

Experimental study of Th-bearing LaPO₄ (780 °C, 200 MPa): Implications for monazite and actinide orthophosphate stability

RENAUD PODOR AND MICHEL CUNEY

Center de Recherches sur la Geologie des Matières Premières Minérales et Énergétiques, Groupement de Recherches between CNRS and CREGU, no. 77, B. P. 23, 54501 Vandœuvre-Les-Nancy Cedex, France

ABSTRACT

A complete solid solution has been hydrothermally synthesized between the two end-members LaPO₄ and (Ca_{0.5}Th_{0.5})PO₄ at 780 °C and 200 MPa, indicating that there is no limitation in temperature and pressure conditions corresponding to those of granitic magmas for Th insertion in natural monazites. The composition limits of the (A_{1-2x}³⁺ B_x²⁺ C_x⁴⁺)PO₄ compounds crystallized in the monazite structure-type are determined by both $r_{\text{average}} = (1 - 2x)^{[9]}r_{\text{A}^{3+}} + x^{[9]}r_{\text{B}^{2+}} + x^{[9]}r_{\text{C}^{4+}}$ and $r_{\text{ratio}} = (1 - x)^{[9]}r_{\text{A}^{3+}} + x^{[9]}r_{\text{B}^{2+}} / (1 - x)^{[9]}r_{\text{A}^{3+}} + x^{[9]}r_{\text{C}^{4+}}$ parameters (where $^{[9]}r_{\text{A}}$ is the ionic radius of the A element in ninefold coordination). The upper and lower values of these parameters are $1.216 \text{ \AA} \geq r_{\text{average}} \geq 1.107 \text{ \AA}$ and $1.238 \geq r_{\text{ratio}} \geq 1$. The incorporation of large amounts of trans-uranium elements in the monazite structure is deduced from this model. The limitations and geochronological inferences of this model are discussed.

INTRODUCTION

Natural monazite is a mixed lanthanide orthophosphate REEPO₄ with REE = La, Ce, Nd. . . Monazite may contain significant amounts of radioactive elements in its structure (Gramaccioli and Segalstad 1978) and is the principal Th ore and a major REE ore. ThO₂ is generally present in monazite in concentrations from a few hundred parts per million up to 31.5 wt% (Overstreet 1967; Boatner and Sales 1988). The natural thorium orthophosphate end-member (Ca_{0.5}Th_{0.5})PO₄, brabantite, has been described only once (Rose 1980). Natural monazite with compositions intermediate between 31.5 wt% ThO₂ and 57 wt% ThO₂ (brabantite) has never been reported.

Natural substitution of Th in the structure of REEPO₄ involves two types of substitutions: (1) replacement of PO₄³⁻ by SiO₄⁴⁻, which compensates the charge imbalance created by the substitution of Th⁴⁺ for REE³⁺, and (2) coupled substitution of Ca²⁺ + Th⁴⁺ for 2 REE³⁺ (Anthony 1965; McCarthy et al. 1978). The latter type of substitution promotes a solid solution between (Ca_{0.5}Th_{0.5})PO₄ and REEPO₄. Hikichi et al. (1978) experimentally showed the existence of complete solid solutions in the systems CePO₄-ThSiO₄ and CePO₄-(Ca_{0.5}Th_{0.5})PO₄ at 1400 °C and 1 atm.

This study consists of the hydrothermal synthesis at geologic conditions (780 °C, 200 MPa) and the characterization by X-ray diffraction of the solid solution between LaPO₄ and (Ca_{0.5}Th_{0.5})PO₄ end-members. The geometrical conditions for the stability of the compounds (A_{1-2x}³⁺ B_x²⁺ C_x⁴⁺)PO₄ in the monazite structure-type and the stability of solid solutions between REEPO₄ (REE³⁺ = La³⁺ to Gd³⁺), (Ca_{0.5}An_{0.5})PO₄ (An⁴⁺ = Th⁴⁺ to Pu⁴⁺) and other end-members are discussed. These results have

direct implications for the use of monazite in U-Pb geochronology and the use of monazite-type compounds as a matrix for nuclear waste disposal.

MATERIALS AND METHODS

The method used for the preparation of Th- and Ca-rich monazites is similar to that of Anthony (1957). Hydroxide gels of La(OH)₃, Ca(OH)₂, and Th(OH)₄ were coprecipitated by addition of NH₄OH to an aqueous solution containing determined stoichiometric proportions of LaCl₃·7H₂O, CaCl₂, and Th(NO₃)₄·3H₂O. The precipitates were dried and heated at 600 °C for 30 min.

Samples for high-temperature, high-pressure experiments were prepared by loading 200 mg of 30 m orthophosphoric acid and 150 mg of solids in a gold capsule. Experiments were conducted in cold seal vessels at 780 ± 15 °C and 200 ± 1 MPa according to the procedure described by Podor et al. (1995).

ANALYTICAL METHODS

Monazite was analyzed on a CAMECA SX 50 electron microprobe equipped with four wavelength-dispersive spectrometers. The instrument operating conditions were 15 kV accelerating voltage, 10 nA probe current, and 1 μm probe diameter. The M lines were used in the Th analyses with PET crystals, L lines were used in the La analysis with PET crystals, and K lines were used in the Ca and P analyses with PET crystals.

Powder X-ray diffractograms were obtained by using a Guinier camera with CuKα (λ = 1.54059 Å) radiation. Si powder was used as an internal standard for each sample. The θ values were determined by scanning the diffractogram using the SCANPI crystallographic computer

TABLE 1. Experimental conditions and composition of initial mixtures and final products

