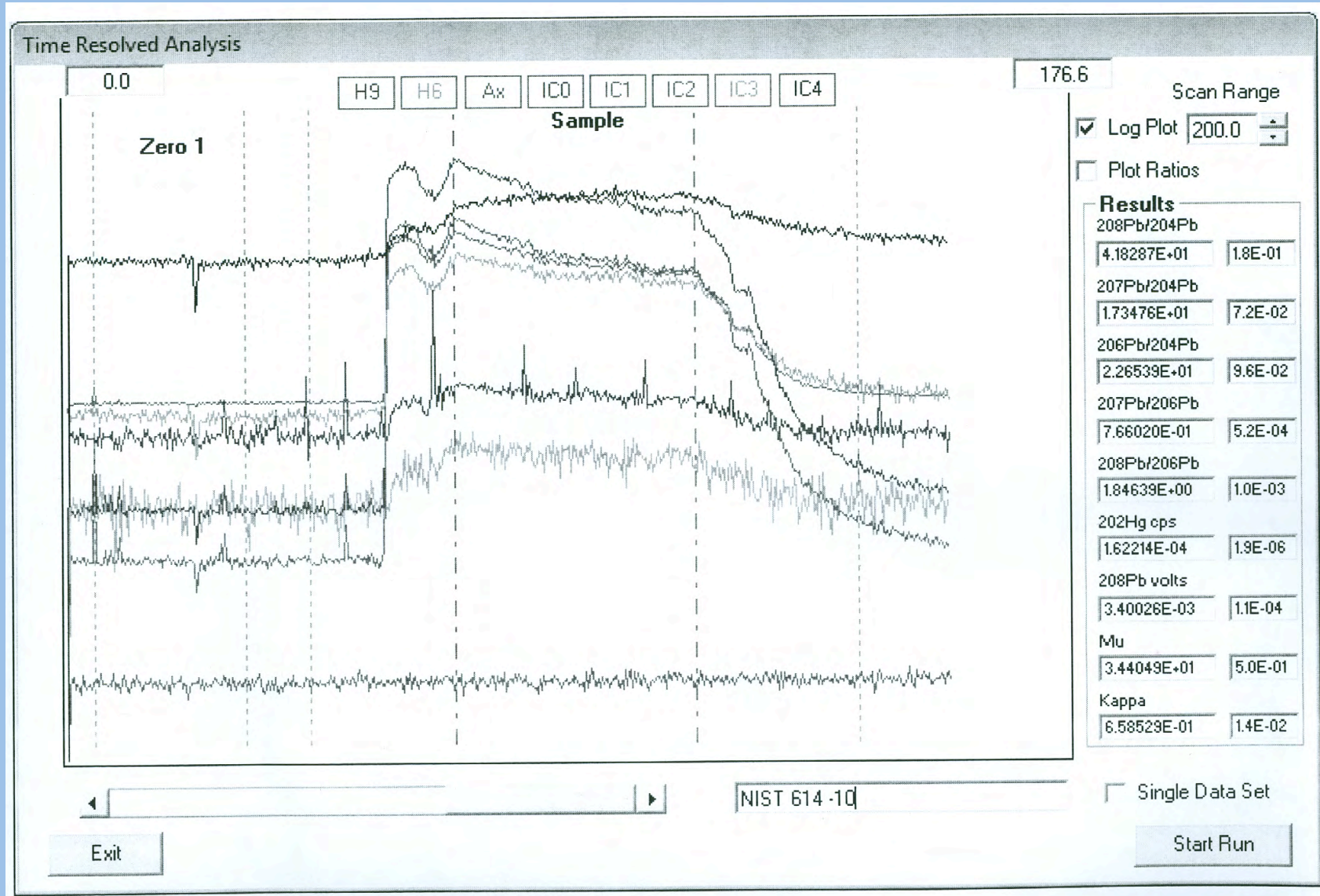


# Faraday – ion counter calibration



Simonetti et al. (2008)

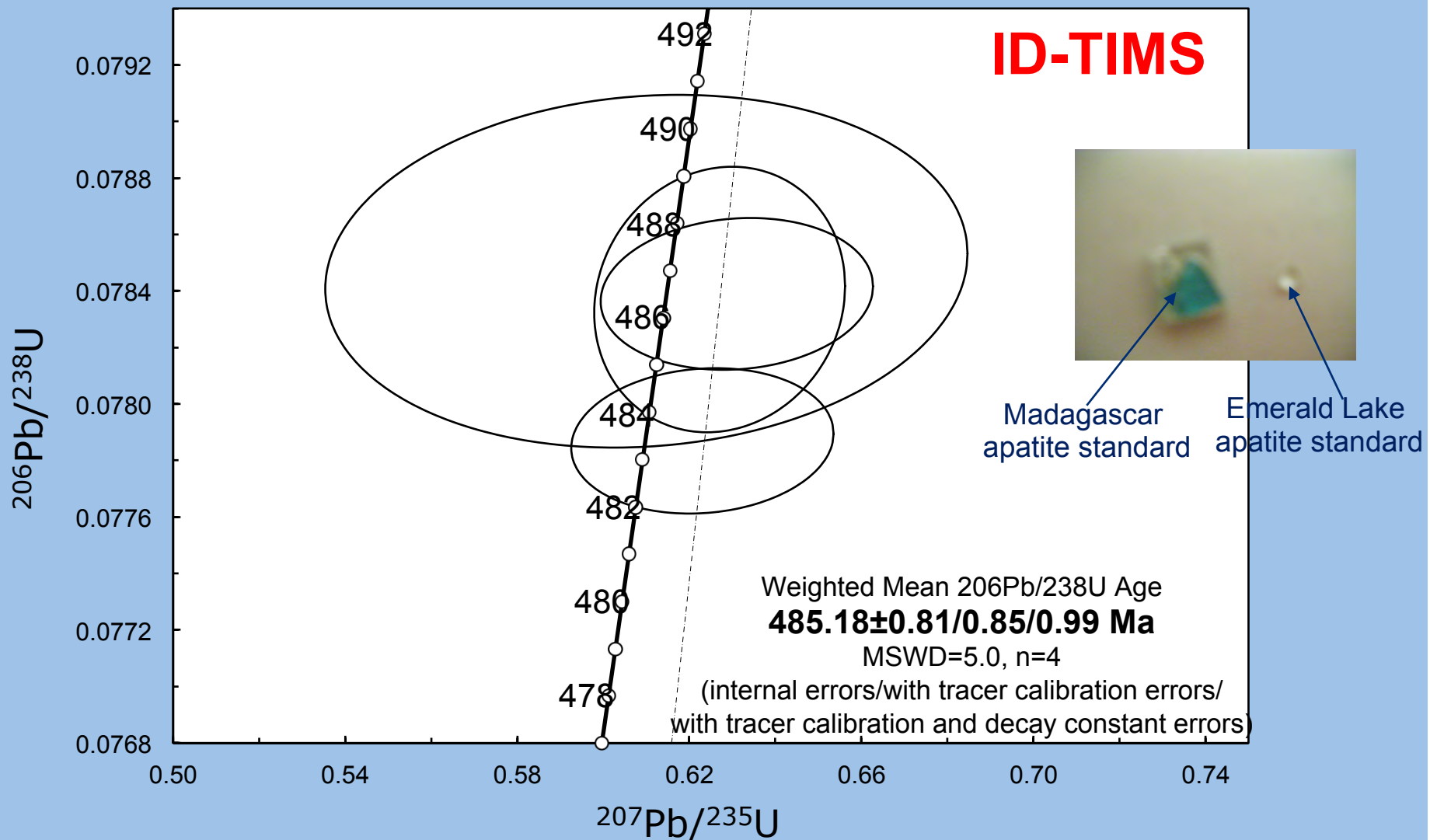
# Time-Resolved Analysis (TRA) Software – NuPlasma II



# In-situ common Pb – Faradays

- Samples containing more abundant Pb contents, typically >10 ppm
- Lots of flexibility for the cup configuration, i.e. more Faraday collectors available than needed
- The instrumental mass bias can be corrected using simultaneous aspiration of Tl (via desolvationg nebuliser), or using the “Standard-Sample” bracketing technique

