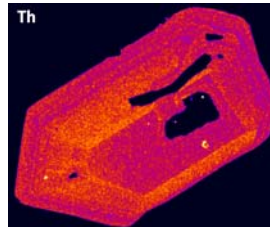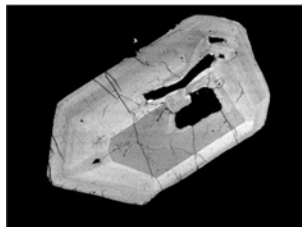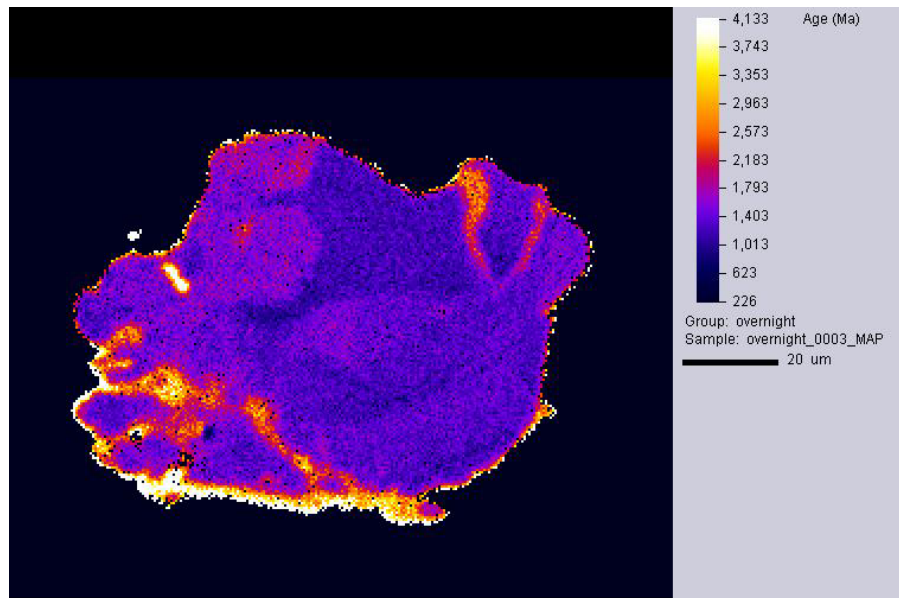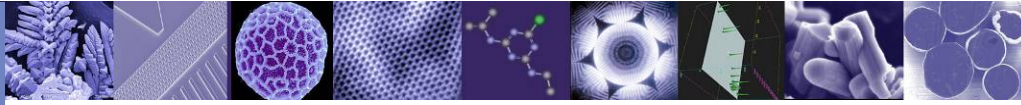# Monazite Age Dating

Monazite Age Dating

Introduction

Determining the age of a rock or rock unit (either relative or absolute) is one of the most fundamental tasks in geology. Because of this routine need, monazite age dating rapidly became a commonly used tool for those involved in field geology. Even though monazite typically occurs only as an accessory mineral, it can be found in wide variety of rocks, making it a perfect candidate for establishing the ages of many different rock-types. Monazite is a rare-earth phosphate $(Ce,La,Nd,Th)PO_4$ that can contain appreciable amounts of thorium. Because of the high thorium content, the mineral typically contains enough lead, even in relatively young rocks, to be measurable using an electron microprobe. The ratio of the Pb to Th and U can then be used to determine the age of the mineral and therefore the rock.
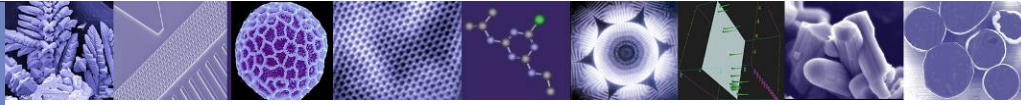
Some argue that mass spectrometers are the better tool for precise age dating, because they can differentiate the isotopic ratios of the Th, U and Pb. Therefore, they can, for example, differentiate radiogenic Pb from non-radiogenic Pb, which can have some impact on the measured age. However, the monazite electron microprobe ages also have many advantages over those from mass spectrometers. They are comparatively fast, easier to obtain, less expensive, and have a much better spatial resolution. Therefore, it is always important to consider the application at hand when selecting the analytical technique.

Monazite Analysis

Measuring the full composition of a monazite can be quite involved giving the number of minor and trace elements common to the mineral (Table 1). The most important of the trace elements is lead, because of the dependence on it in the determination of the age. The concentration of lead varies, but typically is in the few tenths of a percent down to few hundredths of a percent, or less. For the rare earth elements (REE) in monazite, it is the small energy differences between the X-ray lines (Fig. 1) that provide the challenge in the analyses. These are examples of why wavelength dispersive spectrometers (WDS) are the preferred X-ray spectrometer for these types of analyses. Energy dispersive spectrometers (EDS) do not provide the energy resolution or detection limits required for analyses of sufficient accuracy to be used in monazite age dating.

