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

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ABSTRACT

A complete solid solution has been hydrothermally synthesized between the two end-members LaPO₄ and (Ca₀.5Th₀.5)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 (Aᵢ⁺²ₓBᵢ⁺Cᵢ⁺)PO₄ compounds crystallized in the monazite structure-type are determined by both $r_{\text{average}} = (1 - 2x) \cdot mR_{A⁺} + x \cdot mR_{B⁺} + x \cdot mR_{C⁺}$ and $r_{\text{ratio}} = (1 - x) \cdot mR_{A⁺} + x \cdot mR_{B⁺}/(1 - x)$ parameters (where $mR_A$ is the ionic radius of the A element in ninefold coordination). The upper and lower values of these parameters are 1.216 Å $\leq r_{\text{average}} \leq 1.107$ Å 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 REE₃PO₄ 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 (Ca₀.5Th₀.5)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 REE₃PO₄ involves two types of substitutions: (1) replacement of PO₄³⁻ by SiO₂⁻, which compensates the charge imbalance created by the substitution of Th⁺ for REE⁺, and (2) coupled substitution of Ca⁺⁺ + Th⁺⁺ for 2 REE⁺⁺ (Anthony 1965; McCarthy et al. 1978). The latter type of substitution promotes a solid solution between (Ca₀.5Th₀.5)PO₄ and REE₃PO₄. Hikichi et al. (1978) experimentally showed the existence of complete solid solutions in the systems CePO₄-ThSiO₄ and CePO₄-(Ca₀.5Th₀.5)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 (Ca₀.5Th₀.5)PO₄ end-members. The geometrical conditions for the stability of the compounds (Aᵢ⁺²ₓBᵢ⁺Cᵢ⁺)PO₄ in the monazite structure-type and the stability of solid solutions between REE₃PO₄ (REE⁺⁺ = La⁺⁺ to Gd⁺⁺), (Ca₀.5An₀.5)PO₄ (An⁺⁺ = Th⁺⁺ to Pu⁺⁺) 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)₃, and Th(OH)₃ were coprecipitated by addition of NH₄OH to an aqueous solution containing determined stoichiometric proportions of LaCl₃·7H₂O, CaCl₂, and Th(NO₃)₃·3H₂O. 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 ($\lambda = 1.54059$ 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.
La(OH)₃, CaO, and Th(OH)₄ in the initial mixture. Electrospun monazites corresponded to the mole fractions of lanthanum, calcium, and thorium oxides in the synthesis. Electron microprobe and transmission electron microprobe data are summarized in Table 1. The mole fractions contained well-crystallized monazite crystals ranging in size from 0.2 to 2 μm in diameter. The electron microprobe analyses showed that the compositions of synthesized monazite crystals were 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, xLa, and the sum of the mole fractions of Th and Ca, (xTh + xCa) (Fig. 2a). Kelly et al. (1981) have shown that Th incorporated in monazite is tetravalent. Then, the Th⁴⁺ = La⁵⁺ substitution is charge-compensated by the Ca²⁺ = La⁴⁺ 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 (Caₓ₅Thₓ₃)PO₄

The (Caₓ₅Thₓ₃)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 a₀ = 6.706(1), b₀ = 6.918(1), and c₀ = 6.417(1) Å and β₀ = 103.65(4°). All the peaks observed were indexed in the P2₁/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 (Caₓ₅Thₓ₃)PO₄ are consistent with those determined in this study. The corresponding mineral is named brabantite (Rose 1980). Its composition is (Ca₁₁₋ₓ⁺₀·₆ₓ⁺₀·₀₂₁Mg₀·₀₂₁Al₀·₀₀₁Fe₀·₀₀₁)₂₋₀·₆ₓ⁺₀·₀₂₁Th₀·₉ₓ⁺₀·₀₂₁(P₁·₈ₓ₋₀·₂₋₀·₂ₓ⁺₀·₀₂₁Si₀·₇ₓ₋₀·₂₋₀·₂ₓ⁺₀·₀₂₁)O₆.
and the unit-cell parameters are $a = 6.726$, $b = 6.933$, and $c = 6.447$ Å and $\beta = 103.53^\circ$.

