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THE EPIGENE ALTERATION OF ALLANITE

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ABSTRACT

Phases formed during the weathering of allanite are in response to extremely local conditions, including pε, pH, and element concentrations. In the weathering environment in western Virginia, secondary monazite and cerianite are primary sinks for *REE* and Th produced by the alteration of allanite. Bastnäsite is limited spatially to areas buffered to higher pH, such as fractures within the allanite. Furthermore, the individual *REE* have different rates of loss; the *REE* patterns reflect the preferential removal of light *REE* as predicted by thermodynamic data. The oxidation of Ce^{3+} produces a more insoluble phase (cerianite), leading to the relative enrichment of Ce in alteration products. Th apparently enters relatively insoluble compounds or is scavenged by goethite.

Keywords: allanite, bastnäsite, cerianite, monazite, rhabdophane, florencite, rare-earth elements, thorium, epigene alteration, weathering, Bunker Hill pegmatite, Virginia.

SOMMAIRE

Les minéraux néoformés au cours du lessivage de l'allanite témoignent de facteurs (pε, pH et concentrations d'éléments) d'importance très locale. Dans le milieu du lessivage actuel en Virginie occidentale, monazite secondaire et cérianite sont les hôtes principaux des terres rares et du thorium ainsi libérés. La bastnäsite est limitée aux milieux tamponés à un pH plus élevé, dans les fissures dans l'allanite par exemple. De plus, les terres rares sont libérées à des taux différents; les terres rares légères sont mobilisées davantage, comme le prédisent les données thermodynamiques. L'oxydation du Ce^{3+} conduit à un minéral moins soluble (cérianite), et un enrichissement relatif en Ce dans les produits d'altération. Le Th entrerait dans des composés relativement insolubles ou serait capté par la goethite.

(Traduit par la Rédaction)

Mots-clés: allanite, bastnäsite, cerianite, monazite, rhabdophane, florencite, terres rares, thorium, altération épigénétique, lessivage, pegmatite de Bunker Hill, Virginie.

INTRODUCTION

Allanite, the *REE*-rich member of the epidote group, is commonly altered on a megascopic or microscopic scale to distinct crusts, patches and coatings; also, it may show anomalous optical or X-ray-diffraction properties. Watson (1917) summarized the physical attributes of the crusts, noting an apparent zonation and variation in color, from reddish brown to brownish yellow to greyish buff to nearly white. The causes of the alteration are varied, but predominant processes include metamictization and chemical attack.

Since Watson's (1917) work, many researchers have investigated the products of alteration and attempted to identify the processes and phases produced (Table 1). The purpose of this paper is to describe the chemical alteration of allanite from the Bunker Hill pegmatite, Virginia, in light of recent X-ray and neutron-activation analyses of the mineral and its alteration products, and available thermodynamic data. Furthermore, the fractionation effects of chemical alteration on the rare-earth elements (*REE*) and thorium are described.

CHEMICAL ALTERATION

The equilibrium solubility of a mineral is a function of pε[1], pH, temperature, pressure, complexation (inorganic and organic), extent of structural defects, degree of crystallinity, hydrolysis, ionic strength and common-ion effects. Metamictization brought on by the decay of U- and Th-series radionuclides causes structural dislocations that reduce the degree of crystallinity and increase the susceptibility to chemical weathering (Mitchell 1973).

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†Deceased.

[1] pε is a parameter expressing the redox state of an aqueous solution and is equal to the negative log of the activity of electrons in solution. The use of pε has been recommended as a better representation of the redox state of an aqueous solution than Eh (*cf.* Stumm & Morgan 1981, Nordstrom & Munoz 1986).

TABLE 1. MINERALS REPORTED AS RESULTING FROM THE CHEMICAL ALTERATION OF ALLANITE

Bastnäsite
Calcite
Calkinsite[1]
Celadonite
Cerianite
Chlorite
Florencite[2]
Fluorite
Gibbsite
Glauconite
Goethite
Halloysite (7Å)
Halloysite (10Å)[Endellite]
'Hydromica'
Hydroxylbastnäsite
Illite
Kaolinite
Lanthanite
Magnetite
Monazite
Montmorillonite
'REE-bearing Phosphate-Silicate'
Rhabdophane
Sericite
Synchysite
Thorite
Thorogummite
"Vudyavrite"[3]

[1] Not actually identified, but hypothesized (Saebø 1961). [2] Presence attributed to alteration of monazite; however, possibly related to allanite alteration. [3] Complex REE colloid, $Ce_mTi_nSi_p(O,OH)_q.rH_2O$ (Vlasov, 1966). Data from: Adams & Young (1961), Černý & Černá (1972), Hata (1939), Hess (1908), Littlejohn (1981a,b), Meintzer (1981), Mineyev et al. (1962), Mineyev et al. (1973), Mitchell (1966), Mitchell & Redline (1980), Palache et al. (1951), Riesmeyer (1967), Rimsaite 1982a,b), Rimsaite (1984), Saebø (1961), Silver & Grunenfelder (1957), Sverdrup et al. (1959), Takubo & Ueda (1948), Vlasov (1966), Watson (1917) and this study.

The remaining solubility factors are inherent to the aqueous phase. Temperature and pressure are regulated by epigene conditions, and pε and pH reflect the chemical characteristics of the aqueous phase that result from interactions with the atmosphere and solid mineral phases. Complexation and hydrolysis reactions ultimately result in the formation of clay minerals, various hydrous oxides, carbonates, phosphates, fluorides, sulfates, and organic complexes, and in the transport and removal of elements in solution.

