

Heavy minerals (HM) in provenance study

Heavy minerals

- high-density grains ($> 2.8 \text{ g/cm}^3$) in clastic sedimentary rocks
- Heavy minerals (HM) represent the detrital occurrence of essential rock-forming minerals (e.g. garnet, pyroxenes, amphiboles) or accessories (e.g. zircon, tourmaline, apatite)
- They typically comprise $< 1\%$ of siliciclastic sediments
- Heavy minerals may give precise information about the types of rock from which the sediment was eroded (provenance of sedimentary rocks and changes in provenance)
- provide a high-resolution tool for subdividing and correlating clastic successions that lack age-diagnostic fossils (important applications in hydrocarbon exploration)
- Heavy minerals may form naturally concentrates of economically valuable minerals (placers - deposits considerable commercial significance). Cassiterite, gold, diamonds, chromite, monazite, and rutile - are widely exploited from placer deposits.

Structure of the lecture

- Factors governing heavy mineral assemblages (HMA)
- Sampling
- Separations of HM
- Heavy mineral data processing and evaluating
- Important HM

Processes controlling HM assemblages

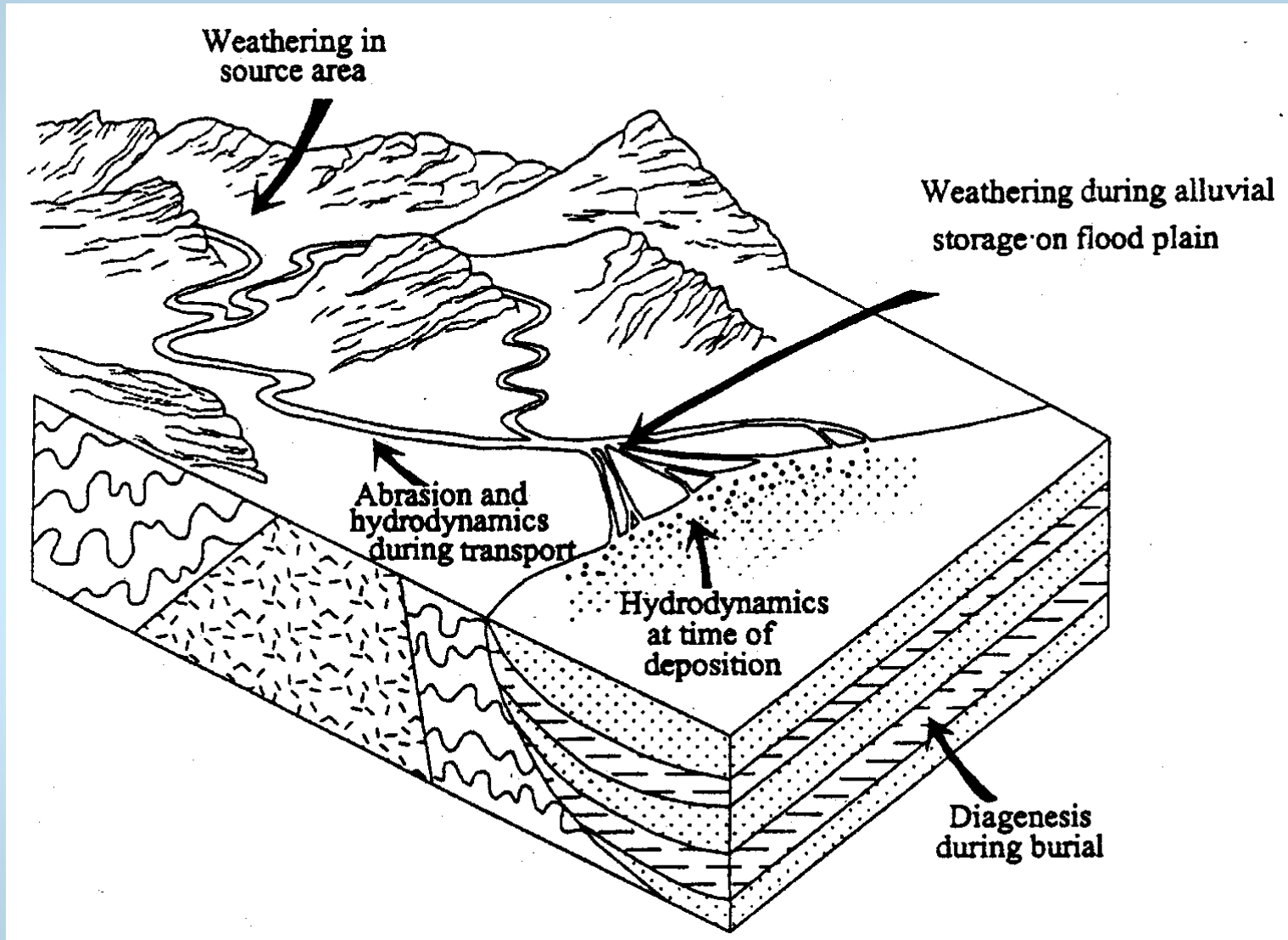
1. Mineralogical composition of the source rocks
 - Heavy mineral assemblage is not controlled only by the mineralogical composition of the source region.
 - The original provenance signal is modified by several other processes:
2. Weathering in the source area
3. Abrasion of HM during transport
4. Hydraulic processes
5. Diagenetic processes and dissolution of HM
6. Weathering in outcrops (sedimentary rocks)

Processes 2-6 can cause an originally homogeneous sandstone body, derived from a single source, to now contain markedly heterogeneous heavy mineral assemblages. Alternatively, sandstones from different sources, originally with different suites of HMA, may now possess similar HMA.

=> uncritical use of HMA may yield erroneous conclusions!!!

The most important overprinting processes on MHA are hydrodynamics and diagenesis

Path from accessory minerals to heavy minerals



Schematic diagram showing processes controlling HMA in sandstones, Morton, Halsworth (1999)

1. Source rock

- composition of heavy mineral assemblages is controlled by the mineralogical composition of the source region
- Despite the complex overprinting processes that affect heavy mineral distribution in sandstones, HM assemblages nevertheless retain fundamental provenance information.
- For correct interpretation of provenance, it is critical that the parameters used are inherited from the source area and are not modified to any great extent by processes operative during the sedimentation cycle.
- Recent sediments are the most suitable for provenance studies. They well reflect provenance information; older sandstones are progressively less rich in heavy minerals
- Problem with **sediment recycling** - especially for very mature sediments
The mineralogical "maturity" of the heavy mineral assemblages of sandstones is quantitatively defined by a **zircon-tourmaline-rutile (ZTR) index** (Hubert 1962). The ZTR index is the percentage of the combined zircon, tourmaline, and rutile grains among the transparent, detrital HM. Because of their high mechanical and chemical stability, zircon, tourmaline, and rutile are concentrated with quartz. In most arkoses and graywackes, the average ZTR index is low. The ZTR index is over 90% in most quartzite sandstones.

2. Weathering of the parent rocks

The degree to which heavy mineral assemblages are modified by weathering in the source area depends on three main factors:

- the composition of the heavy mineral suite (controlled by the **parent rock lithology**),
- the physiographic setting (**geomorphology**)
- **Climate**

Parent rock lithology :

- Ultramafic rocks - minerals unstable to weathering (olivine, pyroxene)
- S-type granites: stable minerals (zircon, monazite, apatite)

Geomorphology:

- If the transport processes are rapid (**rugged relief**) than the detritus is quickly removed without significant modification by chemical weathering.
- Under transport-limited conditions (**flat relief**), weathering products have a longer time to react with soil and groundwaters. In this situation, extensive modification of the heavy mineral suite could occur before the sediment reaches the transport system.

2. Weathering of the parent rocks

Climate:

- Although a number of heavy minerals are unstable during soil-forming processes, studies of both present-day and ancient examples indicate that source-area weathering does not significantly affect the diversity of heavy mineral suites prior to incorporation of sediment into the transport system.

Tropical climate:

- tropical climate leads to the generation of acidic groundwaters through bacterial degradation of organic matter - low pH - acidic groundwaters cause extensive dissolution of unstable heavy minerals (phosphate dissolution - apatite, monazite)
- relative order of stability of heavy minerals in soil profiles:
 - zircon, rutile, tourmaline, kyanite, andalusite and sillimanite showing high stability
 - apatite, monazite, olivine and pyroxene showing very low stability.

Arid climate:

- red-beds - sediments rich in Fe^{3+} - may form in arid, desert climates.
- extensive dissolution of Fe-Mg minerals (olivine, opx, cpx, Ca-hbl; Walker et al. 1967, 1978)
- Fe enters into solution through decomposition of these minerals - oxidized to Fe^{3+} , imparting the typical reddish coloration to the sediments
- Apatite, rutile, tourmaline and zircon are generally abundant in the red-bed sediments

2. Weathering of the parent rocks

Experimental works on the stability of heavy minerals (Nickel 1973, Pettijohn 1941, Lång 2000) showed that minerals have markedly different relative stabilities in different pH conditions. Stability pattern of HM in soil profiles at pH values of 3.6 and 5.6 bears a strong resemblance, but strongly contrasts with that at pH of 10.6. The acidic conditions associate with podzol formation.

stable




unstable

pH 3,6	pH 5,6	pH 10,6
zirkon, rutil	zirkon, rutil	zirkon, rutil
		granát , staurolit
Ca amfibol		Ca amfibol
		apatit
kyanit	kyanit	kyanit
staurolit	turmalín, staurolit	turmalín
turmalín		
epidot	epidot	epidot
	Ca amfibol	
granát	granát	
apatit	apatit	

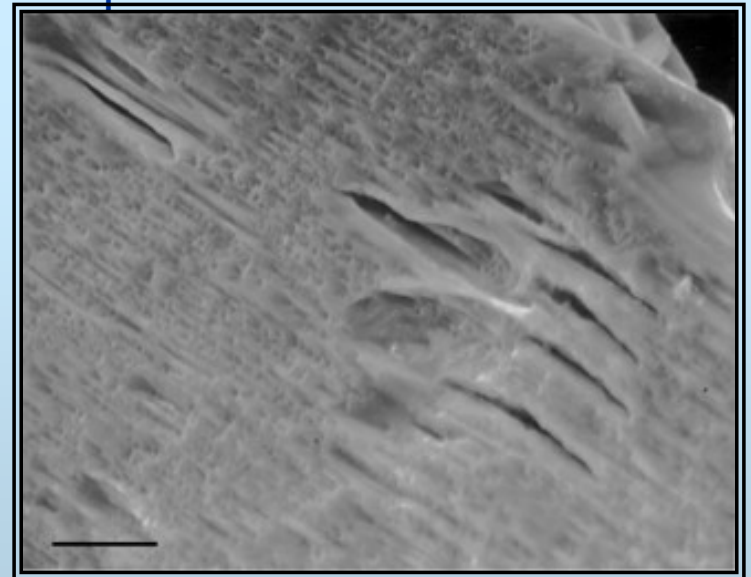
3. Mechanical abrasion

- Mechanical abrasion takes place during transport - causes grains to diminish in size (fracturing and rounding of grains).
- There have been a number of experimental studies which have determined the relative mechanical stability of heavy minerals, (Freise 1931, Thiel 1940, 1945 and Dietz 1973).
- Monazite is experimentally determined as the least mechanically stable mineral of all

		stable
Friese (1931)	Thiel (1945)	
tumalín	turmalín	
spinel		
rutil		
staurolit	staurolit	
augit	titanit	
granát	granát	
epidot	epidot	
apatit		
zirkon	zirkon	
	Ca amfibol	
	rutil	
	apatit	
	augit	
kyanit	kyanit	
olivín		
andalusit		
diopsid		
monazit		
	unstable	

3. Mechanical abrasion

- There is no evidence from natural river systems with extremely long transport distances that heavy mineral diversity decrease in downstream through this process (Morton, Smale 1990; Russell, 1937; Shukri, 1949; van Andel, 1950)
- The effects of abrasion on HMA during transport therefore appear to be generally negligible.
- Mechanical abrasion may have a significant effect only in exceptional circumstances with high energy - glacial transport or aeolian dune sands (Folk 1975, Cormier 1998).
- Chattermark trails (0,5-100 μm) related to glacial transport have an ordered orientation (Cormier 1998).
- Similar chattermarks on garnet can be formed by chemical etching in soils (Folk & Orr 1983) or during sediment diagenesis (Bull et al. 1980).



Chattermarked garnets; SEI, scale bar 10 μm , (Cormier 1998).

4. Hydraulic processes

- The hydraulic behaviour of HM is a complex, with many factors involved.
- Settling of sedimentary particles is governed principally by **grain size** and **density**, although **grain shape** is another potentially significant factor.

Grain size and density

- Because heavy minerals are denser than quartz and feldspar grains, they behave differently during transport and deposition.
- The size of heavy minerals in sandstones differs from that of the light minerals, with the denser heavy minerals having finer mean grain sizes than the associated quartz and feldspar.

- Rubey (1933) introduced the **concept of hydraulic equivalence**
- grains with the same settling velocity are deposited together
- settling velocity is a function of grain size and grain density
- smaller, denser minerals are deposited with larger, less dense ones
- Hydraulic equivalent size is defined as the difference in size between a given heavy mineral and the size of a quartz sphere with the same settling velocity in water (Rubey, 1933)

4. Hydraulic processes

The transport and deposition of HM also depends on how grains are entrained in the flow, on the nature of the transporting medium (water/air), on the mode of dispersal within the transporting medium, and on the grain size distribution in the parent rocks controls the grain size availability in the sediment. The behaviour of heavy mineral grains during transport is therefore affected by a combination of processes.

The entrainment potential of heavy mineral grains

Heavy minerals, once deposited during transport, are more difficult to re-entrain in the transporting medium than quartz (Slingerland, 1977, Komar and Wang, 1984).

=> HM tend to remain at more proximal depositional sites compared with the light minerals.