The LaPO$_4$-(Ca$_{0.5}$Th$_{0.5}$)PO$_4$ 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$_{1-x}$Th$_x$)PO$_4$ 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 $a$, $b$, $c$, and unit-cell volumes $V_0$ are plotted vs. Th mole fraction in monazite (Fig. 3a). The unit-cell constants $a$, $b$, and $c$ decrease linearly with increasing Th content (Fig. 3a), whereas $b$ 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 LaPO$_4$ up to (Ca$_{0.5}$Th$_{0.5}$)PO$_4$. No phase transition has been observed between the two pure phases, consistent with complete solid solution between the two end-members LaPO$_4$ and (Ca$_{0.5}$Th$_{0.5}$)PO$_4$ under these conditions. This conclusion was confirmed by Raman spectroscopy where variations of the vibrational-band frequencies with increasing Th-Ca substitution in (La) monazite are correlated for many of the observed bands (Podor 1995). Hikichi et al. (1978) obtained a complete solid solution between CePO$_4$ and (Ca$_{0.5}$Th$_{0.5}$)PO$_4$, but their experiments were at atmospheric pressure and $T = 1400^\circ$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$^{+}$) in monazite. The mean ionic radius of the cation site is:

$$r_{\text{cat}}^{+} = (1 - 2x) r_{\text{La}}^{+} + x r_{\text{Th}}^{+} + x r_{\text{Ca}}^{+}$$  \hspace{1cm} (1)

Using the ionic radii of Shannon (1976), linear correlations between the mean ionic radius of the cation site in (La$_{1-x}$Th$_x$)PO$_4$ and the unit-cell parameters can be established (Figs. 3a and 3b):

\begin{align*}
ap_0 &= 1.728[r_{\text{cat}}^{+}] + 4.748 & (2) \\
b_0 &= 2.049[r_{\text{cat}}^{+}] + 4.595 & (3) \\
c_0 &= 1.222[r_{\text{cat}}^{+}] + 5.032 & (4) \\
\beta_0 &= -5.031[r_{\text{cat}}^{+}] + 109.377 & (5)
\end{align*}

These results are comparable with those obtained (Podor et al. 1995) for the correlations between $a$, $b$, $c$, $\beta$, and $[r_{\text{cat}}^{+}]$ for the U- and Ca-bearing monazite and with those obtained by Ni et al. (1995) in the REEPO$_4$ family. The c-parameter increase with increasing mean ionic radius is less in the REEPO$_4$ series than in the U- 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 Th$^{4+}$-Th$^{4+}$ repulsion along [001].

**Figure 2.** (a) Linear correlation between mole fractions of Th and those of Ca in (La$_{1-x}$Th$_x$)PO$_4$. $R^2 = $ correlation coefficient. (b) Linear correlation between the sum of Th and Ca mole fractions and those of La in synthetic (La$_{1-x}$Th$_x$)PO$_4$. 

**Table 1.** Continued

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<th>O (at%)</th>
<th>P (at%)</th>
<th>La (at%)</th>
<th>Th (at%)</th>
<th>Ca (at%)</th>
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Determination of the compositional stability range of the solid solution \((\text{A}^{3+} \_2 \text{B}^{2+} \text{C}^{4+})\text{PO}_4\)

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 \((\text{A}^{3+} \_2 \text{B}^{2+} \text{C}^{4+})\text{PO}_4\) intermediate compounds are defined between the two end-members \(\text{A}^{3+}\text{PO}_4\) and \(\text{B}^{2+}\text{C}^{4+}\text{PO}_4\). The compositional stability range of \((\text{A}^{3+} \_2 \text{B}^{2+} \text{C}^{4+})\text{PO}_4\) in the monoclinic system (monazite group) depends on the relative stabilities of the \(\text{A}^{3+}\text{PO}_4\) and \(\text{B}^{2+}\text{C}^{4+}\text{PO}_4\) compounds.

In the case of the \(\text{A}^{3+}\text{PO}_4\) compounds, the ionic radii of the trivalent elements that phosphates crystallized with the monazite structure range between \(\frac{r_\text{Sr}}{2} = 1.216 \text{ Å}\) and \(\frac{r_\text{Ce}^{4+}}{2} = 1.107 \text{ Å}\). The first heavy REE to form a REEPO\(_4\) 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 \(\text{B}^{2+}\text{C}^{4+}\text{PO}_4\) compounds in the monoclinic system can be estimated by comparing two parameters: (1) the mean ionic radii \(\langle r_\text{B}^{2+} \rangle + \langle r_\text{C}^{4+} \rangle /2\) of the atoms in the cation site and (2) the \(\langle r_\text{B}^{2+} \rangle/\langle r_\text{C}^{4+} \rangle\) ratio, where \(\langle r_\text{B}^{2+} \rangle\) and \(\langle r_\text{C}^{4+} \rangle\) are the ionic radii of the \(\text{B}^{2+}\) and \(\text{C}^{4+}\) ions in the ninefold coordination.

