The Canadian Mineralogist
Vol. 36, pp. 107-116 (1998)

LATRAPPITE: A RE-INVESTIGATION

ROGER H. MITCHELL[1]

Department of Geology, Lakehead University, Thunder Bay, Ontario P7B 5E1

JIN BEOM CHOI AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

CATHERINE A. McCAMMON

Bayerisches Geoinstitut, Universität Bayreuth, D-95440, Bayreuth, Germany

PETER C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana 46556-0767, U.S.A.

ABSTRACT

Compositional data are presented for latrappite and other niobium-rich perovskite-group minerals from the Oka, Kaiserstuhl and Magnet Cove carbonatite complexes. Latrappite is shown to be a member of a continuous solid-solution involving $CaTiO_3$, $NaNbO_3$, $Ca_2NbFe^{3+}O_6$ and $Ca_2Nb_2O_7$. ^{57}Fe Mössbauer spectrometry demonstrates that only ferric iron is present in latrappite. The crystal structure of latrappite, determined by Rietveld analysis, is similar to that of $CaTiO_3$ perovskite. It differs in that replacement of Ti by Nb and Fe^{3+} results in greater distortion and tilting of the TiO_6 framework polyhedra relative to $CaTiO_3$. Revised unit-cell parameters of latrappite are: *a* 5.4479(3), *b* 5.5259(3), *c* 7.7575(5) Å, *V* 233.54 Å^3, space group *Pbnm*.

Keywords: perovskite, latrappite, Rietveld analysis, crystal structure, Mössbauer spectrometry, electron microscopy.

SOMMAIRE

Nous présentons des données nouvelles sur la composition de la latrappite et autres membres riches en niobium du groupe de la pérovskite provenant des complexes carbonatitiques de Oka, Kaiserstuhl et Magnet Cove. La latrappite est membre d'une solution solide continue impliquant les pôles $CaTiO_3$, $NaNbO_3$, $Ca_2NbFe^{3+}O_6$ et $Ca_2Nb_2O_7$. La spectrométrie ^{57}Fe de Mössbauer démontre que le fer est uniquement sous forme ferrique. La structure cristalline de la latrappite, affinée par analyse de Rietveld, ressemble à celle de la pérovskite $CaTiO_3$. Elle en diffère par replacement du Ti par Nb et Fe^{3+}, qui mène à un distorsion de la maille et une inclinaison des octaèdres TiO_6 de la trame, par rapport à la structure du pôle $CaTiO_3$. Les paramètres réticulaires révisés de la latrappite sont: *a* 5.4479(3), *b* 5.5259(3), *c* 7.7575(5) Å, *V* 233.54 Å^3, groupe spatial *Pbnm*.

(Traduit par la Rédaction)

Mots-clés: pérovskite, latrappite, analyse Rietveld, structure cristalline, spectrométrie de Mössbauer, microscopie électronique par transmission.

INTRODUCTION

Nickel & McAdam (1963) described a new Nb-rich variety of perovskite from the Oka carbonatite complex (Quebec). It was initially called *niobian perovskite*, as Nickel & McAdam (1963) considered that the names *dysanalyte* and *knopite* were unnecessary for Ca-, Nb-rich perovskites (*sensu lato*). The mineral was subsequently named *latrappite* by Nickel (1964) on the grounds that, unlike perovskite ($CaTiO_3$), the Nb content was greater than the Ti content. The name latrappite was accepted by the International Mineralogical Association (IMA) nomenclature committee on this basis as an approved name for the mineral species.

Subsequently, latrappite was reported in carbonatite associated with the Kaiserstuhl alkaline complex (Van

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[1] *E-mail address*: rmitchel@gale.lakeheadu.ca

Wambeke 1980), from which Nb-rich perovskite, commonly known by the varietal names *dysanalyte* or *knopite*, had been previously described (Knop 1877, Hauser 1908, Meigen & Hugel 1913). These two localities remain the only known occurrences of a Ca–Nb-rich perovskite-group mineral, although Nb-bearing perovskite is known from the Magnet Cove carbonatite (Arkansas).

It is important to note that the material analyzed by Nickel & McAdam (1963) is a complex solid-solution, and Nickel (1964) did not define a distinct compositional end-member representing the latrappite component. This is unfortunate, as an end-member component is required for thermodynamic modeling of perovskite solid-solutions. Hence, we consider that although latrappite as defined by Nickel (1964) does indeed represent a valid mineral species in terms of current IMA criteria for mineral nomenclature, the name is inappropriate from a crystallochemical-thermodynamic standpoint as it does not represent a distinct end-member composition. It is not the purpose of this work to redefine latrappite; the main objective is to re-investigate material from the type localities of latrappite and "dysanalyte", and to provide data which may subsequently be of use in any redefinition, as Mitchell (1996) has noted that the structure and composition of these perovskite-group minerals is inadequately characterized.

EXPERIMENTAL

Sample provenance

The sample of latrappite studied was collected from the type locality at Oka (Quebec) by employees of the St. Lawrence Columbium and Metals Corporation and deposited in the mineralogical collection of the Royal Ontario Museum (Toronto) as specimen number M26142. Samples of "dysanalyte" were provided by Dr. J. Keller from the mineralogical collection at the University of Freiburg. These were originally collected from the type locality at the Badloch Quarry, Kaiserstuhl complex (Germany). Other samples of latrappite and Nb-bearing perovskite from Oka and Magnet Cove were collected by Drs. A.N. Mariano and R.H. Mitchell.

