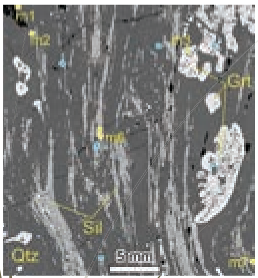
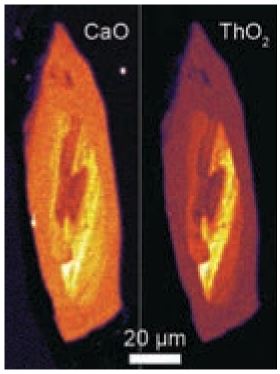
UMASS AMHERST ETH zürich

MAS

16th European Workshop
Trondheim, Norway
23 May 2019



U-Th-Pb_{total} dating of REE-phosphate by electron microprobe: review and progress



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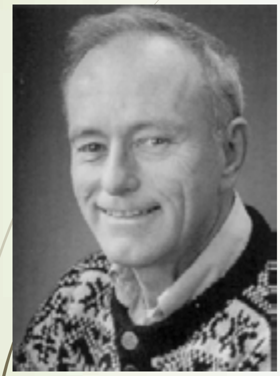
In memory of Prof. Peter Robinson

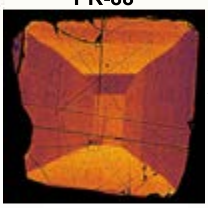
UMASS · AMHERST geosciences

GEOLOGICAL SURVEY OF NORWAY - NGU -



1932 (NH, USA)
2019 (Trondheim, Norway)

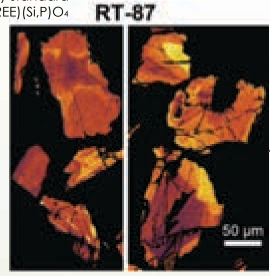
PR-88



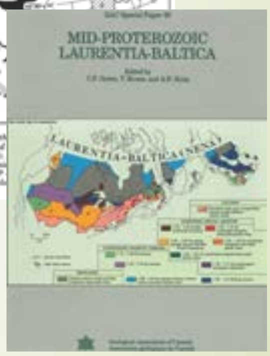
Wendell syncline intrusive

Monazite age consistency standard $(Ca,Th,REE)(Si,P)O_4$

RT-87



Tucker et al. (1990)
Proterozoic evolution and age-province boundaries in the central part of the Western Gneiss Region, Norway: Results of U-Pb dating of accessory minerals from Trondheimsfjord to Geiranger



Outline

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

1. Introduction to REE-phosphate (Monazite & Xenotime)
2. Electron microprobe U-Th-Pb$_{total}$ dating technique
3. Analytical considerations
   - Monazite and Xenotime identification
   - Characterization: element mapping
   - Challenges for quantitative analysis
     - Choice of spectrometer
     - Background acquisition
     - Peak interference correction
     - Beam damage
     - etc.
4. Applications
   - Archean aluminous quartzite (Montana)
   - Upper Granite Gorge (Grand Canyon, Arizona)
   - Challenge: Young monazite with low actinide content

What are monazite & xenotime?

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
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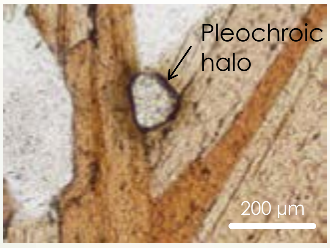
- Monazite = light rare-earth element (REE) phosphate (monoclinic structure).
- Xenotime = Heavy REE-phosphate + Y (tetragonal structure).
- Common substitutions:

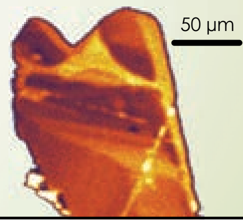
REE substitution	light REE^{3+}	⬄	heavy REE^{3+}
Cheralite substitution	2 REE^{3+}	⬄	Ca^{2+} + $(U,Th)^{4+}$
Huttonite/Coffinite subst.	REE^{3+} + P^{5+}	⬄	Si^{4+} + $(U,Th)^{4+}$
Gasperite/Chernovite subst.	P^{5+}	⬄	As^{5+}
Sulfate substitution	REE^{3+} + P^{5+}	⬄	M^{2+} + S^{6+} (M = Ca, Sr…)

Monazite-(Ce) in pegmatite Tveit, Norway.
Photo mindat.org

Monazite in biotite schist
Photo Smith College (MA)

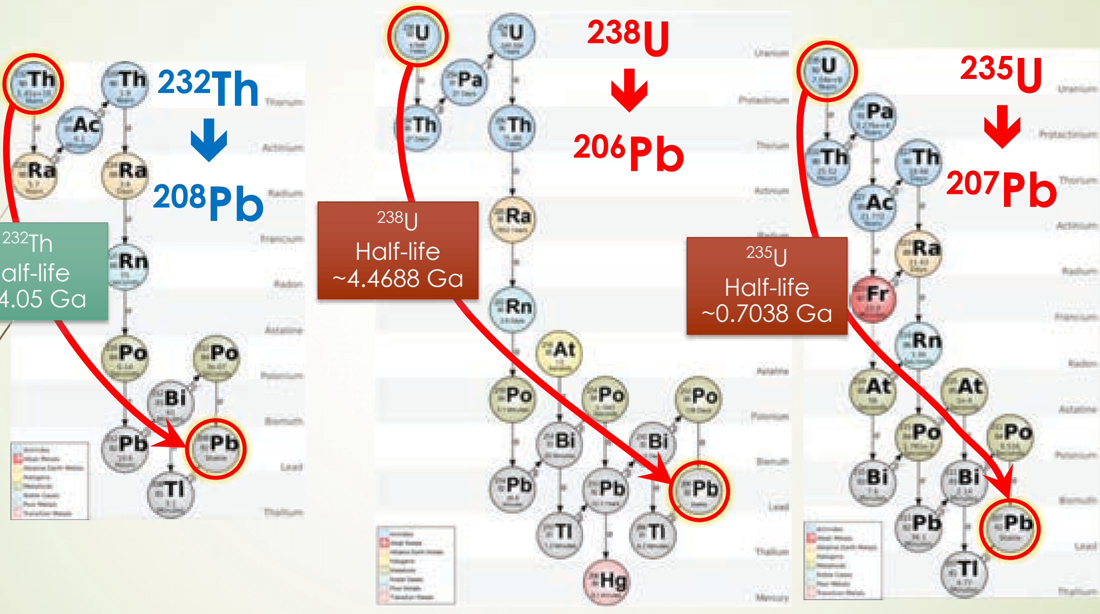


Th-zoning in monazite
(Athabasca Granulite Terrane, Canada)



U and Th decay series

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications



Electron Microprobe U-Th-Pb$_{total}$ dating

1) Introduction
2) U-Th-Pb$_{total}$ dating
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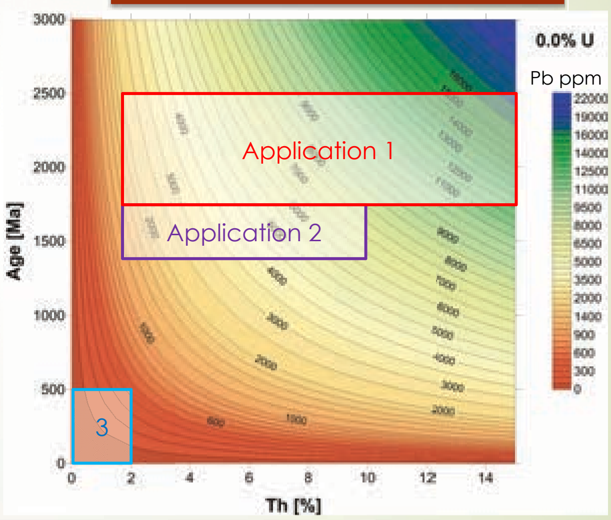
- **Assumption: no "common" Pb (^{204}Pb)** included when mineral grows:
  - Most REE-phosphate < 2-3 ppm ^{204}Pb.
  - Might also be valid for uraninite (UO_2), thorite ($ThSiO_4$), and other (U,Th)-bearing minerals.
  - Monazite ~ Th-richer.
  - Xenotime ~ U-richer.
  - Low grade Mnz/Xnt ~ actinide-poor.
- Two major approaches to **calculate an U-Th-Pb$_{total}$ age**:
  - From multiple compositionally ***heterogeneous domains*** and of (assumed) ***identical age*** = **CHIME** or **CH**emical Th–U-Pb$_{total}$ **I**sochron **ME**thod.
  - Average of several analyses from a compositionally ***homogeneous domain*** = **"single domain" method.**

Pb$_{total}$ = ^{206}Pb + ^{207}Pb (from ^{238}U, ^{235}U) + ^{208}Pb (from ^{232}Th) + ^{204}Pb ("common" Pb)



U-Th-Pb$_{total}$ age equations – Single domain

- Age calculated assuming the measured Pb comes only from decay of U and Th.
- **"Single domain"** means that **one compositionally homogeneous domain** in a grain is analyzed, and an age is calculated by averaging ~5 to 8 analyses.
- **Parslow et al. (1985), Bowles (1990):** First age obtained in uraninite & monazite based on total Pb, Th, U measurement, followed by **Montel et al. (1994, 1996):**
  - ^{208}Pb from ^{232}Th
  - ^{206}Pb from ^{238}U
  - ^{207}Pb from ^{235}U
  - ^{204}Pb = common lead ~ 2-3 ppm Assumed to be 0 (zero)
  - U, Th, and Pb in ppm or wt-%
  - t = time (in years)
  - λ^{xxx} = decay constant

$$Pb = \left[\frac{Th}{232}(e^{\lambda^{232}*t}-1)\right]*208 + \left[\frac{U}{238}0.9928(e^{\lambda^{238}*t}-1)\right]*206 + \left[\frac{U}{235}0.0072(e^{\lambda^{235}*t}-1)\right]*207 + {}^{204}Pb \approx 0$$

Story of the technique: see Montel et al. (2018), Chemical Geology 484

U-Th-Pb$_{total}$ age equations – CHIME

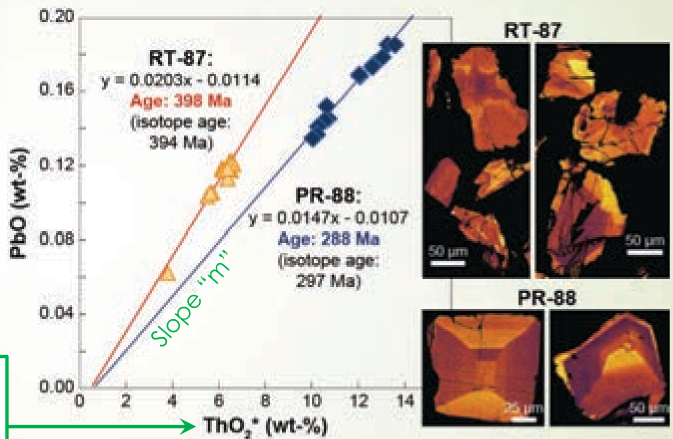
- **Suzuki & Adachi (1991):** PbO content vs. ThO_2^* of various monazite compositions; the slope is function of the age T:

$$T = \frac{1}{\lambda^{232}} \ln\left(1 + m * \frac{W_{ThO_2^*}}{W_{PbO}}\right)$$

Analysed domains MUST be of the same (assumed) age otherwise = age mixture & meaningless age!

