

Monazite alteration mechanisms and depletion measurements in kaolins

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Abstract

Two widely different kaolin deposits of Greece were studied in order to compare the impact of the alteration mechanism to the presence of thorium and rare earth elements (REE) in the deposits and to find a measure for their migration during the alteration processes. Halloysite and kaolinite coexist in gneissic weathering profiles, developed under a temperate climate in the Leucogia area, NE Greece. The kaolin occurrences of Kos island, Aegean sea, Greece, are products of hydrothermal alteration of rocks of rhyolitic composition. Monazite is found as an accessory mineral in both areas and it is the only mineral that contains lanthanum, cerium and neodymium and in addition thorium, in the kaolins of Leucogia area. To resolve the genetic relationship between monazite and its alteration products, the mineralogy of the primary rocks and kaolins and their microtextures were examined, and bulk rock chemical analyses were performed in order to correlate major and trace elements behaviour with the alteration mechanisms.

In the gneissic weathering profiles of the Leucogia area, monazite (Ce) is partially altered to a ThSiO_4 or Th-OH silicate microcrystalline phase with very low concentrations of light rare earth element (LREE). The relict monazite crystals are depleted in thorium. The depletion and/or the enrichment of the various elements in the bulk sample appear to be related to mineral breakdown rather than to mild leaching of primary minerals by meteoric water. The only element that is apparently immobile is thorium and this element can be used as a measure for the depletion in this environment. Monazite (Ce), in the hydrothermally altered rhyolitic rocks of Kos island, is altered to P-bearing crandallite–goyazite. During this alteration process, LREE are depleted with respect to the fresh monazite crystals. Phosphorus, which was found to be the only element with an immobile behaviour, can be used as a reference to evaluate the amount of REE leached during monazite alteration in this hydrothermal environment.

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1. Introduction

Lanthanide abundances are extremely important indices of mantle and crustal geochemical evolution. To a significant extent, lanthanide distribution patterns in soils, sediments, and crystalline rocks are determined by processes occurring during chemical weath-

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ering. Lanthanide behaviour under conditions prevailing near the earth's surface is also of considerable environmental importance because lanthanides serve as geochemical proxies for actinides in contaminated sites. In hydrothermally altered rocks, REE are removed in solution from the altered zones probably because of the higher solubility of lanthanides in the hydrothermal fluids (Poitrasson et al., 1996). The nature of REE redistribution during mineralogical reactions associated with weathering or hydrothermal alteration is very poorly understood (Mc Lennan, 1989). Several studies have suggested REE mobility during low-temperature alterations but there is little agreement regarding the overall magnitude or, for fractionation among the REE (e.g. Nesbitt, 1979; Duddy, 1980; Dickin and Jones, 1983; Middelburg et al., 1988; Teutsch and Kolodny, 1995). In most rocks, REE behaviour is largely controlled by accessory minerals, including phosphates such as monazite (Taunton et al., 2000a). Contrasted styles of monazite alteration show that the conditions of fluid–rock interaction will not only affect the aqueous geochemistry of the lanthanides, actinides and lead, and the relative stability of the different minerals holding these elements. Variations in these conditions will also lead to various possible chemical exchanges between the crystalline phase and the hydrothermal fluids (Poitrasson et al., 1996).

Monazite, a monoclinic orthophosphate with the general formula $[(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4]$ is a light rare earth element (LREE) mineral that may contain appreciable concentrations of the radioactive element Th into its crystal structure. It commonly occurs as an accessory phase in metapelites, leucocratic gneisses, granites, rhyolites and in metamorphosed quartzofeldspathic rocks. Taunton et al. (2000a,b), studying lanthanide distributions during granite weathering, found that the Ce enrichment relative to the trend defined by all weathered granite samples is due to loss of other elements. Kaolinite is one of the clay minerals, whose role in removing REE from aqueous solutions has been demonstrated by recent laboratory experiments (Aja, 1998). Kaolinite in surface weathering systems is scavenging significant amounts of REE and Th from aqueous solutions (Putter et al., 2002).

Halloysite and kaolinite coexist in gneissic weathering profiles, formed under temperate climate conditions in the Leucogia area, NE Greece. The kaolin

deposits of Leucogia lie on fine to coarsely crystalline and thinly bedded leucocratic amphibolite facies gneisses and schist-gneisses. They extend over an area of $\sim 20 \text{ km}^2$ and their thickness ranges from 1 to 50 m depending on the topographic relief. The kaolins consist mostly of kaolinite and halloysite in various proportions and a gradual transition from fresh rock to kaolin is observed. Fresh rocks are mainly composed of quartz, feldspars (microcline, sodic plagioclase) and muscovite. Previous workers (Michailidis and Tsirambides, 1986; Tsirambides and Michailidis, 1990) suggested a residual origin for the kaolins. According to Papoulis and Tsoilis-Katagas (2001a), the kaolinization process seems to follow two alteration paths: (i) Sodic plagioclase $\rightarrow$ halloysite $\rightarrow$ kaolinite. (ii) K-rich feldspars $\rightarrow$ kaolinite.

The kaolin occurrences of the Kefalos peninsula, SW Kos island, are associated with rhyolitic rocks of Pliocene age (Boven et al., 1987). These rocks exhibit perlitic texture and are mainly composed of quartz, Na-plagioclase, K-feldspar and volcanic glass. The kaolin occurrences are white in color, commonly stained reddish by iron oxides, and extend over an area of about 0.5 km^2 . The kaolinization process of Kos island rhyolites seems to follow also two main alteration paths: (i) K-feldspar $\rightarrow$ mixed-layer kaolinite-smectite $\rightarrow$ kaolinite $\rightarrow$ dickite. (ii) Na-plagioclase $\rightarrow$ kaolinite $\rightarrow$ dickite (Papoulis and Tsoilis-Katagas, 2001b). A minor amount of kaolinite could also originate from the alteration of volcanic glass.

Monazite was found as an accessory phase in most lithologies of the two kaolin deposits studied here. Replacement of monazite by a Th-silicate phase and by crandallite-goyazite was observed in the lithologies of the Leucogia and Kos island kaolin deposits, respectively. This process liberated a large proportion of the Th, LREE and P, originally contained in monazites. Although there is a considerable recent literature devoted to the changes monazite undergoes during hydrothermal alteration (e.g. Jefferies, 1985; Cathelineau, 1987; Schandl and Gorton, 1991; Smith et al., 1999; Hecht and Cuney, 2000; Poitrasson et al., 2000; Mathieu et al., 2001), weathering (e.g. Taunton et al., 2000a,b; Putter et al., 2002), and their chemical implications, a more complete understanding of REE chemistry during weathering and hydrothermal alteration would provide additional constraints on the understanding of these processes.

This study was undertaken with the aim to provide an improved understanding to the mechanism of the migration of elements, the genetic relation between monazite and its alteration products and to provide depletion measurements in weathering and hydrothermal environments.

2. Experimental methods

The mineralogical composition of bulk rocks and of the clay fractions ($<2\ \mu\text{m}$) of the samples were determined by X-ray diffraction, using a Philips diffractometer PW1050/25, with Ni-filtered $\text{CuK}\alpha$ radiation. Powders from oriented clay-aggregate samples were scanned at $1^\circ\ 2\theta/\text{min}$ from 3 to $60^\circ\ 2\theta$. Clay minerals were identified from three XRD patterns (air-dried at 25°C , ethylene-glycolated, and heated at 490°C for 2 h) of the clay-size fraction ($<2\ \mu\text{m}$) extracted by the standard sedimentation technique in deionized water.