Electron-microprobe analysis

Perovskite-group minerals were analyzed by standard wavelength-dispersion (Cameca SX–50 electron microprobe) or energy-dispersion (Hitachi 570 SEM) methods at the University of Manitoba and Lakehead University, respectively.

Wavelength-dispersion analysis used the following operating conditions and standards: accelerating voltage 15 kV, beam current of 20 nA; Sr and Ti ($SrTiO_3$), Fe (almandine), Na (albite), Ca (diopside), Ba (witherite), Th (thorite), Nb (Nb_2O_5), Ta (microlite); accelerating voltage 20 kV, beam current 40 nA; La ($L\alpha$) [$LaVO_4$], Ce($L\alpha$) [monazite], Pr ($L\beta$), Nd ($L\alpha$), Sm ($L\beta$) [rare-earth-bearing glass standards of Drake & Weill (1972)].

Compositions determined by X-ray energy-dispersion spectrometry (EDS) were obtained using a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm Mn*K*). EDS spectra were acquired for 300 seconds (live time) with an accelerating voltage of 20 kV and beam current of 0.86 nA. X-ray spectra were collected and processed with the LINK ISIS–SEMQUANT software package. The following standards were used; Na, La, Ce, Pr, Nd, Nb, Ti (Khibina loparite), Ca, Fe (Magnet Cove perovskite), Sr ($SrTiO_3$), Ba ($BaSiO_3$) and metallic Th and Ta. A well-characterized multi-element standard for the rare-earth elements (*REE*) was used, as experience has shown that this gives more accurate data than single-*REE* standards when using EDS spectrum-stripping techniques. However, peak profiles used for the analytical X-ray lines were obtained using single *REE* fluoride standards. The accuracy of the EDS method was cross-checked by wavelength-dispersion electron-microprobe analysis of some samples.

Mössbauer spectrometry

Approximately 17 mg of latrappite was finely ground under acetone in an agate mortar and mounted over a 19.63 mm² area on cellophane foil using water-soluble glue. The effective thickness of the sample was 1.8 mg Fe/cm², this being the ideal thickness for this composition (Long *et al.* 1983). A Mössbauer spectrum was recorded at room temperature (293 K) in transmission mode on a constant-acceleration Mössbauer spectrometer (Bayerisches Geoinstitut) with a nominal 50 mCi ^{57}Co source in a 6 μm α-Fe–Rh matrix. The velocity scale was calibrated relative to a 25 μm α-foil using the positions certified for the National Bureau of Standards standard reference material No. 1541. We obtained line widths for the outer lines of α-Fe of 0.28 mm/s at room temperature. The spectra were fitted to Lorentzian lineshapes using the commercially available fitting program NORMOS, written by R.A. Brand and distributed by Wissenschaftliche Elektronik GmbH, Germany.

X-ray diffraction

The sample was ground in alcohol to less than 5 μm using an automated grinder. The resulting powder was spread on a 4-μm thick prolene film over an area of approximately 80 mm², the boundary of which was defined by a thin-wire ring glued onto the prolene film with hairspray. The thin film of powder was finely serrated with a razor blade and then covered with prolene to fix the powder during data collection. Step-scan diffraction-intensity data were collected at the University of Manitoba on a Siemens D5000 X-ray diffractometer in the 2θ range 8–140° in steps of 0.02° 2θ, with a step-counting time of 20 s and Cu$K\alpha_1$ radiation. The sample was rotated at 120 rpm during the $\theta/2\theta$ scan in order to minimize further any preferred orientation and crystal-size effects.

Rietveld refinement

The Rietveld refinement was done in the space group *Pbnm* using the program DBWS–9006PC (Sakthivel & Young 1990). Diffraction peaks were modeled using the Thompson–Cox–Hastings modified pseudo-Voigt profile function corrected for asymmetry up to 29° 2θ, and the background was refined using a fifth-order polynomial. Structural variables were atomic coordinates, cation-site occupancies and an overall isotropic-displacement factor; non-structural variables were the scale factor and parameters for background correction, peak shape and asymmetry, and the correction for preferred orientation. Individual isotropic-displacement parameters were fixed at values taken from single-crystal structure refinements of other perovskites (Buttner & Maslen 1992), and the overall isotropic-displacement parameter was refined to scale these values. Refinement was terminated when the maximum shift-to-error ratio was less than 0.01.

High-resolution transmission electron microscopy (HRTEM)

TEM samples were prepared by gently crushing the XRD powder under acetone in an agate mortar and allowing drops of the suspension to evaporate on a holey carbon TEM grid. Observations were made using a JEOL JEM–2010 instrument (University of New Mexico) operated at 200 kV. Under these conditions, the maximum point-to-point resolution of the microscope is 1.9 Å. HRTEM images and selected-area diffraction patterns were obtained from numerous grains in various orientations.

