

## PINK LANTHANITE-(Nd) FROM WHITIANGA QUARRY, COROMANDEL PENINSULA, NEW ZEALAND

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### ABSTRACT

Lanthanite-(Nd) occurs in tuffaceous, altered andesitic agglomerate in the Whitianga quarry, Coromandel Peninsula, New Zealand. The usual platy habit is represented, together with more unusual blocky equant crystals. The former show the new forms {201}, {102} and {111}, and the latter, {111}. ICP-MS analyses show that the distribution of REE (and Ga) is consistent with the formulation  $(\text{Nd}_{0.63}\text{La}_{0.59}\text{Ce}_{0.35}\text{Pr}_{0.15}\text{Sm}_{0.10}\text{Gd}_{0.069}\text{Y}_{0.06}\text{Eu}_{0.03}\text{Dy}_{0.02}\text{Ga}_{0.01})_{\Sigma 2.04}(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ ; the REE sum of 2.04 is due solely to rounding errors. The find represents the first occurrence of this rare mineral in New Zealand. The mineral formed under comparatively oxidizing conditions. The REE are probably scavenged by warm waters circulating through underlying greywackes of the Manaia Hill Group. We also characterized the lanthanite-(Nd) by X-ray diffraction (powder method) and Raman spectroscopy.

*Keywords:* lanthanite-(Nd), rare-earth elements, composition, X-ray diffraction, Raman spectroscopy, Coromandel Peninsula, New Zealand.

### SOMMAIRE

Nous décrivons la lanthanite-(Nd) présente dans un agglomérat andésitique tuffacé altéré à la carrière de Whitianga, péninsule de Coromandel, en Nouvelle-Zélande. L'habitus en plaquettes habituel y est développé, ainsi qu'une morphologie plus inhabituelle en blocs. Les plaquettes montrent les formes {201}, {102} et {111}, et les cristaux en blocs, {111}. Les analyses effectuées par l'approche ICP-MS révèlent une distribution des terres rares (et Ga) qui concorde avec la formule  $(\text{Nd}_{0.63}\text{La}_{0.59}\text{Ce}_{0.35}\text{Pr}_{0.15}\text{Sm}_{0.10}\text{Gd}_{0.069}\text{Y}_{0.06}\text{Eu}_{0.03}\text{Dy}_{0.02}\text{Ga}_{0.01})_{\Sigma 2.04}(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ ; la somme des terres rares supérieure à 2.00 est due aux erreurs d'arrondi. Il s'agit du premier exemple de cette espèce rare en Nouvelle-Zélande. La lanthanite-(Nd) s'est formée en milieu relatif-

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vemen oxydant. Les terres rares auraient été lessivées par de l'eau tiède circulant au travers des roches andésitiques sous-jacentes du Groupe de Manaia Hill. Nous nous sommes aussi servis de la diffraction X (méthode des poudres) et de la spectroscopie de Raman pour caractériser la lanthanite-(Nd).

(Traduit par la Rédaction)

*Mots-clés:* lanthanite-(Nd), terres rares, composition, diffraction X, spectroscopie de Raman, péninsule de Coromandel, Nouvelle-Zélande.

## INTRODUCTION

Minerals of the lanthanite group,  $(\text{REE})_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ , are rare secondary species typically formed by the alteration or weathering of other minerals carrying the rare-earth elements (REE) (Anthony *et al.* 2003). Various REE can dominate the metal site. So far, lanthanite-(La), lanthanite-(Nd) and lanthanite-(Ce) have been formally described (Coutinho 1955, Ansell *et al.* 1976, Cesbron *et al.* 1979, Roberts *et al.* 1980, Bevins *et al.* 1985, Atencio *et al.* 1989, Coimbra *et al.* 1989).

In 2001, one of the authors (R.M.) discovered bright pink, thin bladed crystals in the Whitianga quarry, Coromandel Peninsula, New Zealand. At first, these were thought to be barite, but XRD and EDS analyses proved that they are in fact members of the lanthanite group.