Thermodynamic data are available for only a few minerals identified or considered possible in the alteration products of allanite: cerianite $(Ce^{4+},Th)O_2$, monazite-(La), thorite[2], and thorianite; on the other hand, data are available for many of the aqueous ions and complexes possibly present in groundwater solutions that react with allanite (Appendix A). These data permit the construction of solubility diagrams for La, Ce, Y, Yb, and Th using the methods described by Butler (1964) and the MODEL and SIMNLIN computer procedures (SAS Institute Inc. 1982). Ligand concentrations in Figure 1 are those of typical groundwater as used by Langmuir & Herman (1980), plus a typical value for ΣCO_3 (Hem 1970). Figure 2 is similar to Figure 1 except that the concentrations of ΣCO_3, ΣSO_4, and ΣF are lower, as anticipated under epigene conditions over a felsic to intermediate plutonic or metamorphic terrane.

In both Figures, the activity of the *REE* in solution seems to be governed by the relatively insoluble *REE* fluorides, except at extremely high levels of pH. Variation in fluoride stability among the individual *REE* is evident; Bilal & Becker (1979) found that in general, the stability of the fluoride salts increases with atomic number, but that salts of the middle *REE* (Sm, Eu) are more stable than the immediately adjacent, heavier *REE* fluorides. Although no *REE* fluorides (as REF_3) have been identified in any reported epigene associations, substitution in fluorite is probably substantial (*cf.* Möller 1983).

Phosphate solubility is indicated by data for $LaPO_4$; as determined by Carron *et al.* (1958), the solubility increases with atomic number, except that as with the fluorides, phosphates of the middle *REE* are less soluble than the immediately heavier *REE* phosphates. At pH values greater than 10, *REE hydroxides are less soluble than REE* phosphates.

Carbonates phases are less soluble than the hydroxide phases below a pH of 10.8 (La), 8.6 (Y), and 6.8 (Yb) (Fig. 1) or a pH of 8.4 (La) and 6.3 (Y) (Fig. 2), but are more soluble at all levels of pH for Vb (FIg. 2) at a lower activity of ΣCO_3. Moreover, the heavy *REE* carbonates and hydroxides are generally less soluble below a pH of 8 than the light-*REE* carbonates.

The solubility curves of Ce phases display the effect of the oxidation of Ce and the resulting dominance of CeO_2 at higher pε and pH. In all cases, the solubility of the compounds resulting from the hydrolysis of Ce is greater than those of other *REE* at a pε of 8, whereas it is variable at lower values of pε. Thorium stability is governed by the solubility of thorite below a pH of about 13.

The *REE* and actinides substitute for calcium in one of the two *A* sites in the structure of allanite (Dollase 1971). During the breakdown of allanite, these *A*-site cations are apparently removed in solution; the remaining elements (mostly Si, Al, and Fe) may form aluminosilicates or are partly removed in solution (Mineyev *et al.* 1973, Littlejohn 1981a). Furthermore, Littlejohn (1981a) has suggested that under hypogenic alkaline conditions, the breakdown of allanite could be described as a two-step process that results in the initial production of thorite, bastnäsite, and a montmorillonoid clay mineral, followed by further reaction resulting in fluorite, synchysite and chamosite. A similar reaction has been suggested by Mneyev *et al.* (1973) for hypogene and epigene alteration, resulting in the production of bastnäsite, fluorite, kaolinite, and magnetite.

In both examples, the *REE* components of allanitei result in the formation of bastnäsite, although Littlejohn (1981a) has also included the precipitation of thorite and synchysite. The formation of the various clay minerals is dependent on pH, $[Al^{3+}]$, and $[H_4SiO_4]$.

GEOLOGY AND SECONDARY MINERALOGY OF THE PEGMATITE

The samples of allanite and the products of its

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[2] Speer (1980) considered thorite, not huttonite, to be the stable species of $ThSiO_4$ under surficial conditions (*cf.* Langmuir & Herman 1980).

