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**Parisite-(Nd), ideally  $\text{CaNd}_2(\text{CO}_3)_3\text{F}_2$ , a new mineral from Bayan Obo  
Fe-Nb-REE deposit, Inner Mongolia, China**

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**Abstract**

Parisite-(Nd) (IMA2024-013), ideally  $\text{CaNd}_2(\text{CO}_3)_3\text{F}_2$ , as the Nd-dominant analogue of parisite-(Ce), occurs in dolomitic marble in the Bayan Obo Fe-Nb-REE deposit, Inner Mongolia, China. It is associated with calcite, aegirine, magnetite, hematite, fluorite, riebeckite, bastnäsite-(Ce), barite, aeschynite-(Ce), aeschynite-(Nd), monazite, and parisite-(Ce). Parisite-(Nd) occurs as subhedral to anhedral irregular grains from 0.02 mm to 1 mm. Parisite-(Nd) is transparent, yellowish-brown color, with pale yellow streak and displays vitreous to resinous lustre. Cleavage is distinct on pseudo-{001}; fracture is uneven, or conchoidal. The Mohs hardness is 4 to 5, and it is brittle. Calculated density of parisite-(Nd) is 4.357 g/cm<sup>3</sup>. Parisite-(Nd) is pseudo-uniaxial (+),  $\omega = (1.679)$ ,  $\varepsilon = (1.754)$ . The empirical formula is  $(\text{Ca}_{0.945}\text{Fe}_{0.058}\text{Sr}_{0.015}\text{Ba}_{0.007})_{\Sigma 1.025}(\text{Nd}_{0.967}\text{Ce}_{0.529}\text{La}_{0.191}\text{Pr}_{0.137}\text{Gd}_{0.070}\text{Sm}_{0.029}\text{Th}_{0.022}\text{Y}_{0.016}\text{Nb}_{0.011}\text{Ho}_{0.003})_{\Sigma 1.975}(\text{CO}_3)_3\text{F}_{1.893}\text{OH}_{0.023}$ . The Raman spectrums of parisite-(Nd) are observed strong and sharp peaks at 1113, 1090, 825, 635 and 1608 cm<sup>-1</sup> and moderate to weak bands centered at 255, 392, 739, 924, 1183, 1228, 1296, 1640, 2247, 2924 and 3065 cm<sup>-1</sup>. X-ray powder diffraction and TEM studies give the following results: monoclinic, space group: *Cc* (# 9),  $a = 12.3283(13)$  Å,  $b =$

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7.1185(4) Å,  $c=28.4633(37)$  Å,  $\beta = 98.529(14)^\circ$ ,  $V = 2470.28(42)$  Å<sup>3</sup>,  $Z = 12$ .

**Keywords:** parisite-(Nd), new mineral, Ca-REE fluorocarbonate, Bayan Obo deposit, Inner Mongolia, China

## Introduction

Parisite-(Nd) is a new member mineral in calcium-rare earth element (Ca-REE) fluorocarbonates. So far, four mineral species have been discovered in the Ca-REE fluorocarbonate mineral series (Donnay and Donnay, 1953). Bastnäsite, REECO<sub>3</sub>F and synchysite, CaREE(CO<sub>3</sub>)<sub>2</sub>F are considered as the end members of this polysomatic mineral series. Parisite, CaREE<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>F<sub>2</sub>, and röntgenite, CaREE<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>F<sub>2</sub> are considered as intermediate members (Ni *et al.*, 1993; Wu *et al.*, 1998; Zeug *et al.*, 2021). Rare earth elements are easy to replace each other in mineral crystal structures because of their similar properties. Cerium is the most common rare element in Ca-REE fluorocarbonates. All the Ce-dominant analogues including bastnäsite-(Ce), röntgenite-(Ce), synchysite-(Ce) and parisite-(Ce) have been found in nature. The La-dominant analogues of bastnäsite-(La) and parisite-(La), Nd-dominant analogues of bastnäsite-(Nd) and synchysite-(Nd), Y-dominant analogues of bastnäsite-(Y) and synchysite-(Y) are also reported (Smith *et al.*, 1960; Vainshtein *et al.*, 1961; Mineev *et al.*, 1970; Scharm and Kühn, 1983; Miyawaki *et al.*, 2013; Menezes Filho *et al.*, 2018). Parisite-(Nd) is the Nd-dominant analogue of parisite-(Ce) and parisite-(La).

Parisite-(Ce) has generated considerable interest because of its economic importance as the primary source rare earth elements for industrial use (Morteani, 1991). Parisite-(Ce), as one of the most common rare earth minerals, was first reported by J.J. Paris in 1835 from the emerald mine at Muzo in Colombia, South America (Warren and Palache, 1911). It occurs as an accessory mineral in differentiated alkalic massifs, granite pegmatites, and REE-rich carbonatites. It distributes in many localities, for example the carbonatite orebody of Mountain Pass, California (Castor, 2008), the carbonatite complex Amba Dongar, India (Doroshkevich *et al.*, 2009), the alkaline granite-syenite pegmatites of the Mount Malosa pluton in Malawi (Guastoni *et al.*, 2010), the ultramafic lamprophyre-carbonatite complex near Delitzsch, Germany (Seifert *et al.*, 2000),

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the Bayan Obo Fe–Nb–RE deposit, Inner Mongolia, China (Zhang and Tao, 1986). It has been reported with a chemical composition of  $\text{Ca}_{1.02}(\text{Ce}_{0.94}\text{La}_{0.50}\text{Nd}_{0.37}\text{Pr}_{0.10}\text{Sm}_{0.05})_{\Sigma=1.96}(\text{CO}_3)_3\text{F}_{1.51}$  from Muso mine Colombia (NMNH no. 122145)(Ni *et al.*, 2000). The crystal structure of parisite-(Ce) was once controversial. In an earlier study, its structure was defined as hexagonal symmetry with space group  $R\bar{3}$ ,  $a=7.18 \text{ \AA}$ ,  $c=8.41 \text{ \AA}$  (Donnay and Donnay, 1953). Until the work of Ni *et al.* (2000), the crystal structure of parisite-(Ce) was refined to monoclinic symmetry with space group  $C2/c$  or  $Cc$  and unit cell of  $a = 12.305(2)$ ,  $b = 7.1053(5)$ ,  $c = 28.250(5) \text{ \AA}$ , and  $\beta = 98.257(14)^\circ$ . Parisite-(La) only discovered in the Mula mine, Brazil has been approved as a new mineral (IMA2016-031) with chemical composition of  $\text{Ca}_{0.98}(\text{La}_{0.83}\text{Nd}_{0.51}\text{Ce}_{0.37}\text{Pr}_{0.16}\text{Sm}_{0.04}\text{Y}_{0.03})_{\Sigma=1.94}\text{C}_{3.03}\text{O}_{8.91}\text{F}_{2.09}$  and crystal structure of monoclinic (pseudo-trigonal), space group:  $C2$ ,  $Cm$ , or  $C2/m$ ,  $a = 12.356(1) \text{ \AA}$ ,  $b = 7.1368(7) \text{ \AA}$ ,  $c = 28.299(3) \text{ \AA}$ ,  $\beta = 98.342(4)^\circ$ ,  $V = 2469.1(4) \text{ \AA}^3$  and  $Z = 12$  (Menezes Filho *et al.*, 2018). Parisite-(Nd) was once reported in Bayan Obo deposit in the literature, but only REE assemblage information was provided, and no complete chemical compositions and crystal structure were given (Zhang and Tao, 1986). So it is not officially recognized by IMA CNMNC list (Jambor *et al.*, 1988).