Monazite's textures, morphology and chemical composition of its alteration products were determined at the laboratory of Electron Microscopy and Microanalysis, University of Patras using a Scanning Electron Microscope (SEM) (JEOL 6300) equipped with an energy dispersive spectrometer (EDS). The chemical composition of the minerals was determined using natural and synthetic standards and 20 kV accelerating voltage with 10 nA beam current. Special analytical conditions with lower beam current and short counting times (10 s) were applied for the analysis of hydrated Th-silicates to minimize mineral alteration during analysis.

Chemical analyses of bulk samples for both major and trace elements were performed using ICP on HClO_4/HF solutions; SiO_2 was determined using the X-ray Fluorescence method after LiBO_2 fusion and Zr was measured by the xylenol orange colorimetric method.

3. Results

3.1. Mineralogy

Quartz, feldspars (microcline, oligoclase) and muscovite are the dominant minerals in the gneisses of the

Leucogia area. Biotite, epidote and chlorite are additional phases occurring in small amounts. Zircon, monazite and in few samples a Th-silicate and/or Th–OH silicate are accessory mineral phases identified by optical or analytical scanning electron microscopy. Kaolinite, halloysite, illite-smectite interstratification, smectite and discrete illite are the clay mineral phases, detected by XRD in the kaolins of the Leucogia area weathering profiles. Kaolinite increases significantly upwards from the unaltered parent gneiss to the upper horizons, whereas halloysite decreases (Papoulis and Tsolis-Katagas, 2001a).

Kaolinite, dickite, mixed-layer kaolinite-smectite, smectite and illite are the clay minerals detected in the altered rhyolite of Kos island. Cristobalite and quartz are also present in most of the samples in considerable amounts. Kaolinite content increases from the unaltered rhyolite to completely kaolinized rocks. From the X-ray Diffraction patterns and SEM, it is evident that dickite grows progressively at the expense of kaolinite. Mixed-layer kaolinite-smectite is an intermediate stage in the kaolinization process of feldspars. Smectite and illite are present in few samples and in small amounts (Papoulis and Tsolis-Katagas, 2001b). Barite, pyrophyllite, monazite, halite and in few samples crandallite-goyazite and apatite occur as accessory phases and were identified using SEM observations and microanalyses.

3.2. Composition of REE and Th bearing phases

The only mineral of the Leucogia gneisses that contains the elements La, Ce, Nd and Th is monazite (Fig. 1a,b). Microanalyses of epidote and zircon which are also present, reveal that neither of them contains the above elements in detectable amounts (0.01%). Monazite crystals are found as inclusions in biotite and rarely in epidote; they are very rich in Ce_2O_3 and to a lesser degree in La_2O_3 and Nd_2O_3 and may be termed monazite-(Ce). The highest ThO_2 content found in the investigated unaltered monazite crystals is 5.0 wt.% and decreases with advancing alteration (Table 1, analyses 1, 2 and 3). The microanalyses of monazite crystals from the Leucogia kaolins revealed that there is a remarkable difference in REE content between the unaltered and altered parts of the monazite. The unaltered monazites have lower total REE than the altered residual grains. An increase in La, Ce and Nd

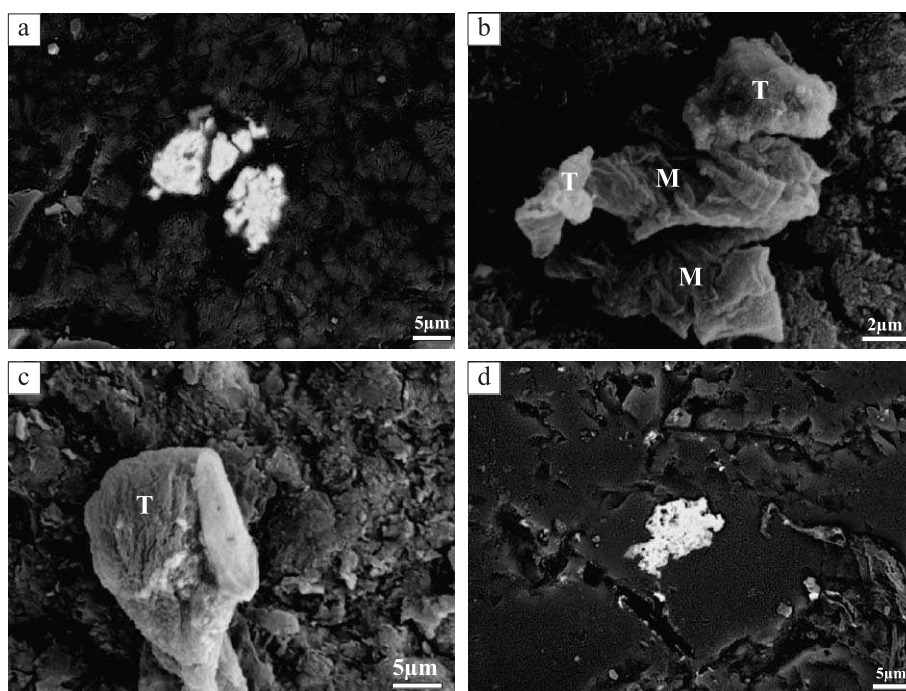


Fig. 1. SEM micrographs showing: (a) Monazite (white crystals). (b) Monazite (M) altered in its rims to thorium silicate (T). (c) Thorium silicate (T). (d) Thorium silicate (white crystals) showing microporous texture (Leucogia area).

oxides in the residual monazite, results in a decrease in CaO and ThO₂ (Table 1), confirming the coupled substitution of these elements within the rare earth site ($2\text{RE}^{3+} = \text{Ca}^{2+} + \text{Th}^{4+}$). However, a more complex coupled substitution at two independent sites may be

Table 1
Representative microanalyses of monazite (Ce) and its alteration products

	1	2	3	4	5
SiO ₂	3.36	2.95	1.95	16.27	20.54
Al ₂ O ₃	2.96	2.08	0.00	0.00	0.00
P ₂ O ₅	20.13	21.86	20.19	0.00	0.00
Ce ₂ O ₃	34.79	34.80	37.62	0.00	0.00
La ₂ O ₃	17.16	20.08	24.45	0.00	0.00
Nd ₂ O ₃	11.86	12.68	10.79	0.00	0.78
Pr ₂ O ₃	0.00	0.00	2.04	0.04	0.00
Sm ₂ O ₃	0.00	0.00	0.00	0.00	0.00
Ho ₂ O ₃	0.00	0.00	0.00	0.00	0.00
ThO ₂	5.00	1.51	0.14	83.69	68.98
CaO	3.83	1.82	1.23	0.00	0.00
Total	99.09	97.78	98.41	100	90.30

Leucogia area; (1) unaltered monazite; (2, 3) residual monazite; (4) thorium silicate; (5) Th–OH silicate (?).

more suitable for the actual crystal structure, since the isolated tetrahedral anionic group of monazite was found containing also Si⁴⁺ and sometimes Al³⁺ besides P⁵⁺. Thorium therefore may also be incorporated into monazite via the coupled substitution $\text{REE}^{3+} + \text{P}^{5+} \rightleftharpoons \text{Th}^{4+} + \text{Si}^{4+}$, which leads to an isostructural with monazite thorium silicate phase (thorite or huttonite), through the partial destruction of the phosphate framework. The ThSiO₄ phase has been found as a microcrystalline and microporous alteration product of monazite with the alteration starting from the grain margins and proceeding to the inner parts of the monazite grains (Fig. 1b,c,d). Some Th-silicate analyses show very low totals (Table 1, analysis 5) suggesting the presence of (OH) groups in the structure and possible formation of a Th–(OH) silicate phase.