In this paper, we present new X-ray-diffraction, laser Raman and ICP-MS analytical data on lanthanite from this occurrence, which broadens the existing worldwide dataset on this rare species, and we tentatively suggest the conditions necessary for its crystallization. A chemical analysis of the REE distribution using ICP-MS methods showed that  $\text{Nd} > \text{La} > \text{Ce} > \text{Pr} > \text{Sm} > \text{Gd} \approx \text{Y}$ , and thus the material is formally lanthanite-(Nd).

## GEOLOGICAL SETTING

Whitianga quarry (also known as McCleods quarry) is located near Whitianga, Coromandel Peninsula, New Zealand ( $36^\circ 51.8' \text{ S}$ ,  $175^\circ 37.8' \text{ E}$ ; Fig. 1). The Coromandel Peninsula forms part of the Late Cenozoic Hauraki volcanic region of New Zealand's North Island. It is considered to be a precursor to the presently active Taupo Volcanic Zone, which lies to the southeast (Adams *et al.* 1994). The oldest units on the Coromandel Peninsula are the Late Jurassic low-grade metagreywacke sequences of the Manaia Hill Group (Adams *et al.* 1994). On top of this folded basement were deposited Oligocene and Early Miocene sedimentary sequences, with the latter (the Colville Formation and Waitemata Group) recording the onset of volcanism. From detailed mapping of the Coromandel Peninsula, Skinner (1976, 1993) distinguished three groups of volcanic rocks, the Coromandel (andesitic to dacitic; 18.0–7.6 Ma), Whitianga (predominantly rhyolitic; 10.0–5.3 Ma) and Kerikeri groups (basaltic to andesitic; 9.1–4.6 Ma; see also Adams *et al.* 1994).

The quarry exposes andesitic lavas and volcaniclastic rocks belonging to the Beesons Island Volcanic Suite, part of the Coromandel Group. These have been extensively altered hydrothermally to various propylitic, argillic and siliceous assemblages, and have been dated at 13.9–15.5 Ma (Adams *et al.* 1994). Recent geophysical investigations by Malengreau *et al.* (2000) point to the existence of a major Late Miocene rhyolitic caldera (15 km diameter) in the region, centered on Whitianga.

The Beesons Island Volcanic Suite at the quarry consists of an alternating sequence of andesitic lavas and agglomerates (Telford & Caryer 2005). Fine- to medium-grained massive andesite is exposed at the quarry base and appears to have filled a former valley. This is covered by a layer of volcanic agglomerate 20–25 meters thick consisting of clasts of andesite and metasedimentary rocks in a hydrothermally altered ash. This is overlain in turn by another andesitic lava flow up to 20 meters thick and a second layer of agglomerate, 2–3 meters thick. The uppermost layer consists of andesitic lava some 10–15 meters thick.

Andesite exposed at the quarry is generally massive and microporphyrific, and fractures easily owing to pervasive argillic alteration along joint and fracture planes. Fine-grained pyrite occurs as joint and fracture linings. The lanthanite was found in a single block of andesite some  $2 \text{ m}^3$  in size, lying in a narrow layer of tuff in the main volcanic agglomerate unit, intimately associated with clinoptilolite, by far the most common zeolite present in the quarry. Clinoptilolite occurs throughout the quarry along joint planes as stalactitic aggregates of thin, colorless to pale yellow tabular crystals. A carbonate-rich zone on the eastern edge of the quarry, away from the lanthanite-bearing zone, carries calcite and minor aragonite.

## ANALYTICAL METHODS

Powder XRD measurements were made using a Philips PW1730 instrument with  $\text{CuK}\alpha$  radiation. Qualitative analyses (energy-dispersion spectroscopy, EDS) of carbon-coated polished grain mounts were performed using a Cambridge Stereoscan 120 SEM. The ICP-MS analyses (Varian 810-MS) were carried out by the School of Earth Sciences, University of Melbourne, using a hand-picked sample. Calibration was based on dilutions of the USGS BHVO-1 rock standard with accuracy better than 3% across the mass