Now parisite-(Nd) has been approved as a new mineral species by the Commission of New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2024-013) (Bosi *et al.*, 2024). Type material is deposited in the collections of the National Research Center for Geoanalysis, Baiwanzhuang Street 26, Beijing, People's Republic of China (holotype), catalogue Number NRCGA2024001, and the Geological Museum of China, Yangrouhutong Street 15, Xicheng District, Beijing, People's Republic of China, catalogue number GMCTM2024003 (cotype).

## Occurrence

Parisite-(Nd) was found in dolomitic marble in the Bayan Obo Fe-Nb-REE deposit, 130 km north of the city of Baotou, Inner Mongolia, China. Bayan Obo deposit is hosted by Palaeo- to Mesoproterozoic sedimentary rocks of the Bayan Obo Group (Nie *et al.*, 2002; Liu *et al.*, 2022). It comprises six formations, Dulahala Formation (H<sub>1</sub>-H<sub>3</sub>), Jianshan Formation (H<sub>4</sub>-H<sub>5</sub>), Halahuoqite Formation (H<sub>6</sub>-H<sub>8</sub>), Bilute Formation (H<sub>9</sub>-H<sub>10</sub>), Baiyinbaolage Formation (H<sub>11</sub>-H<sub>12</sub>), and Hujiertu Formation (H<sub>13</sub>-H<sub>18</sub>) (Ling *et al.*, 2012; Yang *et al.*, 2017) (Fig.1).

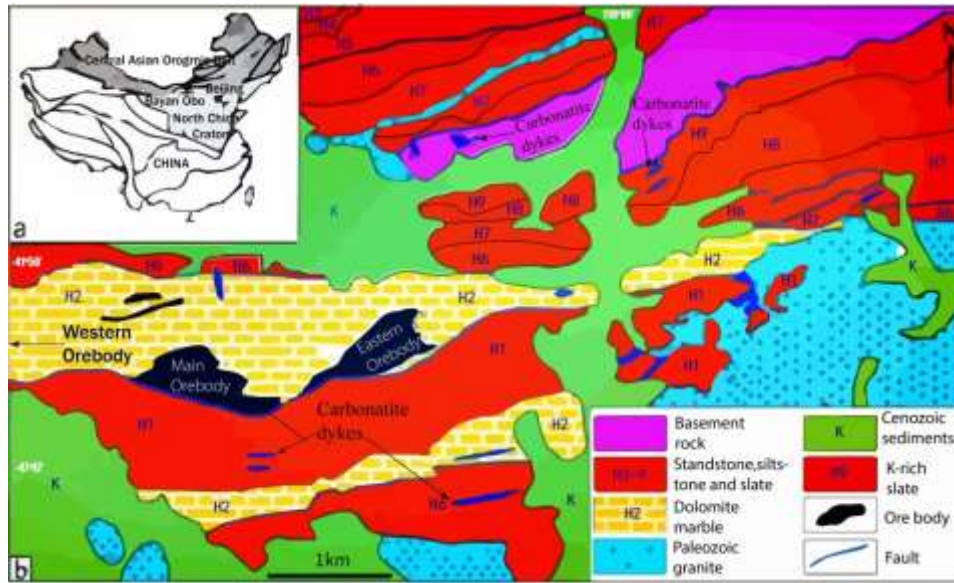


Figure 1. Geological sketch map of the Bayan Obo REE-Nb-Fe deposit (modified from [Ling et al., 2013](#); [Liu et al., 2022](#))

The specimens were picked up in magnetite ores within H8 formation in the eastern part of the mine ( $109^{\circ}57.666'E$ ,  $41^{\circ}47.951'N$ ) ([Fig.2](#)). Parisite-(Nd) was associated with calcite, aegirine, magnetite, hematite, fluorite, riebeckite, bastnäsite-(Ce), barite, aeschynite-(Ce), aeschynite-(Nd), monazite, and parisite-(Ce). The ore-forming mechanism of Bayan Obo deposits is still controversial. There are many different viewpoints on mineralization age including (1) Mesoproterozoic to Neoproterozoic, 1360-789 Ma; (2) Caledonian, 485-386 Ma; (3) Hercynian, 277-255 Ma ([Yuan, 2012](#); [Xie et al., 2019](#)). The models on the genesis of the Bayan Obo REE deposit include: (1) genetically related to carbonatite magmatism; (2) hydrothermal alteration of carbonate sedimentary rocks; (3) carbonatite volcanic eruptions and so on ([Ren et al., 1994](#); [Smith, 2007](#); [Zhu et al., 2015](#); [Yang et al., 2017](#)). The formation of REE mineralized dolomite might be related to interaction and reaction between the carbonatite magmas and/or associated fluids with sedimentary carbonate rocks, with the REE-bearing carbonatite magmas having undergone intense fractionation enrichment process ([Yang et al., 2024](#)). Parisite-(Nd) might be a product of bimetasomatism Ca-Mg-carbonate rock and/or carbonatite, and Na-, F-rich postmagmatic hydrothermal solutions.



Figure 2. The outcrop of specimen on which the new mineral parisite-(Nd) was found from main ore of Bayan Obo REE-Nb-Fe ore deposit

### **Appearance, physical and optical properties**

Parisite-(Nd) occurs as subhedral to anhedral irregular grains from 0.02mm to 1mm in maximum dimension. The a:b:c ratio calculated from unit-cell parameters is 1: 0.5774: 2.3088. Parisite-(Nd) shows thin, tabular and hexagonal crystal habits, but most of the grains are broken and fractured. Parisite-(Nd) is transparent, yellowish-brown color (Fig.3), with pale yellow streak. It displays vitreous to resinous lustre. It has no fluorescence under shortwave (254nm) and longwave (366nm) ultraviolet radiation. The Mohs hardness is between 4 and 5, which is estimated from comparison with fluorite and parisite-(Ce). Cleavage is distinct on pseudo-{001} and parting was not observed. The fracture is uneven, or conchoidal, and the mineral tenacity is brittle. Density was not measured due to the limited crystals available and nanometric crystal size. The calculated density is  $4.357 \text{ g/cm}^3$  on the basis of empirical formula and unit-cell volume from powder XRD data.

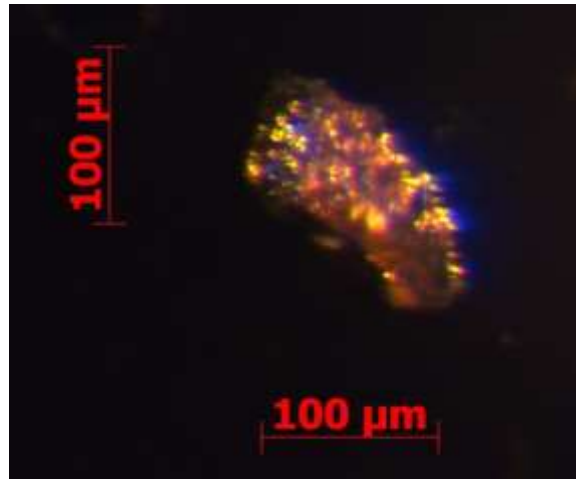


Figure 3. A microscopic view of yellowish-brown parasite-(Nd)

Under the polarizing microscope (Fig.4), parasite-(Nd) is colorless to brownish yellow in transmitted light with weak pleochroism. The other main optical characteristics of parasite-(Nd) are parallel extinction, interference color from third-order bluish yellow to fourth-order white, uniaxial and optically positive. In transmitted light parasite-(Nd) is colourless, pseudo-uniaxial (+),  $\omega = (1.679)$ ,  $\varepsilon = (1.754)$  (the value not determined, data referenced from Zhang and Tao, 1986). The pleochroism is invisible.

