Electron-microprobe dating of monazite

Nicole Malz
Institute of Mineralogy, TU Bergakademie Freiberg

Abstract. Monazite (LREE, ThO$_2$)PO$_4$ is an accessory mineral in leucogranites and metapelites. It crystallizes with zircon from granitic melts. During metamorphism the formation of monazite is possible at a wide range of conditions. High contents of Th and its decay to Pb during geological time spans provide the prerequisite for a dating method without analysis of isotopic ratios. Monazite Th-U-Pb ages can be calculated from a bulk chemical analysis by electron-microprobe (EMP). This analytical technique is non-destructive and in-situ with a great spatial resolution. Besides the characteristics of monazite and the properties of EMP this paper is focused on the different age calculation methods that have been developed during the last years.

Introduction

The dating of minerals is an essential procedure for understanding the formation processes and emplacement of rocks, and to distinguish between different magmatic and/or metamorphic events. Monazite is the second most used mineral for U/Pb-dating besides zircon. Although monazite is an accessory mineral, it is very common in a wide variety of rocks, e.g. in granites, rhyolites, pegmatites, gneisses, as well as in carbonatites, charnockites, migmatites, quartz veins and alluvial deposits (BOATNER

It has been demonstrated that monazite does not incorporate common Pb, thus no correction of the Pb content is needed. It is assumed that monazite behaves as a perfect structure and is very stable through geologic times.

In most cases, Pb diffusion in monazite can be neglected. According to HARRISON ET AL. (2002) would a heating episode of 10 Ma duration at a temperature of 700°C result in a diffusion profile with a characteristic length-scale of only 0.25 μm.

There are various case studies showing that monazite is able to preserve several age stages (e.g. DAHL ET AL. 2005b, FINGER ET AL. 2002). Furthermore they
showed that the Th-U-Pb system is not reset until upper sillimanite grade of metamorphism (SMITH ET AL. 1990).

The electron microprobe (EMP) is used for monazite dating because of its many advantages in contrast to other techniques. It is an in-situ and non-destructive technique with an excellent spatial resolution (about 1µm). Due to that one is able to measure several monazites in one thin section or several grains mounted in epoxy resin quite quickly. The only requirement one has is a polished, lead-free thin section, but there are several new techniques which can handle this.

Mineral-chemistry of monazite

Monazite - (LREE, ThO$_2$)PO$_4$ - is one of the most radioactive minerals after uraninite and thorite, containing high amounts of Th (up to 20 wt% ThO$_2$) and comparably low contents of U (up to 2 wt% UO$_2$). Monazite can also be the main host for Th and U in many rocks (HARRISON ET AL. 2002).

Although it is so strongly radioactive, monazite does not become metamict (HARRISON ET AL. 2002). Thermal annealing seems to be an important factor to restore the damaged structure. According to experiments from MELDRUM ET AL. (1997) it is not possible to amorphize a natural monazite grain above a critical temperature of 175°C.

Due to the high content of Th and U, radiogenic Pb accumulates in monazite within geological time spans and the content gets higher than the detection limit of the electron microprobe within about 100 Ma (MONTEL ET AL. 1996).

The general formula of monazite is ABO$_4$. The A-site usually contains large cations like LREE$^{3+}$, Ca$^{4+}$ or Th$^{4+}$, whereby the B-site is occupied by small cations that are tetrahedrally coordinated such as P$^{5+}$ (HARRISON ET AL. 2002).

The typical monazite grains tend to show rounded and irregular shapes and they often occur in clusters or trails (SCHERRER ET AL. 2000). The interference colors vary from third order blue to fourth order green or yellow. A useful characteristic to find monazite in a thin section are the pleochroitic halos common in biotite, chlorite and cordierite. But one has to be aware that they appear also due to a few other minerals like zircon. In contrast to tetragonal zircon, the monoclinic monazite mostly displays oblique optical extinction.

Sample preparation

Monazite can be analyzed by electron microprobe in two different kinds of samples. Either one can use a polished rock thin section coated with carbon or mounted and then polished mineral separates in epoxy resin.

