

Zoned porphyroblasts of metamorphic monazite in the Anakeesta Formation, Great Smoky Mountains, North Carolina

DAVID W. MOHR

Department of Geology
Texas A&M University
College Station, Texas 77843

Abstract

Monazite has widespread occurrence in pelitic schists of the Anakeesta Formation which were metamorphosed to staurolite–kyanite grade. This monazite is of strictly metamorphic origin. In a few very graphitic metashales, monazite forms zoned euhedral porphyroblasts 50–150 μm in size. Microprobe analyses of these porphyroblasts for P, Ca, Th, Y, and the rare-earth elements La, Ce, Pr, Nd, Sm, and Gd revealed significant relations among the elements. Virtually all thorium is accommodated by the charge-coupled substitution $\text{Th}^{4+} + \text{Ca}^{2+} = 2\text{REE}^{3+}$. Zonation for Th and Ca is sharply gradational and separates distinct cores and rims; cores show thorium enrichment over rims by a factor of 2.5. Increase in thorium content correlates with a small increase in average atomic number of analyzed REE from 58.65 to 58.76 and is most clearly seen in enrichment in gadolinium and depletion in lanthanum. These trends can be explained by a decrease in ionic size with increasing atomic number of rare-earth elements and a slight decrease in unit-cell dimensions of monazite due to increased content of Th and Ca. However, yttrium is slightly enriched in the rims and does not follow this trend.

Introduction

Monazite is a rare-earth phosphate of the formula $\text{REE}^{3+}(\text{PO}_4)^{3-}$. Possible substitutions in the chemical formula include Th^{4+} , Ca^{2+} , and Y^{3+} for REE, and Si^{4+} for phosphorus. Although monazite is a common accessory mineral in metamorphic as well as igneous rocks very little discussion of metamorphic monazite is available in the literature. Indeed, metamorphic monazite may often be misidentified as zircon in thin section, as for example by Mohr and Newton (1983). Most published analyses of monazite are bulk analyses, and the question of zoning of monazite crystals over its full composition has not often been addressed. This paper reports the occurrence and discusses the chemistry of zoned monazite porphyroblasts in black metashale of the Anakeesta Formation in western North Carolina.

Survey of literature

Perhaps the best summary of metamorphic monazite is that of Overstreet (1967), who states that within metamorphosed sediments, monazite is most abundant in metashale. The mineral is widespread at sillimanite and higher grades and is commonly seen in the staurolite and kyanite zones. At garnet or lower grades monazite is rare, and its place is taken by allanite or sphene. Furthermore, monazite crystals in mica schists are frequently too large to

have been of detrital origin, and they often contain inclusions of metamorphic minerals. Thus a metamorphic origin is favored. No microprobe analyses and very few bulk analyses of metamorphic monazite are available in the literature (Donnot *et al.*, 1973; Serdyuchenko and Kochetkov, 1974).

Analyses of igneous, pegmatitic, and hydrothermal monazites are reported to show the following compositional trends. Thorium content of monazite tends to increase with increasing temperature of formation for all modes of occurrence, from nil in hydrothermal monazites to well over 10 wt.% in igneous crystals (Overstreet, 1967). For most analyzed monazites, relative abundances of the lighter REE (La–Gd) are close to those reported for average granite and average shale (Herrmann, 1969).

With regard to world-wide occurrences of monazite, absolute abundances of La and Ce decrease while those of Nd, Sm, and Gd increase as the average atomic number of all REE increases (Murata *et al.*, 1967). Lee and Bastron (1967) confirmed this trend in REE abundances for monazites from a single granitic pluton, and correlated increasing average atomic number of REE with increasing thorium content. Ionic radii of yttrium and REE heavier than Gd are smaller than those of the La–Gd family of elements. Thus, Y and heavier REE show relatively low affinity for the monazite crystal structure (Felsche, 1976). Analyses of coexisting mona-

zite and other minerals which contain REE show strong fractionation of the lighter REE into monazite (Åmli, 1975; Ilupin *et al.*, 1971).

