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Gasparite-(Ce) and monazite-(Nd): two new minerals to the monazite group from the Alps*

by *Stefan Graeser*[1,2] and *Hans Schwander*[2]

Abstract

Gasparite-(Ce) and monazite-(Nd), two new minerals from the Penninic region of the Alps are described.

Gasparite-(Ce), (Ce, REE)AsO_4, represents the arsenate analogue of monazite, $CePO_4$. Space group symmetry, consequently, is $P2_1/n$, cell parameters [a = 6.937(3), b = 7.137(4), c = 6.738(6) Å; β = 104.69(5)°] are significantly larger than in monazite. Refractive indices [n_x = 1.810(8), n_y = 1.825(8), n_z = 1.92(1); 2V(+) = 40–45°], too, are clearly higher than in monazite. Gasparite-(Ce) is associated with various other arsenic oxide minerals like cafarsite, chernovite, and REE-minerals like synchisite.

Monazite-(Nd) is another new monazite mineral in which Nd is clearly predominant over Ce. The simplified mineral formula is $(Nd_{.44}Ce_{.27}La_{.04}Pr_{.08}Sm_{.14}Gd_{.03})_1(P_{.99}Si_{.01})_1O_4$. Cell parameters are very close to those of ordinary monazite-(Ce): a = 6.745(4), b = 6.964(4), c = 6.435(4) Å; β = 103.65(4)° whereas optical constants are slightly higher [n_x = 1.793(2), n_y = 1.795(2), n_z = 1.860(5) for 589 nm]. The mineral occurs together with numerous REE-minerals such as: xenotime, gadolinite, bastnaesite, allanite, and common monazite-(Ce).

Both minerals and mineral names were approved by the "Commission on New Minerals and Mineral Names, I. M. A." prior to publication. Type material of both minerals is preserved at the Natural History Museum, and at the Mineralogical Institute, Basel.

Keywords: New minerals, gasparite-(Ce), monazite-(Nd), arsenates, monazite group, REE distribution, Alpine fissure minerals.

Riassunto

Gasparite-(Ce) e monazite-(Nd), due nuove specie di minerali provenienti dalla regione Penninica delle Alpi Centrali, sono descritti.

Gasparite-(Ce), (Ce,REE)AsO_4 rappresenta un equivalente arseniato alla monazite, $CePO_4$. Simmetria del gruppo spaziale è $P2_1/n$, i parametri della cellula, però, sono più grandi che nella monazite [a = 6.397(3), b = 7.137(4), c = 6.738(6) Å; β = 104.69(5)°]. L'indice di rifrazione è anche chiaramente più alto che quello della monazite: n_x = 1.810(8), n_y = 1.825(8), n_z = 1.92(1); 2V(+) = 40–45°. Gasparite-(Ce) è associata con altri minerali d'ossido-arsenico come la cafarsite, chernovite e minerali di terre rare, come la sinchisite.

Monazite-(Nd) è un nuovo tipo di monazite in cui l'elemento Nd è chiaramente dominante su Ce. La formula simplificata del minerale è $(Nd_{.44}Ce_{.27}La_{.04}Pr_{.08}Sm_{.14}Gd_{.03})_1(P_{.99}Si_{.01})_1O_4$. I parametri della cellula sono quasi identici con quelli della monazite-(Ce): a = 6.745(4), b = 6.964(4), c = 6.435(4) Å; β = 103.65(4)°, le costanti ottiche però sono leggermente più alte: n_x = 1.793(2), n_y = 1.795(2), n_z = 1.860(5) (589 nm). Il minerale è associato con il rutilo e vari minerali di terre rare (REE) come xenotime, gadolinite, bastnaesite, allanite e monazite-(Ce).

Tutti due minerali e i loro nomi erano stati approvati, prima di essere stati pubblicati, dalla comissione I. M. A. I tipi dei due nuovi minerali sono conservati al Museo di Scienze Naturali e all'Istituto di Mineralogia di Basilea.

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* Dedicated to Professor Ernst Niggli on the occasion of his 70th birthday.