In heavy mineral separates it is difficult to find monazite, as it is masked by predominant rutile and sphene (titanite) grains, even if the mineral separation has been optimized. With such samples, age calculations can be done very quickly but the petrographical positions of the grains remain unknown, which is quite a great
disadvantage. Another crucial factor is that grains smaller than 20-30 μm are
discarded by mineral separation. MONTEL ET AL. (1996) stated that the average
grain size of monazite in granites is about 20 μm and that crystals enclosed in
other minerals are even smaller and therefore can not be measured.

In polished thin sections the petrographical positions of the grains remain
visible. But it is sometimes hard to determine monazite using microscope optics.
A lot of experience is needed for that. And even if one finds a high-relief mineral,
it is hard to decide whether it is monazite, xenotime or zircon (MONTEL ET AL.
1996).

The optical identification of monazite in polarized light under the microscope is
always problematic due to small grain sizes of 20 – 200 μm. The most efficient
way to determine monazite in both kinds of samples is to use a backscattered
electron image (BSE) and search for minerals with high reflection. The
identification can be confirmed by a semi quantitative analysis with EDS (energy
dispersive X-ray spectrometer) or by positioning the WDS (wavelength dispersive
X-ray spectrometer) on the Th, Ce and P emission peaks. With this technique it is
also possible to detect much smaller crystals than can be seen with optical
microscopes.

No matter if one uses use polished thin sections or mineral separates, it is
necessary that the sample is lead-free polished, if the EMP should be used for
measuring. Conventional polishing lead disks contaminate the sample by
depositing lead at grain boundaries and are therefore not suitable. SCHERRER ET
AL. (2000) presented a new technique which uses ND-PE (low pressure
polyethylene) disks. They achieve nearly the same preparation efficiency and need
less time than conventional disks. But the most cost and time efficient method is
to polish the preparates with industrial pure diamond powder (0.5 – 2 μm) on
clothes.

Analytical procedures

Principles of measurement

For the EMP dating precise analyses of Th, U, Pb and Y are required.
Furthermore, for the ZAF correction of raw signals, the analysis of all other
elements, as LREE, P, Si and Ca are needed. The analytical precision for the
detection of Pb and U is achieved by long counting times and/or high analysis
currents, due to the low concentrations of these elements at < 1 wt%. One should
be aware, that high beam currents in combination with a long-term analysis
(several minutes) increase the analysis current and the risk to damage the sample
and/or the carbon coating and to get false results (STORMER ET AL. 1993). Thus,
one has to compromise between the accuracy of the measurements and the
analysis current.
In fact, these are not the only problems one will be confronted with by doing EMP analysis. Difficulties arise from a number of factors (e.g. choice of standard material, element detection limits, inter-element interferences etc.) which are discussed in many publications (e.g. PYLE ET AL. 2002; HARRISON ET AL. 2002) and are presented in an overview in the following passage.

**Problems of measurement**

The main difficulties doing EMP analysis arise from the presence of other X-ray lines interfering with peaks or background positions of elements required for measurement. Therefore the choice of analyzed lines and background positions are the key to the procedure.

Due to the fact that a considerable number and concentrations of LREE (light rare earth elements, e.g. La, Ce, Pr, Sm, Nd, Pr, Eu, Gd) can occur in monazite, the quantitative analysis is not trivial. Thus, a careful selection of X-ray lines is required that the peak overlap can be kept to a minimum. There exist several methods to correct for peak overlap (AML AND GRIFFIN 1975; DONOVAN ET AL. 1993; FIALIN ET AL. 1997; ROEDER 1985) but it appears to be more straightforward to choose lines with negligible interferences, if possible.

Owing to the fact that X-ray lines of the LREE are very closely spaced together, it is better to use global instead of local background positions. SCHERRER ET AL. (2000) showed in experimentations that for elements from Pr to U it is better to measure the upper and lower background on the two closest overlap positions surrounding the peak of interest. Neither UMα nor UMβ are free of significant peak interferences related to the Th content. Thus, a correction procedure is required based on the analytical lines ThMα and UMβ, but no correction for ThMγ and YLγ is needed for UMβ (SCHERRER ET AL. 2000). Dependent on the analytical instrumentation, the analysis of the PbMα or the PbMβ peak is suitable. However, in each configuration, the PbMo peak is influenced by the flank of the YLγ peak. This requires a correction procedure by linear regression, as monazite can have 0-4 wt% Y₂O₃. Therefore, the quantification of monazite using WDS requires careful selection of analytical settings and is quite time-consuming.

