# Dyrnaesite-(La) a new hyperagpaitic mineral from the Ilímaussaq alkaline complex, South Greenland

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# ABSTRACT

The new mineral, dyrnaesite-(La), is found in the Ilímaussaq alkaline complex, South Greenland. The holotype material originates from an arfvedsonite lujavrite sheet as an accessory mineral. Dyrnaesite-(La) is pale yellowish green, with no cleavage and an irregular fracture. Density is  $3.68(2)/3.682$  g/cm<sup>3</sup> (measured/ calculated). It is biaxial, negative,  $2V\alpha = 47(1)/48$  (measured/calculated);  $\alpha = 1.6226(5)$ ,  $\beta = 1.6852(10)$ ,  $\gamma = 1.6982(2)$ ;  $X = c$ ,  $Y = a$ ,  $Z = b$ . The average values of microprobe analyses are (wt.%) P<sub>2</sub>O<sub>5</sub> 37.17, SiO<sub>2</sub> 0.15, CaO 0.90, Na<sub>2</sub>O 20.06, La<sub>2</sub>O<sub>3</sub> 16.44, CeO<sub>2</sub> 20.23, Pr<sub>2</sub>O<sub>3</sub> 1.40, Nd<sub>2</sub>O<sub>3</sub> 3.47, Sm<sub>2</sub>O<sub>3</sub> 0.24, Dy<sub>2</sub>O<sub>3</sub> 0.06,  $Y_2O_2$  0.06.

The crystal structure was solved from single-crystal X-ray diffraction data. Dyrnaesite-(La) is orthorhombic, *Pnma*;  $a = 18.4662(7)$  Å,  $b = 16.0106(5)$  Å,  $c = 7.0274(2)$  Å,  $V = 2077.7(2)$  Å<sup>3</sup>,  $Z = 4$ . The structural formula calculated from the diffraction data and microprobe analysis is  $\text{Na}_{7.89}(\text{Ce}_{0.94}\text{Ca}_{0.06})_{\Sigma1.00}(\text{Ca}_{0.12}\text{La}_{1.14}\text{Ce}_{0.40}\text{Pr}_{0.10}\text{Nd}_{0.24})_{\Sigma2.00}(\text{PO}_4)_{6}$ , the simplified formula is Na<sub>8</sub>Ce<sup>4+</sup>  $REE_2(\text{PO}_4)_6$ . The crystal structure is related closely to that of vitusite-(Ce), but is distinct from it in several aspects. The five strongest lines of the powder X-ray diffraction pattern are (d Å,  $(1\%)$ , (hkl)); 6.57 (100) (101), 4.62 (40) (301, 230, 400), 3.50 (40) (331), 2.80 (86) (232, 402), 2.67 (54) (060,630).

KEYWORDS: dyrnaesite-(La), new mineral, optical properties, chemical analyses, X-ray data, vitusite, Ilímaussaq.

#### Introduction

SODIUM silicates and phosphates enriched in Zr, Ti, Nb and rare-earth elements (REE) are typical minerals in the agpaitic and hyperagpaitic nepheline syenites in the Ilímaussaq alkaline complex, South Greenland, as rock-forming minerals and in pegmatites. In this complex the hyperagpaitic minerals include semenovite-(Ce), naujakasite, vuonnemite, lomonosovite and vitusite-(Ce). Dyrnaesite-(La) is also formed under hyperagpaitic conditions.

Dyrnaesite-(La) was recorded as an unknown mineral from various lujavrite localities in the

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Ilímaussaq alkaline complex by [Buchwald and](#page-8-0) [Sørensen \(1961\)](#page-8-0) and [Sørensen \(1962\),](#page-8-0) who introduced the name 'green mineral'. Later, [Engell](#page-8-0) [\(1973\)](#page-8-0) reported the presence of dyrnaesite-(La) from sheet-like lujavrite bodies on the Taseq slope, where the mineral was found in an arfvedsonite-rich as well as an aegirine-rich lujavrite. The present investigation is based on material donated by John Engell. The mineral is chemically and structurally related closely to vitusite-(Ce) first described from the Ilímaussaq alkaline complex, South Greenland and the Lovozero alkaline massif, Kola by [Rønsbo](#page-8-0) et al. [\(1979\)](#page-8-0).