Exp.	Days	Initial mixture	P ₂ O ₅ (wt%)	CaO (wt%)	La ₂ O ₃ (wt%)	ThO ₂ (wt%)
P193	14	(La _{0.36} Th _{0.31} Ca _{0.31})-oxide mixture	30.06 ± 0.72	7.57 ± 0.53	26.32 ± 2.85	36.05 ± 2.17
P194	14	(La _{0.2} Th _{0.4} Ca _{0.4})-oxide mixture	30.46 ± 0.24	9.39 ± 0.74	16.12 ± 4.30	44.03 ± 3.57
P204	14	(La _{0.28} Th _{0.36} Ca _{0.36})-oxide mixture	30.04 ± 0.39	5.14 ± 0.35	39.21 ± 1.49	25.61 ± 1.04
P205	14	(Th _{0.5} Ca _{0.5})-oxide mixture	30.44 ± 0.47	12.49 ± 0.48	0.00 ± 0.00	57.07 ± 0.85
P221	14	(La _{0.2} Th _{0.4} Ca _{0.4})-oxide mixture	30.27 ± 0.46	10.17 ± 0.35	12.01 ± 2.03	47.54 ± 1.91
P230	14	(La _{0.8} Th _{0.1} Ca _{0.1})-oxide gels	30.83 ± 0.43	2.09 ± 0.11	55.86 ± 0.51	11.22 ± 0.47
P231	14	(La _{0.6} Th _{0.2} Ca _{0.2})-oxide gels	31.00 ± 0.47	4.64 ± 0.22	41.46 ± 1.00	22.89 ± 0.64
P232	14	(La _{0.4} Th _{0.3} Ca _{0.3})-oxide gels	30.92 ± 0.31	7.03 ± 0.33	27.48 ± 1.42	34.56 ± 1.22
P233	14	(La _{0.2} Th _{0.4} Ca _{0.4})-oxide gels	30.91 ± 0.52	9.47 ± 0.22	14.21 ± 0.79	45.41 ± 0.72
P234	14	(Th _{0.5} Ca _{0.5})-oxide gels	30.98 ± 0.30	11.78 ± 0.27	0.03 ± 0.14	57.20 ± 0.37
P259	14	(La _{0.9} Th _{0.05} Ca _{0.05})-oxide gels	30.88 ± 1.14	19.23 ± 3.02	61.19 ± 1.18	6.662 ± 0.61
P260	14	(La _{0.95} Th _{0.025} Ca _{0.025})-oxide gels	30.70 ± 0.42	19.28 ± 2.27	65.20 ± 0.59	3.42 ± 0.37
P274	1	(La _{0.6} Th _{0.2} Ca _{0.2})-oxide gels	31.35 ± 0.61	4.59 ± 0.21	41.40 ± 1.10	22.67 ± 0.91
P275	7	(La _{0.6} Th _{0.2} Ca _{0.2})-oxide gels	31.16 ± 0.54	4.45 ± 0.24	42.33 ± 1.40	22.06 ± 1.18
P276	12	(La _{0.6} Th _{0.2} Ca _{0.2})-oxide gels	31.27 ± 0.53	4.82 ± 0.19	40.65 ± 1.11	23.26 ± 0.88
P277	18	(La _{0.6} Th _{0.2} Ca _{0.2})-oxide gels	31.03 ± 0.63	4.65 ± 0.20	41.17 ± 0.95	23.15 ± 0.78
P278	23	(La _{0.6} Th _{0.2} Ca _{0.2})-oxide gels	31.11 ± 0.33	4.62 ± 0.24	41.12 ± 1.34	23.14 ± 1.07
P279	30	(La _{0.6} Th _{0.2} Ca _{0.2})-oxide gels	31.24 ± 0.37	4.79 ± 0.19	40.43 ± 1.22	23.53 ± 0.92

Note: All experiments were performed at 780 °C, 200 MPa, and 30 *m* (H₃PO₄).

program (Werner 1990) and the unit-cell parameters were refined with the U-FIT program (Evain 1992).

RESULTS

Equilibrium conditions in the system

Eleven typical compositions of LaPO₄ containing Th and Ca were synthesized for this study. Final products contained well-crystallized monazite crystals ranging in size from 0.2 to 2 μm in diameter. The electron microprobe data are summarized in Table 1. The mole fractions of lanthanum, calcium, and thorium oxides in the synthesized monazites corresponded to the mole fractions of La(OH)₃, CaO, and Th(OH)₄ in the initial mixture. Electron microprobe and transmission electron microprobe analyses showed that the compositions of synthesized monazites are homogeneous. A kinetic study was conducted to determine the minimum experiment duration to reach equilibrium. The Th available in the initial gel was

completely incorporated in monazite after 24 h so that the concentration of Th in monazite was independent of experiment duration (Fig. 1). Increasing experiment duration above 24 h led only to an increase of the crystal size. The crystal shapes were very well defined even when the crystals were small.

Mechanism of Th and Ca substitution in monazite

A linear correlation is shown between mole fraction of La, x_{La} , and the sum of the mole fractions of Th and Ca, ($x_{Th} + x_{Ca}$) (Fig. 2a). Kelly et al. (1981) have shown that Th incorporated in monazite is tetravalent. Then, the Th⁴⁺ = La³⁺ substitution is charge-compensated by the Ca²⁺ = La³⁺ substitution (Fig. 2b). This type of charge compensation mechanism was also proposed by Bowie & Horne (1953) and Frondel (1948) to explain the Ca-Th substitution in natural monazites.

Synthesis of the compound (Ca_{0.5}Th_{0.5})PO₄

The (Ca_{0.5}Th_{0.5})PO₄ end-member was synthesized for the first time hydrothermally in [H₃PO₄] = 30 *m*, at *T* = 780 °C and *P* = 200 MPa. This compound was obtained by hydrothermal reaction between an homogeneous and stoichiometric mixture of Th(OH)₄ and Ca(OH)₂ with a molar excess of phosphoric acid in aqueous solution. The synthetic crystals were 20–100 μm in size. X-ray data show this compound to be isostructural with monazite. Calculated unit-cell parameters are *a*₀ = 6.706(1), *b*₀ = 6.918(1), and *c*₀ = 6.417(1) Å and β₀ = 103.65(4)°. All the peaks observed were indexed in the *P*2₁/*n* space group. This compound was synthesized for the first time at atmospheric pressure by Pfoertsch and McCarthy (1978) at 1200 °C and Hikichi et al. (1978) at 1400 °C. The unit-cell parameters determined by these authors for (Ca_{0.5}Th_{0.5})PO₄ are consistent with those determined in this study. The corresponding mineral is named brabantite (Rose 1980). Its composition is (Ca_{1.000}Mg_{0.065}Mn_{0.021}Al_{0.068}Fe_{0.003})_{Σ=1.157}Th_{0.936}(P_{1.832}Si_{0.177})O₈

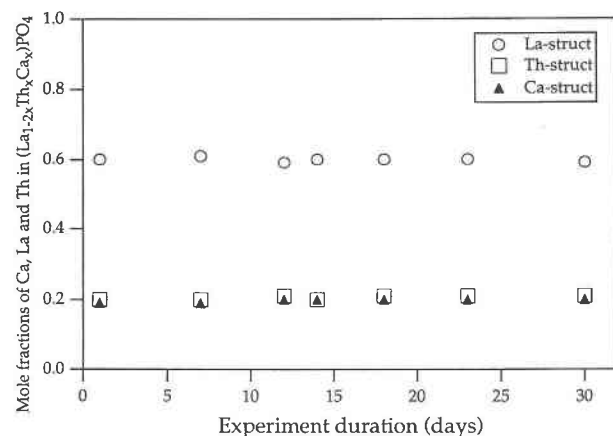


FIGURE 1. Substitution of Th and Ca in (La_{0.6}Th_{0.2}Ca_{0.2})PO₄ vs. experiment duration.

