HÅLENIUSITE-(La) FROM THE BASTNÄS DEPOSIT, VÄSTMANLAND, SWEDEN: A NEW REE OXYFLUORIDE MINERAL SPECIES

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ABSTRACT

Håleniusite-(La), a new mineral species whose ideal formula is (La,Ce)OF, is cubic and has a unit-cell parameter a equal to 5.6282(5) Å, $V = 178.28(5)$ Å^3, for $Z = 4$. The strongest five lines in the X-ray powder-diffraction pattern obtained with a Guinier–Hägg camera [d in Å (I_{obs})(hkl)] are: 3.25(100)(111), 2.815(31)(200), 1.991(61)(220), 1.697(46)(311) and 1.292(15)(331). The crystal structure was refined in space group $Fm3m$ from powder data using the Rietveld method, to an R_F value of 5.1%. The mineral is shown to be isostructural with fluorite, and the average metal–anion distance is 2.437(1) Å for håleniusite-(La). D(calc.) ≈ 6.5 g/cm^3. The atomic ratio La/(La + Ce) is 0.506 ± 0.001 (range 0.485–0.528). Håleniusite-(La) is powdery, with a distinct yellow color. It is associated with bastnäsite-(La), brochantite, ferriallanite-(Ce) and quartz in the type specimen, and was found on the dumps of the Bastnäs Cu–REE mines in Västmanland, Sweden. Additional specimens from the same locality contain cerite-(Ce), molybdenite and amphibole. Håleniusite-(La) is a secondary mineral, formed by alteration of primary bastnäsite-(La), most likely *via* a decarbonation reaction, $(La, Ce)CO_3F \rightarrow (La, Ce)OF + CO_2$. The name of this new mineral honors Ulf Hålenius, Professor of Mineralogy at the Swedish Museum of Natural History.

Keywords: håleniusite-(La), new mineral species, REE oxyfluoride, lanthanides, Bastnäs, Sweden.

SOMMAIRE

La håléniusite-(La), nouvelle espèce minérale dont la formule idéale est (La,Ce)OF, a une symétrie cubique et un paramètre réticulaire a égal à 5.6282(5) Å, $V = 178.28(5)$ Å^3, pour $Z = 4$. Les cinq raies les plus intenses du spectre de diffraction X, méthode des poudres, tel qu'obtenu avec une chambre Guinier–Hägg [d en Å (I_{obs})(hkl)], sont: 3.25(100)(111), 2.815(31)(200), 1.991(61)(220), 1.697(46)(311) et 1.292(15)(331). La structure cristalline a été affinée dans le groupe spatial $Fm3m$ avec la méthode de Rietveld, jusqu'à une valeur R_F de 5.1%. Le minéral possède la structure de la fluorite, et la distance moyenne de métal à anion est 2.437(1) Å. La densité calculée est égale à 6.5 g/cm^3. Le rapport La/(La + Ce) est 0.506 ± 0.001, et varie entre 0.485 et 0.528. La håléniusite-(La) est pulvérulente et de couleur jaune. Elle est associée à la bastnäsite-(La), brochantite, ferriallanite-(Ce) et quartz dans l'échantillon-type. Nous l'avons découverte dans des haldes de mines désaffectées de cuivre et de terres rares à Bastnäs, Västmanland, en Suède. Des échantillons additionnels du même endroit contiennent cérite-(Ce), molybdénite et une amphibole. La håléniusite-(La), d'origine secondaire, s'est formée par altération de la bastnäsite-(La) primaire, tout probablement par une réaction de décarbonatation, $(La, Ce)CO_3F \rightarrow (La, Ce)OF + CO_2$. Le nom choisi honore Ulf Hålenius, Professeur de Minéralogie au Musée d'Histoire Naturelle de Suède.

(Traduit par la Rédaction)

Mots-clés: håléniusite-(La), nouvelle espèce minérale, oxyfluorure de terres rares, lanthanides, Bastnäs, Suède.

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Introduction

In this note, we present information on a new mineral species, håleniusite-(La), the first naturally occurring rare-earth (REE) oxyfluoride to be approved by the IMA Commission on New Minerals and Mineral Names (#2003–028). It was discovered as a secondary phase at the Bastnäs deposit, Skinnskatteberg District, Västmanland County, Sweden (lat. 59°51'N, long. 15°35'E). The mineral is named in honor of Professor Ulf Hålenius (b. 1951), head of the Department of Mineralogy of the Swedish Museum of Natural History, for his contributions to the spectroscopy of minerals and the mineral sciences in general.