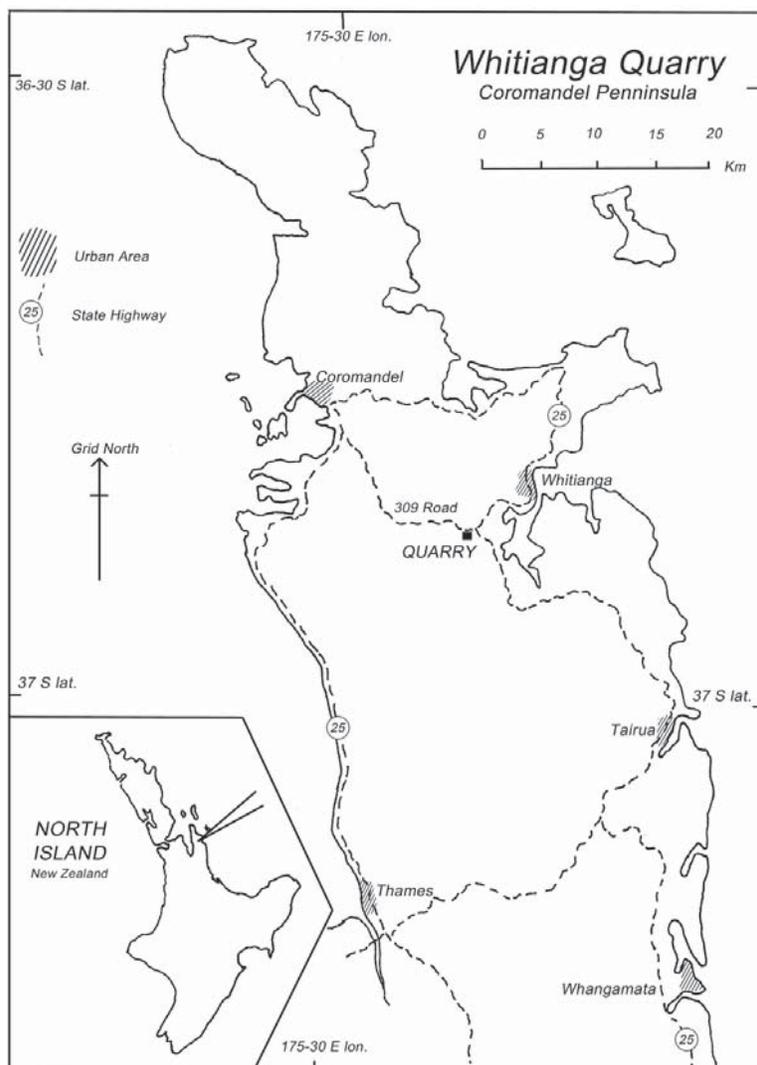


FIG. 1. Map showing the location of the Whitianga quarry in relation to the Coromandel Peninsula of New Zealand.

range, and 1% for  $M > 85$ . Our ability to measure accurately elemental concentrations spanning several orders of magnitude by inductively coupled plasma – mass spectrometry (ICP–MS) is important for this study. Laser Raman spectra were recorded using a Renishaw Raman spectrophotometer. Spectra were accumulated for 30 s using the 514 nm line of a 25 mW  $\text{Ar}^+$  ion laser. Crystal blades were oriented E–W in a horizontal plane, and perpendicular to the laser beam, using  $180^\circ$  sampling geometry through an uncoated  $50\times$  objective of a Leica microscope.

## RESULTS AND DISCUSSION

### *Crystallography*

The lanthanite-(Nd) displays two habits, the most common being lustrous glassy, vivid pink, thin bladed crystals up to 1 mm in size (Fig. 2a). Vivid pink, blocky equant crystals were more rarely encountered (Fig. 2b). Both forms occur in solution cavities in highly altered fine-grained grey-green feldspathic crystal tuff. Colorless, glassy, prismatic crystals of clinoptilolite (to 0.5