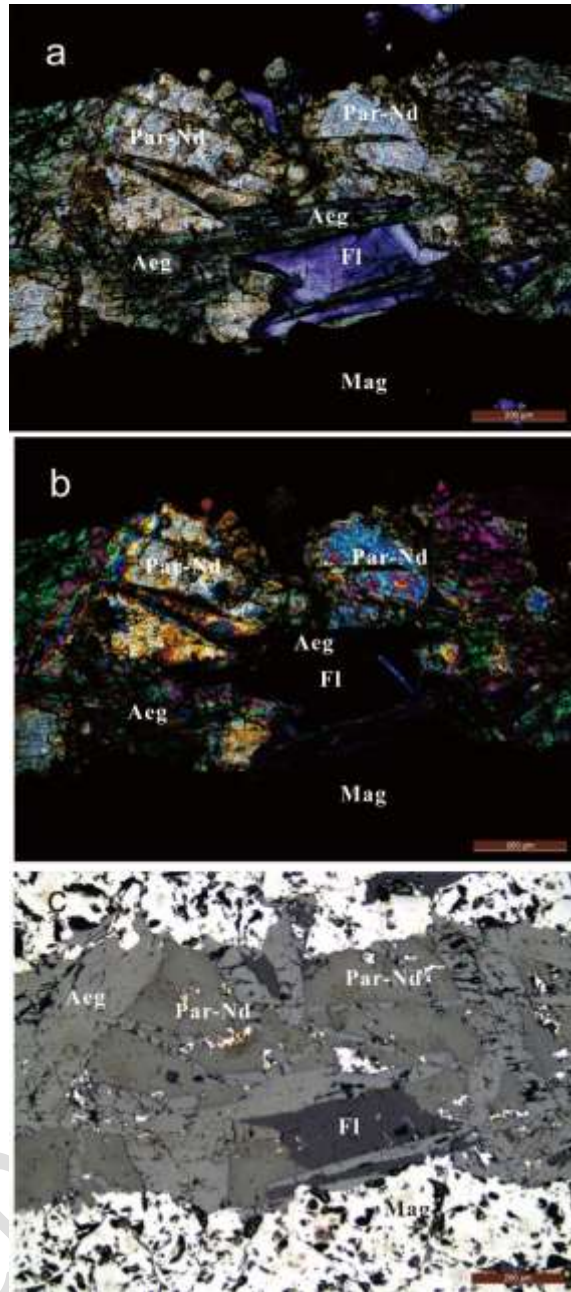


Figure 4. Photomicrographs of parisite-(Nd) (Par-Nd) associated with fluorite (Fl), aegirine (Aeg) and magnetite (Mag). (a) transmitted light; (b) cross polarized light; (c) reflected light

### Raman Spectroscopic characterization

The Raman spectrum of parisite-(Nd) between 100 and 3600  $\text{cm}^{-1}$  was recorded using a Renishaw inVia Reflex system, using a solid-state laser with a wavelength of 532 nm and a thermoelectric cooled CCD detector, with 1  $\text{cm}^{-1}$  resolution and a spot size of 2  $\mu\text{m}$  and compared with associated bastnäsite-(Ce) and parisite-(Ce) (Fig. 5).

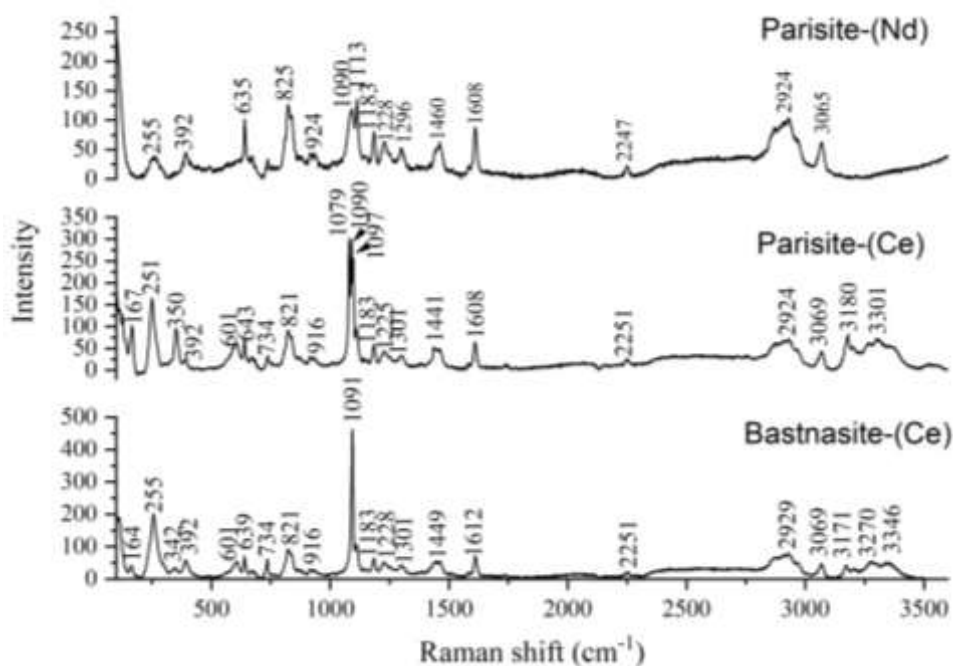


Figure 5. Raman spectra of parisite-(Nd) with comparison to parisite-(Ce) and bastnäsite-(Ce)

The strong and sharp peaks of parisite-(Nd) are observed at 1113, 1090, 825, 635 and 1608  $\text{cm}^{-1}$  and moderate to weak bands centered at 255, 392, 739, 924, 1183, 1228, 1296, 1640, 2247, 2924 and 3065  $\text{cm}^{-1}$ . The Raman spectrum of parisite-(Nd) is similar with the spectra of parisite-(Ce) and bastnäsite-(Ce), but the vibration of  $\text{CO}_3^{2-}$  show some different. The  $\text{CO}_3^{2-}$  complex exhibits four internal vibrational modes: (1) a symmetric stretching vibration ( $\nu_1$ ), (2) an out-of-plane bending vibration ( $\nu_2$ ), (3) a doubly degenerate asymmetric stretching vibration ( $\nu_3$ ) and (4) in-plane bending vibration ( $\nu_4$ ) (White, 1974). The most intense Raman band is assigned to  $\nu_1$  vibration at  $\sim 1100 \text{ cm}^{-1}$ . The vibration spectrum of the  $(\text{CO}_3)^{2-}$  in bastnäsite-(Ce) is relatively symmetrical, and the  $\nu_1$  Raman scattering peak is located at  $1091 \text{ cm}^{-1}$ . The  $\nu_1$  Raman band is split into three bands at  $\sim 1079 \text{ cm}^{-1}$ ,  $\sim 1090 \text{ cm}^{-1}$  and  $\sim 1097 \text{ cm}^{-1}$  in parisite-(Ce), while two bands at  $\sim 1090 \text{ cm}^{-1}$  and  $\sim 1113 \text{ cm}^{-1}$  in parisite-(Nd). These differences of  $\nu_1$  Raman spectrum of fluorinated carbonates are probably dependent on the chemical compositions (Frost and Dickfos, 2007). The band assigned to the  $\nu_2(\text{CO}_3)^{2-}$  vibration is supposed to locate at  $\sim 924 \text{ cm}^{-1}$  and  $\sim 825 \text{ cm}^{-1}$  in parisite-(Nd), which is a little higher than the band positions at  $\sim 916 \text{ cm}^{-1}$  and  $\sim 821 \text{ cm}^{-1}$  in parisite-(Ce) and bastnäsite-(Ce). The parisite-(Nd) spectrum shows  $\nu_3(\text{CO}_3)^{2-}$  vibration band at ca.  $1460 \text{ cm}^{-1}$  in comparison with  $1441 \text{ cm}^{-1}$  in parisite-(Ce) and  $1449 \text{ cm}^{-1}$  in bastnäsite-(Ce). The bands in the range of  $600\sim 740 \text{ cm}^{-1}$  are supposed to be classified as the  $\nu_4$