The name is after the base camp area, Dyrnæs (animal headland), north of the town of Narsaq, Kujalleq Kommune, South Greenland. The camp was used during the geological mapping of the Ilímaussaq alkaline complex in the period

1957–1983. The mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, IMA No. 2014-070. The type material is preserved in the

TABLE 1. Unit-cell data, physical and optical properties of dyrnaesite-La and vitusite-(Ce).\*

|                            | Dyrnaesite-(La)   | Vitusite- $(Ce)$ *         |
|----------------------------|---|----------------------------|
| Ideal formula              | $\text{Na}_8\text{Ce}^{4+}REE_2(\text{PO}_4)_6$                           | $Na_3REE(PO_4)$            |
| Crystallography            |   |                            |
| Space group                | Pnma  | $Pc2_1b$                   |
| a                          | 18.4662(7) Å  | $5.3356(8)$ Å              |
| h                          | 16.0106(5) Å  | 18.6722(9) Å               |
| $\overline{c}$             | 7.0274(2) Å   | 14.0546(9) Å               |
| V                          | $2077.7(2)$ Å <sup>3</sup>  | $1400.2(5)$ Å <sup>3</sup> |
| Z                          | 4   | 8                          |
| <b>Physical properties</b> |   |                            |
| Colour                     | pale yellowish green  | white                      |
| Streak                     | white   | white, pink                |
| Lustre                     | vitreous, transparent   | vitreous,<br>transparent   |
|                            | Non-fluorescent   | Non-fluorescent            |
| Hardness                   | n.d.  | 4.5                        |
| Tenacity                   | brittle   | brittle                    |
| Cleavage                   | none observed   | ${100}$ and ${010}$        |
| Fracture                   | irregular   |                            |
| Density<br>$(meas.)$ **    | $3.68(2)$ g/cm <sup>3</sup>   | 3.70 $g/cm^3$              |
| Density<br>$(calc.)$ ***   | 3.682 $g/cm^{3}$  |                            |
| <b>Optical properties</b>  |   |                            |
| optic sign                 |   |                            |
| $\alpha^{***}$             | 1.6226(5)   | 1.6038(5)                  |
| β                          | 1.6852(10)  | 1.6465(5)                  |
| γ                          | 1.6982(2)   | 1.6490(5)                  |
| $2V\alpha$ , meas.         | 47(1)   | 28.5                       |
| $2V\alpha$ , calc.         | 48  |                            |
|                            | $X=c$ , $Y=a$ , $Z=b$   | $X=a, Y=b,$<br>$Z = c$     |
| Pleochroism                | pale yellowish green<br>with the strongest<br>colour parallel to $\alpha$ |                            |
| Twinning                   | ${210}$ and ${230}$   | ${160}$ and ${120}$        |
|                            |   |                            |

\*Rønsbo et al. (1976); crystal structure data Mazzi and Ungaretti (1994) for a sub-cell.

\*\*By flotation in heavy liquids.

\*\*\*Using the empirical formula.

\*\*\*\*The refractive indices, for  $\lambda$  = 589 nm, were obtained using the microrefractometer spindle stage technique [\(Medenbach, 1985\)](#page-8-0) and under the application of the  $\lambda - T$ variation method.

mineralogical collection of the Natural History Museum, University of Copenhagen, Denmark under the specimen number 2014.53.