Zonation of monazite over its full composition range has not often been observed. For pegmatitic occurrences, Åmli (1975) reports unzoned monazite inclusions within apatite, and Watkinson and Mainwaring (1976) report very slight zoning in massive monazite, with enrichment of Ca and depletion of La and Ce in the cores of crystals. For monazite in granite, Silver *et al.* (1980) report substantial depletion of Th, Ca, and Y and variable enrichment in La, Ce, Nd, Sm, and Gd in crystal cores. A thorium-free monazite found in a quartz vein shows depletion of Nd, Sm, Gd, and Y and enrichment in La and Ce towards the core (Bernstein, 1982).

Geologic setting and description

Monazite crystals occur in metashales of the Anakeesta Formation of late Precambrian depositional age, in an outcrop belt west of the town of Bryson City, North Carolina. Stratigraphy and structure of this area are discussed by Mohr (1973), and metamorphism of pelitic units is described by Mohr and Newton (1983). The Anakeesta Formation consists of beds of gray to black graphite-bearing metashale, on which are imposed closely-spaced staurolite and kyanite isograds which separate wide zones of garnet grade and of staurolite-kyanite grade.

Monazite occurs in virtually all metashale of staurolite-kyanite grade. Most beds contain only anhedral monazite of matrix size (50–100 μm). Euhedral porphyroblasts of monazite (50–150 μm) are restricted to a few beds of black metashale whose matrix size is only 5–10 μm . These beds lack monazite of matrix size. In the garnet zone allanite, now metamict, is the characteristic REE mineral, but monazite crystals (to 50 μm) are found in a few units. In thin section, all monazite crystals show high birefringence and pale greenish-yellow color.

The euhedral porphyroblasts of monazite show simple morphologies with {110} prism and {111} pyramid forms (Fig. 1). These porphyroblasts occur within crystals of kyanite, plagioclase, and biotite as well as within the matrix, and, in turn they contain matrix-size inclusions of graphite, quartz, and rutile (Fig. 2). Zoned porphyroblasts were found in a few beds in which biotite has high Mg/(Mg+Fe) ratios near 0.80 (Mohr and Newton, 1983). Cores are marked by greater numbers of inclusions (Fig. 1) and slightly deeper color and in a few cases by slightly lower birefringence than the rims. Core-rim boundaries are optically quite sharp and commonly euhedral; thicknesses of rims are approximately 15–25 μm .

Method of analysis

One kyanite-zone sample of black metashale, labeled NC-35, contains a number of zoned, euhedral monazite porphyroblasts set in a schistose matrix of 5–10 μm . This

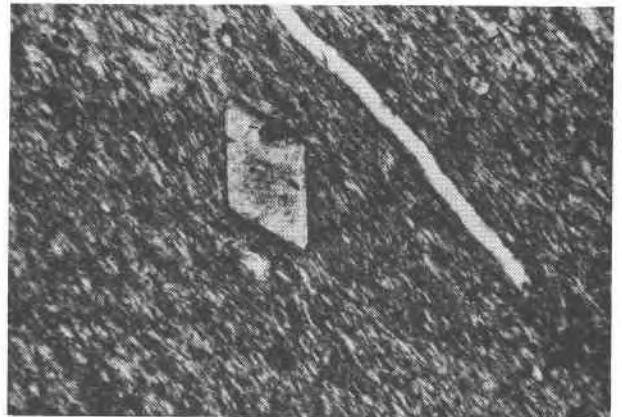


Fig. 1. Photomicrograph showing monazite porphyroblast (crystal 1 of analyses) and surrounding matrix. Long axis of crystal is 200 microns. Zoning is visible with small inclusions more abundant within the core.

sample has a Mg/(Mg+Fe) ratio in biotite of 0.76 and closely resembles samples 135 and GS-113 of Mohr and Newton (1983) in mineralogy, mineral chemistry, and stratigraphic position. Four of these porphyroblasts, re-