In most cases, it is not necessary to do a complete mineral analysis for each age determination. It is sufficient to determine an average composition for the monazite grains involved and then enter this bulk composition (Si, P, Ca, La, Ce, Pr, Nd, Sm, Gd, Dy and F) as fixed values for the later analyses. This will allow the matrix correction routine to correct the measured elements, without having to reproduce the complete analyses at each point. More time can then be spent measuring the critical elements. One approach is to measure only Th Mα, U Mβ, Pb Mα, and Y Lα at each point. Other strategies can also be used. However in every strategy, there is a certain amount of correcting for peak overlaps that must be undertaken. This particular configuration minimizes the number and severity of the corrections. However, the Pb Mα peak will still have to be corrected for the overlap by Y, and the U Mβ peak will have to be the overlap by Th.

Typically, these analyses are run at a 15kV accelerating voltage and at a high beam current, commonly in the range of 200nA. The counting time used depends on the concentration of Pb. If an additional spectrometer is available with a PET crystal on it, Pb can be measured on multiple spectrometers, improving the count rate. When possible multiple analyses are preferred over long counting times.

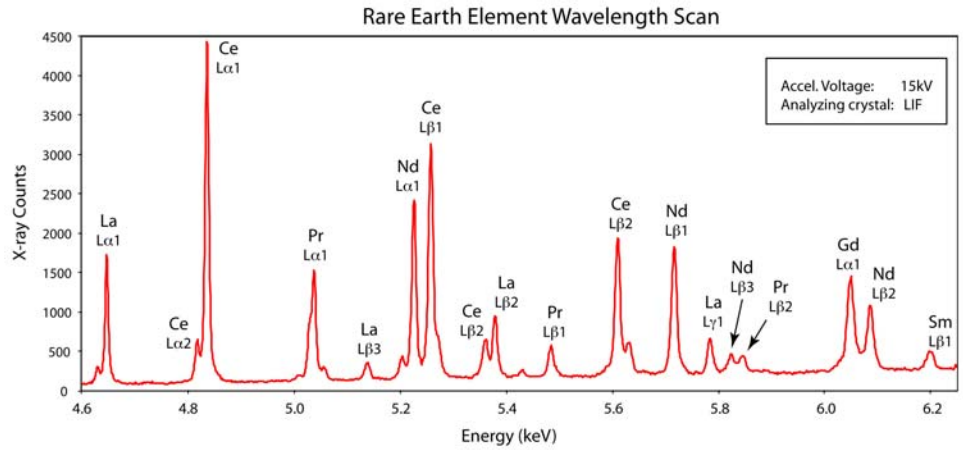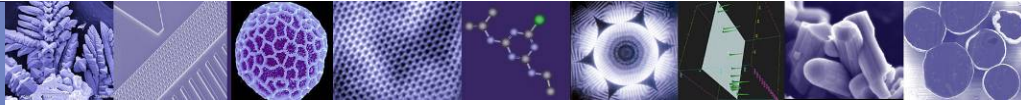| Element	Wt.%
CaO	0.97
Ce_2O_3	29.75
Dy_2O_3	0.109
F	0.50
FeO	0.016
Gd_2O_3	0.753
La_2O_3	14.21
Nd_2O_3	11.41
P_2O_5	29.2
PbO	0.804
Pr_2O_3	3.22
SiO_2	0.78
Sm_2O_3	0.98
Tb_2O_3	0.049
ThO_2	6.54
UO_2	0.119
Y_2O_3	0.73

Figure 1. Wavelength scan showing the rare earth element X-ray lines over the energy range occupied by the elements La to Gd.

Table 1. Average monazite composition from the Vermillion Migmatite Complex, northern Minnesota.

Method Used for Age Determination

JEOL's MonaziteAge program follows the dating procedure outlined originally by Suzuki and Adachi (1991, 1994), and Suzuki and others (1994). It can be used with both Th-rich phases and more U-rich phases, such as zircon or xenotime. It allows the user to calculate the age of a monazite grain from a single analytical point or from a set of analyses. When multiple analyses are used to determine a single age, the method will correct for non-radiogenic lead or for lead leaching that may have taken place. When creating age maps, the method uses the same procedure as that for a single analysis, but applies it to each pixel.