Calculation of ThO_2^* = ThO_2 + equivalent ThO_2 from UO_2:

$$ThO_2^* = ThO_2 + \left(\frac{UO_2 * W_{ThO_2}}{W_{UO_2} * (e^{\lambda^{232}*t} - 1)}\right) * \left(\frac{e^{\lambda^{235}*t} + 137.88 * e^{\lambda^{238}*t}}{138.88} - 1\right)$$



For U-rich minerals (xenotime, uraninite, ± zircon…), use UO_2^* = UO_2 + equivalent UO_2 from ThO_2.

Story of the technique: see Montel et al. (2018), Chemical Geology 484

Analytical considerations

- **Focus on the single-domain technique (Montel et al.).** Nonetheless, all analytical considerations presented here are valid for the CHIME, too!

STEP BY STEP…

- **Thin section preparation:** fine polishing, carbon coating (> 20 nm) OR (preferred) dual aluminum (15-20 nm) + carbon* (5-10 nm) coating.
- **Identification of accessory phases:** Full thin section element mapping by WDS.
- **Element mapping of individual grains:** ~10-20 grains, identify homogeneous domains.
- **Quantification of the element maps.**
- *Optional: Ultra-high resolution element mapping to obtain an **age map** (>10-12 hours per grain).*
- **Complete quantitative analysis** with special care on U, Th, Pb measurement.
- **Data interpretation.**

** Carbon overcoating helps preventing oxidation of Al*

1) Introduction
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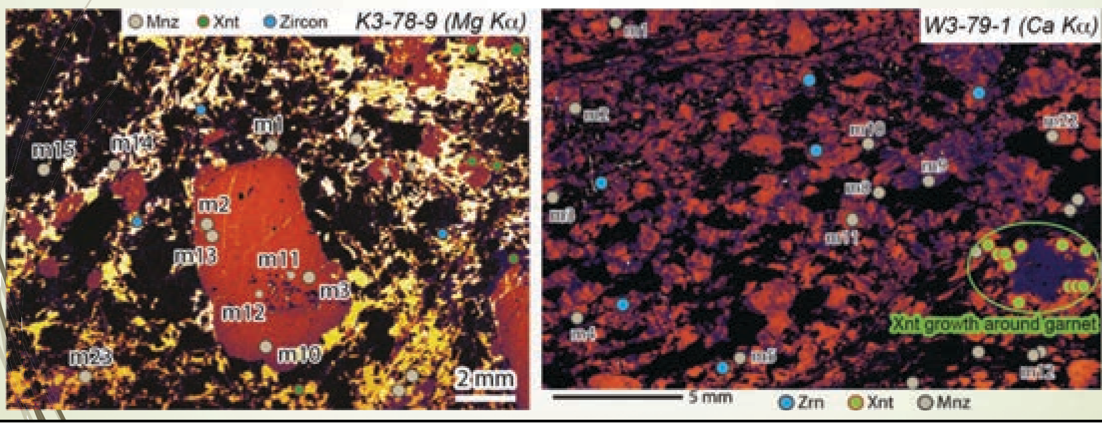
Full thin-section element mapping

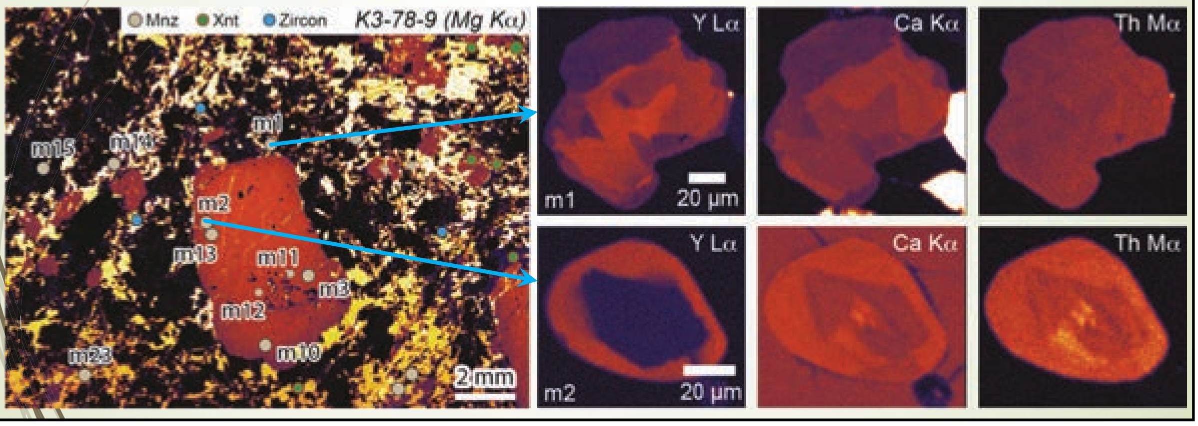
- **WDS stage mapping** of Ce/La Lα (Mnz), Y Lα (Xnt), Ca/P Kα (Ap), Zr Lα (Zrn) + one major element + BSE image. Overlay all element maps and highlight the accessory phases.
- **Identify 10-20 grains of interest** (structural considerations, shape of grains, location with regards to other minerals, heterogeneities at sample level, etc.)
- **Conditions:** 15 keV, >200 nA, 20-30 µm step & beam size, ~20-30 msec per step, Σ 4-5 h.



Single-grain element mapping

1) Introduction
2) U-Th-Pbtotal dating
3) Analytical settings
4) Applications

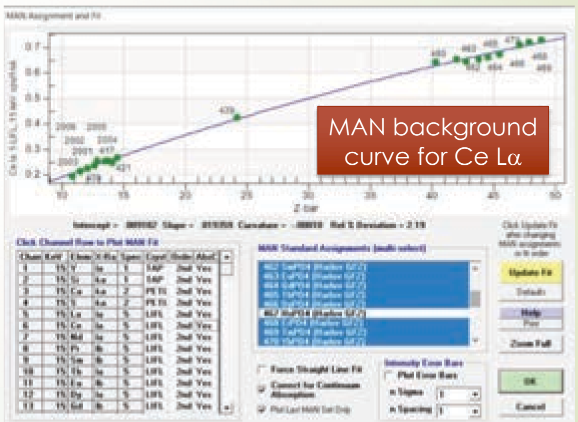
- **WDS beam mapping** of U Mβ, Th Mα, Y Lα, Ca Kα, Si Kα to reveal major compositional zoning and to identify homogeneous domains.
- To ease comparison, **treat each group of element maps similarly** (same intensity level, brightness, and contrast adjustments).
- **Conditions for monazite mapping:** 15 keV, >200 nA, beam mapping, 0.5 µm step size, focused beam (~0.7 µm w/ LaB_6), 20-30 msec dwell time, Σ ~5-10 min per grain.



Single-grain element mapping – *QUANTITATIVE*

1) Introduction
2) U-Th-Pbtotal dating
3) Analytical settings
4) Applications

- Element maps of U, Th, Y, Ca and Si are **quantified** to ***ease comparison*** of grains within a sample and between samples, and to obtain an ***approximate actinide content***.
- Quantification run through **CalcImage** (ProbeSoftware, Inc.):
  - Full ZAF or ϕ(ρz) matrix correction on each pixel;
  - Interference correction (Th Mγ on U Mβ);
  - Background correction from a standard-calibrated bkg curve using the Mean Atomic Number (MAN) background correction (Donovan & Tingle, 1996).



Basic principle: Bkg intensity of a specific element is proportional to the average atomic number (Z-bar).

Background curve is obtained by measuring a specific element in 5 or more standards of different average atomic number (Z-bar).

Standard used must be free of that element, and without any peak interference at the X-ray line position.

Single-grain element mapping – *QUANTITATIVE*

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  - Interference correction (Th Mγ on U Mβ);
  - Background correction obtained from a standard-calibrated bkg curve using the Mean Atomic Number (MAN) background correction (Donovan & Tingle, 1996).
- For accurate quantification, ALL elements must be measured. **BUT…** We only have U, Th, Y, Ca, and Si maps, and we are missing the major elements (P, REE).
- **Accuracy test considering various assumptions:**
  - Treat maps with only the acquired element (no constrained element);
  - Gd- or Ce-rich monazite with fixed P_2O_5 content (30 wt%) and Gd_2O_3 or Ce_2O_3 by difference;
  - Ce-rich monazite with lower P_2O_5 content (25 wt%);
  - Average monazite composition: 30 wt% P_2O_5, 13% La_2O_3, 3% Pr_2O_3, 11% Nd_2O_3, Ce_2O_3 by difference.

Single-grain element mapping – *QUANTITATIVE*

1) Introduction
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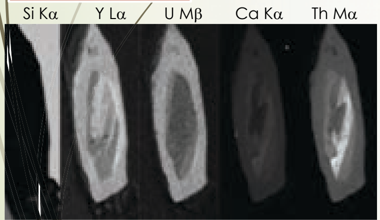
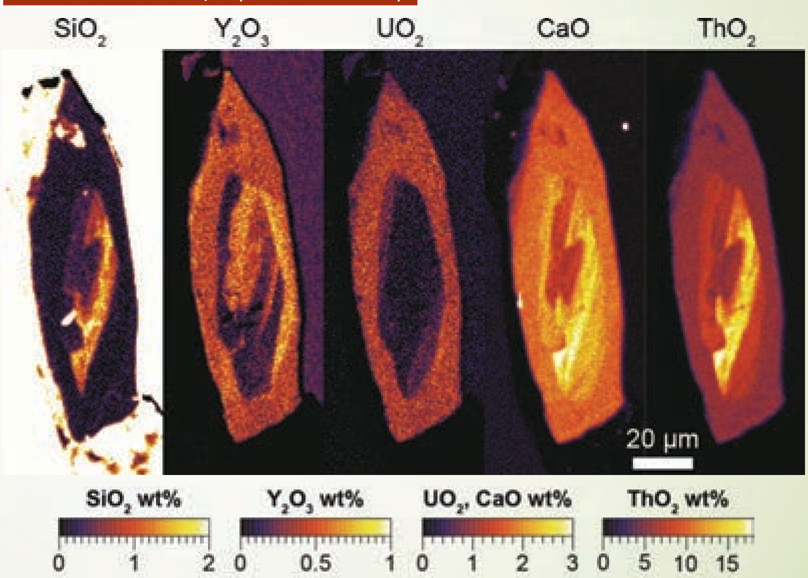
On each pixel…
- Full matrix correction;
- Background correction;
- Interference correction (here Th Mγ on U Mβ).