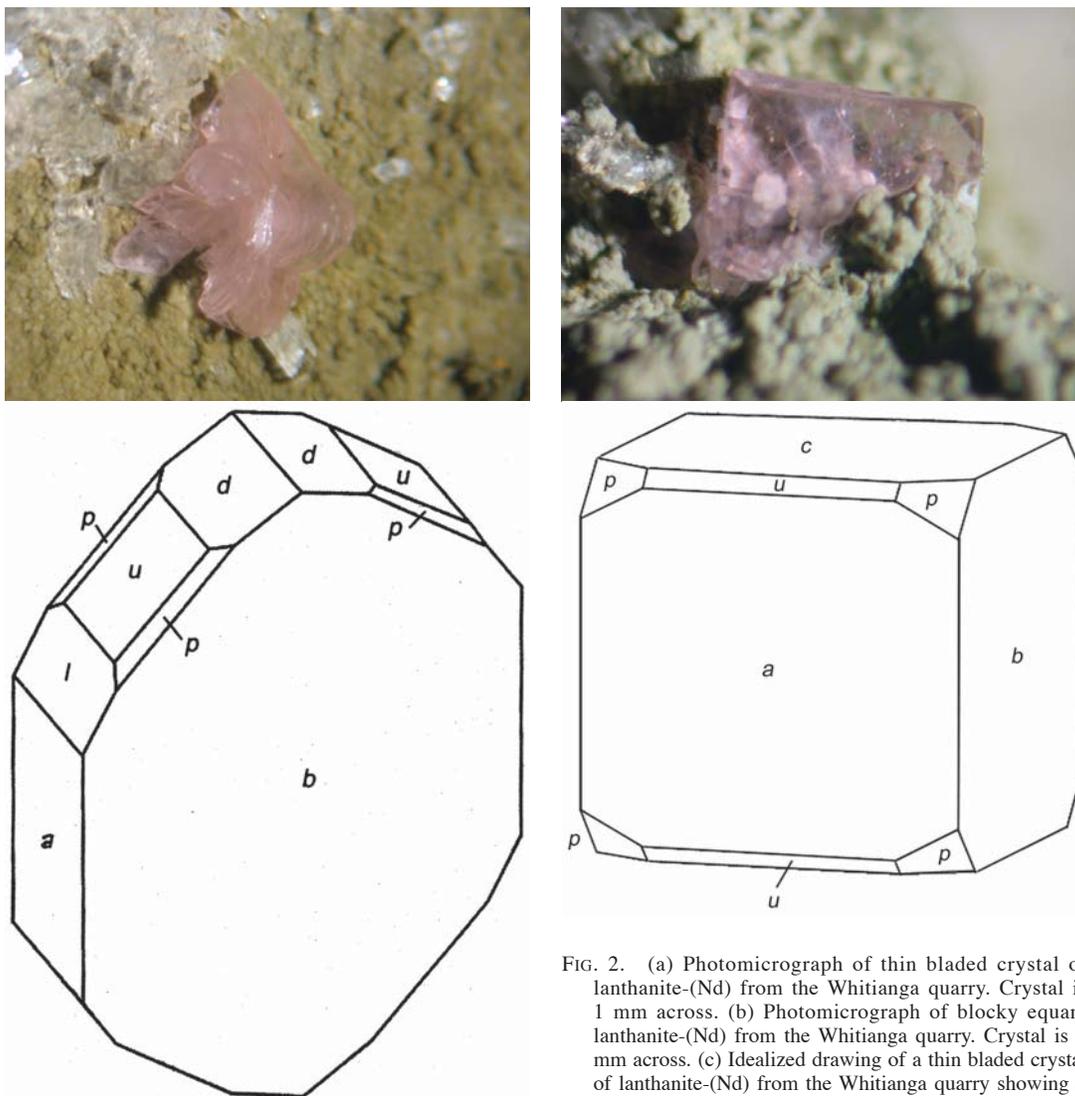


FIG. 2. (a) Photomicrograph of thin bladed crystal of lanthanite-(Nd) from the Whitianga quarry. Crystal is 1 mm across. (b) Photomicrograph of blocky equant lanthanite-(Nd) from the Whitianga quarry. Crystal is 1 mm across. (c) Idealized drawing of a thin bladed crystal of lanthanite-(Nd) from the Whitianga quarry showing  $a$   $\{100\}$ ,  $b$   $\{010\}$ ,  $d$   $\{102\}$ ,  $l$   $\{201\}$ ,  $p$   $\{111\}$ , and  $u$   $\{101\}$ . (d) Idealized drawing of a blocky equant crystal of lanthanite-(Nd) from the Whitianga quarry showing  $a$   $\{100\}$ ,  $b$   $\{010\}$ ,  $c$   $\{001\}$ ,  $p$   $\{111\}$  and  $u$   $\{101\}$ .