The relationship between the weight percent of ThO_2, UO_2, and PbO in a Th- or U-rich mineral, and that mineral's age, can be defined by Equation (1) (Figure 1) [Suzuki and Adachi (1991, 1994) and Suzuki, and others (1994)]. It can be solved using an initial guess for the age, and then calculating the corresponding amount of PbO. A new, better age estimate is then made, and a new PbO value is determined. This iterative process continues until the value for PbO converges on the measured value.

$$\frac{PbO}{W_{Pb}} = \frac{ThO_2}{W_{Th}} \{ \exp(\lambda_2 t) - 1 \} + \frac{UO_2}{W_U} \left\{ \frac{\exp(\lambda_5 t) + 138 \exp(\lambda_8 t)}{139} - 1 \right\} \quad (1)$$

(for monazite)

$$ThO_2^* = ThO_2 + \frac{UO_2\, W_{Th}}{W_U \{ \exp(\lambda_2 t) - 1 \}} \left\{ \frac{\exp(\lambda_5 t) + 138 \exp(\lambda_8 t)}{139} - 1 \right\} \quad (2)$$

$$PbO = m\, ThO_2^* + b \quad (3)$$

$$T_s = \frac{1}{\lambda_2} \ln(1+m) \frac{W_{Th}}{W_{Pb}} \quad (4)$$

(for zircon & xenotime)

$$UO_2^* = UO_2 + \frac{139\, ThO_2\ W_U \{ \exp(\lambda_2 t) - 1 \}}{W_{Th} \{ \exp(\lambda_5 t) + 138 \exp(\lambda_8 t) - 139 \}} \quad (5)$$

$$PbO = m\, UO_2^* + b \quad (6)$$

$$m\, \frac{W_{Th}}{W_{Pb}} = \frac{\exp(\lambda_5 T_s) + 138 \exp(\lambda_8 T_s)}{139} - 1 \quad (7)$$

where: $\Rightarrow$ W is the molecular weight of each oxide,

$\quad W_{Th}$ = 264
$\quad W_U$ = 270
$\quad W_{Pb}$ = 224 (for monazite)
$\qquad\quad$ = 222 (for zircon and xenotime)

$\Rightarrow \lambda$ is the decay constant of each isotope,

$\quad$ (232) $\lambda_2 = 4.9475 * 10^{-11}$ / year,
$\quad$ (235) $\lambda_5 = 9.8485 * 10^{-10}$ / year,
$\quad$ (238) $\lambda_8 = 1.55125 * 10^{-10}$ /year

$\Rightarrow$ t is the apparent age determined from each analysis.

$\Rightarrow$ ThO_2^* is the equivalent amount of ThO_2 that would be required to produce the measured amount of PbO, if there was no UO_2 in the mineral.

$\Rightarrow$ UO_2^* is the equivalent amount of UO_2 that would be required to produce the measured amount of PbO, if there was no ThO_2 in the mineral.
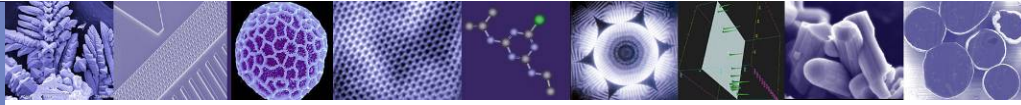
$\Rightarrow$ Ts is the age determined from the slope of PbO versus ThO_2^* (or UO_2^*).

$\Rightarrow$ m is the slope of the least square fit curve in Figure 2.

$\Rightarrow$ b is the intercept of the least square fit curve.

Table 2. Formulae for age calculations.

Using the above approach, an estimated age can be determined for each analysis. If many analyses are made, an average of the results can be used to estimate the average age of the rock. However, these calculations are based on a number of assumptions. First, it is assumed that the monazite grains contain no non-radiogenic lead. If the monazite formed with a measurable quantity of lead initially, then the age determined by the above described method will be older than is actually the case. Likewise, the method assumes that all of the lead that formed in the mineral grain, from the radioactive decay of Th and U, stayed within the grain throughout its geologic history. Any leaching of the lead will produce younger ages than is actually the case. To account for these possibility of either a loss in PbO or some initial PbO, Suzuki and Adachi (1991, 1994) proposed an isochron method for determining the final age of the sample.

Figures 2, 3 and 4 show three hypothetical scenarios: 1) a set of monazite grains that contain no radiogenic Pb, and did not later loose any of the Pb created internally, (2) monazite grains that contain some non-radiogenic Pb from when the grains formed, and (3) grains that lost some of their radiogenic Pb.