The limiting values of these parameters can be determined from results reported in the literature. Pepin et al. (1981) showed that monazite-structured \((\text{Ca}^{2+} \text{Th}^{4+})\text{PO}_4\) and \((\text{Ca}^{2+} \text{U}^{4+})\text{PO}_4\) compounds are stable, while \((\text{Ca}^{2+} \text{Ce}^{4+})\text{PO}_4\) is not stable. The lower limit of the \(\langle r_\text{B}^{2+} \rangle + \langle r_\text{C}^{4+} \rangle /2\) parameter is inferred to be just larger than the value of the average ionic radius of \(\text{Ca}^{2+}\) and \(\text{Ce}^{4+}\) in the ninefold coordination, \(\langle r_\text{B}^{2+} \rangle + \langle r_\text{C}^{4+} \rangle /2\) parameter is determined by the mean ionic radius in the \((\text{Pb}^{2+} \text{Th}^{4+})\text{PO}_4\) compound and is equal to 1.215 Å. This, thus, the limits of the mean ionic radii for the monazite structure to be stable range between:

\[
1.215 \AA \geq \langle r_\text{B}^{2+} \rangle + \langle r_\text{C}^{4+} \rangle /2 \geq 1.10 \AA
\]

The upper limit of the second parameter is given by the \(\langle r_\text{B}^{2+} \rangle/\langle r_\text{C}^{4+} \rangle\) ratio \(\langle r_\text{B}^{2+} \rangle/\langle r_\text{C}^{4+} \rangle = 1.35 \text{ Å, Shannon 1976}\). Monoclinic \((\text{Pb}^{2+} \text{Th}^{4+})\text{PO}_4\) is stable (Quarton et al. 1984), whereas \((\text{Sr}^{2+} \text{U}^{4+})\text{PO}_4\) does not crystallize in the monoclinic form (Rose 1980; \(\langle r_\text{Sr}^{2+} \rangle = 1.31 \text{ Å, Shannon 1976}\). Moreover, the stability of \((\text{Mg}^{2+} \text{Th}^{4+})\text{PO}_4\) in the monazite group has not been demonstrated \(\langle r_\text{Mg}^{2+} \rangle = 0.966 \text{ Å, calculated from the values given by Shannon 1976}\). Thus, the lower limit of the second parameter is given by the stability of \((\text{Ca}^{2+} \text{Th}^{4+})\text{PO}_4\) with \(\langle r_\text{Ca}^{2+} \rangle = 1.135 \text{ Å}\). The limits of \(\langle r_\text{B}^{2+} \rangle/\langle r_\text{C}^{4+} \rangle\) are:

\[
1.238 \geq \langle r_\text{B}^{2+} \rangle/\langle r_\text{C}^{4+} \rangle \geq 1.041
\]

More generally, the stability of the intermediate compounds \((\text{A}^{3+} \_2 \text{B}^{2+} \text{C}^{4+})\text{PO}_4\) can be described by the two parameters:

\[
r_{\text{average}} = \frac{(1 - 2x)\langle r_\text{A}^{3+} \rangle + x\langle r_\text{B}^{2+} \rangle + x\langle r_\text{C}^{4+} \rangle}{(1 - 2x) + x + x}
\]

\[
r_{\text{ratio}} = \frac{(1 - 2x)\langle r_\text{A}^{3+} \rangle + x\langle r_\text{B}^{2+} \rangle + x\langle r_\text{C}^{4+} \rangle}{(1 - 2x)\langle r_\text{B}^{2+} \rangle + x\langle r_\text{B}^{2+} \rangle + x\langle r_\text{C}^{4+} \rangle}
\]
**Figure 3.** (a) Linear correlation between unit-cell parameters \((a_0, b_0, c_0)\) (Å) of synthetic \((\text{La}_{1-x}\text{Th}_x\text{Ca}_x)\)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 \(\beta\) angle of synthetic \((\text{La}_{1-x}\text{Th}_x\text{Ca}_x)\)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 \((\text{La}_{1-x}\text{Th}_x\text{Ca}_x)\)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 \(B^{3+}\) and one atom of \(C^{4+}\). The \(r_{\text{ratio}}\) parameter describes the coupled substitution of one atom of \(B^{3+}\) in one site \(A^{3+}\), and of one atom of \(C^{4+}\) in another \(A^{3+}\) site.