mm) are commonly associated with the lanthanite-(Nd), and in all cases appear to have crystallized earlier. Minute, cubic and framboidal pyrite and flattened discoidal or prismatic siderite are present in some cases. In most cases, the siderite appears to be contemporaneous with lanthanite-(Nd).

The bladed crystals of lanthanite consist of individuals flattened on  $\{010\}$  and terminated by  $\{100\}$ ,  $\{201\}$ ,  $\{101\}$ ,  $\{102\}$ ,  $\{10\bar{2}\}$ ,  $\{\bar{1}01\}$  and  $\{20\bar{1}\}$ . On some crystals,  $\{111\}$  can be observed (Fig. 2c). The

blocky equant crystals display the forms  $\{100\}$ ,  $\{010\}$ ,  $\{001\}$  and  $\{111\}$  (Fig. 2d). Reported forms are  $\{001\}$ ,  $\{010\}$ ,  $\{100\}$ ,  $\{101\}$ ,  $\{122\}$  and  $\{121\}$ , with crystals commonly flattened on  $\{010\}$  and twinned on  $\{101\}$  (Roberts *et al.* 1980, Anthony *et al.* 2003). Bladed crystals of lanthanite from the Whitianga quarry displays the additional forms  $\{201\}$ ,  $\{102\}$  and  $\{111\}$ , and are markedly flattened on  $\{010\}$ . The blocky crystals have faces similar to those previously reported, with the new form  $\{111\}$  and are slightly flattened on  $\{100\}$ .

### X-ray diffraction

Powder XRD data were indexed by comparison with the ICDD file for lanthanite-(Nd), PDF 42-0593. Cell constants were refined using least-squares methods (Langford 1973) for 25 peaks. Observed and calculated  $d$  values are listed in Table 1, along with five observed peaks not used in the refinement, indexed using Powder-Cell (Kraus & Nolze 1996). The derived constants are  $a$  9.452(4),  $b$  16.908(10),  $c$  8.923(6) Å,  $V$  1426.1(6) Å<sup>3</sup>. Lanthanite is orthorhombic, space group  $Pbn\bar{b}$ , with  $a$  9.476(4),  $b$  16.940(8),  $c$  8.942(4) Å for lanthanite-(Nd) (Roberts *et al.* 1980, Anthony *et al.* 2003).

### Laser Raman spectroscopy

The laser Raman spectra of Whitianga lanthanite-(Nd) (Table 2) between 200 and 1800 cm<sup>-1</sup> are dominated by a single extremely intense and sharp peak at 1093 cm<sup>-1</sup>, attributed to  $\nu_s(\text{CO}_3)$ . The peak at 1365 cm<sup>-1</sup> can be attributed to  $\nu_{as}(\text{CO}_3)$ . Other peaks between 1400 and 1500 cm<sup>-1</sup> can be ascribed to internal vibrational modes of the carbonate ions. The H-O-H symmetric and antisymmetric stretching modes of H<sub>2</sub>O show a typical bell-shaped curve with a maximum at 3280 and shoulders at 2865, 3070 and 3470 cm<sup>-1</sup>. The weak H-O-H in-plane bending mode is present at 1636 cm<sup>-1</sup> (White 1974, Griffith 1974, 1987, Roberts & Beattie 1995).