In the alteration zone of Kos island kaolins, monazite found as inclusions in biotite (Fig. 2a,b) is the only mineral that contains the elements La, Ce and Nd. Apatite, which is also present, does not contain REE in detectable amounts. All monazite crystals analyzed have Ce as the dominant cation and may be termed monazite-(Ce). Aside from the REE oxide content,

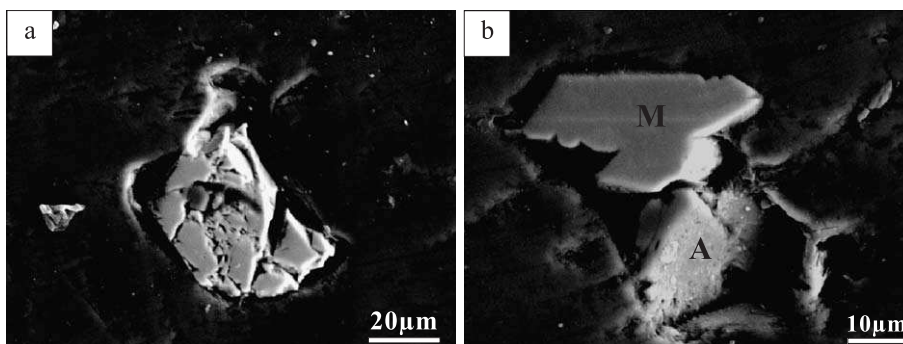


Fig. 2. SEM micrographs showing: (a) Monazite inclusion in biotite. (b) Apatite (A) coexisting with monazite (M) in biotite (Kos island).

which closely approaches the theoretical value, minor amounts of CaO have been detected in some crystals (Table 2). The ThO₂ content of monazite in Kos island is below the detection limits (0.01%) and it is consistent with the Th content of hydrothermal monazite or of monazite found in low-temperature metapelites and in hydrothermal veins (Franz et al., 1996). Samples containing altered monazite may also contain small grains of P-bearing crandallite-goyazite, presumably formed from the REE and P liberated during monazite alteration (Hecht and Cuney, 2000). The crandallite-goyazite series minerals have a composition midway between the (Ca,REE)Al₃(PO₄)₂(OH₅·H₂O) and (Sr,REE)Al₃(PO₄)₂(OH₅·H₂O) end members, respec-

tively. Their REE oxide content (Ce₂O₃) is very low, approaching 3 wt.% (Table 2).

4. Alteration chemistry of the host rocks

Major and trace element analyses of 1 representative gneissic rock and 13 altered samples from the Leucogia area, showing various degrees of kaolinization are given in Table 3. The lowest potassium, calcium and sodium and the highest LOI contents are found in samples from the uppermost part of the profile (L34, L38, L58), where the alteration process is most advanced. The high positive correlation coefficient between Al₂O₃ and LOI (0.92) and the high negative loadings between LOI and SiO₂ (−0.88), Al₂O₃ and SiO₂ (−0.96) indicate that LOI and Al₂O₃ contents increase in the more altered samples (Table 4). These correlations may be attributed to the alteration (kaolinization) of oligoclase and microcline during the weathering. The Na₂O content of the kaolinized rocks ranges between 0.09 and 4.02 wt.%, with its lower values observed in the uppermost part of the profile, suggesting that sodic plagioclase is practically completely altered in the more altered samples.

The potassium content in the kaolin deposit, which is considered to be a good measure of the degree of alteration of the primary rocks, ranges between 0.78% and 4.91%, and decreases upwards in the profile, suggesting also that the alteration is more advanced in the upper horizons. Petrographic and geochemical evidence, however, indicate that K-feldspars exhibit less intense weathering characteristics relative to plagioclase. Remnants of K-feldspars are commonly preserved in samples with completely kaolinized plagioclase.

Table 2

Representative microanalyses of: (1) unaltered monazite, (2) monazite, (3, 4, 5) crandallite-goyazite, and (6) apatite, from Kos island

	1	2	3	4	5	6
SiO ₂	0.00	0.00	0.00	0.00	0.00	0.38
P ₂ O ₅	25.06	26.66	28.53	29.11	29.06	38.30
Ce ₂ O ₃	35.91	37.99	3.22	2.21	2.90	0.00
La ₂ O ₃	31.07	29.73	0.00	0.00	0.68	0.00
Nd ₂ O ₃	6.50	6.09	0.00	0.00	0.00	0.00
Pr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	0.00	0.00	40.80	39.48	38.62	0.00
ThO ₂	0.00	0.00	0.00	0.00	0.00	0.00
SrO	0.00	0.00	7.58	7.51	5.34	0.00
Na ₂ O	0.00	0.00	0.00	0.45	0.00	0.00
CaO	0.75	0.00	7.73	8.75	9.48	57.74
Fe ₂ O ₃	0.00	0.00	0.00	0.00	0.00	2.48
MnO	0.00	0.00	0.00	0.00	0.00	0.68
F	0.00	0.00	0.00	0.00	0.00	0.06
Cl	0.00	0.00	0.00	0.00	0.00	0.32
Total	99.30	99.47	87.85	87.57	87.04	99.96

Major and trace element analyses of parent rock* and kaolinized rocks from Leucogia

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	LOI	Total
L24	74.93	0.17	12.58	0.95	<0.01	0.16	0.45	3.49	3.55	0.02	1.45	1.69	99.44
L28	73.22	0.24	10.53	1.18	0.01	0.28	0.21	3.68	2.94	0.02	3.90	2.22	98.43
L32b	68.23	0.28	15.65	1.61	<0.01	0.36	0.27	0.67	2.65	0.02	3.00	6.66	99.40
L34	53.56	0.15	29.36	0.69	<0.01	0.21	0.15	2.04	1.13	0.04	2.00	11.35	100.68
L38	68.94	0.28	15.61	1.97	0.07	0.40	0.14	0.21	3.37	0.05	3.10	5.53	99.34
L42	70.56	0.33	17.67	1.07	<0.01	0.27	0.15	0.10	1.49	0.01	0.95	7.05	99.65
L44	70.81	0.55	16.40	1.19	0.01	0.31	0.28	0.09	0.78	0.03	1.75	8.39	100.59
L45	69.72	0.15	15.08	1.66	0.01	0.31	0.23	2.77	2.72	0.03	1.90	4.74	99.32
L50	71.38	0.29	14.50	1.19	0.01	0.31	0.34	2.35	3.16	0.02	2.35	3.82	99.72
L54	72.50	0.20	13.84	1.96	0.08	0.36	0.08	0.79	4.91	0.03	1.60	3.57	99.92
L58	53.37	0.84	24.86	2.96	0.04	1.03	0.54	0.85	2.95	0.06	2.30	10.77	100.57
L95	75.68	0.37	12.84	1.35	0.01	0.22	0.37	0.99	4.05	0.02	0.55	3.98	100.43
L98	77.44	0.48	9.72	2.86	0.01	0.17	0.50	1.72	2.66	0.04	0.95	3.21	99.76
L102*	73.36	0.16	13.41	1.33	0.04	0.26	1.10	4.02	3.45	0.07	0.35	3.52	101.07

cients between the elements Eu and Ce, La, Nd, and Sm and Ce, La, indicate that these components are generally following the same geochemical path during