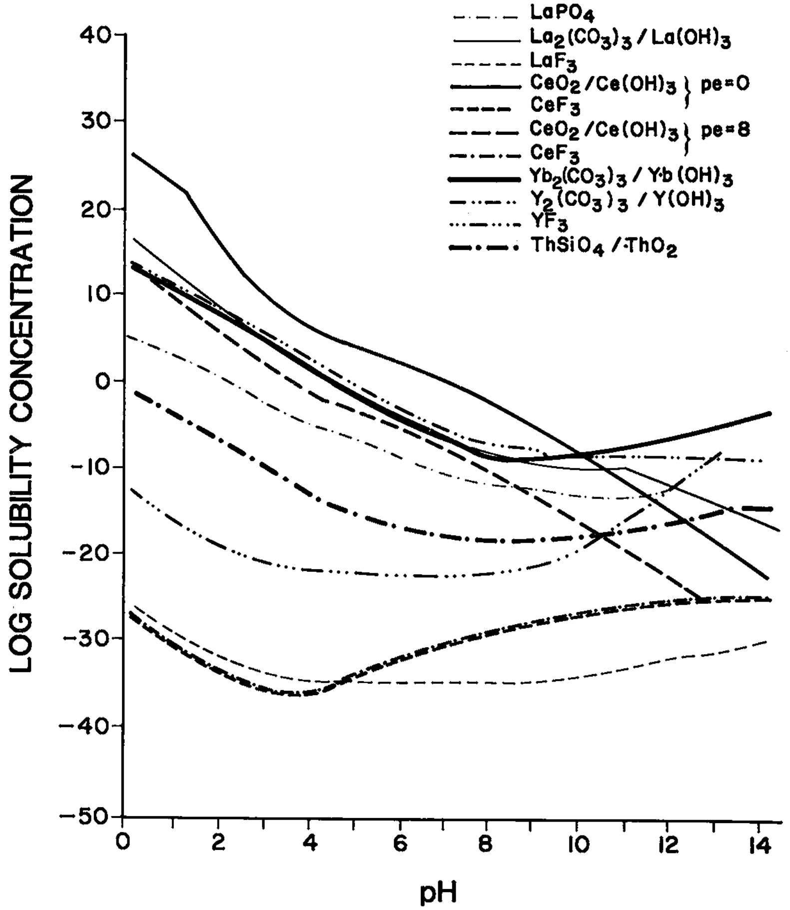

FIG. 1. Solubility diagram for various species of La, Ce, Yb, Y, and Th as a function of pH. Curves for Ce are representative of solubilities at pε 0 and pε 8. Concentrations: ΣLa 1 ppm, ΣCe 1 ppm, ΣYb 1 ppm, ΣY 1 ppm, ΣTh 1 ppb, ΣCO_3 100 ppm, ΣF 0.3 ppm, ΣPO_4 0.1 ppm, ΣSO_4 100 ppm, and ΣSiO_4 9 ppm.

alteration used in this study were derived from the Bunker Hill permatite (Mitchell & Redline 1980, Meintzer 1981) and nearby outcrops of a similar, or perhaps the same, pegmatite body. The pegmatite is located in northwestern Amherst County, 7.4 km southeast of Buena Vista, Virginia. The samples were obtained as float immediately adjacent to the pegmatite, or from *in situ* saprolitic material.

The pegmatite, including the saprolitic portion, is overlain by an ultisol that extends downward about 0.65 m to the base of the B_3 soil horizon. The soil consists of 3.61–7.25 wt.% organic material (based on loss on ignition), quartz, kaolinite, halloysite (7 Å) (or disordered kaolinite) and minor vermiculite, gibbsite, and goethite. Reaction pH (Harriss & Adams 1966) varies from 4.0 to 5.8 in the O, *A*, and *B* horizons, and from 5.8 to 7.75 in the *C* horizon and pegmatite saprolite.

Allanite occurs in the first intermediate zone of the pegmatite, in an assemblage of allanite, biotite, quartz and perthite. A partial composition of the allanite, as determined by instrumental neutron-activation analysis and atomic-absorption spectroscopy, is given in Table 2.

Minerals attributable to the alteration of *REE*-bearing phases occur either as part of the predominantly reddish orange rind that surrounds or replaces allanite, or within fractures in the allanite. Mitchell & Redline (1980) and Meintzer (1981) described the minerals as resulting from the weathering of the pegmatite: bastnäsite, monazite, cerianite, florencite, thorogummite, kaolinite, halloysite (7 Å), halloysite (10 Å), illite, gibbsite, goethite, and lithiophorite. Since their studies, clear to purple fluorite, distributed along thin fractures within the allanite, has been identified in thin section.

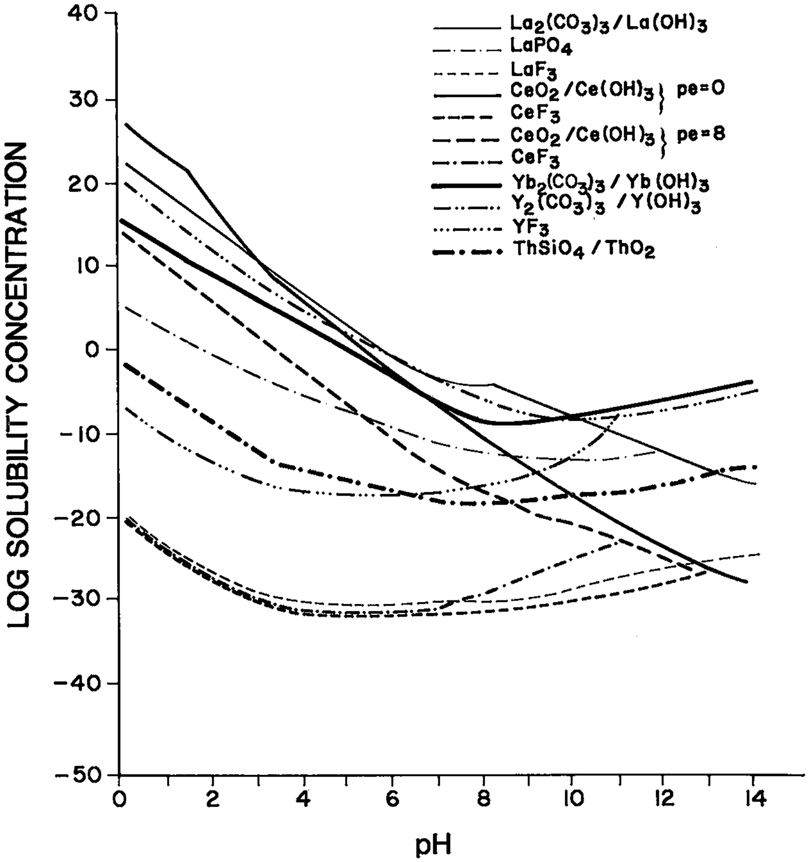

FIG. 2. Solubility diagram for various species of La, Ce, Yb, Y, and Th as a function of pH. Curves for Ce are representative of solubilities at pε 0 and pε 8. Concentrations: ΣLa 1 ppm, ΣCe 1 ppm, ΣYb 1 ppm, ΣY 1 ppm, ΣTh 1 ppb, ΣCO_3 1 ppm, ΣF 0.3 ppb, ΣPO_4 0.1 ppb, ΣSO_4 6 ppm, and ΣSiO_4 9 ppm.