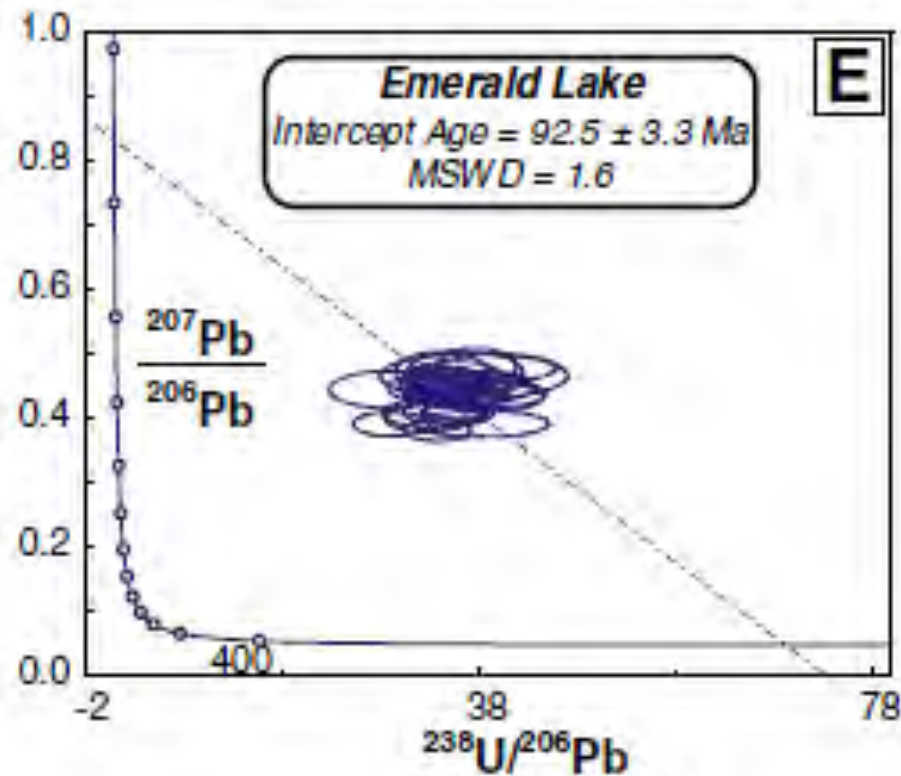
# Madagascar apatite standard



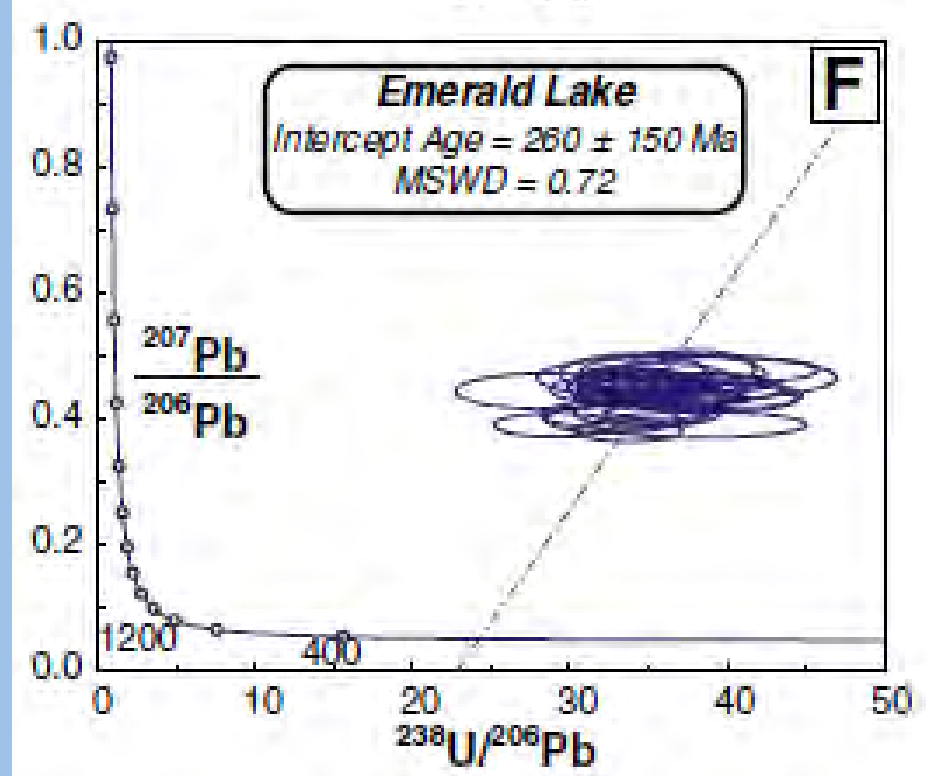
The apatite standard **was supplied** by Stuart N. Thomson, University of Arizona

# Emerald Lake Apatite – *Memorial University (Chew et al., 2011)*

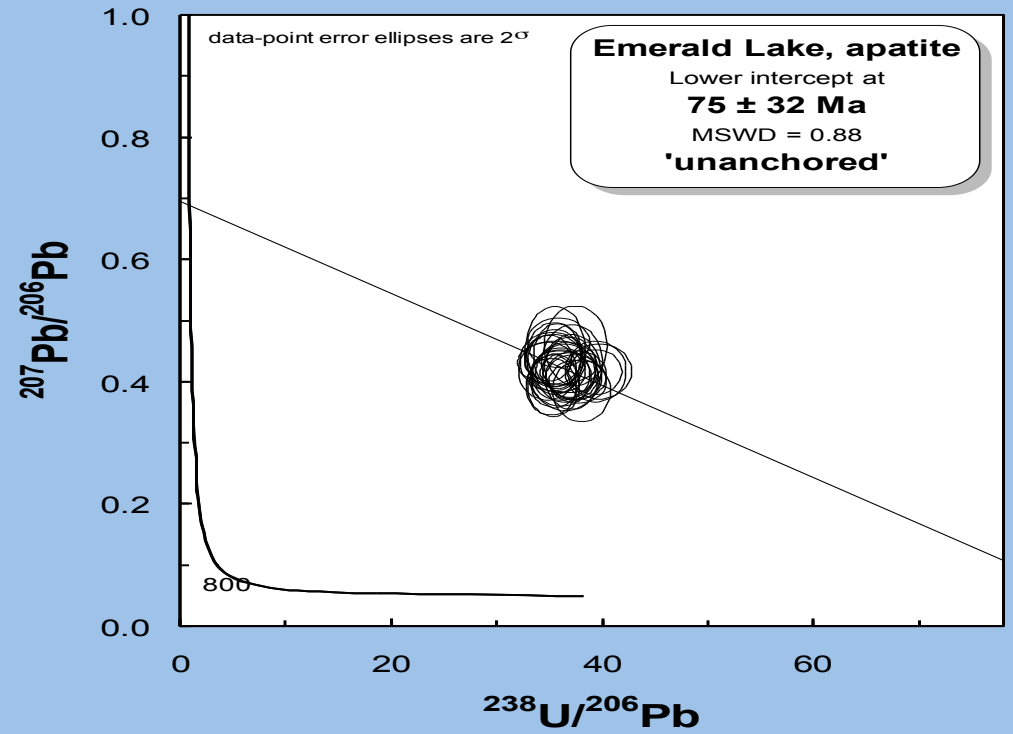
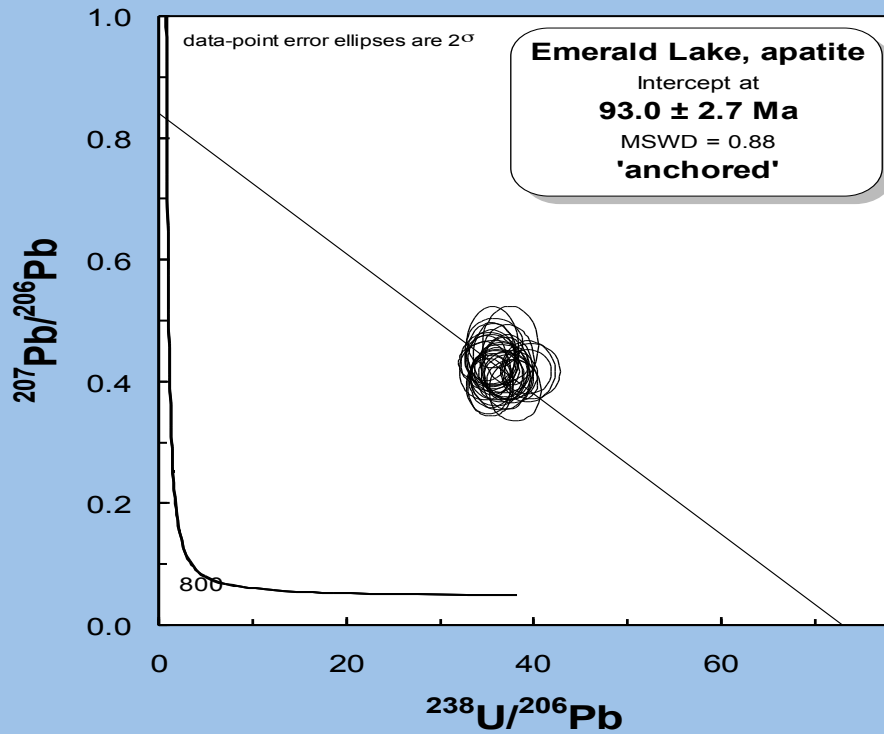
‘Anchored’



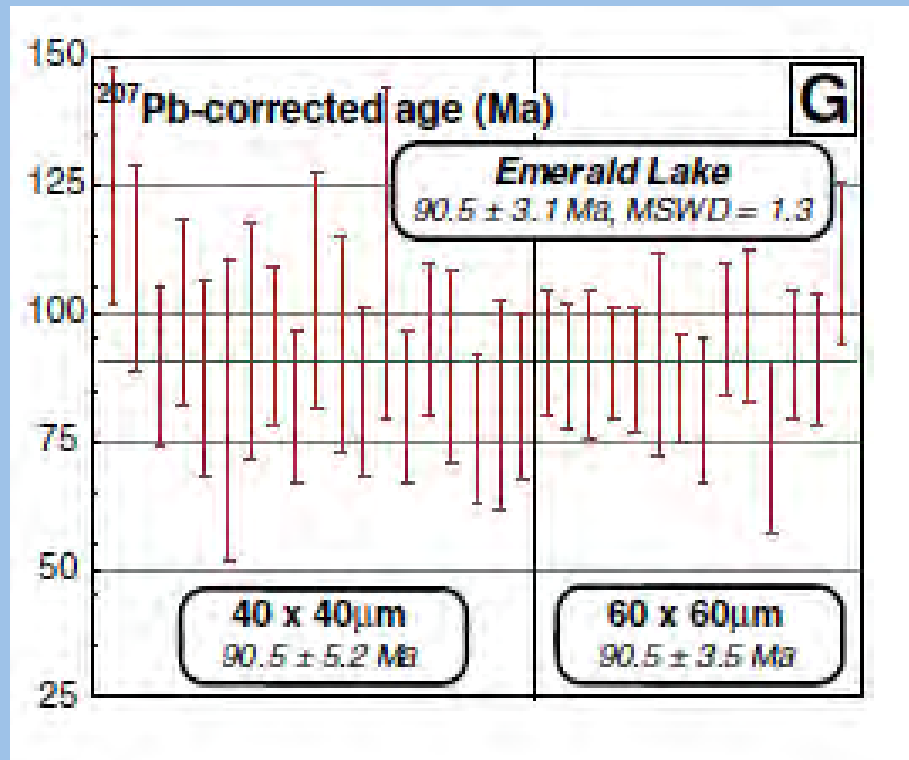
‘Unanchored’



# Emerald Lake Apatite – *University of Notre Dame*

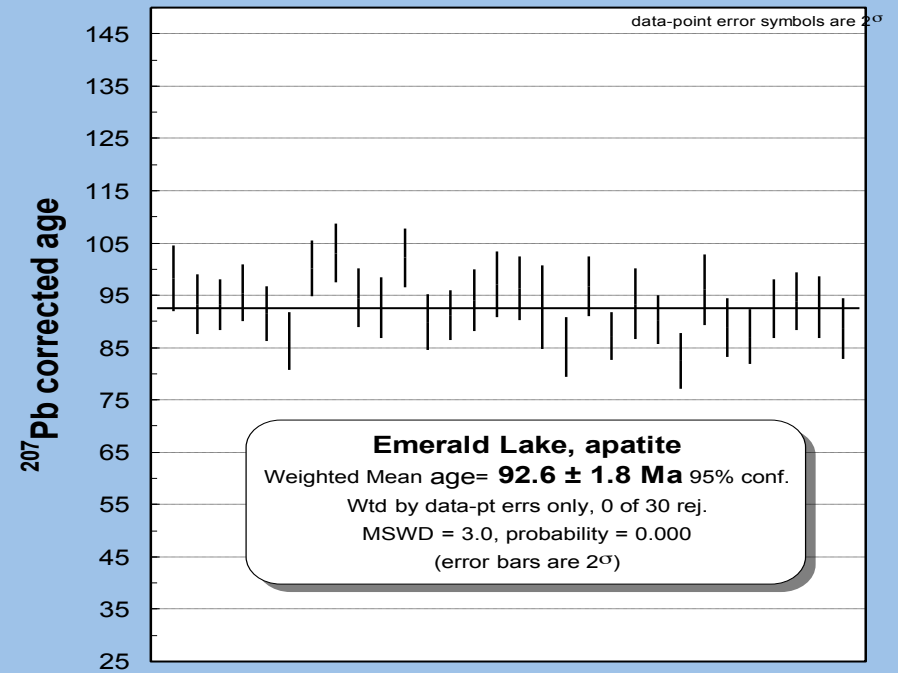


## Memorial University



Chew et al. (2011)