4. Hydraulic processes

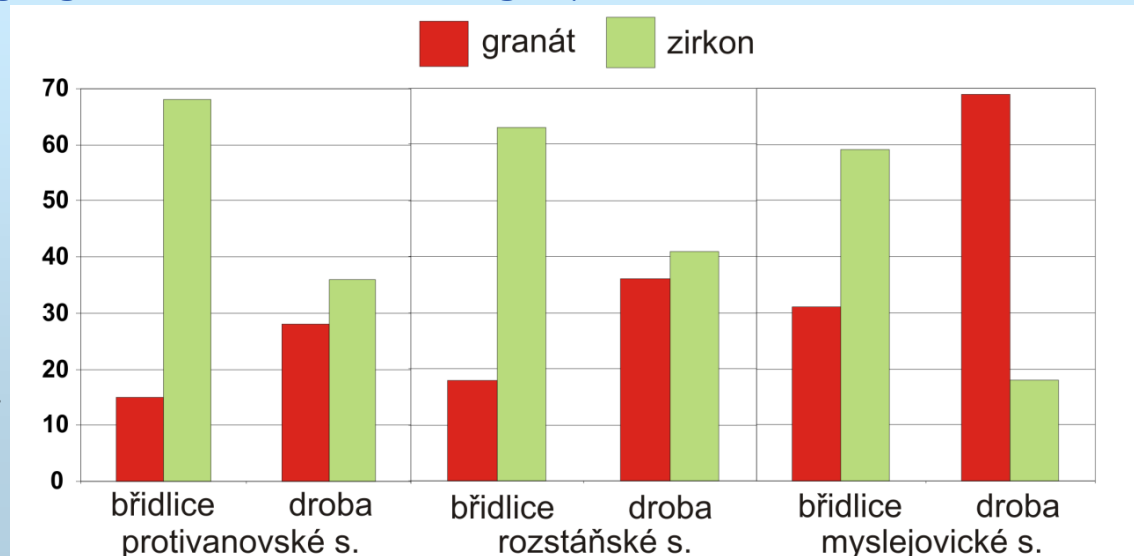
Grain shape

- The original definition of hydraulic equivalence by Rubey (1933) assumes that the heavy mineral grains are spherical.
- Many mineral grains are not spherical (notably mica, amphibole and kyanite - platy, tabular habit)
- Briggs et al. (1962) showed that grain shape can be as important as density in controlling the hydraulic behaviour of heavy minerals.
- mica (density 2.8 - 3.0 g/cm³) - sand-size mica particles (platy habit) are hydraulically equivalent to silt-sized light minerals (Doyle et al., 1983).

4. Hydraulic processes

- Grain size distribution in the source rocks controls the grain size availability in the sediment
- If a certain heavy mineral is available only in the very fine grain size fraction (e.g. monazite), it will be absent from the coarser fraction even if the hydraulic equivalence concept requires it to be there.
- Garnet or tourmaline tend to form relatively large grains in the source rock; rutile, zircon or monazite are very small in many cases.
- Well correlation was observed between content of garnet in HM and sediment grain size (Morton 1985). With increasing grain size of sediments increases garnet content in HM.
- Similar feature was observed in sediments of the Drahany Upland - garnet and zircon content in HMA vary in relation to sediment grain size. High zircon is common in shales and high garnet in associated graywackes.

Zircon and garnet in HMA from fine-grain shales (břidlice) and graywackes (droba) at three representative localities (Drahany Upland)



4. Hydraulic processes

- Two complementary methods are used to counteract the effects of hydraulic processes on HMA.
 - 1) To minimize the effects of hydraulic behaviour use limited size range (usually 63-125 μm) of sediments.
 - 2) The alternatively approach is to undertake varietal studies, which concentrate on chemical variations seen within one mineral group (eg. garnet group; range in density for garnet group is 3,57 - 4,30 g/cm^3 - redistribution of garnet with different chemical composition during hydraulic processes was not observed.

5. Dissolution of HM during burial diagenesis

Very important process

heavy mineral suites react to burial diagenesis by dissolution of unstable phases (intrastratal solution) and growth of secondary minerals.

there have not yet been enough case studies to confidently predict mineral dissolution patterns under all circumstances

Several major factors govern HM dissolution during deep burial:

- Composition of HM assemblage (stable/unstable HM)
- Pore fluid temperature (=> deep of burial)
- Pore fluid composition (chemistry, pH, Eh)
- Pore fluid circulation (porosity)
- time
- stability of the heavy minerals

5. Dissolution of HM during burial diagenesis

Fluid temperature

- The relationship between burial depth and dissolution is a result of increasing porefluid temperature as a result of geothermal gradient

Pore-fluid circulation

- dissolution rate of HM correlates with rate of pore-fluid movement through the rock
- zones protected from pore-fluid circulation (due to cementation or original low porosity) contain more diverse HM assemblages than the surrounding friable sandstones

5. Dissolution of HM during burial diagenesis

Decline in heavy mineral diversity with increasing burial depth, interpreted as resulting from intrastratal solution is usually observed in siliciclastic sediments.

Heavy minerals show evidence of surface corrosion as they approach the levels at which they disappear.

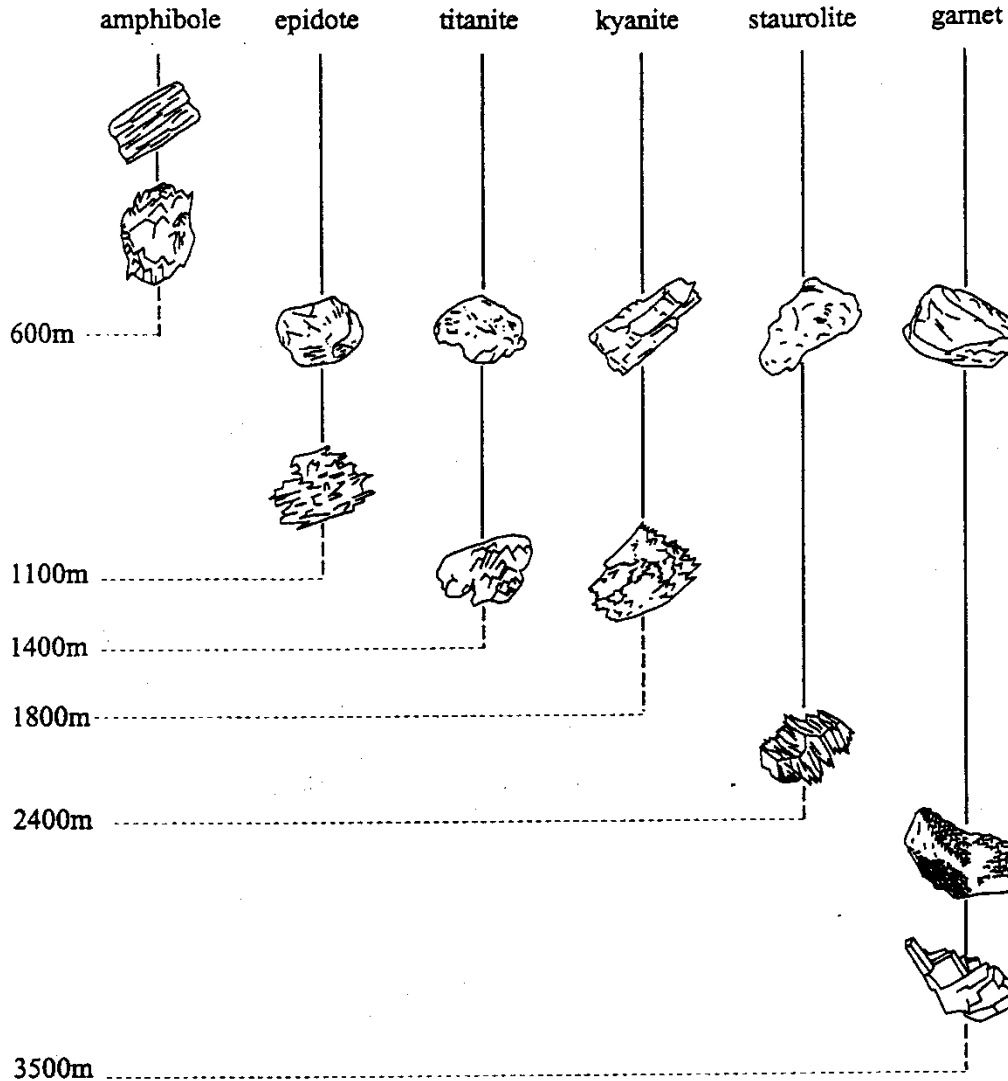
HM suites become steadily less diverse as burial increases due to elimination of heavy mineral species through dissolution, beginning with olivine, pyroxene, calcic amphibole, followed by epidote, titanite, kyanite and staurolite.

Rutile, tourmaline and zircon rarely display signs of etching, and are apparently stable (so-called ultrastable HM).

The provenance-sensitive minerals monazite and chrome spinel also appear to be generally stable

5. Dissolution of HM during burial diagenesis

A.C. Morton, C.R. Hallsworth / *Sedimentary Geology* 124 (1999) 3-29



Burial depth distribution of heavy minerals in sandstones (North Sea), showing the decrease in mineral diversity with increasing burial caused by dissolution of unstable minerals (Morton, 1984).

e.g. garnet

uncorroded detrital garnet

zone with surface corrosion

garnet disappearing from HM

5. Dissolution of HM during burial diagenesis


	US Gulf Coast (Milliken 1988)	North Sea (Morton, Hallsworth 1999)	
<p>stable</p>  <p>unstable</p>	apatit, chloritoid, monazit, spinel	apatit, monazit, spinel, TiO ₂ minerály, turmalín, zirkon	
	TiO ₂ minerály, turmalín, zirkon	chloritoid	
	granát	granát	3 500 m
		staurolit	2 400 m
		kyanit	1 800 m
	titanit	titanit	1 400 m
	epidot	epidot	1 100 m
	kyanit		
	Ca amfibol	Ca amfibol	600 m
	pyroxen	andalusit, sillimanit pyroxen olivín	

The effects of burial diagenesis on heavy mineral assemblages in the central North Sea (Morton, 1984) and in the Gulf Coast (Milliken 1988).

5. Dissolution of HM during burial diagenesis

- The stability patterns and the burial depths at which individual heavy minerals disappear from heavy mineral assemblages differ significantly from basin to basin.
- The stability patterns crucially depends on fluid activity and chemistry
- The stability patterns for HM according to Pettijohn

unstable



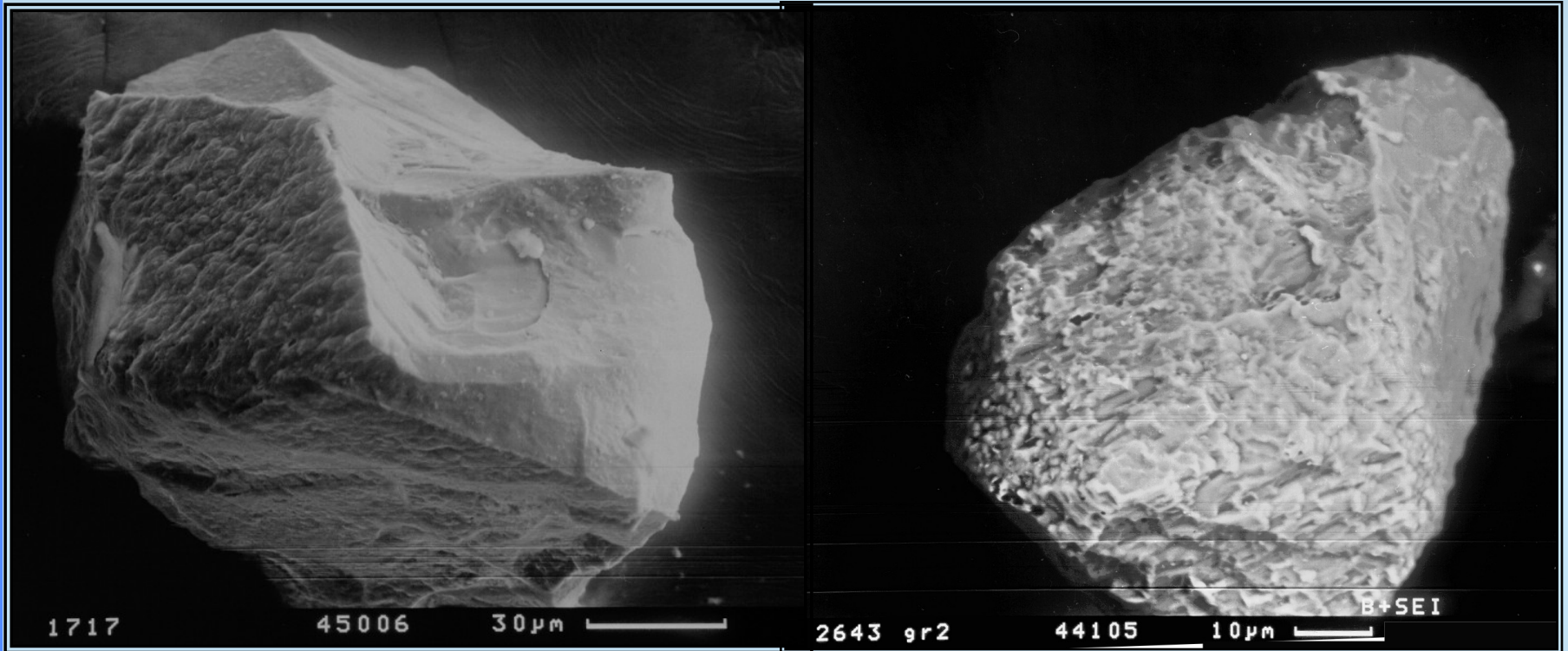
Olivine
Sillimanite
Pyroxene
Spinel
Andalusite
Amphibole
Epidote
Kyanite
Staurolite
Apatite
Garnet
Zircon
Tourmaline
Rutile

stable

5. Dissolution of HM during burial diagenesis

- The observation of grain surface corrosion is strong evidence for the widespread operation of dissolution processes during deep burial
- corrosion features are well visible by two widely available methods;
 - optical petrography and
 - scanning electron microscopy (SEM); - SEI secondary electron image is used to examine the three-dimensional geometry of corrosion features on grain surfaces)
- Different surface corrosive textures are observed:
 - Etch pits
 - Chattermark trail
 - Rough surface
 - Faceted surface
 - Mammillated surface