#### **Occurrence**

The Ilímaussaq alkaline complex belongs to the late Precambrian Gardar province of South Greenland (e.g. [Upton, 2013](#page-8-0)). The complex was emplaced in four pulses [\(Sørensen, 2006](#page-8-0)). The first pulse led to the formation of an incomplete augite syenite shell. Alkaline granites found as remnants at the top of the intrusion represent the second pulse. The major part of the complex, the layered peralkaline nepheline syenite, was presumably formed by two separate magma pulses (e.g. [Sørensen, 2006\)](#page-8-0). The roof sequence ( pulaskite, foyaite, sodalite foyaite and naujaite) was formed by downwards crystallization from the third magma pulse, whereas the kakortokite-lujavrite sequence was formed by the last. The eudialyte-bearing kakortokite forms the layered floor cumulates and grades upwards into the lujavrite. The lujavrite series is at least 500 m thick ([Sørensen](#page-8-0) et al., 2006) and represents the latest magmatic stage. Lujavrite dykes and sheets intrude and enclose naujaite rafts and the overlying sodalite foyaite and naujaite ([Sørensen](#page-8-0) et al., 2006). The characteristic agpaitic mineral, eudialyte, is present in the kakortokite and some lujavrite but is uncommon [\(Sørensen and Larsen, 2001\)](#page-8-0) in the latest formed lujavrite, where steenstrupine-(Ce) and other hyperagpaitic minerals such as vitusite- (Ce), naujakasite and vuonnemite occur.

At the Taseq slope numerous lujavrite sheets and dykes cut the naujaite. The investigated material, sample 85708III, originates from the largest and ∼10 m thick sheet ([Engell, 1973](#page-8-0)). Dyrnaesite-(La) occurs as 0.2–0.7 mm subhedral grains in a hyperagpaitic arfvedsonite lujavrite, i.e. a trachytoid melanocratic nepheline syenite. The main minerals are lath-shaped arfvedsonite, albite and microcline along with nepheline and sodalite, whereas aegirine and analcime are only present in minor amounts. Dyrnaesite-(La) is a primary late magmatic mineral and the most common REE-bearing phase in this sample making a total of 4% by modal analysis ([Engell, 1973\)](#page-8-0).

#### Descriptive mineralogy

The unit-cell data plus the physical and optical properties of dyrnaesite-(La) are listed in Table 1

<span id="page-2-0"></span>

FIG. 1. Microphotograph of dyrnaesite-(La) in thin section. Approximate size  $0.2$  mm  $\times$   $0.5$  mm.

and compared to those of vitusite-(Ce) ([Rønsbo](#page-8-0) et al.[, 1979](#page-8-0)). It is worth noting the differences between the refractive indices for dyrnaesite-(La) and vitusite-(Ce), usable for a quick identification of the minerals. A microphotograph of dynaesite is given in Fig. 1.

#### **Chemistry**

The chemical composition of dyrnaesite-(La) was established by use of the electron microprobe technique. The analyses were performed on JEOL 8200 using standards and spectral lines as described by [Rønsbo \(1989\).](#page-8-0) To diminish loss in sodium intensity and analytical inaccuracy, the analyses were performed with a defocused electron beam on  $~\sim$ 10 μm. Furthermore, the sodium determinations were made by an acceleration potential of 10 kV [\(Rønsbo](#page-8-0) et al., 1979).

Cerium can obtain both trivalent and tetravalent states in minerals, and based on the crystal structure of dyrnaesite-(La) (Balić-Žunić, 2017) and the valence balance, it is most appropriate to consider its valence state to be  $Ce^{4+}$  in this mineral. Therefore the content of this REE is listed as  $CeO<sub>2</sub>$  in [Table 2.](#page-3-0)

The analytical results for 9 grains, 63 points in total, are listed in [Table 2](#page-3-0) (analysis 1) together with a new analysis for vitusite-(Ce) from the Ilímaussaq alkaline complex (analysis 2) as well as the data published by [Rønsbo](#page-8-0) et al. (1979) (analysis 3).