The most significant correlation coefficients of major and trace elements from parent rocks and kaolinized gneisses of Leucogia

[illegible]

the alteration processes. Most of the REE and Th show also high positive correlation coefficients with Al_2O_3 and high negative correlation coefficients with SiO_2 indicating their close relationship to the alteration. The chondrite normalized REE distribution patterns of samples from different weathering horizons are shown in Fig. 3. The less altered samples show higher values of the lighter REE: La, Ce, Pr, Nd, Eu and Gd and lower values of the heavier REE (Tb, Dy, Ho, Er, Tm, Yb and Lu) compared with the parent rock. With advancing alteration, all the REE are enriched and the samples with the higher values in REE are the most altered samples, showing that the heavier REE (Tb, Dy, Ho, Er, Tm, Yb and Lu) are depleted first during monazite alteration (the only mineral of the Leucogite gneisses that contains REE is monazite). The lower values of the heavier REE (Tb, Dy, Ho, Er, Tm, Yb and Lu) compared with the parent rock observed in the less altered samples may be attributed to the fact that the amount of clay minerals in these samples is not enough to absorb these heavier REE.

Major and trace element analyses of slightly altered rhyolite and altered samples with different degrees of kaolinization, from Kos island, are presented in Table 5. The lowest K_2O , CaO , Na_2O and Ba and the highest Al_2O_3 and LOI contents are found in samples in which the alteration is more advanced (samples K9, K11).

The most significant correlation coefficients of major and trace elements from parent rocks and kaolinized rocks of Kefalos, Kos island, are presented in Table 6a. The correlation coefficients between LOI–

K_2O , Na_2O –LOI, K_2O – Na_2O , Ba– K_2O and Ba– Na_2O are -0.85 , -0.92 , $+0.94$, $+0.76$ and $+0.76$, respectively (Table 6a). The high correlation coefficients found between K_2O , Na_2O and Ba indicate that these components decrease in the more altered samples, following the same geochemical path. The high negative correlation coefficient found between K_2O and LOI shows that LOI increases in the more altered samples, following the opposite geochemical path. These correlations may be attributed to the alteration (kaolinization) of K-feldspar and Na-plagioclase during the hydrothermal alteration. A minor amount of kaolinite could also originate from the alteration of volcanic glass, as it has been observed in few thin sections. The correlation coefficients between Ce, La and Nd are extremely high (0.99) denoting a very similar behaviour of these elements during fluid–rock interaction.

Al_2O_3 is strongly correlated with P_2O_5 , Fe_2O_3 and Sr; these components increase in the more altered samples (Table 5, samples K11 and K9), following the same geochemical path, it is therefore concluded that Fe_2O_3 , P_2O_5 and Sr increase in amount with advancing kaolinization by enrichment. The most significant correlation coefficients of major and trace elements from parent rocks, oxidized rocks and kaolinized rocks of Kos are presented in Table 6b. The negative correlation coefficient between Fe_2O_3 and Sr shown in this table is attributed to the low Sr values in the oxidized samples K7 and K12 which have not been included in Table 6a. The elements Cr, Cu and Zn are strongly correlated with Fe_2O_3 and not to kaolinization

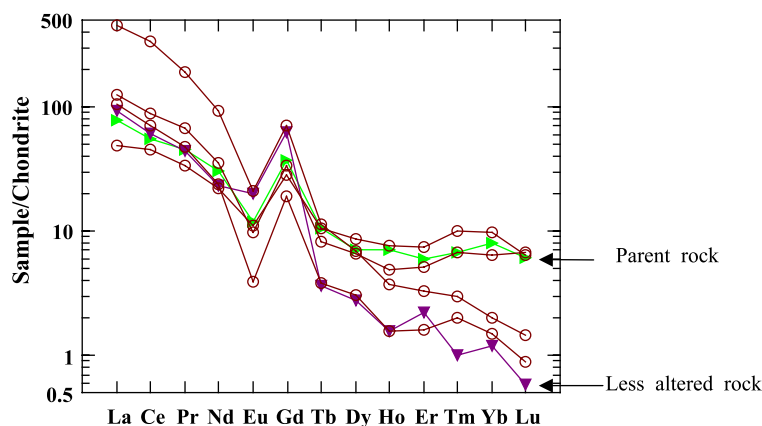


Fig. 3. Chondrite normalized REE distribution pattern of samples from different weathering horizons of the Leucogite kaolins. Analyses normalized to chondrite values from Nakamura, 1974.

Table 5

Major and trace element analyses of parent rocks* (rhyolite slightly enriched in SiO₂), oxidized rock[#] and kaolins of Kefalos, Kos island, listed according to their degree of alteration

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	LOI	Total
K14*	78.80	0.15	10.63	0.17	0.01	0.01	0.59	4.26	3.85	0.02	0.10	0.80	99.39
K15*	77.50	0.14	11.71	0.83	0.06	0.09	0.62	4.45	3.91	0.02	0.13	0.46	99.92
K7 [#]	30.63	0.32	7.24	48.10	0.05	0.14	0.22	0.06	0.08	0.06	2.59	10.88	100.37
K8	66.21	0.63	14.99	0.97	0.01	0.05	0.12	0.26	0.26	0.11	3.80	12.46	99.87
K18	71.49	0.57	15.12	0.50	<0.01	0.03	0.12	0.07	0.90	0.09	0.93	10.11	99.93
K5	67.71	0.48	16.98	1.60	<0.01	0.74	0.10	1.11	0.01	0.08	2.06	9.49	100.36
K10	70.86	0.54	17.05	3.32	<0.01	0.04	0.13	0.14	0.03	0.13	0.61	7.41	100.26
K13	59.89	0.56	17.83	3.73	<0.01	0.03	0.12	0.19	0.96	0.13	2.30	14.46	100.20
K6	63.95	0.64	19.66	1.95	0.10	0.05	0.14	0.12	0.01	0.13	2.62	11.33	100.70
K12 [#]	42.96	0.35	21.73	19.16	<0.01	0.01	0.12	0.08	0.51	0.17	0.69	14.09	99.87
K11	60.44	0.19	25.83	1.13	<0.01	0.02	0.09	1.13	0.14	0.19	0.75	11.94	100.85
K9	55.16	0.42	26.04	5.20	0.06	0.03	0.10	0.07	0.47	0.14	0.59	12.55	100.83