5. Dissolution of minerals during diagenesis



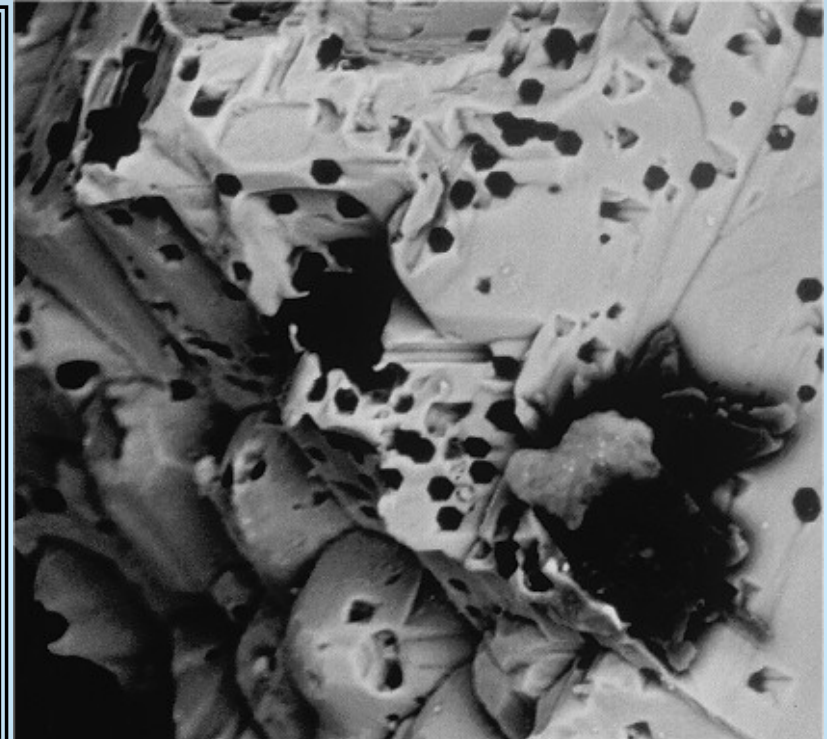
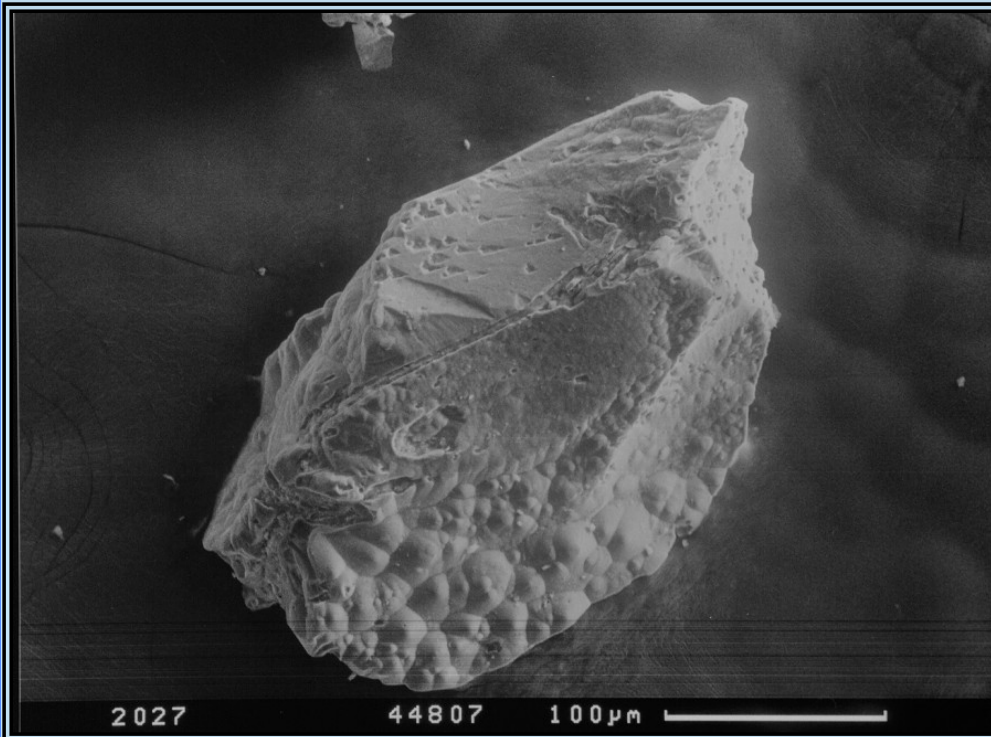
(left) - Initial stage of garnet dissolution - rough surface (Drahany Upland, burial temperature 120-180 °C); (right) - Intensively altered garnet - rough surface (Drahany Upland, burial temperature 200-300 °C).

5. Dissolution of minerals during diagenesis

Initial stage of garnet dissolution - chattermark trails- preferential dissolution along garnet edges



5. Dissolution of minerals during diagenesis

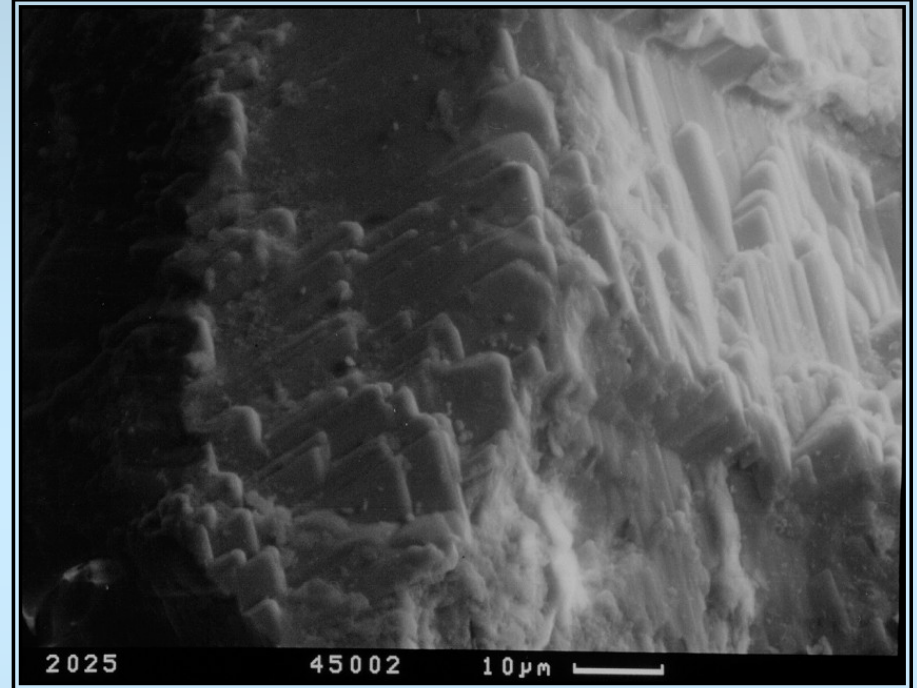
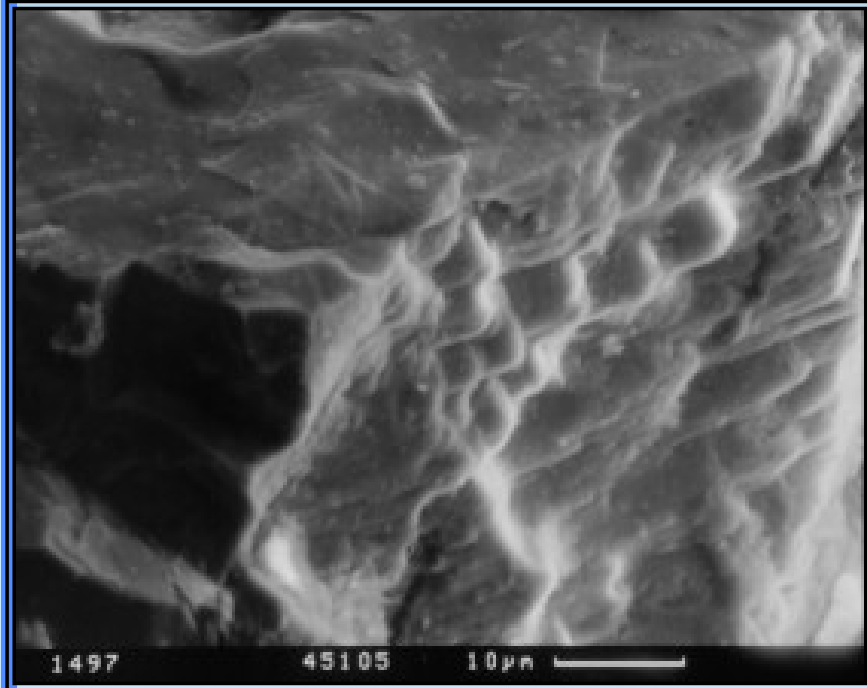


Complex etching patterns (intensively altered detrital garnets (Drahaney Upland)
Left - etch pits and mammillated surface ; right - etch pits and faceted surface

etch pits can be randomly distributed or preferentially distributed

5. Dissolution of minerals during diagenesis

Faceted surface on garnet (Drahany Upland)



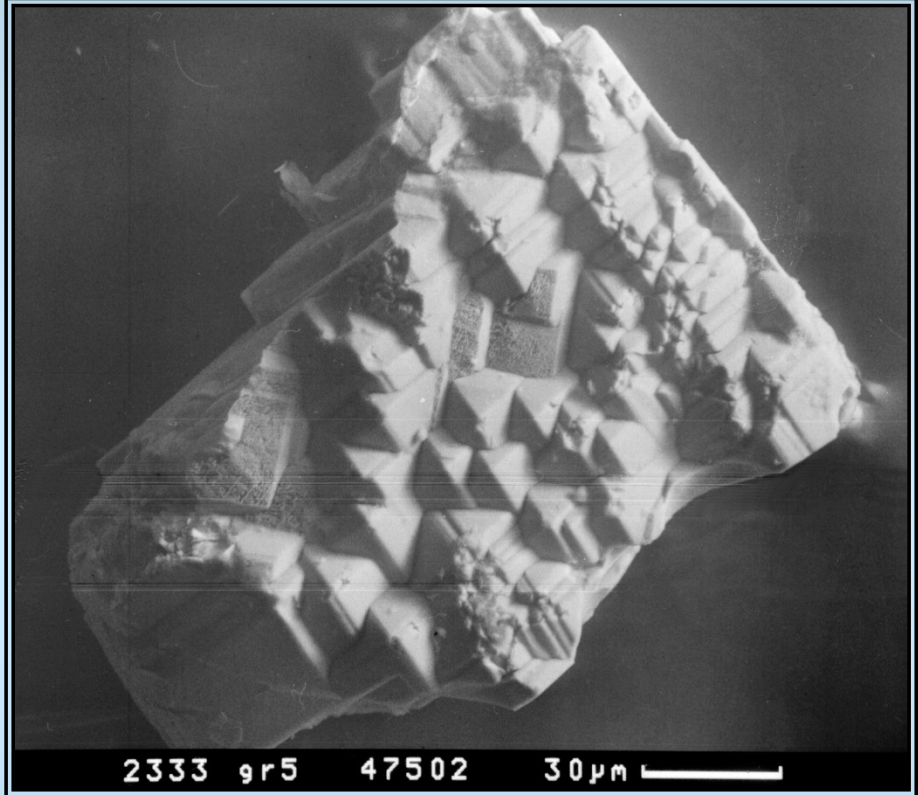
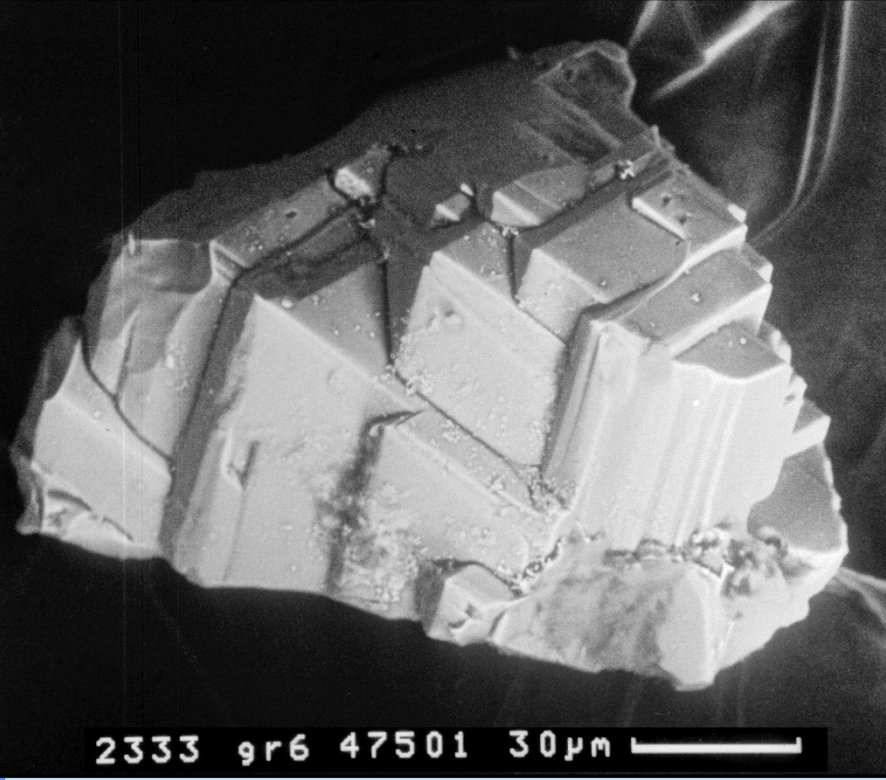
(left) slightly faceted garnet with hummocky surfaces

(right) garnet with small, sharp facets

faceted surface = angular surfaces on garnets; systematic etching is caused by preferential dissolution along octahedral and cubic planes of garnet (Hansley 1987).

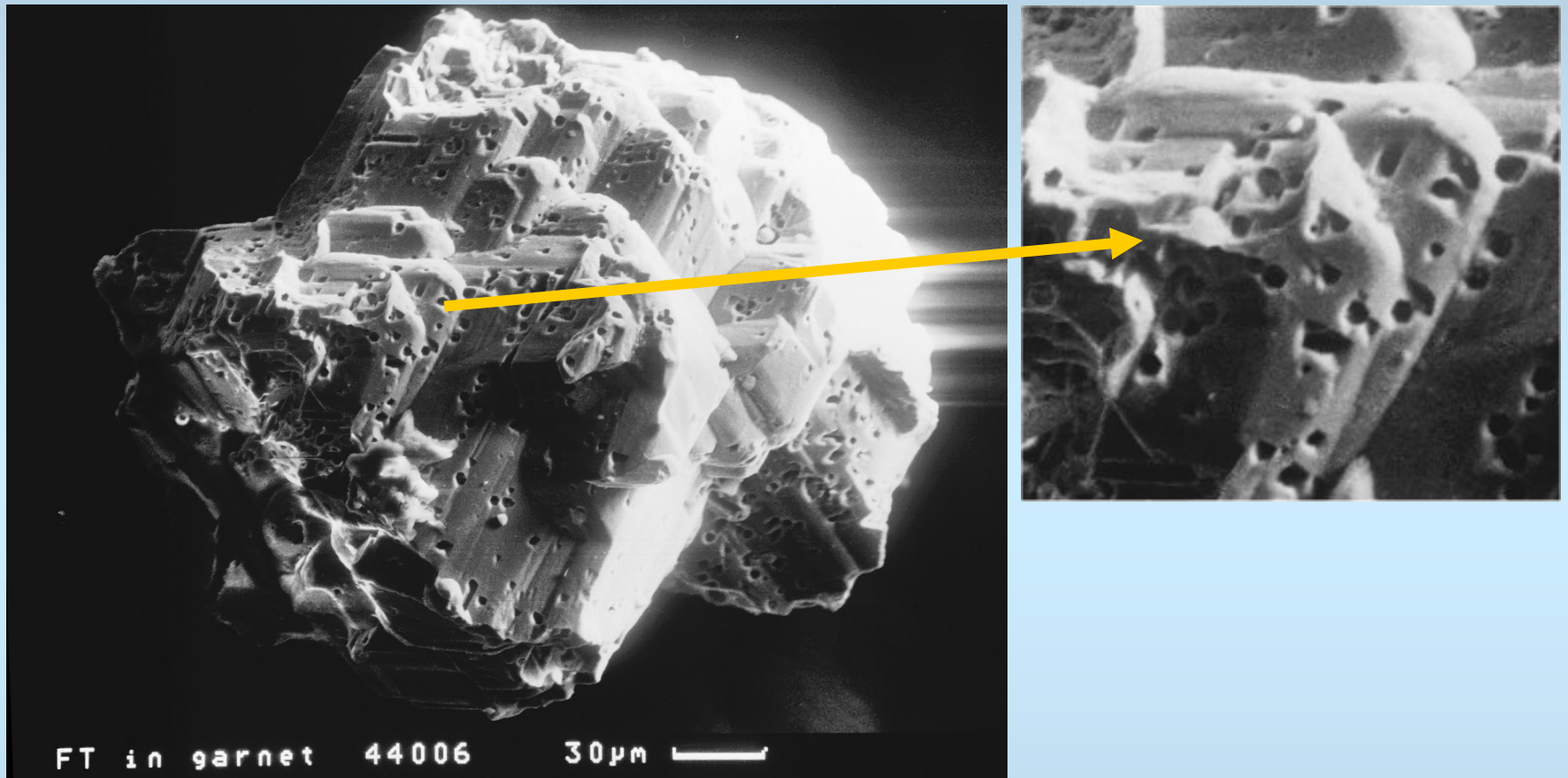
There is a continuum from slightly faceted grains with hummocky surfaces (left), to grains with small, sharp facets (right) to skeletal grains (2 next slides).