The initial example (Fig. 2) assumes that the monazite grains contain no initial lead, that thorium occurs as the only radioactive element in the system, and that the grains had no subsequent loss of lead during its history. Plotted in Figure 2 is the amount of lead versus the amount of thorium at two different times. When the grains formed (t=0), there would be no lead in the system, but the amount of thorium each monazite grain contained varied from grain to grain. As such, each monazite grains would plot along the X-axis, as illustrated in Figure 2A. Over time, the amount of PbO would increase in each grain due to the radioactive decay of the thorium, but the specific amount would differ depending on the initial amount of ThO_2. However the ratio of ThO_2 / PbO would be constant from grain to grain, regardless of the amount of ThO_2. Therefore all of the analyses should plot along a line, and the slope of the line would be a function of the age of the mineral grains (Fig. 2B).
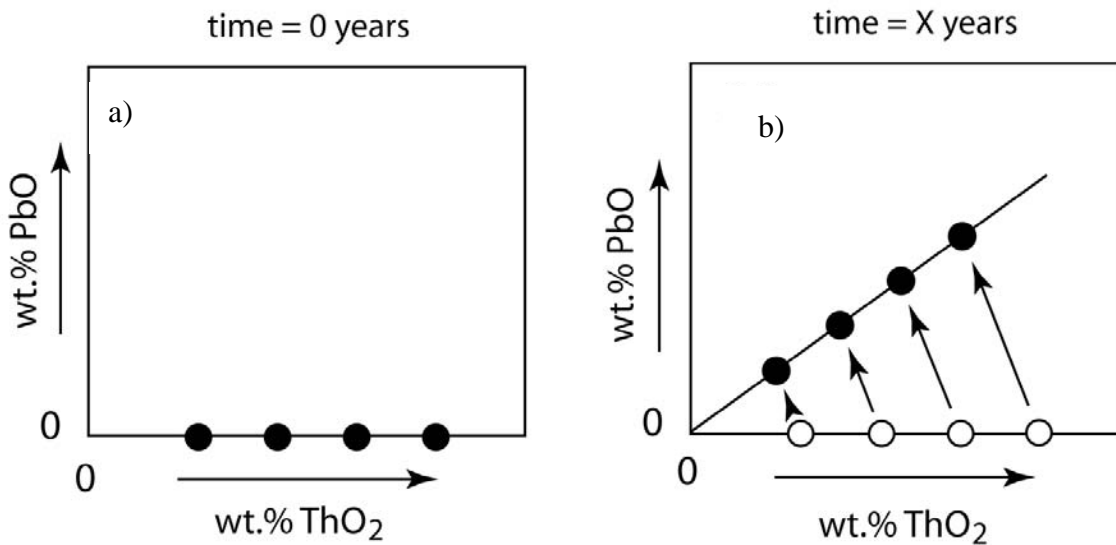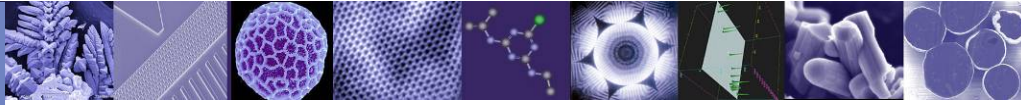

Figure 2. Plots representing a hypothetical set of monazite grains from a single rock that contained no initial PbO, but with a range of ThO_2 contents. Over time, each grain produces radiogenic lead in proportion to its original thorium abundance. The age of the grains can be determined from the slope of the curve.
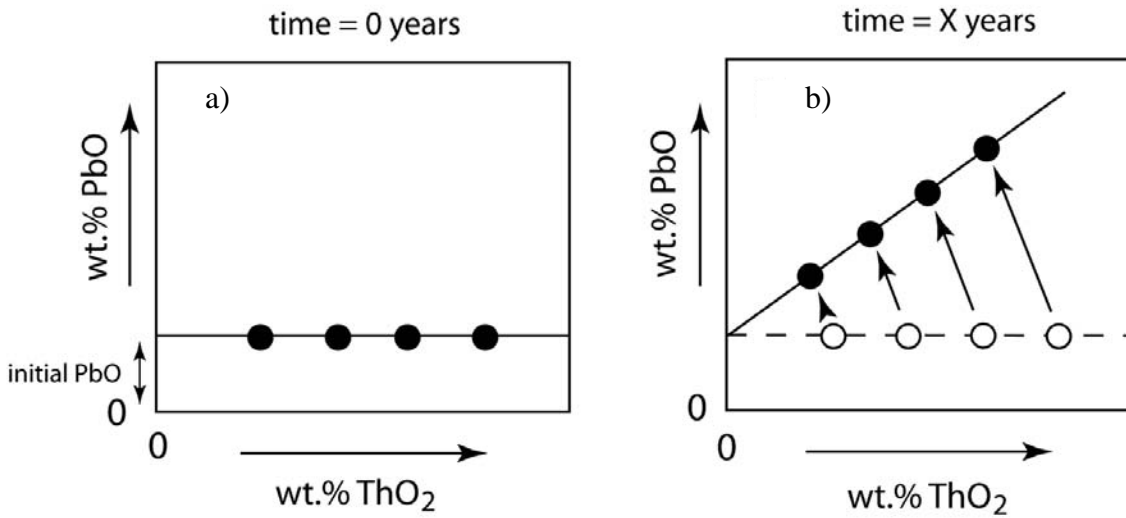
Case 2: Some initial PbO, but no loss of PbO

Figure 3. Plots representing a hypothetical set of monazite grains that contained a uniform amount of initial non-radiogenic lead. Over time each monazite grain will produce radiogenic lead in proportion to its original thorium abundance. Therefore the grains will contain both the radiogenic and non-radiogenic lead.