### Chemical composition

The EDS analyses indicate that the major REE present are La, Nd and Ce, with (La,Nd) > Ce. There is no evidence of zoning in back-scattered electron images. Results of the ICP-MS analyses (Table 3) accurately provide the REE distribution in the Whitianga lanthanite. The content of Nd (31.9 wt% Nd<sub>2</sub>O<sub>3</sub>) is slightly greater than that of La (29.1 wt% La<sub>2</sub>O<sub>3</sub>) and

considerably more than that of Ce (17.2 wt% Ce<sub>2</sub>O<sub>3</sub>). The mineral carries negligible amounts of the heavy REE, as expected, although small but significant amounts of Dy are present. We detected Tb, Ho, Er Yb and Lu in trace amounts, with relative abundances in the order Tb > Er > Ho > Yb > Lu, but together, they contribute less than 1% of the REE present. A small amount of Ga is present in the structure. On the basis of the stoichiometry of lanthanite, the normalized REE plus Ga distribution is (Nd<sub>0.627</sub>La<sub>0.590</sub>Ce<sub>0.346</sub>Pr<sub>0.149</sub>Sm<sub>0.102</sub>Gd<sub>0.069</sub>Y<sub>0.064</sub>Eu<sub>0.026</sub>Dy<sub>0.017</sub>Ga<sub>0.010</sub>) $\Sigma$ 2.000, or (Nd<sub>0.63</sub>La<sub>0.59</sub>Ce<sub>0.35</sub>Pr<sub>0.15</sub>Sm<sub>0.10</sub>Gd<sub>0.069</sub>Y<sub>0.06</sub>Eu<sub>0.03</sub>Dy<sub>0.02</sub>Ga<sub>0.01</sub>) $\Sigma$ 2.04(CO<sub>3</sub>)<sub>3</sub>•8H<sub>2</sub>O; the REE sum of 2.04 in this case is due solely to rounding errors. The pink color of the lanthanite-(Nd) from the Whitianga Quarry is ascribed to the presence of large amounts of Nd, whose salts with simple O-donor ligands are invariably pink to rose red.

A triangular La-Nd-Ce diagram for the lanthanite group is shown as Figure 3. Unlike material reported elsewhere, lanthanite-(Nd) from the Whitianga Quarry contains significantly large amounts of the three REE Nd, La and Ce. Previous analyses of lanthanite-group minerals (Table 4) show either high Nd and La with low Ce, or high Ce with low Nd and La. The present material thus extends the known compositional range of the lanthanite group, although there is no obvious reason why solid solution should not be complete between any of the various end-members of the light REE. In line with the analysis, the chondrite-normalized REE pattern

TABLE 1. POWDER XRD DATA\* FOR LANTHANITE-(Nd) FROM THE WHITIANGA QUARRY

$l$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$hkl$	$l$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$hkl$
100	8.419	8.454	0 2 0	10	2.686	2.687	0 6 1
12	4.725	4.726	2 0 0	10	2.574	2.574	2 4 2
13	4.462	4.462	0 0 2	6	2.273	2.276	4 2 0
28	4.218	4.227	0 4 0	6	2.160	2.163	3 0 3
13	4.129	4.125	2 2 0	6	2.129	2.128	2 6 2
12	3.941	3.946	0 2 2	6	2.091	2.088	4 0 2
12	3.843	3.859	1 4 0	9	2.056		0 8 1
12	3.818	3.820	0 4 1	8	2.028	2.027	4 2 2
15	3.243	3.244	2 0 2	7	2.020	2.019	2 5 3
10	3.145	3.151	2 4 0	7	2.009	2.010	4 4 1
15	3.026		0 4 2	5	1.931	1.931	1 4 4
12	2.994	2.999	1 5 1	6	1.873	1.872	4 4 2
21	2.816	2.818	0 6 0	5	1.822	1.822	3 5 3
15	2.700	2.701	1 6 0	5	1.637		1 10 1
12	2.694		1 2 3	5	1.561		1 10 2

\* Calculated lines are those included in the least-squares refinement of unit-cell data.