Due to different equipment of the microprobes, no general agreement on the best lines and background positions exist because they are all a function of the spectrometer configuration. To figure out the most precise contents of Th, U and Pb accurate investigations of the WDS signal have to be done. With long counting times, high probe currents and a state-of-the-art instrument, the detection limit of Pb can be as low as ±80 ppm (HARRISON ET AL. 2000).

For calibration of measurements the used standard materials should be well characterized. ThP₂O₇ achieved good results for Th, and UO₃ for elemental U. For Pb either well-characterized crocoite (PbCrO₄) or vanadinate (Pb₅(VO₄)₃Cl) should be used instead of galena (PbS), avoiding interferences of Pb and S (SCHERRER ET AL. 2000).
Age calculation procedures

The main limitation for dating single monazite by EMP is the rather poor precision of about ±45 up to ±120 Ma (COCHERIE AND ALBAREDE 2001) which depends on the measured concentration of Pb and thus the age of the mineral. But it can decrease after statistical treatment of a set of homogeneous ages to ±20 to ±30 Ma. The calculated errors depend almost entirely on the Pb content. Since it is the radiogenic product of Th and U, the error is furthermore directly related to the Th and U content. Another limitation results in the fact, that neither thorogenic and uranogenic Pb can be separated, nor the common Pb. According to PARRISH (1990) the amount of common Pb is negligible compared to radiogenic contents. One should be aware, that discrimination of discordant ages is not possible by EMP, because one just gets measurements of the contents of Th, U and Pb and try to calculate an age. The theoretical basis for the easiest way of calculating an age is the same as for the so-called chemical ages used in geochronology. With measuring the concentrations of Th, U and Pb one can calculate an age (t) by solving the following equation:

\[ \text{Pb} = \frac{\text{Th}}{232} \left[ \exp(\lambda_{232} t) - 1 \right] 208 + \frac{U}{238.04} 0.9928 \times \left[ \exp(\lambda_{235} t) - 1 \right] 206 + \frac{U}{238.04} 0.0072 \times \left[ \exp(\lambda_{238} t) - 1 \right] 207 \]  

(1)

where Pb, Th and U are in ppm, and \( \lambda_{232} \), \( \lambda_{235} \), \( \lambda_{238} \) are the radioactive decay constants of \(^{232}\text{Th}\), \(^{235}\text{U}\), and \(^{238}\text{U}\) respectively (MONTEL ET AL. 1996).

Average weighted age method

The easiest way for obtaining an age with EMP measurements is to use a program, e.g. Isoplot/Ex developed by LUDWIG (1999). When the ages are calculated and all lay within the analytical error of their individual ages, the group of monazites can assumed to be homogeneous. Ages, that seem to be geochronologically abnormal and that do not plot within the error of all points, can be automatically rejected (LUDWIG 1999). For the case, that two or more populations of ages appear, each homogeneous group can by studied as an individual group.

This method can be used, if the measured monazites contain nearly constant U and Th concentrations (COCHERIE ET AL. 2005).

\( \text{Pb} = f(\text{Th}^*) \)

This method was proposed by SUZUKI AND ADACHI (1991 a, b). Referring to COCHERIE ET AL. (2005) it can be used for monazites that exhibit a fairly constant Th/U ratio but a significant U and Th heterogeneity. By knowing the age of each point, the U content can be converted into the equivalent Th content, that would
have produced the same amount of Pb and is then added to the measured Th content, named Th*. The slope from the regression line of the diagram gives a Th*-Pb age. The higher the Th and U variability, the lower gets the age error.

The intercept of the line with the Pb axis gives no information about common Pb or Pb loss. Since adding an amount of common Pb at the lowest or highest point would lead to opposite effects. In spite of that negative intercepts related to a common Pb effect on some points of high Th content, could be interpreted as Pb loss. To avoid such artifacts, COCHERIE ET AL. (1998) proposed therefore adding a virtual point at the origin affected by an error of ± 150 ppm for Pb and Th*. If the isochron is completely forced through the origin, it gives the direct age in almost all cases. The precision is around 20 Ma (COCHERIE ET AL. 2005).