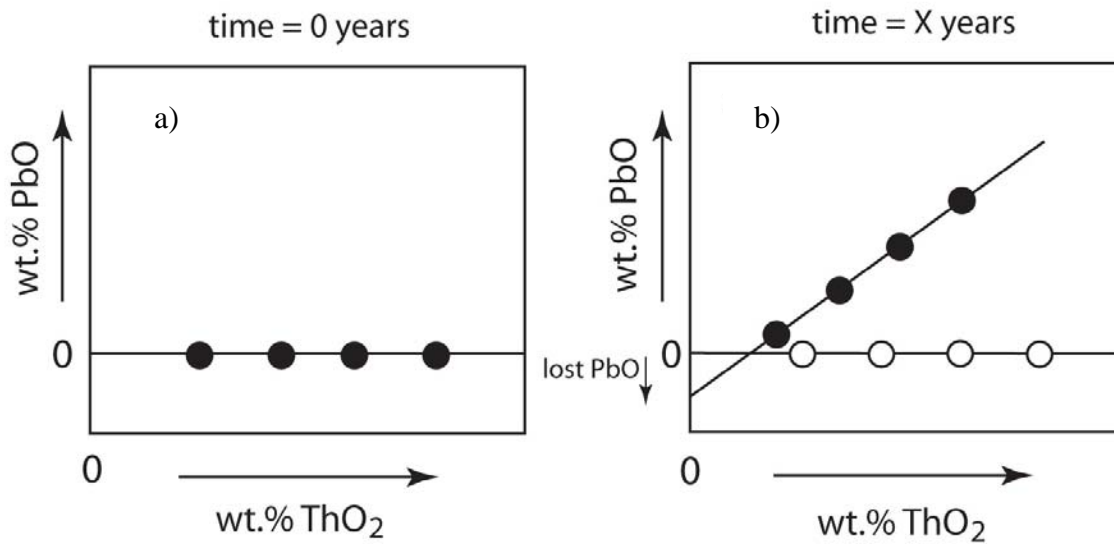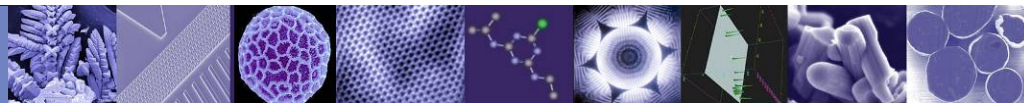## Case 3: No initial PbO, but some PbO loss

Figure 4. Plots of a theoretical monazite system that has undergone leaching of some of its lead. The intercept in this system is negative.

A second possibility is that the monazite grains originally contained some non-radiogenic lead (Case 2 - Fig. 3A). Over time, the radiogenic lead will be added to the non-radiogenic lead. Since these two lead isotopes are indistinguishable using an electron microprobe, calculated ages based solely on the total amount of thorium, uranium, and lead will result in an overestimation. However, the amount of non-radiogenic lead can be estimated from the plot in Figure 3B. The non-radiogenic lead is equal to the Y-intercept of the least square fit line to the compositional data, and the true age of the sample can still be calculated from the slope.

A third possibility is that some of the radiogenic lead leached from the mineral grains (Case 3 – Fig. 4). In this case, the age will be underestimated. If the monazite grains are all nearly uniform in size, and all underwent a similar process, then the amount of lost PbO can again be estimated (Fig. 4). In this example, the intercept of the least square fit line is negative (Fig. 4B), which is a measure of the lost lead. The true age can again be determined from the slope. If the leach rate were not uniform, then a more complicated model would have to be applied to the system.

To simplify the calculations using this isochron method, the less abundant radioactive element is eliminated by calculating the equivalent amount of the primary radioactive element that would be required to produce the measured lead content. For monazite, one calculates the amount of ThO_2 that would be required to produce the measured amount of PbO assuming that there was no UO_2 present in the mineral grain. This can be carried out using Equation (2) in Figure 1. However, in order to complete this calculation, the age of the mineral must be known. Therefore these calculations require an iterative process, and the following procedure is used (for monazite):

1) Use Equation (1) to calculate an age from each analysis point.
2) Calculate ThO_2* (the equivalent required ThO_2, if there had been no UO_2 present, to produce the measured PbO) for each analysis using Equation (2) and the original estimated age.
3) Determine a least square fit to the data PbO versus ThO_2*.
4) Use the slope of this line and Equation (4) to determine a new age for the system.
5) Use this new age to recalculate the ThO_2* content for each analysis.
6) Repeat steps 3-5 until the calculated age converges.

A similar process is used for minerals with a higher uranium than thorium content; then Equations 5, 6 and 7 are used.

Application

The JEOL MonaziteAge program can be used for individual measurements, groups of individual analyses, or to map the 2D distribution of the age within a monazite grain. Individual ThO_2, UO_2 and PbO compositions can be entered individually into the age calculator (Fig. 5). The resulting age is output to a screen from which it can be saved.