5. Dissolution of minerals during diagenesis



Deeply etched faceted garnet - skeletal garnet (Drahany Upland, diagenetic temperature > 200 C)

5. Dissolution of minerals during diagenesis



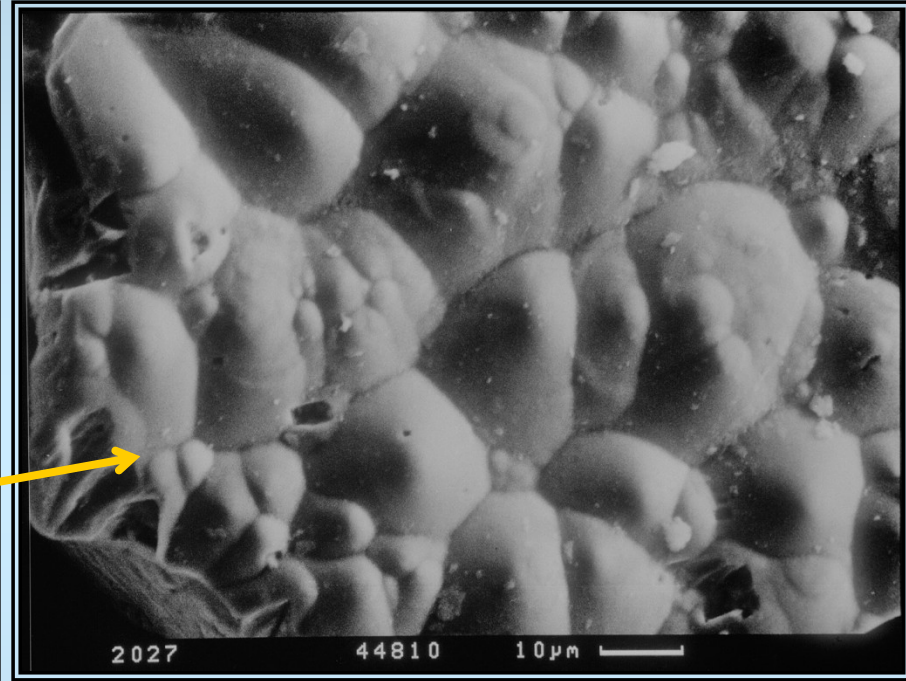
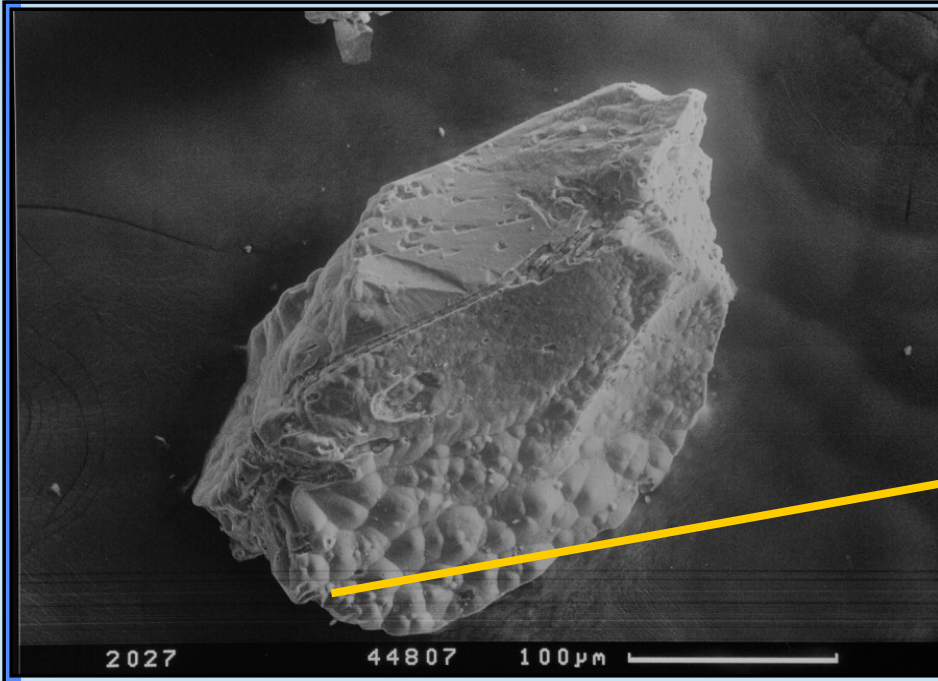
Deeply etched faceted garnet - skeletal garnet (Drahany Upland, diagenetic temperature > 200 C)

Complex etching patterns (faceted surface and etch pits)

The origin of faceted garnets in sandstones: dissolution or overgrowth?

- Faceted garnets have only been reported from late diagenetic sandstones. Garnet in recent sediments and soils may be pitted, but do not display crystallographically controlled facets.
- The earliest explanation of such facets was interpreted as overgrowths (Sauer 1900; Simpson 1976). The main arguments of this hypothesis are crystallographic similarity between garnet facets and euhedral authigenic overgrowths on quartz and feldspar.
- Several studies demonstrated that chemical corrosion (HF, NaOH) does produce facets on garnet surfaces, but the surface textures were not identical to those produced by natural processes (Bramlette 1929, McMullen 1959),
- Experiments with dicarboxylic acid solutions (Hansley 1987) created facets on garnets identical to those developed on naturally etched garnets.
- Warm diagenetic fluids reacted with organic material causing the generation of organic acids and CO_2 . Between $T \sim 80\text{-}130\text{ }^\circ\text{C}$ is the zone of maximum generation of organic acids during diagenesis of organic-rich sediments and occurrence of skeletal garnets (Hansley 1987).
- Garnet (almandine, pyrope, grossular, spessartine, uvarovite) is typical high-T and high-P mineral. Hydro-garnets (hydro-grossular and hydro-andradite) are the only garnets, that could be formed under diagenetic conditions ($T \sim 50\text{ }^\circ\text{C}$ Kuzel 1968). Well developed facets are observed on garnet with variable chemical composition.

5. Dissolution of HM during burial diagenesis

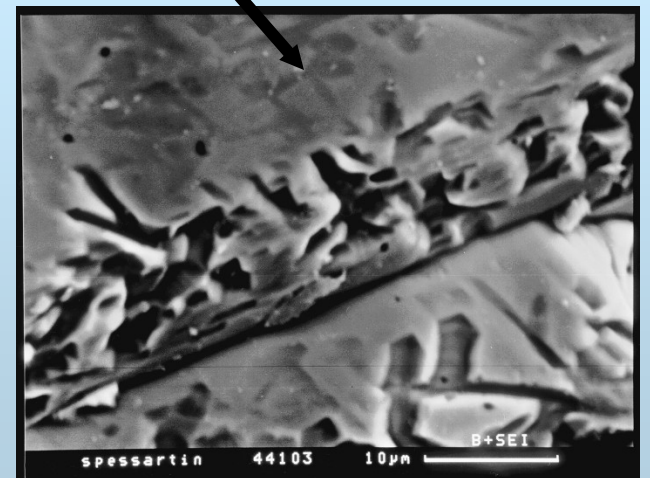
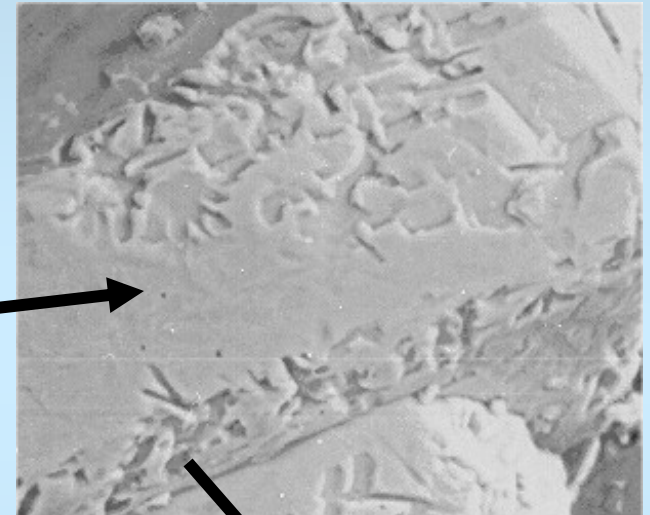
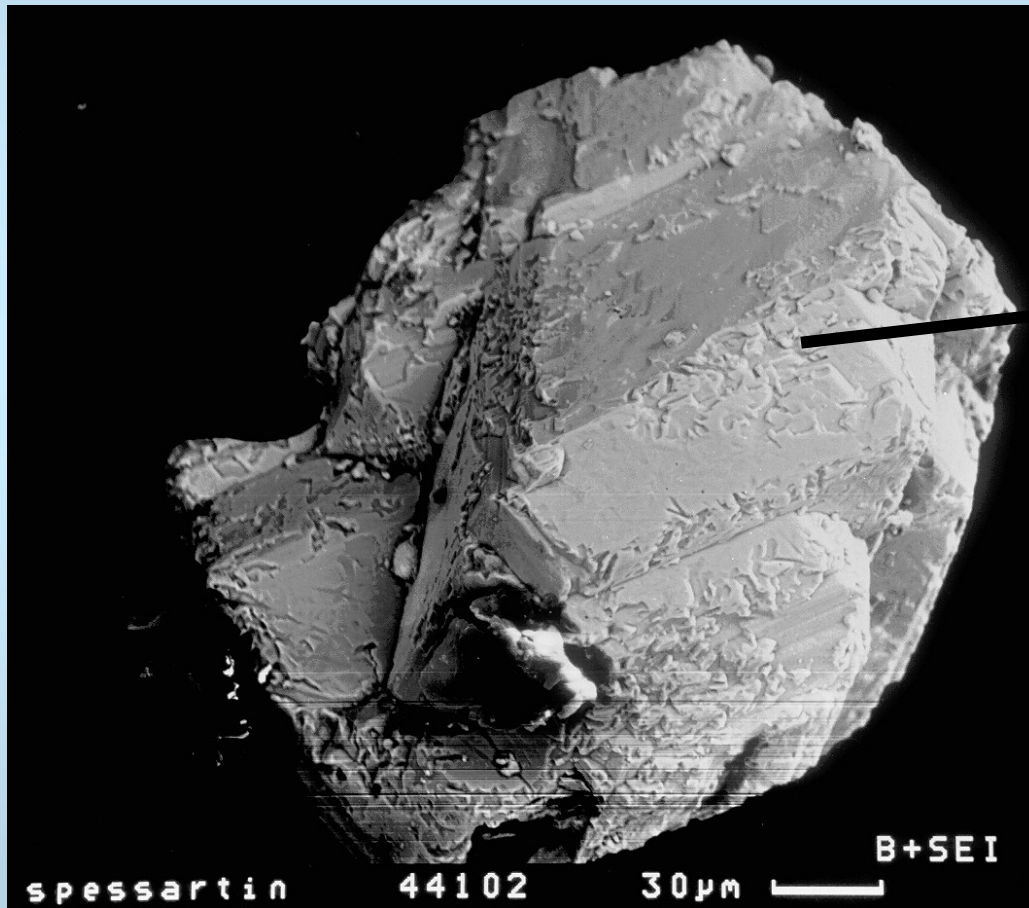


Complex etching patterns (intensively altered detrital garnets (Drahany Upland) - etch pits and mammillated surface

Mammillated surface formed during experimental dissolution of garnet by 1% oxalic acid solution (Hansley 1987)

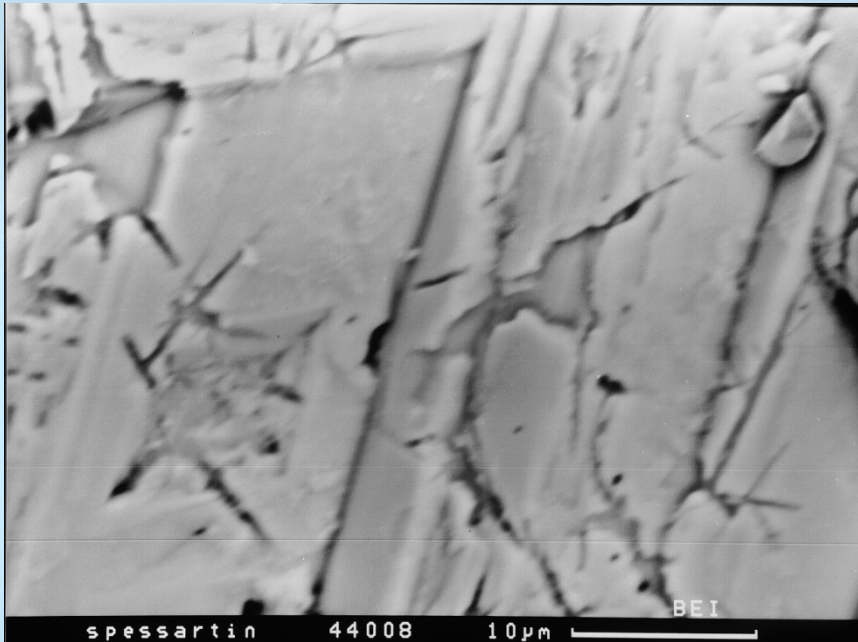
5. Dissolution of HM during burial diagenesis

Garnet dissolution - skeletal garnet and fission-tracks?



