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BASTNAESITE IN FRACTURES OF THE EYE–DASHWA LAKES PLUTON, ATIKOKAN, NORTHWESTERN ONTARIO

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ABSTRACT

Bastnaesite $CeFCO_3$ has been identified in fractures of the Eye–Dashwa lakes pluton near Atikokan, Ontario. In this locality, it is a secondary mineral formed by alteration of monazite, and it contains La replacing Ce. Its cell dimensions are *a* 7.09(1), *c* 9.78(8) Å. The leaching of Ce and La from monazite, with concentration in nearby fractures, provides an example of the retardation of radionuclide migration from potential vaults dug in crystalline rocks for nuclear waste disposal.

Keywords: bastnaesite, fractures, Eye–Dashwa pluton, rare earths, Ontario, nuclear waste.

SOMMAIRE

La bastnaesite $CeFCO_3$ a été identifiée dans des fractures du pluton des lacs Eye et Dashwa, près d'Atikokan en Ontario. En cet endroit, elle est d'origine secondaire et s'est formée par altération de la monazite. Elle contient du lanthanum substitué au cérium. Les dimensions de la maille hexagonale sont *a* 7.09(1), *c* 9.78(8) Å. Le lessivage du Ce et du La de la monazite, suivi de leur concentration dans des fractures voisines, fournit un exemple du retardement de la migration des radio-nuclides à partir d'éventuels souterrains creusés dans les roches cristallines pour y enfouir les résidus nucléaires.

(Traduit par la Rédaction)

Mots-clés: bastnaesite, fractures, pluton des lacs Eye et Dashwa, terres rares, Ontario, résidus nucléaires.

INTRODUCTION

The Eye–Dashwa lakes pluton, located about 30 km northeast of Atikokan, Ontario, occurs in the Superior structural province of the Canadian Shield. It is an egg-shaped body that has intruded a series of tonalitic and granitic gneisses (Brown *et al.* 1980). Petrographic examination revealed that the pluton is zoned, with a granodioritic rim and a granitic core (Kamineni & Brown 1981). The pluton has recently been investigated in detail as a part of a program of generic research to assess the suitability of bodies of crystalline rock for disposal of nuclear fuel wastes. These studies include numerous techniques from the disciplines of geology, geophysics and hydrogeology. The petrology of the pluton, and the mineralogy and geochemistry of fracture-filling minerals, have been investigated in detail.

MODE OF OCCURRENCE

The Eye–Dashwa lakes pluton is intersected by a series of fractures that are commonly coated or filled by epidote or chlorite (or both), with minor amounts of titanite, sericite, fluorite and hematite (Kamineni *et al.* 1980). Calcite, kaolin, montmorillonite and gypsum, termed low-temperature fillings, are either associated with epidote and chlorite or occur independently in minute fractures that cross-cut the epidote-filled fractures. The calcite-filled fractures intersect epidote-filled fractures, this clearly demonstrates that low-temperature minerals filled the fractures. These minerals show zonal distribution in boreholes: gypsum is concentrated at depth below 500 m and calcite, in the zone above 500 m.

Two types of calcite are recognized in the fractures: (1) thin flakes coating epidote and bluish chlorite, and (2) equidimensional crystals arranged randomly in fractures, the arrangement of which gives rise to numerous vugs. Bastnaesite, in the form of fine flakes, is associated with flaky calcite in samples collected in a road cut within the Eye–Dashwa lakes pluton; it was discovered during electron-microscope examinations of fracture-filling minerals. It also occurs commonly as thin and fine flaky coatings on epidote fracture fillings (Fig. 1).

CHEMICAL COMPOSITION AND X-RAY DATA

Samples with natural (unpolished) fracture surfaces containing mineral matter were cut into 1×1×0.5 cm slabs and coated with carbon.