TABLE 1. Continued

Exp.	Total (wt%)	O (at%)	P (at%)	La (at%)	Th (at%)	Ca (at%)
P193	94.22 ± 4.31	66.61	16.50	6.30	5.32	5.26
P194	98.49 ± 2.15	66.64	16.60	3.83	6.45	6.48
P204	97.73 ± 3.30	66.66	16.55	9.41	3.79	3.58
P205	99.40 ± 4.37	66.56	16.53	0.00	8.33	8.58
P221	99.89 ± 1.10	66.6	16.53	2.86	6.98	7.03
P230	97.10 ± 1.34	66.78	16.84	13.29	1.65	1.45
P231	98.01 ± 1.01	66.77	16.86	9.83	3.35	3.20
P232	99.17 ± 1.61	66.77	16.82	6.51	5.05	4.84
P233	98.03 ± 3.23	66.73	16.77	3.36	6.62	6.51
P234	100.25 ± 0.83	66.77	16.8	0.01	8.34	8.09
P259	96.57 ± 3.44	66.76	16.84	13.99	0.98	0.87
P260	97.76 ± 1.76	66.73	16.79	15.53	0.50	0.45
P274	90.15 ± 4.39	66.82	16.97	9.77	3.30	3.14
P275	94.92 ± 1.83	66.80	16.91	10.01	3.22	3.05
P276	95.83 ± 3.13	66.79	16.93	9.59	3.38	3.30
P277	97.22 ± 1.36	66.79	16.87	9.75	3.38	3.20
P278	96.80 ± 2.15	66.80	16.90	9.73	3.38	3.18
P279	95.82 ± 1.38	66.80	16.93	9.55	3.43	3.29

and the unit-cell parameters are $a = 6.726$, $b = 6.933$, and $c = 6.447$ Å and $\beta = 103.53^\circ$.

The LaPO₄-(Ca_{0.5}Th_{0.5})PO₄ solid solution

X-ray powder data indicate that all compounds synthesized have a monoclinic structure similar to the monazite crystal structure (Pepin and Vance 1981; Ni et al. 1995). Refined unit-cell parameters for (La_{1-2x}Th_xCa_x)PO₄ have been calculated for the different values of the mole fraction x . The results are reported in Table 2 with other values obtained from the literature.

The unit-cell parameters a_0 , b_0 , c_0 , β_0 , and unit-cell volumes V_0 are plotted vs. Th mole fraction in monazite (Fig. 3). The unit-cell constants a_0 , b_0 , and c_0 decrease linearly with increasing Th content (Fig. 3a), whereas β_0 increases with increasing x (Fig. 3b). The substitution of two atoms of La by one atom of Th and one atom of Ca involves a regular contraction of the unit-cell volumes (Fig. 3c) from LaPO₄ up to (Ca_{0.5}Th_{0.5})PO₄. No phase transition has been observed between the two pure phases, consistent with complete solid solution between the two end-members LaPO₄ and (Ca_{0.5}Th_{0.5})PO₄ under these conditions. This conclusion was confirmed by Raman spectroscopy where variations of the vibrational-band frequencies with increasing Th-Ca substitution in (La)_{1-2x}monazite are correlated for many of the observed bands (Podor 1995). Hikichi et al. (1978) obtained a complete solid solution between CePO₄ and (Ca_{0.5}Th_{0.5})PO₄, but their experiments were at atmospheric pressure and $T = 1400^\circ\text{C}$.

DISCUSSION

Relations between the lattice parameters and the ionic radius of the cation site

The decrease of the unit-cell parameters is correlated with the decrease of the ionic radius of the cation site (cat^{3+}) in monazite. The mean ionic radius of the cation site is:

$$^{[9]}r_{\text{cat}^{3+}} = (1 - 2x) ^{[9]}r_{\text{La}^{3+}} + x ^{[9]}r_{\text{Ca}^{2+}} + x ^{[9]}r_{\text{Th}^{4+}} \quad (1)$$

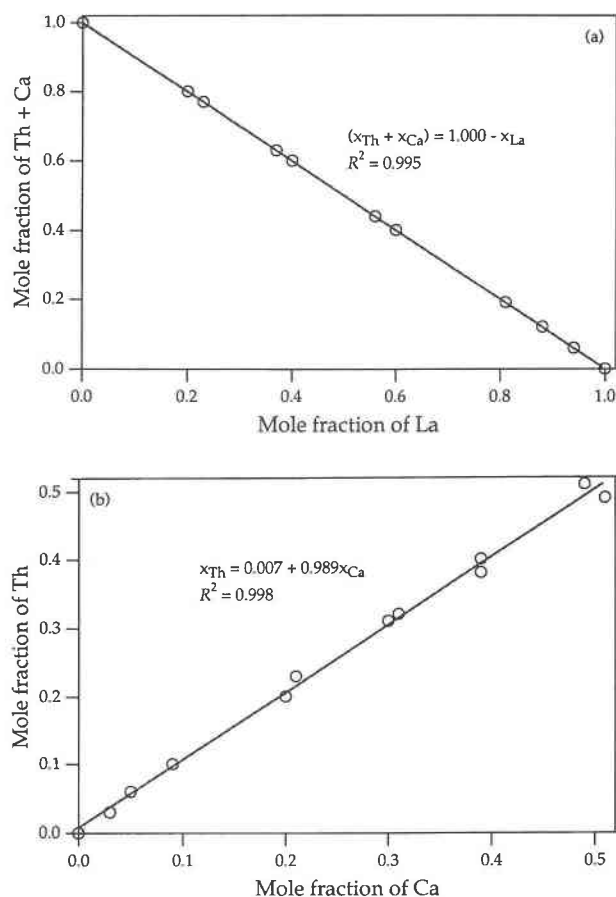


FIGURE 2. (a) Linear correlation between mole fractions of Th and those of Ca in (La_{1-2x}Th_xCa_x)PO₄. R^2 = correlation coefficient. (b) Linear correlation between the sum of Th and Ca mole fractions and those of La in synthetic (La_{1-2x}Th_xCa_x)PO₄.