bending mode. A sharp intensity band is observed at  $635\text{ cm}^{-1}$  in parisite-(Nd), and two bands are observed at  $\sim 601\text{ cm}^{-1}$  and  $\sim 643\text{ (639)}\text{ cm}^{-1}$  in parisite-(Ce) and bastnäsite-(Ce). A weaker peak at  $\sim 739\text{ cm}^{-1}$  or  $\sim 734\text{ cm}^{-1}$  is observed in three samples. The positions of the  $\nu_4$  bands perhaps show the divergence of ionic radius of the Nd and Ce cation in the carbonate structure. A number of low wavenumber bands are observed for parisite-(Nd) at  $\sim 392\text{ cm}^{-1}$  and  $\sim 255\text{ cm}^{-1}$ . These two bands and another two bands around  $350\text{ (342)}\text{ cm}^{-1}$  and  $167\text{ (164)}\text{ cm}^{-1}$  are also observed in the Raman spectra of parisite-(Ce) and bastnäsite-(Ce). These bands are described as lattice modes involving halogen and F (Frost and Dickfos, 2007). The Raman spectrum of all three fluoro-carbonate minerals in the  $2800\text{ to }3500\text{ cm}^{-1}$  spectral range is reported in Figure 5. Raman bands are observed at  $2924$  and  $3065\text{ cm}^{-1}$ . These bands are attributed to water stretching vibrations (Frost *et al.*, 2013). For parisite-(Nd) OH units are likely to replace F in a complex structure.

### Chemical composition

The chemical composition of parisite-(Nd) was studied with a JXA-iHP200F electron microprobe, operating in wavelength-dispersive mode with excitation voltage of 15kV, specimen beam current 20nA, and  $5\text{ }\mu\text{m}$  beam diameter. The analytical data of 13 spots with ranges and standards employed are given in Table 1. There is insufficient material for a direct determination of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Thus, the calculation of the empirical formula was done in following steps: (1) calculation of the REE site cations/Ca site cations ratio; (2) when REE site cations/Ca site cations =2, the normalization of the empirical formula to 3 cations (REE site cations + Ca site cations); (3) calculation of the OH content (in apfu) from charge balance considering  $3\text{ CO}_3^{2-}$  groups and the calculated F content. The  $\text{CO}_2$  was calculated to 24.44 wt% for charge neutrality. The empirical formula is  $(\text{Ca}_{0.945}\text{Fe}_{0.058}\text{Sr}_{0.015}\text{Ba}_{0.007})_{\Sigma 1.025}(\text{Nd}_{0.967}\text{Ce}_{0.529}\text{La}_{0.191}\text{Pr}_{0.137}\text{Gd}_{0.070}\text{Sm}_{0.029}\text{Th}_{0.022}\text{Y}_{0.016}\text{Nb}_{0.011}\text{Ho}_{0.003})_{\Sigma 1.975}(\text{CO}_3)_3\text{F}_{1.893}\text{OH}_{0.023}$ . The simplified formula is  $\text{Ca}(\text{Nd,Ce,La,Pr,Gd})_2(\text{CO}_3)_3\text{F}_2$ . The ideal formula is  $\text{CaNd}_2(\text{CO}_3)_3\text{F}_2$ , which requires (wt. %) CaO 10.26%,  $\text{Nd}_2\text{O}_3$  61.56%, F 6.95%,  $\text{CO}_2$  24.16%,  $\text{O}=\text{F}-2.93$ , total 100 wt.%. The ratio of rare earth to calcium is close to 2: 1. Neodymium plays an absolutely dominant role in rare earth elements, and this feature is different from parisite-(Ce) and parisite-(La).

Table 1. Chemical data (in wt %) for parisite-(Nd)

Constituent	Mean	Range	Stand. Dev. ( $\sigma$ )	Reference Material
F	6.60	5.26-7.70	0.60	topaz
La <sub>2</sub> O <sub>3</sub>	5.70	4.78-6.73	0.58	LaP <sub>5</sub> O <sub>14</sub>
Ce <sub>2</sub> O <sub>3</sub>	15.93	12.80-17.33	1.41	CeP <sub>5</sub> O <sub>14</sub>
Pr <sub>2</sub> O <sub>3</sub>	4.14	3.58-4.47	0.25	PrP <sub>5</sub> O <sub>14</sub>
Nd <sub>2</sub> O <sub>3</sub>	29.81	25.94-31.68	1.69	NdP <sub>5</sub> O <sub>14</sub>
Sm <sub>2</sub> O <sub>3</sub>	0.94	0.70-1.20	0.17	SmP <sub>5</sub> O <sub>14</sub>
Gd <sub>2</sub> O <sub>3</sub>	2.33	1.82-3.14	0.44	GdP <sub>5</sub> O <sub>14</sub>
Ho <sub>2</sub> O <sub>3</sub>	0.09	0-0.27	0.08	HoP <sub>5</sub> O <sub>14</sub>
Y <sub>2</sub> O <sub>3</sub>	0.33	0.11-0.51	0.13	YP <sub>5</sub> O <sub>14</sub>
CaO	9.71	8.45-10.67	0.64	wollastonite
FeO	0.77	0-2.41	0.59	fayalite
SrO	0.28	0.06-0.40	0.10	celestine
ThO <sub>2</sub>	1.07	0.25-2.76	0.78	ThO <sub>2</sub>
Nb <sub>2</sub> O <sub>5</sub>	0.28	0-1.12	0.30	KNbO <sub>3</sub>
BaO	0.19	0-1.83	0.50	barite
H <sub>2</sub> O*	0.21			
CO <sub>2</sub> *	24.44			
-O=F	2.77			
<b>Total</b>	<b>100.05</b>			

\* H<sub>2</sub>O and CO<sub>2</sub> from formula calculation.

## Crystallography

The crystal structure of parisite-(Nd) sample could not be determined by single-crystal X-ray studies due to the nature of nanometric crystals aggregate and its structural complexity. Therefore, the X-ray powder diffraction and selected-area electron diffraction were, instead, carried out for the crystallographic characterization.