TABLE 2. LASER-RAMAN DATA FOR LANTHANITE-(Nd) FROM THE WHITIANGA QUARRY

cm <sup>-1</sup>	Rel. Int.	cm <sup>-1</sup>	Rel. Int.	cm <sup>-1</sup>	Rel. Int.
233	1	1294	5	1581	10
277	2	1365	12	1612	8
356	1	1394	6	1615	8
372	1	1418	2	1636	4
686	5	1454	2	1702	3
732	8	1459	2		
762	9	1487	6		O-H stretch
968	3	1505	7		
1093	100	1513	6	2865	84
1173	3	1557	8	3072	96
1286	3	1559	8	3280	100
1292	5	1576	9	3471	94

Wavenumbers in cm<sup>-1</sup>, all  $\pm 1$  cm<sup>-1</sup>. Relative intensities in %.

TABLE 3. THE COMPOSITION OF LANTHANITE-(Nd) FROM THE WHITIANGA QUARRY

Ga <sub>2</sub> O <sub>3</sub> wt%	0.29	Sm <sub>2</sub> O <sub>3</sub> wt%	5.39	Er <sub>2</sub> O <sub>3</sub> wt%	0.07
Y <sub>2</sub> O <sub>3</sub>	2.18	Eu <sub>2</sub> O <sub>3</sub>	1.40	Yb ppm	111
La <sub>2</sub> O <sub>3</sub>	29.1	Gd <sub>2</sub> O <sub>3</sub>	3.79	Lu	11.1
Ce <sub>2</sub> O <sub>3</sub>	17.2	Tb <sub>2</sub> O <sub>3</sub>	0.31	Hf	2.32
Pr <sub>2</sub> O <sub>3</sub>	7.44	Dy <sub>2</sub> O <sub>3</sub>	0.94	Pb	1.63
Nd <sub>2</sub> O <sub>3</sub>	31.9	Ho <sub>2</sub> O <sub>3</sub>	0.06	Th	1.77

The composition is normalized to two atoms of the rare-earth elements per formula unit. These data were acquired by ICP-MS analysis.

for lanthanite-(Nd) from the Whitianga quarry (Fig. 4) exhibits a strong concave downward curve reflecting strong enrichment in the light REE, with a significant negative Ce anomaly, characteristic of an oxidizing environment. The negative Ce is due to oxidation of  $Ce^{3+}$  to  $Ce^{4+}$  by  $O_2$ . This is favored by higher pH values, which would in turn lead to a higher activity of  $CO_3^{2-}$ . Formation under oxidizing conditions explains why

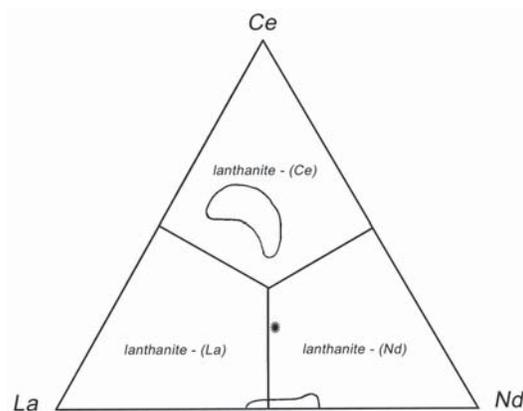


FIG. 3. The composition of lanthanite-group minerals in terms of the elements La, Nd and Ce (adapted from Atencio *et al.* 1989); \*: Whitianga Hill lanthanite-(Nd), circled fields: compositions reported from other localities.

lanthanite is commonly Ce-poor, and La and Nd dominate the REE distribution. A similar relationship has been noted for lanthanite from other localities (Cesbron *et al.* 1979, Roberts *et al.* 1980, Nagashima *et al.* 1986, Coimbra *et al.* 1989, Akagi *et al.* 1996).