The chemical similarities between the two minerals are obvious except for Na, where the difference is  $~\sim$ 4 wt.% Na<sub>2</sub>O. The empirical formulae from the microprobe analysis (based on 24 O apfu) for dyrnaesite-(La) and vistusite-(Ce) are, respectively:  $Na_{7.44}Ca_{0.19}Ce_{1.35}La_{1.16}Nd_{0.24}$  $Pr_{0.10}Sm_{0.02}Y_{0.01}(P_{6.02}Si_{0.03})O_{24}$  and  $Na_{9.00}Ca_{0.19}$  $Ce<sub>1.37</sub>La<sub>1.16</sub>Nd<sub>0.24</sub>Pr<sub>0.10</sub>Sm<sub>0.02</sub>Y<sub>0.01</sub>(P<sub>5.97</sub>Si<sub>0.03</sub>)O<sub>24</sub>.$ The valence balance confirms that Ce is tetravalent in dyrnaesite and trivalent in vitusite. The simplified formula of dyrnaesite-(La) is  $Na_8Ce^{4+}REE_2(PO_4)_6.$ 

## Crystallography

#### Powder X-ray diffraction data

Due to the alteration of dyrnaesite-(La) and inclusions of silicate minerals, it was impossible to obtain a powder X-ray diffraction pattern free of interference from other minerals. To be able to distinguish between dyrnaesite-(La) reflections and those from the alteration products and inclusions, in preliminary work a number of powder patterns were made on different dyrnaesite-(La) grains using a Guinier-Hägg camera, with quartz as the internal standard. Using this method, it was possible to exclude reflections from different silicates such as arfvedsonite, albite and microcline. The only other phosphate observed on exposures was monazite. The best powder X-ray pattern, measured on a Bruker AXS D8 diffractometer with primary  $Ge<sub>111</sub>$  monochromator in the reflection Bragg-Brentano geometry is listed in [Table 3](#page-4-0) together with data for vitusite-(Ce) for comparison.

# Single-crystal X-ray diffraction study

A crystal fragment of  $0.002$  mm<sup>3</sup> was investigated using a four-circle X-ray diffractometer equipped with a CCD detector. The crystal structure is orthorhombic,  $Pnma$ , with unit-cell parameters  $a =$ 18.4662(7) Å,  $b = 16.0106(5)$  Å,  $c = 7.0274(2)$  Å,  $V = 2077.7(2)$  Å<sup>3</sup>, Z = 4. The crystal structure was determined by direct methods and refined anisotropically to an R factor of 0.037. The refinement revealed two REE sites with equal electron numbers (55.8) but different coordinations that characterized them as a predominately  $Ce^{4+}$  site and a predominately  $La^{3+}$  site, with proportions of multiplicities of 1:2, respectively. Besides five Na sites with close to full occupancy, a sixth Na site with only 13% occupancy was identified. Taking into account the electron numbers at REE sites and their characteristics plus the occupancies of Na sites, and considering the results of electron microprobe analysis, the structural formula of dyrnaesite-(La)