Few natural occurrences of REE oxyfluorides were known previous to our discovery. One is the Cínovec (Zinnwald) granite, in the Czech Republic, famous as an example of W–Sn mineralization. In samples from deep boreholes (*ca.* 400 m), rare opaque grains interstitial to quartz and zinnwaldite were found to consist of a submicroscopic intergrowth of fluocerite-(La) and two unnamed (Ce, La) oxyfluorides (Johan & Johan 1994). The crystal symmetries of the oxyfluorides are somewhat unclear because they were determined from powder data; one phase was found to be cubic with an *a* parameter equal to 5.470 Å, and the other one is probably hexagonal with *a* = 7.007 and *c* = 9.840 Å.

The REE oxyfluorides, with the general stoichiometric formula *Ln*OF, are well known synthetic compounds (Zachariasen 1951, Mann & Bevan 1970). For *Ln* = La to Er, there are two polymorphs: a rhombohedral form (the β phase) is stable at room temperature, but at elevated temperatures (750–900 K), it inverts to a cubic fluorite-type structure (the α phase, space-group symmetry *Fm3m*). This change is a first-order transition, and it is normally not possible to preserve the cubic symmetry by quenching. The mechanism behind the structure transformation is not known, but it is possibly related to an order–disorder reaction among the anions (Petzel *et al.* 1993, Müller & Petzel 1995, Fergus 1996, Achary *et al.* 1998).

Occurrence and Physical Description

The Bastnäs deposit in the Riddarhyttan ore field is known for its unique REE mineralization, dominated by cerite, ferriallanite and bastnäsite. Chalcopyrite, bismuthinite and molybdenite are the major sulfides found. These minerals occur in skarn assemblages together with tremolite and talc, in a zone up to 0.6 m wide (Geijer 1921, Holtstam *et al.* 2003). Although originally worked as a copper mine, about 160 metric tonnes of REE ore produced from Bastnäs were sold between 1860 and 1919 (Carlborg 1923).

The holotype specimen was collected by Mr. J. Langhof at the mine dumps of Bastnäs (close to an open pit known as "the Cerite mine") in 1986, and is now preserved in the type-mineral collection of the Swedish Museum of Natural History in Stockholm (catalogue no. 20030025). It consists mainly of ferriallanite-(Ce), and what used to be coarsely crystalline bastnäsite-(La), now largely replaced by håleniusite-(La), with a distinct yellow color. The original bastnäsite plus lesser amounts of quartz seem to have been interstitial, filling a cavity about 5 cm across, in the mass of ferriallanite-(Ce). The alteration goes deep, with a layer of håleniusite-(La) a few millimeters in thickness covering the bastnäsite. Small portions with håleniusite-(La), invariably accompanied by irregular voids (Fig. 1), also are found within the unaltered bastnäsite.

On the type specimen, håleniusite-(La) is partially covered with tiny crystals of brochantite, forming aggregates or crusts on the rough surfaces of the new mineral (Fig. 2). Brochantite is a common product of copper sulfide oxidation at Bastnäs.

In the original description of bastnäsite from Bastnäs (known as "basiskt fluor-cerium" at the time; Hisinger 1838), an "earthy" variety of the mineral was mentioned. An early 19th century label in the Uppsala University collection refers to a lemon-yellow, earthy bastnäsite; the corresponding specimen (catalogue no. 198/1) has been examined by us and is confirmed to contain håleniusite (from an X-ray powder pattern) plus bastnäsite, cerite, ferriallanite, molybdenite and amphibole. Note that the bastnäsite samples show some variations in their La:Ce ratio at Bastnäs, and it must be understood that a Ce-dominant analogue of håleniusite-(La) probably is present here as well (*cf.* below).

Individual crystallites of håleniusite-(La) have dimensions less than 1 μm across, and for that reason the standard physical and optical parameters could not be determined. From the crystal symmetry and chemical composition, we expect the mineral to be optically isotropic, with $n_{calc} \approx 1.9$. It is non-fluorescent under shortwave UV radiation. The calculated density, based on the composition and the unit-cell volume (*cf.* below), is 6.5 g/cm³.