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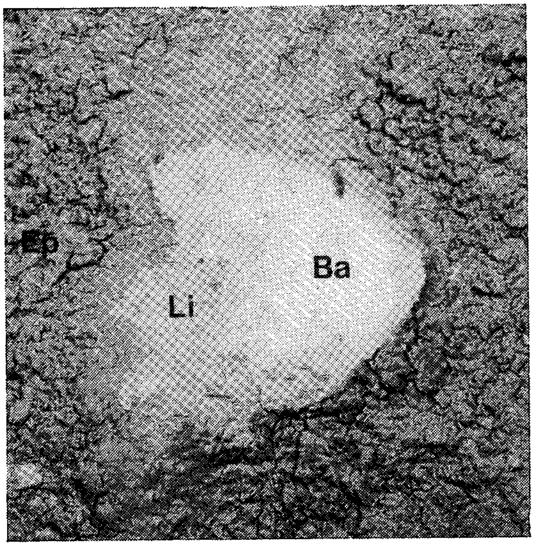

Fig. 1. Scanning electron micrograph of fracture surface showing epidote (Ep), iron oxide (Li) and bastnaesite (Ba).

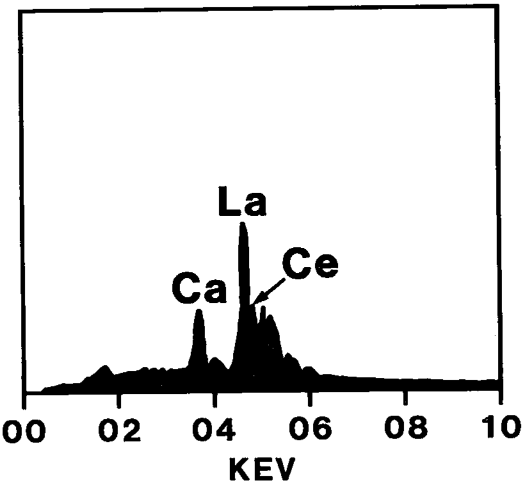

Fig. 3. Energy-dispersion spectrum of bastnaesite showing La and Ce peaks. The Ca peak is due to calcite associated with bastnaesite. The sample (ATK 40) was collected on the southeastern rim of the Eye–Dashwa lakes pluton in a road cut on Highway 622.

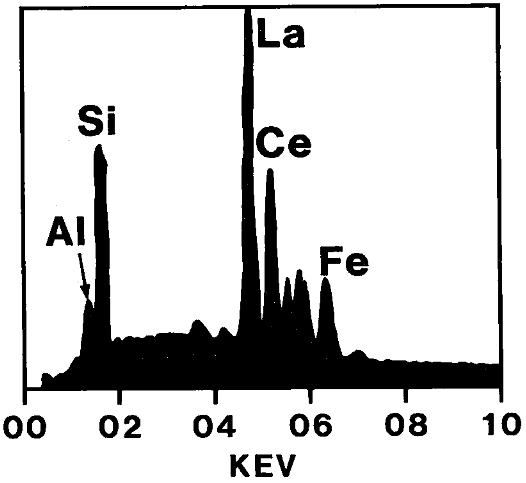

Fig. 2. Energy-dispersion spectrum of bastnaesite in Figure 1, displaying prominent Ce and La peaks. Fe, Ca, Al, Si and Mn are probably from epidote and limonite. The sample (ATK 20) was collected on the southeastern rim of the Eye–Dashwa lakes pluton in a road cut on Highway 622.

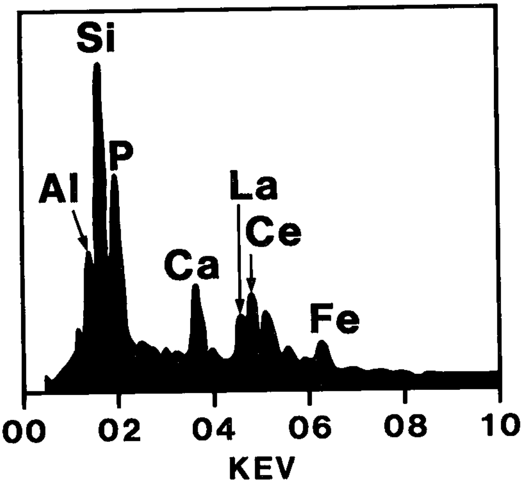

Fig. 4. Energy-dispersion spectrum of monazite showing P, Ce and La peaks. Al, Si, Ca and Fe peaks are due to the adjacent epidote grain. Location is the same as sample ATK 20.