COMPOSITION

Latrappite

The composition of latrappite (Table 1) given by Nickel & McAdam (1963) was obtained by gravimetric methods and represents an average bulk composition. The presence of Si, Mg and S in their sample indicates that this material was contaminated with minor amounts of other minerals. Our studies (this work) have shown that calcite, pyrochlore, magnetite and clinohumite may be present as inclusions in samples of latrappite from Oka. Regardless of the presence of small amounts of contaminants, the mineral was shown by Nickel & McAdam (1963) to be rich in Ca, Nb, Fe and Ti, and thus distinct in composition from Na-, *REE*- and Nb-rich perovskite-group minerals such as loparite-(Ce) and lueshite.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF LATRAPPITE

Wt.%	1	2	3	4	5	6	7	8	9	10
Nb_2O_5	47.60	46.44	47.61	47.91	40.53	39.12	35.23	49.7	47.9	43.90
Ta_2O_5	0.24	0.32	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.
TiO_2	9.73	8.94	10.39	8.89	11.71	13.96	17.51	9.8	9.3	10.05
ThO_2	n.d.	n.d.	0.04	0.07	n.d.	n.d.	n.d.	n.d.	0.1	n.d.
Fe_2O_3	6.16	8.39	6.26	6.89	9.91	9.77	10.09	5.8	5.9	9.71
La_2O_3	0.52	0.53	0.49	0.45	0.70	0.77	1.11	0.3	1.1	-
Ce_2O_3	1.04	1.25	1.10	0.98	1.66	1.76	2.36	0.7	1.5	2.03
Pr_2O_3	0.06	0.11	0.08	0.05	0.10	0.22	0.24	0.5	0.8	-
Nd_2O_3	0.27	0.29	0.26	0.26	0.36	0.48	0.71	0.6	0.4	-
MnO	0.41	0.32	0.30	0.34	0.27	0.24	0.26	0.3	0.5	0.77
MgO	2.16	1.67	1.80	1.89	1.54	1.15	0.88	2.1	2.2	2.20
CaO	26.65	27.06	25.24	26.97	29.82	28.25	28.29	24.3	24.2	25.95
SrO	0.17	0.11	0.18	0.22	0.19	0.19	0.24	0.2	0.3	n.d.
Na_2O	3.94	3.85	4.79	3.96	2.33	3.09	2.90	4.9	4.3	4.03
Total	98.95	99.28	98.54	98.88	99.12	99.00	99.93	100.1	99.3	98.64
Structural formulae based on 3 atoms of oxygen										
Nb	0.573	0.560	0.575	0.574	0.486	0.468	0.420	0.597	0.588	0.529
Ta	0.003	0.002	-	-	-	-	-	-	-	-
Ti	0.195	0.179	0.209	0.177	0.234	0.278	0.347	0.194	0.190	0.202
Fe	0.123	0.169	0.126	0.153	0.198	0.195	0.180	0.116	0.114	0.194
Mn	0.009	0.007	0.007	0.008	0.006	0.005	0.006	0.007	0.011	0.017
Mg	0.086	0.066	0.072	0.075	0.061	0.045	0.035	0.083	0.089	0.088
ΣB	0.989	0.983	0.989	0.987	0.985	0.991	0.988	0.997	0.992	1.030
La	0.005	0.005	0.005	0.004	0.007	0.007	0.011	0.003	0.011	-
Ce	0.010	0.012	0.011	0.009	0.016	0.018	0.023	0.007	0.015	0.020
Pr	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.004	0.008	-
Nd	0.003	0.003	0.003	0.003	0.003	0.005	0.007	0.006	0.004	-
Ca	0.760	0.774	0.722	0.766	0.848	0.801	0.800	0.693	0.704	0.742
Sr	0.003	0.002	0.003	0.003	0.003	0.003	0.004	0.003	0.005	-
Na	0.203	0.199	0.248	0.204	0.120	0.159	0.148	0.253	0.226	0.208
ΣA	0.985	0.996	0.993	0.990	0.998	0.995	0.995	0.969	0.973	0.970
Mol.% end-members										
$SrTiO_3$	0.25	0.16	0.26	0.32	0.27	0.27	0.34	0.29	0.45	-
LOP	3.07	3.47	3.07	2.73	4.41	4.84	6.68	2.85	6.32	2.39
LU	20.82	20.24	25.04	20.90	11.31	15.06	13.27	25.68	22.38	21.84
LATRAP	14.74	20.14	14.70	18.21	23.48	22.76	20.98	13.61	13.78	23.57
PEROV	21.55	19.07	22.79	19.54	24.67	29.43	35.66	21.22	16.54	23.90
$Ca_2Nb_2O_7$	39.57	36.92	34.16	38.31	35.86	27.64	23.08	36.37	40.53	28.30

Total Fe calculated as Fe_2O_3; LOP = Na(REE)Ti_2O_6; LU = $NaNbO_3$; LATRAP = Ca_2NbFeO_6; PEROV = $CaTiO_3$. Compositions: 1- 3, this work; 4, Mitchell (1996); 5-7, this work; 8-9, Chakhmouradian (1996); 10, Nickel & McAdam (1964).Totals of compositions 8 & 9 include 1.0 and 0.8 wt.% ZrO_2, respectively n.d. = not detected

Table 1 presents compositions of latrappite from the type locality obtained by electron-microprobe analysis (this work, Mitchell 1996, Chakhmouradian 1996). Back-scattered electron images show that minor compositional zoning, primarily with respect to Nb and Fe, is present. The compositions, recast into the nomenclature scheme for perovskite-group minerals suggested by Mitchell (1996), are also given in Table 1. In this scheme of recalculation, Fe is considered to be entirely in the ferric state (see below). These data show that latrappite may be regarded primarily as a quaternary solid-solution between $CaTiO_3$ (perovskite *sensu stricto)*, $NaNbO_3$ (lueshite), $Ca_2NbFe^{3+}O_6$, and $Ca_2Nb_2O_7$. Other end-member perovskite-group compounds such as tausonite or loparite account for less than 10 mol.% of the composition. The synthetic end-member $Ca_2NbFe^{3+}O_6$ is a *B*-site double perovskite (Filipyev & Fesenko 1965, Chakhmouradian & Mitchell 1998), and $Ca_2Nb_2O_7$ is a layered derivative