X-Ray Crystallography

A small, high-purity sample (< 1 mg) was taken for collection of a powder-diffraction pattern, using a 40.16-mm Guinier–Hägg camera, Cu*K*α radiation and Si as internal standard. The films were evaluated with an automated film-scanner system (Johansson *et al.* 1980). The nine observed Bragg peaks could be indexed with a face-centered cubic unit-cell, and least-squares refinement yielded an *a* of 5.6282(5) Å and *V* equal to 178.28(5) Å³. The indexed powder-diffraction pattern is given in Table 1. The figure of merit, which indicates the completeness and accuracy of measured interplanar spacings of the present dataset (Smith & Snyder 1979) is F_9 = 66 (0.0154, 9), suggesting good quality of the data.
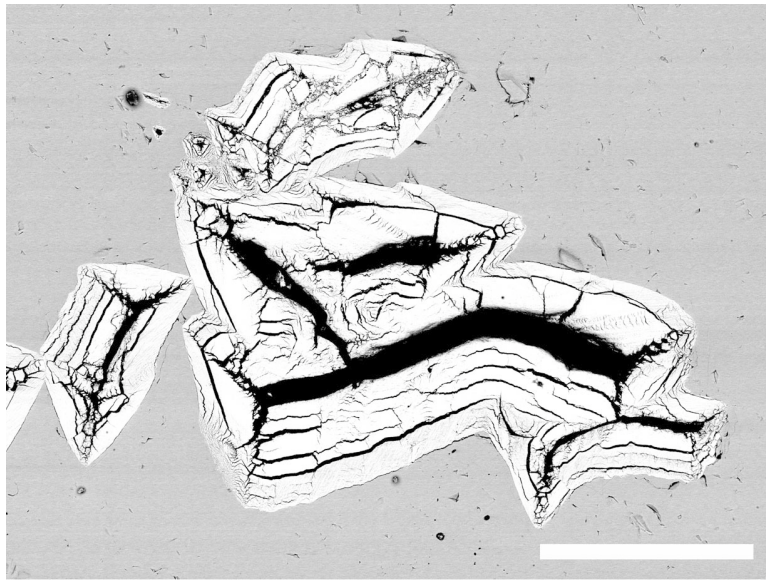
FIG. 1. Back-scattered electron (BSE) micrograph of a section of bastnäsite-(La) showing partial alteration to håleniusite-(La), which is white on the image. Black areas are voids. The scale bar equals 100 μm.
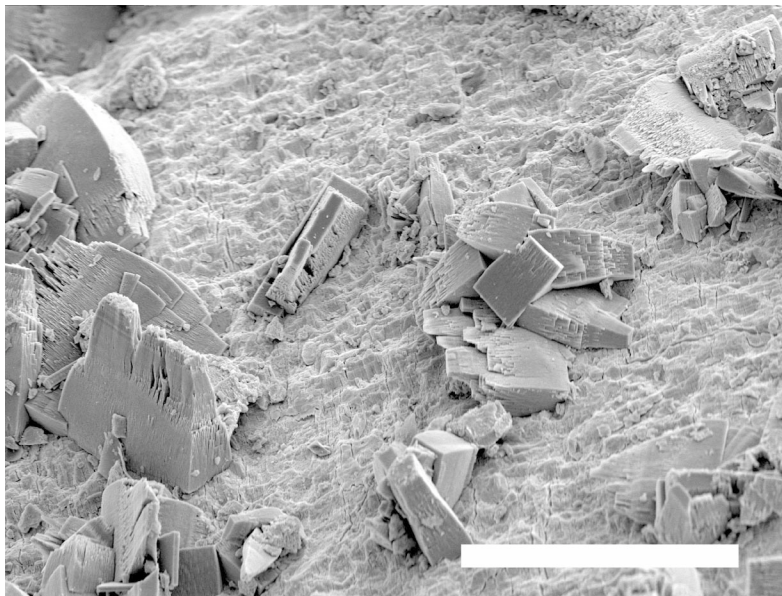

FIG. 2. Secondary electron microscope (SEM) image showing aggregates of brochantite crystals that have grown on håleniusite-(La). The scale bar equals 100 μm.

Another powder pattern was recorded with a STOE STADI/P diffractometer, CuKα radiation, a sample in symmetrical transmission mode, and a linear position-sensitive detector covering 4.6° in 2θ. The reflection profiles were found to be close to Lorentzian and show a broadening of lines corresponding to a domain size of *ca.* 300 Å. The diffractometer dataset was used to confirm the fluorite-type structure by the Rietveld method. The program FullProf (Rodriguez-Carjaval 2000) was used, and all 17 reflections for 2θ ≤ 130° were included in the refinement. The (La, Ce) and (O, F) atoms were located in the 4*a* (0, 0, 0) and 8*c* (¼, ¼, ¼) positions, respectively, of the *Fm3m* unit cell. A total of 12 parameters were refined, yielding $R_F = 5.1\%$ and a χ^2 value of 0.86. The refined thermal-displacement parameters