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Gasparite-(Ce)

INTRODUCTION

The mineral was found by the expert mineral collector GIOVANNI GASPARI (Crodo, Italy) on the south-eastern slope of Pizzo Cervandone/Italy during summer 1984. On the occasion of a visit in Crodo, the mineral attracted our attention because of its uncommon colour and shape and was taken back to Basel for closer examination. From X-ray diffraction and optical studies it became obvious that the mineral must be very close in chemical composition to the synthetic compound $CeAsO_4$, a fact which could be proved later by chemical analyses. In recognition of his extremely valuable collecting activity that has provided mineralogical research with numerous interesting mineral samples, we have named the mineral gasparite according to its finder's name and added the suffix -(Ce) for the Ce-dominant composition.

OCCURRENCE

Pizzo Cervandone (in Italian) or Cherbadung (in local Swiss dialect) is a remarkable mountain peak between V. Devero in Italy and Binntal in Switzerland. The whole region belongs to the Penninic Mte.-Leone nappe, consisting partly of meta-sediments together with predominant gneisses which were influenced by lower amphibolite zone metamorphism: the mesocoic meta-sediments are partly kyanite-bearing. As the nappe has an almost horizontal position, the geological situation is more or less identical on both sides of the border. The formation of fissure minerals in the whole region has been strongly influenced by the remobilisation process of hercynic Cu-As-ores (tennantite, chalcopyrite) during Alpine metamorphism. These migrating arsenic bearing solutions resulted in the generation of a large number of highly special minerals, mainly arsenate and arsenite minerals (GRAESER, 1966; GRAESER and ROGGIANI,

Fig. 1 Pseudomorph of gasparite after barrel-shaped synchisite (length 5-6 mm) (Foto E. Offermann).

1970). The formation of this new arsenate monazite, too, is a product of this process.

The first find of gasparite consisted of a strange crystal aggregate of about 5 mm in length made up by pseudo-rhombohedral crystals (up to 0.5 mm). The whole aggregate clearly represents a pseudomorph after some (pseudo-)hexagonal mineral (Figs. 1–3). From the study of further samples, on which gasparite could be found as a reaction rim around partly unaltered primary material it became obvious that it was the Ca–Ce-carbonate mineral synchisite which was replaced by gasparite. Synchisite is quite common in the Cervandone-region and occurs in its characteristic barrel-shaped pseudohexagonal habit. The procedure that led to the formation of gasparite consists of a reaction of the carbonate mineral synchisite with As-bearing solutions with consequent replacement of CO_3^{2-} by AsO_4^{3-}, a process that in a similar way caused the crystallisation of the various other arsenic-oxide-minerals. Associated minerals are: rutile, anatase, magnetite, hematite, synchisite, chernovite, cafarsite, etc.

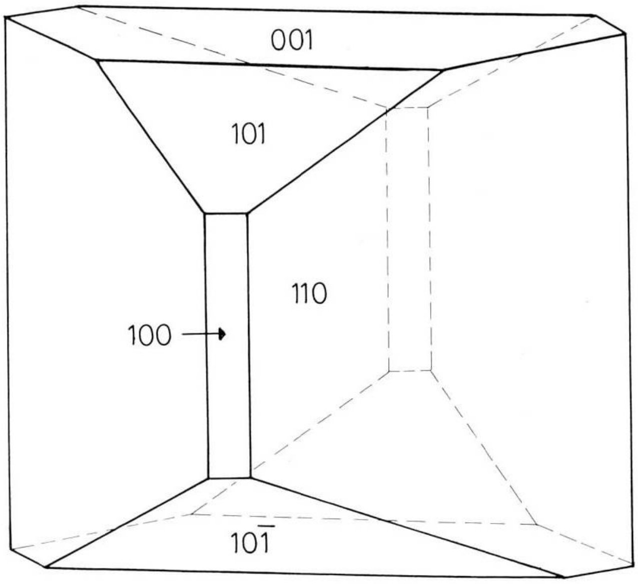

Fig. 2 Pseudo-rhombohedral habit of gasparite. Constructed after goniometrical measurement.