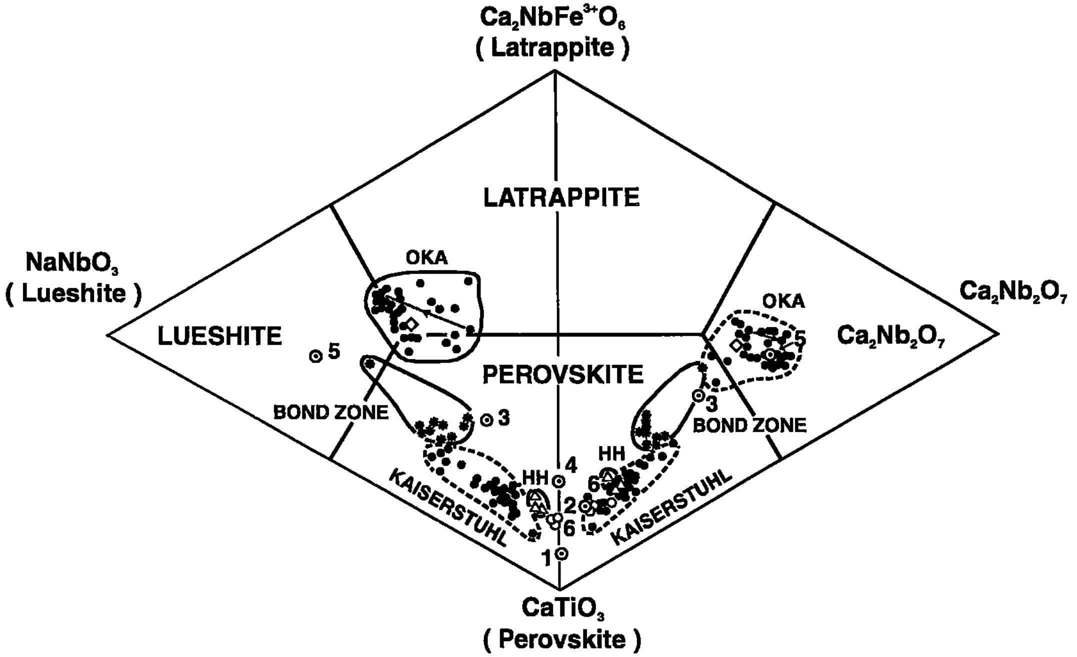

FIG. 1. Compositions (mol.%) of latrappite, "dysanalyte" and niobium perovskite plotted in the ternary systems $NaNbO_3$ – $CaTiO_3$ – $Ca_2NbFe^{3+}O_6$ and $CaTiO_3$ – $Ca_2NbFe^{3+}O_6$ – $Ca_2Nb_2O_7$. Numbered compositions of niobian perovskite or "dysanalyte" are for: 1. Oka (this work); 2. Magnet Cove (Lupini *et al.* 1992); 3. Kaiserstuhl (Meigen & Hugel 1913); 4. Kaiserstuhl (Hauser 1908); 5. Kaiserstuhl latrappite (Van Wambeke 1980); 6. Calgon Pit, Magnet Cove carbonatite (Chakhmouradian & Mitchell, unpubl. data). Samples from the Oka alkaline complex (Quebec) include latrappite (OKA) from the type locality (Nickel & McAdam 1963), and niobian perovskite from the Bond Zone carbonatite and Husereau Hill okaite (HH).

of the perovskite structure (Scheunemann & Müller-Buschbaum 1974).

Table 1 and Figure 1 demonstrate clearly that the composition of latrappite from Oka is dominated by significant amounts of the $Ca_2NbFe^{3+}O_6$ and $Ca_2Nb_2O_7$ components. Nickel (1964) did not consider either of these compounds as the potential end-member perovskite to which the name latrappite might be applied. Interestingly, $Ca_2NbFe^{3+}O_6$ had previously been recognized by Tikhonenkov & Kazakova (1957) as a major component of "dysanalyte" from the Kaiserstuhl complex, but the component was not given a specific name. Mitchell (1996) has suggested that the name *latrappite* be retained for the $Ca_2NbFe^{3+}O_6$ component. However, it could be argued, because of the dominance of the $Ca_2Nb_2O_7$ component in material from the type locality, that the name latrappite be given to this component and that dysanalyte be retained for $Ca_2NbFe^{3+}O_6$ on the grounds of historical precedence. It should be noted that in terms of current nomenclature, "*dysanalyte*" is merely a varietal name for Nb-bearing perovskite.

"Dysanalyte"

Representative compositions of "dysanalyte" from the Kaiserstuhl carbonatite complex are given in Table 2 and illustrated in Figure 1. These data show that "dysanalyte" exhibits considerable within- and between-grain compositional variation, but is not as enriched in Nb as latrappite. Table 2 and Figure 1 demonstrate that "dysanalyte" is primarily a solid solution involving $CaTiO_3$, $NaNbO_3$, and $Ca_2Nb_2O_7$, and that the latrappite ($Ca_2NbFe^{3+}O_6$) component is typically less than 12 mol.%. Many compositions are best regarded as sodian niobian perovskite.