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|                                | Dyrnaesite (La)                      |           |        | Vitusite-(Ce) |        |           |  |
|--------------------------------|--------------------------------------|-----------|--------|---------------|--------|-----------|--|
|                                | $[1]$                                | <b>SD</b> | $[2]$  | <b>SD</b>     | $[3]$  | <b>SD</b> |  |
| $P_2O_5$                       | 37.17                                | 0.28      | 36.44  | 0.35          | 36.27  | 0.18      |  |
| SiO <sub>2</sub>               | 0.15                                 | 0.04      | 0.17   | 0.07          | 0.25   |           |  |
| CaO                            | 0.90                                 | 0.17      | 0.92   | 0.11          | 0.92   |           |  |
| Na <sub>2</sub> O              | 20.06                                | 0.60      | 23.98  | 0.38          | 23.15  | 0.49      |  |
| La <sub>2</sub> O <sub>3</sub> | 16.44                                | 0.34      | 16.22  | 0.44          | 15.56  | 0.36      |  |
| CeO <sub>2</sub>               | 20.23                                | 0.36      |        |               |        |           |  |
| Ce <sub>2</sub> O <sub>3</sub> |                                      |           | 19.28  | 0.22          | 19.95  | 0.11      |  |
| Pr <sub>2</sub> O <sub>3</sub> | 1.40                                 | 0.21      | 1.37   | 0.18          | 1.24   |           |  |
| Nd <sub>2</sub> O <sub>3</sub> | 3.47                                 | 0.15      | 3.36   | 0.13          | 4.39   |           |  |
| $Sm_2O_3$                      | 0.24                                 | 0.13      | 0.24   | 0.10          | n.a.   |           |  |
| $Dy_2O_3$                      | 0.06                                 | 0.08      | 0.06   | 0.08          | n.a.   |           |  |
| $Y_2O_3$                       | 0.06                                 | 0.04      | 0.05   | 0.03          | n.a.   |           |  |
| Total                          | 100.18                               |           | 102.09 |               | 101.73 |           |  |
|                                | Number of cations based on 24 O apfu |           |        |               |        |           |  |
| P                              | 6.02                                 |           | 5.97   |               | 5.98   |           |  |
| Si                             | 0.03                                 |           | 0.03   |               | 0.05   |           |  |
| Ca                             | 0.19                                 |           | 0.19   |               | 0.19   |           |  |
| Na                             | 7.44                                 |           | 9.00   |               | 8.74   |           |  |
| La                             | 1.16                                 |           | 1.16   |               | 1.12   |           |  |
| Ce                             | 1.35                                 |           | 1.37   |               | 1.42   |           |  |
| Pr                             | 0.10                                 |           | 0.10   |               | 0.09   |           |  |
| Nd                             | 0.24                                 |           | 0.24   |               | 0.31   |           |  |
| Sm                             | 0.02                                 |           | 0.02   |               | n.a.   |           |  |
| Dy                             | 0.00                                 |           | 0.00   |               | n.a.   |           |  |
| Y                              | 0.01                                 |           | 0.01   |               | n.a.   |           |  |

<span id="page-3-0"></span>TABLE 2. Microprobe analysis of dyrnaesite-(La) and vitusite-(Ce).

[1] Dyrnaesite-(La),  $n = 63$ ; [2] Vitusite-(Ce), type material from Ilímaussaq alkaline complex, this paper,  $n = 36$ ; [3] Vitusite-(Ce), type material from Ilímaussaq alkaline complex (Rønsbo et al., 1979).

SD – standard deviation; n.a. – not analysed.

results as  $Na_{7.89}(Ce_{0.94}Ca_{0.06})_{\Sigma1.00}(La_{1.14}Ce_{0.40}Pr_{0.10}$  $Nd_{0.24}Ca_{0.12}\Sigma_{2.00}(PO_4)_6$ . Although there is more Ce than La in the summary chemical formula, the REE suffix for the mineral is (La), because Ce is predominantly concentrated in the specific  $Ce<sup>4+</sup>$  site where no significant presence of other REE is expected or observed, whereas La dominates in the site occupied by all *REE* species.

The crystal structure is related closely to that of vitusite-(Ce) ([Mazzi and Ungaretti, 1994](#page-8-0)). There are four main differences in the crystallography and crystal structures of the two minerals:

(1) Dyrnaesite-(La) has a 1.5 times larger unit cell compared to the sub-cell, or 3/16 of the 8x super-cell of vitusite-(Ce) ([Mazzi and Ungaretti,](#page-8-0) [1994\)](#page-8-0). The corresponding directions of the crystal lattices are  $a_d = b_v$ ,  $b_d = 3a_v$ ,  $c_d = 1/2c_v$  (subscripts indicating dyrnaesite-(La) and vitusite-(Ce) sub-cell, respectively).