X-ray powder diffraction data were collected with a Rigaku Xtalab Synergy single-crystal diffractometer (CuK $\alpha$  radiation) in Gandolfi powder mode at 50kV and 1mA. The unit-cell parameters were refined using the program by [Holland and Redfern \(1997\)](#). A monoclinic unit cell of parisite-(Ce) by [Ni \*et al\* \(2000\)](#) was referenced to index the diffraction spots. Unit cell parameters refined from the powder data are as follows: monoclinic symmetry with space group *Cc* (# 9),  $a = 12.3283(13)$ ,  $b = 7.1185(4)$  Å,  $c = 28.4633(37)$  Å,  $\beta = 98.529(14)^\circ$ ,  $V = 2470.28(42)$  Å<sup>3</sup>,  $Z = 12$ .

The complete X-ray powder diffraction data of parisite-(Nd) is shown in [Table 2](#) and compared with parisite-(Ce) and parisite-(La) in [Figure 6](#). Based on the obtained XRD patterns of

parisite-(Nd), the results show that these values are in agreement with the measured  $d$ -spacings for parisite-(Ce), with most of the absolute value of difference less than 0.02 Å. The diagnostic reflexes with  $d$ -values (Å) of 14.336, 6.926, 4.720, 3.558, 2.835, 2.056, 1.959 and 1.880 for parisite are recognized. The interplanar spacings in  $c$  axis direction of parisite-(Nd) have some difference with those of parisite-(Ce) due to the substitution of Nd to Ce.

Table 2. X-ray powder diffraction data ( $d$  in Å,  $I$  in %) for parisite-(Nd)

$h$	$k$	$l$	$I_{\text{cal}}$	$I_{\text{meas}}$	$d_{\text{cal}}$	$d_{\text{meas}}$
<b>0</b>	<b>0</b>	<b>2</b>	<b>100.0</b>	<b>75</b>	<b>14.074</b>	<b>14.336</b>
<b>0</b>	<b>0</b>	<b>4</b>	<b>38.9</b>	<b>28</b>	<b>7.037</b>	<b>6.926</b>
<b>0</b>	<b>0</b>	<b>6</b>	<b>73.2</b>	<b>61</b>	<b>4.691</b>	<b>4.720</b>
$\bar{3}$	<b>1</b>	<b>1</b>	<b>78.1</b>	<b>80</b>	<b>3.559</b>	<b>3.558</b>
0	2	4	10.3	22	3.176	3.114
<b>0</b>	<b>2</b>	<b>6</b>	<b>53.4</b>	<b>100</b>	<b>2.836</b>	<b>2.835</b>
$\bar{3}$	<b>3</b>	<b>1</b>	<b>47.4</b>	<b>43</b>	<b>2.055</b>	<b>2.056</b>
<b>0</b>	<b>2</b>	<b>12</b>	<b>24.5</b>	<b>39</b>	<b>1.959</b>	<b>1.959</b>
<b>3</b>	<b>3</b>	<b>5</b>	<b>19.4</b>	<b>29</b>	<b>1.881</b>	<b>1.880</b>
0	4	0	9.9	14	1.780	1.777
6	2	4	12.0	20	1.662	1.663
3	3	11	8.1	10	1.544	1.542
6	2	10	6.1	8	1.415	1.415
$\bar{3}$	5	1	3.8	8	1.345	1.350
9	1	3	5.0	16	1.292	1.291
3	3	17	3.5	12	1.243	1.245

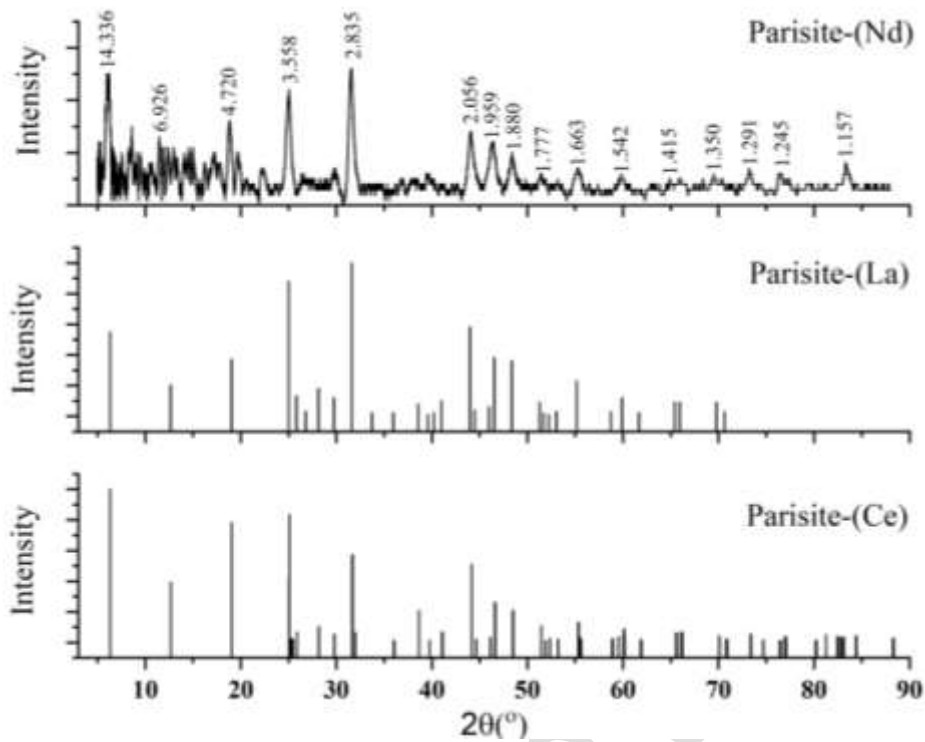


Figure 6. Powder X-ray diffraction patterns of parisite-(Nd) in this work with comparison to parisite-(Ce) (Ni *et al.*, 2000) and parisite-(La) (Menezes Filho *et al.*, 2018)

For TEM studies, two perpendicular TEM foils of about 80nm thickness were prepared with a FEI Scois 2 focus ion beam (FIB) device at Beijing SHRIMP Center, Institute of Geology, Chinese Academy of Geological Sciences, and analyzed by a JEM-2100 (HR) Transmission Electron Microscope equipped with a double-tilt holder, a Gatan digital camera, and an INCA Energy TEM100 energy-dispersive spectroscopy instrument at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, operated at 200 kV. Images of one foil and its location in polished section before cutting are shown in Figure 7. Before TEM testing on parisite-(Nd), the TEM instrument underwent camera constant calibration using a standard polycrystalline gold sample. Following calibration, the camera constant was determined to be  $L\lambda = 9.26 \text{ mm}\cdot\text{\AA}$ . Six different SAED patterns were acquired along two distinct Kikuchi lines within the same area of one TEM foil and simulated in Kikuchi maps using SingleCrystal program (Figure 8 and 9), while three different SAED patterns (Figure 10) were captured along a Kikuchi line in another TEM foil.