5. Dissolution of HM during burial diagenesis

fission-tracks ?



Garnet surface (Drahany Upland;
BSE)



For comparison - fission-tracks
in apatite (optical microscope)

5. Dissolution of HM during burial diagenesis

stability of the heavy minerals - internal factors

- Variability in chemical composition of minerals forming solid solutions: garnet, tourmaline, epidote, amphibole, pyroxene
- Intensity of alteration from source rock (ilmenite - leukoxenization; zircon - metamictization)
- Effect of surface quality (grains with large surface dissolves more intensively than grains with small surface, due to larger reaction area)
- Effect of external irradiation (fission-tracks)

Effect of variability in chemical composition on burial dissolution

Garnet

- Ca content probably governs the stability of the garnets, preferential dissolution of the more calcium-rich garnets was observed in some sedimentary units (Morton, 1987; Milliken, Mack 1990; Smale and van der Lingen 1989).
- Morton and Hallsworth (1999) distinguished with increasing depth of burial the zone (i) rich in detrital garnet (with variable chemistry); zone (ii) where intrastratal dissolution of Ca-rich garnet was observed; followed by zone (iii) at which detrital garnet disappear from HM assemblages (below about 3500 m).
- On the other hand, in the Moravo-Silesian Culm basin and in Anglo-Welsh basin preferential dissolution of the more calcium-rich garnets was not observed (Čopjaková 2001; Haughton and Farrow 1989)
- In experimental studies (Nickel 1973, Schott and Petit 1987, Sverdrup 1990) the correlation between dissolution rate and garnet chemistry was not observed. All major garnet end-member (almandine, pyrope, grossular, andradite) yield similar dissolution rate. Only significant correlation between dissolution rate and pH of solutions was observed; the lowest dissolution rate is near neutral pH 5-8, with increasing and decreasing pH dissolution rate grows.

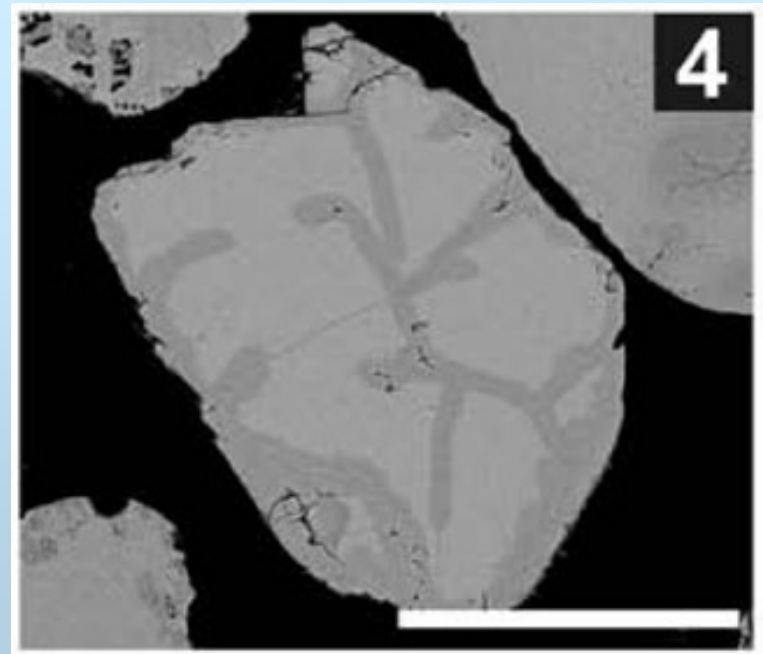
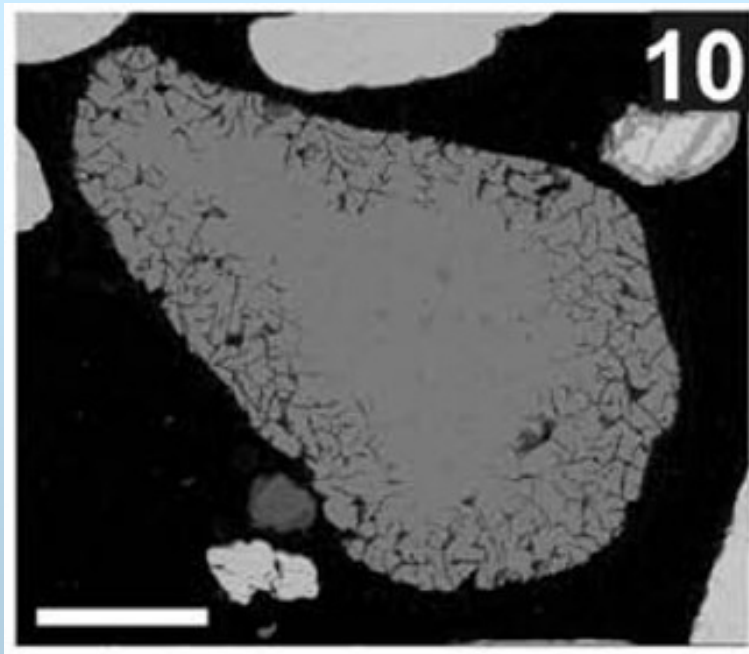
Monazite

- Preferential dissolution exclusively of Th-rich monazite (LREEPO_4) was observed by some authors. Th-poor monazite seems to be more stable.

5. Dissolution of HM during burial diagenesis

Cr-rich spinel

- Papers concerning postdepositional alteration of Cr-rich spinels are only rare (Lumpkin 2001; Pownceby 2005).
- Cr-rich spinels are usually considered stable in diagenetic conditions
- Diagenetic changes on Cr-rich spinels (Pownceby 2005):
 - network of microcracks at Cr-spinel rim
 - chemical changes - altered dark rim - depletion in Fe and Mg; bad stoichiometry; deficit in A-site



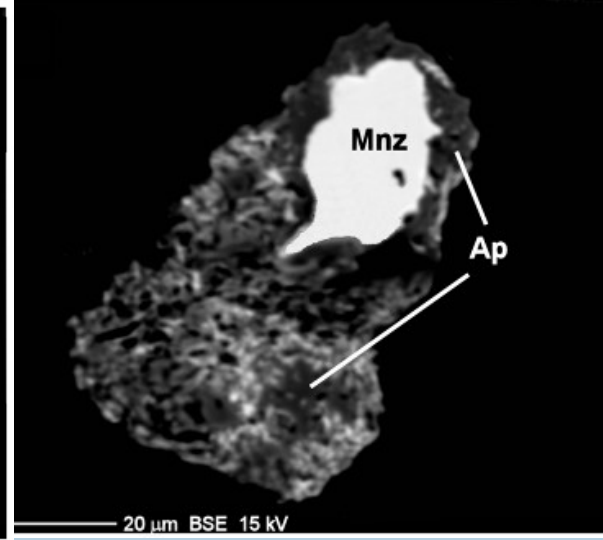
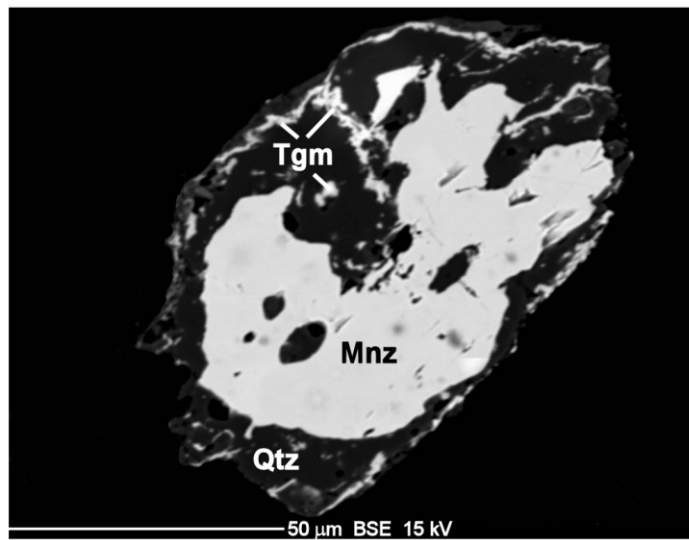
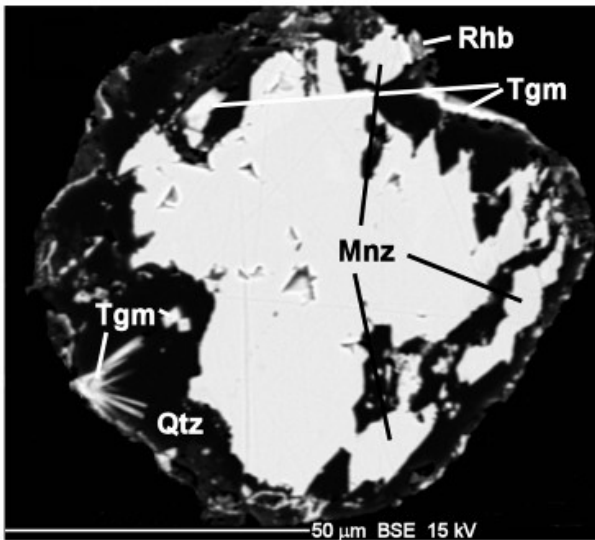
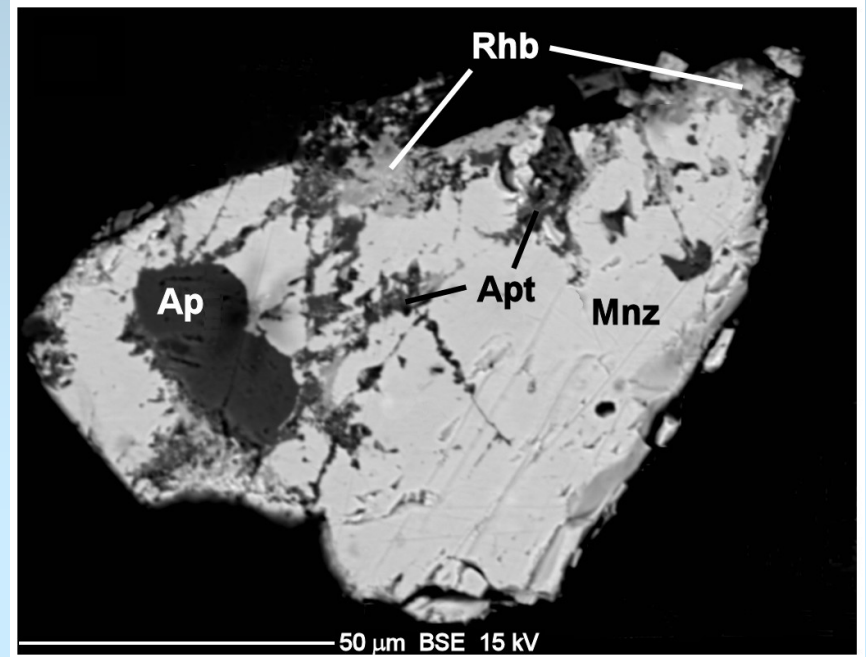
5. Dissolution of HM during burial diagenesis

Monazite

- Published papers on the degradation of monazite during diagenesis to burial metamorphism are scarce.
- Monazite is typically present in heavy mineral assemblages and it is usually considered relatively stable in such sedimentary environments (Morton and Hallsworth, 1999).
- Detrital monazite has been reported even from amphibolite-facies metasediments (Williams, 2001; Krenn et al., 2008).
- The idea that monazite may decompose during diagenetic conditions has been debated recently (Cuney and Mathieu, 2000; Mathieu et al. 2001; Hecht and Cuney, 2000).
- These authors reported microcrystalline Th-OH silicate as the principal phase of monazite degradation.
- Detrital monazite dissolution and replacement by florencite in siliciclastic sediments was observed by Wanagi and Pagel (2011)

5. Dissolution of HM during burial diagenesis

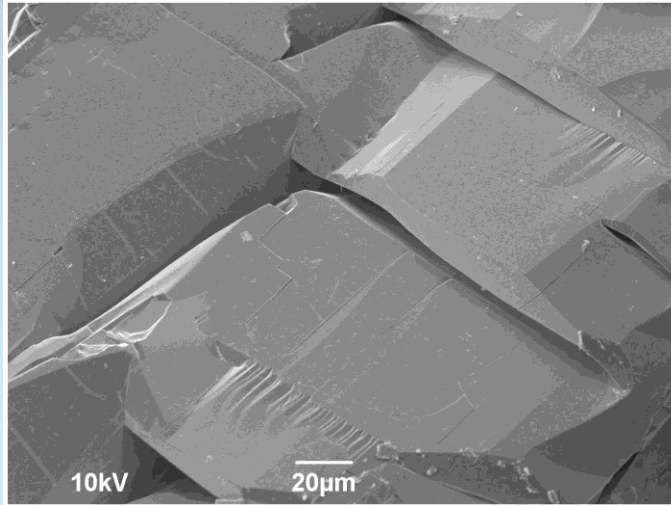
altered detrital monazite in BSE image
monazite dissolution with subsequent
precipitation of authigenic fluorapatite,
rhabdophane and hydrated Th-Si phase
(Drahany Upland) in relation to a deep burial
(T ~ 200-250 °C)