(2) The symmetries of the two structures belong to different space groups (Pnma and  $Pc2_1b$ , respectively). Compared to dyrnaesite-(La), vitusite-(Ce) lacks the  $m$  mirror planes (100) [(010) in dyrnaesite-(La) orientation] and has the c glides instead. The symmetry is correspondingly lower and belongs to the  $m2m$ and not the *mmm* class. This means that also [100] and [001] ([010] and [001] in dyrnaesite-(La) orientation)  $2<sub>1</sub>$  axes and (010) ((100) in dyrnaesite-(La) orientation)  $n$  glides present in dyrnaesite-(La) are missing in vitusite-(Ce). The higher symmetry in dyrnaesite-(La) is especially expressed in the  $Ce^{4+}$  site in the structure which lies in the Wyckoff position 4c. Also, two of the P sites, two full Na sites, a predominantly vacant Na site and four O sites lie at 4c positions. Vitusite-(Ce) has no atoms with this coordination symmetry because it lacks mirror planes.

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# <span id="page-4-0"></span>TABLE 3. Powder diffraction data for dyrnaesite-(La), compared to vitusite-(Ce).

(continued)





\*Rønsbo et al. (1979), measured on a Guinier-Hägg camera.

(3) The vacancies in dyrnaesite-(La), concentrated in one of the Na sites, make the fundamental difference in the chemical formulae of the two minerals.

(4) Vitusite-(Ce) shows super-lattices with  $5a$ ,  $8a$ and 11a super-cell periods. No satellite reflections and thus no super-lattices or modulations of the crystal structure are observed for dyrnaesite-(La).

The details of the crystal structure analysis and the full description of the crystal structure can be found in Balić-Žunić [\(2017\)](#page-8-0).

#### Alterations of dyrnaesite-(La)

Dyrnaesite-(La) is typically altered, but the degree varies from grain to grain, and in the same thin section unaltered grains can be found together with almost completely altered ones.

Back-scattered electron images of a grain showing the characteristic alteration features are given in Fig.  $2a$  and b. The primary dyrnaesite-(La) is altered initially to a homogeneous Ca bearing

<span id="page-6-0"></span>REE-phosphate with a total oxide sum of 85.9% (the rest is supposed to be  $H_2O$ ) and a  $(REE + Ca)/P$ ratio of 1.0 [\(Table 4](#page-7-0), analysis 1). The mineral probably belongs to the rhabdophane group, REE  $(PO<sub>4</sub>)·nH<sub>2</sub>O$ . However, the observed total is lower than for rhabdophane-(Ce), where the expected total should be ∼93% in accordance with the general formula  $REE(PO<sub>4</sub>) \cdot 1H<sub>2</sub>O$ .

Rhabdophane analysis with a low total has been described by Göb et al. [\(2011\)](#page-8-0) and explained by porosity. But our back-scattered electron image (Fig. 2b) shows no porosity, suggesting an unknown hydrated La, Ce phosphate having the general formula  $REE(PO<sub>4</sub>) \cdot nH<sub>2</sub>O$ ,  $n = 1.9$ . This phase is penetrated by veins of a younger generation of alteration (Fig. 2b), most probably an intergrowth of two phases having a maximum grain size of ∼1 µm. This intergrowth also encircles the former dyrnaesite-(La) grain (Fig. 2b). The composition of this mixture is listed in [Table 4](#page-7-0), analysis 2. The determined oxide total is 90.3% and the analysis corresponds to  $(Ca + REE)/P$  ratio on 0.99. The chemical data indicate that the crystals with the highest mean atomic number are rhadophane-(Ce) (Fig. 2b). Alteration of vitusite-(Ce) to a mixture of rhabdophane and monazite has been described by Pekov et al. [\(1997\),](#page-8-0) and they concluded, that the pseudomorph called erikite- (Ce), established as a mineral species by [Bøggild](#page-8-0) [\(1903\)](#page-8-0), is formed by alteration of vitusite-(Ce) at a late stage in the evolution of the Ilímaussaq alkaline complex due to falling alkalinity. Our results show that the erikite-like alteration products could just as well be an alteration after dyrnaesite-(La).