Groups of monazite analyses can be read in from text files or from JEOL quantitative analysis files. An age can then be determined from each individual point, or an isochron age can be determined from the entire set (Fig. 6). An isochron method fits a least square fit curve to the data set and the slope of the curve corresponds to the age. A positive y-intercept for the curve would suggest the monazite grains contain some initial non-radiogenic lead, and a negative y-intercept suggest some of the radiogenic lead has been leached from the grains.
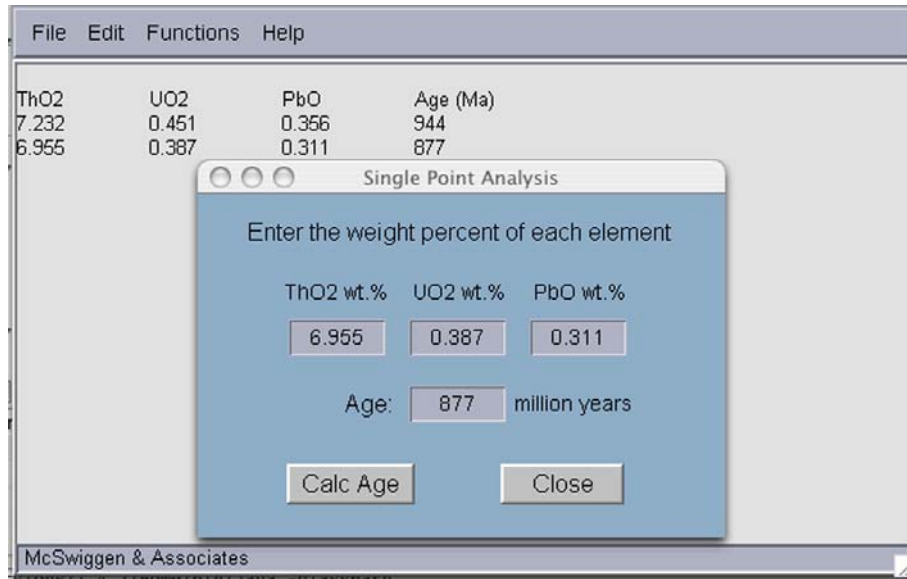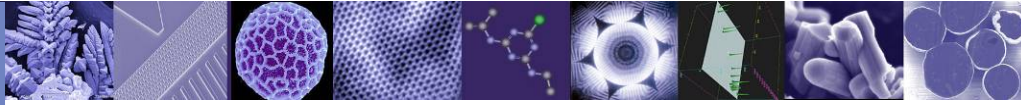
Figure 5. The Single Point Analysis window allows the user to enter the weight percent ThO$_2$, UO$_2$, and PbO from an analysis one point at a time.
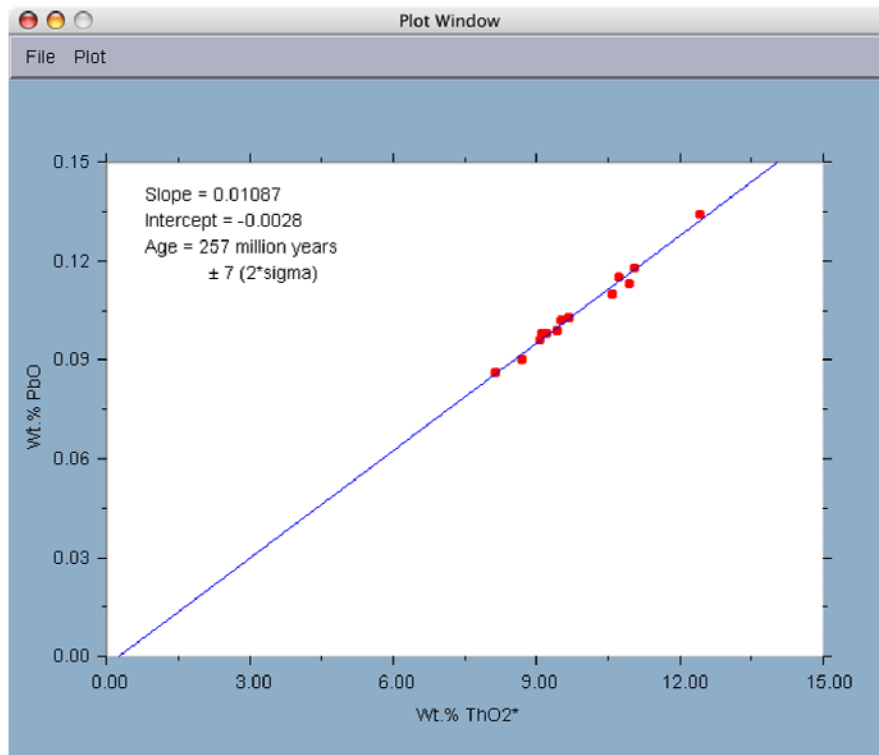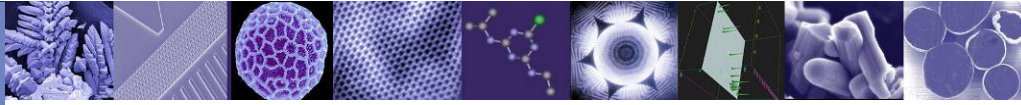

Figure 6. A plot of monazite grains using the isochron method to determine the age. The data from Suzuki and Adachi (1994).