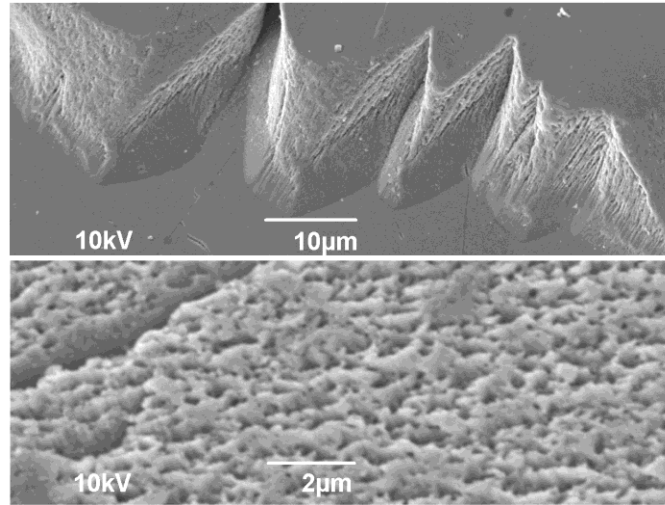
Experimental alteration of synthetic monazite

temperature 150°C, duration 3 months, 2 M solutions

non-altered monazite



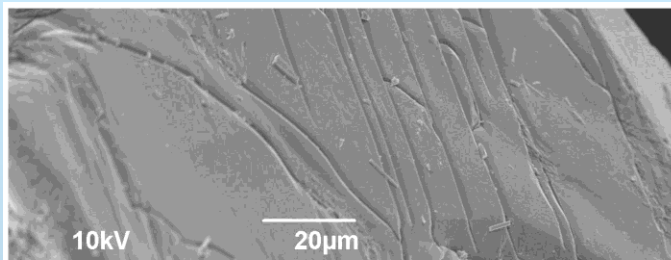
Cl⁻ rich solution



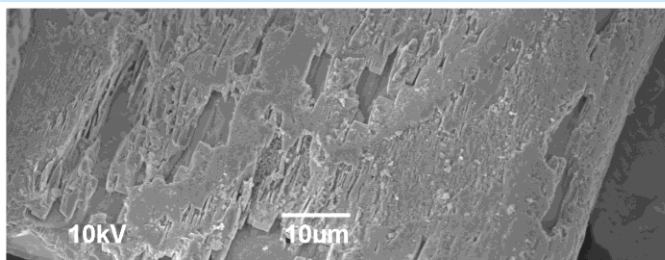
preferential dissolution of selected faces

etch pits

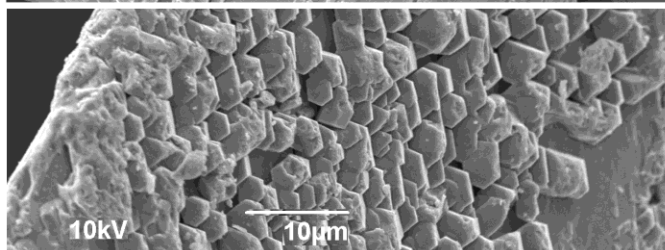
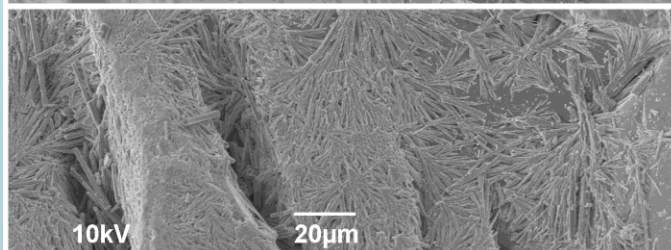
OH⁻ rich solution



F⁻ rich solution



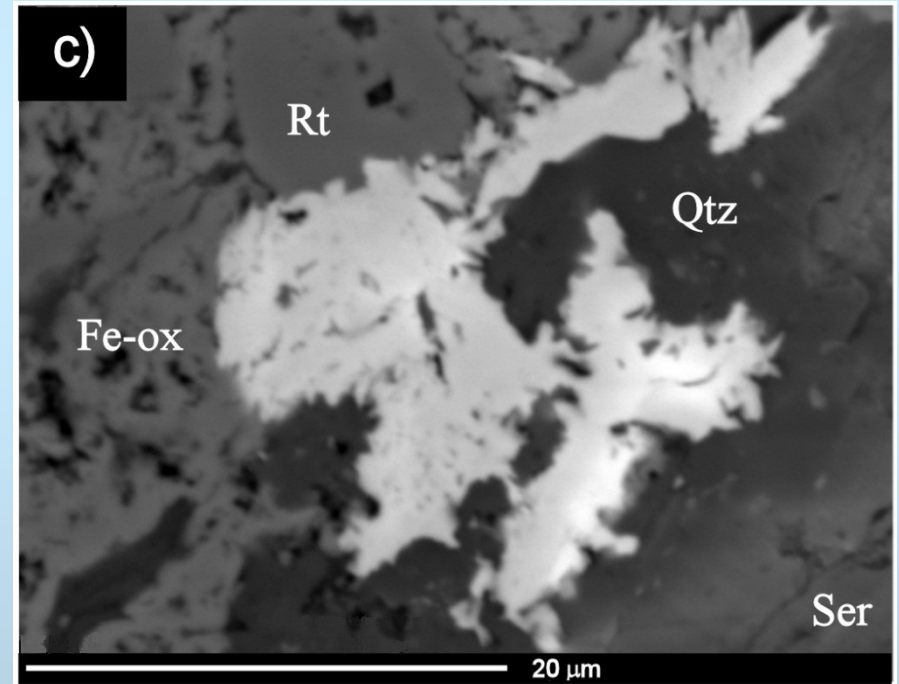
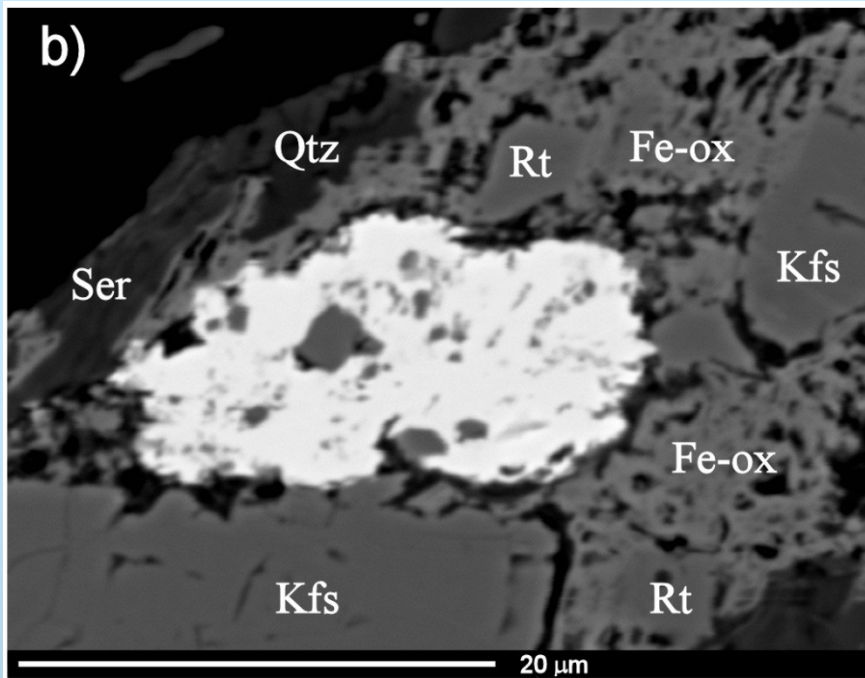
etch grooves to intensive dissolved surface - rough surface



dissolution of monazite and subsequent precipitation of newly-formed REE-phases

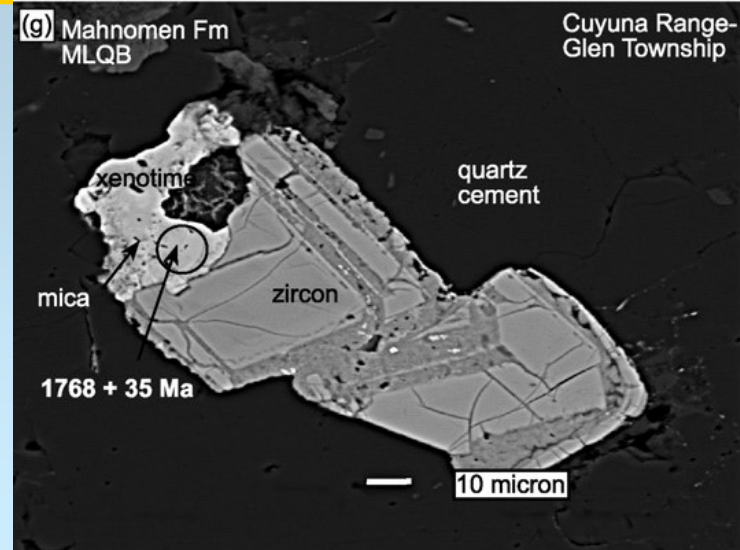
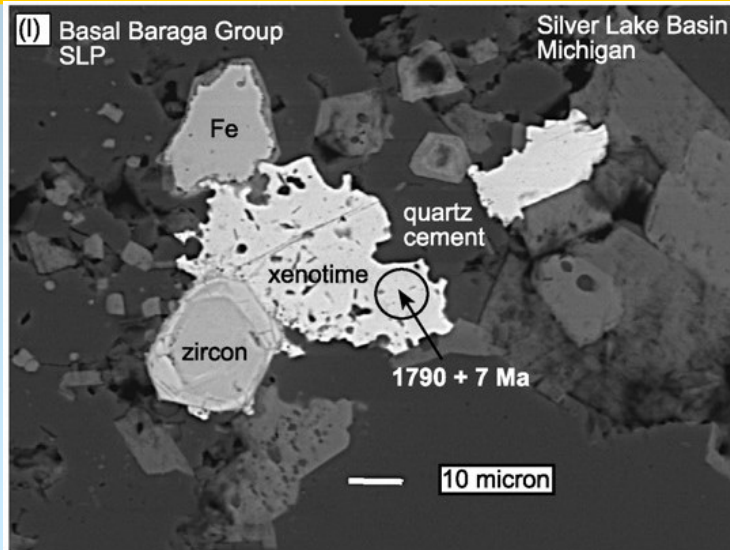
Formation of authigenic minerals during diagenesis

- Observed formation of authigenic tourmaline, TiO_2 oxides, apatite, monazite, xenotime
- It is problem to distinguish between authigenic and detrital origin (shape, texture, chemical composition, mineral association)
 - Irregular shape are common for many diagenetic minerals
 - contain inclusions of other diagenetic minerals

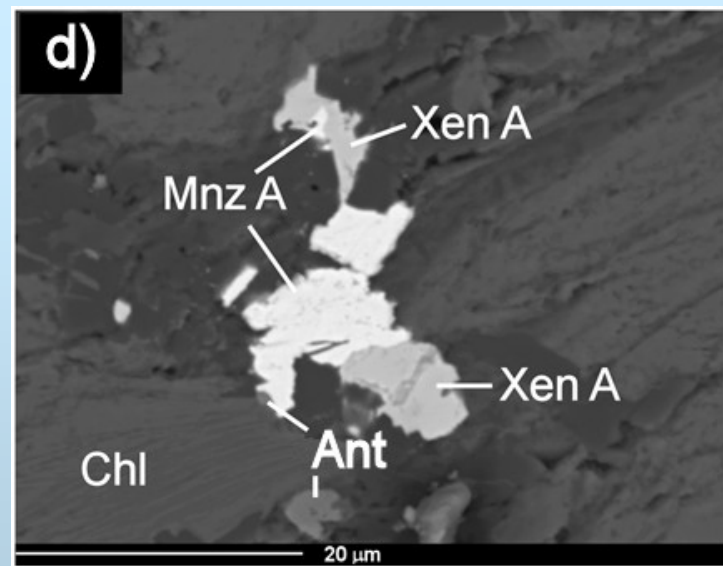
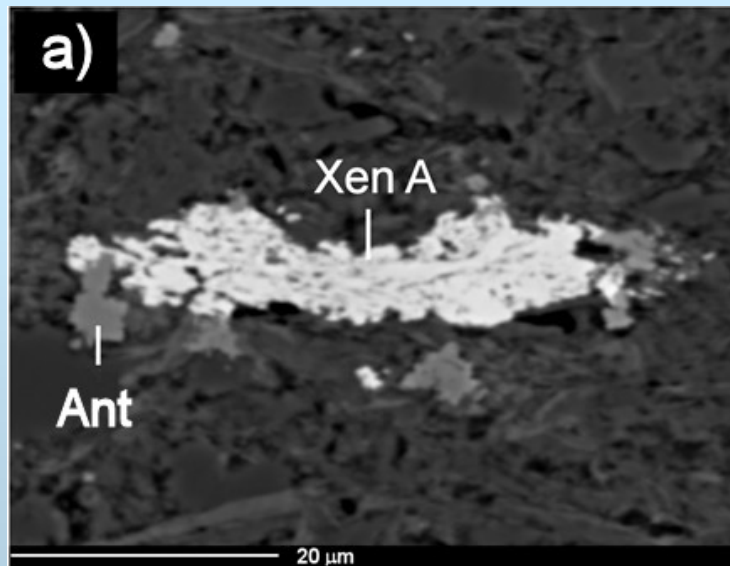


authigenic monazite, bright phase in the BSE image (Protivanov Formation, Drahany Upland)

Formation of authigenic minerals during diagenesis



Early diagenetic **xenotime** - typically forms overgrowths on detrital zircon (Vallini et al. 2007)




Authigenic **xenotime** - formation during a deep burial (Protivanov Fm., Drahany Upland)

6. Weathering at outcrop of sedimentary rocks

- Sandstones at outcrops are likely to be invaded by acidic groundwaters
- The most critical mineral is apatite, which is stable in deep burial but is exceptionally unstable under weathering.
- Hester (1974) showed that garnet and epidote are absent in weathered samples, but they are present in unweathered sandstones (Alabama and Georgia).
- If sandstones have been exposed at the surface for long periods, extensive alteration of HM assemblages may have occurred.
- It is crucial to collect fresh material.