Monazite commonly forms thin light red to pinkish grey and dark reddish brown, waxy crusts on the alteration rind, intermixed with cerianite and halloysite (7 Å). The reddish coloration probably arises from amorphous iron oxides. Results of partial analysis of a crust of this type are given in Table 2 (sample L47).

Rhabdophane was not identified with certainty in any secondary material from the pegmatite samples. However, material recovered from the second outcrop to the south-southwest contains mixtures of monazite (dominant) and rhabdophane. Based on morphology and different unit-cell dimensions obtained by X-ray diffraction, this monazite is thought to be primary.

Clay minerals in the crusts primarily consist of disordered kaolinite and some halloysite (7 Å). Minor amounts of halloysite (10 Å) and illite also are present. It is assumed that the halloysite (7 Å) represents, at least in part, dehydrated halloysite (10 Å), as humidity of soil and saprolite was not maintained from time of sampling to X-ray analysis.

Bastnäsite was noted by Mitchell & Redline (1980) to occur in lighter-colored zones and as thin white veins within the rind. In addition, bastnäsite and cerianite were found as a botryoidal crust on a quartz seam that cuts a weathered allanite, and they commonly occur as thin pale blue to very light grey crusts on broken surfaces of fresh allanite. The latter occurrence of bastnäsite is the predominant one.

GEOCHEMISTRY

Several samples were selected for chemical analysis, including: (1) Two crystals of fresh allanite that exhibit only partial metamictization (samples L14 and L43). (2) A pseudomorph after allanite removed from a depth of about 1.5 m and separated into L41

TABLE 2. CHEMICAL COMPOSITION OF ALLANITE AND PRODUCTS OF ALTERATION

	L14	L43	Mean	L41	L42	L47
Al_2O_3,wt.%	16.1	16.9	16.5	18.5	19.6	16.3
Fe_2O_3*	10.4	7.63	9.0	25.5	28.3	7.50
MgO	0.91	0.42	0.66	0.22	0.10	0.26
CaO	10.7	12.1	11.4	0.21	0.23	0.17
Na_2O	nd	nd	nd	nd	0.10	
K_2O	0.46	0.47	0.46	1.00	0.56	0.45
La,ppm	24600 (3.)	17800 (3.)	21200	2260 (1.)	822 (1.)	21100 (3.)
Ce	61200 (2.)	44100 (2.)	52650	6010 (2.)	3250 (1.)	101000 (2.)
Nd	23800 (11.)	19200 (11.)	21500	1450 (13.)	nd	20000 (11.)
Sm	2000 (1.)	4130 (1.	3065	261 (1.)	235 (1.)	3150 (1.)
Eu	12.0(1.)	11.7(1.)	11.9	4.03(2.)	1.28(3.)	29.2 (1.)
Gd	1890 (23.)	1750 (23.)	1820	341 (35.)	230 (35.)	2930 (5.)
Tb	219 (6.)	213 (6.)	216	52.4 (8.)	38.2 (6.)	249 (8.)
Yb	122 (4.)	52 (4.)	87.0	16.0 (7.)	8.35(8.)	91.5 (5.)
Lu	nd	nd	nd	0.89(14.)	0.78(14.)	9.98(10.)
Th	3330 (3.)	3030 (3.)	3180	4420 (5.)	8350 (5.)	2150 (4.)

*total iron as Fe_2O_3. nd: not detected. blank: not determined. Percentage uncertainty for INAA values for REE and Th given in brackets.

L14: Allanite, Bunker Hill Pegmatite, Amherst Co., Va.
L43: Allanite, Bunker Hill Pegmatite, Amherst Co., Va.
Mean: Arithmetic mean of analyses for allanites, L14 & L43.
L41: Core section of pseudomorph after allanite, Bunker Hill Pegmatite, Amherst Co., Va.
L42: Outer section of pseudomorph after allanite, Bunker Hill Pegmatite, Amherst Co., Va.
L47: Monazite-Cerianite-Halloysite(7Å) crust from allanite, Bunker Hill Pegmatite, Amherst Co., Va.

Concentration of REE, Th, and Fe was determined by instrumental neutron activation analysis using the methods outlined in Allen & Mason (1973) and Meintzer (1981). Counts for ^{153}Gd 103-KeV peak and ^{141}Ce 145-KeV peaks were corrected for addition effects of ^{233}Pa resetting from activation of Th. Correction equal to 5% and 2.5%, respectively of the ^{233}Pa 312KeV peak were applied.

(core) and L42 (outermost portion). This pseudomorph is typical of the weathering rind, except that in this case the allanite has been completely altered. (3) A pale red to light grey alteration rind (L47) composed of monazite, cerianite, and halloysite (7 Å). The rind was removed from an allanite crystal occurring within the soil overlying the pegmatite body.

The abundance of *REE* in the samples (normalized to C1 chondrite concentrations) is indicated in Figure 3. Figure 4 is a plot of the abundance of the *REE* in the alteration pseudomorph (L41, L42) and the crust (L47) normalized to the value of the arithmetic mean of the two allanite samples (L14 and L43).