Original maps

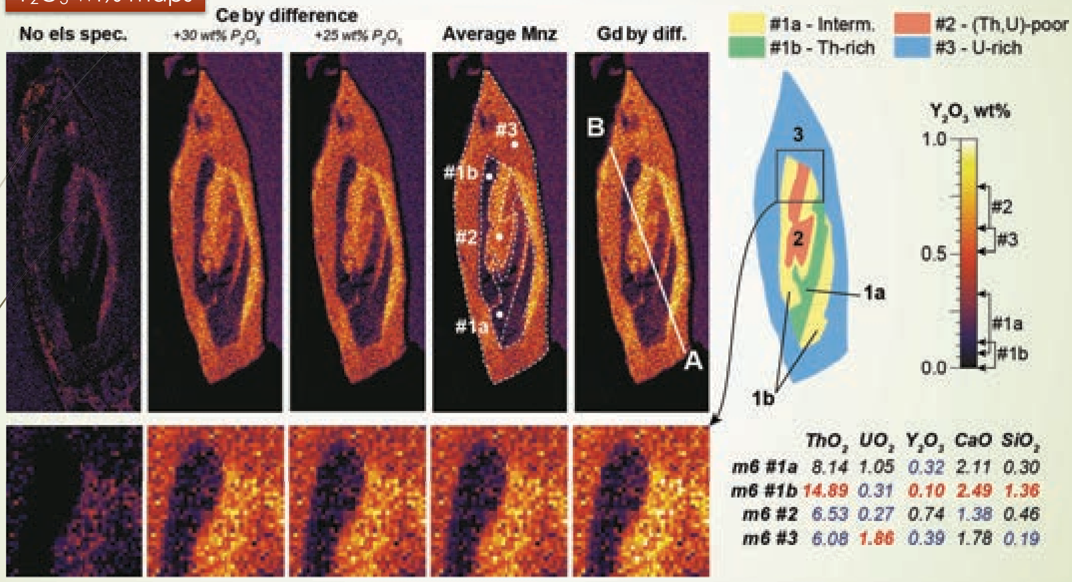


Quantitative maps (in oxide wt-%)



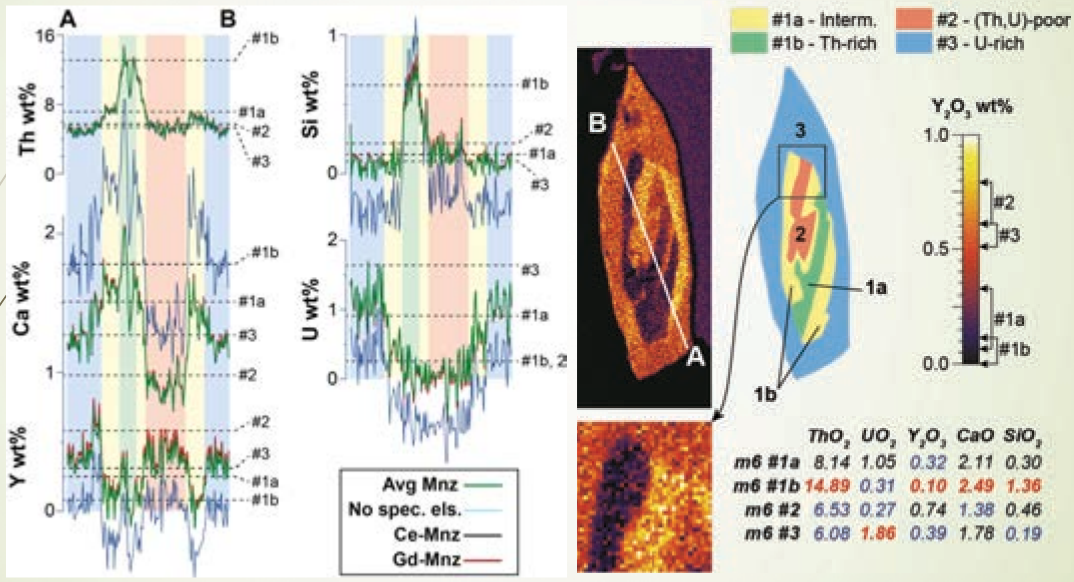
Single-grain element mapping – *QUANTITATIVE*

Y_2O_3 wt% maps



	ThO_2	UO_2	Y_2O_3	CaO	SiO_2
m6 #1a	8.14	1.05	0.32	2.11	0.30
m6 #1b	14.89	0.31	0.10	2.49	1.36
m6 #2	6.53	0.27	0.74	1.38	0.46
m6 #3	6.08	1.86	0.39	1.78	0.19

Single-grain element mapping – *QUANTITATIVE*



	ThO_2	UO_2	Y_2O_3	CaO	SiO_2
m6 #1a	8.14	1.05	0.32	2.11	0.30
m6 #1b	14.89	0.31	0.10	2.49	1.36
m6 #2	6.53	0.27	0.74	1.38	0.46
m6 #3	6.08	1.86	0.39	1.78	0.19

Erratum: This figure is wrong in the Book of Tutorials and Abstracts…

1) Introduction
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Preparation of U-Th-Pb + REE-analysis setup

- **Trace element analysis:** low Pb content (and sometimes also low U, low Th).
  - **High current** analysis (>100-200 nA).
  - **Optimum acceleration voltage** for optimum ***spatial resolution*** (15 keV, ~1 µm diameter sphere; submicron analysis possible at 6-10 keV), optimized ***X-ray production***, and ***minimum beam damage effect***.
  - **Long counting time** (> 5-10 min on peak) for ***high-precision*** (>1%) analysis.
  - **Choice of spectrometer**: Maximize count rate & peak-to-background ratio for ***high sensitivity***: normal or large area monochromator, H-type spectrometer, P-10 or Xe-sealed detector, etc.
  - **Measure major elements first** to prevent beam damage effect.
  - **Combined EDS-WDS analysis** for major elements (e.g., in Mnz: P ± major REEs [?]).
  - *Alternative option (not discussed here): combined analysis with (1) low and (2) high beam current analysis for major and minor/trace elements (e.g., 20 nA, and then 200 nA).*

- **Very important considerations…**
  - ***Background correction*** (as peak-to-background ratio approaches one);
  - ***Potential beam damage*** (Al-coating is preferred);
  - ***Peak interference(s)*** (especially on U and Pb, but also on REE!).

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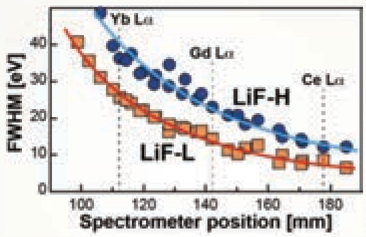
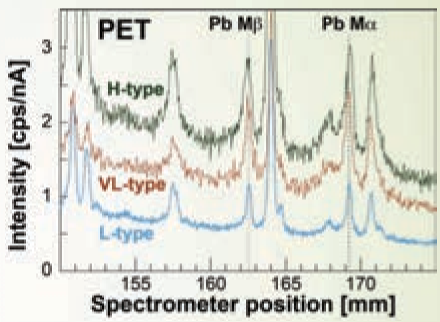
Choice of spectrometer

- **Superiority of large (L) or very large (VL) monochromator:** higher count rate (2-3x for L, 4-6x for VL) and excellent spectral resolution.
- **H-type spectrometer** (100mm Rowland) yields excellent count rate but poorer spectral resolution.





	Standard	X-ray	keV	Net peak [cps/nA] J-type Ar, LP	J-type Xe	L-type Xe	L-type Ar, HP	H-type Xe	VL-type Ar, HP	Peak-to-background ratio J-type Ar, LP	J-type Xe	L-type Xe	L-type Ar, HP	H-type Xe	VL-type Ar, HP
PET	Pyromorph.	Pb Mα	2.35	61.1	66.5	141.2	145.1	239.3	266.4	27.0	124.9	195.7	242.9	116.1	179.8
PET	ThO_2	Th Mα	3.00	72.5	151.6	397.1	-	563.1	-	15.9	82.1	153.7	-	78.3	-
PET	UO_2	U Mβ	3.34	69.3	166.4	336.5	280.4	636.0	420.2	11.4	80.2	83.1	63.0	74.5	56.7
LiF	$LaPO_4$	La Lα	4.65	-	22.2	62.2	88.7	91.8	-	-	101.1	137.8	106.6	78.3	-
LiF	$NdPO_4$	Nd Lα	5.23	-	37.1	98.9	121.0	137.0	-	-	104.2	125.7	100.2	75.7	-
LiF	$TbPO_4$	Tb Lα	6.27	-	54.3	144.7	164.3	172.6	-	-	70.3	82.2	63.0	48.4	-
LiF	$DyPO_4$	Dy Lα	6.49	-	57.0	184.1	168.1	177.2	-	-	61.4	73.2	61.5	42.2	-
LiF	$HoPO_4$	Ho Lβ	7.52	-	36.1	114.0	89.5	98.8	-	-	26.8	25.7	21.5	16.7	-

1) Introduction
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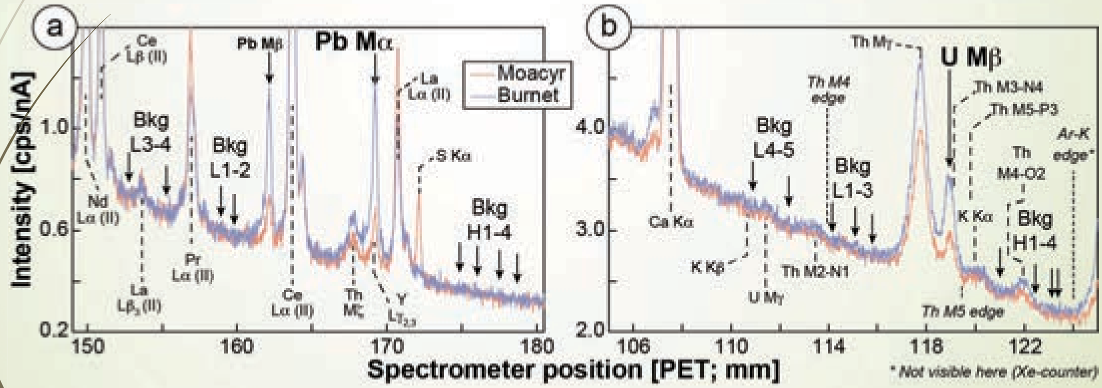
Background acquisition

- Complex spectrum especially around Pb M-lines with multiple potential ***peak & background interferences***.
- Analysis of ***background-only on first analysis point***, and ***then peak-only analysis*** to minimize beam damage effect (abnormal increase of background intensity).
- **Precise and accurate background correction is extremely important** for trace element acquisition ➔ ***Multipoint background acquisition.***



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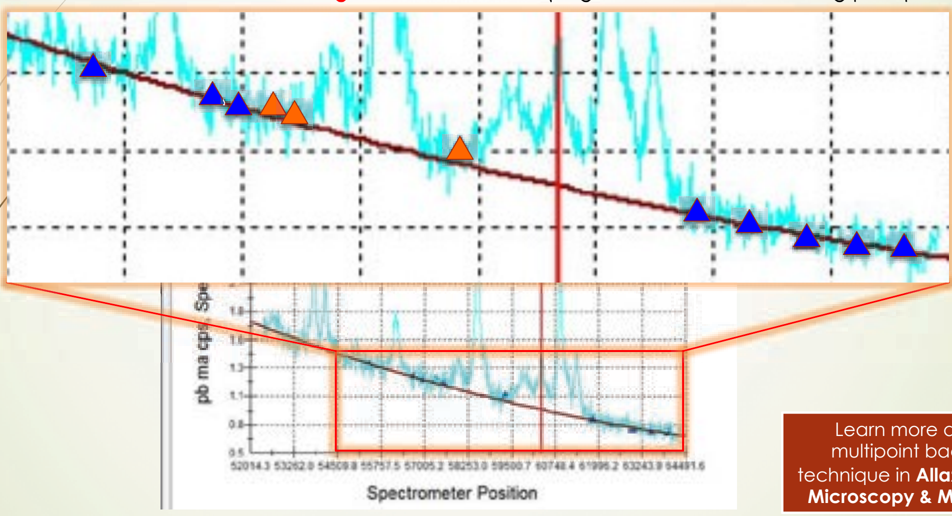
Flat Earth! Flatness is a matter of scale…

So why would you assume your X-ray background is linear?