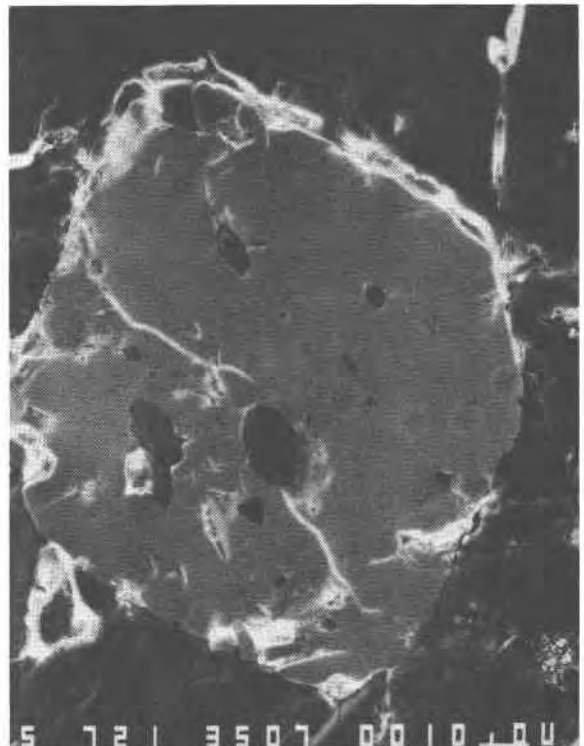


Fig. 2. Normal-backscatter SEM picture of monazite crystal 4 of the analyses. Graphite (black flakes), quartz (dark gray grains), and rutile (medium gray crystals) form inclusions. The bar in the lower right corner is 10 microns long. The series of 6 round spots from center to edge of the crystal are due to the half-traverse microprobe analyses.

ferred to as crystals 1 through 4, were selected for analysis. The monazites studied contain analyzable amounts of P, Ca, Y, La, Ce, Pr, Nd, Sm, Gd, and Th, as well as minute, unanalyzable amounts of Eu and other heavier REE. Silicon was not detected. Quantitative analyses of the 10 analyzable elements were run on four separate monazite crystals with one full spot traverse (rim to opposite rim) and three half traverses (core to rim) for a total of 31 analyses.

Analyses were performed at the Department of Geology, Southern Methodist University, Dallas, Texas, on a JEOL JXA-733 "Superprobe" equipped with Krisel automation. Beam spot size was 10 μm . Standards used include Wilberforce apatite for Ca and P and a commercial ThO_2 for thorium. Suitable standards for REE and Y are uncommon; those used here are a series of rare-earth oxide-CaO-Al₂O₃-SiO₂ glasses prepared by Drake and Weill (1972). All analyses are reported in elemental atomic abundances normalized to an assumed anionic content of 4 oxygen atoms. Trivalent charge was assumed for all rare-earth elements and yttrium.

Average phosphorus content of the analyzed monazites is 1.027 atoms per 4 oxygens, and the average wt.% oxides total to 99.4. This small departure from stoichiometry is believed to be due to the presence of unanalyzable REE, such as Eu, Tb, Dy, and Ho. Since silicon was not detected, all phosphorus determinations were normalized to 1.000. The sum of all other analyzed cations was also normalized to 1.000. Thus it is not possible to use reported analyses to determine amounts of minor REE, although it can be estimated that the sum of their oxides total to an average of less than one weight percent.

Results of analyses

A half-traverse of crystal 2 revealed only analyses characteristic of rims and no apparent zoning. Traverses of crystals 1, 3, and 4 show clear zonation of Th and Ca (Figs. 3 and 4). Relatively broad cores of essentially constant composition are surrounded by zones about 10

ZONATION OF THORIUM AND CALCIUM

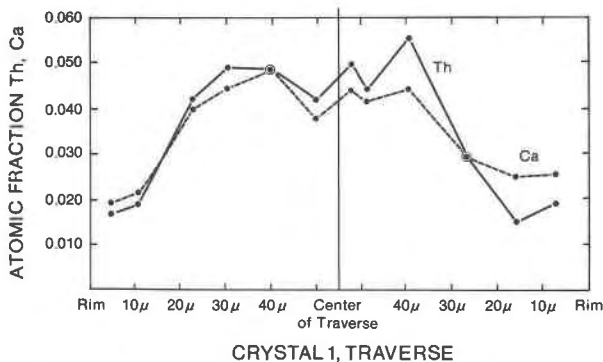


Fig. 3. Zonation of thorium and calcium in a full traverse of crystal 1.