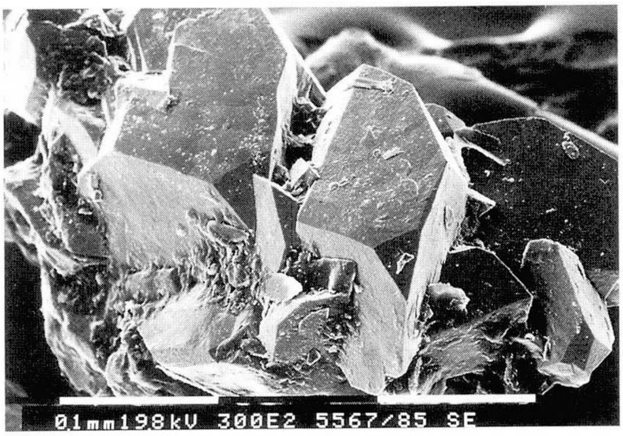

Fig. 3 SEM-picture of ideally shaped gasparite crystals (Foto: SEM laboratory University Basel).

PHYSICAL AND OPTICAL PROPERTIES (TAB. 1)

The fact that gasparite is present exclusively as a reaction product of and mostly as pseudomorph after synchisite makes a visual determination of the mineral quite easy. The crystals themselves, seen under the binocular microscope, display the characteristic habit of flat pseudo-rhombohedrals composed of the following forms: $\{110\}$, $\{101\}$, $\{10\bar{1}\}$, $\{100\}$, $\{001\}$, always in a somewhat rounded appearance. The colour of the mineral is light brown-red, with a typical flesh-like tint. Like other rare earth minerals gasparite-(Ce) shows the characteristic change to bright green colour under the radiation of a common quartz lamp ("quick tanning lamp"). In building up the pseudomorphous aggregates, all crystals appear in the same squamous grouping yet it is difficult to decide whether they have orientated intergrowth or not. The density could not be measured because of the small grain size of single crystals and the porosity and intergrowth with synchisite of the aggregates. The calculated density of 5.63 g/cm^3, however, indicates that gasparite has a much higher density than ordinary monazite.

CHEMICAL ANALYSES

The preliminary study of the mineral by the energy-dispersive-system of the scanning electron microscope proves it to be a pure rare earth arsenate; phosphorous seemed to be completely absent, a diagnosis that was confirmed by subsequent microprobe analyses.

9 chemical analyses were carried out by means of an ARL electron microprobe (Tab. 2). The following standard materials were used: synthetic CeO_2(Ce), $LaAlO_3$(La), $NdAlO_3$(Nd), $GdAlO_3$(Gd), Pr metal(Pr), ThO_2(Th), $Ca_2P_2O_7$(P), $AlAsO_4$(As,Al) and

Tab. 1 Physical and optical data [gasparite-(Ce)].

n_x	= 1.810(8)	Hardness:	327(5) kg/mm^2 (VHN_{50}) =
n_y	= 1.825(8)		4 1/2 - 5 (MOHS)
n_z	= 1.92 (1)	Density:	5.63 g/cm^3 (calculated)
Δ	= 0.11	Fracture:	conchoidal to uneven
$2V_z$	= 40-45° (+)	Cleavage:	not observed
Orientation:	X = b	Twinning:	not observed
	Z: c = 4°	Colour:	brown-red, streak white
(all for Na_D-light)		non-pleochroic	

wollastonite (Ca,Si), quartz (Si), anhydrite (S). Standard deviations for the main components were small [Ce_2O_3 = 28.33 (±.22), As_2O_5 = 39.21 (±0.7) wt.%] but significantly higher for the rest of the rare earth elements and ThO_2.

The I.R. spectrogram (Fig. 4) shows the typical AsO_4-vibrations (at 850 and 804 cm^{-1}), a very distinct band in the region of 451 cm^{-1} may be due to the small silicate content. In comparison to ordinary monazite-(Ce), it is interesting to state that the two minerals, structurally such closely related, yield completely different I.R. spectra.

The GLADSTONE-DALE relationship which can be used to check the compatibility between the mean refractive index, density and chemical data of a new mineral (according to MANDARINO, 1979) yielded a calculated compatibility index with the value "superior" in MANDARINO'S arbitrary scale.

X-RAY CRYSTALLOGRAPHY

Powder diagrams of the previously unknown mineral indicated clearly the relationship to the monazite series with d-spacings perceptibly shifted to larger values (Tab. 4).

The very small crystals were well appropiate for single crystal work which was carried out by Weissenberg and Precession techniques (Tab. 3). The observed extinctions (0k0: only for k = 2n and h0l: only for h + l = 2n are present) are in agreement with the space group symmetry $P2_1/n$ as is consistent for monazite minerals. The unit cell parameters in table 3 were computed by least squares refinement from the powder data. The cell volume is considerably larger for gasparite than for other monazite minerals.