Age mapping is also a very useful tool for understand the history of individual monazite grains. Monazite grains may have experienced a very long history, during which they may have undergone different stages of growth. Each of these different growth zones may have discretely different ages. The ability to distinguish these different ages can mean the difference between unraveling the timing within an orogenic event versus reporting an age that is an average of hundreds of millions of years of events.

An element map can be a misleading indicator of whether the monazite grains represent multiple ages. Many, if not most, monazite grains show some compositional zoning. For example, both the backscattered electron image of the grain shown in Figure 7 and its corresponding element maps (Fig. 8) show distinct compositional zoning. However the age map of the same grain shows that it is quite uniform in age (Fig. 9)
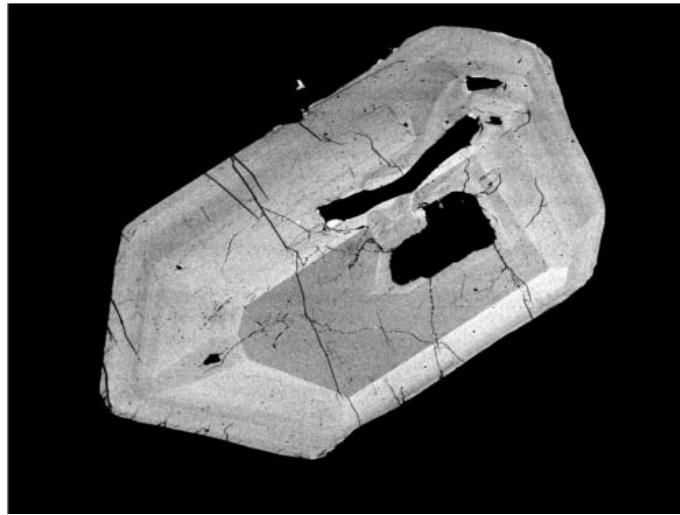

Figure 7. Backscattered electron image of a monazite grain showing distinct compositional zoning form core to rim.
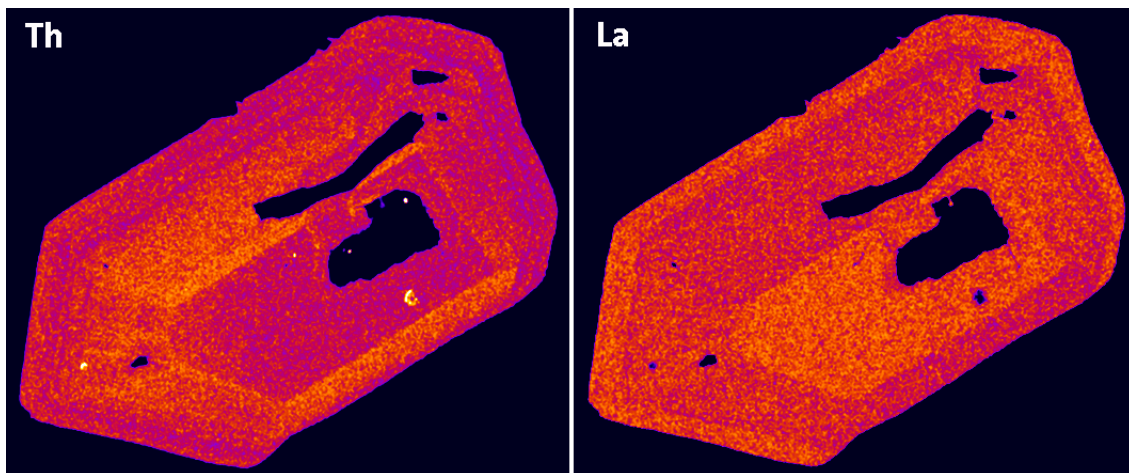