## University of Notre Dame





**CASE STUDY-**

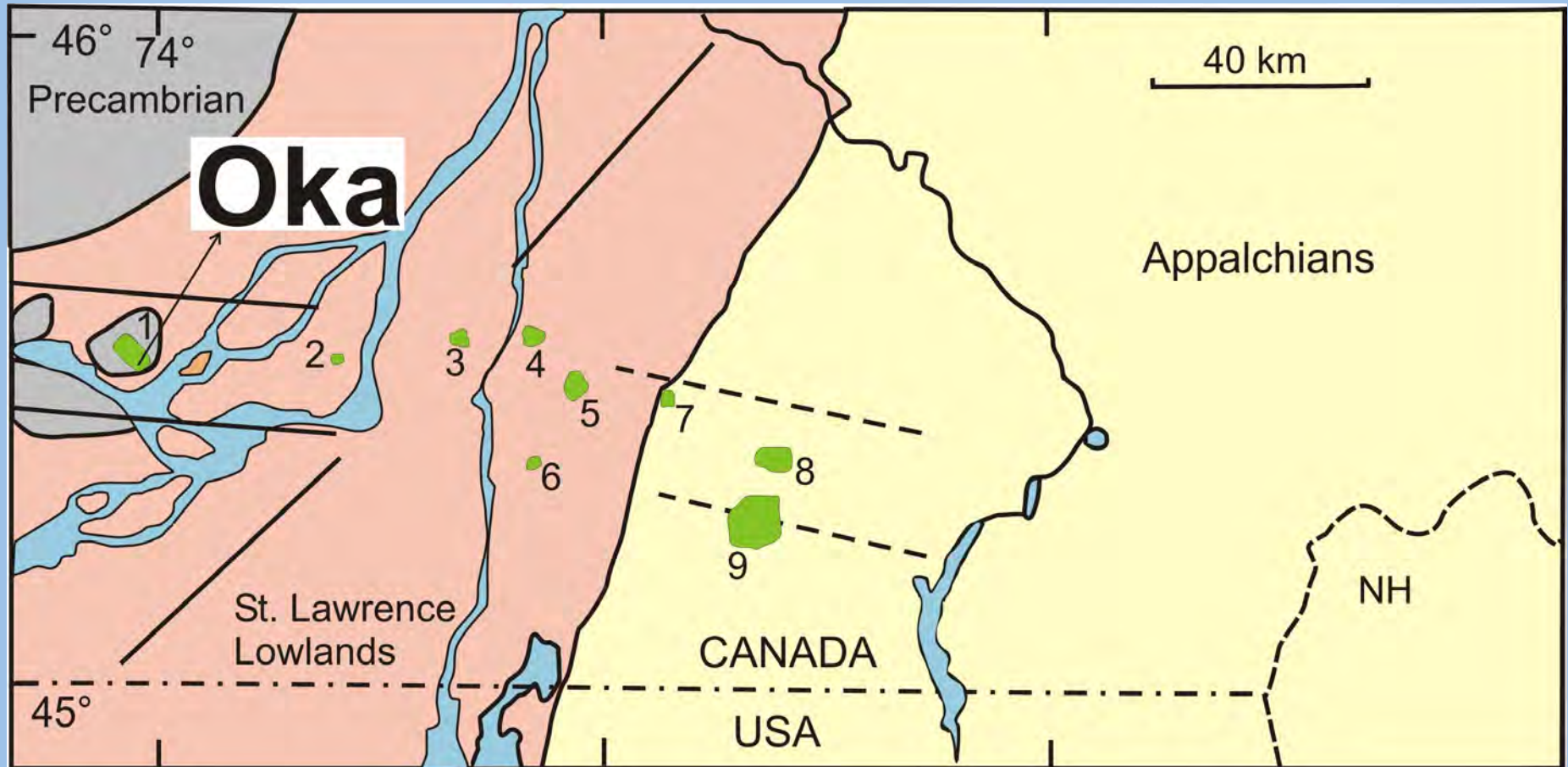
**OKA CARBONATITE COMPLEX, QUEBEC (CANADA)**



# Monteregian Igneous Province (MIP) – Plume relationship?

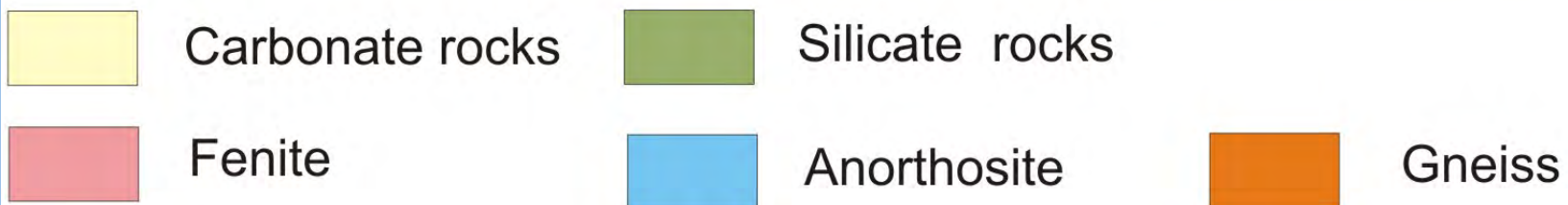
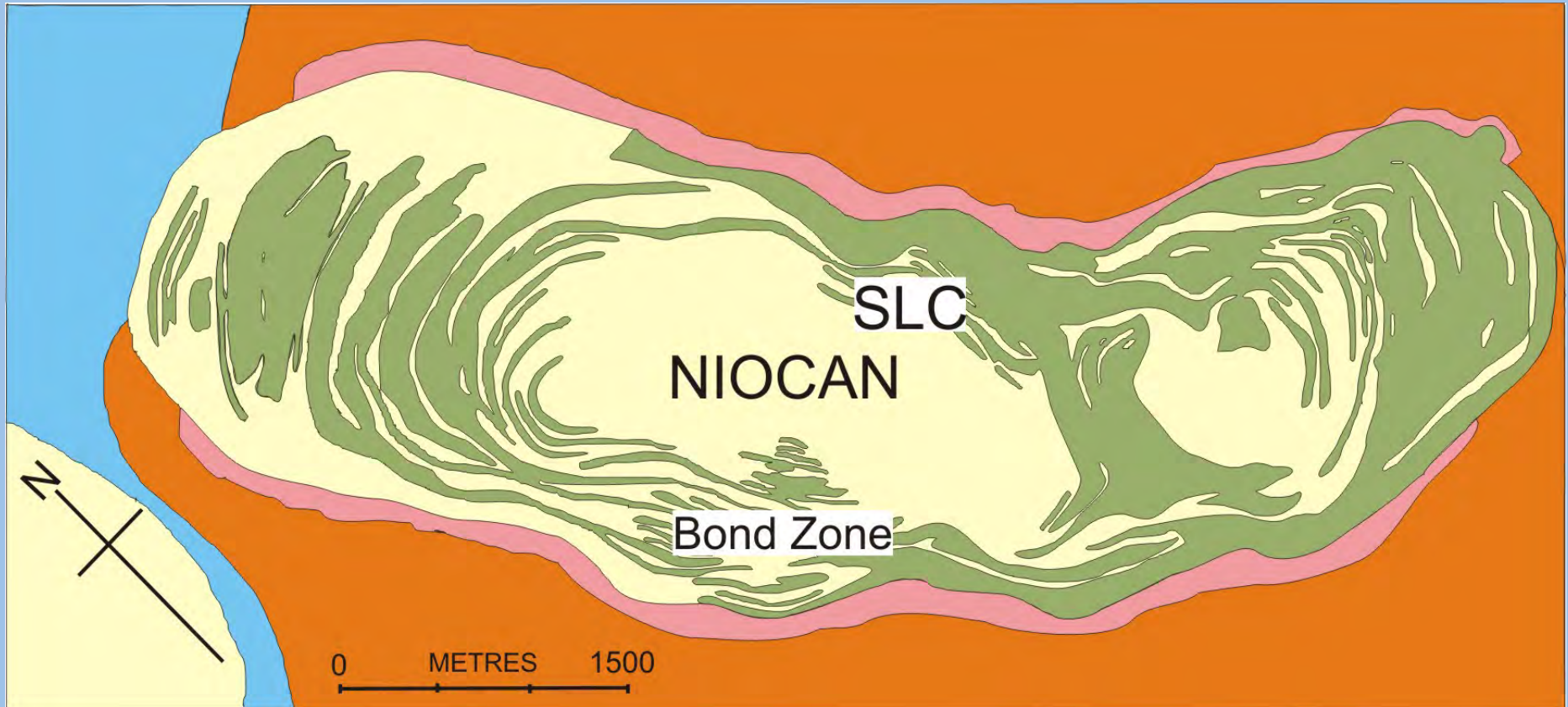


# Monteregian Igneous Province (MIP)



1- Oka; 2-Royal; 3-Bruno; 4-St. Hilaire; 5-Rougemont; 6-Johnson; 7-Yamaska; 8-Shefford; 9-Brome;

# Oka Carbonatite Complex





# Field Relations



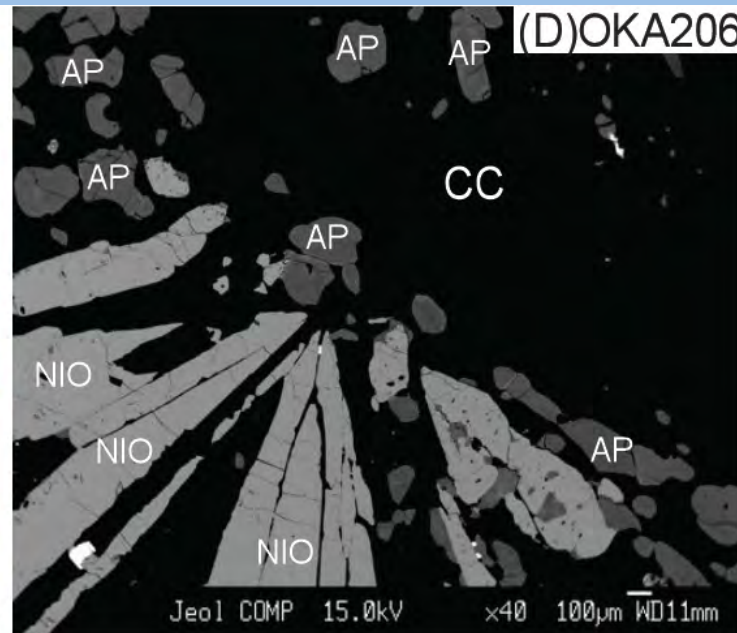
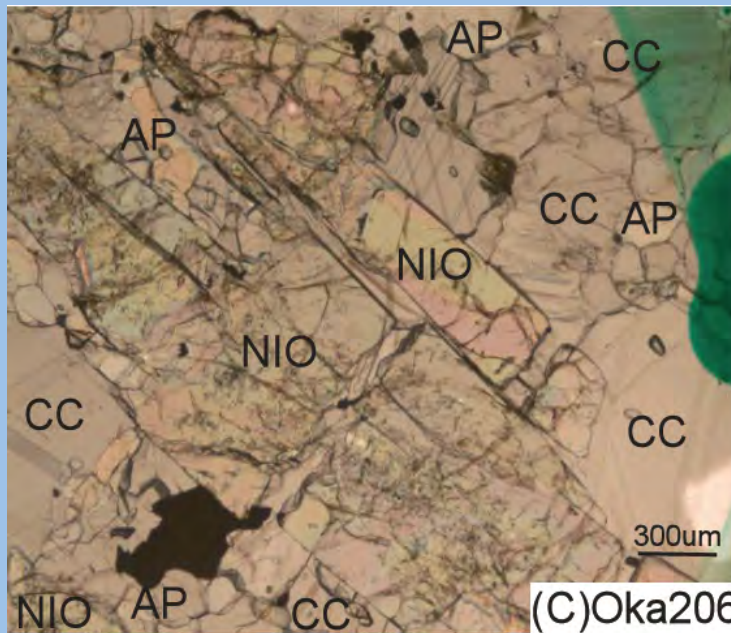
Carbonatite & ijolite breccia