Using the ionic radii of Shannon (1976), linear correlations between the mean ionic radius of the cation site in (La_{1-2x}Th_xCa_x)PO₄ and the unit-cell parameters can be established (Figs. 3a and 3b):

$$a_0 = 1.728^{[9]}r_{\text{cat}^{3+}} + 4.748 \quad (2)$$

$$b_0 = 2.049^{[9]}r_{\text{cat}^{3+}} + 4.595 \quad (3)$$

$$c_0 = 1.222^{[9]}r_{\text{cat}^{3+}} + 5.032 \quad (4)$$

$$\beta_0 = -5.031^{[9]}r_{\text{cat}^{3+}} + 109.377 \quad (5)$$

These results are comparable with those obtained (Podor et al. 1995) for the correlations between a_0 , b_0 , c_0 , β_0 , and $^{[9]}r_{\text{cat}^{3+}}$ for the U- and Ca-bearing monazite and with those obtained by Ni et al. (1995) in the REEPO₄ family. The c -parameter increase with increasing mean ionic radius is less in the REEPO₄ series than in the U-Ca- and Th-Ca-bearing monazite series. Hugues et al. (1995) have also observed that the contraction of the REE site in cheralite occurs principally along interchain equatorial bonds in (001) and explained this specific behavior by enhanced Th⁴⁺-Th⁴⁺ repulsion along [001].

TABLE 2. Unit-cell constants of (La_{1-2x}Th_xCa_x)PO₄

Exp.	Compound	x	a ₀ (Å)	b ₀ (Å)	c ₀ (Å)	β ₀	V ₀ (Å ³)
	LaPO ₄	0.000	6.790	7.040	6.470	104.40	299.00
	LaPO ₄	0.000	6.837	7.077	6.510	103.24	306.50
	LaPO ₄	0.000	6.825	7.057	6.482	103.21	303.90
	LaPO ₄	0.000	6.682	7.044	6.539	104.25	307.20
	LaPO ₄	0.000	6.8313	7.0705	6.5034	103.27	
P7	LaPO ₄	0.000	6.845	7.082	6.512	103.29	307.54
P260	(La _{0.94} Th _{0.05} Ca _{0.03})PO ₄	0.028	6.838	7.076	6.510	103.31	306.53
P259	(La _{0.84} Th _{0.06} Ca _{0.06})PO ₄	0.055	6.839	7.075	6.510	103.31	306.56
P230	(La _{0.81} Th _{0.10} Ca _{0.09})PO ₄	0.094	6.818	7.047	6.497	103.34	303.77
P231	(La _{0.600} Th _{0.204} Ca _{0.196})PO ₄	0.200	6.792	7.019	6.478	103.40	300.46
P204	(La _{0.561} Th _{0.226} Ca _{0.213})PO ₄	0.220	6.790	7.016	6.476	103.42	300.09
P232	(La _{0.397} Th _{0.308} Ca _{0.294})PO ₄	0.301	6.769	6.991	6.461	103.50	297.35
P193	(La _{0.373} Th _{0.315} Ca _{0.312})PO ₄	0.313	6.768	6.992	6.458	103.51	297.16
P194	(La _{0.229} Th _{0.385} Ca _{0.286})PO ₄	0.385	6.738	6.953	6.439	103.60	293.19
P233	(La _{0.204} Th _{0.401} Ca _{0.395})PO ₄	0.398	6.741	6.959	6.440	103.59	293.66
P234	(Ca _{0.5} Th _{0.5})PO ₄	0.500	6.705	6.918	6.415	103.65	289.15
P205	(Ca _{0.5} Th _{0.5})PO ₄	0.500	6.706	6.916	6.417	103.72	289.03
	(Ca _{0.5} Th _{0.5})PO ₄ ^[6]	0.500	6.726	6.933	6.447	103.53	
	(Ca _{0.5} Th _{0.5})PO ₄ ^[7]	0.500	6.681	6.926	6.421	103.54	288.42
	(Ca _{0.5} Th _{0.5})PO ₄ ^[8]	0.500	6.713	6.916	6.419	103.75	

Determination of the compositional stability range of the solid solution (A_{1-2x}B_x²⁺C_x⁴⁺)PO₄

All the results reported in this part correspond to compounds that are stable in the temperature range 1000–1400 °C in air. Some compounds that crystallize in the monoclinic system (monazite group) in this temperature range have polymorphic modifications at lower or higher temperatures.

The (A_{1-2x}B_x²⁺C_x⁴⁺)PO₄ intermediate compounds are defined between the two end-members A³⁺PO₄ and (B_{0.5}C_{0.5})PO₄. The compositional stability range of (A_{1-2x}B_x²⁺C_x⁴⁺)PO₄ in the monoclinic system (monazite group) depends on the relative stabilities of the A³⁺PO₄ and (B_{0.5}C_{0.5})PO₄ compounds.

In the case of the A³⁺PO₄ compounds, the ionic radii of the trivalent elements that phosphates crystallized with the monazite structure range between ⁹r_{La³⁺} = 1.216 Å and ⁹r_{Gd³⁺} = 1.107 Å. The first heavy REE to form a REEPO₄ that does not crystallize in the monoclinic system is Tb (Ivanov and Sin'Kova 1967; Milligan et al. 1983; Hikichi et al. 1989) which has an ionic radius is 1.095 Å in the ninefold coordination (Shannon 1976). The trans-plutonium (from Am to Es) phosphates crystallize in the monazite group (Hobart et al. 1983; Haire et al. 1983). The ionic radii of these elements in the ninefold coordination can be estimated by linear extrapolation from the values given by Shannon (1976) in the sixfold and eightfold coordination. They are ranging from 1.135 Å to 1.107 Å.

The stability of the (B_{0.5}C_{0.5})PO₄ compounds in the monoclinic system (monazite group) can be described by comparing two parameters: (1) the mean ionic radii (⁹r_{B²⁺} + ⁹r_{C⁴⁺})/2 of the atoms in the cation site and (2) the ⁹r_{B²⁺}/⁹r_{C⁴⁺} ratio, where ⁹r_{B²⁺} and ⁹r_{C⁴⁺} are the ionic radii of the B²⁺ and C⁴⁺ ions in the ninefold coordination.