Background acquisition – Multipoint Background

- ***Multipoint background acquisition*** allows to…
  - Accurately constrain the **background curvature**;
  - Minimize the risk of **background interference** (bkg can be removed during post-processing).



Learn more about the multipoint background technique in **Allaz et al. (2019) Microscopy & Microanalysis**

Background acquisition – Multipoint Background

1) Introduction
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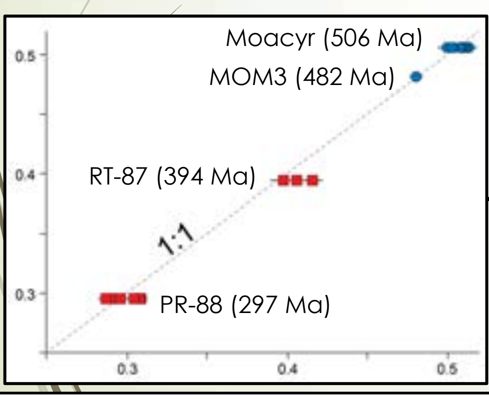
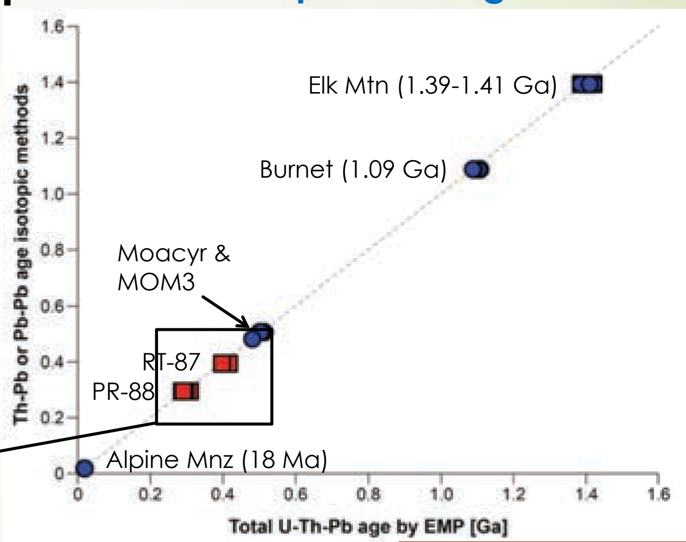
- **Technique validated by…**
  - Blank test correction;
  - Comparison of EPMA monazite age with isotopic ages in multiple age consistency standards.





Blue: $^{208}Pb/^{232}Th$ age
Red: $^{207}Pb/^{206}Pb$ age

Learn more about the multipoint background technique in **Allaz et al. (2019) Microscopy & Microanalysis**

Beam damage

1) Introduction
2) U-Th-Pb$_{total}$ dating
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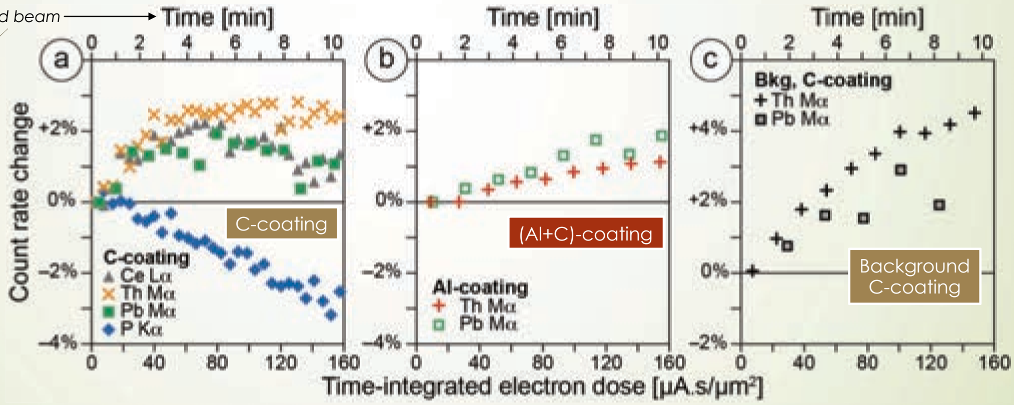
- High beam current + focused beam + long counting time = **high electron dose!**
- Beam damage almost unavoidable.
- P must be analyzed first, along with major elements. **Solution = EDS!**
  P analyzed by EDS + test in progress for major REE (Ce, La, Nd, Sm).
- Beam damage effect on elements analysed later not fully evaluated…

200 nA, focused beam



Beam damage – U, Th, and Pb analyses

1) Introduction
2) U-Th-Pb$_{total}$ dating
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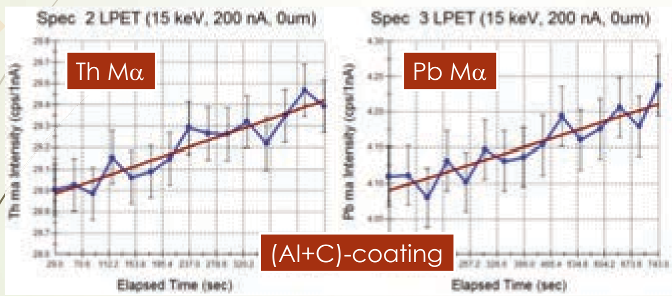
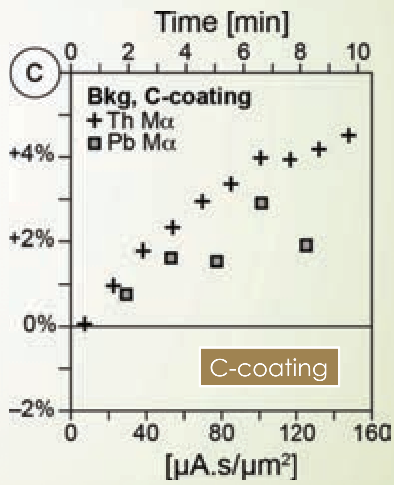
- **MUST analyze U, Th, and Pb first** to enable time dependent intensity correction (TDI)
  ➔ beam damage effect is compensated for in these elements.
- **Background-only analysis on a separate point** within a homogeneous domain
  ➔ minimizes risk of increasing background intensity due to beam damage.





Element	U	Th	Pb	Age [Ma]
Wt-% no TDI	0.086%	10.59%	1.15%	2241
Wt-% w/ TDI	0.084%	10.45%	1.13%	2226
TDI correction	-1.7%	-1.3%	-2.0%	-0.7%

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Peak interference correction – Pb and U

- **Age accuracy** strongly depends on Pb-measurement (most of the time) and U or Th (sometimes) ➔ ***accurate peak interference correction*** must be applied.
- **Use Donovan et al. (1993) peak interference correction** routine in Probe for EPMA: peak interference correction included within the ZAF correction (double-iteration).

- Major interferences on **Pb Mα**:
  - **Th Mζ**;
  - **Y Lγ$_{2,3}$**: **WARNING, peak shift** (50 * 10^{-5} sinθ in monazite compared to xenotime [YPO_4]);
  - **La Lα (II)**: Usually small ***(PHA in differential mode)*** but important when La-content is high.
- For xenotime, prefer **Pb Mβ** to avoid strong interference from Y Lγ$_{2,3}$ on Pb Mα.

- Major interferences on **U Mβ**:
  - **Th Mγ:** most important correction;
  - **Sm Lβ$_{2,15}$ (II):** often minor and insignificant;
  - **K Kα:** not present in Mnz or Xnt, but secondary fluorescence effect potentially important;
  - Problem of ***absorption edges from Th*** in Th-rich grains (background problem…).

1) Introduction
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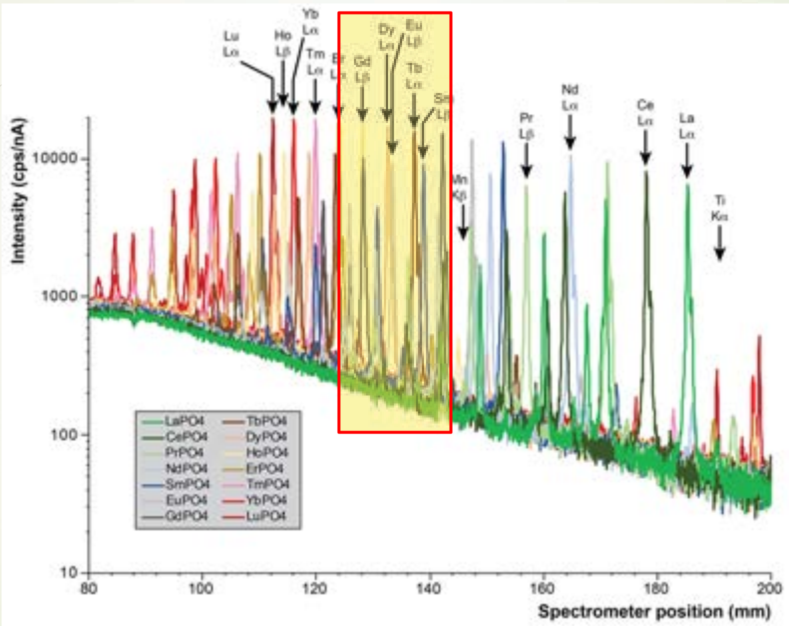
Peak interference correction – REE



Peak interference correction – REE, example Gd

- **Many interferences on REE!!!** Some element X-ray lines cannot be found "interference-free", example with Gd…

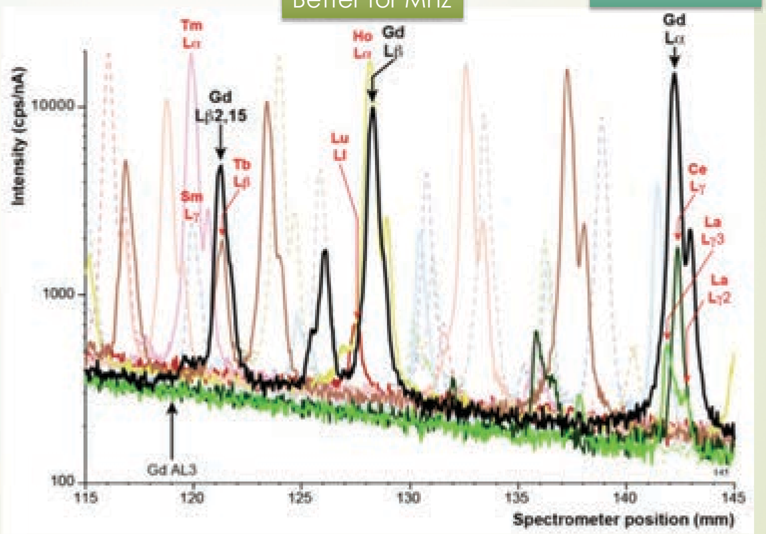
Gd Lα: suitable for xenotime, not for monazite due to strong interference with Ce Lγ & La $L\gamma_{2,3}$

Gd Lβ: suitable for monazite (lower count rate), not for xenotime due to strong interference From Ho Lα.