# Niocalite?



Source: Webminerals



Chen et al. (in press, *Can. Mineral.*)

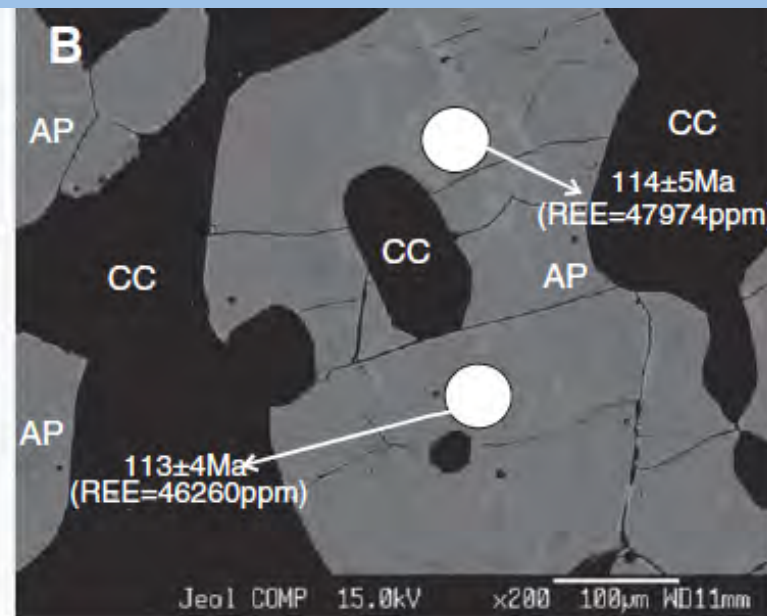
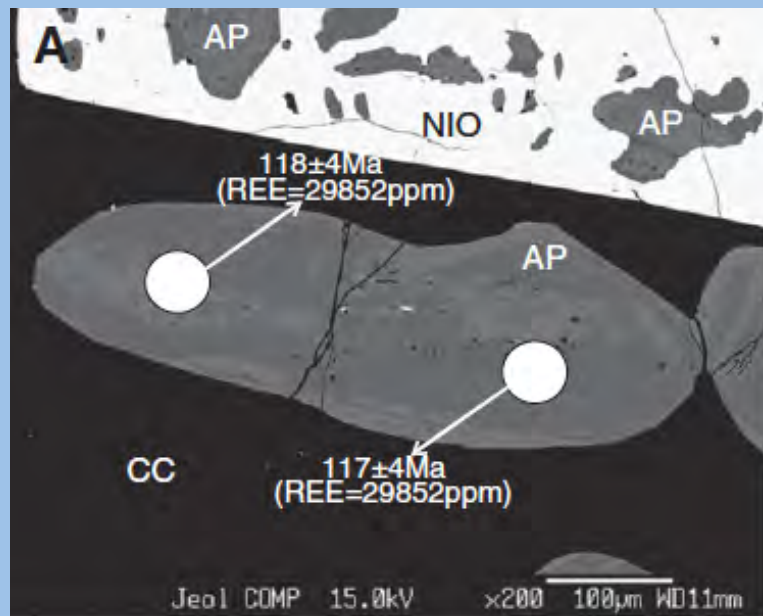
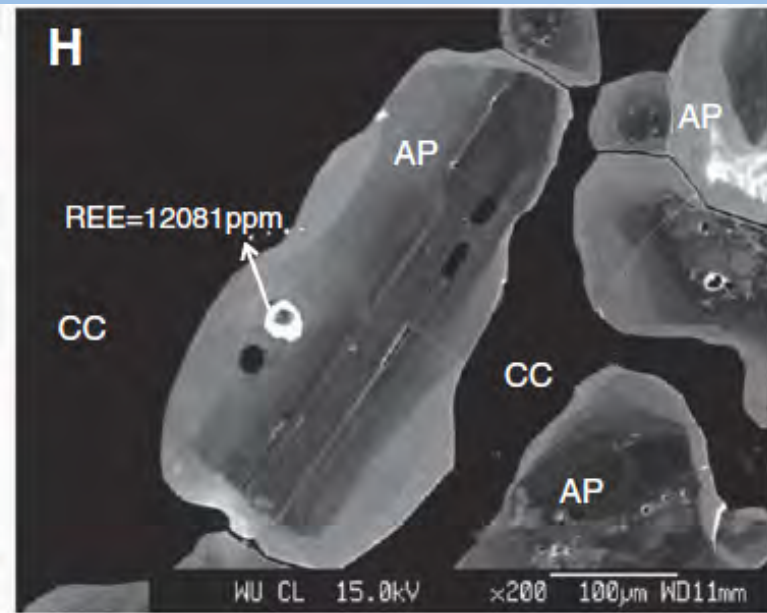
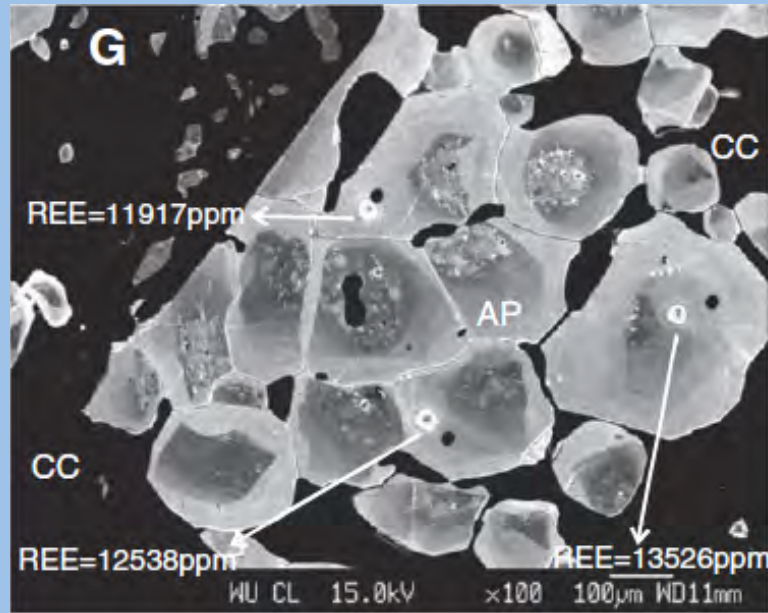
# OBJECTIVES

- Conduct a detailed chemical, isotopic and geochronological investigation of the Oka carbonatite complex using constituent and accessory minerals at high spatial resolution – **outline petrogenetic history**
- Mantle sources – **plume involvement?**

# Methodology

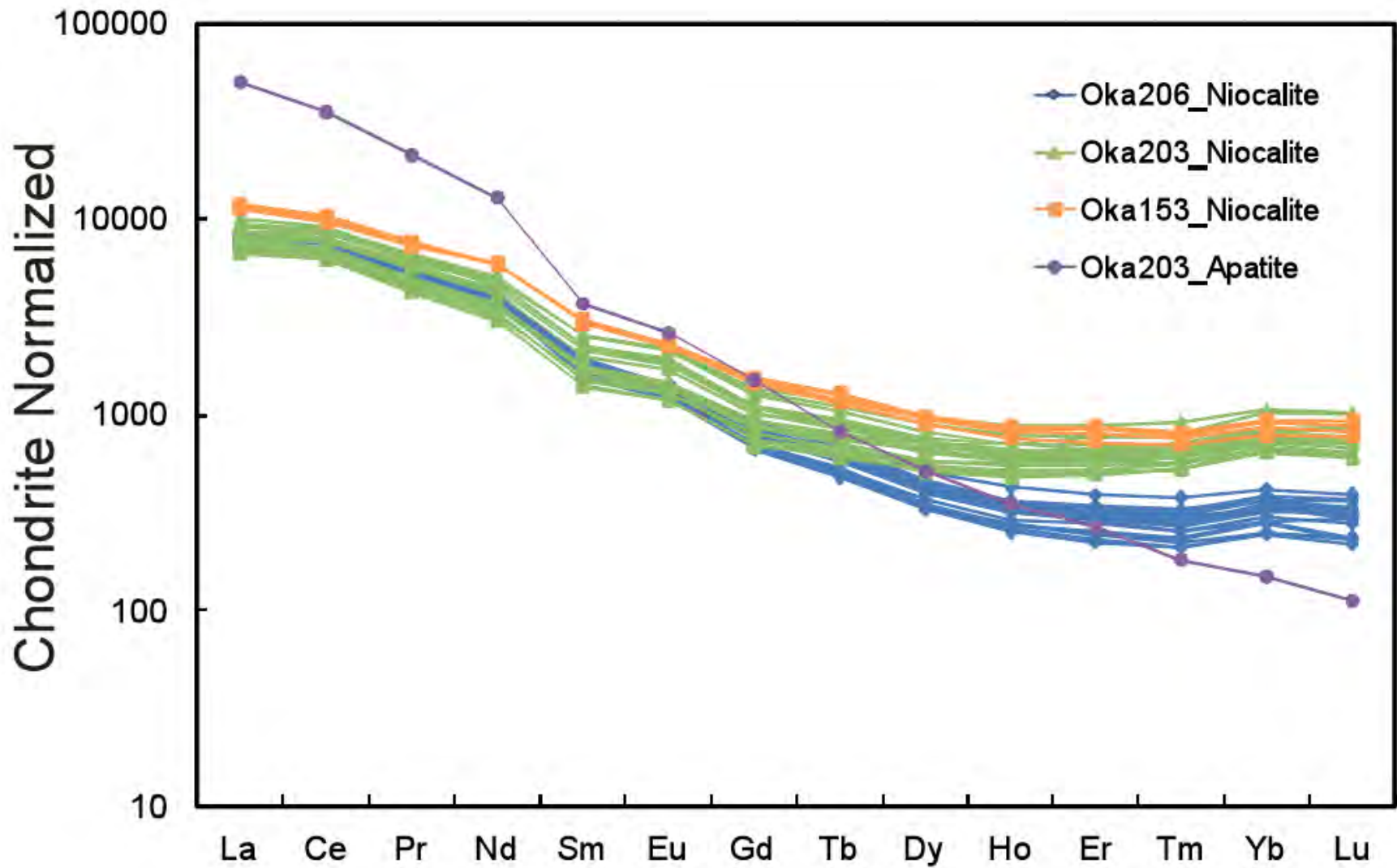
- Major element chemistry & cathodoluminescence imaging of *apatite*, *calcite*, *perovskite*, and *niocalite* conducted by Electron Microprobe (EMP) analysis
- In-situ trace element chemistry obtained by LA-HR-ICP-MS (Element2)
- In-situ Sr, Nd, Pb and U-Pb age dating conducted by LA-MC-ICP-MS (NuPlasmas) & HR-ICP-MS (Element2)