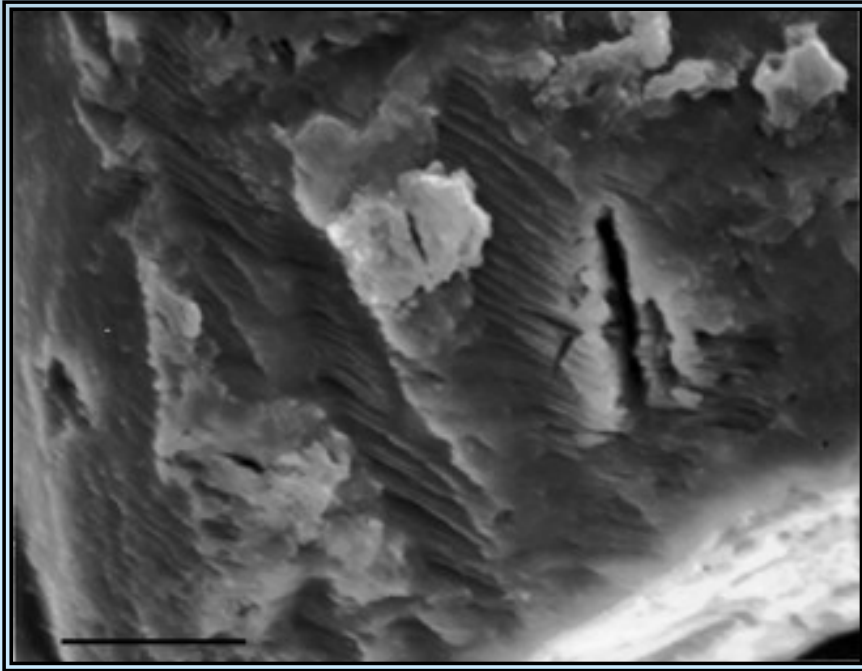
6. Weathering at outcrop of sedimentary rocks

Morton (1982) and Lang (2000) identified a dissolution profile in sediments in relation to exposure and subaerial weathering

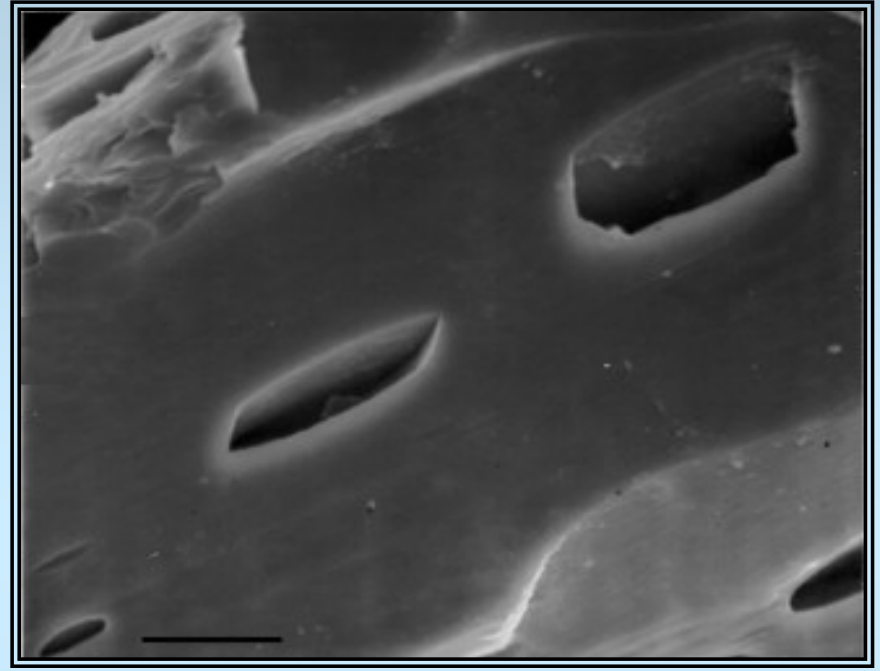
a) Morton (1982)	b) Lang (2000)	
amfibol	apatit	 <p>nestabilní</p> <p>stabilní</p>
titanit	titanit	
apatit	amfibol	
epidot		
granát	granát	
staurolit	epidot	
kyanit		
zirkon	zirkon	
turmalín		
TiO ₂ minerály		

Stability of HM during subaerial weathering; a) sandstones of Thanet Fm., pH < 7; b) glacial sediments with pH 4,5.

6. Weathering at outcrop of sedimentary rocks



Conchoidal fracturing on garnet surface, SEI, scale bar 10 μ m, (Cormier 1998)



Etch pits on garnet surface, SEI, scale bar 10 μ m, (Cormier 1998).

Chemical weathering of garnet in soil zone of glaci-fluvial sediments - etch pits and conchoidal fracturing on garnet are similar to dissolution marks in relation to deep burial.

Sampling and sample preparation

Do not collect weathered rocks (if possible)-weathering could affect heavy mineral assemblage.

Take a sufficient amount of the rock-usually more than 3 kg (it depends on the content of heavy minerals).

Take samples of the same grain size.

Sample preparation (disintegration)

- Use the same procedure for all samples
- For sandstones-ideally mechanical disintegration (crushing)
- If possible, do not use chemical disintegration (HCl dissolves phosphates, magnetite, etc..)
- If needed, use diluted acetic acid instead of HCl (to removing carbonate cement)
- Use the same grain fraction, usually 63-125 μm (Be careful if you are using data of other researchers)

Separation of the HM assemblages

separation of complete HM assemblages:

- using heavy liquids with density about 2.9 g.cm^{-3}
tetrabromethane $\text{C}_2\text{H}_2\text{Br}_4$ 2.96 g/cm^3 , bromoform - toxic
non-toxic liquids - polytungstenates (short lifetime due to the recrystallization)
- Sedimentation or centrifugation (time consuming)
- Panning - less convenient- frequently used during stream sediments sampling-obtaining HM assemblage in situ.

obtaining of monomineral fractions

- using heavy liquids of the density higher than 2.9 g.cm^{-3} , e.g. Clerici solution (4.25 g.cm^{-3} , toxic)
- magnetic separation
- manual separation under binocular microscope
- Chemical separation - e.g. for zircon, when the rest of HM assemblage is dissolved and is not important.
- Technical problem of separation of HM assemblage bellow $50 \mu\text{m}$. Such small grains have tendency to keep in suspension. It would be useful for study of monazite or zircon, because majority of grains remain in the undersize fraction

Heavy mineral analysis

- heavy mineral analysis should be based on the counting of more than 200 non-opaque grains (usually 200-300 grains) under optical microscope, binocular microscope or scanning electron microscope
- determination of not recognized minerals - EMPA, XRD
- Two alternative ways to generate provenance sensitive data are possible:
 - **Conventional heavy mineral analysis** - uses the entire heavy mineral assemblage
 - **Varietal heavy mineral analysis** - concentrates on the attributes of individual mineral species
- To maximize the provenance information a combined approach is recommended

Data processing

data processing and evaluation:

Conventional heavy mineral analysis

- absolute and relative (percentage) abundance of individual minerals in HMA
- presence/absence of certain mineral
- ratios of abundance of individual minerals - The minerals selected for provenance sensitive ratio determination should meet two criteria:
 - (i) they are **stable during diagenesis**
 - (ii) they have **similar densities and grain sizes**, which are the main controls on hydrodynamic behaviour.

apatite-tourmaline index = $100 \cdot \text{Ap} / (\text{Ap} + \text{Tu})$

garnet-zircon index = $100 \cdot \text{Grt} / (\text{Grt} + \text{Zr})$

monazite-zircon index = $100 \cdot \text{Mnz} / (\text{Mnz} + \text{Zr})$

chrome spinel-zircon index = $100 \cdot \text{CrSp} / (\text{CrSp} + \text{Zr})$

Data processing

Multivariate statistical methods:

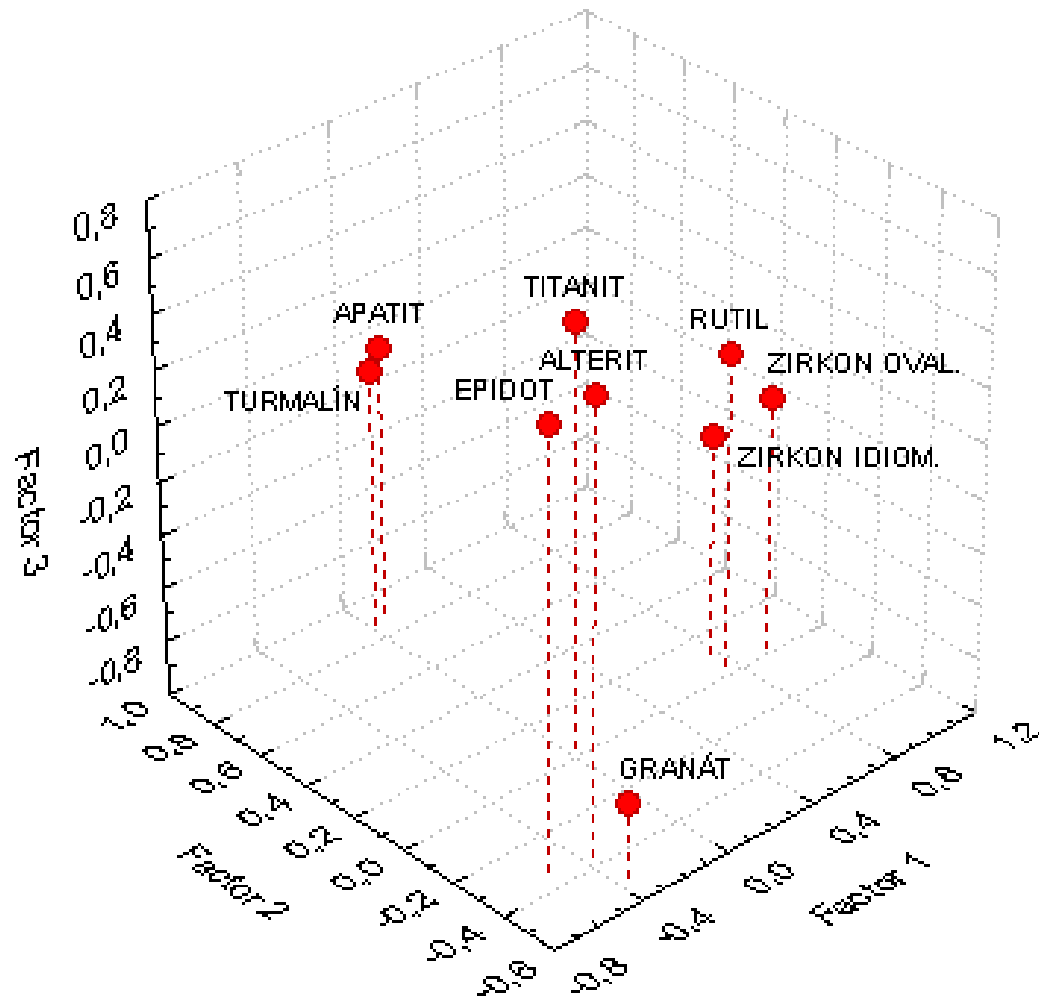
Among the variety of multivariate methods appropriate to the statistical analysis of heavy mineral data are:

- factor analysis (Q-mod or R mod)
- cluster analysis, fuzzy cluster analysis
- discriminant analysis

These methods provide a reduction of variables and an objective classification of samples

example of processed data

Analysis of heavy mineral data - R-mode factor analysis



Protivanovské souvrství

Varietal heavy mineral analysis

- optical methods (color and shape of minerals - tourmaline, amphibole, garnet)
 - color varieties of tourmaline (Krynine, 1946; Mange-Rajetzky, 1995) can be provenance-diagnostic.
 - ... outdated methods
- study of crystal morphology - crystal morphology of the zircon is regarded as a petrogenetic indicator (Pupin, 1976).
- At present, the most common studies involving geochemical study (using EMPA) of selected mineral species (Garnet is very useful due to its wide distribution in various types of rocks, variable chemical composition and the stability during transportation and diagenesis)
- Moreover, study of mineral inclusions in selected minerals
- Dating of individual monazite, zircon, xenotime grains - single-grain dating techniques - sensitive high-resolution ion microprobe (SHRIMP) and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP MS)
- Fission track (apatites, zircons) - cooling history

Varietal heavy mineral analysis

Chemical composition of HM:

- analysis of the chemical composition (garnets, tourmaline, staurolite, spinel group, amphiboles, pyroxenes, olivines, ilmenite, rutile, apatite, monazite...)
- Particularly electron microprobe analysis, which became widely available in the 1990s.
 - Major elements
 - Trace elements detectable by electron microprobe
 - F, Cl, Cr, Ti in amphibole group,
 - F, Mn, Zn, V in tourmaline
 - Ti, Mn, Zn, V in Cr-rich spinel
 - Na, P, Ti, Y, Cr, V in garnet
- electron microprobe - about 100-300 ppm detection limit for majority of trace elements
- The most frequently used garnet, tourmaline, Cr-spinel (Garnet is very useful due to its wide distribution in various types of rocks, variable chemical composition and the stability during transportation and diagenesis)
- Utilization of chemical composition of olivine, amphibole and pyroxene is limited owing their low stability during diagenesis.

Varietal heavy mineral analysis

Chemical composition of HM:

- More recently, more sophisticated technology has been developed, such as laser ablation inductively-coupled plasma mass spectrometry (LA-ICP MS) - enable high-precision determination of trace elements and isotopic compositions of single-mineral grains
- 0.X - X ppm detection limit for trace elements
- Using LA-ICP MS in provenance studies:
 - Trace elements in garnets (Čopjaková et al. 2005)
 - Trace elements in zircon (Belousova et al. 2002)
 - Trace elements in apatite (Morton and Yaxley 2007)

Detrital garnets

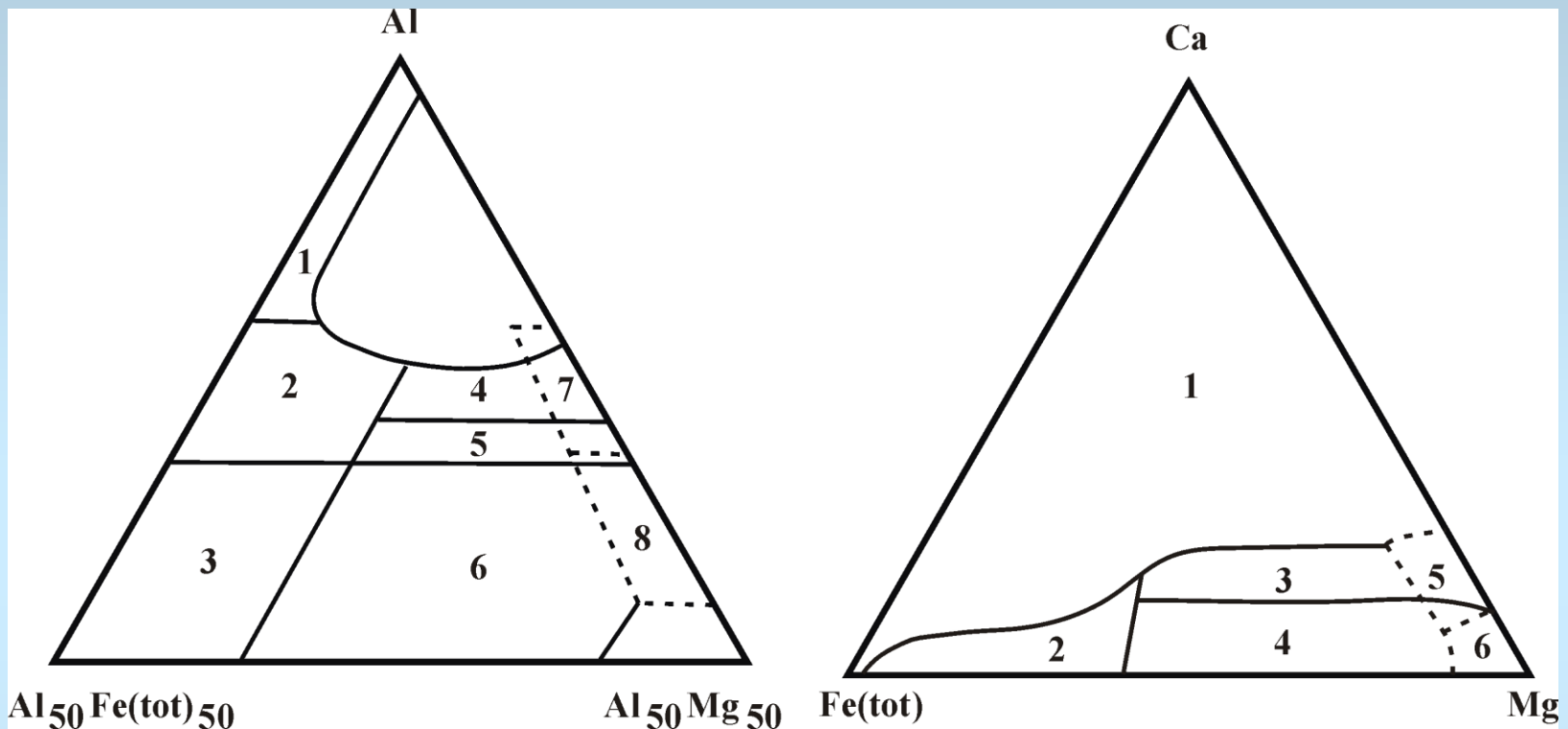
- relatively stable
- Variability of its chemical composition reflect the conditions of formation.
- Garnet is common accessory mineral in magmatic, metamorphosed and sedimentary rocks.
- variability in garnet chemical composition and character of zonation of major to trace elements play important role for geothermobarometric calculation, drawing of the PT paths of the metamorphosed rocks and study of metamorphic reactions.
- In the case of sedimentary rocks, the garnet is frequently used for provenance study, lithostratigraphy of sedimentary complexes and correlation of sedimentary rocks.