The upper limit of \(r_{\text{average}}\) is given by the ionic radius of La in LaPO\(_4\) \((^{(9)}r_{\text{La}} = 1.216\text{ Å})\), whereas the lower limit of this parameter is given by the ionic radius of Gd in GdPO\(_4\) \((^{(9)}r_{\text{Gd}} = 1.107\text{ Å})\). Consequently,

\[
1.216\text{Å} \geq r_{\text{average}} \geq 1.107\text{Å} \tag{10}
\]

The limits of \(r_{\text{ratio}}\) that have been obtained for \(x = 0\) and \(x = 0.5\) are:

\[
1.238 \geq r_{\text{ratio}} \geq 1 \tag{11}
\]

The stability range of the \((A^{3+}_{1-x}, B^{3+} C^{4+})\)PO\(_4\) compounds is plotted as a function of the three parameters \(x\), \(r_{\text{average}}\), and \(r_{\text{ratio}}\) (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 \((A^{3+}_{1-x}, B^{3+} C^{4+})\)PO\(_4\) in the monazite structure-type vs. mole fraction of \(B^{3+}\) or \(C^{4+}\), \(r_{\text{average}}\), and \(r_{\text{ratio}}\).
Pressure also influence the limits of $r_{\text{average}}$ and $r_{\text{ratio}}$ parameters. For example, monoclinic lanthanum phosphate is stable in the temperature range 200–600 °C, 200 > $P$ > 50 MPa, under hydrothermal conditions (Akers et al. 1993). The polymorphic transformation of the ($\text{Ca}_x\text{U}_y\text{O}_3$)PO$_4$ compound from orthorhombic to monoclinic form is lowered down to 700 °C, at $P = 200$ MPa and in 30 m H$_2$PO$_4$ (Dusausoy et al. 1996).

**Variations of the stability range of the solid solution (A$_{x}$B$_{1-x}$)$\text{PO}_4$ with temperature and pressure**

The limits of the $r_{\text{average}}$ 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 $T = 400$ °C for LaPO$_4$, $T = 450$ °C for NdPO$_4$ and $T = 500$ °C for EuPO$_4$ (Bondar et al. 1976; Hikichi et al. 1989; Akers et al. 1993). Two polymorphous 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 $T = 550$ °C for GdPO$_4$ and $T = 600$ °C for TbPO$_4$ and DyPO$_4$ (Bondar et al., 1976). The second modification temperatures are $T = 1200$ °C for GdPO$_4$, $1100 > T > 800$ °C for TbPO$_4$ and $T \sim 800$ °C for DyPO$_4$ (Ivanov and Sin’Kova 1967; Hikichi et al. 1989).

Moreover, the limits of the $r_{\text{ratio}}$ parameter also vary with temperature. Dusausoy et al. (1996) have shown that the ($\text{Ca}_x\text{U}_y\text{O}_3$)PO$_4$ synthetic compound has an irreversible polymorphic modification from orthorhombic to monoclinic form at $T > 1000$ °C and atmospheric pressure. The ($\text{Ca}_x\text{Th}_y\text{O}_3$)PO$_4$ compound does not undergo this type of phase transformation.

**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 $[\text{Th}]_{\text{PO}_4}^{4+}/[\text{Th}]_{\text{PO}_4}^{2+}$ 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 RE$^{4+}$ = Pb$^{2+}$ + [U, Th$^{4+}$] and (2) the valence state IV; The substitution mechanism is 2 RE$^{4+}$ = Ca$^{2+}$ + 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 Steenkanpkraal (Tilton and Nicolaysen 1957) presents $^{206}$Pb/$^{208}$Pb of 77 and the monazite from Baltor granite in Pakistan shows $^{208}$Pb/$^{208}$Pb as low as 385 (Parrish 1990). The stability domain determined from Equations 10 and 11 leads to the evi-
idence 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 U$^{4+}$ or Th$^{4+}$ incorporation.

The second point (2) is not supported by the model proposed in this work. Indeed, the concentrations of Ca$^{2+}$, Pb$^{2+}$, U$^{4+}$, and Th$^{4+}$ in the cation site are always relatively low in comparison with the REE$^{3+}$ concentrations. The diffusion of Pb corresponds to a displacement of divalent cation in a trivalent cation network. This displacement can only occur with coupled Th$^{4+}$ or U$^{4+}$ displacement to respect charge balance in the REE$^{3+}$ 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).

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