ZONATION OF THORIUM AND CALCIUM

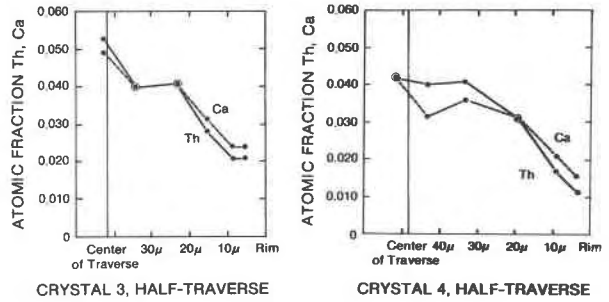


Fig. 4. Zonation of thorium and calcium in half-traverses of crystals 3 and 4.

μm across showing noticeable decrease in Th and Ca, followed by rims showing only slight further decrease. These cores correspond to those visible optically (Fig. 1). All traverses show a slight excess of Th to Ca in the cores and a slight deficiency in the rims.

In order to determine relative zonation of REE and Y exclusive of Th and Ca elemental abundances of REE and Y were normalized to yield a sum of 1.000. Although traverse plots of resulting values show some tendency toward zoning, this tendency is obscured by analytical scatter. To resolve these uncertainties, analyses were averaged for cores (13 analyses) and rims (15 analyses). Averages for total analyses are given in Table 1 and for REE + Y in Table 2. For each analyzed cation in Table 1, a statistical standard error

$$\left(\sqrt{\frac{\sigma^2}{N}} \right)$$

was computed. In order to estimate statistical validity of

Table 1. Average analyses of cores and rims of all analyzed monazite crystals. Phosphorus and total metal cations have each been normalized to 1.000 per 4 oxygen atoms. Each uncertainty value is equal to two times the standard error of analysis for each element (see text).

ELEMENT	CORE	RIM
P	1.000	1.000
TH	0.045 \pm 0.003	0.018 \pm 0.002
CA	0.041 \pm 0.002	0.022 \pm 0.002
Y	0.024 \pm 0.002	0.030 \pm 0.002
LA	0.202 \pm 0.003	0.232 \pm 0.002
CE	0.374 \pm 0.004	0.387 \pm 0.003
PR	0.037 \pm 0.002	0.038 \pm 0.001
ND	0.192 \pm 0.004	0.195 \pm 0.002
SM	0.031 \pm 0.002	0.031 \pm 0.002
GD	0.054 \pm 0.002	0.047 \pm 0.002
SUM OF REE + Y	0.914 \pm 0.005	0.960 \pm 0.002
	13 ANALYSES	15 ANALYSES

Table 2. Recalculation of analyses of Table 1 for REE + Y, in which the sum of REE + Y has been normalized to 1.000. Also shown is the standard error of the averages for each element and an assessment of the validity of observed zonation for each element (see text).

ELEMENT	N CORE	N RIM	ΔN	ΣSE	$\Delta N/ SE$
Y	0.026	0.031	+ 0.005	0.0021	+ 2.4
La	0.221	0.242	+ 0.021	0.0030	+ 7.0
Ce	0.410	0.403	- 0.007	0.0036	- 1.9
Pr	0.040	0.040	0	0.0015	0
Nd	0.210	0.203	- 0.007	0.0035	- 2.0
Sm	0.034	0.032	- 0.002	0.0020	- 1.0
Gd	0.059	0.049	- 0.010	0.0018	- 5.6

13 ANALYSES 15 ANALYSES

observed zonation, a factor was computed for each element equal to the difference in composition between rim and core divided by the sum of the standard errors (Table 2). Zoning is considered clearly significant if the magnitude of this factor exceeds a value of 2 and insignificant if it is less than 1.

Results show zoning to be most marked for Gd (enriched in cores) and La (enriched in rims). Cerium, Nd, and Sm may show slight enrichment in the cores whereas yttrium is enriched in the rims.