Monazite-(Nd)

INTRODUCTION

In 1983 we received several mineral samples collected by DR. V. MATTIOLI (Milan) for identification. Among these there was one very strangely rose-red coloured mineral which, af-

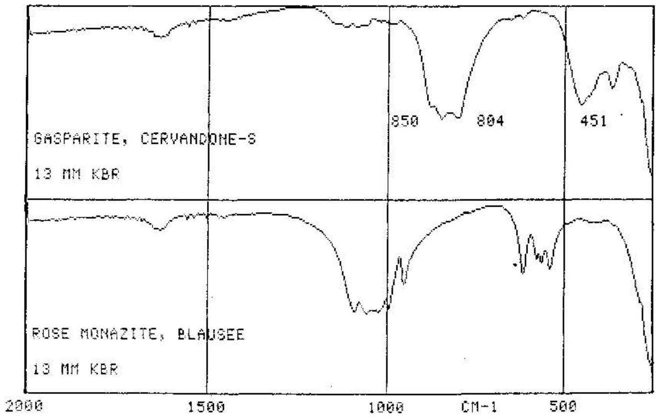

Fig. 4 I.R. spectrogram of gasparite-(Ce) with AsO_4-vibrations (At 850 and 804 cm^{-1}) compared with ordinary monazite-(Ce) [Rose monazite-(Ce) from Blausee, Binntal - PE 883, MPI, Basel].

Tab. 2 Chemical data of gasparite-(Ce).

	mean of 9 analyses	calculated for simplified formula
Ce_2O_3	28.33 wt.%	30.23 wt.%
La_2O_3	12.07	12.82
Nd_2O_3	11.02	11.73
Pr_2O_3	3.89	4.13
ThO_2	1.95	-
CaO	1.36	-
SiO_2	0.64	-
Al_2O_3	0.06	-
SO_3	0.99	-
As_2O_5	39.21	41.09
Total	99.52	100.00

based on O = 4:

empirical formula:

$(Ce_{.47}La_{.20}Nd_{.18}Pr_{.06}Ca_{.07}Th_{.02})_{1.0}(As_{.94}S_{.03}Si_{.03})_{1.0}O_4$

simplified formula:

$(Ce_{.52}La_{.22}Nd_{.19}Pr_{.07})_{1.0}AsO_4$

Tab. 3 Unit-cell parameters (gasparite, synth. $CeAsO_4$).

	Gasparite-(Ce)	synth. $CeAsO_4$ 1)
a	6.937(3)Å	6.9596 Å
b	7.137(4)	7.1576
c	6.738(6)	6.7378
β	104.69(5)°	104.71°
V	322.7(2)$Å^3$	324.64 $Å^3$
Z	4x[(Ce,La,Nd,Pr)AsO_4]	4x[$CeAsO_4$]

1) SWANSON et al. (1966)

Tab. 4 X-ray powder diffraction data.

I/I_o	d_{meas}	d_{calc}	hkl	ICPDS: 15-772[1]	
		5.41	$\bar{1}01$	5.42	6
		4.81	011	4.82	12
		4.31	$\bar{1}11$	4.32	12
30	3.59	3.60 3.57	111 020	3.61	10
77	3.355	3.355	200	3.368	60
100	3.156	3.151	120	3.161	100
34	3.035	3.036	210	3.046	25
70	2.966	2.964	012	2.978	35
44	2.709	2.706	$\bar{2}02$	2.710	25
31	2.519	2.530 2.506	$21\bar{2}$ 112	2.533	20
20	2.233	2.235	031	2.240	20
45	2.003	2.004	212	2.008	30
30	1.9245	1.9285 1.9214	103 032	1.930	30
30	1.8905	1.8952	320	1.902	16
32	1.8113	1.8167 1.8021	$\bar{3}22$ 222	1.822	20
34	1.7787	1.7782	132	1.7817	25
18	1.7225	1.7232	321	1.7293	12
20	1.6725	1.6775 1.6742	400 $\bar{4}02$	1.6791	12
16	1.6333	1.6330	410	1.6385	16
16	1.3592			1.3634	10
14	1.3050			1.3109	8
14	1.2730			1.2784	8