Gd $L\beta_{2,15}$: less interferences (Tm Lα, Tb Lβ), but ~30% intensity of Lα…

Better for Mnz

Better for Xnt



All major peak interferences…

Approximate interference % (no matrix correction), using average & max values for Mnz/Xnt composition (from literature).

Element	Xtal	Interfering element: Interference	cps/nA	Approx. % interf. corr.: Mnz avg	Mnz max	Xnt avg	Xnt max
Y Lα	TAP	Sr $L\beta_3$	4.60	0.2%	9.2%	No data for Sr in Xnt	
Sr Lα	TAP	Si Kβ + sat.	2.98	0.8%	6.0%		
Si Kα	TAP	Nd Lα (III)	0.62	1.2%	3.3%	<0.1%	0.3%
As Lα	TAP	Tb Mβ	7.85	<0.1%	0.4%	4.9%	8.4%
		Dy Mα	5.67	0.3%	2.1%	27.5%	39.7%
		Sm Mγ	1.70	0.4%	2.1%	0.8%	2.9%
Th Mα	PET	No significant interference					
Ca Kα	PET	No significant interference					
S Kα	PET	No significant interference					
U Mβ	PET	K Kα	7.40	Variable (fluorescence)			
		Th Mγ	2.10	7.7%	42.5%	0.5%	11.1%
		Sm $L\beta_{2,15}$ (II)	0.17	0.3%	1.2%	0.1%	0.3%
K Kβ	PET	U Mγ	4.10	Variable (fluorescence)			
		Tm Lα (II)	6.70	Variable (fluorescence)			
		Ca Kα	0.55	Variable (fluorescence)			
Pb Mα	PET	Y $L\gamma_{2,3}$	0.51	2.1%	12.0%	Prefer Pb Mβ	
		Th $M\zeta$	0.22	3.2%	17.8%	0.3%	6.0%
		La Lα (II)	0.04	1.9%	3.9%	<0.1%	<0.1%
P Kα	PET	Y Lβ	0.26	<0.1%	<0.1%	0.2%	0.2%

For xenotime only

Element	Xtal	Interference	
Pb Mβ	PET	Ce Lα (II)	Not determined (insignificant in Xnt)

Element	Xtal	Interfering element: Interference	cps/nA	Approx. % interf. corr.: Mnz avg	Mnz max	Xnt avg	Xnt max
La Lα	LiF	Nd Ll	0.18	0.2%	0.6%	0.8%	2.8%
Ce Lα	LiF	No significant interference					
Nd Lα	LiF	Ce Lβ	0.45	1.2%	1.6%	0.4%	1.1%
		La $L\beta_6$	0.36	0.5%	1.0%	0.1%	0.2%
Pr Lβ	LiF	No significant interference					
Sm Lβ	LiF	Tb Lα	0.60	<0.1%	0.2%	1.0%	1.7%
Tb Lα	LiF	Sm Lβ	0.56	1.2%	3.3%	0.1%	0.5%
Eu Lβ	LiF	Dy Lα	17.90	23.0%	141%	Prefer Eu Lα	
Dy Lα	LiF	No significant interference					
Er Lα	LiF	Tb Lβ	12.30	5.2%	14.6%	1.8%	3.1%
Gd Lβ	LiF	Ho Lα	126.50	6.1%	14.8%	Prefer Gd Lα	
		Sm $L\beta_{2,4}$	0.23	0.2%	0.9%	<0.1%	0.1%
Tm Lα	LiF	Sm Lγ	20.30	116%	542%	2.5%	8.7%
		Dy Lβ	1.73	2.3%	13.9%	2.1%	3.0%
		Gd $L\beta_{9,10}$	0.65	2.8%	8.1%	0.5%	1.3%
Yb Lα	LiF	Tb $L\beta_{2,15}$	0.95	0.7%	2.0%	0.2%	0.3%
		Dy $L\beta_{5,6}$	0.88	2.1%	13.2%	1.1%	1.6%
		Sm $L\gamma_3$	0.50	5.3%	24.7%	<0.1%	0.2%
Ho Lβ	LiF	Yb Lα,n	0.41	0.3%	1.4%	0.4%	1.9%
		Dy $L\beta_{2,15}$	0.24	0.3%	2.5%	0.2%	0.6%

For xenotime only

Element	Xtal	Interference	
Eu Lα	LiF	Pr $L\beta_{2,15}$, Ce $L\gamma_5$, La Lγ	Not determined (insignificant in Xnt)
Gd Lβ	LiF	Nd $L\beta_{2,15}$, La $L\gamma_{2,3}$	

Approximate % interference correction:

$$\%interference \approx \frac{I^A_{interf}/C^B_{interf}}{I^A_{std}/C^A_{std}} * \frac{C^B_{unk}}{C^A_{unk}}$$

Example of an analytical setup (Mnz & Xnt)

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

Sr and As rarely present in significant quantities

U, Th, and Pb analysed first & on dedicated spectrometers.

K not present in Mnz, but interferes with U (secondary fluorescence problem)

Complete set of REE analysis (can be simplified, e.g., by removing some HREE when analysing Mnz)

P analysed by EDS

SP	El.	Line	Xtal	Peak [mm]	Peak [10^5.sinθ]	Recommanded standard	Time [s] Peak	Time [s] Bkg#	Bkg Type	Major and minor peak interferences (see Table 7)	
1	Y	Lα	TAP	69.70	24890	YPO_4	180	-	MAN	Sr Lβ	(1)
1	Sr*,**	Lα	TAP	74.77	26705	Strontianite	180	-	MAN	Si Kβ + satellite peaks	
1	Si	Kα	TAP	77.10	27535	Microcline	180	-	MAN	Nd Lα (III)	
1	As*,**	Kα	TAP	105.36	37630	As-pyrite, GaAs	180	-	MAN	Tb Mβ; Dy Mα; Sm Mγ	
2	Th	Mα	L-PET	132.44	47300	$CaTh(PO_4)_2$, ThO_2	550	50##	MPB	-	
2	Ca	Kα	L-PET	107.50	38395	Apatite	60	-	MAN	-	
2	S	Kα	L-PET	172.09	61460	Sulfate or sulide	60		MAN	-	
3	U	Mβ	L-PET	119.04	42470	UO_2	600	50##	MPB	K Kα; Th Mγ; Sm $L\beta_2$ (II)	
3	K	Kβ	L-PET	110.64	39515	K-feldspar	100	-	MAN	U Mγ; Tm Lα (II); Ca Kα	
4	Pb	Mα	L-PET	169.24	60445	Pyromorphite	700	50##	MPB	Y $L\gamma_{2,3}$; Th Mζ; La Lα (II)	(2)
5	La**	Lα	L-LiF	185.38	66205	$LaPO_4$	30	-	MAN	Nd Ll	(3)
5	Ce	Lα	L-LiF	178.12	63615	$CePO_4$	30	-	MAN	-	(3)
5	Nd	Lα	L-LiF	164.82	58864	$NdPO_4$	30	-	MAN	Ce Lβ; La $L\beta_6$	(3)
5	Pr**	Lβ	L-LiF	157.08	56100	$PrPO_4$	30	-	MAN	-	(3)
5	Sm	Lβ	L-LiF	138.97	49630	$SmPO_4$	30	-	MAN	Tb Lα	(3)
5	Tb*	Lα	L-LiF	137.41	49075	$TbPO_4$	60	-	MAN	Sm Lβ	
5	Eu	Lβ	L-LiF	133.58	47705	$EuPO_4$	60	-	MAN	Dy Lα	(4)
5	Dy	Lα	L-LiF	132.66	47380	$DyPO_4$	60	-	MAN	-	
5	Er*	Lα	L-LiF	123.98	44280	$ErPO_4$	60	-	MAN	Tb Lβ	
5	Gd	Lβ	L-LiF	128.32	45830	$GdPO_4$	60	-	MAN	Ho Lα; Sm $L\beta_2$	(4)
5	Tm*	Lα	L-LiF	119.96	42845	$TmPO_4$	60	-	MAN	Sm Lγ; Dy Lβ; Gd $L\beta_{9,10}$	(5)
5	Yb	Lα	L-LiF	116.13	41475	$YbPO_4$	60	-	MAN	Tb $L\beta_{2,15}$; Dy $L\beta_{3,6}$; Sm $L\gamma_2$	
5	Ho*	Lβ	L-LiF	114.40	40855	$HoPO_4$	60	-	MAN	Yb Lα,η; Dy $L\beta_{2,15}$	
5	Lu*	Lα	L-LiF	112.62	40220	$LuPO_4$	60	-	MAN	Ho $L\beta_{3,6}$; Dy $L\beta_{2,15}$; Eu Lγ	
-	P	Kα	EDS	2.01 keV		$CePO_4$	300	-	EDS	Y Lβ	(6)

Application 1: *Archean aluminous quartzite (MT, USA)*

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

- “Simple” case of old samples with “a lot” of Pb (> 7000 ppm).
- One sample analyzed so far (preliminary data).
- Quantitative element maps.
- First attempt at combined EDS-WDS analysis including some REE.

Application 2: *Upper Granite Gorge (Grand Canyon, AZ)*

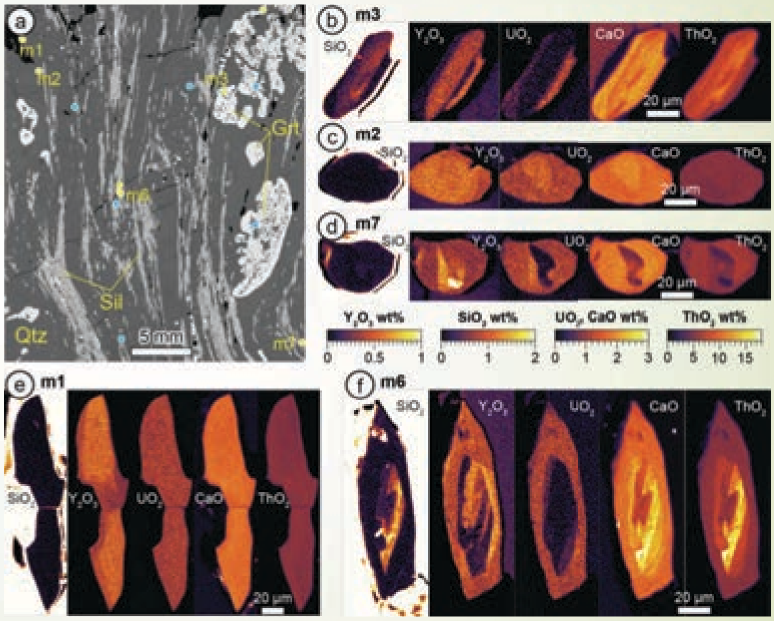
- Complexly zoned monazite, multiple ages, yet still a high Pb-amount (> 1000 ppm).
- Relationship between major minerals & monazite growth.
- Sensitivity of the method: can distinguish ages better than ±1% of the age.