# Apatite - Major & Trace Element Chemistry



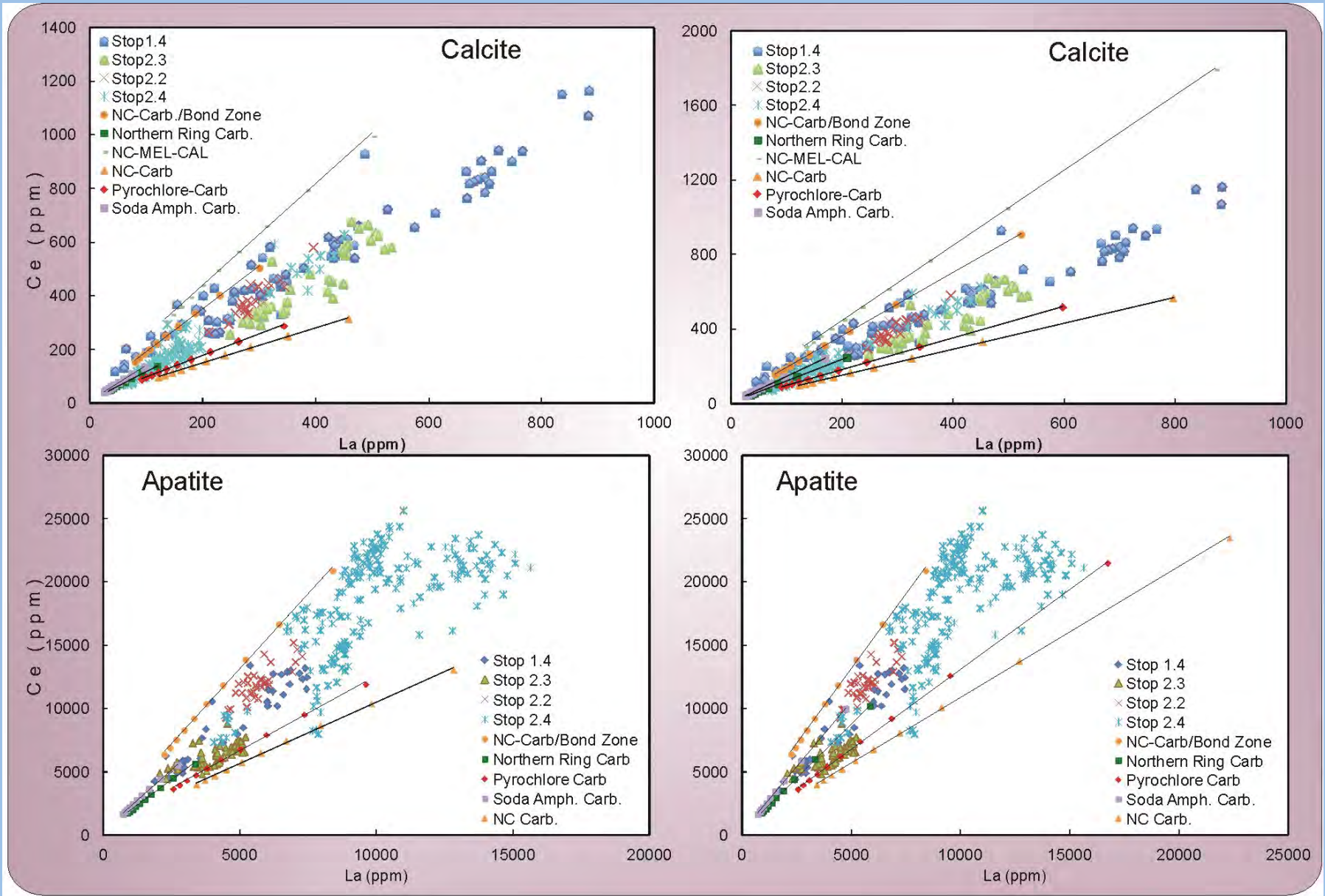


# Trace Element Chemistry – Apatite & Niocalite



Chen et al. (in press, *Can. Mineral.*)

# Equilibrium & Fractional Crystallization Modeling

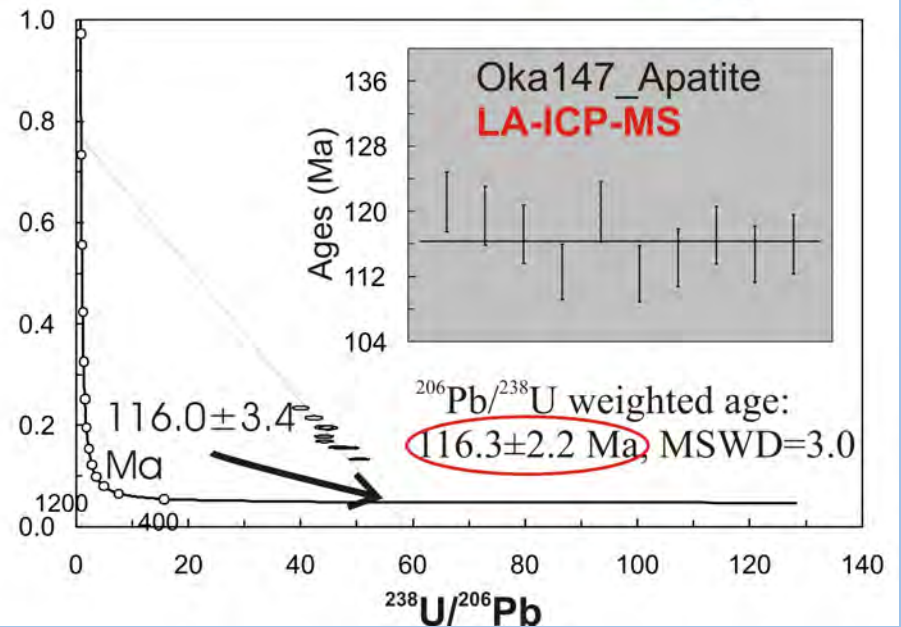
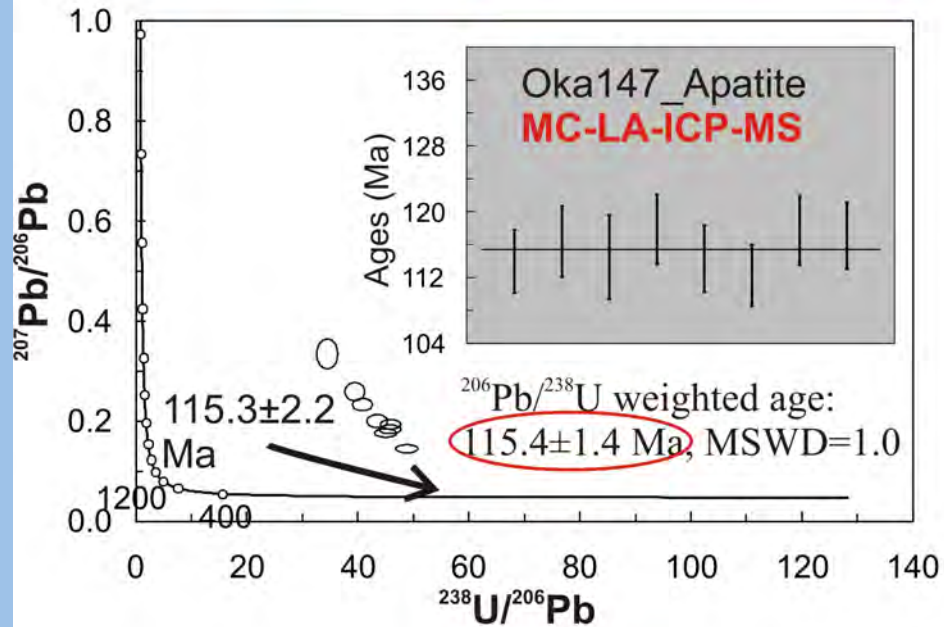