The occurrence of lanthanite-(Nd) in the Whitianga quarry, its intimate association with clinoptilolite, negative chondrite-normalized Ce anomaly and occurrence in solution cavities in altered pyritic andesitic tuffs, suggest low-*T* aqueous fluid transport of the REE with

TABLE 4. THE COMPOSITION OF LANTHANITE-(Nd) FROM VARIOUS LOCALITIES

Location	1	2	3	4	5	6
Nd <sub>2</sub> O <sub>3</sub> wt%	39.99	39.57	44.46	42.14	41.92	31.93
La <sub>2</sub> O <sub>3</sub>	35.60	38.71	29.94	33.53	39.06	29.12
Pr <sub>2</sub> O <sub>3</sub>	9.49	6.76	9.83	14.63	-	7.44
Sm <sub>2</sub> O <sub>3</sub>	7.51	6.20	7.00	5.66	7.81	5.39
Gd <sub>2</sub> O <sub>3</sub>	3.09	3.82	3.30	2.47	7.23	3.79
Eu <sub>2</sub> O <sub>3</sub>	3.00	0.64	1.52	1.09	2.27	1.40
Dy <sub>2</sub> O <sub>3</sub>	0.81	1.01	0.65	0.49	1.50	0.94
Y <sub>2</sub> O <sub>3</sub>	0.40	1.63	0.91	-	-	2.18
Ce <sub>2</sub> O <sub>3</sub>	0.06	0.50	2.11	-	0.03	17.23
Ga <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	0.29
Tb <sub>2</sub> O <sub>3</sub>	-	0.23	0.19	-	-	0.31
ThO <sub>2</sub>	0.06	-	-	-	-	<0.01
Ho <sub>2</sub> O <sub>3</sub>	-	0.57	0.04	-	-	0.06
Er <sub>2</sub> O <sub>3</sub>	-	0.35	0.06	-	0.19	0.07

The compositions are normalized to two atoms of rare-earth elements per formula unit. Columns: 1 Curitiba, Parana, Brazil (Roberts *et al.* 1980), 2 Santa Isabel, São Paulo, Brazil (Coimbra *et al.* 1989), 3 Hizzen-cho, Saga Prefecture, Japan (Nagashima *et al.* 1986), 4 Bethlehem, Pennsylvania, USA (Atencio *et al.* 1989), 5 Higashi, Saga Prefecture, Japan (Akagi *et al.* 1996), 6 This study.

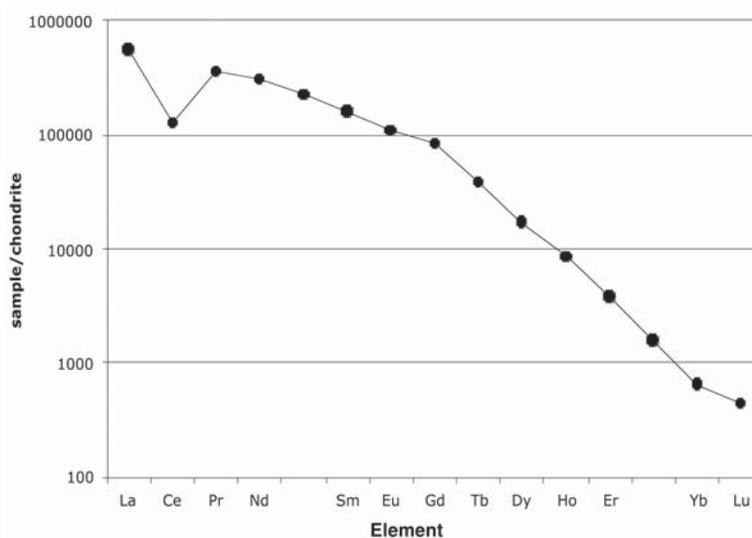


FIG. 4. Chondrite-normalized rare-earth-element abundances in lanthanite-(Nd) from the Whitianga quarry. Note that the abundances for Pm and Tm have been interpolated.

subsequent precipitation in a carbonate-rich environment. The original source of REE may have been the underlying greywacke sequence of the Manaia Hills Group. Black (1970) reported allanite-(Ce) and allanite-(La) from metasedimentary units of the Manaia Hill Group near Paritu, in the northwestern part of the Coromandel Peninsula, and ascribed their formation to the remobilization of the REE from the Manaia Hill Group sedimentary rocks by fluids associated with intrusion of the Paritu pluton. The Whitianga quarry is located on the edge of the Whitianga Caldera (Malengreau *et al.* 2000), which may have provided the heat source for fluid circulation in the present case.

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