Application 3: *Detrital and low-grade monazite (upstate NY)*

- Detrital monazite in sandstone (provenance study).
- Low-grade metamorphic or hydrothermal overgrowth, very low Pb content (~100 ppm).

Application 1: *Archean aluminous quartzite (MT, USA)*

- Quantified element maps.
- Monazite-poor sample.
- Recognize **similar compositional domains** between grains (e.g., U-rich rim, Y-rich and U-poor core, etc.).
- At least **two major events** identified:
  - U-poor core: 2.42 Ga = maximum deposition time age.
  - U-rich rim: 1.72-1.73 Ga = Big Sky orogeny, metamorphism.



Application 1: *Archean aluminous quartzite (MT, USA)*

- Complete analysis of U, Th, Pb, P, REE, Si, Ca… (without S, As, Sr).
- Data comparison: (a) **shared background** (= multipoint bkg applied to multiple X-ray lines), (b) **MAN** correction, (c) **EDS** (major REE only).
- Best results with shared backgrounds (less negative values), very similar MAN results.

WDS vs. EDS

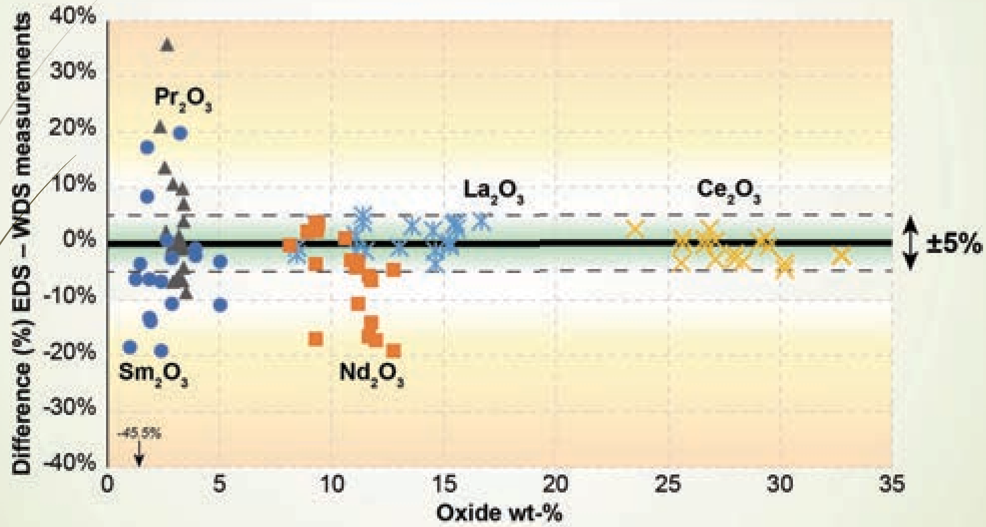
		Burnet	Moacyr	AA09-34B				
		Age ref. standard		m6 #1a	m7 core	m6 #3	m7 rim	m2 all
La_2O_3	*Shared*	9.27	14.56	13.61	16.67	15.54	15.58	15.49
	EDS	9.6	14.9	14.0	17.3	16.1	16.0	16.0
	Diff.	3.5%	2.4%	3.2%	4.0%	3.8%	2.8%	3.5%
Ce_2O_3	*Shared*	29.38	29.05	23.55	29.46	26.84	26.67	26.65
	EDS	29.7	29.1	24.2	29.3	27.5	26.5	26.8
	Diff.	1.1%	0.2%	2.6%	-0.6%	2.5%	-0.5%	0.7%
Pr_2O_3	*Shared*	3.54	3.23	2.37	2.94	2.67	2.60	2.65
	EDS	3.2	3.3	2.9	2.9	3.6	3.0	2.7
	Diff.	-8.7%	1.5%	20.9%	-0.1%	35.8%	13.6%	2.1%
Nd_2O_3	*Shared*	9.44	11.14	8.19	10.66	9.40	8.99	9.35
	EDS	9.8	10.6	8.2	10.8	9.6	9.2	9.7
	Diff.	3.4%	-4.5%	-0.5%	1.0%	2.1%	1.9%	3.7%
Sm_2O_3	*Shared*	3.30	1.87	1.09	1.84	1.46	1.33	1.56
	EDS	3.9	2.2	0.9	2.0	0.8	1.2	1.5
	Diff.	19.5%	17.1%	-18.7%	8.2%	-45.5%	-6.5%	-3.7%

		Burnet	Moacyr	AA09-34B				
		Age ref. standard	Age ref. standard	m6 Core #1a	m7 Core	m6 Rim #3	m7 Rim	m2 All grain
	Age	1085 ±[illegible]	505 ±[illegible]	2421 ±[illegible]	2478 ±[illegible]	1717 ±[illegible]	1730 ±[illegible]	1757 ±[illegible]
P_2O_5	EDS	27.45	28.35	29.22	30.18	30.01	29.56	29.83
SiO_2	MAN	1.38	1.07	1.28	0.11	0.18	0.36	0.09
CaO	MAN	0.85	0.46	2.43	0.86	1.74	1.89	1.84
Y_2O_3	MAN	0.50	1.22	0.11	0.94	0.38	0.26	0.45
La_2O_3	Shared	9.27	14.56	13.61	16.67	15.54	15.58	15.49
La_2O_3	MAN	9.26	14.54	13.57	16.64	15.81	15.58	15.43
La_2O_3	EDS	9.6	14.9	14.0	17.3	16.1	16.0	16.0
Ce_2O_3	Shared	29.38	29.05	23.55	29.46	26.84	26.67	26.65
Ce_2O_3	MAN	29.34	29.02	23.47	29.49	26.77	26.66	26.69
Ce_2O_3	EDS	29.7	29.1	24.2	29.3	27.5	26.5	26.8
Pr_2O_3	Shared	3.54	3.23	2.37	2.94	2.67	2.60	2.65
Pr_2O_3	MAN	3.57	3.29	2.37	2.96	2.67	2.69	2.65
Pr_2O_3	EDS	3.2	3.3	2.9	2.9	3.6	3.0	2.7
Nd_2O_3	Shared	9.44	11.14	8.19	10.66	9.40	8.99	9.35
Nd_2O_3	MAN	9.44	11.14	8.16	10.85	9.37	8.88	9.33
Nd_2O_3	EDS	9.8	10.6	8.2	10.8	9.6	9.2	9.7
Sm_2O_3	Shared	3.30	1.87	1.09	1.84	1.46	1.33	1.56
Sm_2O_3	MAN	3.33	1.90	1.14	1.88	1.56	1.38	1.61
Sm_2O_3	EDS	3.9	2.2	0.9	2.0	0.8	1.2	1.5
Eu_2O_3	Shared	-0.09	-0.03	0.09	0.18	0.24	0.22	0.23
Eu_2O_3	MAN	-0.08	0.00	0.14	0.23	0.36	0.32	0.28
Gd_2O_3	Shared	1.40	0.85	0.68	1.36	1.06	0.93	1.20
Gd_2O_3	MAN	1.46	0.85	0.68	1.41	1.02	0.85	1.18
Tb_2O_3	Shared	0.26	0.08	0.02	0.14	0.02	0.03	0.09
Tb_2O_3	MAN	0.25	0.10	0.04	0.16	0.08	0.07	0.11
Dy_2O_3	Shared	0.94	0.24	0.12	0.44	0.18	0.16	0.24
Dy_2O_3	MAN	0.83	0.23	0.09	0.43	0.17	0.13	0.23
Ho_2O_3	Shared	0.09	0.03	0.04	0.07	0.01	0.00	0.02
Ho_2O_3	MAN	0.01	-0.01	-0.07	0.00	-0.06	-0.08	-0.04
Er_2O_3	Shared	0.13	0.05	0.01	0.06	0.03	0.02	0.02
Er_2O_3	MAN	0.09	0.03	-0.04	0.03	-0.01	-0.03	-0.02
Tm_2O_3	Shared	0.01	0.00	0.01	0.01	0.00	0.00	-0.01
Tm_2O_3	MAN	0.00	0.01	-0.03	0.01	-0.01	-0.02	-0.01
Yb_2O_3	Shared	0.03	0.02	0.01	0.00	-0.01	-0.01	-0.01
Yb_2O_3	MAN	0.01	0.01	-0.05	-0.01	-0.03	-0.04	-0.03
ThO_2	MPB	9.93	6.59	15.16	2.49	6.15	7.05	5.93
UO_2	MPB	0.29	0.12	0.32	0.86	1.88	1.71	2.07
PbO	MPB	0.51	0.15	1.78	0.86	0.98	1.01	1.04

Application 1: Analysis of REE by EDS vs. WDS

1) Introduction
2) U-Th-Pbtotal dating
3) Analytical settings
4) Applications

- Same analysis point, difference between EDS results vs. WDS results.
- Ce and La are mostly within ±5%, Nd and less abundant elements more problematic…



Application 1: Analysis of REE by EDS vs. WDS

1) Introduction
2) U-Th-Pbtotal dating
3) Analytical settings
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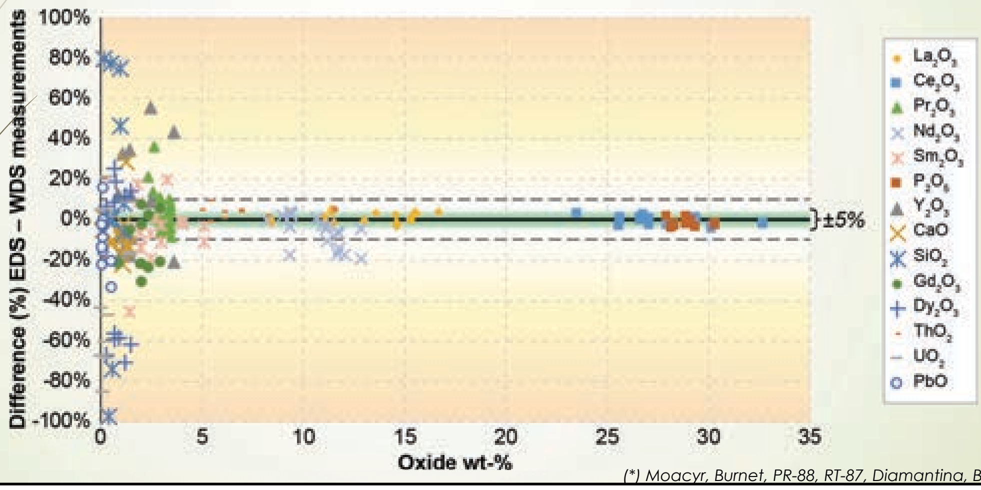
- Additional comparison in ***monazite reference standard (*)***: WDS data from **JEOL-8200** electron microprobe, SEM-EDS data from JEOL-6390 SEM using the a **Thermo UltraDry 30mm² EDS** detector ***(standard-based analysis)***.
- All elements in monazite ➔ within ±10% for elements as low as 2-3 wt-%, problem after…