Figure 8. Element maps for Th and La showing as that seen in the backscattered electron image in Figure 7.
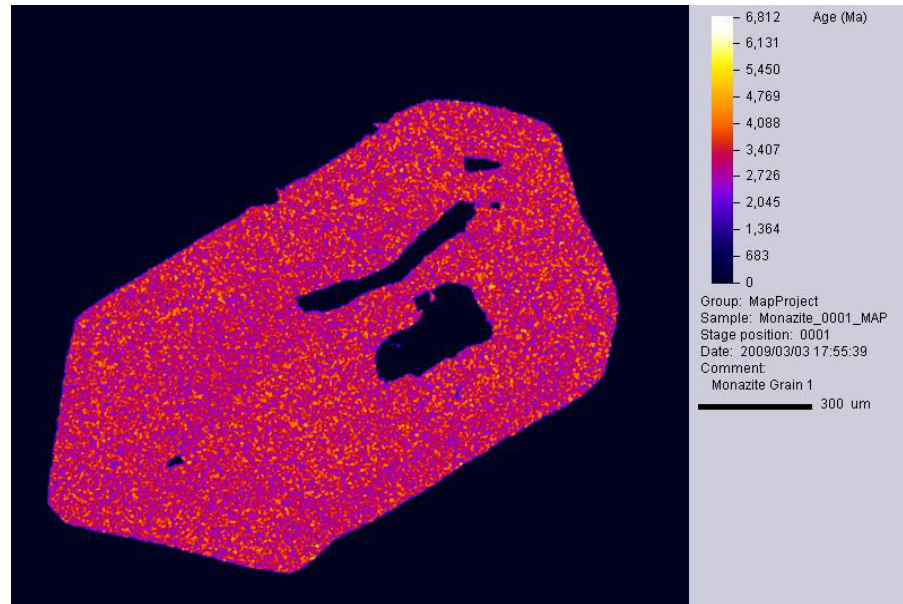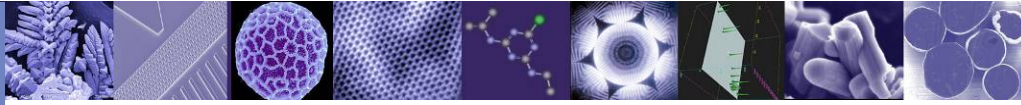
Figure 9. The age maps of the same monazite grain in Figures 7 and 8 shows that it is very uniform in age and must have formed over a short period of time.

In contrast, the monazite grain shown in Figure 10 has significant differences in the measured age within it. The oldest bands (yellow) appear along the edge of the grain and along cracks running through the grain. These are zone where the Th has been leached, resulting in a very old, erroneous age. These areas must be avoided when trying to decipher the growth ages. The other zones (blues) may represent geologic events that triggered monazite grain growth and are suitable for further investigation.
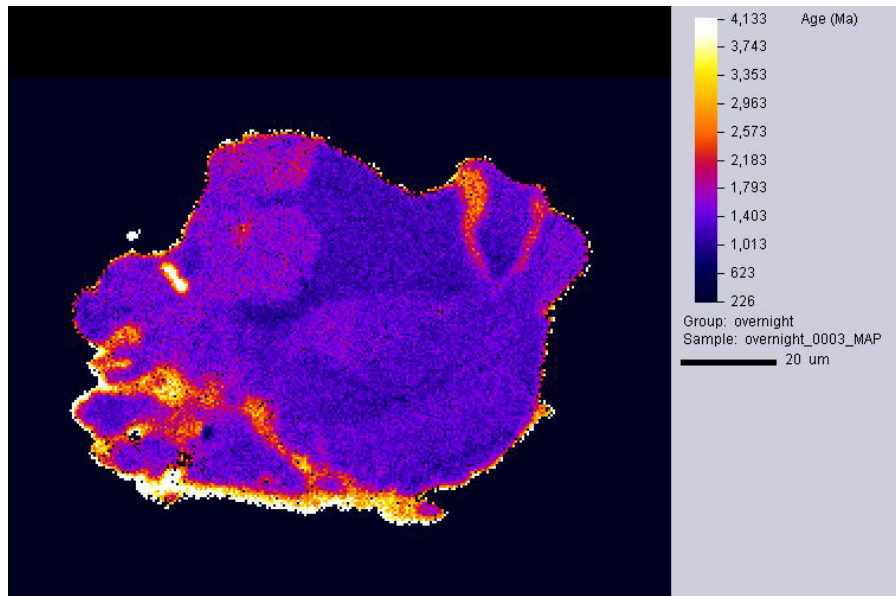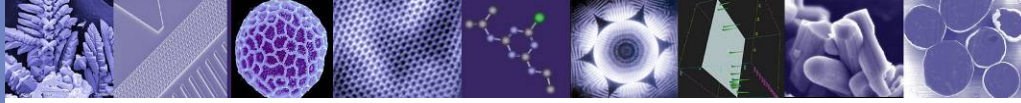

Figure 10. Age map of a monazite grain that contains both evidence of multiple ages of mineral growth (blues) and later alteration (yellow,) which leached Th along the grain boundary and cracks within the grain.

References

Suzuki, K., and Mamoru Adachi, 1991, Precambrian provenance and Silurian metamorphism of the Tsubonosawa paragneiss in the South Kitakami terrane, northeast Japan, revealed by the chemical Th-U-total Pb isochron ages of monazite, zircon and xenotime. *Geochemical Journal,* vol. 25, p. 357-376.

Suzuki, K., and Mamoru Adachi, 1994, Middle Precambrian detrital monazite and zircon from the Hida gneiss on Oki-Dogo Island, Japan: their origin and implications for the correlation of basement gneiss of southwest Japan and Korea. Tectonophysics, vol. 235, p. 277-292.

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