Finally, atomic weight percentages were computed for REE and Y from an average of all monazite analyses, and normalized to the average abundances of these elements in North American shales (Haskin *et al.*, 1966). Figure 5 displays this computation as a function of ionic radius (Felsche, 1976). Results show a generally flat curve for La, Ce, Pr, Nd, and Sm, but the normalized abundance of Gd is too high by a factor of 2. However, Cullers *et al.* (1974) report similarly high Gd abundances for bulk analyses of Silurian metashales in Maine. Such a generally flat curve is typical of most monazite analyses and suggests little fractionation of the La-Gd family of REE between monazite and other phases. Yttrium is far less concentrated in monazite by a factor of 10. This relation, along with the fact that heavier REE are present in abundances below the level of quantitative analysis, is interpreted to indicate strong fractionation of the La-Gd family of REE into monazite, which accords with nearly all other reported analyses.

Discussion

Incorporation of Th^{4+} ions into a monazite crystal structure requires a charge-balanced substitution of other elements; the two leading candidates are Ca^{2+} for REE^{3+} and Si^{4+} for P^{5+} . Analyses presented here show that at metamorphic temperatures, even in the presence of abundant quartz, by far the dominant charge-coupled substitution for thorium is $\text{Th}^{4+} + \text{Ca}^{2+} = 2\text{REE}^{3+}$. The analyzed amounts of thorium (5 wt.% ThO_2 in the cores

and 2 wt.% in the rims) are compatible with Overstreet's (1967) estimate of the amounts of thorium to be expected in monazites of this metamorphic grade.

Bowie and Horne (1953) report that increase in Th content of monazite is correlated with a slight decrease in unit-cell volume of this mineral. This should be expected, since both Th^{4+} and Ca^{2+} have smaller ionic radii than do La^{3+} , Ce^{3+} , and Nd^{3+} (Krauskopf, 1967). Thus increase in Th and Ca in monazite might be expected to correlate with a shifting of relative abundances of REE and Y toward increasing abundance of those elements with smaller ionic radii. Among analyzed elements Gd and Y should show greatest relative enrichment, while La should show strongest relative depletion.

Observed zoning for REE and Y in analyzed monazites is plotted as a function of ionic radius in Figure 6. Error bars represent maximum uncertainty of analysis and are equivalent to two times the sum of standard errors (Table 2). Values used for ionic radii are those of Felsche (1976) for 8-fold coordination and M-O bonding. The ionic radius of yttrium was estimated to be 0.15 Å lower than that of lanthanum (Krauskopf, 1967). The analyzed REE show a clear correlation of increasing core enrichment with decreasing ionic radius, but yttrium does not follow this trend. For the analyzed REE, the relation seen in Figure 6 may be explained by increasing stability of the heavier analyzed REE in the slightly smaller unit cell resulting from increased content of Th and Ca. Although departure of yttrium from this trend may be due to changing fractionation ratios of this element between monazite and other minerals, this hypothesis could not be tested.

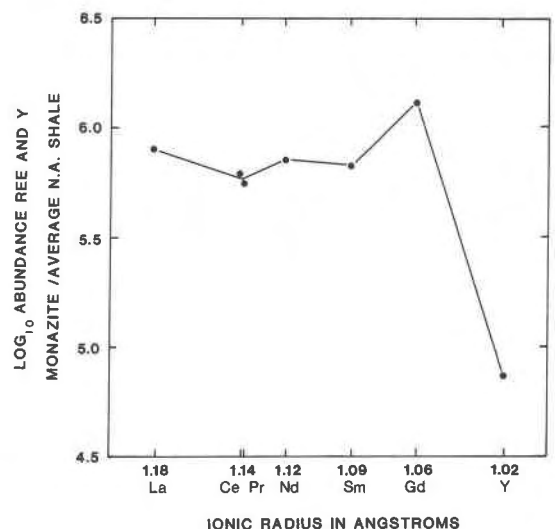


Fig. 5. All monazite analyses were averaged and resulting abundances of REE and Y were normalized to those of average North American shale (Haskin *et al.*, 1966), and then plotted as a function of ionic radius. Results show an essentially flat curve for the La-Gd family of REE, but marked decline for Y.