# U-Pb age dating

Nu Plasma II  
Multicollector  
ICP-MS

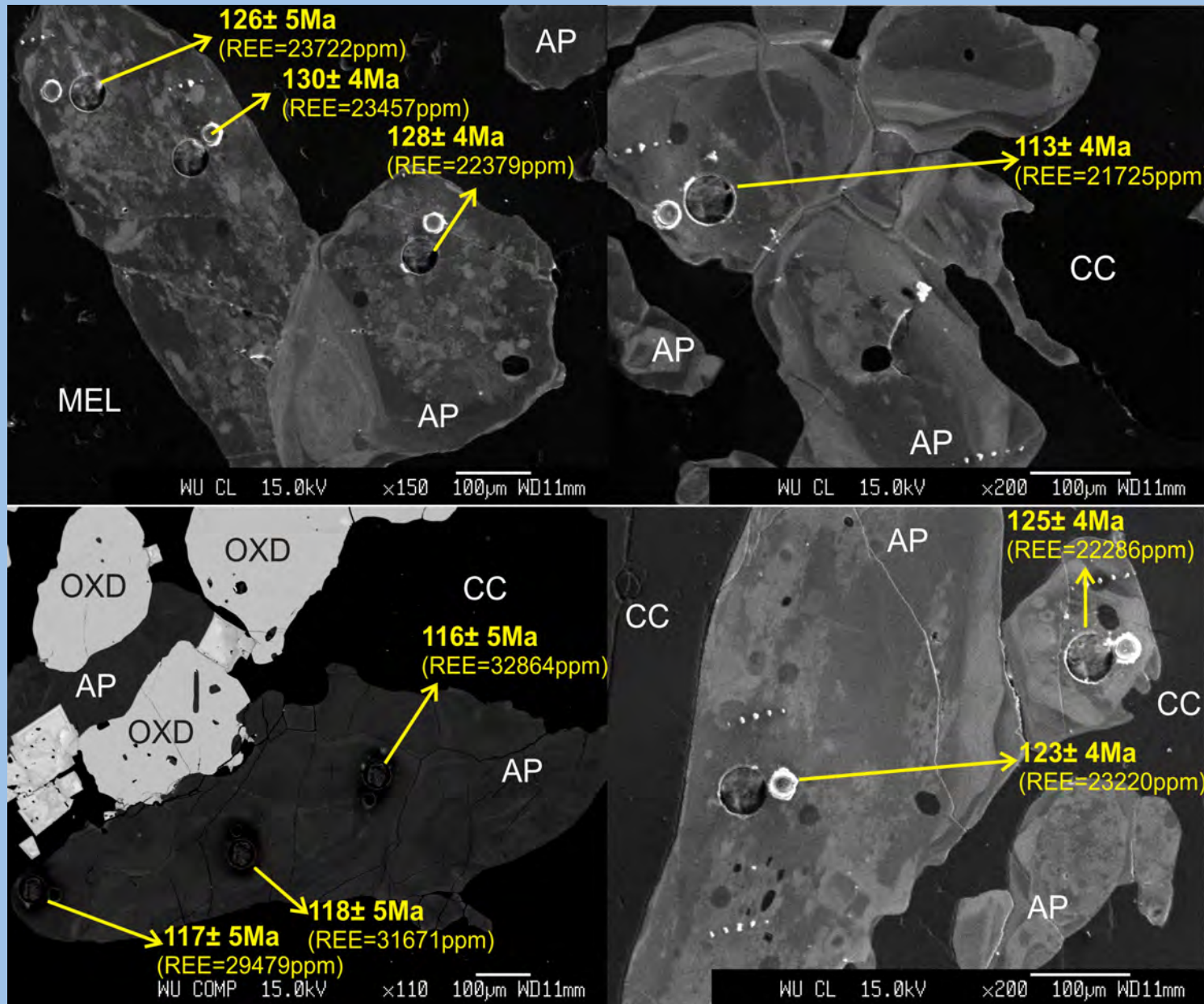


Thermo Finnigan  
Element2 ICP-MS

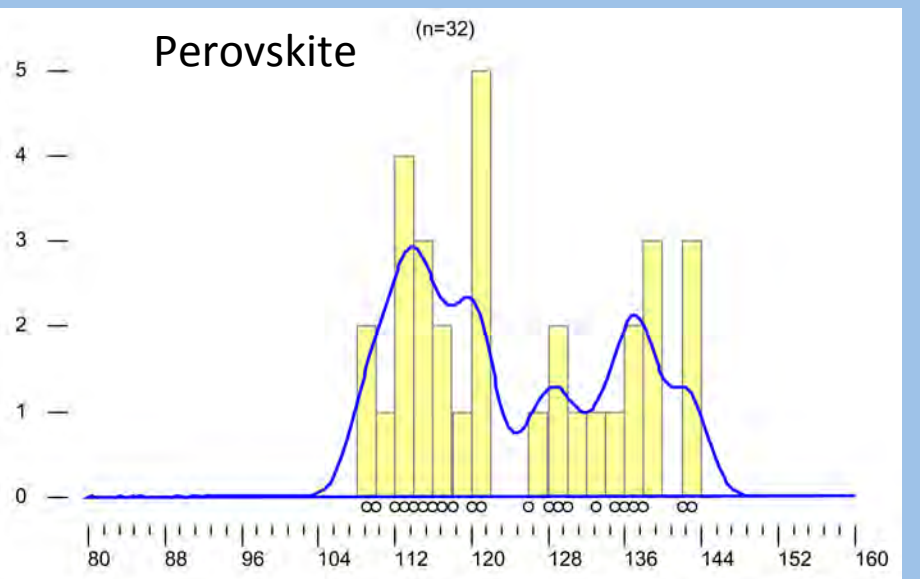
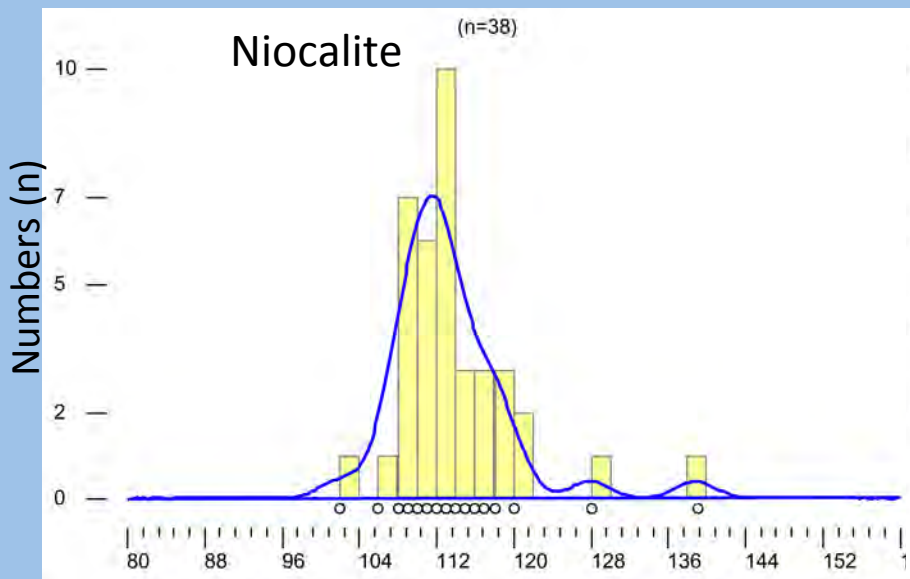
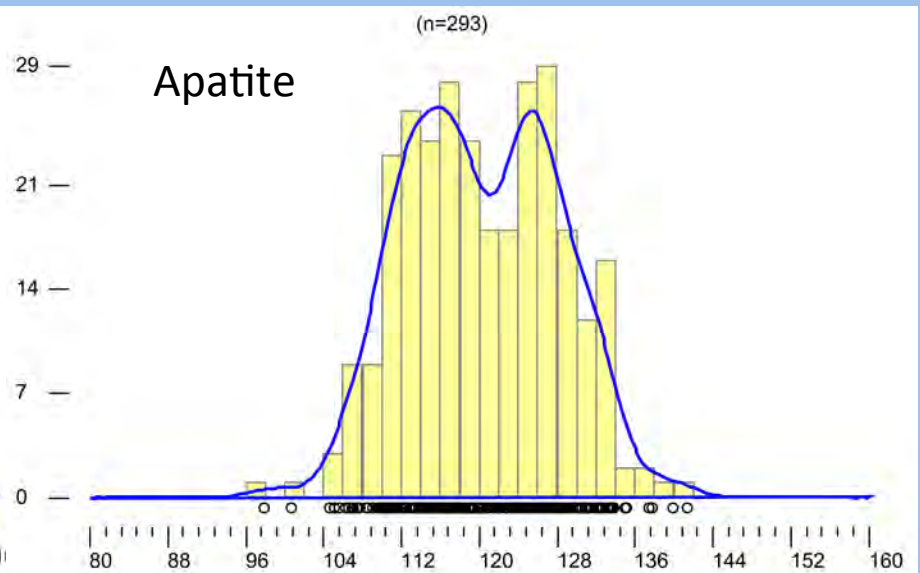
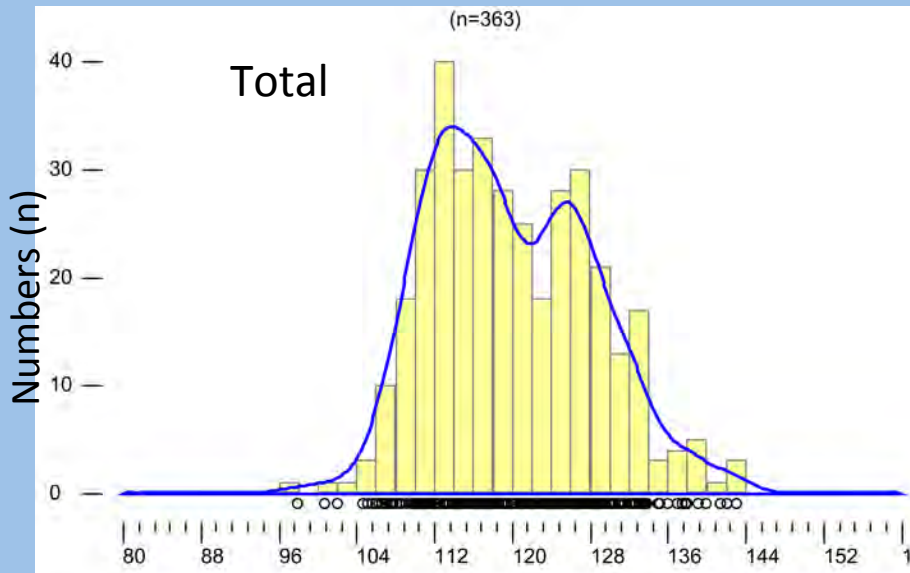




# U-Pb Age vs. Chemistry



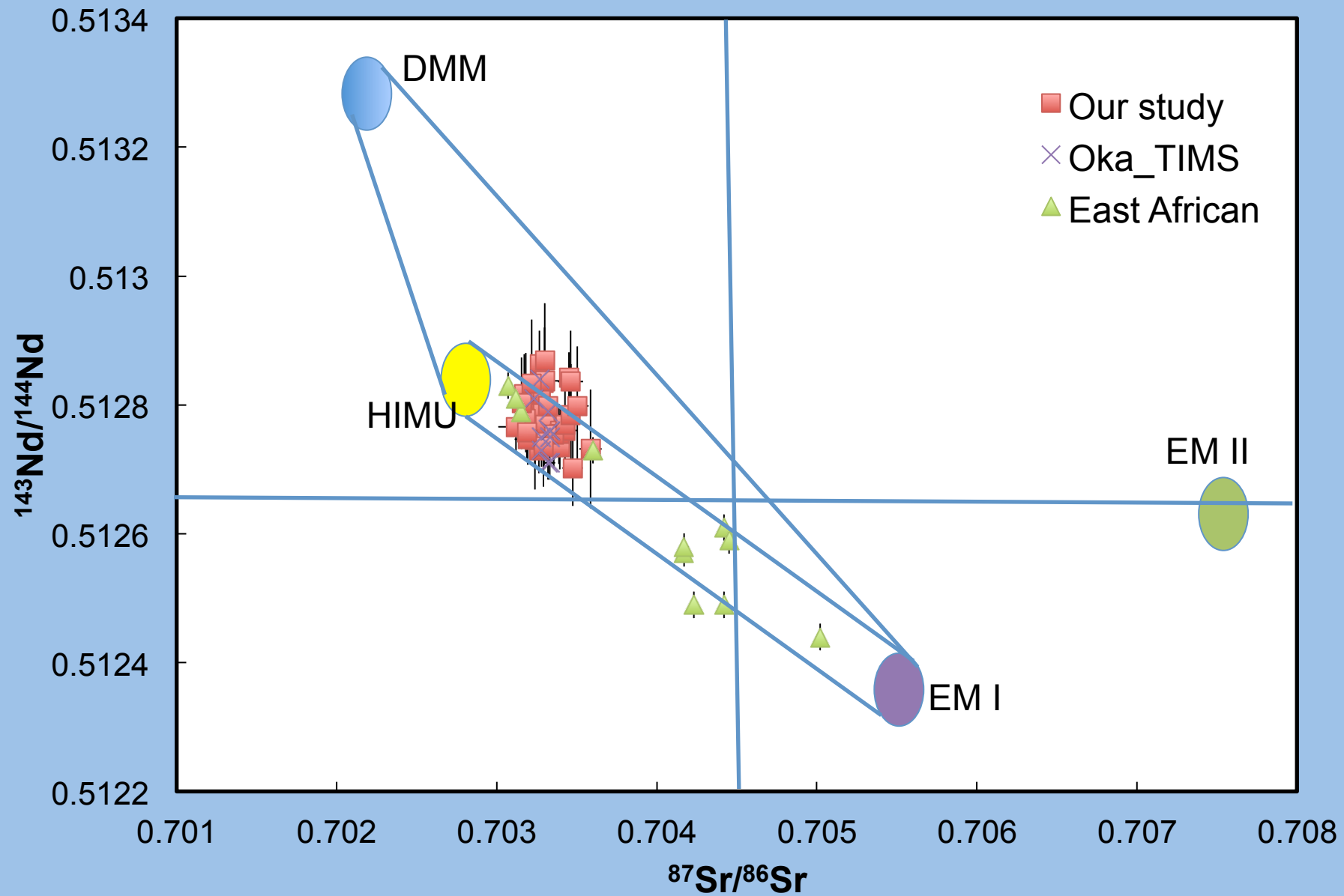
Chen & Simonetti (2013, *Chem. Geol.*)