(*) Moacyr, Burnet, PR-88, RT-87, Diamantina, Bananeira

1) Introduction
2) U-Th-Pb$_{total}$ dating
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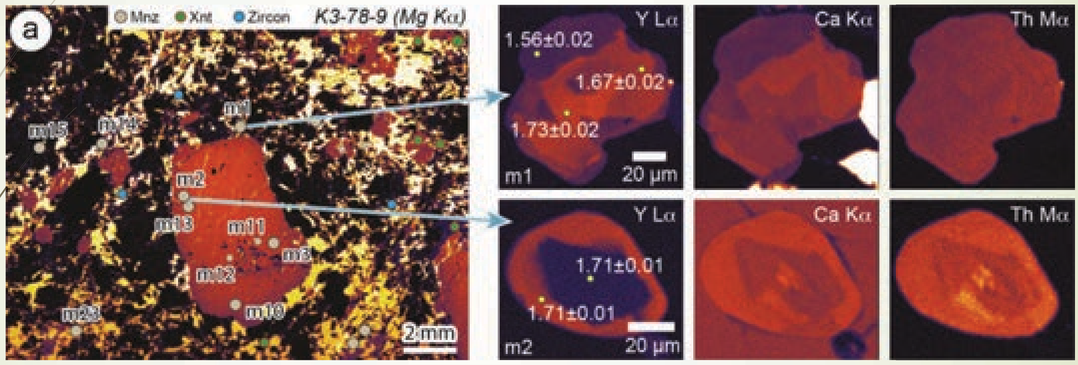
4) Applications

Application 2: *Upper Granite Gorge (Grand Canyon, AZ)*

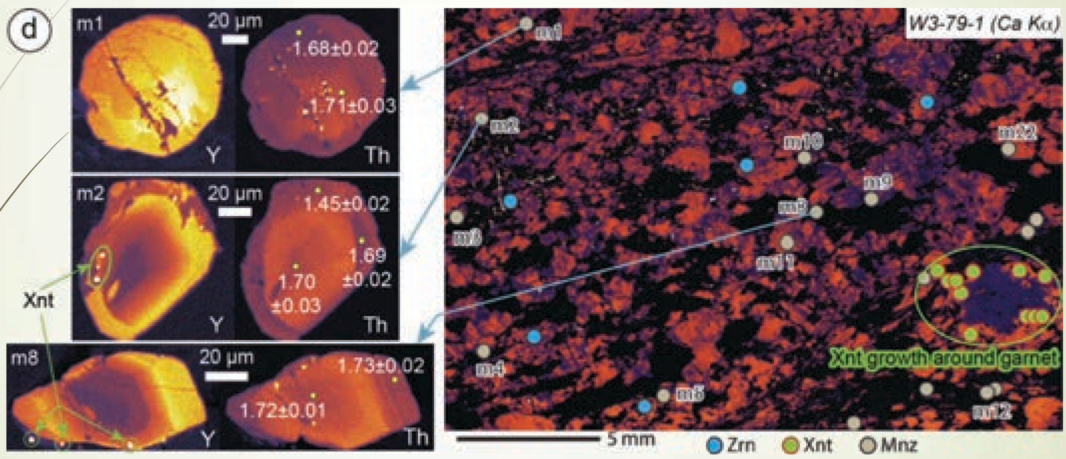
- Samples from high-amphibolite to granulite facies.
- Example of key-relationship between major rock-forming minerals and age / monazite compositional domains.



1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

Application 2: *Upper Granite Gorge (Grand Canyon, AZ)*

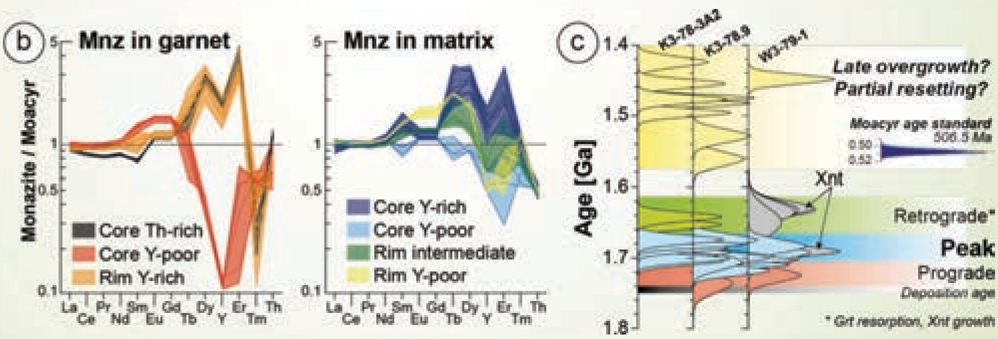
- One sample shows a clearly distinct growth pattern between core & rim.
- Clear growth of xenotime after garnet resorption (based on structure observation).



Application 2: *Upper Granite Gorge (Grand Canyon, AZ)*

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

- Distinct composition for monazite included in garnet. All record an old age 1.73 to 1.71 Ga **= *prograde stage***.
- Matrix monazite ~1.69 Ga **= *peak of metamorphism***.
- Clear ***retrograde*** event identified in several samples, and correlated with xenotime growth (garnet resorption).
- ***"Enigmatic" age*** from ~1.55 to 1.42 Ga (late overgrowth or partial resetting?).



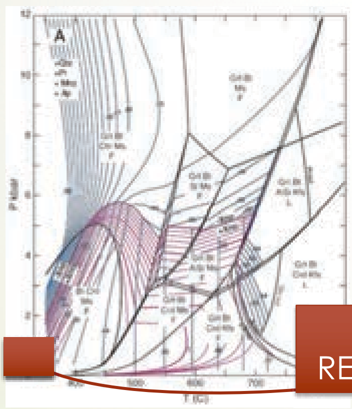
Application 3: *Young monazite, low (U,Th)-content*

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

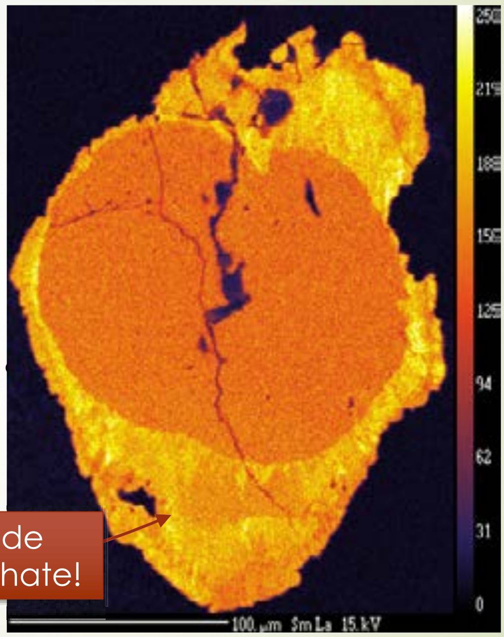
- Monazite (and xenotime) mostly dated in medium- to high-grade metamorphic or magmatic samples.
- ***REE-phosphate stable at low T***, BUT… (U,Th)-poor.

PT-stability *(Spear & Pyle, 2010)*

Occurrence of low-grade REE-phosphate in claystone, marl, metacherts and sandstone:
Burnotte et al., 1989; Cabella et al., 2001; Evans et al., 2002; Storm & Spear, 2002; Rasmussen & Muhling, 2007; Rasmussen et al., 2007; Mahan et al., 2010.



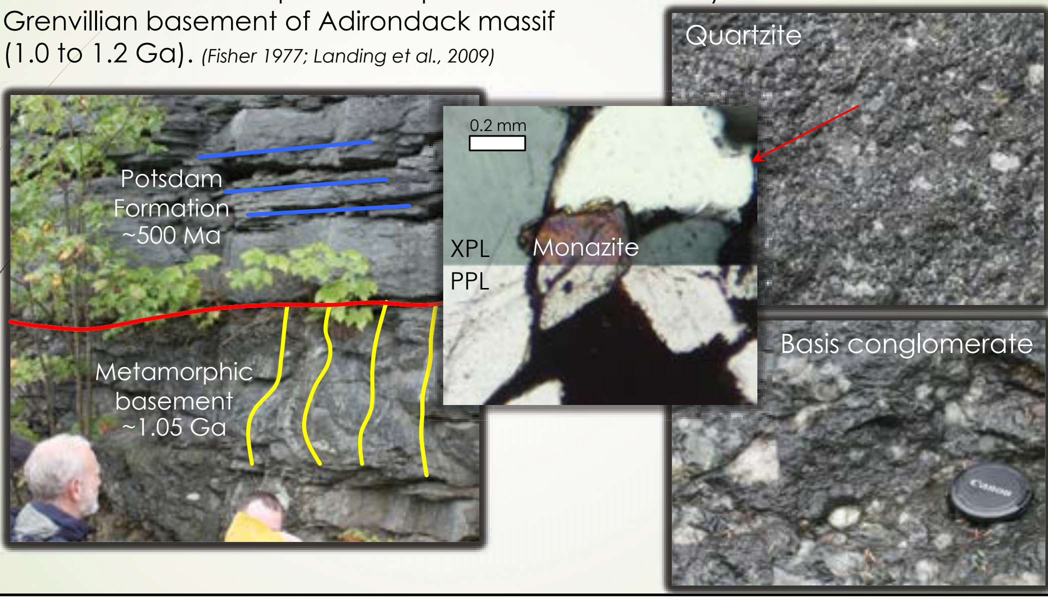
Low grade REE-phosphate!