Clusters of monazite are found in lujavrite from several localities in the Ilímaussaq alkaline complex [\(Danø and Sørensen, 1959\)](#page-8-0), and they suggested that monazite was a secondary phase formed after decomposition of eudialyte. In the investigated samples from the Taseq slope, two different types of monazite clusters are found. In the one type, monazite occurs as anhedral grains intergrown with dyrnaesite- (La) and its alteration products [\(Fig. 3](#page-7-0) and [Fig. 4\)](#page-7-0). In the second type of clusters, monazite is lath-formed [\(Fig. 3](#page-7-0)), and dyrnaesite-(La) is not observed. The two types of monazite can also be distinguished by their chemical composition. Whereas the Th content is  $\leq 0.1$  wt.% ThO<sub>2</sub> in monazite intergrown with dyrnaesite-(La) [\(Table 4](#page-7-0), analysis 3), the content varies between 9.3 and 0.6 wt.% ThO<sub>2</sub> [\(Table 4](#page-7-0), analysis 4) in the lath-shaped monazite. [Engell \(1973\)](#page-8-0) mentioned the presence of steenstrupine-(Ce) in some of the investigated lujavrites, and [Rønsbo](#page-8-0) et al. (1979) described co-existing steenstrupine-(Ce) and vitusite- (Ce) from another locality in the Ilímaussaq alkaline complex. This suggests that the Th-rich monazite clusters represent altered steenstrupine-(Ce) and not dyrnaesite-(La).



FIG. 2. Back-scattered electron images of dyrnaesite-(La). (a) Typical altered dyrnaesite-(La) with hydrated REE phosphate and monazite. (b) Enlarged segment of [Fig. 1](#page-2-0)a, showing the relationship between unaltered dyrnaesite-(La),  $REE(PO<sub>A</sub>)$ <sup>1</sup>.9H<sub>2</sub>O and intergrowth of two *REE* phosphate minerals. The phase with the highest mean atomic number might be rhabdophane-(Ce).

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|                                | $[1]$  | SD.  | $[2]$ | SD   | $[3]$  | SD.  | [4]    | SD.  |
|--------------------------------|--|------|-------|------|--------|------|--------|------|
| $P_2O_5$                       | 29.67  | 0.19 | 29.82 | 0.68 | 31.52  | 0.23 | 29.37  | 0.75 |
| SiO <sub>2</sub>               | 1.18   | 0.03 | 1.33  | 0.17 | 0.04   | 0.04 | 1.98   | 0.55 |
| CaO                            | 7.61   | 0.10 | 4.64  | 0.53 | 0.12   | 0.09 | 0.10   | 0.08 |
| Na <sub>2</sub> O              | 0.87   | 0.06 | 0.55  | 0.10 | n.d.   |      | n.d.   |      |
| La <sub>2</sub> O <sub>3</sub> | 19.13  | 0.52 | 21.50 | 0.66 | 28.68  | 1.17 | 23.34  | 1.10 |
| Ce <sub>2</sub> O <sub>3</sub> | 21.63  | 0.26 | 25.53 | 0.94 | 32.73  | 0.63 | 33.34  | 0.97 |
| Pr <sub>2</sub> O <sub>3</sub> | 1.49   | 0.50 | 2.10  | 0.38 | 2.20   | 0.23 | 2.55   | 0.31 |
| Nd <sub>2</sub> O <sub>3</sub> | 3.74   | 0.19 | 4.39  | 0.16 | 5.27   | 0.51 | 6.62   | 0.58 |
| ThO <sub>2</sub>               | n.a.   |      | n.a.  |      | 0.06   | 0.08 | 2.84   | 1.03 |
| FeO                            | 0.08   | 0.12 | n.d.  |      | n.d.   |      | 0.04   | 0.04 |
| $\text{Al}_2\text{O}_3$        | 0.46   | 0.06 | 0.42  | 0.08 | n.d.   |      | n.d.   |      |
| Total                          | 85.86  |      | 90.28 |      | 100.62 |      | 100.18 |      |
|                                | Number of cations based on $1.0 P + Si$ apfu |      |       |      |        |      |        |      |
| $\mathbf{P}$                   | 0.95   |      | 0.95  |      | 1.00   |      | 0.93   |      |
| Si                             | 0.05   |      | 0.05  |      | 0.00   |      | 0.07   |      |
| Ca                             | 0.31   |      | 0.19  |      | 0.00   |      | 0.00   |      |
| Na                             | 0.07   |      | 0.04  |      | 0.00   |      | 0.00   |      |
| La                             | 0.27   |      | 0.30  |      | 0.40   |      | 0.32   |      |
| Ce                             | 0.30   |      | 0.36  |      | 0.45   |      | 0.45   |      |
| Pr                             | 0.02   |      | 0.03  |      | 0.03   |      | 0.03   |      |
| Nd                             | 0.05   |      | 0.06  |      | 0.07   |      | 0.09   |      |
| Th                             | n.a.   |      | n.a.  |      | n.d.   |      | 0.09   |      |
| Fe                             | 0.00   |      | 0.00  |      | n.d.   |      | 0.00   |      |
| Al                             | 0.02   |      | 0.02  |      | n.d.   |      | n.d.   |      |