The "dysanalyte" studied typically exhibits all stages of replacement by a variety of niobian titanates. Replacement can range from minor effects along the edge of crystals to total replacement. The initial stage of replacement in some instances involves formation of a calcium-bearing pyrochlore-like mineral, which is replaced in turn by a complex intergrowth of niobian rutile and $(Nb,Ti,Fe,Ta)_2O_5$ (Table 3). In other instances, the latter minerals appear to form as a direct

TABLE 2. REPRESENTATIVE COMPOSITIONS OF "DYSANALYTE"

Wt.%	1	2	3	4	5	6	7	8	9	10
Nb_2O_5	10.93	16.03	18.99	22.02	23.26	28.29	30.75	32.01	33.63	50.35
Ta_2O_5	0.23	0.29	1.84	2.02	2.20	0.86	1.15	1.12	1.12	0.55
TiO_2	43.47	39.13	34.84	33.18	33.14	29.48	28.71	27.64	25.06	15.16
ZrO_2	0.68	0.42	0.06	0.18	0.09	0.21	0.20	0.14	0.30	0.85
Fe_2O_3	3.42	4.10	5.63	5.03	4.86	5.19	4.52	4.97	5.23	5.41
La_2O_3	1.23	0.93	0.60	0.56	0.45	0.53	0.43	0.39	0.36	0.20
Ce_2O_3	2.87	2.52	1.73	1.61	1.55	1.29	1.34	1.15	0.97	0.33
Pr_2O_3	0.26	0.16	0.19	0.17	0.02	0.10	0.24	0.06	0.05	0.04
Nd_2O_3	0.59	0.65	0.47	0.46	0.37	0.34	0.29	0.23	0.13	0.05
MnO	n.d.	0.04	0.08	n.d.	n.d.	0.06	0.12	n.d.	0.20	0.07
MgO	n.d.	0.05	0.06	0.12	0.09	0.17	0.23	0.22	0.25	n.d.
CaO	33.85	32.71	32.84	31.87	30.89	28.77	27.76	27.69	28.06	20.00
SrO	0.31	0.30	n.d.	0.08	0.08	0.21	0.23	0.18	0.17	0.29
Na_2O	1.41	1.93	1.90	2.20	2.66	3.67	4.28	4.40	3.82	6.67
Total	99.25	99.26	99.23	99.50	99.66	99.17	100.25	100.20	99.35	99.97
Structural formulae based on 3 oxygens										
Nb	0.121	0.179	0.214	0.249	0.262	0.322	0.348	0.363	0.387	0.591
Ta	0.002	0.002	0.012	0.014	0.015	0.006	0.008	0.008	0.008	0.004
Ti	0.797	0.725	0.653	0.623	0.621	0.559	0.541	0.521	0.480	0.296
Zr	0.008	0.005	0.001	0.002	0.001	0.003	0.002	0.002	0.004	0.011
Fe	0.063	0.076	0.106	0.095	0.091	0.098	0.085	0.094	0.100	0.106
Mn	-	0.001	0.002	-	-	0.001	0.003	-	0.004	0.002
Mg	-	0.002	0.002	0.004	0.003	0.006	0.009	0.008	0.009	-
ΣB	0.991	0.990	0.990	0.987	0.993	0.995	0.996	0.996	0.992	1.040
La	0.011	0.008	0.006	0.005	0.004	0.005	0.004	0.004	0.003	0.002
Ce	0.026	0.023	0.016	0.015	0.014	0.012	0.012	0.011	0.009	0.003
Pr	0.002	0.001	0.002	0.002	-	0.001	0.002	0.001	-	-
Nd	0.005	0.006	0.004	0.004	0.003	0.003	0.003	0.002	0.001	-
Ca	0.885	0.864	0.877	0.853	0.825	0.777	0.745	0.744	0.765	0.556
Sr	0.004	0.004	-	0.001	0.001	0.003	0.003	0.003	0.003	0.004
Na	0.067	0.092	0.092	0.107	0.129	0.179	0.208	0.214	0.188	0.341
ΣA	1.000	0.998	0.987	0.997	0.976	0.980	0.977	0.979	0.969	0.906
Mol. % end-members										
$SrTiO_3$	0.38	0.38	-	0.10	0.10	0.28	0.30	0.24	0.23	0.43
LOP	6.61	5.55	3.90	3.77	3.13	3.14	3.10	2.48	2.15	1.07
LU	4.40	7.36	7.99	9.59	12.18	17.40	20.34	21.23	18.89	37.97
LATRAP	6.92	8.45	11.90	10.72	10.43	11.27	9.76	10.76	11.60	13.23
$Ca_2Nb_2O_7$	6.09	8.93	12.16	14.97	14.34	14.58	15.14	15.61	20.68	28.55
PEROV	75.60	69.33	64.06	60.85	59.82	53.34	51.37	49.68	46.45	18.75

Total Fe calculated as Fe_2O_3; Compositions 1-9 this work; 10 Van Wambeke (1980) n.d. = not detected. LOP = $Na(REE)Ti_2O_6$; LU = $NaNbO_3$; LATRAP = Ca_2NbFeO_6; PEROV = $CaTiO_3$.