The limiting values of these parameters can be deter-

mined from results reported in the literature. Pepin et al. (1981) showed that monazite-structured (Ca_{0.5}Th_{0.5})PO₄ and (Ca_{0.5}U_{0.5})PO₄ compounds are stable, while (Ca_{0.5}Ce_{0.5})PO₄ is not stable. The lower limit of the (⁹r_{B²⁺} + ⁹r_{C⁴⁺})/2 parameter is inferred to be just larger than the value of the average ionic radius of Ca²⁺ and Ce⁴⁺ in the ninefold coordination, ⁹r_{cat} limit > 1.10 Å (The value for the ionic radius of Ce⁴⁺ is calculated as an average of the eightfold and tenfold coordination ionic radii, and ⁹r_{Th⁴⁺} = 1.09 Å.) The upper limit of the parameter (⁹r_{B²⁺} + ⁹r_{C⁴⁺})/2 is determined by the mean ionic radius in the (Pb_{0.5}Th_{0.5})PO₄ compound and is equal to 1.215 Å. Thus, the limits of the mean ionic radii for the monazite structure to be stable range between:

$$1.215 \text{ Å} \geq (\text{}^9\text{r}_{\text{B}^{2+}} + \text{}^9\text{r}_{\text{C}^{4+}})/2 > 1.10 \text{ Å} \quad (6)$$

The upper limit of the second parameter is given by the ⁹r_{Pb²⁺}/⁹r_{Th⁴⁺} ratio (⁹r_{Pb²⁺} = 1.35 Å, Shannon 1976). Monoclinic (Pb_{0.5}Th_{0.5})PO₄ is stable (Quarton et al. 1984), whereas (Sr_{0.5}U_{0.5})PO₄ does not crystallize in the monoclinic form (Rose 1980; ⁹r_{Sr²⁺} = 1.31 Å, Shannon 1976). Moreover, the stability of (Mg_{0.5}Th_{0.5})PO₄ in the monazite group has not been demonstrated (⁹r_{Mg²⁺} = 0.966 Å, calculated from the values given by Shannon 1976). Thus, the lower limit of the second parameter is given by the stability of (Cd_{0.5}Th_{0.5})PO₄ (with ⁹r_{Cd²⁺} = 1.135 Å). The limits of ⁹r_{B²⁺}/⁹r_{C⁴⁺} are:

$$1.238 \geq \text{}^9\text{r}_{\text{B}^{2+}}/\text{}^9\text{r}_{\text{C}^{4+}} \geq 1.041 \quad (7)$$

More generally, the stability of the intermediate compounds A_{1-2x}B_x²⁺C_x⁴⁺PO₄ can be described by the two parameters:

$$r_{\text{average}} = (1 - 2x)\text{}^9\text{r}_{\text{A}^{3+}} + x(\text{}^9\text{r}_{\text{B}^{2+}} + \text{}^9\text{r}_{\text{C}^{4+}}) \quad (8)$$

$$r_{\text{ratio}} = \frac{(1 - 2x)\text{}^9\text{r}_{\text{A}^{3+}} + x\text{}^9\text{r}_{\text{B}^{2+}}}{(1 - 2x)\text{}^9\text{r}_{\text{A}^{3+}} + x\text{}^9\text{r}_{\text{C}^{4+}}} \quad (9)$$

The r_{average} parameter corresponds to the ionic radius of

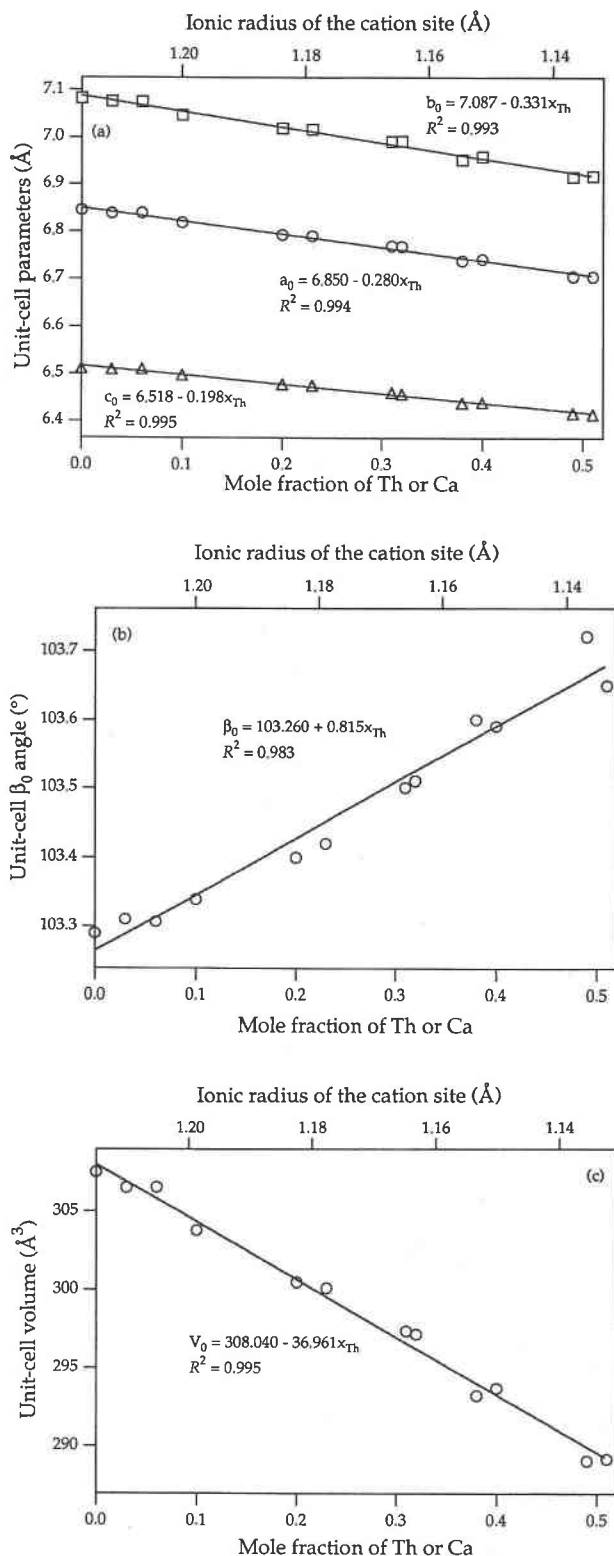


FIGURE 3. (a) Linear correlation between unit-cell parameters (a_0 , b_0 , c_0) (\AA) of synthetic $(\text{La}_{1-2x}\text{Th}_x\text{Ca}_x)\text{PO}_4$ with mole fraction x of Th or Ca, and with the ionic radius of the cation site (open circle: a_0 , open square: b_0 , open triangle: c_0). (b) Linear correlation between unit-cell β_0 angle of synthetic $(\text{La}_{1-2x}\text{Th}_x\text{Ca}_x)\text{PO}_4$ with mole fraction x of Th or Ca and with the ionic radius of the cation site. (c) Variations of unit-cell volume V_0 of synthetic $(\text{La}_{1-2x}\text{Th}_x\text{Ca}_x)\text{PO}_4$ vs. mole fraction x of Th or Ca, and vs. the ionic radius of the cation site.

the cation site when $1 - 2x$ atoms of A^{3+} are substituted by one atom of B^{2+} and one atom of C^{4+} . The r_{ratio} parameter describes the coupled substitution of one atom of B^{2+} in one site A^{3+} , and of one atom of C^{4+} in another A^{3+} site.