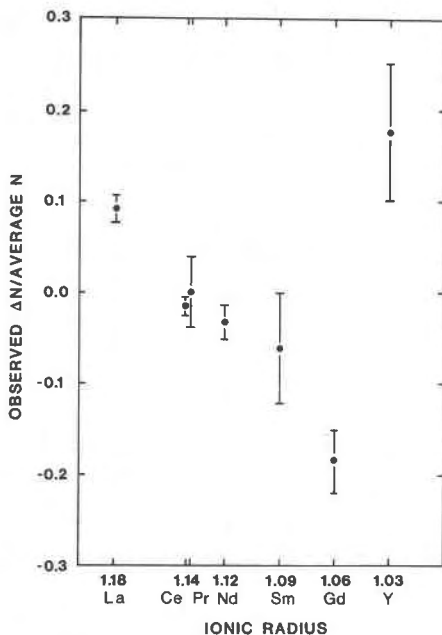


Fig. 6. The extent of zonation of analyzed rare earth elements and yttrium (ΔN /average N) are plotted as a function of ionic radius. Data for this figure are derived from Table 2 and error bars shown are equal to two times the sum of standard errors (see text). For analyzed REE, increasing enrichment in the core correlates well with decreasing ionic radius, but yttrium does not follow this trend.

A few similar studies of monazite chemistry are available in the literature. Lee and Bastron (1967) present a series of bulk analyses of monazites, showing a wide range of thorium contents (14.80 to 5.92 wt.% ThO_2) from a single granitic pluton. The authors did not report abundances of Ca, Si, or P. Thus it is not possible to assess the type of charge-balanced substitution which could accommodate thorium, but their data show a number of interesting trends. Seven analyses, in which ThO_2 contents are all less than 10 wt.%, show trends similar to those of this study. The major exception is a sharp drop, rather than a slight increase, of yttrium abundance with decreasing ThO_2 content. Six other analyses, in which ThO_2 contents are greater than 10 wt.%, show no significant trends. Silver *et al.*, (1980) report zoning of monazite crystals from another granitic pluton. Thorium content ranges from 2.6 wt.% in the core to 8.1 wt.% in the rim. Although zonation of Ca follows that of Th, most thorium is accommodated by charge-coupled substitution involving silicon. Increasing abundance of Th is accompanied by increasing content of Y, appearance of the heavy REE holmium in sufficient quantity for analysis, and decreasing content of all members of the La–Gd family of REE. These trends may be explained by decrease in unit-cell dimensions of monazite with increasing contents of Th and Ca. However, incomplete analyses (Lee and Bastron,

1967) and extensive Th–Si substitution (Silver *et al.*, 1980) make such an explanation less certain.

Bernstein (1982) reports strong zonation of REE and Y in thorium-free monazite from an epithermal quartz vein. Calcium content of analyzed monazite is quite small (~ 0.01 atoms per 4 oxygens). Relative zonation of each REE, as well as Y, is a direct function of ionic size. From core to rim, La shows greatest depletion, Pr shows little change, and Y shows strongest enrichment. These results suggest that in the near-absence of Th and Ca, the REE with the largest ions have the greatest affinity for the monazite crystal structure.

Conclusion

Analyses of monazite porphyroblasts in graphitic meta-shales of staurolite–kyanite grade show that, at these metamorphic conditions, virtually all thorium present is accommodated by a charge-coupled substitution of Th + Ca for two REE. For analyzed rare-earth elements, increase in Th and Ca is correlated with a slight relative enrichment of the heavier REE and depletion in lanthanum. It is suggested that relative zoning of REE ions is related to their ionic size and is due to decrease in unit-cell volumes of monazite caused by increasing contents of Th and Ca. Such a model accounts for observed trends of rare-earth elements, but does not account for the trends seen in yttrium abundances.

Inspection of published monazite analyses from non-metamorphic occurrences lends some support to these hypotheses, although many uncertainties remain. In particular the analyses of Bernstein (1982) suggest that monazite whose Th and Ca contents are minimal have greatest affinity for the largest REE ions. This affinity may be due to an increase in unit-cell dimensions of monazite attendant upon near-absence of Th and Ca.

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