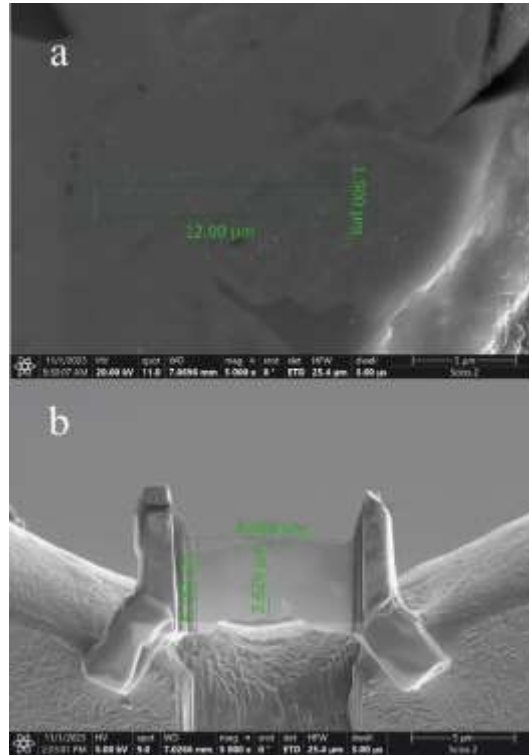


Figure 7. Images of TEM foil of parasite-(Nd) by FIB sampling for SAED analysis

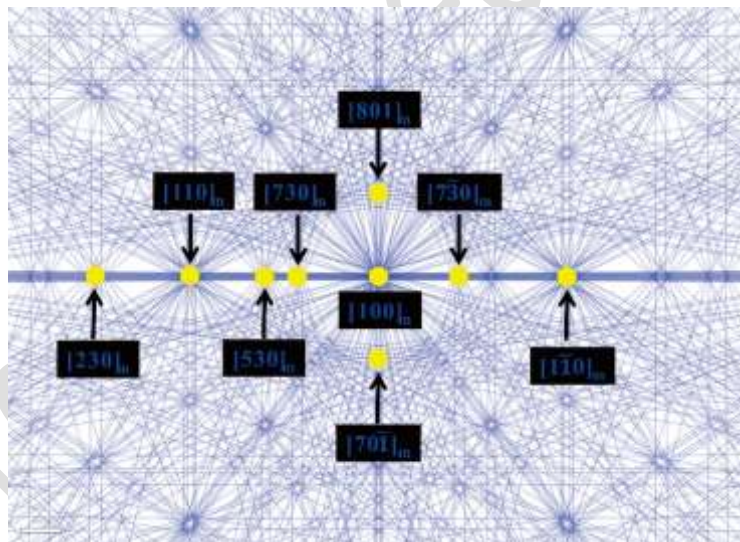


Figure 8. Kikuchi map of parasite-(Nd) simulated using SingleCrystal software (Palmer, 2015). The labeled Kikuchi poles in the diagram correspond to the zone axes of SAED patterns in

Figure 9

The solid angles calculated from the patterns match with the patterns generated from the structure of parasite-(Ce) (Fig.9). A series of SAED patterns were taken along two kikuchi lines. Figure 9 shows the SAED patterns and the indices of the diffraction spots of zones  $[100]$ ,  $[7\bar{3}0]$ ,  $[1\bar{1}0]$ ,  $[730]$ ,  $[801]$  and  $[70\bar{1}]$ , which conform to the monoclinic symmetry of parasite-(Ce). Figure

10 shows the SAED patterns of the diffraction spots of zones [001], [809] and [403]. We also measured the angles between adjacent planes in the SAED patterns of parisite-(Nd). The measured angles of parisite-(Nd) agree well with the calculated angles of parisite-(Ce), with the absolute value of difference less than  $1^\circ$  (Table 3).

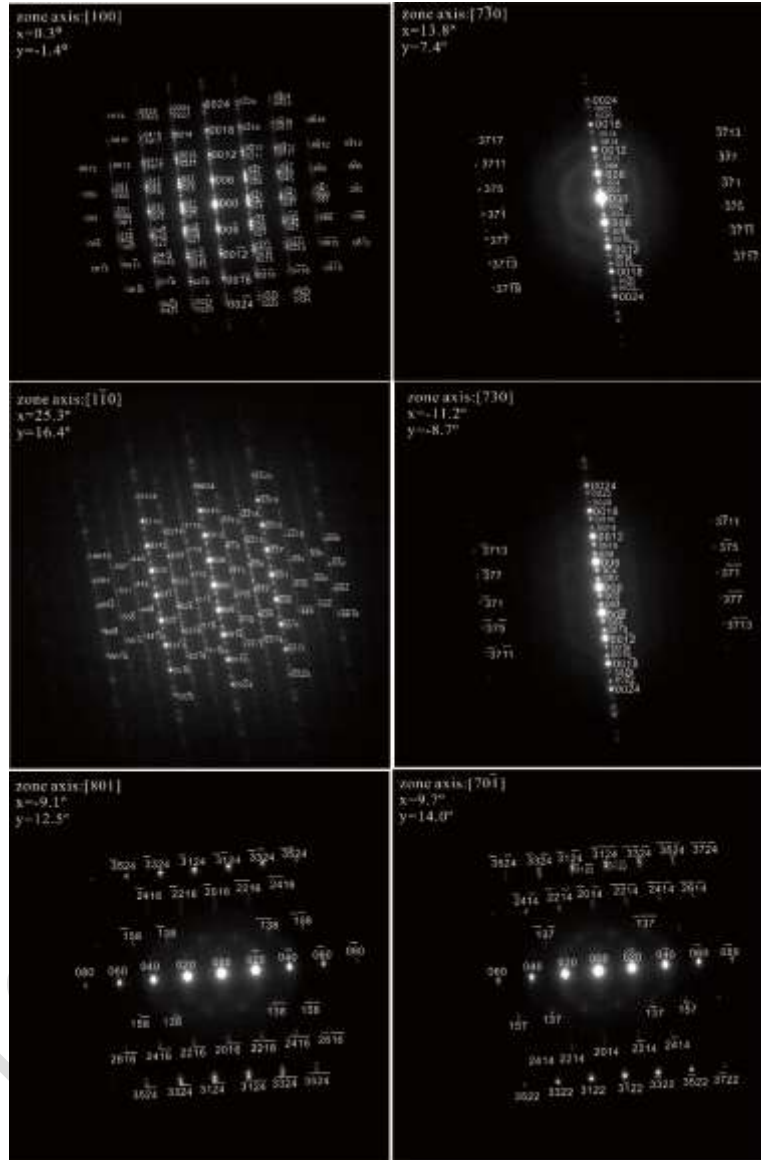


Figure 9. SAED patterns of parisite-(Nd) from 6 different zone axes around [001] axis with the diffraction spots of zones [100],  $[7\bar{3}0]$ ,  $[1\bar{1}0]$ , [730], [801] and  $[70\bar{1}]$

Table 3. Measured angles of parisite-(Nd) in comparison with calculated angles of parisite-(Ce)

Planes ( <i>hkl</i> )	Angle between planes	
	Measured	Calculated
(006)/(0 $\bar{2}$ 0)	90	90
(006)/(0 $\bar{2}$ 6)	53.24	52.67
(0 $\bar{2}$ 0)/(0 $\bar{2}$ 6)	36.94	37.33