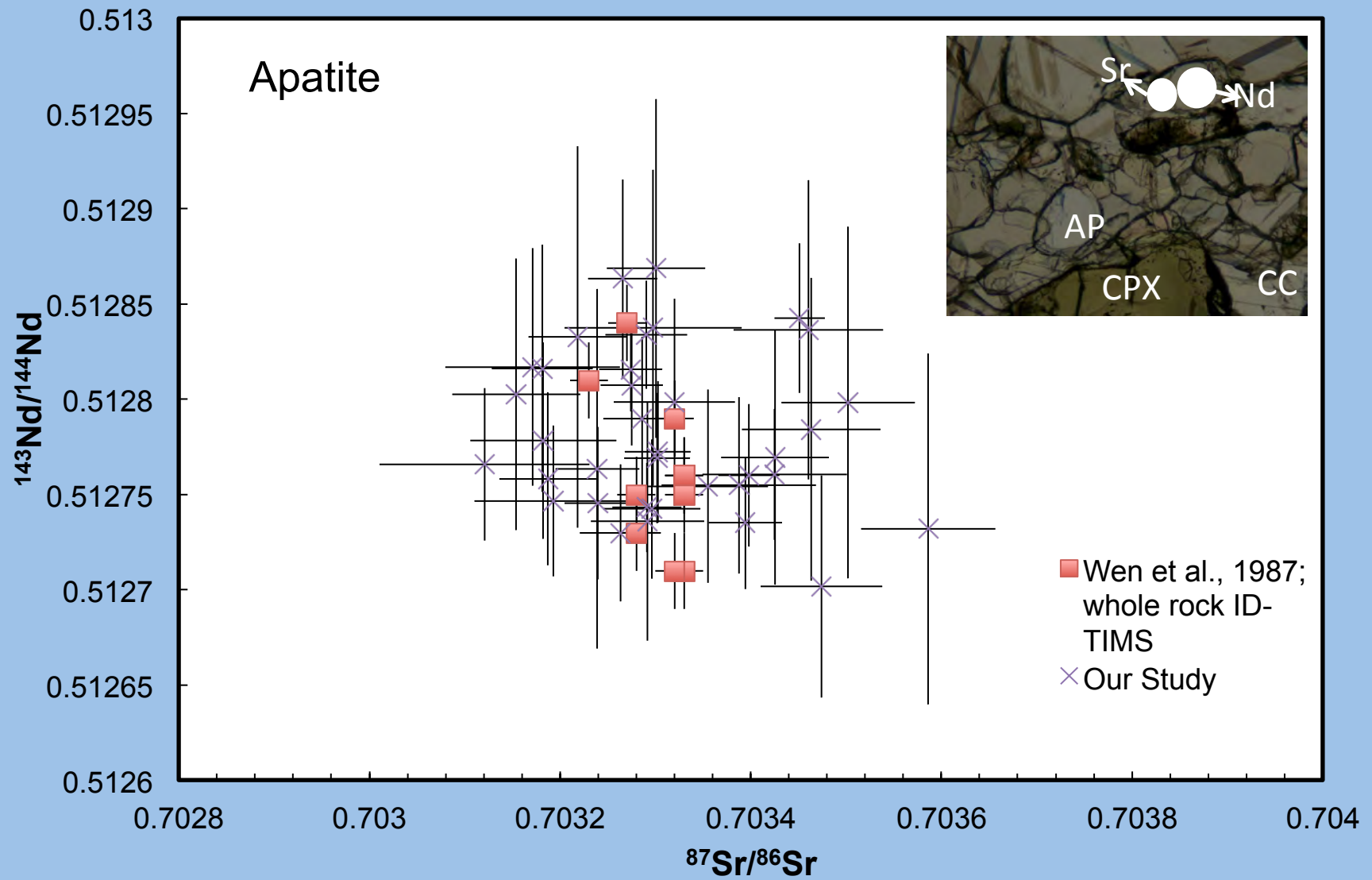
$^{206}\text{Pb}/^{238}\text{U}$  age (Ma)

$^{206}\text{Pb}/^{238}\text{U}$  age (Ma)