The upper limit of r_{average} is given by the ionic radius of La in LaPO_4 ($^{(9)}r_{\text{La}^{3+}} = 1.216 \text{ \AA}$), whereas the lower limit of this parameter is given by the ionic radius of Gd in GdPO_4 ($^{(9)}r_{\text{Gd}^{3+}} = 1.107 \text{ \AA}$). Consequently,

$$1.216 \text{ \AA} \geq r_{\text{average}} \geq 1.107 \text{ \AA} \quad (10)$$

The limits of r_{ratio} that have been obtained for $x = 0$ and $x = 0.5$ are:

$$1.238 \geq r_{\text{ratio}} \geq 1 \quad (11)$$

The stability range of the $(\text{A}_{1-2x}^{3+}\text{B}_x^{2+}\text{C}_x^{4+})\text{PO}_4$ compounds is plotted as a function of the three parameters x , r_{average} , and r_{ratio} (Fig. 4). The volume obtained is a prism that describes the stability domain of monazites. Each point included in this volume corresponds to the composition of a product that crystallizes with the monazite structure. A line segment joining two points in this vol-

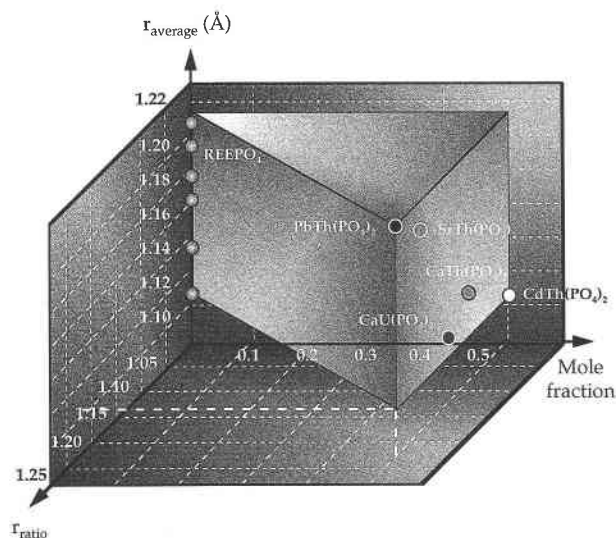


FIGURE 4. Stability domain of the compounds $(\text{A}_{1-2x}^{3+}\text{B}_x^{2+}\text{C}_x^{4+})\text{PO}_4$ in the monazite structure-type vs. mole fraction of B^{2+} or C^{4+} , r_{average} , and r_{ratio} .

ume represents a solid solution between the two compositions.

The existence of partial solid solutions between $(\text{REE}_{1-2x}\text{Ca}_x\text{Pu}_x)\text{PO}_4$ and $(\text{REE}_{1-2x}\text{Ca}_x\text{Np}_x)\text{PO}_4$ can be deduced from this figure. The value of x is estimated to be equal to 0.45 when REE is La or Ce, referring to equations (10) and (11). Seaborg (1978) has shown that very small amounts of Pu and Np are sometimes present in natural monazite. Actinide-doped LaPO_4 single crystals containing 1.7 wt% $^{238}\text{UO}_2$, 5 wt% $^{242}\text{PuO}_2$, 2 wt% $^{237}\text{NpO}_2$, 0.2 wt% $^{241}\text{Am}_2\text{O}_3$, and 0.2 wt% $^{246}\text{Cm}_2\text{O}_3$ have been prepared by the flux technique (Kelly et al. 1981).

The ionic radii of Y^{3+} , In^{3+} , and Sc^{3+} in the ninefold coordination can be calculated from the values given by Shannon (1976) for the sixfold and eightfold coordinations. They are 1.075, 0.98, and 0.932 Å, respectively. The end-members are not stable because they plot outside the prism, but the $(\text{Ca}_{0.5}\text{Th}_{0.5})\text{PO}_4$ or $(\text{Ca}_{0.5}\text{U}_{0.5})\text{PO}_4$ compounds can incorporate small amounts of A^{3+}PO_4 ($\text{A}^{3+} = \text{In}^{3+}$, Sc^{3+} , Y^{3+}).

The decrease of the unit-cell parameters with increasing (Th, Ca) and (U, Ca) substitutions will favor the insertion of cations with low ionic radii. The use of both r_{average} and r_{ratio} parameters shows that $(\text{Ca}_{0.5}\text{Th}_{0.5})\text{PO}_4$ and $(\text{Ca}_{0.5}\text{U}_{0.5})\text{PO}_4$ end-members can incorporate significant amounts of heavy rare-earth elements. Partial solid solutions such as $(\text{Ca}_x^{2+}\text{U}_x^{4+}\text{HREE}_{1-2x}^{3+})\text{PO}_4$ are stable for values of x close to 0.5. Indeed, substitution of light rare-earth elements by heavy rare-earth elements and Y increases with increasing Th and U substitution in monazite has been shown by Brouand and Cuney (1990).

Variations of the stability range of the solid solution $(\text{A}_{1-2x}^{3+}\text{B}_x^{2+}\text{C}_x^{4+})\text{PO}_4$ with temperature and pressure

The limits of the r_{average} parameter vary with temperature at atmospheric pressure. X-ray diffraction studies on (lanthanum-europium) orthophosphates have shown one polymorphic modification between an hexagonal form (stable at low temperature) and a monoclinic form (stable at high temperature). The modification temperatures are $T = 400^\circ\text{C}$ for LaPO_4 , $T = 450^\circ\text{C}$ for NdPO_4 and $T = 500^\circ\text{C}$ for EuPO_4 (Bondar et al. 1976; Hikichi et al. 1989; Akers et al. 1993). Two polymorphic modifications have been found for the transitional compounds GdPO_4 , TbPO_4 , and DyPO_4 : from hexagonal to monoclinic form and from monoclinic to tetragonal form. The first modification temperatures are $T = 550^\circ\text{C}$ for GdPO_4 and $T = 600^\circ\text{C}$ for TbPO_4 and DyPO_4 (Bondar et al., 1976). The second modification temperatures are $T > 1200^\circ\text{C}$ for GdPO_4 , $1100 > T > 800^\circ\text{C}$ for TbPO_4 and $T \sim 800^\circ\text{C}$ for DyPO_4 (Ivanov and Sin'Kova 1967; Hikichi et al. 1989).