Sample	Ba	Co	Cr	Cu	Li	Nb	Ni	Sc	Sr	V	Y	Zn	Zr	La	Ce	Nd
K14*	931	16	10	4	20	14	7	1	83	4	7	11	61	17	34	14
K15*	965	14	10	3	14	14	7	1	79	6	11	22	72	19	36	17
K7 [#]	79	21	137	51	5	9	38	5	139	135	15	181	69	17	39	19
K8	130	17	25	10	3	11	36	9	806	67	8	12	115	15	38	15
K18	194	7	18	4	20	11	6	10	439	83	4	7	53	18	42	13
K5	142	7	18	4	3	9	10	25	318	100	5	16	92	36	82	30
K10	150	7	25	4	3	10	8	14	439	94	44	17	91	50	139	49
K13	244	9	38	16	5	10	18	27	759	104	4	12	98	16	45	18
K6	781	11	22	13	3	11	20	8	467	75	5	15	115	19	38	20
K12 [#]	320	11	132	43	3	8	22	20	885	225	3	47	68	39	89	36
K11	339	4	23	7	5	4	7	14	1087	107	1	10	35	62	160	58
K9	469	5	48	6	3	9	10	10	1106	109	1	9	85	10	21	11

Major elements in wt.%, trace elements in ppm. H₂O=loss at 110 °C, LOI=loss at 1000 °C.

processes (Table 6a,b). The amounts of Fe₂O₃, Sr, Zn, Cu and Cr are increasing in the most altered samples more radically than the other elements (Table 5, samples K11 and K9), suggesting that hydrothermal fluids may add Fe₂O₃ and Sr, (Thorpe, 1982), Zn, Cu and Cr to the altered rhyolite. Varnavas and Cronan (1991), in their study of the submarine hydrothermal field off Kos, reported Fe, Sr, Cu and Zn concentrations in the submarine hydrothermal waters from Kefalos Bay, of 14.0, 10.2, 1.1 and 1.4 µg/l, respectively.

4.1. Discussion on the behaviour of REE and thorium during monazite alteration

Monazite in the Leucogia gneisses is altered to a microcrystalline and microporous Th-silicate (thorite or huttonite) or to a Th–OH silicate phase, with the alteration starting from the grain margins and proceeding to the inner parts of the grain. Relict monazite and Th-silicate are commonly found in the same sites,

suggesting mobility of Th over very small distances. The remaining monazite crystals are enriched in Ce, La and Nd (Table 1) and this enrichment in the altered samples is attributed to the high mobility of other elements. A significant amount of the elements Ce, La and Nd is released during the alteration of monazite to Th-silicate. However, the decrease in these elements in the altered weathering profiles is minimized due to the presence of clay minerals (Condie, 1991; Coppin et al., 2002; Yang et al., 2002) and especially kaolinite. Kaolinite flakes absorb a large part of the released Ce, La and Nd. Halloysite absorbs less REE than kaolinite because of its crystal form (usually tubular). The significant increase of the amount of thorium during the weathering procedure is only due to the depletion of other elements. Thorium, being less mobile during the alteration of monazite, it is soon bound in the formation of the Th-silicate structure and as a result it can be used as a reference to evaluate the amounts of other elements depletions. From the cor-

Table 6

(a) The most significant correlation coefficients of major and trace elements from parent rocks and kaolinized rocks of Kefalos, Kos island

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Ba	Sr	Zr	Cu	Zn	Cr	Ce	La
Nd	−0.13	0.40	0.01	−0.31	−0.27	−0.40	0.54	0.10	−0.33	0.24	−0.33	−0.14	0.15	−0.08	0.99	0.99
La	−0.05	0.35	−0.09	−0.27	−0.22	−0.36	0.46	0.04	−0.33	0.17	−0.41	−0.25	0.13	−0.18	0.99	
Ce	−0.10	0.36	−0.02	−0.33	−0.29	−0.41	0.52	0.11	−0.41	0.23	−0.37	−0.19	0.09	−0.09		
Cr	−0.88	0.71	0.90	−0.62	−0.65	−0.53	0.66	0.74	−0.40	0.80	0.31	0.48	−0.40			
Zn	0.43	−0.39	−0.07	0.44	0.47	0.29	−0.40	−0.51	0.34	−0.56	0.32	−0.16				
Cu	−0.58	0.26	0.32	−0.40	−0.46	−0.36	0.47	0.66	−0.13	0.42	0.54					
Zr	−0.23	−0.09	0.37	−0.26	−0.27	−0.34	0.04	0.32	−0.14	0.00						
Sr	−0.91	0.86	0.54	−0.71	−0.73	−0.63	0.87	0.81	−0.48							
Ba	0.42	−0.30	−0.26	0.82	0.76	0.76	−0.55	−0.68								
LOI	−0.89	0.69	0.50	−0.92	−0.92	−0.85	0.83									
P ₂ O ₅	−0.85	0.87	0.50	−0.84	−0.87	−0.83										
K ₂ O	0.71	−0.66	−0.42	0.97	0.94											
Na ₂ O	0.77	−0.68	−0.49	0.98												
CaO	0.77	−0.68	−0.46													
Fe ₂ O ₃	−0.70	0.60														
Al ₂ O ₃	−0.89															

(b) The most significant correlation coefficients of major and trace elements from parent rocks, oxidized rocks and kaolinized rocks of Kefalos, Kos island

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Ba	Sr	Zr	Cu	Zn
Cr	−0.93	−0.08	0.90	−0.23	−0.39	−0.33	0.21	0.44	−0.37	0.12	−0.13	0.97	0.79
Zn	−0.78	−0.51	0.98	0.03	−0.16	−0.18	−0.22	0.10	−0.30	−0.33	−0.14	0.83	
Cu	−0.91	−0.21	0.91	−0.17	−0.34	−0.30	0.13	0.41	−0.32	0.00	−0.07		
Zr	0.07	−0.03	−0.15	−0.23	−0.20	−0.28	0.02	0.23	−0.07	0.01			
Sr	−0.28	0.88	−0.18	−0.68	−0.62	−0.52	0.88	0.75	−0.33				
Ba	0.47	−0.09	−0.35	0.77	0.76	0.77	−0.42	−0.67					
LOI	−0.63	0.55	0.24	−0.91	−0.92	−0.84	0.79						
P ₂ O ₅	−0.36	0.86	−0.07	−0.80	−0.77	−0.71							
K ₂ O	0.53	−0.45	−0.26	0.95	0.95								
Na ₂ O	0.57	−0.49	−0.27	0.96									
CaO	0.43	−0.59	−0.08										
Fe ₂ O ₃	−0.87	−0.37											
Al ₂ O ₃	−0.08												

relations between Th and Ce, La and Nd abundances presented in Fig. 4, however, it is evident that these elements are enriched in the unaltered monazite bearing samples, confirming that in these samples Ce, La, Nd and Th remain in the structure of monazite crystals, it may thus be inferred that the depletion in these samples can be measured by all these elements.

In samples with monazite partially altered to Th-silicate, the depletion can be measured only by thorium (Fig. 4a,d,e). The elements Ce and La follow the same geochemical path (Fig. 4c) during the weathering procedure, and show equal depletion during monazite alteration. The absorption of these elements by clay minerals does not seem to affect their geochemical behaviour. The only difference noted in the

geochemical behaviour of these two elements was in the order of their depletion. Fig. 5a,b,c shows that La is the first element which is depleted during monazite alteration. Note that Nd is not following the same geochemical path showing rather similar behaviour with thorium (Fig. 5a,b,d), and some explanations for this behaviour are given below.