were $B = 4.3(1)$ Å^2 for (La, Ce) and $B = 6.6(4)$ Å^2 for (O, F). The large B values indicate that there may be ordered regions in the structure locally, with extensive relaxations of the cations and anions ions that are slightly displaced from their ideal sites in the structure. The refinement validates the hypothesis that the new mineral species is isostructural with fluorite and that the average structure has (La, Ce) metal atoms with eight anionic ligands, forming a regular cube (Fig. 3). The metal-to-anion distance is calculated to be 2.437(1) Å. Although many aspects of the synthetic REE oxy-fluorides have been studied in the past, there seems to be no structural *refinements* done on compounds of this family.

CHEMICAL COMPOSITION

The chemical composition of the new mineral was determined using both wavelength-dispersion (WDS) and energy-dispersion (EDS) X-ray spectrometry on carbon-coated polished samples embedded in epoxy resin (Table 2). For the WDS analyses, a Cameca SX50 electron microprobe was used. The accelerating voltage was 20 kV, with a beam current of 15 nA and beam diameter of 1 μm. We used as standards pure synthetic REE phosphates (LnLα, SmLβ), YPO₄ (YLα), wollastonite (CaKα, SiKα) and LiF (FKα). Data were reduced with a Cameca version of the PAP (Pouchou & Pichoir 1991) routine. EDS analyses were carried out with an electron microscope (Hitachi S4300) fitted with a solid-state Si(Li) detector at 20 kV and 10 nA using the INCA software package (Oxford Instruments). In this case, the concentration of oxygen was determined directly from the OKα peak in the energy spectrum.

The three dominant REE in håleniusite-(La) are La, Ce and Nd, accounting for more than 95% of the cations in the mineral. For all analytical points taken together, the mean atomic La/(La + Ce) value is 0.506, with a standard error of 0.001 (the median value is 0.507), which forms the basis for naming the mineral håleniusite-(La). The total range is 0.485–0.528, thus indicating that some points actually are Ce-dominant. Associated bastnäsite-(La) has the composition $(La_{0.46}Ce_{0.44}Nd_{0.08}Pr_{0.02})CO_3F$ on average.

As expected, the molar volume of LnOF compounds decreases with atomic number, as a consequence of decreasing ionic radii of the cations involved. The curve in Figure 4 is supported by data from two different studies of the synthetic compounds (at room temperature). Clearly, håleniusite-(La) has a much smaller unit-cell volume than that expected from the average atomic number of its REE constituents (based on the chemical analyses).

Nonstoichiometry could be the reason for the discrepancy, and possibly it also offers an explanation why the cubic modification is stable (or at least metastable) at room temperature. The oxide CeO_2, corresponding to the mineral cerianite, has the cubic (*Fm3m*) fluorite-type

TABLE 1. X-RAY POWDER-DIFFRACTION DATA
FOR HÅLENIUSITE-(La) FROM THE BASTNÄS DEPOSIT, SWEDEN

I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l
100	3.252	3.249	1	1	1
31	2.815	2.814	2	0	0
61	1.991	1.990	2	2	0
46	1.6969	1.6970	3	1	1
9	1.6246	1.6247	2	2	2
5	1.4072	1.4071	4	0	0
15	1.2916	1.2912	3	3	1
9	1.2582	1.2585	4	2	0
12	1.1486	1.1488	4	2	2

Guinier–Hägg camera, λ = 1.5406 Å. Indexed on a cell having *a* = 5.6282(5) Å. Intensities are taken from diffractometer data.
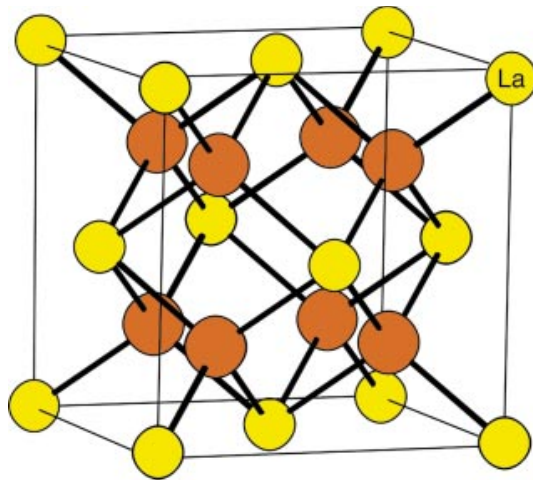