The *REE* are depleted not only in the pseudomorph, relative to the concentration in the original allanite, but even more so in the outermost section (L42) relative to the core (L41). Despite the overall depletion in *REE*, the chondrite-normalized plots of all three alteration products reflect the relative enrichment of light *REE* and the distinctive negative Eu anomaly of the original allanite. Positive Ce anomalies are present in the alteration products, but not in the original allanite, and are best-developed in the outer part of the pseudomorph (L42) and in the monazite–cerianite–halloysite (7 Å) crust (L47).

In comparison with fresh allanite, L47 exhibits little change in the concentration of the individual *REE* except for a relative enrichment of Eu and Ce (Fig. 4). The small variation of La_N/Yb_N (164 in fresh allanite and 156 in L47) indicates insignificant fractionation of the heavy *REE* relative to the light *REE*. The samples of the alteration pseudomorph show losses of all *REE* relative to fresh allanite and, in addition, they show fractionation effects resulting in a relative gain in heavy *versus* light *REE*: La_N/Yb_N is decreased to 95 and 66 for L41 and L42, respectively. In addition, europium in L41 shows a relative enrichment similar to that in L47.

Thorium is relatively immobile during the weathering process, as is indicated by the increased Th/ΣREE_N, Th/La, Th/Ce values in the alteration peudomorph (Table 3). These values, however, are lower in the monazite–cerianite–halloysite (7 Å) crust (L47) than in the fresh allanite.

DISCUSSION

Allanite is unstable under surface conditions and, moreover, its alteration is hastened by breakdown of the crystal structure through metamictization. With the onset of hydrolysis, the movement of the

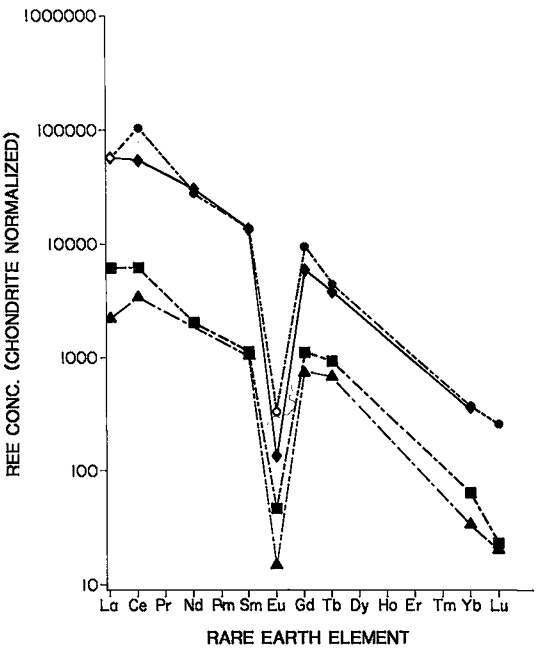

FIG. 3. C1-chondrite-normalized plot of *REE*: mean alllanite (L14 and L43) (diamond), core of alteration pseudomorph after allanite (L41) (square), outermost portion of alteration pseudomorph after allanite (L42) (triangle), and monazite–cerianite–halloysite (7Å) (L47) (dot). Average C1-chondrite values of Evensen *et al.* (1978) multiplied by 1.5 to allow for loss of volatiles have been used for normalization.

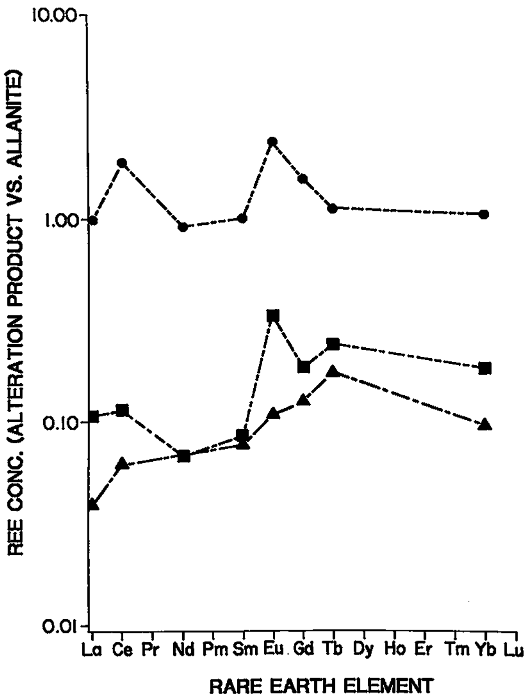

FIG. 4. Alteration products of allanite normalized against average composition of allanite; core of alteration pseudomorph after allanite (L41) (square), outermost portion of alteration pseudomorph after allanite (L42) (triangle), and monazite–cerianite–halloysite(7Å) (L47) (dot).

constituents of allanite is dependent largely on pε–pH conditions and the activities of various complexes in the groundwater, *e.g.*, $(CO_3)^{2-}$, $(PO_4)^{3-}$, F^- $(SO_4)^{2-}$, and organic complexes. In addition, the rate of flow of groundwater is important in controlling the activity of ionic species, as the activities of the various species commonly increase with greater contact-time with specific compounds.