(a) Some microprobe analyses of monazite from monazite coexisting with Th-silicate bearing samples (e.g. Table 1, analysis 2) show that the remnants of monazite crystals are enriched in Nd, implying thus that Nd remains in the monazite during its alteration to Th-silicate, (b) Nd was found to be absorbed by clay minerals probably easier than Ce and La absorbed in kaolinite, and (c) Th–OH silicate contains a low

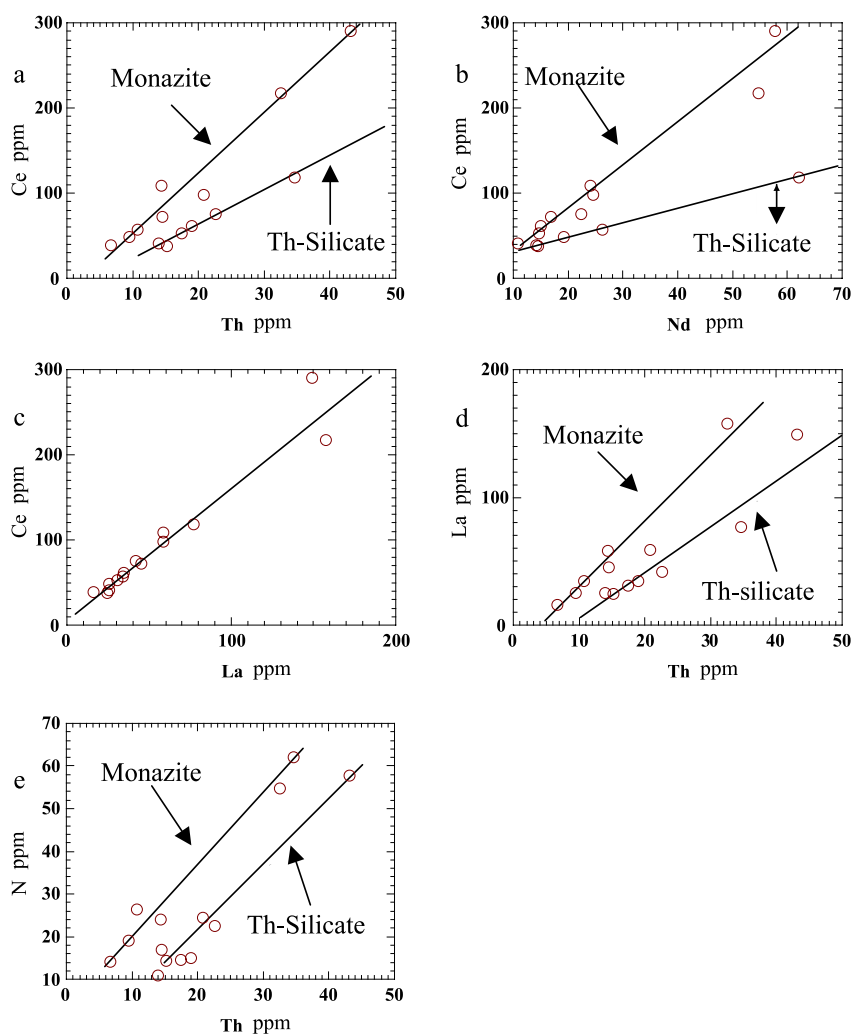


Fig. 4. Correlations between: (a) Th and Ce; (b) Nd and Ce; (c) La and Ce; (d) Th and La; (e) Th and Nd abundances in the unaltered monazite (Monazite), in altered monazite and monazite partially altered to Th-silicate bearing samples (Th-silicate), from Leucogia area.

amount of Nd and below detection limits Ce and La, reducing Nd depletion (Table 1, analysis 6).

Depletion measurements in the altered monazite coexisting with Th-silicate bearing samples, based on Th, suggest loss of almost 85% of the original rock constituents. If we use Nd as a measure of depletion, the results will be less accurate (77%) because of the depletion of Nd, and if we use Ce, the values (66%) will be even less accurate than those of Nd. It should be noted, however, that in the altered samples with unaltered monazite, the depletion measurements using Ce as a depletion measure will be more accurate (86%

depletion). The slightly higher value obtained could be attributed to the radioactivity of Th.

Assuming thorium as an immobile element, the whole rock average Th/Nd ratio increases from 0.46 in the parent rock to 0.68 in the most altered rock and corresponds to leaching of 24% of Nd during monazite dissolution. The whole rock average Th/La ratio increases from 0.21 to 0.45 and corresponds to leaching of 53% of La, and the whole rock average Th/Ce ratio increases from 0.17 to 0.29 and corresponds to leaching of 41% of Ce during monazite dissolution.

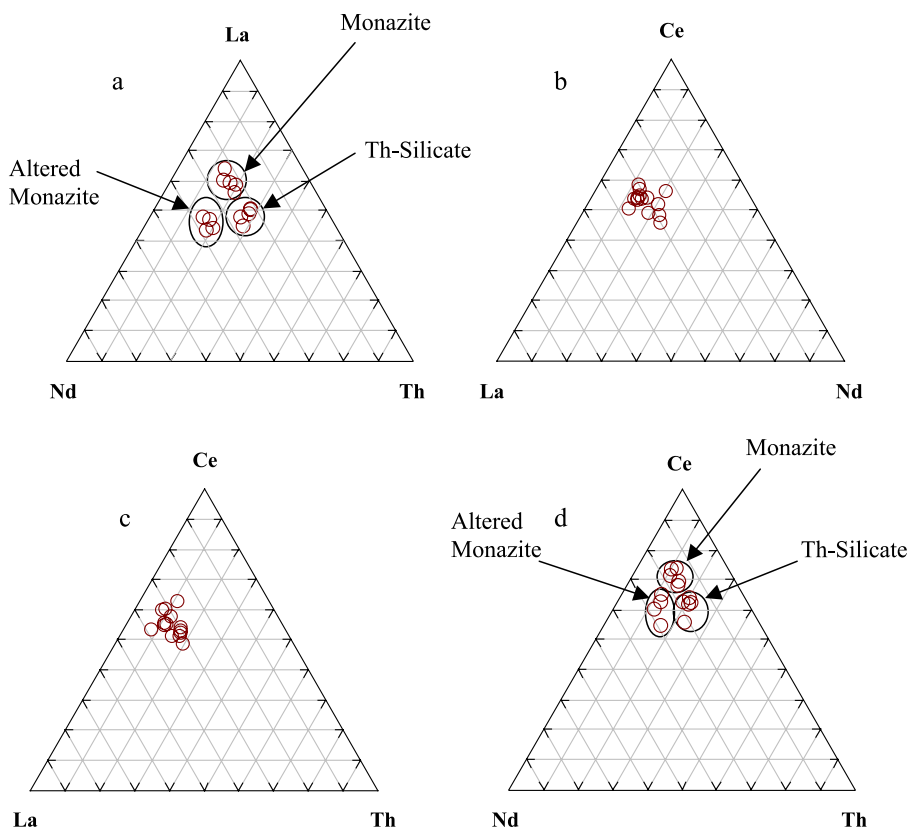


Fig. 5. Variation of Ce, La, Nd and Th concentrations in unaltered monazite bearing samples (Monazite), in altered monazite bearing samples (Altered Monazite) and in monazite partially altered to TH-silicate bearing samples (Th-Silicate), from Leucogia area.