FIG. 3. The atomic structure and unit cell of håleniusite-(La). Note that the O and F atoms must be randomly distributed over the anion positions (darker spheres) to maintain the cubic symmetry.

structure with a = 5.41 Å at room temperature (Strunz & Nickel 2001) and thus is isostructural with the cubic oxyfluorides stable at higher temperatures. The close structural relationship makes it likely that solid solution is possible between the two types of compounds. If a portion of the Ce is in the tetravalent state, the unit-cell volume would be reduced, and O would substitute for F; *i.e.*, a more general formula for the natural mineral would be $(La_{(1-y)}[Ce^{3+}_{(y-x)}Ce^{4+}_{x}])O_{(1+x)}F_{(1-x)}$. Such a possibility is not supported by the present WDS data (Table 2), which indicate F > O for håleniusite-(La). However, the general formula is in good agreement with the EDS analyses, which gave O > F, *i.e.*, $0.05 < x < 0.1$. Bastnäsite analyzed under identical conditions gave O/F = 3.01(4), which is the stoichiometric value assuming no OH substitution of F in bastnäsite (confirmed with FTIR spectroscopy), so one might conclude that the EDS analyses of håleniusite-(La) are more accurate than the WDS analyses of this mineral. As O^{2-} and F^- are isoelectronic ionic species, the question of nonstoichiometry among the anions cannot be resolved by structure refinements of intensity data obtained in ordinary X-ray-diffraction experiments. Note that the Ce-rich cubic oxyfluoride reported from Cínovec (Johan & Johan 1994) has an F-deficient composition, *ca.*

$(Ce,La)O_{1.2}F_{0.6}$, and an even smaller unit-cell volume than håleniusite-(La) (*cf.* Fig. 4).

To obtain infrared absorption data, powdered samples with håleniusite-(La) were dispersed in liquid paraffin on a CaF_2 plate. Spectra were recorded from 600 to 2000 cm^{-1} with 128 scan cycles and a spectral resolution of 4 cm^{-1}, using a FTIR microscope-spectrometer (Bruker Equinox 55). In this spectral range, and with a pure sample, there are practically no features at all (Fig. 5), which is in agreement with the absence of hydrous or carbonic components. For samples with remnants of bastnäsite present, there is a characteristic strong absorption band at *ca.* 870 cm^{-1} attributed to vibrations of the $(CO_3)^{2-}$ groups (Akhmanova & Orlova 1966).

CONDITIONS OF FORMATION

Bastnäsite has been reported as a relatively common product of alteration of REE minerals (*e.g.*, allanite and fluocerite) from localities worldwide, but there are few descriptions of minerals forming directly from the bastnäsite. In the Bayan Obo Fe–REE–Nb deposit, Smith *et al.* (1999) found evidence for reactions between apatite and bastnäsite that produced monazite, fluorite and calcite. In the case of håleniusite-(La) from Bastnäs, no reactants other than bastnäsite itself seem to be involved, and we suggest the simple reaction (La,Ce) $CO_3F \rightarrow$ (La,Ce)OF + CO_2. This model is supported by the textural relations, and the fact that the REE composition of the primary phase is inherited by håleniusite-(La). Note that the alteration process suggested is

TABLE 2. CHEMICAL COMPOSITION OF HÅLENIUSITE-(La)
OBTAINED BY WDS AND EDS SPECTROMETRY

| element | EDS | | | WDS |
| | area A | area B | oxide | |
n	46	52		7
La wt%	36.3 ± 1	37.0 ± 0.8	La_2O_3	39.29 ± 0.31
Ce	36.6 ± 0.8	35.5 ± 0.6	Ce_2O_3	39.00 ± 0.25
Pr	1.5 ± 0.7	1.3 ± 0.8	Pr_2O_3	4.06 ± 0.19
Nd	6.3 ± 0.7	6.0 ± 0.6	Nd_2O_3	7.60 ± 0.08
Sm	0.0	0.0	Sm_2O_3	0.28 ± 0.09
			Gd_2O_3	0.27 ± 0.11
			Y_2O_3	0.08 ± 0.06
			SiO_2	0.38 ± 0.06
O	9.6 ± 0.6	10.3 ± 0.6	CaO	0.02 ± 0.06
F	10.0 ± 0.8	9.8 ± 0.5	F	11.7 ± 0.5
			O = F	−4.93
Total	100.3	99.9	Total	97.75
La *apfu*	0.45	0.47		0.431
Ce	0.45	0.44		0.425
Nd	0.08	0.07		0.082
Pr	0.02	0.02		0.044
Sm				0.003
Gd				0.003
Y				0.001
Si				0.011
Ca				0.001
O	1.04	1.12		0.95
F	0.92	0.90		1.10