[1] Natl.B.Stds (1966): synthetic $CeAsO_4$

ter chemical and X-ray diffraction studies was identified as monazite with strong predominance of Nd over Ce. According to the Levinson rule for rare earth minerals it had to be named monazite-(Nd) and this represented a new member of the monazite series. Shortly afterwards a notice appeared in "The American Mineralogist" (68, 1983) which mentioned the "description" of monazite-(Nd) from the Marmara bauxite in Greece (MAKSIMOVIC and PANTO, 1980) which consisted only of a chemical analysis without any optical, physical or structural data, published without the approval of the "Commission on New Minerals and Mineral Names, I.M.A.". In the meantime, the members of this Commission had agreed that decriptions of new mineral published without approval should not be recognized. On the suggestion of DR. J.A. MANDARINO, chairman of the Commission, the mineral was resubmitted to the Commission as proposal (86-52) for a new mineral and subsequently was approved as monazite-(Nd).

OCCURRENCE

The first material containing this mineral was collected by members of the "Gruppo Mineralogico Lombardo" (Milan) in gneiss blocks on the moraine of the north-slope of Pta. Glogstafel in Val Formazza, Italy. The minerals occur in small fissures or druses of aplitic to pegmatitic veins in a schistose gneiss with abundant white mica. According to the petrological work of JOOS (1969), this rock belongs to the so-called Lebendun-series which is built up mainly by metamorphic psephite gneisses.

The small fissures in the aplitic parts of the rock are especially rich in rutile and various other minerals. An X-ray diffraction study of these revealed that all of them are rare earth minerals: *Xenotime* is quite frequently present in translucent greenish crystals; *gadolinite* occurs in needle shaped colourless crystals of limpid aspect; *bastnaesit* as long-prismatic beige crystals which are always somewhat corroded, *allanit* seems to have grown as a rockforming mineral (anhedral reddish-black elongated specimens); *monazite-(Ce)* is present in almost colourless clear crystals of pseudo-rhombohedral habit. Among all these, one mineral was particularly conspicuous because of its bright rose-red colouring, which by closer examination turned out to be a Nd-dominant monazite—the monazite-(Nd). As a preliminary publication, these REE-minerals were discribed in a well illustrated article by V. MATTIOLI (1985).

PHYSICAL AND OPTICAL PROPERTIES (TAB. 5)

Though it is a proper member of the monazite group, monazite-(Nd) is quite different from ordinary monazite-(Ce) in habit as well as in colour. It forms longprismatic crystals which are mostly translucent or sometimes milky but always bright rose in colour. After detection of this new monazite mineral we be-

Tab. 5 Physical and optical data of rose monazites.

	Monazite-(Nd) Pta. Glogstafel, Italy		Rose monazite-(Ce) Blausee, Binntal, Switzerland
n_x	1.793 (2)		1.783 (2)
n_y	1.795 (2)	(Na_D)	1.784 (2)
n_z	1.860 (5)		1.830 (5)
Δ	0.067		0.047
$2V_z$ (+)	18-20°		15-17°
Density (calc)	5.43 g/cm^3		5.34 g/cm^3

came interested in other monazites of the region which are slightly rose coloured, quite different from the orange-yellow colour of common monazite-(Ce). Yet, a subsequent study of such monazites revealed that, though the Nd contents are slightly elevated relative to Ce, they all represent common monazites-(Ce) (see Tab 6).

CHEMICAL ANALYSES

Chemical analyses were carried out on monazite-(Nd) from Glogstafel and rose monazite-(Ce) from Binntal by means of an ARL electron microprobe. Standards were the same as used in the case of gasparite with same additions: metallic Sm, U, synthetic TiO_2, ZrO_2 and

Tab. 6 Chemical analyses: monazite-(Nd) and rose monazite-(Ce).