Although LREEs are generally considered immobile, several studies have shown that LREE may be mobile during hydrothermal alteration of igneous rocks under specific conditions (Mc Lennan and Taylor, 1979; Wood and Williams-Jones, 1994; Mathieu et al., 2001).

Monazite and apatite were found as inclusions in biotite in the alteration zone of Kos island kaolins. However, as shown from the microanalyses presented in Table 2, monazite is the only mineral that hosts REE. Apatite shows no signs of any alteration, it is therefore supposed that its presence in the kaolins of Kos does not affect the mobility of P. Monazite crystals are partially altered and a significant part of the elements Ce, La and Nd is depleted during its alteration to P-bearing crandallite-goyazite. Only a small part of the amount of Ce in monazite is held in the structure of the newly formed crandallite-

goyazite during the alteration of monazite to P-bearing crandallite-goyazite (Table 2) and partially, Ce is depleted along with La and Nd. The depletion of these elements is reduced due to the presence of clay minerals and especially kaolinite and dickite. Kaolinite and dickite flakes may absorb a significant part of the released Ce, La and Nd. The absorption of these elements from clay minerals seems to be similar because they decrease in the altered samples following the same geochemical path. This is documented in Fig. 6 where Ce, La, Nd and P_2O_5 concentrations in hydrothermally altered rhyolite samples from Kos, bearing unaltered monazite and crandallite-goyazite, are plotted in various variation diagrams (Fig. 6a,b). Phosphorus in the parent rocks is accommodated exclusively in the monazite and apatite structures. Phosphorus was found to be the only element with an immobile behaviour, it is therefore suggested that it

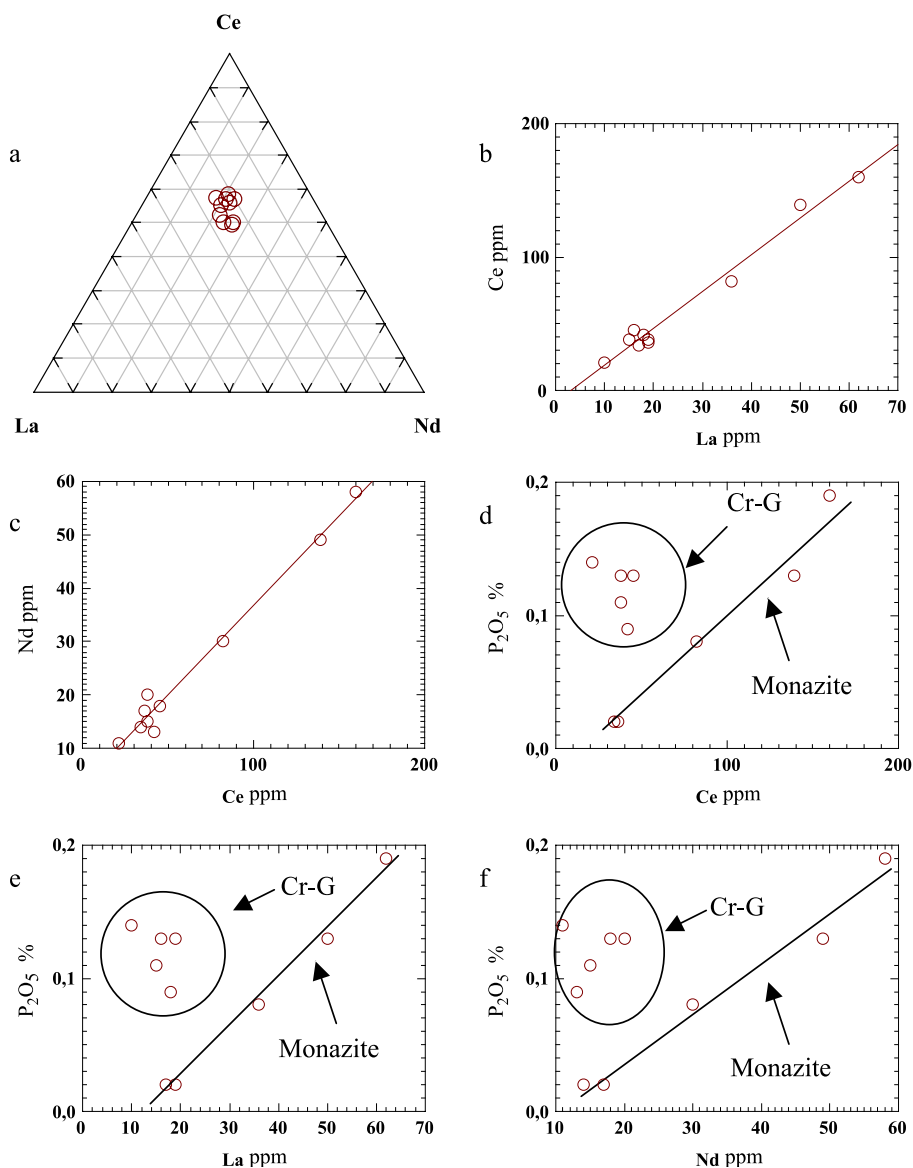


Fig. 6. Ce, La, Nd and P_2O_5 concentrations in hydrothermally altered rhyolite samples from Kos island. Note the similarity in the geochemical behaviour of the elements Ce, La, Nd and P_2O_5 in the samples with unaltered monazite and the similarity of the geochemical behaviour of the elements Ce, La and Nd in all samples. Cr-G: Crandallite-Goyazite bearing samples.

may be used as a measure for the depletion in this hydrothermal environment. Depletion measurements based on P suggest a loss of almost 75% of the original rock constituents. P, being considered as an immobile element, the whole rock average P/Nd ratio increases from 1430 in the parent rock to 12,730 in the most altered rock and corresponds to leaching of

89% of Nd during monazite dissolution. Following the same procedure, the leaching of Ce and La was calculated to be 92%. The loss of Ce, La and Nd is similar (89–92%) confirming that the amount of Ce in the crandallite-goyazite structure is insignificant. In samples with unaltered monazite, the amounts of P, Ce, La and Nd are increasing during the hydrothermal