Application 3: *Young monazite, low (U,Th) content*

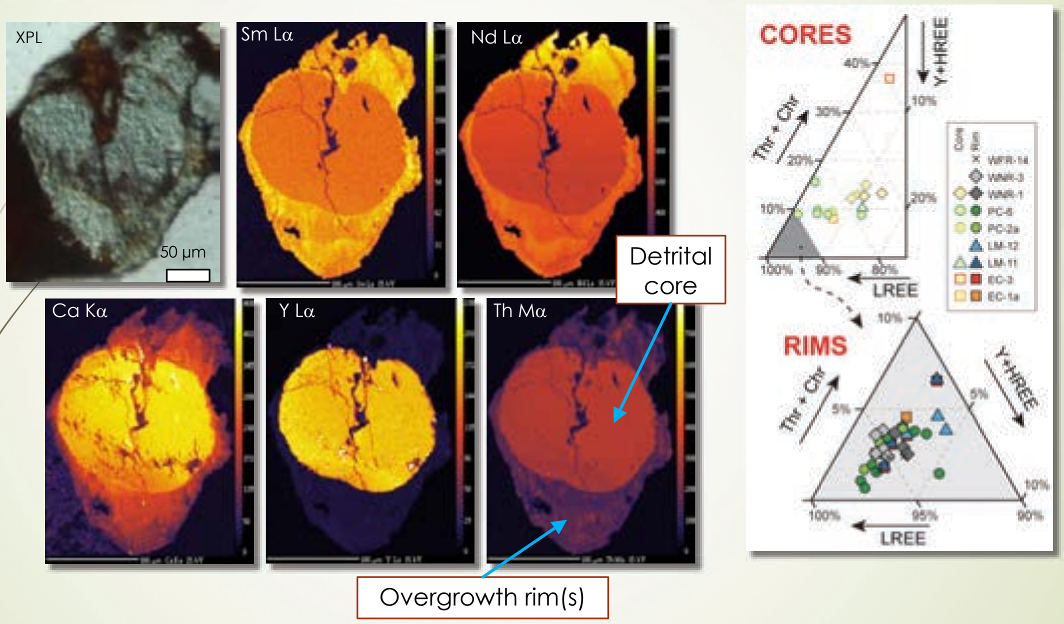
1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

Potsdam Formation: quartzite deposited unconformably around 510-490 Ma on Grenvillian basement of Adirondack massif (1.0 to 1.2 Ga). *(Fisher 1977; Landing et al., 2009)*



Application 3: *Young monazite, low (U,Th) content*

1) Introduction
2) U-Th-Pb$_{total}$ dating
3) Analytical settings
4) Applications

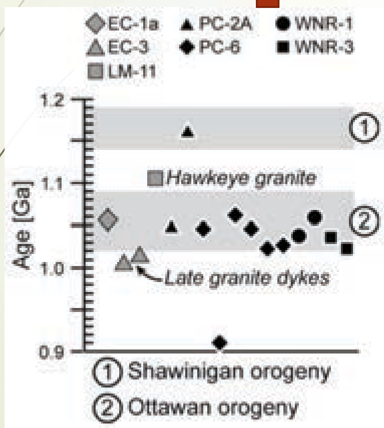


Application 3: *Young monazite, low (U,Th) content*

1) Introduction
2) U-Th-Pb total dating
3) Analytical settings
4) Applications

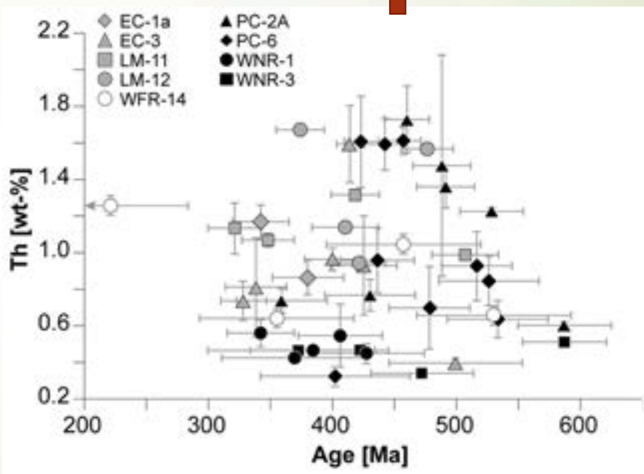
Similar to zircon, monazite can be used for provenance study *(e.g., Hietpas et al. 2010)*

Detrital cores



Authigenic rims

?????



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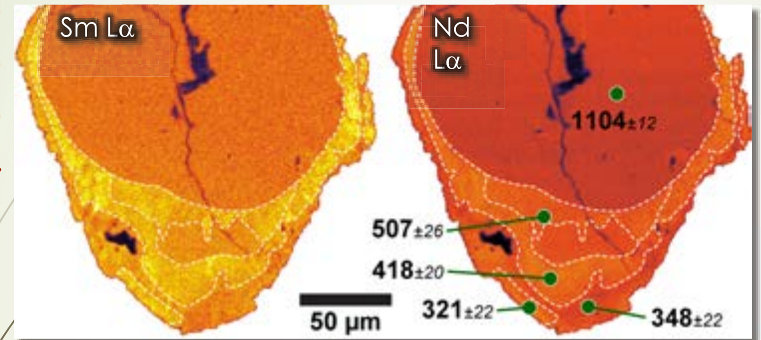


0) Detrital Mnz
1) Deposition (diagenesis)
2) Salinic orogeny?
3) Neo-Acadian orogeny?
4) Alleghenian orogeny?

2σ error

Average chemistry of some key elements (a.p.f.u.)

	Core	Rim 1	Rim 2	Rim 3	Rim 4
Ca	**0.045**	**0.022**	**0.017**	**0.009**	**0.006**
La	**0.149**	**0.192**	**0.168**	**0.217**	**0.171**
Ce	0.386	0.442	0.438	0.440	0.437
Nd	**0.185**	**0.208**	**0.229**	**0.197**	**0.229**
Sm	**0.041**	**0.048**	**0.057**	**0.048**	**0.057**

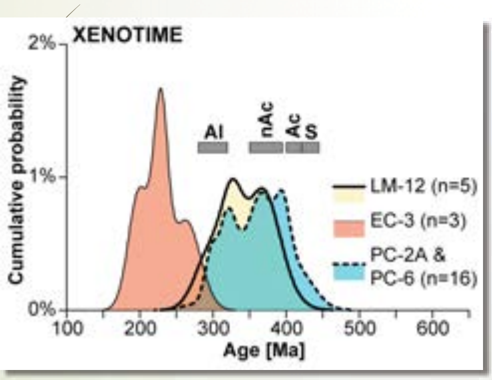
Component %

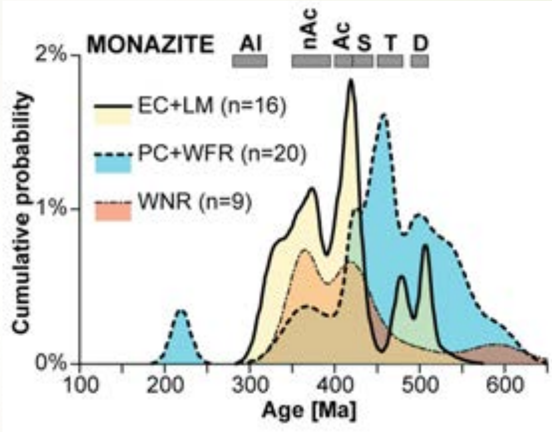
LREE	79.6	95.9	95.8	96.6	96.8
HREE+Y	10.0	0.8	1.0	1.0	0.9
Chr+Thr	10.5	3.3	3.2	2.4	2.3

More info: Allaz et al. (2013) *American Mineralogist 98*

Application 3: *Young monazite, low (U,Th) content*

- Each homogeneous domain = one Gaussian probability curve
- Curves cumulated for each area:
  - EC+LM = North
  - PC+WFR = East
  - WNR = South *(borehole)*





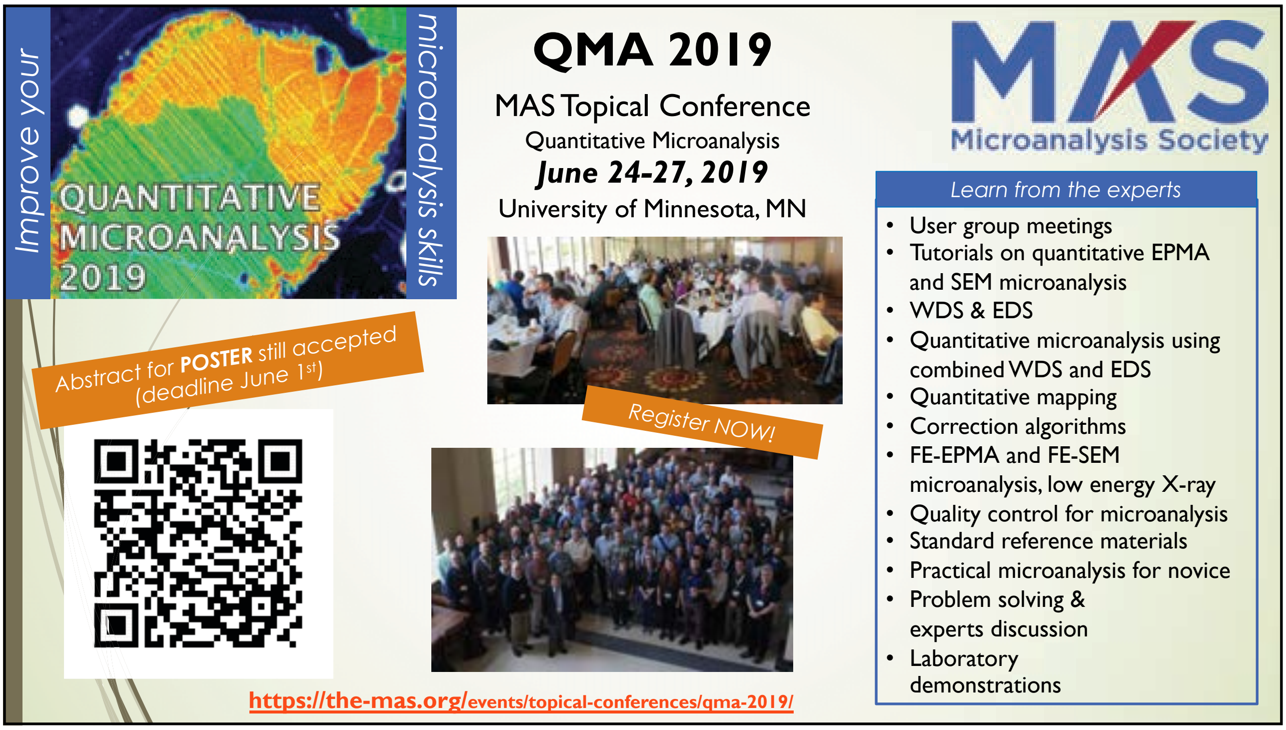
D: Deposition time, diagenesis
T: Taconic orogeny
S: Salinic orogeny
Ac: Acadian orogeny
nAc: Neo-Acadian orogeny
Al: Alleghenian orogeny

More info: Allaz et al. (2013)
American Mineralogist 98

Conclusions

- Electron microprobe dating of monazite and xenotime offers…
  - **High spatial resolution**;
  - **Excellent age accuracy and precision** (better than ±1% for old / actinide-rich samples);
  - **Limitations** arise for too-young monazite (<50-200 Ma) and when actinide-content is low;
  - **Complete composition** of the monazite to help with data interpretation;
  - **In situ technique** ➔ can relate the growth of a monazite domain to other minerals.
- Need to pay attention to…
  - **Background correction** (multipoint background acquisition);
  - **Peak interferences**;
  - Problem of **beam damage**; (Al+C)-coating is preferred.
- **Element maps** can be quantified, even without mapping for all major elements.
- **Combined EDS-WDS is the future:** analyse major elements on EDS and reserve the power of WDS for the minor/trace elements, or for elements with strong peak overlaps.

- During the EMAS week, Moacyr gained ~55 ppq of Pb ➔ Sometimes it's good to age, it makes the analysis easier!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