Chemical composition of tourmaline

- Owing to its chemical and physical durability, the tourmaline is common in the HM assemblage
- Useful for study of significantly modified ultrastable HM assemblage
- In the past, the tourmaline color was frequently used for provenance study, but this information is not very trustworthy.

- In the last decades, there is a progress in study of chemical composition of garnet using EMPA
- The classification diagrams for estimating of the detrital tourmaline origin were published by Henry and Guidotti (1985), Henry and Dutrow (1992).
- When study detrital tourmalines, take care about authigenic tourmaline overgrows which could forming during diagenesis. Its chemical composition could be highly distinct from original detrital core

Discrimination plots of the tourmaline



- 1 Li-rich granitoids, pegmatites and aplites
 - 2 Li-poor granitoids and associated pegmatites and aplites
 - 3 Fe³⁺-rich quartz-tourmaline rocks
 - 4 metapelites and metapsamites coexisting with an Al saturating phase
 - 5 metapelites and metapsamites not coexisting with an Al saturating phase
 - 6 Fe³⁺-rich quartz-tourmaline rocks, metapelites and calc-silicate rocks
 - 7 low Ca ultramafics, Cr- and V-rich metasediments
 - 8 metacarbonates
- according to Henry and Guidotti (1985)

Spinel

Spinel play an substantial role among HM assemblage of sedimentary rocks.

The most important are spinels rich in Cr-spinel, gahnite and hercynite molecule.

Cr-spinels are crucial for provenance study of mafic and ultramafic rocks and represent important mineral for paleogeographic reconstruction.

Al-spinels

Název	A-pozice	B-pozice	Charakter
Hercynit	$\text{Fe}^{(2+)}$	Al_2	Normální
Spinel	Mg	Al_2	Normální
Gahnit	Zn	Al_2	Normální
Galaxit	$\text{Mn}_{0,71}\text{Al}_{0,29}$	$\text{Mn}_{0,9}\text{Al}_{1,71}$	29% Inverzní

Fe-spinels

Název	A-pozice	B-pozice	Charakter
Magnetit	$\text{Fe}^{(2+)}$	$\text{Fe}^{(2+)}\text{Fe}^{(3+)}$	Inverzní
Magnesioferrit	$\text{Mg}_{0,1}\text{Fe}^{(2+)}_{0,9}$	$\text{Mg}_{0,9}\text{Fe}^{(2+)}_{1,1}$	Z 90% inverzní
Franklinit	Zn	$\text{Fe}^{(2+)}_2$	Normální
Jaccobsit	$\text{Mn}_{0,85}\text{Fe}^{(2+)}_{0,15}$	$\text{Mn}_{0,15}\text{Fe}^{(2+)}_{1,85}$	Z 15% Inverzní
Trevorit	$\text{Fe}^{(2+)}$	$\text{Fe}^{(2+)}\text{Ni}$	Inverzní

Cr-spinels

Název	A-pozice	B-pozice	Charakter
Ferrochromit	$\text{Fe}^{(2+)}$	Cr_2	Normální
Magnesiochromit	$\text{Mg}^{(2+)}$	Cr_2	Normální

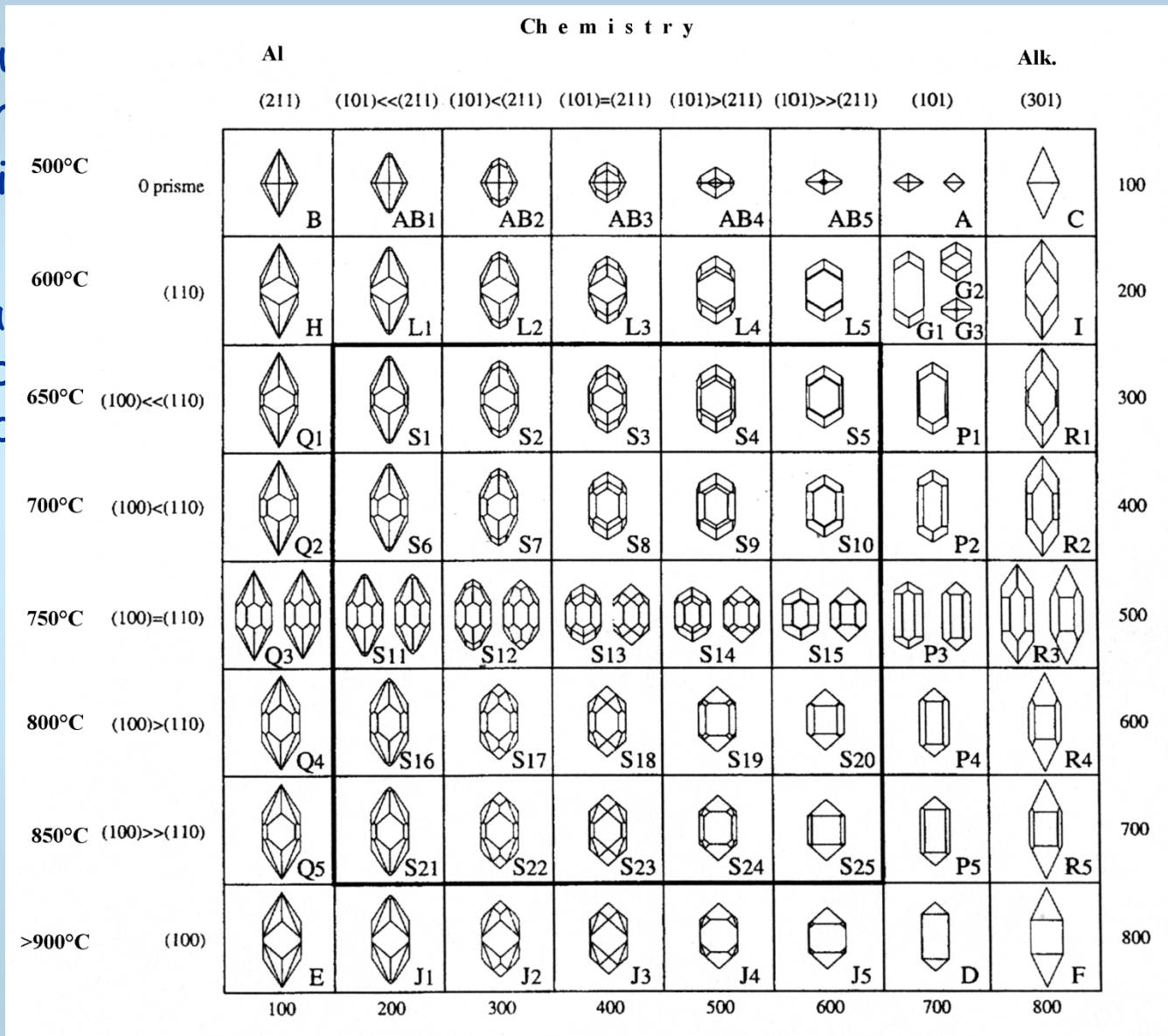
Zircon typology

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electron



Monazite

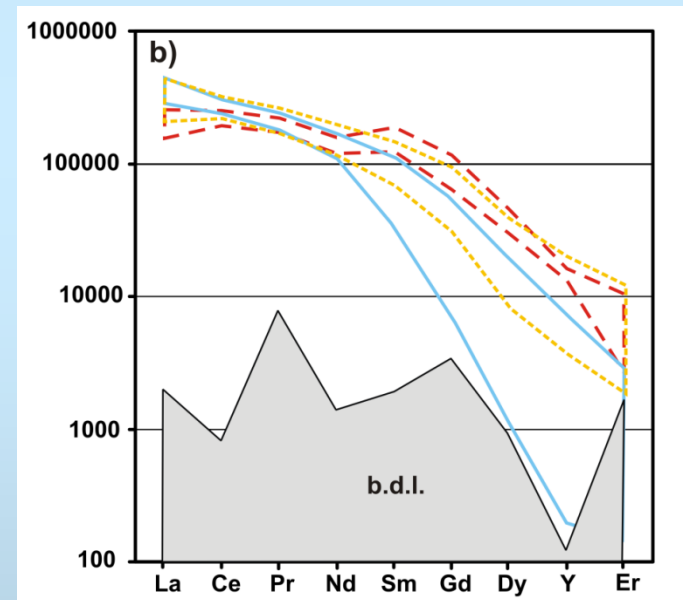
- monazite - monoclinic LREE phosphate - LREEPO_4
- It is useful mineral for age determination - CHIME (CHEMical Th-U-total Pb Isochron METHOD) dating
 - big advantage for provenance studies

chemical composition of monazite

The most common is monazite-(Ce), but La, Nd and Sm dominant members were found in the nature as well.

The shape of REE pattern is dependent on the chemical composition of the parent rock

monazite commonly contains several wt.% of U, Th, Ca and Si.

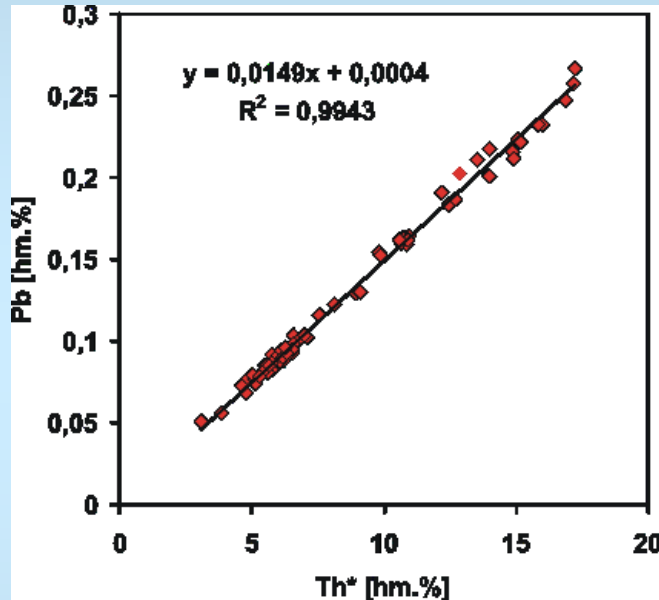


Chondrite normalized REE pattern of monazite from selected pebbles of Račice conglomerates, Drahany Upland.

Monazite-dating

CHIME monazite dating - using electron microprobe

based on the U, Th and Pb content in monazite on the assumption of none or negligible amount of common lead in monazite (Parrish 1990).



Isochrone Th*-Pb for detrital monazite of Viséan age from graywackes from Drahanu Upland

- The homogeneity of the data set is verified by construction of the isochrone Th*-Pb, which could reveal if the studied rock/HM assemblage contains or not monazites of different ages.
- Th* stands for theoretical Th content which would produce the same amount of Pb as determines for the calculated age.
- Th* allow us to take into consideration different decay constants for ^{232}Th , ^{238}U a ^{235}U , and therefore samples of the same age have to lie on the line passing the origin of the coordinate system.

Fission track analysis

- Based on analysis of radiation damage trails ("fission tracks") within detrital apatite or zircon grains - extracted from clastic sediments
- Each fission track is created by spontaneous fission of a single atom of ^{238}U
- ^{238}U is the only isotope with a decay rate that is relevant to the significant production of natural fission tracks
- Initial length of fission tracks; - apatite 16 μm ; - zircon 11 μm
- The number of tracks in grain depends on ^{238}U content and time
- Fission tracks are selectively dissolved and enlarged by etching in dilute nitric acid
- uranium content in apatite (zircon) needs to be determined independently



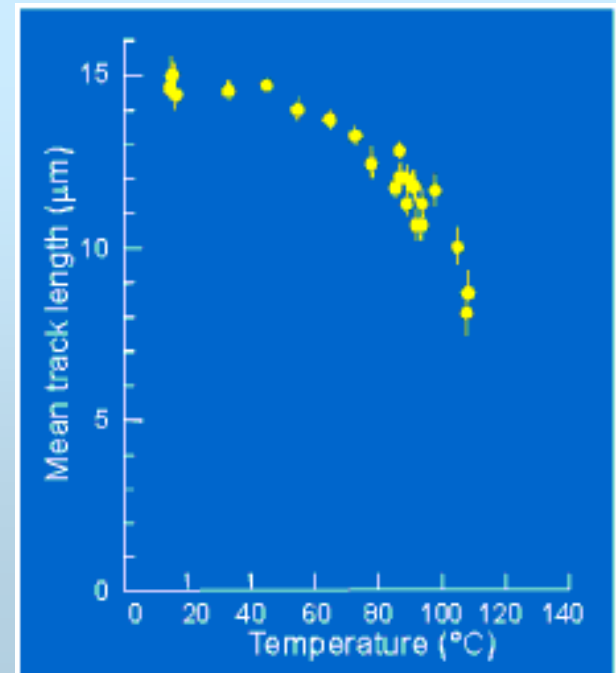
Etched spontaneous fission tracks in an apatite crystal.

(www.geotrack.com.au/afta-overview.htm)

Fission track analysis

- if we measure ^{238}U content and the number of tracks, we can measure the time over which tracks have accumulated - the fission track age
- at temperatures greater than $\sim 70^\circ\text{C}$, the ages are progressively reduced to zero at around 120°C - for apatite.
- at temperatures greater than $\sim 200^\circ\text{C}$, the ages are progressively reduced to zero at around 320°C - for zircon.
- The reduction in fission track - because the radiation damage constituting each fission track is progressively repaired, at a rate which increases with temperature. This repair is manifested as a decrease in the length of individual tracks.
- Chlorine content exerts a significant control on fission track annealing rates in apatite
- The fission-track dating technique is widely used in understanding the thermal evolution in sedimentary basin

The reduction of fission track length in apatite with increasing temperature (www.geotrack.com.au/afta-overview.htm)



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