Moreover, the limits of the r_{ratio} parameter also vary with temperature. Dusaosoy et al. (1996) have shown that the $(\text{Ca}_{0.5}\text{U}_{0.5})\text{PO}_4$ synthetic compound has an irreversible polymorphic modification from orthorhombic to monoclinic form at $T > 1000^\circ\text{C}$ and atmospheric pressure. The $(\text{Ca}_{0.5}\text{Th}_{0.5})\text{PO}_4$ compound does not undergo this type of phase transformation.

Pressure also influence the limits of r_{average} and r_{ratio} parameters. For example, monoclinic lanthanum phosphate is stable in the temperature range $200\text{--}600^\circ\text{C}$, $200 > P > 50$ MPa, under hydrothermal conditions (Akers et al. 1993). The polymorphic transformation of the $(\text{Ca}_{0.5}\text{U}_{0.5})\text{PO}_4$ compound from orthorhombic to monoclinic form is lowered down to 700°C , at $P = 200$ MPa and in 30 m H_3PO_4 (Dusaosoy et al. 1996).

Limitations of the model

Other compounds of general formula ABO_4 such as vanadates, LaVO_4 (Rice and Robinson 1976), chromates, PbCrO_4 (JC-PDS file no. 8-209) or silicates, ThSiO_4 (Hikichi et al. 1978) crystallize in the $P2_1/n$ space group (monazite type). Their stability domain is not represented in Figure 4, and their stability limits cannot be determined by Equations 10 and 11. A fourth parameter must be defined to describe the stability of these compounds. The $^{[9]}r_{\text{A}^{n+}}/^{[9]}r_{\text{DO}_4^{n-}}$ ratio must be taken into account. However, presently available structural data are too limited to determine the limits of this fourth parameter.

GEOLOGICAL IMPLICATIONS

The experimental data presented in this paper demonstrate that Th substitution in monazite is unlimited in temperature and pressure conditions corresponding to those of granitic magmas, provided that charge compensation is assured by a divalent cation of similar ionic radius (generally Ca^{2+}). Therefore, the compositional gap between naturally occurring Th-rich monazite and brabantite may result only from the fact that the compositions of the fluids or silicate melts required to crystallize these intermediate compositions are not reached in nature.

Monazite Th-U-Pb isotopic systematics have great potential for determining the absolute chronology of a detailed sequences of geologic events (Copeland et al. 1988; Parrish 1990; Kingsbury et al. 1993; Suzuki et al. 1994). For an accurate age-dating of zones in a single monazite grain, it is necessary that (1) Pb was not incorporated at the time of monazite formation, and that (2) monazite remain immune to radiogenic Pb loss (Pb diffusion in monazite must be limited at low temperature).

The first point is not supported by the model proposed in this work. From purely chemical-physical considerations, Pb can be incorporated during the formation of monazite at: (1) the valence state II; The substitution mechanism is $2\text{REE}^{3+} = \text{Pb}^{2+} + [\text{U}, \text{Th}]^{4+}$ and (2) the valence state IV; The substitution mechanism is $2\text{REE}^{3+} = \text{Ca}^{2+} + \text{Pb}^{4+}$. This type of substitution mechanism cannot be observed in natural monazites because Pb does not occur in the tetravalent state in nature.

In fact, some analytical data do indicate incorporation of noticeable amounts of "common lead" in monazite. For example, the monazite from Steenkanpakraal (Tilton and Nicolaysen 1957) presents $^{206}\text{Pb}/^{204}\text{Pb}$ of 77 and the monazite from Baltor granite in Pakistan shows $^{206}\text{Pb}/^{204}\text{Pb}$ as low as 385 (Parrish 1990). The stability domain determined from Equations 10 and 11 leads to the evi-

dence that Pb can replace Ca in its original site. In this case, Pb can be substituted to rare-earth elements during monazite formation. Then, charge compensation is assumed by U⁴⁺ or Th⁴⁺ incorporation.

The second point (2) is not supported by the model proposed in this work. Indeed, the concentrations of Ca²⁺, Pb²⁺, U⁴⁺, and Th⁴⁺ in the cation site are always relatively low in comparison with the REE³⁺ concentrations. The diffusion of Pb corresponds to a displacement of divalent cation in a trivalent cation network. This displacement can only occur with coupled Th⁴⁺ or U⁴⁺ displacement to respect charge balance in the REE³⁺ network. This type of double diffusion mechanism is highly energetic and the jumping probability is necessarily very weak. Thus, Pb diffusion in monazite is naturally limited. These results confirm the hypothesis that radiogenic lead is stable in the structure of natural monazites (Suzuki et al. 1994). Parrish (1990) has estimated a closure temperature of 725 ± 25 °C for monazite, a result confirmed by numerous other studies (Copeland et al. 1988; Kingsbury et al. 1993).

ACKNOWLEDGMENTS

The high-pressure and temperature experiments were performed in the Experimental Laboratory of the Centre de Recherches Pétrographiques et Géochimiques (CRPG)-France. The authors thank A. Rouillier (CRPG), J. Ghanbaja, and J. M. Claude (Univ. Nancy I) for their technical and analytical support.