The compositional variations are given as standard deviations (± 1 σ); *n* is the number of points analyzed. The compositions are recast in terms of atoms per formula unit (*apfu*) on the basis of one cation.
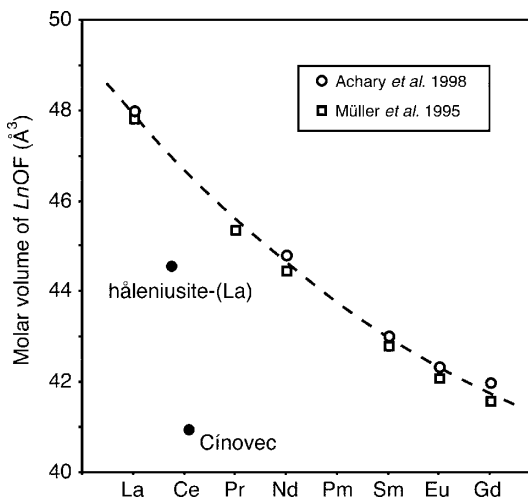

FIG. 4. Molar volumes *versus* REE composition of the oxyfluorides.

accompanied by a volume reduction of the solid phase amounting to *ca.* 38%, which explains the porosity of the aggregates (*cf.* Fig. 1).

This kind of devolatilization of a fluorocarbonate can be predicted to occur at increased temperatures from theoretical constraints on phase relations (Williams-Jones & Wood 1992), and has been verified in experimental work in the system (Ce,La)–F–H–C–O (*e.g.*, Hsu 1992). The thermal limit of stability of bastnäsite, $Ln(CO_3)F$, is sensitive to overall pressure (*P*), and in cases where Ln = Ce, to oxygen fugacity, $f(O_2)$. At P = 1 kbar, bastnäsite-(La) is stable up to 860°C, and bastnäsite-(Ce), up to 760°C [with $f(O_2)$ defined by the magnetite–hematite buffer; Hsu 1992]. Such high temperatures are not realistic when considering the geological situation, and we can thus expect that the formation of håleniusite-(La) occurred at $P \ll 1$ kbar. Ozaki *et al.* (1996) reported the complete breakdown of natural bastnäsite of an unspecified REE composition to oxyfluoride above 460°C under atmospheric conditions. Preliminary microthermometric data obtained on fluid inclusions in bastnäsite from Bastnäs (Holtstam & Broman 2002) indicate that the mineral originally crystallized slightly below 400°C.

Although secondary, the new mineral species must have formed at conditions different than those typical for late-stage assemblages with, *e.g.*, lanthanite-(Ce) and hydroxyl-bearing Cu sulfates (brocanthite, wroewolfeite, among others), that occur within the deposit. The latter are low-temperature (<100°C) minerals characteristic of a supergene environment.

A different mechanism for the formation of a REE oxyfluoride is feasible in nature. Alteration of fluocerite may proceed by hydrolysis: $Ln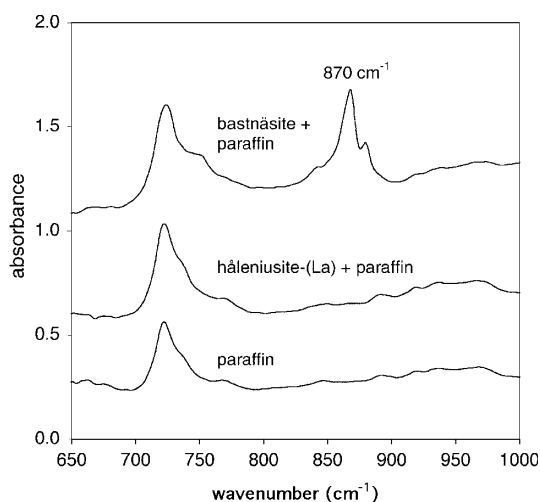F_3 + H_2O \rightarrow LnOF + 2$ HF(aq). Such a process also requires high temperatures and could be relevant in the development of a hydrothermal–magmatic system, such as the case of the complex assemblage in the Cínovec granite, as described by Johan & Johan (1994).

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FIG. 5.   Infrared spectra for liquid paraffin, håleniusite-(La) and bastnäsite.

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