The carbon-coated samples were examined under an ETEC scanning electron-microscope equipped with a Kevex energy-dispersion spectrometer, located in the laboratories of the Geological Survey of Canada. On the back-scattered image, the bastnaesite grains appear as bright spots. These spots could not be analyzed quantitatively, but their chemical characteristics can be documented qualitatively. Energy-dispersion spectra of the bright spots from two samples show CeLα and LaLα peaks (Figs. 2, 3). From these spectra, it is evident that the samples of bastnae-

TABLE 1. X-RAY-DIFFRACTION DATA FOR BASTNAESITE

hkl	d (Observed)	d (Calculated)	I/I_O
002	4.85 Å	4.890 Å	6
110*	3.58	3.545	8
112*	2.87	2.879	10
030*	2.04	2.097	8
220	1.78	1.773	1
222*	1.66	1.666	3
224*	1.43	1.435	3
140	1.35	1.340	<1
142*	1.29	1.292	6

Hexagonal, a 7.09 (1), c 9.78 (8) Å.* lines used in unit-cell refinement, indexed with a 7.129, c 9.774 Å

site contain both the rare-earth elements Ce and La. One of the samples shows Mn, Fe and Ca peaks (Fig. 2) also, which are due to limonite and epidote in the vicinity. The Ca peak in Figure 3 represents calcite associated with bastnaesite. Some other grains, also appearing as bright spots displaying Ce$L\alpha$, La$L\alpha$ and P$K\alpha$ lines (Fig. 4), were noted in one sample, and they are inferred to be monazite. The Al, Si, Ca and Fe lines in Figure 4 are due to an adjacent epidote grain.

Powder photographs of bastnaesite were prepared using a Debye–Scherrer camera with Cu$K\alpha$ radiation. The observed d values were processed using a least-squares refinement program. The results are listed in Table 1.

ORIGIN OF BASTNAESITE

Reported occurrences of bastnaesite have been listed by Palache *et al.* (1951). All of them appear to have formed either in pegmatitic or contact zones of granitic rocks. The various associations may be summarized as follows: 1) with allanite, cerite and fluocerite in amphibole skarn at Bastnas, Sweden, 2) as an alteration product of tysonite near Fahlun, Sweden, 3) with allanite, cerite and tornebohmite as pebbles in gold placers derived from alkali syenites in the Kyshtym district in the Urals, U.S.S.R., 4) with glaucophane and chevkinite in a contact zone of pegmatite and alkali granite in the region of Torendrika–Ifsina, Madagascar, 5) with cerite, fluorite, allanite and tornebohmite in a contact zone with pegmatitic facies of an alkali granite, and with fluocerite in pegmatite in Colorado, U.S.A. and 6) with fluorite in a brecciated contact zone in Gallinas Mountains, New Mexico, U.S.A. More recently, Černý & Černá (1972) and Littlejohn (1981) have reported bastnaesite from the Canadian Shield. In both these occurrences, bastnaesite was shown to be an alteration product of allanite.

Additional occurrences include bastnaesite associated with alkalic rocks and carbonatites at Mountain Pass, California (Pray & Sharp 1951, Kapustin 1971). Bastnaesite in this occurrence was noted both as an accessory mineral and independent veinlets. Semenov *et al.* (1961) described bastnaesite in the erosion zone of an alkaline massif and suggested that it formed by supergene enrichment from parisite. Maksimovic & Panto (1978) reported bastnaesite formed in a residual weathered zone in the Grebnik bauxite deposits, Yugoslavia, where it is associated with monazite and synchysite.