With the exception of Ce, the *REE* are not pε-dependent in aqueous solutions under epigenetic conditions; the extent of dissolution and movement is dependent on the stability of complexes at the prevailing pH. The available thermodynamic data suggest varying degrees of stability among *REE* complexes and of solubility among species, as evident in Figures 1 and 2. These differences bring about a certain degree of fractionation evidenced by nonuniform losses of *REE* during breakdown of *REE*-bearing minerals (*cf.* Balashov *et al.* 1964, Nesbitt 1979, Bilal & Becker 1979, Bilal & Koss 1980a,b). The loss of *REE* during chemical weathering of allanite from the Bunker Hill pegmatite is accompanied by a relative enrichment of heavy relative to light *REE* (Fig. 4), in agreement with a range of pH values of 3 to 10 based on carbonate–hydroxide solubility control (Fig. 2). A dominant fluoride sink, in contrast, should have produced an enrichment of light *REE* according to the thermodynamic data (Figs. 1,2).

TABLE 3. THORIUM AND RARE-EARTH-ELEMENT RATIOS

Ratio	Mean Allanite	L41	L42	L47
$Th/\Sigma REE_N$	0.094	1.28	4.17	0.043
Th/Ce	0.060	0.74	2.57	0.021
Th/La	0.15	1.96	10.2	0.10
Ce_N/Yb_N	157	97	101	287
Ce_N/La_N	0.95	1.02	1.52	1.84
Ce/Ce*	1.18	1.47	1.78	2.34

Ce*: Equivalent to that value of Ce obtained were a smooth curve drawn from La to Nd.
REE_N,etc: Chondrite-normalized value.
Mean allanite: value based on allanite samples, L41 & L43.
L41: Core of allanite alteration pseudomorph,Bunker Hill pegmatite.
L42: Outer part of allanite alteration pseudomorph, Bunker Hill pegmatite.
L47: Monazite-cerianite-halloysite (7Å) crust from allanite, Bunker Hill pegmatite.

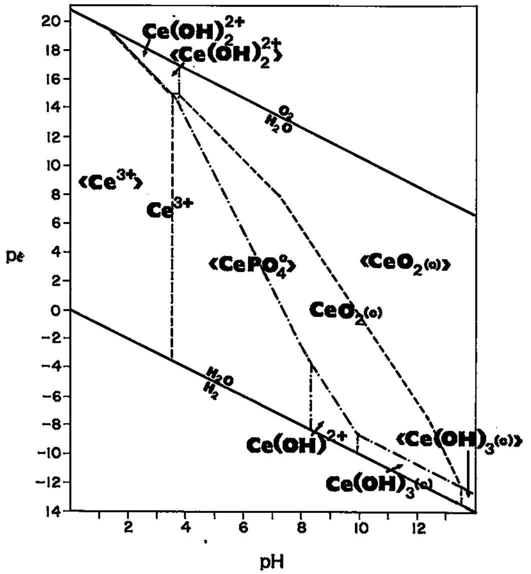

FIG. 5. Diagram of pε–pH for cerium species. Unbracketed species and dash-dot lines delineate dominance fields of hydrolysis products. Bracketed species and dashed lines delineate dominance fields with addition of phosphate. ΣCe 0.1 ppm, ΣPO_4 0.1 ppm.

This nonuniformity of loss and, in particular, the resultant relative enrichment of the Sm–Ho group of *REE* have been observed in previous studies (*cf.* Mineyev *et al.* 1973, Bilal & Becker 1979, Carron *et al.* 1958). The enrichment of Sm through Tb in this study (Fig. 4) may also be indicative of this change in stability, although the lack of data for Tb, Dy, and Ho preclude a definite statement.

Ce, on the other hand, can be oxidized to its tetravalent state in aqueous solutions, and the dominant species over a wide range of pε–pH conditions, considering hydrolysis only, is cerianite (Fig. 5). The lack of data for monazite-(Ce) or cerium carbonate precludes the comparison of their solubilities with cerianite or other *REE* species, although in light of the data for monazite-La and $CePO_4^0$ (aq), one might speculate that the stability field of cerianite would be curtailed considering the magnitude of PO_4^{3-} and CO_3^{2-} activities common in groundwater (Fig. 5).

Supergene cerianite contains little Th (A.N. Mariano, pers. comm.) and may possibly incorporate a small amount of trivalent *REE*. The precipitation of cerianite therefore can effect further fractionation of the *REE*, as is manifested by Ce anomalies in precipitates or solutions. The positive Ce anomalies shown by the weathering products studied (Fig. 4) result from this process. Furthermore, this process would explain the extreme enrichment of Ce observed by Watson (1917) in a crust formed on allanite from Little Friar Mtn., Virginia. In areas of lower pH, such as higher in the weathering profile, Ce^{3+} may be the dominant Ce species (as predicted in Fig. 5) and, thus, would be similar to La with respect to its mobility. The comparatively greater loss of Ce in a sample from the Il'men Mountains, U.S.S.R., observed by Mineyev *et al.* (1962), possibly indicates a low-pε regime, resulting in trivalent and more mobile Ce.

The Th released from the breakdown of allanite is probably precipitated as relatively insoluble thorite (or its hydrated form, thorogummite) in most groundwater conditions, unless, owing to low concentrations, it is incorporated solely in cerianite or other *REE* species. $Th(OH)_4$ may exist metastably, but has never been identified in nature; except under very acidic or extremely alkaline conditions, thorite should remain the dominant species. Removal of Th, therefore, is limited and probably occurs owing to organic or inorganic complexes such as $Th(HPO_4)_2^0$, $Th(SO_4)PO_4^0$, ThF_2^{2+}, or $Th(OH)PO_4^0$, as suggested by Langmuir & Herman (1980). This lack of mobility is indicated by the high values of Th/*REE* (Table 3) for the alteration pseudomorph, and reflects a lower extent of Th removal compared to that of the *REE*. The retention of thorium would also explain the increased level of radioactivity observed in the outer crusts of alteration pseudomorphs (Hata 1939).