<span id="page-7-0"></span>TABLE 4. Microprobe analysis of hydrated REE phosphates and monazite.

[1] Hydrated REE-phosphate, [Fig. 1](#page-2-0)b,  $n = 6$ ; [2] intergrowth of two REE phosphates, Fig. 1b,  $n = 6$ ; [3] Th-free monazite,  $n = 15$ ; [4] Th-bearing monazite,  $n = 4$ .

SD – standard deviation; n.a. not analysed; n.d. not detected.



FIG. 3. Back-scattered electron image of dyrnaesite-(La) with inclusions of anhedral monazite and two clusters with lath-formed monazite.



Monazite Partly altered dyrnaesite-(La)

FIG. 4. Back-scattered electron image of altered dyrnaesite-(La) with clusters of anhedral monazite.

## <span id="page-8-0"></span>Conclusion

Due to close compositional and structural relationships, it is difficult to distinguish dyrnaesite-(La) and vitusite-(Ce) on the basis of chemical analysis, and very difficult to distinguish them on the grounds of their powder diffraction patterns, especially if they appear in mixtures with other minerals and/or if they are measured with a diffractometer with lower resolution than the one used in this work or in the original description of vitusite-(Ce) [\(Table 3](#page-4-0)). Interplanar spacings for the main diffraction maxima of the two minerals are slightly larger for vitusite-(Ce). In addition, some of the prominent diffraction maxima in vitusite-(Ce) are split, whereas they closely overlap in dyrnaesite-(La). This is observed for maxima at 4.62, 3.86, 2.80, 2.67 and 1.930 Å in dyrnaesite-(La) to which correspond pairs with d values  $4.66 + 4.63$ ,  $3.89 + 3.87$ ,  $2.81 +$ 2.80,  $2.69 + 2.67$  and  $1.945 + 1.935$  Å in vitusite-(Ce). Apart from this, the two minerals could be distinguished by the presence or absence of some weak maxima which are forbidden in the counterpart. In this way, diffraction maxima with  $k \neq 3n$ from the dyrnaesite-(La) pattern do not have counterparts in vitusite-(Ce), whereas the diffraction maxima of vitusite-(Ce) with  $l = 2n + 1$  do not have equivalents in dyrnaesite-(La). Due to small differences in powder patterns, it might be necessary to use single-crystal diffraction to classify a specimen as dyrnaesite-(La) or vitusite-(Ce). Unit-cell parameters, space-group symmetry and the presence of satellite reflections along the  $a^*$  axis in vitusite-(Ce) and their absence in dyrnaesite-(La), are clearly distinguishing characteristics of the two minerals.

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