Th/Pb = f(U/Pb)

COCHERIE AND ALBAREDE (2001) introduced this as a simpler method as the three-dimensional Concordia-diagram which is explained later and COCHERIE ET AL. (2005) stated that it is quite a precise method for monazites exhibiting significant Th and U variations with a precision of ±5 to ±10 Ma. The visualization is easier due to the fact, that only two dimensions were viewed. The isochrones are straight lines in such a diagram (Fig. 1). The change of slope is very weak for ages younger than 2000 Ma but increases significantly for ages older than 3000 Ma.

The intercepts with the axes are just a function of the ages and do not give any information about Pb loss or common Pb. An easy way to assess whether the regression line of the measured points belongs to an isochron is to plot theoretical isochrones on both sides. The ages can be calculated at the intercepts using the following equations:

\[
(\text{Th} / \text{Pb})_0 = 1 / \left( 1 - e^{-\lambda_{232} \cdot t_{\text{Th-Pb}}} \cdot \frac{M_{208}}{M_{232}} \right) \]

\[
(\text{U} / \text{Pb})_0 = 1 / \left( \frac{M_{208}}{M_{238}} \cdot 0.9928 \cdot e^{\lambda_{238} \cdot t_{\text{U-Pb}}} - 1 \right) \cdot \frac{1}{1 - e^{-\lambda_{235} \cdot t_{\text{U-Pb}}} \cdot \frac{M_{235}}{M_{238}} + \frac{M_{207}}{M_{235}} \cdot 0.0072 \cdot e^{\lambda_{235} \cdot t_{\text{U-Pb}}} - 1} \right)
\]

where Pb, Th and U are concentrations in ppm; (Th/Pb)_0 is the intercept with the Th/Pb axis, (U/Pb)_0 is the intercept with the U/Pb axis, \( \lambda_{232}, \lambda_{235}, \lambda_{238} \) are the decay constants.

If the calculated ages are indistinguishable within the errors with an acceptable MSWD (mean standard weighted deviation) of ~ 1, the conditions are correct for calculating a more precise probable age and concordance is assumed. The best age is calculated on the point with the lowest error.

Besides these perfect conditions for calculating an isochron, three less favorable cases can occur, referring to COCHERIE AND ALBAREDE (2001):
Fig. 1 Typical isochron distribution in a Th/Pb vs. U/Pb diagram. a) The isochrones are not parallel, b) although they appear so for young ages (modified after COCHERIE AND ALBAREDE 2001).

1) The measurements define a regression line, parallel to a theoretical isochron and the U-Pb and Th-Pb ages are indistinguishable within the errors, but the MSWD is large. This can be caused by maybe two events that show perhaps similar U/Th variations and are homogeneous domains. Another reason can be that Pb diffusion took place.

2) The measurement leads to a regression line crossing the theoretical isochrones. The U-Pb and Th-Pb ages are significantly different and the MSWD is large.

3) The data fit well with the regression line, the MSWD is acceptable, but it crosses the theoretical isochrones. The U-Pb and Th-Pb ages are significantly different. This and the second case can appear, when at least two events are recorded on areas of different U/Th composition.

Based on these different cases that can occur, this method is also a tool to control whether the studied monazites are monogenetic or polygenetic at the scale of two (or more) events separated by ~20-60 Ma, according to their age (COCHERIE AND ALBAREDE 2001).

Three-dimensional method

This method is able to calculate independently the Th-Pb age and the U-Pb age and then, according to COCHERIE AND ALBAREDE (2001), to control the concordancy of both. Referring to KUIPER (2005), an EMP analysis does not indicate, whether the mineral is isotopically discordant or not. She states that the concordia of all three isotope systems does not lie on a plane (see Fig. 2) due to their different decay constants and therefore can not be plotted in two dimensions, as suggested by COCHERIE AND ALBAREDE (2001). For using the three-dimensional method one has to be aware, that in EMP analyses element concentrations rather than isotopes are measured. For example the concentration
of U isotopes can only be estimated by their natural occurrence, which is 0.72% $^{235}$U and 99.28% $^{238}$U. The Pb concentration is made up of $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb assuming no common Pb is involved.