As noted before, numerous phases resulting from the breakdown of allanite under endogene and epigene conditions have been reported (Table 1). Much of the original material is removed in solutions: Watson (1917) determined that up to 75% of the original constituents of allanite had been removed from the samples he examined. One may conclude that the resulting phases are varied; as suggested by the thermodynamic data, the mineralogy of the secondary phases of *REE*- and Th- bearing species will vary from site to site depending on the groundwater conditions enumerated above. A member of the bastnäsite – thorbastnäsite – hydroxyl-bastnäsite series is commonly reported in alteration parageneses, allegedly owing to the stability of this carbonate, whereas the comparative rarity of lanthanite, calkinsite, or synchysite is, in part, due to the requirement of greater activities of ΣCO_3, H_2O, and Ca^{2+} in the mineral-generating solution (*cf.* Saebø 1961, Littlejohn 1981a). The formation of bastnäsite within the inner fractures of the Bunker Hill allanite is attributed to precipitation from carbonate- and fluoride-bearing groundwater in a zone of relatively high pH buffered by silicate hydrolysis. Under these conditions, mobility of the elements is limited.

Contrary to the suggestions of Vlasov (1966), the occurrence of cerianite is probably not as rare as previously considered. The stability field of cerianite is broad and compares in pε–pH space with those of goethite or hematite (Fig. 7.23 of Garrels & Christ 1965). Therefore, in rocks containing *REE*-bearing minerals and secondary goethite or hematite, one would anticipate the occurrence of cerianite if the activities of ΣPO_4 and ΣCO_3 were sufficiently low. The fact that Mineyev *et al.* (1973) found magnetite as the common iron-bearing mineral indicates that the pε of the solutions producing bastnäsite may have been too low to produce cerianite. This would be expected at the low pε anticipated at depth in endogene or deuteric solutions. The fields of magnetite and cerianite do not overlap except where pH exceeds 8, pε is less than –5, and activities of S^{2-}, and $H_4SiO_4^0$ are low.

The presence of available phosphate in the groundwater is indicated by the formation of *REE* phosphates. Secondary monazite is common as thin crusts in the Amherst Co. occurrences, although it is typically restricted to the outer portions of the alteration pseudomorphs, where it is mixed with cerianite. The presence of monazite and the lack of calcium phosphate minerals are probably indicative of weakly acidic conditions of formation and the lower solubility of the rare-earth phosphates. Although they are associated with primary monazite, rare florencite and rhabdophane also are present and may represent additional phases resulting from the precipitation of *REE* from the groundwater solutions emanating from the altering allanite.

Thorite and thorogummite were not identified in materials formed by alteration of allanite, although they would be anticipated on the basis of the thermodynamic data. As the concentration of Th is low in the Amherst County allanite, the low levels of Th released are probably incorporated into other minerals such as cerianite, bastnäsite, or monazite, or are scavenged along with *REE* by goethite, as reported by Koons *et al.* (1980) and reviewed by Langmuir & Herman (1980).

The remainder of the alteration products makes up the bulk of the alteration pseudomorph and consists of a mixture of clay minerals, quartz, goethite, and gibbsite, plus undetermined amorphous to very poorly crystalline ferric and aluminum hydroxides and silica. Under the regime of intense weathering present in western Virginia, the assemblage of ferric and aluminum hydroxides plus silica is transformed to goethite and halloysite (10 Å), with subsequent alteration of the halloysite (10 Å) to halloysite (7 Å) and kaolinite.

In summary, the alteration of allanite is primarily dependent on the climatic and groundwater conditions, which impose definite physicochemical domains. The alteration products represent a continuing change toward more stable species for the specific conditions. General reactions, such as have been proposed by Mineyev *et al.* (1973) and Littlejohn (1981a), may be used to define certain conditions of alteration characterized by specific pε, pH, and chemical potentials. The conditions present in this study area apparently are more oxidizing and less alkaline than those studied by Mineyev *et al.* (1973): the stable species are goethite and cerianite instead of bastnäsite and magnetite. Bastnäsite is present only in the more alkaline areas, such as adjacent to the primary allanite or in fractures of granitic rocks, where silicate hydrolysis buffers the pH at relatively high levels. This bastnäsite is a minor reservoir of the *REE* and thorium, but samples were not large enough for analysis by means available during this study. In areas where the pH is lower and the pε and activity of PO_4 are greater, such as around the Bunker Hill pegmatite, the alteration of allanite has resulted in the formation of secondary monazite and cerianite as primary sinks for the *REE* and Th, as summarized in the following two-part reaction:

$$1.\quad \underset{\text{allanite}}{12(Ce,La,Ca)_2(Al,Fe)_3Si_2O_7SiO_4O(OH)} + 102H_2O + 8H^+ \rightarrow$$

$$\underset{\text{cerianite}}{8CeO_2} + 8La(OH)^{2+} + 8Ca^{2+} + \underset{\text{goethite}}{18FeO(OH)} + \underset{\text{gibbsite}}{18Al(OH)_3} + 36\ H_4SiO_4$$

$$2.\quad + 8H_3PO_4 \rightarrow \underset{\text{cerianite}}{8CeO_2} + \underset{\text{monazite-(La)}}{8LaPO_4} +$$

$$\underset{\text{halloysite (10 Å)}}{9Al_2Si_2O_5(OH)_4{\bullet}2H_2O} + 18H_4SiO_4 +$$

$$35H_2O + 18\ FeO(OH) + 8Ca^{2+} + 16H^+$$

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APPENDIX A. INORGANIC AQUEOUS SPECIES AND SOLIDS AT 25°C AND 10^5 PASCALS