	Monazite-(Nd) (Pta. Glogstafel) 3 analyses	rose Monazite-(Ce) (Binntal) 6 analyses
Ce_2O_3	19.85 wt.%	30.43 wt.%
La_2O_3	2.48	14.17
Pr_2O_3	6.47	4.67
Nd_2O_3	30.32	14.58
Sm_2O_3	8.81	3.11
Gd_2O_3	2.26	1.96
ZrO_2	0.77	-
P_2O_5	28.65	29.93
SiO_2	0.22	0.30
MnO	-	0.40
Total	99.83	99.74

based on O = 4:

Monazite-(Nd):

$(Nd_{.44}Ce_{.29}Sm_{.12}Pr_{.09}La_{.04}Gd_{.03}Zr_{.02})_{1.03}(P_{.97}Si_{.01})_{.98}\ O_4$

Monazite-(Ce):

$(Ce_{.44}La_{.21}Nd_{.20}Pr_{.07}Sm_{.04}Gd_{.03}Ca_{.01})_{1.0}(P_{.99}Si_{.02})_{1.01}\ O_4$

apatite (P). The results of the analyses are compiled in table 6.

X-RAY CRYSTALLOGRAPHY

Monazite-(Nd) was studied by Weissenberg and Precession techniques. It seems that the cell parameters (and cell volume) are slightly smaller than in ordinary monazites which might be a consequence of the fact that the ion radius of Nd is slightly shorter than the Ce and La radii. The rose coloured monazite-(Ce) yields the powder pattern of common monazites.

DISCUSSION

In comparison to standard lanthanide patterns of monazites, the three investigated monazite group minerals reveal characteristical differences (see Table 8):

Our rose coloured monazite-(Ce) shows

Tab. 7 X-ray diffraction data (of rose monazites).

	Monazite-(Nd) (Pta.Glogstafel/I)	Rose Monazite-(Ce) (Binntal/CH)
a	6.745(4)Å 1)	6.76(1)Å 1)
b	6.964(4)	7.00(1)
c	6.435(4)	6.45(1)
β	103.65(4)°	104.0(2)
V_o	293.7(2)Å^3	296.2(7)Å^3

I	d in Å	hkl	d in Å	I
30	4.15	$\bar{1}11$	4.16	20
10	3.51	111	3.49	20
60	3.280	200	3.273	70
100	3.080	120	3.081	100
50	2.846	$\bar{1}12$	2.861	80
30	2.590	$\bar{2}02$	2.596	30
40	2.425	$\bar{2}12$	2.431	30
30	2.177	031	2.184	40
30	1.9541	212	1.9594	50
20	1.8835	$\bar{3}21$	1.8917	20
30	1.8634	103	1.8606	40
20	1.7514	222	1.7550	30
30	1.7301	132	1.7330	30
20	1.6845	321	1.6838	20

1) lattice parameters refined from d-spacings.

Tab. 8 Rare earth patterns of monazite minerals.

	(1)	(2)	(3)	(4)
La_2O_3	23.84	20.56	3.53	21.82
Ce_2O_3	46.56	44.15	28.28	51.22
Pr_2O_3	5.30	6.78	9.22	7.03
Nd_2O_3	18.64	21.15	43.20	19.92
Sm_2O_3	3.68	4.51	12.55	-
Gd_2O_3	1.98	2.84	3.22	-

(1) Average REE contents in monazites (MERTIE, 1960)

(2) rose monazite-(Ce), Binntal (mean of 6 analyses, this work)

(3) monazite-(Nd), Pta. Glogstafel (mean of 3 analyses, this work)

(4) gasparite-(Ce), Pizzo Cervandone (mean of 9 analyses, this work)

*) REE-oxide values recalculated to a total of 100%

only a small difference: the abundance of the rare earth elements is slightly shifted towards the heavier elements, yet, the influence of the traces of Mn on the colouring is not known. An extreme difference becomes obvious in the case of monazite-(Nd): La and Ce are strongly depleted whereas Nd and Sm are enriched by a factor of two to three. The chemical composition of the accompanying monazite-(Ce) from Pta. Glostafel was checked semiquantitatively by EDAX system on a scanning electron microscope; it yielded the pattern of common monazite-(Ce). Finally, the arsenate mineral gasparite-(Ce) fits quite well into the average lanthanide pattern of monazites though the heavier rare earth elements seem to be more or less absent.

MANNUCCI et al. (1986) have reported a comprehensive study on pegmatitic and fissure monazites of the Alps and found a very unifom REE pattern, for fissure minerals and pegmatitic ones as well. The Nd-content in particular shows an extremely narrow variance with values between 7-10 wt% Nd_2O_3. The occurrence of the red monazite-(Nd) seems to represent a very local and unique phenomenon.

Acknowledgments

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