TABLE 3. Fe–Ti–Nb-BEARING OXIDES REPLACING "DYSANALYTE"

wt%	1	2	3	4	5	6	7	8	9	10
Nb_2O_5	50.02	50.63	49.13	47.24	42.80	52.99	47.34	32.22	26.89	33.00
Ta_2O_5	1.61	1.48	2.45	2.59	3.22	3.12	1.85	2.24	2.24	2.57
TiO_2	33.02	32.18	35.69	38.68	41.97	32.64	38.09	59.72	65.81	57.65
Fe_2O_3	14.24	14.34	11.58	12.13	11.73	11.79	12.58	5.83	3.82	5.62
Total	98.89	98.63	98.85	100.64	99.72	100.54	99.86	100.01	98.76	98.84

1-7 $(Nb,Ti,Fe,Ta)_2O_5$; 8-10 niobian rutile. Total Fe expressed as Fe_2O_3.

product of the replacement of perovskite. A description of the replacement process will be given in a subsequent paper.

Although Van Wambeke (1980) has described latrappite (with Nb > Ti) from this locality (Table 2, anal. 10), we did not encounter in our work any Nb-rich compositions similar to those of the Oka material that could be described as latrappite. Note that the latrappite analyzed by Van Wambeke (1980) is compositionally unlike latrappite from the type locality in being relatively rich in Na, and hence contains greater amounts of the $NaNbO_3$ component.

Niobian perovskite

Niobian perovskite is common in the Bond Zone and at Husereau Hill in the Oka complex. Table 4 gives representative compositions for these and other Nb-bearing perovskites from Oka. Figure 1 shows that perovskite from the Bond Zone is similar in composition to the most Nb-rich "dysanalyte" from Kaiserstuhl. Table 4 also gives compositional data for Na- and *REE*-poor niobian perovskite from Magnet Cove. These minerals represent solid solutions involving $CaTiO_3$ (dominant), and minor $Ca_2NbFe^{3+}O_6$, $Ca_2Nb_2O_7$ and $REE_2Ti_2O_7$, and are clearly unlike niobian cerian perovskite described from agpaitic undersaturated alkaline complexes (Mitchell & Chakhmouradian 1996). Figure 1 is interpreted to indicate that there is possibly a continuous solid-solution among $CaTiO_3$, $Ca_2NbFe^{3+}O_6$, $Ca_2Nb_2O_7$, and $NaNbO_3$.

MÖSSBAUER SPECTROMETRY

The Mössbauer spectrum of latrappite (Fig. 2) is similar to previously published spectra of perovskite (Muir *et al.* 1984) and shows a simple Lorentzian doublet with a center shift of 0.388 ± 0.005 mm/s

TABLE 4. REPRESENTATIVE COMPOSITIONS OF NIOBIAN PEROVSKITE

Wt%	1	2	3	4	5	6	7	8
Nb_2O_5	28.76	31.59	33.94	44.21	10.19	2.69	8.66	9.38
Ta_2O_5	0.79	0.59	2.42	0.39	0.89	n.d.	0.16	0.33
TiO_2	25.66	26.76	24.61	16.80	40.47	51.55	42.43	42.44
ThO_2	n.d.	n.d.	n.d.	n.d.	0.49	0.31	n.d.	0.12
Fe_2O_3	8.10	5.72	5.31	7.55	5.15	2.49	5.12	5.70
La_2O_3	0.93	0.50	1.02	0.76	2.51	0.55	1.05	1.60
Ce_2O_3	1.96	1.81	1.58	1.27	5.55	2.15	2.26	2.38
Pr_2O_3	n.d.	n.d.	n.d.	n.d.	0.12	0.16	n.d.	n.d.
Nd_2O_3	0.77	0.04	0.67	0.09	1.41	0.67	0.54	0.38
CaO	28.51	26.83	25.44	23.52	30.76	37.68	37.46	37.49
SrO	0.61	0.54	0.58	0.57	0.57	0.50	0.16	0.33
Na_2O	3.39	4.31	4.90	6.03	1.38	0.34	0.28	0.15
Total	99.48	98.68	100.47	101.19	99.49	99.09	98.12	100.30
Structural formulae based on 3 atoms of oxygen								
Nb	0.333	0.365	0.393	0.514	0.116	0.029	0.096	0.102
Ta	0.006	0.004	0.017	0.003	0.003	-	0.001	0.002
Ti	0.495	0.515	0.474	0.325	0.768	0.920	0.781	0.772
Fe	0.156	0.110	0.102	0.146	0.097	0.044	0.105	0.104
ΣB	0.990	0.994	0.986	0.988	0.984	0.993	0.983	0.980
La	0.008	0.005	0.009	0.007	0.023	0.002	0.009	0.014
Ce	0.018	0.017	0.015	0.012	0.051	0.019	0.020	0.021
Pr	-	-	-	-	0.001	0.001	-	-
Nd	0.007	-	0.006	-	0.013	0.006	0.005	0.003
Th	-	-	-	-	0.003	0.002	-	-
Ca	0.783	0.735	0.648	0.649	0.832	0.958	0.983	0.972
Sr	0.009	0.008	0.009	0.009	0.008	0.007	0.004	0.005
Na	0.169	0.214	0.243	0.301	0.068	0.016	-	0.007
ΣA	0.994	0.979	0.930	0.978	0.999	1.011	1.021	1.022
Mol.% end-members								
$SrTiO_3$	0.82	0.72	0.78	0.79	0.74	0.59	0.35	0.05
LOP	5.31	3.28	4.99	3.48	13.46	4.01	0.13	2.09
LU	15.68	21.08	23.42	30.53	2.33	0.19	-	-
LATRAP	18.00	12.72	11.75	17.13	10.95	4.79	11.65	11.48
$Ce_2Ti_2O_7$	-	-	-	-	-	-	1.70	1.44
$Ca_2Nb_2O_7$	15.47	15.28	17.24	21.52	7.03	1.20	6.38	7.19
PEROV	44.70	46.93	41.82	26.55	65.49	89.22	79.78	77.70

Total Fe calculated as Fe_2O_3; LOP = $Na(REE)Ti_2O_6$; LU = $NaNbO_3$; LATRAP = Ca_2NbFeO_6; PEROV = $CaTiO_3$. Compositions: 1-4 Bond Zone, Oka; 5 Husereau Hill, Oka; 6 LeCullier, Oka; 7-8 Calgon Pit, Magnet Cove. n.d. = not detected.