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(006)/(37 $\bar{1}$ )	89.56	90.03
(006)/(375)	77.89	78.08
(37 $\bar{1}$ )/(375)	11.67	11.94
(006)/( $\bar{1}\bar{1}\bar{3}$ )	60.66	59.55
(006)/( $\bar{1}\bar{1}\bar{9}$ )	28.59	27.65
(006)/( $\bar{3}\bar{3}\bar{1}$ )	90.55	89.95
(006)/( $\bar{3}\bar{3}\bar{7}$ )	67.12	66.20
(00 $\bar{6}$ )/( $\bar{3}\bar{7}\bar{1}$ )	90.44	90.03
(00 $\bar{6}$ )/( $\bar{3}\bar{7}\bar{5}$ )	78.65	78.08
(020)/( $\bar{3}\bar{1}\bar{2}\bar{4}$ )	99.07	99.31
(020)/( $\bar{3}\bar{1}\bar{2}\bar{4}$ )	80.87	80.69
(020)/( $\bar{3}\bar{1}\bar{2}\bar{2}$ )	99.50	99.32
(020)/( $\bar{3}\bar{1}\bar{2}\bar{2}$ )	80.51	80.68

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Measured = measured values based on the SAED patterns of parisite-(Nd) in Figure 9, Calculated = calculated values based on the cell parameters of parisite-(Ce) (Ni *et al.*, 2000)

Parisite-(Nd) is the Nd-dominant analogue of parisite-(Ce), as demonstrated by the consistency between their chemical compositions, powder X-ray diffraction data and TEM results. The ionic radius of Nd<sup>3+</sup> is 0.983 Å, which is close to the ionic radius of Ce<sup>3+</sup> (1.01 Å), and La<sup>3+</sup> (1.032 Å) (Shannon 1976). The rare elements occupy the same position in the parisite crystal structure. So parisite-(Nd) is believed to have the same structure as parisite-(Ce) (Ni *et al.*, 2000).

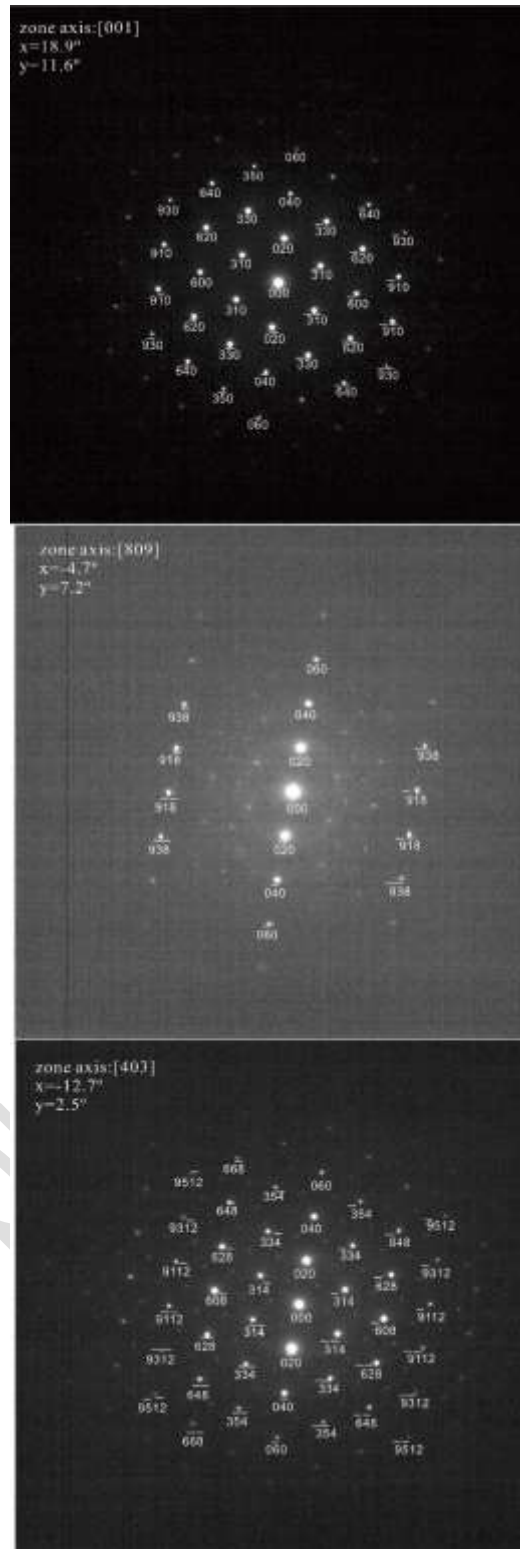


Figure 10. SAED patterns of parisite-(Nd) of the diffraction spots of zones [001], [809] and [403]



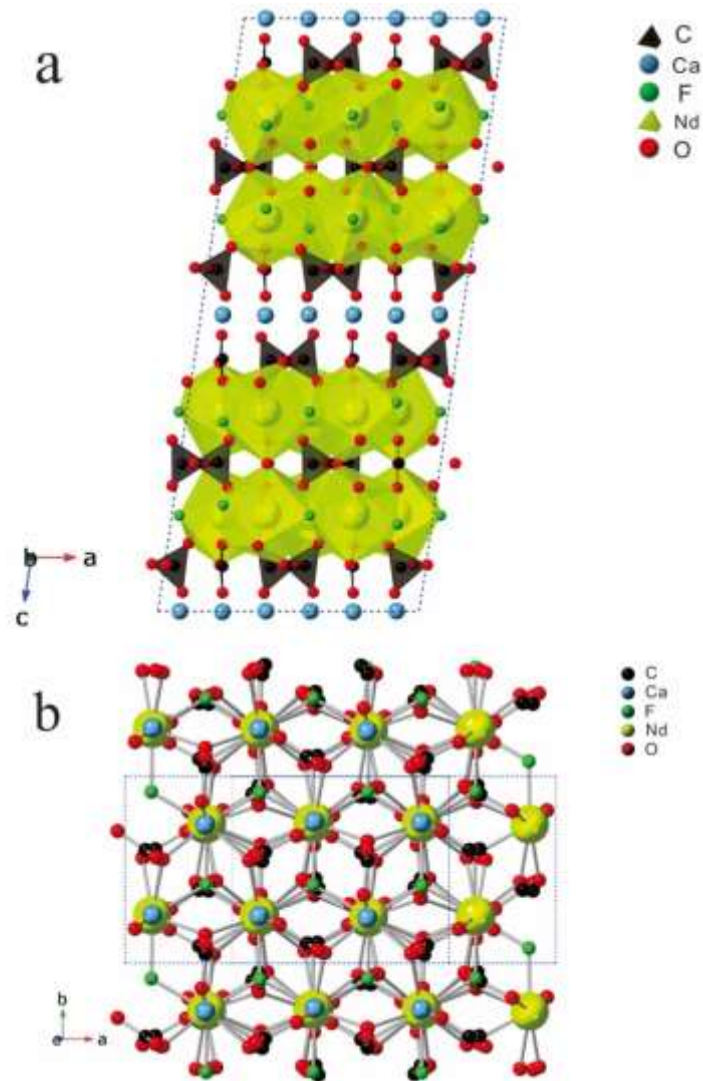


Figure 11. The crystal structure of parisite-(Nd) modified from parisite-(Ce) by [Ni \*et al\* \(2000\)](#) using CrystalMaker software ([Palmer, 2015](#))

## Discussion

As a member of Ca-REE fluocarbonate minerals, minerals chemically or structurally related to parisite-(Nd) including bastnäsite, synchysite, and röntgenite are shown in [Table 4](#) and [Table S1](#). The structure of Ca-REE fluocarbonate family of minerals has been described quantitatively in terms of layers parallel to (001) of the hexagonal or monoclinic cell. There are some ways to describe the structure of Ca-REE fluocarbonate family of minerals. The mostly used notation is proposed to use two end members bastnäsite (*B*) and synchysite (*S*) for the characterization of layer sequences in fluorcarbonate minerals ([Van Landuyt and Amelinckx, 1975](#); [Meng \*et al.\*, 2001a](#); [Meng \*et al.\*, 2001b](#)). Another way for the interpretation of the stacking sequence can be

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defined in terms of vaterite (V) and bastnäsite (B) (Ciobanu et al., 2017; Capitani et al., 2019; Capitani et al., 2020). The structure can also be described in terms of four layers parallel to (001): a REEF structural layer (*d*), a layer of CO<sub>3</sub> groups between two REEF layers (*e*), a layer of Ca (*f*), and a layer of CO<sub>3</sub> groups between calcium and REEF layers (*g*) (Donnay and Donnay, 1953).