Except monazite, none of the above minerals found elsewhere coexisting with bastnaesite was noted in fractures of the Eye–Dashwa lakes pluton. The association of monazite in the present case strongly suggests that Ce and La, the major constituents of bastnaesite, must have been derived from monazite. The mode of occurrence of bastnaesite definitely supports a post-hydrothermal stage for the timing of its crystallization. Flakes of bastnaesite occur as coatings on epidote and chlorite fillings, which were shown have formed during the stage of hydrothermal alteration (Kamineni & Dugal 1982, Stone & Kamineni 1982). Monazite grains occur as accessory minerals within the host rock adjacent to some fractures. From these observations, it is concluded that neither epidote nor monazite is cogenetic with bastnaesite. Monazite, as the source of Ce and La in bastnaesite, is supported further by the fact that energy-dispersion X-ray analysis and microprobe analysis of epidote and titanite occurring in the Eye-Dashwa lakes pluton show no detectable rare-earth elements (Kamineni & Brown 1981).

The occurrence of various secondary minerals, such as epidote, chlorite, calcite, bastnaesite and kaolinite as coatings on fracture surfaces indicates that the fractures represent either ancient or present fluid pathways in the pluton. Fluid circulation along fractures causes alteration along the wallrock; consequently, incongruent leaching and removal of chemical constituents occur in these zones. Evidently, in the case of monazite, fluid passing through fractures subsequent to the formation of epidote, *i.e.*, at a post-hydrothermal cycle of activity, has altered this mineral and released the Ce and La. The fluid percolating along these fractures must have been groundwater rich in CO_2 and F. This implies a supergene origin for the bastnaesite. According to Krauskopf (1955), the precipitation of rare-earth elements depends on a number of factors, the most important being: 1) temperature and pressure, 2) the concentration of rare-earth elements in the solution, 3) the concentration of other ions, 4) the nature of the rare metal ion or ions present, and 5) the solubilities of the various compounds. Rare earths form carbonates in the weathered zone where the concentration of the metal is abnormally high (Krauskopf 1955). Presumably, leaching of monazite along fractures caused high concentrations of Ce and La, leading to the precipitation of bastnaesite.

DISCUSSION

The occurrence of rare-earth-bearing secondary minerals such as bastnaesite in fractures in granite is significant to an understanding of radionuclide migration. Fractures in a crystalline rock barrier may act as pathways into the biosphere for migrating radionuclides from a deeply placed disposal-vault repository.

This migration can be retarded by various processes, such as physisorption, chemisorption and precipitation. The first two processes involve physical and chemical interaction of mineral phases and radionuclides (sorption on mineral surfaces), whereas precipitation involves formation of new minerals from saturated solution. The rare-earth element Ce, which is the main constituent in bastnaesite, is a common fission product in nuclear fuel waste. Bastnaesite provides an excellent example for retardation of migration by precipitation.

Nuclide release from a disposal vault is controlled by the hydrogeological and geochemical interactions in the vicinity of the vault that affect incongruent dissolution of waste, leaching and precipitation (Savage & Chapman 1980). An analogy with these events in nature can be found in the origin of bastnaesite. The events can be visualized as follows: (1) monazite, which is the source of bastnaesite, represents the immobilized fission products, (2) the monazite is leached along fractures by interaction with groundwater and (3) bastnaesite is precipitated from a fluid saturated with Ce and La. These three events provide an excellent example of possible retardation of radionuclide mobility in nature.

Bastnaesite can also be considered a "source term" (Savage & Chapman 1980), a mineral precipitate that incorporates a proportion of the radionuclides leached from a vitrified waste. The "source term" will be important in the assessment of radionuclide migration from a nuclear fuel-waste repository to the biosphere. The materials comprising a "source term" are secondary minerals such as bastnaesite; these minerals seem to be stable over long periods of time. For example, ^{14}C analysis (unpublished work by the authors) of calcium carbonate associated with bastnaesite yields an age greater than 40,000 years. This implies that if the mobilized fuel-waste products from the repository are retarded by precipitation in suitable mineral forms, they may become immobilized either indefinitely, or at last until their radioactivity has dropped off considerably.

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