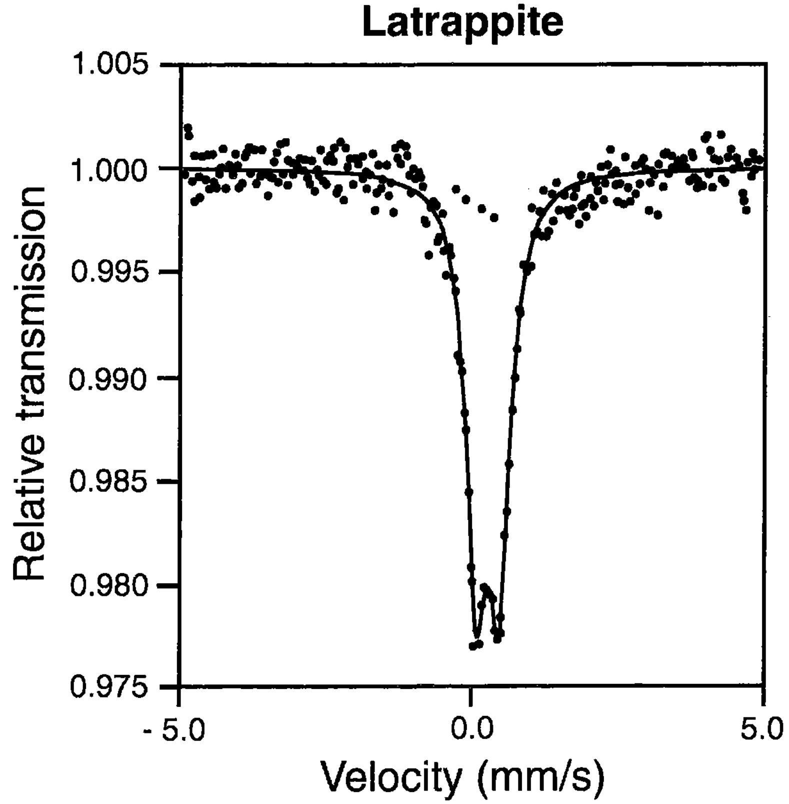

FIG. 2. Mössbauer spectrum of latrappite.

TABLE 5. INDEXED X-RAY POWDER DIFFRACTION PATTERN FOR LATRAPPITE (Pbnm)

I (obs)	d(obs) Å	d(calc) Å	h	k	l
60	3.885	3.884	1	1	0
6	3.465	3.473	1	1	1
100	2.744	2.744	1	1	2
4	2.335	2.336	1	0	3
<1	2.151	2.152	1	1	3
<1	2.082	2.081	1	2	2
<1	2.069	2.069	2	1	2
55	1.940	1.939	0	0	4
<1	1.885	1.884	2	2	1
4	1.746	1.747	1	3	0
10	1.735	1.735	1	1	4
2	1.703	1.704	1	3	1
14	1.589	1.588	0	2	4
25	1.578	1.578	3	1	2
10	1.371	1.372	2	2	4
<1	1.362	1.361	0	4	1
8	1.227	1.227	1	1	6
<1	1.114	1.113	2	4	3
<1	1.033	1.032	0	4	5
<1	0.970	0.970	0	0	8

relative to α-Fe, a quadrupole splitting of 0.398 ± 0.005 mm/s, and a line width of 0.44 ± 0.01 mm/s. The hyperfine parameters indicate that: (1) all iron occurs as Fe^{3+}, and (2) Fe^{3+} occupies only one type of site. Systematics between site geometry and the center shift indicate that Fe^{3+} occupies the octahedral site in the perovskite structure (McCammon 1996). Significantly, no peaks arising from Fe^{2+} can be observed. These data are the basis for the calculation of the total Fe content of latrappite as Fe_2O_3 (Table 1), and the assignment of all Fe^{3+} to the $Ca_2NbFe^{3+}O_6$ component.

X-RAY DIFFRACTION AND RIETVELD ANALYSIS

X-ray diffraction

The observed and calculated X-ray powder-diffraction patterns of latrappite are given in Table 5 and Figure 3. In the usual orthorhombic orientation of the perovskite structure, the space group is *Pbnm*, and the cell parameters are: *a* 5.4479(3), *b* 5.5259(3), *c* 7.7575(5) Å [*cf.* Nickel & McAdam (1964), who give *Pcmn*: *a* 5.448, *b* 7.777, *c* 5.553 Å].