REFERENCES CITED

- Akers, W.T., Grove, M., Harrison, T.M., and Ryerson, F.J. (1993) The instability of rhabdophane and its unimportance in monazite paragenesis. *Chemical Geology*, 110, 169–176.
- Anthony, J.W. (1957) Hydrothermal synthesis of monazite. *American Mineralogist*, 42, 904.
- (1965) Crystal morphology of thorium-bearing synthetic monazite. *American Mineralogist*, 50, 1421–1431.
- Boatner, L.A. and Sales, B.C. (1988) Radioactive waste forms for the future: Monazite. In W. Lutze and R.C. Ewing, Ed., *Radioactive waste forms for the future*, p. 495–564. North Holland, Amsterdam.
- Bondar, I.A., Domanskii, A.I., Mezentsseva, L.P., Degen, M.G., and Kalinina, N.E. (1976) A physicochemical study of lanthanide orthophosphates. *Zhurnal Neorganicheskoi Khimii*, 21, 2045–2050 (translated from Russian).
- Bowie, S.H.U. and Horne, J.E.T. (1953) Cheralite, a new mineral of the monazite group. *Mineralogical Magazine*, 30, 93–99.
- Brouand, M. and Cuney, M. (1990) Substitution des radioéléments dans la monazite des granites hyperalumineux. Conséquences pour la définition de leur potentialité métallogénique. *Bulletin de la Société Française de Minéralogie et de Cristallographie*, 2/3, 124–125.
- Copeland, P., Parrish, R.R., and Harrison, T.M. (1988) Identification of inherited radiogenic Pb in monazite and its implications for U-Pb systematics. *Nature*, 333 (6175), 760–763.
- Dusauroy, Y., Ghermani, N.E., Podor, R., and Cuney, M. (1996) Synthesis and crystal-structure of the low-temperature form of CaU(PO₄)₂. *European Journal of Mineralogy*, 8 (4), 667–673.
- Evain, M. (1992) U-FIT program. Institut des Matériaux de Nantes, France.
- Fronzel, C. (1948) Systematic mineralogy of uranium and thorium. *US Geological Survey Bulletin*, 1064, 151–152.
- Gramaccioli, C.M. and Segalstad, T.V. (1978) A uranium- and thorium-rich monazite from a south-alpine pegmatite at Piona, Italy. *American Mineralogist*, 63, 757–761.
- Haire, R.G., Hellwege, H.E., Hobart, D.E., and Young, J.P. (1983) *Journal of the Less-Common Metals*, 93, 358.
- Hikichi, Y., Hukuo, K., and Shiokawa, J. (1978) Solid solutions in the systems monazite (CePO₄)—huttonite (ThSiO₄) and monazite—(Ca_{0.5}Th_{0.5})PO₄. *Nippon Kagaku Kaishi*, 12, 1635–1640 (in Japanese).
- Hikichi, Y., Murayama, K., Ohsato, H., and Nomura, T. (1989) Thermal changes of rare-earth phosphate minerals. *Nippon Kagaku Kaishi*, 19(3), 117–126 (in Japanese).
- Hobart, D.E., Begun, G.M., Haire, R.G., and Hellwege, H.E. (1983) Raman spectra of the transplutonium orthophosphates and trimetaphosphates. *Journal of Raman Spectroscopy*, 14(1), 59–62.
- Hugues, J.M., Foord, E.E., Hubbard, M.A., and Ni, Y. (1995) The crystal structure of cheralite-(Ce), (LREE, Ca, Th, U)(P, Si)O₄, a monazite-group mineral. *Neues Jahrbuch für Mineralogie Monatshefte*, 8, 344–350.
- Ivanov, V.I. and Sin'kova, L.A. (1967) Experimental study of the monazite-xenotime structural relationship in the rare-earth phosphates. *Geokhimiya*, 2, 241–243 (Translated from Russian).
- Kelly, K.L., Beall, G.W., Young, J.P., and Boatner, L.A. (1981) Valence states of actinides in synthetic monazites. In J.G. Moore, Ed., *The Scientific Basis For Nuclear Waste Management* 3, p. 189–195. Plenum, New York.
- Kingsbury, J.A., Miller, C.F., Wooden, J.L., and Harrison, T.M. (1993) Monazite paragenesis and U-Pb systematics in rocks of the eastern Mojave Desert, California, USA, implications for thermochronothermometry. *Chemical Geology*, 110, 147–167.
- McCarthy, G.J., White, W.B., and Pfoertsch, D.E. (1978) Synthesis of nuclear waste monazites, ideal actinide hosts for geological disposal. *Material Research Bulletin*, 13, 1239–1245.
- Milligan, W.O., Mullica, D.F., Beall, G.W., and Boatner, L.A. (1983) The structures of three lanthanide orthophosphates. *Inorganica Chimica Acta*, 70(2), 133–136.
- Ni, Y., Hugues, J.M., and Mariano, A.N. (1995) Crystal chemistry of the monazite and xenotime structures. *American Mineralogist*, 80, 21–26.
- Overstreet, W.C. (1967) The geologic occurrence of monazite. *US Geological Survey Professional Paper*, 530, 327 p.
- Parrish, R.R. (1990) U-Pb dating of monazite and its application to geological problems. *Canadian Journal of Earth Sciences*, 27, 1431–1450.
- Pepin, G.J. and Vance, E.R. (1981) Crystal data for rare earth orthophosphates of the monazite structure-type. *Journal of Inorganic and Nuclear Chemistry*, 43 (11), 2807–2809.
- Pepin, G.J., Davis, D.D., McCarthy, G.J., and Vance, E.R. (1981) Crystal chemistry of some monazite-structured phosphates and silicates. Report 1981, DOE/ET/41 900-7, ESG-EOG-13 351, 37 p., Energy Research Abstract, 6 (19), Abstract no. 29 104.
- Pfoertsch, D.E. and McCarthy, G.J. (1978) Powder diffraction file 31-295.
- Podor, R. (1995) Raman spectra of the actinide-bearing monazites. *European Journal of Mineralogy*, 7, 1353–1360.
- Podor, R., Cuney, M., and Nguyen Trung, C. (1995) Experimental study of the complete solid solution between (La)-monazite and (Ca_{0.5}U_{0.5})PO₄ at 780 °C and 200 MPa. *American Mineralogist*, 80(11–12), 1261–1268.
- Quarton, M., Zouiri, M., and Freundlich, W. (1984) Cristallochimie des orthophosphates doubles de thorium et de plomb. *Comptes Rendus de l'Académie des Sciences, Ser. II*, 299 (12), 785–788.
- Rice, C.E. and Robinson, W.R. (1976) Lanthanum orthophosphate. *Acta Crystallographica*, B32, 2232–2233.
- Rose, D. (1980) Brabantite, CaTh(PO₄)₂, a new mineral of the monazite group. *Neues Jahrbuch für Mineralogie Monatshefte*, 6, 247–257.
- Seaborg, G.T., Ed., (1978) *Benchmark papers in physical chemistry and chemical physics, Vol. 1: Products of modern alchemy*, 512 p. Dowden, Hutchinson and Ross East Stroudsburg, PA.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Suzuki, K., Adachi, M., and Kajizuka, I. (1994) Electron microprobe observations of Pb diffusion in metamorphosed detrital monazites. *Earth and Planetary Science Letters*, 128, 391–405.
- Tilton, G.R. and Nicolaysen, L.O. (1957) The use of monazite for age determination. *Geochimica and Cosmochimica Acta*, 11, 28–40.
- Werner, P.E. (1990) SCANPI program. University of Stockholm, Sweden.

MANUSCRIPT RECEIVED NOVEMBER 10, 1995

MANUSCRIPT ACCEPTED MARCH 5, 1997