La *Species*	ΔG_f°	*Source*
La^{3+}	−683.67	3
$La(OH)^{2+}$	−872.79	1
$La_2(OH)_2^{4+}$	−1741.73	1
$La_3(OH)_5^{4+}$	−3018.10	1
$La_5(OH)_9^{6+}$	−5146.22	1
$La(OH)_3(s)$	−1279.22	1
LaF^{2+}	−985.92	7
$LaF_3(s)$	−1816.19	2
$LaSO_4^+$	−1448.99	6
$La(SO_4)_2^-$	−2202.95	6
$LaH_2PO_4^{2+}$*	−1823.25	6
$LaPO_4(s)$* (monazite-(La)?)	−1830.70	6
$La_2CO_3(s)$	−3141.68	6
$La_2O_3(s)$	−1705.96	6
Ce		
Ce^{3+}	−672.00	5
Ce^{4+}	−503.80	5
$CeOH^{2+}$	−861.77	1
$Ce_2(OH)_2^{4+}$	−1729.81	1
$Ce_3(OH)_5^{4+}$	−3010.49	1
$CeOH^{3+}$	−785.3	4
$Ce(OH)_2^{2+}$	−1020.9	4
$Ce(OH)_3(s)$	−1269.84	1
CeF^{2+}	−976.54	6
$CeF_3(s)$	−1812.57	2
$Ce(SO_4)^+$	−1437.03	6
$Ce(SO_4)_2^-$	−2190.77	6
$CeH_2PO_4^{2+}$	−1815.69	6
$CePO_4^\circ$	−1796.71	6
$CeO_2(s)$ (cerianite)	−1025.38	5
α-$Ce_2O_3(s)$	−1707.94	5

Yb

Yb^{3+}	−762.32	3
$Yb(OH)^{2+}$	−955.51	1
$Yb(OH)_2^+$	−1146.42	1
$Yb(OH)_3^{\circ}$	−1336.18	1
$Yb(OH)_4^-$	−1524.24	1
$Yb(OH)_3(s)$	−1389.84	6
$Yb(SO_4)^+$	−1527.30	6
$Yb(SO_4)_2^-$	−2281.09	6
$Yb_2(CO_3)_3(s)$	−3285.86	6
$Yb_2O_3(s)$	−1726.84	6

Y

Y^{3+}	−693.71	3
YOH^{2+}	−886.90	1
$Y(OH)_2^+$	−1074.38	1
$Y(OH)_4^-$	−1433.94	1
$Y_2(OH)_2^{4+}$	−1780.48	1
$Y_3(OH)_5^{4+}$	−3086.47	1
$Y(OH)_3^{\circ}$	−1256.73	1
$Y(OH)_3(s)$	−1305.24	1
YF^{2+}	−1002.81	6
YF_2^+	−1305.64	6
YF_3°	−1607.89	6
$YF_3(s)$	−1751.05	2
YSO_4^+	−1458.06	6
$Y(SO_4)_2^-$	−2213.05	6
$YH_2PO_4^+$	−1839.23	6
$Y_2(CO_3)_3(s)$	−3145.78	6
$Y_2O_3(s)$	−1816.61	5

Sources:

1. Baes & Mesmer (1976), 2. Barin *et al.* (1977), 3. Barner & Scheuerman (1978), 4. Garrells & Christ (1965), 5. Robie *et al.* (1978), and 6. Smith & Martell (1976). *Ionic strength = 0.5 for determination. ΔG_f° given in kJ/mole.

Th

Species	ΔG_f°
Th^{4+}	−704.59
$ThOH^{3+}$	−923.41
$Th(OH)_2^{2+}$	−1139.30
$Th(OH)_3^+$	−1349.23
$Th\ (OH)_4^{\circ}$	−1562.40
$Th_2(OH)_2^{6+}$	−1848.42
$Th_4(OH)_8^{8+}$	−4595.05
$Th_6(OH)_5^{9+}$	−7575.00
ThF^+	−1032.19
ThF_2^{2+}	−1349.42
ThF_3^+	−1657.70
ThF_4°	−1958.95
$ThF_4(s)$	−2003.72
$ThF_4 \cdot 2.5H_2O(s)$	−2613.74
$ThSO_4^{2+}$	−1480.30
$Th(SO_4)_2^{\circ}$	−2249.32
$Th(SO_4)_3^{2-}$	−2998.25
$Th(SO_4)_4^{4-}$	−3731.29
$ThH_3PO_4^{4+}$	−1858.11
$ThH_2PO_4^{3+}$	−1861.46
$Th(H_2PO_4)_2^{2+}$	−3016.25
$ThHPO_4^+$	−1855.60
$Th(HPO_4)_2^{\circ}$	−3013.32
$Th(HPO_4)_3^{2-}$	−4150.95
$Th(HPO_4)_2 \cdot 4H_2O(s)$	−3985.26
$ThO_2(s)$ (thorianite)	−1168.78
$ThSiO_4(s)$ (thorite)	−2048.78

Sources: for thorite, Schuiling *et al.* (1976); in all other cases, Langmuir & Herman (1980). ΔG_f° given in kJ/mole.