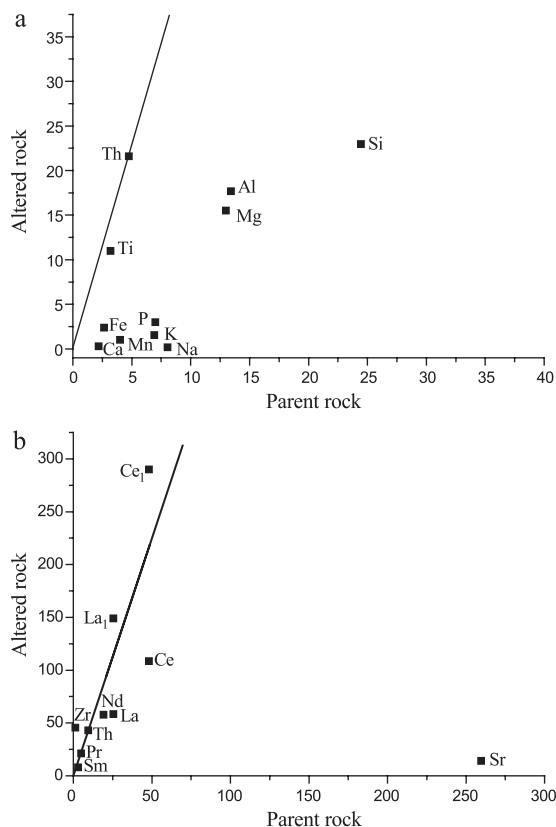


Fig. 7. Isocon plots for major and trace elements using the method of Grant (1986) and assuming constant Th (solid line) during alteration in Leucogia area. Data for major elements (a) are plotted as weight percentage of the oxides, trace elements (b) are in ppm. The values of most of the elements were multiplied by suitable factors (for major elements the factors are the following: SiO_2 : 0.33, TiO_2 : 20, Al_2O_3 : 1, Fe_2O_3 : 2, MnO : 100, MgO : 50, CaO : 2, Na_2O : 2, K_2O : 2, P_2O_5 : 100, Th: 5000 and for trace elements is 1 for all elements). La_1 , Ce_1 : concentrations of La and Ce in altered samples in which monazite is not altered.

alteration, following the same geochemical path (Fig. 6d,e,f). The increase of the above elements is in fact due to the depletion of other mobile elements.

Isocon diagrams (Grant, 1986) for major and trace elements of representative parent and altered rocks from the Leucogia area and Kos island are presented in Figs. 7 and 8, respectively. These figures show the extent of the depletion for selected elements. In the samples of the Leucogia area, assuming Th as immobile, all the major elements are depleted and the order from the most depleted to the less depleted element is the following: $\text{Na} > \text{Ca} > \text{K} > \text{Mn} > \text{P} > \text{Fe} > \text{Si} > \text{Mg} > \text{Al} > \text{Ti}$

(Fig. 7a). In the altered monazite-bearing samples (Fig. 7b), the only element that is enriched is Zr, and Pr and Sm are immobile, whereas in the samples with unaltered monazite the elements Ce and La are not depleted (Ce_1 , La_1). In Kos island assuming P as immobile, the order from the most depleted to the less depleted major element is $\text{K} > \text{Na} > \text{Ca} > \text{Si} > \text{Al} > \text{Ti} > \text{Mg} > \text{Mn} > \text{Fe}$ (Fig. 8a). In samples with altered monazite, Sr and V are enriched (due to hydrothermal fluids) whereas all the other elements are depleted.

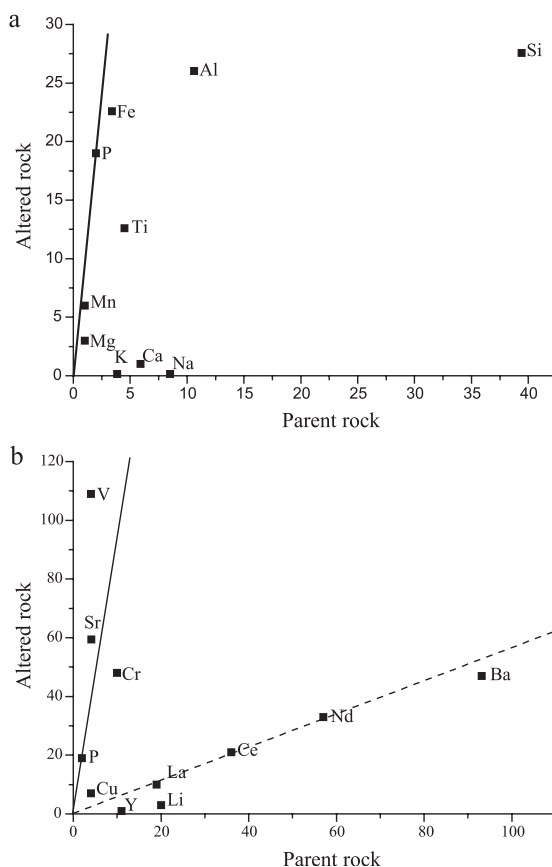


Fig. 8. Isocon plots for major and trace elements of representative parent and altered rocks from Kos island using the method of Grant (1986) and assuming constant P (solid line) during alteration in Kos island. Dashed line shows the equal loss of the elements Ce, La, Nd. Data for major elements (a) are plotted as weight percentage of the oxides, and trace elements (b) are in ppm. The values of most of the elements were multiplied by suitable factors (for major elements the factors are the following: SiO_2 : 0.5, TiO_2 : 30, Al_2O_3 : 1, Fe_2O_3 : 20, MnO : 100, MgO : 100, CaO : 10, Na_2O : 2, K_2O : 1, P_2O_5 : 100, and for trace elements are Ba: 0.1, Sr: 0.05 and 1 for all the other elements).

The dotted line in Fig. 8b shows that the elements Ce, La and Nd are equally depleted.

5. Conclusions

Monazite (Ce), in the gneissic weathering profiles of the Leucogia area, is partially altered to a Th-silicate microcrystalline phase with very low concentrations of LREE. The relict monazite crystals are depleted in thorium. Th, however in the bulk sample is the only element that is apparently immobile, it may be used therefore as a measure for the depletion in this environment. Depletion measurements based on Th indicate a loss of almost 85% of the original rock constituents. If we use Nd for the depletion measurements, the results will be even less accurate (77%) because of the depletion of Nd. The use of Ce for the depletion measurements in altered samples bearing monazite coexisting with Th-silicate results in a loss of 66%. Depletion measurements with Ce in the altered samples with unaltered monazite give more accurate results (86% depletion). The slightly higher value could be attributed to the radioactivity of Th. In these samples, we can also use for the depletion measurements La and Nd.

Monazite (Ce), in hydrothermally altered rhyolitic rocks of Kos island, is altered to P-bearing crandallite-goyazite. During this alteration process, LREE are depleted. Hydrothermal fluids add to the altered rhyolite significant amounts of Sr, Cr, Cu, Zn and Fe. Relative to the parent volcanic rock (rhyolite), the kaolinitic zone is characterized by depletion in Si, Na, K, Ca, Ba and enrichment in Al, Sr, P and Fe (Papoulis and Tsoilis-Katagas, 2001b). Phosphorus is accommodated exclusively in the monazite and apatite structures and it was found to be the only element with an immobile behaviour, it may be used therefore as a measure for the depletion in this hydrothermal environment. Depletion measurements based on P suggest a loss of almost 75% of the original rock constituents. Assuming that P is an immobile element, the whole rock average P/Nd ratios for parent and most altered rocks suggest leaching of 89% of Nd during monazite dissolution. Following the same procedure, the leaching of Ce and La was found to be 92% for both elements. The similar loss values of Ce, La and Nd confirm that the amount of Ce in crandallite-goyazite

structure is insignificant. In samples with unaltered monazite, the amounts of P, Ce, La and Nd are not depleted, on the contrary they are enriched during the hydrothermal alteration following the same geochemical path. The increase of the above elements is due to the depletion of other more mobile elements.

Ce and La followed by Nd are the LREE elements which are depleted first, during monazite alteration in both, weathering and hydrothermal environments.

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