The structure of parisite-(Nd) is regarded as the intermediate product composed of 1:1 ratio of B and S or 2:1 ratio of B and V or *dedgfg* structure along the (001) plane (Figure 11a) (Donnay and Donnay, 1953). Referring to the structure of parisite-(Ce), Nd atoms coordinate to three F atoms in the same (001) layer and six O atoms, three from the neighboring (CO<sub>3</sub>) groups on each side. Ca atoms coordinate with eight O atoms, four from each adjoining (CO<sub>3</sub>) layer; the six shorter Ca-O bonds form a regular octahedron (Figure 11b). The parisite-(Nd) structure consists of stacked (001) layers of the Nd polyhedra and Ca polyhedra. The polyhedra within the layers share edges, and the polyhedra between the layers are connected by apical oxygen atoms and by vertically oriented carbonate groups (Ni et al., 2000).

Not only the nature of the nanometric crystals aggregate of the parisite-(Nd) sample, but also structural complexity makes its crystal structure very difficult to determine. Because the X-ray diffraction power of F, O and C atoms is very weak, it is difficult to calculate the structure factor. In addition, a variety of syntactic intergrowth, polytypes, polysomatic faults, polytypic disorder and twinning have been also found in parisite-(Ce) as well as in parisite-(Nd) in our observation, which brought great difficulties in analysis of X-ray studies (Wu and Meng, 2000; Meng et al., 2001a, 2001b; Ciobanu et al., 2017; Capitani, 2019). Taking parisite-(Ce) as an example, its structure was defined with space group *R3*, *a*=7.18 Å, *c*=8.41 Å in the early study (Donnay and Donnay, 1953). Until the work of Ni et al (2000), the crystal structure of parisite-(Ce) was refined to space group *C2/c* or *Cc* with unit cell of *a* = 12.305(2), *b* = 7.1053(5), *c* = 28.250(5) Å, and  $\beta$  = 98.257(14)°. In this study, it was proposed for the first time that the common 6R polytype of parisite was not found, and it may be 2M polytype. Capitani et al (2019) proposed the discovery of a new polytype with C1 space group may be 2M<sub>2</sub>, and believed that rhombohedral symmetry in parisite was wrong. The structure of parisite-(La) proved the result of simulation calculation with Ni et al (2000)'s work. However, due to inclusions of synchysite, röntgenite or bastnäsite microblocks, no new structure was determined for parisite-(La) (Hålenius et al., 2016; Menezes Filho et al., 2018). In our study, we tried to analyse several particles of parisite-(Nd) many times

on a Rigaku Xtalab Synergy-DS 4-circle diffractometer with CuK $\alpha$  radiation but failed. The X-ray powder diffraction and selected-area electron diffraction were, instead, carried out for the crystallographic characterization to prove the structure of parisite-(Nd) analogue of parisite-(Ce).

Table 4. Minerals and phases chemically/structurally related to parisite-(Nd)

Mineral	Formula	Crystal system	Space group	Cell parameters					Reference
				<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>Z</i>	
Parisite-(Nd)	CaNd <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> F <sub>2</sub>	Monoclinic	<i>Cc</i>	12.3283	7.1185	28.4633	98.529	12	This study
Parisite-(Ce)	Ca(Ce,La) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> F <sub>2</sub>	Monoclinic	<i>Cc</i>	12.3049	7.1056	28.2478	98.2416	12	Donnay and Donnay, 1953
Parisite-(La)	CaLa <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> F <sub>2</sub>	Monoclinic	<i>C2<sub>1</sub></i> , <i>Cm</i> , <i>C2<sub>2</sub></i> / <i>m</i>	12.356	7.1368	28.299	98.342	12	Ni <i>et al.</i> , 2000
Synchysite-(Ce)	Ca(Ce,La)(CO <sub>3</sub> ) <sub>2</sub> F	Monoclinic	<i>C2<sub>1</sub></i> / <i>c</i>	12.329	7.110	18.741	102.68	12	Menezes Filho <i>et al.</i> , 2018
Synchysite-(Nd)	Ca(Nd,La)(CO <sub>3</sub> ) <sub>2</sub> F	Orthorhombic		4.039	6.984	54.27		12	Wang <i>et al.</i> , 1994
Synchysite-(Y)	Ca(Y,Ce)(CO <sub>3</sub> ) <sub>2</sub> F	Monoclinic	<i>C2<sub>1</sub></i> / <i>c</i>	12.039	6.950	18.436	102.45	12	Scharm and Kühn, 1983
Röntgenite-(Ce)	Ca <sub>2</sub> (Ce,La) <sub>3</sub> (CO <sub>3</sub> ) <sub>5</sub> F <sub>3</sub>	Trigonal	<i>R3</i>	7.13		69.4		9	Smith <i>et al.</i> , 1960
Bastnäsit-(Ce)	(Ce,La)(CO <sub>3</sub> )F	Hexagonal	<i>P6<sub>3</sub></i> / <i>c</i>	7.118		9.762		6	Donnay and Donnay, 1953
									Palache <i>et al.</i> , 1951

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Bastnäsite-(La)	(La, Ce)(CO <sub>3</sub> )F	Hexagonal 1	$P\bar{6}2c$				Ni <i>et al.</i> , 1993 Vainsht ein <i>et al.</i> , 1961 Miyaw aki <i>et al.</i> , 2013 Mineev <i>et al.</i> , 1970
Bastnäsite-(Nd)	Nd(CO <sub>3</sub> )F	Hexagonal 1	$P\bar{6}2c$	7.079 2	9.721	6	
Bastnäsite-(Y)	Y(CO <sub>3</sub> )F	Hexagonal 1	$P\bar{6}2c$	6.57	9.48	6	

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## Figure captions

Figure 1. Geological sketch map of the Bayan Obo REE-Nb-Fe deposit (modified from Ling *et al.*, 2013; Liu *et al.*, 2022)

Figure 2. The outcrop of specimen on which the new mineral parisite-(Nd) was found from main ore of Bayan Obo REE-Nb-Fe ore deposit

Figure 3. A microscopic view of yellowish-brown parisite-(Nd)

Figure 4. Photomicrographs of parisite-(Nd) (Par-Nd) associated with fluorite (Fl), aegirine (Aeg) and magnetite (Mag). (a) transmitted light; (b) cross polarized light; (c) reflected light

Figure 5. Raman spectra of parisite-(Nd) with comparison to parisite-(Ce) and bastnäsite

Figure 6. Powder X-ray diffraction patterns of parisite-(Nd) in this work with comparison to parisite-(Ce) (Ni *et al.*, 2000) and parisite-(La) (Menezes Filho *et al.*, 2018)

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[403]

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