If more than one age domain is probed by the microprobe beam, then the total Pb/(U+Th) ratio is lower than that of the oldest age domain, since the older the monazite gets the more Pb originates. This results in an apparent younger age that has neither a geochronological nor a geological meaning.

By dating isotopically discordant material, the Pb concentration of the fastest decay system ($^{235}$U $\rightarrow$ $^{207}$Pb) is underestimated while the Pb concentration of the slowest ($^{232}$Th $\rightarrow$ $^{208}$Pb) is overestimated. The concentration of $^{207}$Pb may be over- or underestimated (KUIPER 2005).

To conclude this three-dimensional method, there are minimum age constraints on $^{207}$Pb/$^{235}$U and $^{207}$Pb/$^{208}$Pb ages and maximum age constraints on $^{208}$Pb/$^{232}$Th ages. EMP data gives always a minimum age constraint on the oldest Pb content.

**Limits of EMP analysis**

The limitations of EMP analyses are based on the detection limit, which are quite diverse for the different elements, and the spatial resolution of about 1-3 μm. Referring to MONTEL ET AL. (1996) there are four different issues when no age can be calculated due to these limitations.

First case: young ages. The youngest age that can be measured is directly related to the detection limit for Pb, which was in the case of MONTEL ET AL. (1996) about 200ppm. When the measured Pb content is lower than the detection...
limit the only thing that can be concluded is that the crystal is younger than a certain value. This value depends again on the minerals Th and U content. If a monazite is very radioactive – therefore contains high amounts of U and Th – the calculated ages can be as low as 30 Ma, but in most cases it has to be 50-100 Ma.

Second case: old ages. Theoretical there is no upper limit of course, based on the low decay constants of U and Th. The only limitations may arise from two features. The first one is the possible absence of monazite in old rocks. The second is due to possible restrictions to the ability of monazite to retain radiogenic Pb at very high concentrations. Measured Pb contents of above 1% are very common in samples older than 1,5Ga.

Third case: small crystals. Monazites in high-grade metamorphic rocks are rather large (100 μm) and therefore it is no problem to measure them. But monazites in granites are smaller, usually 20-50 μm. Such small crystals can only be dated with means of the EMP, no other technique is able to do that. But if the crystals become smaller than the spatial resolution of the EMP, they are not even detectable by means of EMP.

Fourth case: zoned crystals. Monazites containing two or more ages were found in several occasions. When doing age profiles on these crystals, heterogeneities of about 10 ppm were measured, which are not detectable by means of a spatial resolution lower than this. Every time when the spatial resolution is higher than the heterogeneities, different ages would be detected and may yield to intermediate ages by mixing the information.

Conclusion

Monazite is widely distributed as an accessory in a variety of rocks and is thought to be stable under low- to high-grade metamorphism. Observations showed that monazite on one hand is very vulnerable to metamictization and retentive. On the other hand it recrystallizes when the lattice is damaged due to radioactive decay and at changing temperature or fluid conditions. Therefore monazite is a nearly perfect mineral for age dating.

The EMP allows better spatial resolution than any other analytical technique and its great advantage is that it is non-destructive and provides results very fast and cost-efficient. Nevertheless one has to be aware that some skill is needed to handle the analytical method, especially the choice of emission lines and measurement conditions.

Until now a lot of new techniques are developed and will be designed in the future to precise and to ease the measurements. Next to these issues related to EMP hardware, some more sophisticated methods for the model age calculation were contrived which have both their advantages and disadvantages for each case. Combining them can lead to enhanced age resolution.

But besides that one has to bring to mind that discordance of ages can not be directly reconsidered with the means of EMP. Every time one wants to date a
mineral a basic knowledge of it is needed to prove if the calculated age has any geological meaning.

References


JERCOINOC M J, WILLIAMS M L (2005) Analytical perils (and progress) in electron microprobe trace element analysis applied to geochronology: Background acquisition, interferences, and beam irradiation effects. American Mineralogist 90: 526-546


Electron-microprobe dating of monazite


SUZUKI K, ADACHI M (1991a) Precambrian provenance and Silurian metamorphism of the Tsubosawara paragneiss in the South Kitakami terrane, revealed by the chemical Th-U-total Pb isochron ages of monazite, zircon and xenotime. Geochem. J. 25: 357-376