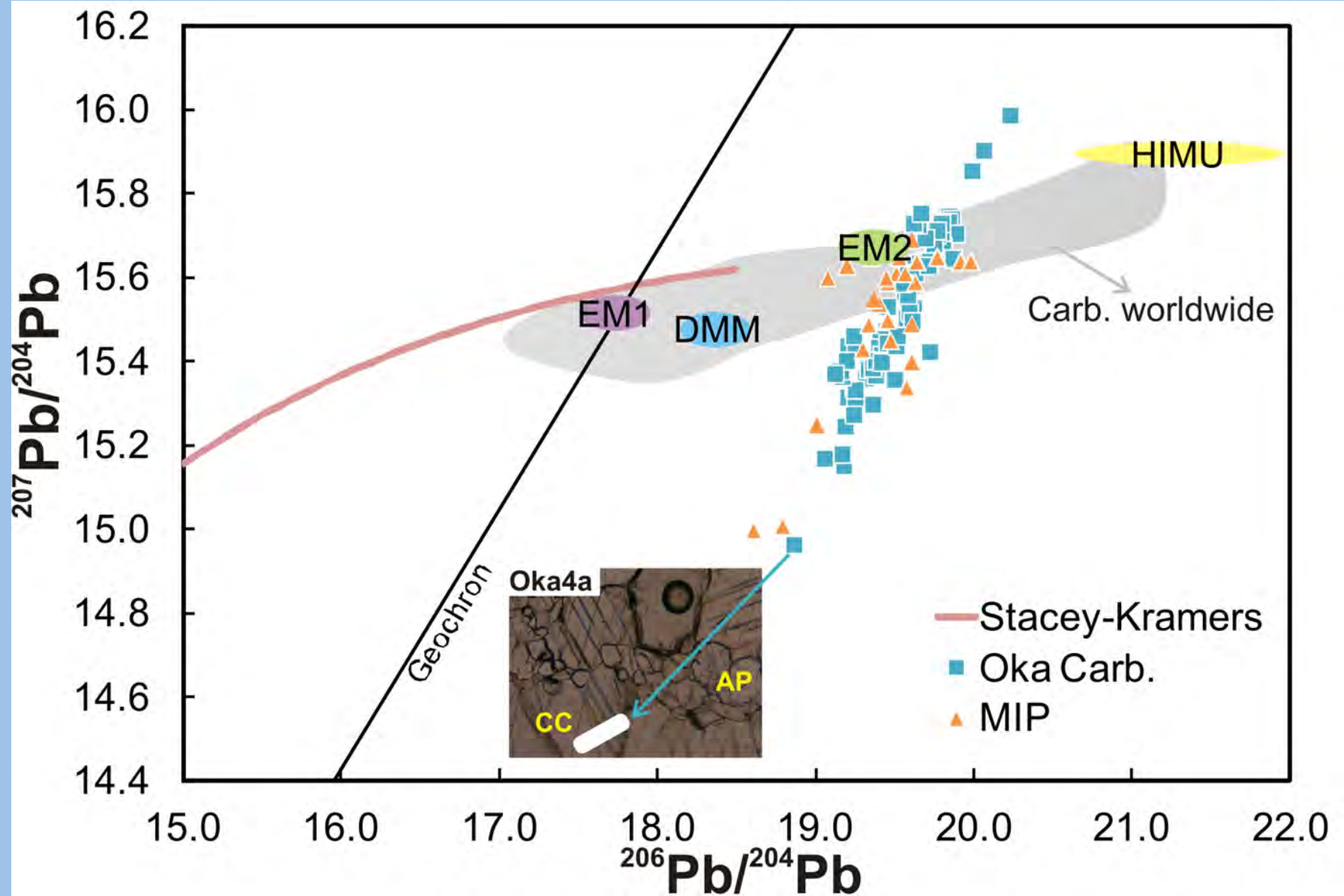
# Nd vs. Sr isotopes



# Nd vs. Sr isotopes

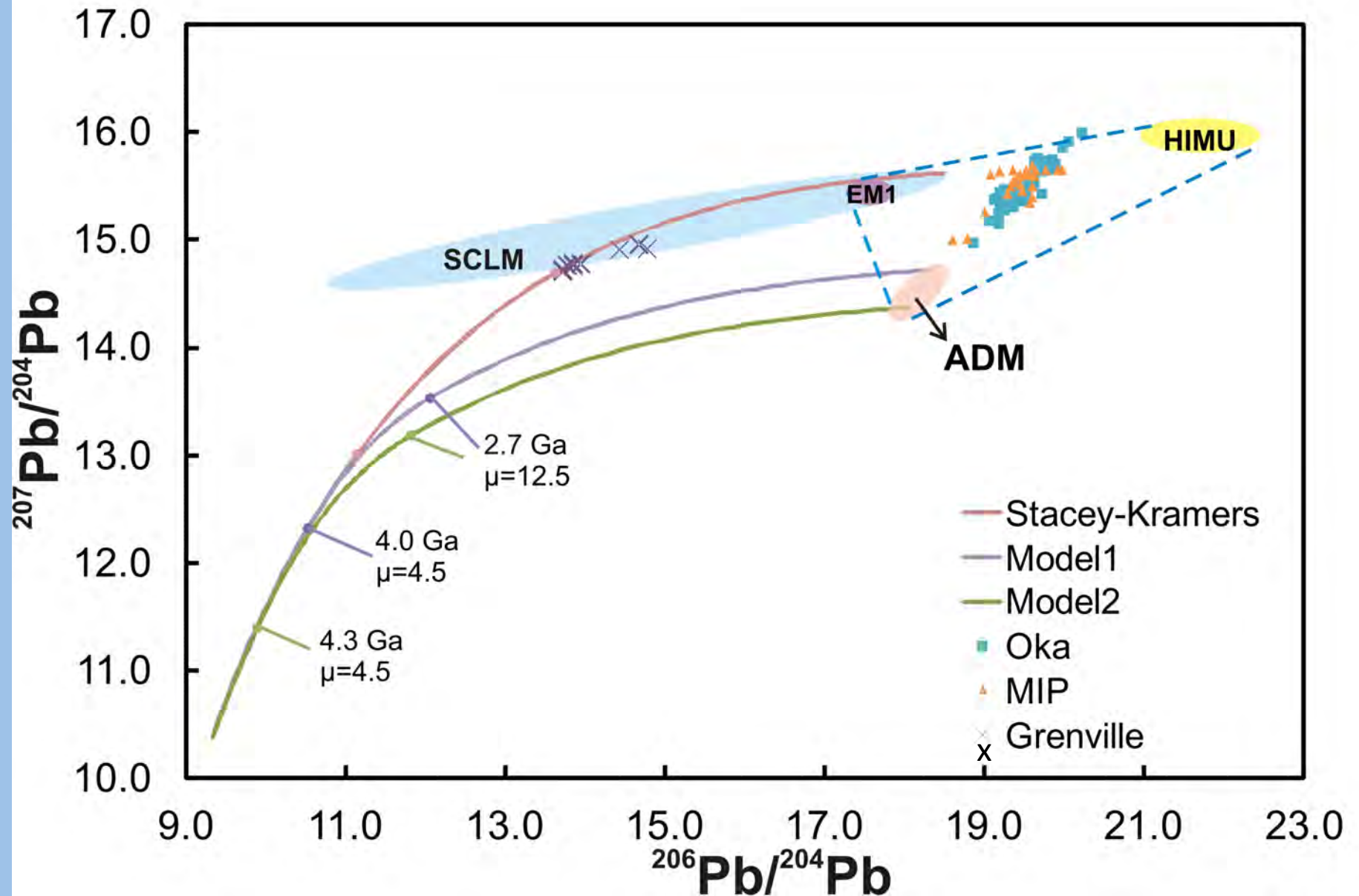


# Pb isotopes

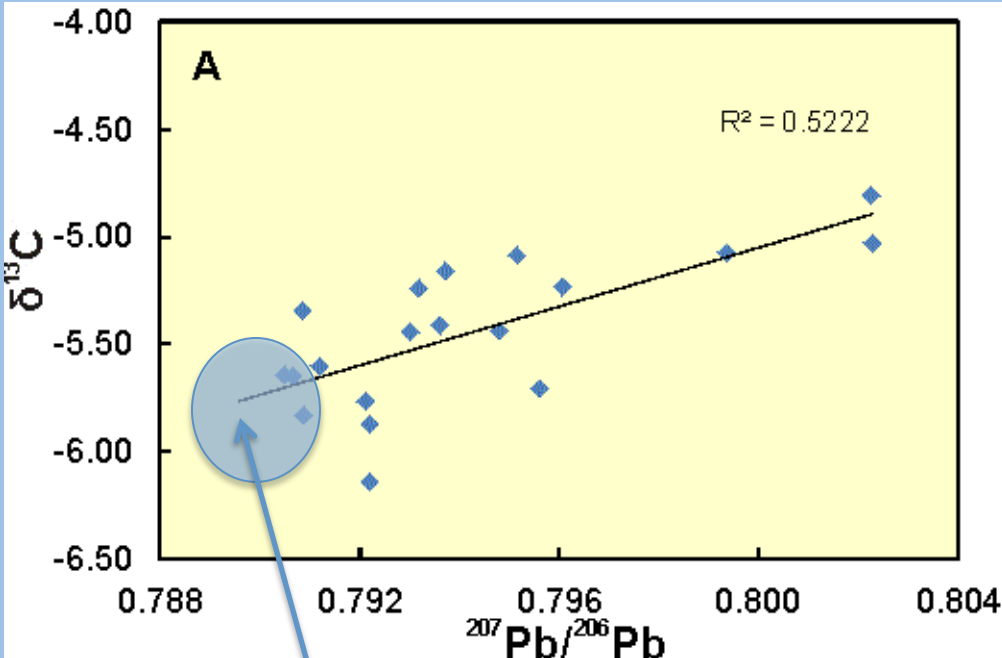




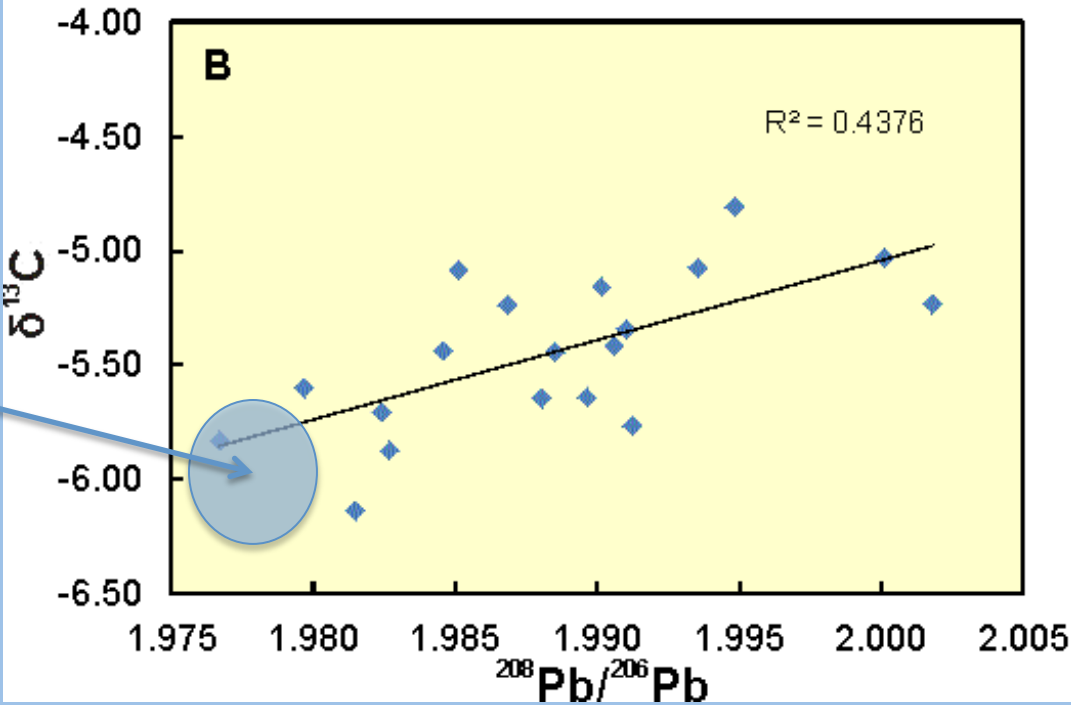
# Pb isotopes – modeling

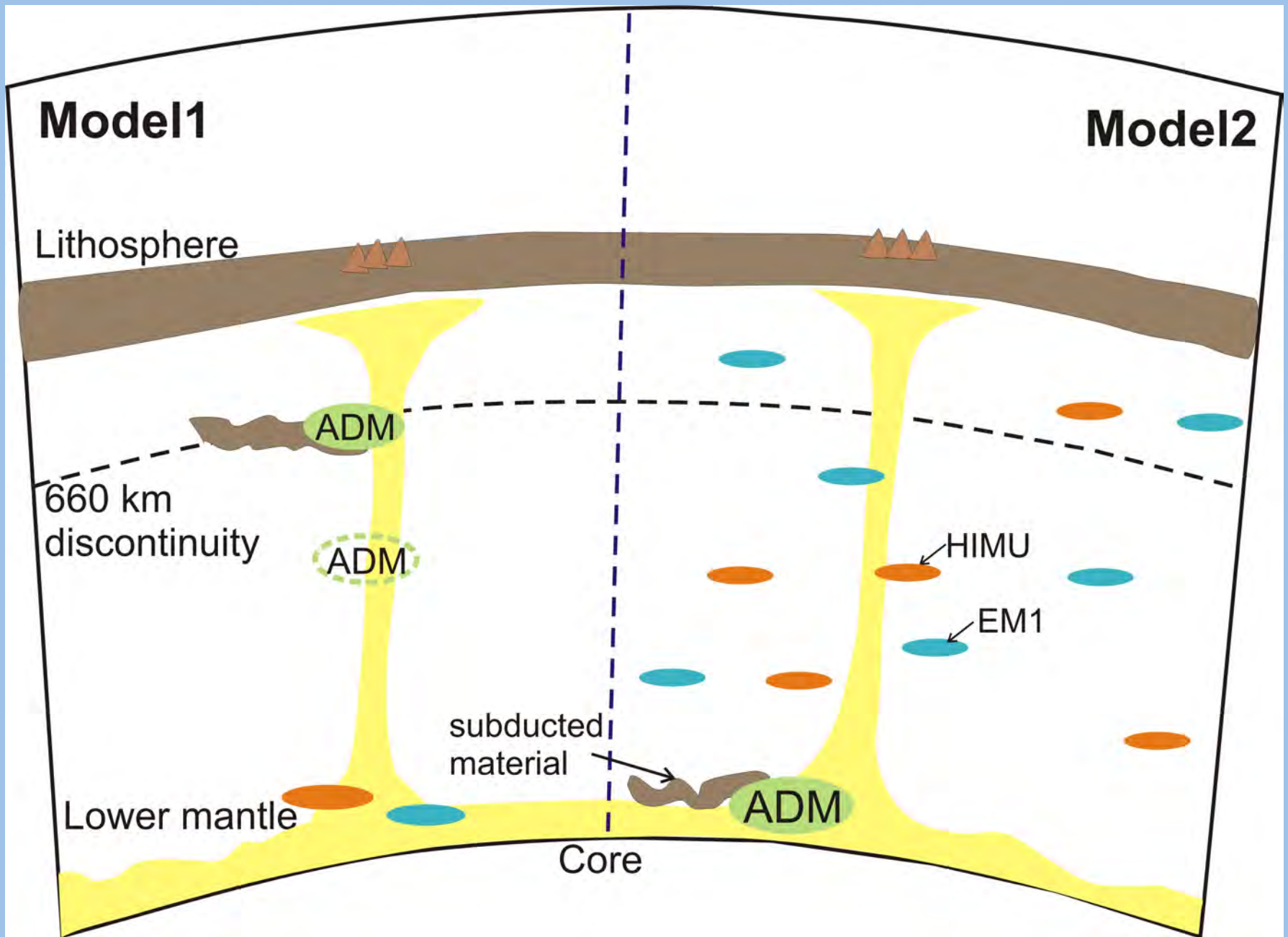


# Pb vs. Carbon isotopes



Inherent mantle heterogeneity  
or  
Subducted component?





Chen & Simonetti (submitted, *Geology*)

# Conclusions

- Combined chemical and radiogenic isotope data indicate that Oka underwent a complex crystallization history involving repeated incursion of small volume melts – not related to **one** parental magma!
- What is the real meaning of **WHOLE ROCK** data??
- Radiogenic isotopes (and carbon) indicate derivation from multiple mantle sources – mantle plume with HIMU-EMI mixture? and presence of an **Ancient Depleted Mantle (ADM)**
- In-situ U-Pb ages indicate a protracted, **bimodal** crystallization history for Oka that spanned between **~127 Ma and ~115 Ma**, as indicated by results from all the accessory minerals studied here

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