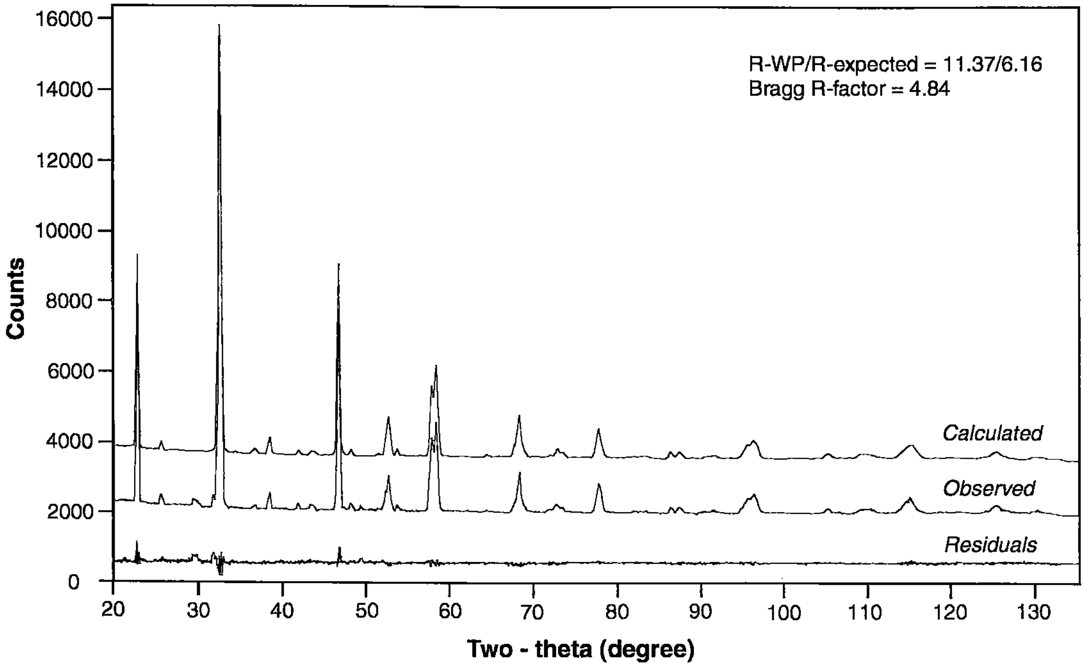

FIG. 3. Rietveld refinement data for latrappite.

As $Ca_2NbFe^{3+}O_6$ is an ordinary, although complex perovskite, we cannot expect its presence to be reflected in the XRD pattern, unless there is a superstructure resulting from the ordering of Nb and Fe; peaks attributable to such ordering were not evident. However, $Ca_2Nb_2O_7$ is expected to produce additional diffraction peaks in the XRD pattern if present in sufficient amounts. The situation is analogous to solid solutions in the $Sr_{1-x}La_xTiO_{3+0.5x}$ series of compounds (Bowden *et al.* 1995). In this series, peaks attributable to the lanthanate perovskite appear in the powder-diffraction pattern only where x exceeds 0.5. As there are no anomalous peaks in the X-ray-diffraction pattern of latrappite that might originate from $Ca_2Nb_2O_7$, it seems reasonable to conjecture that this component must also exceed at least 50 mol.% before its presence might be reflected in the powder pattern.

TABLE 6. CRYSTAL STRUCTURE DATA FOR LATRAPPITE

Atom	X	Y	Z	B
Ca(Na)	-0.0076(3)	0.0359(5)	0.25	0.61
Nb(Fe,Ti)	0	0.5	0	0.40
O1	0.0764(3)	0.4800(2)	0.25	0.53
O2	0.7087(1)	0.2871(1)	0.0364(1)	0.50

Cell parameters: a = 5.4479(3); b = 5.5259(3); c = 7.7575 (5) Å
Space group = ***Pbnm***; V = 233.54 Å^3; Z = 4
Bragg R-factor = 4.84%; R-WP = 11.37%; S = 1.86; D-WD = 0.94

Crystal structure

Structural parameters determined by Rietveld analysis are given in Table 6, and selected bond-lengths and angles, in Table 7. These data show that the structure of latrappite is very similar to that of $CaTiO_3$ (Buttner & Maslen 1992). The principal differences are the longer metal–oxygen bonds in, and greater distortion of, the XO_6 polyhedron in latrappite arising from the introduction of Nb and Fe^{3+} into the structure. In common with $CaTiO_3$ perovskite, the XO_6 polyhedron is compressed along the O1–(X)–O1 axis, but in contrast, there is greater distortion in the equatorial O2 plane, and the (X)–O2 bonds of latrappite differ significantly in length. Significantly different (X)–O1–(X) bond angles for latrappite and perovskite are expressed in the greater tilt of the latrappite XO_6 polyhedra about the [111] axis than found in perovskite (Table 7).

ELECTRON MICROSCOPY

HRTEM studies of solid solution in the systems $Ca_2Nb_2O_7$ – $CaTiO_3$ (Nanot *et al.* 1975), and $Ca_2Nb_2O_7$ – $NaNbO_3$ (Portier *et al.* 1974) have demonstrated the occurrence of slabs of $Ca_2Nb_2O_7$ interleaved with layers of normal perovskite. By analogy, we expect that similar intergrowths should be visible in natural perovskites that are sufficiently rich in the $Ca_2Nb_2O_7$ component. Electron-diffraction patterns and high-resolution images were obtained for about 20 crystals

TABLE 7. LATRAPPITE AND PEROVSKITE: INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Latrappite		Perovskite	
Ca - O(1)	2.496	Ca - O(1)	2.488
-O(1)B	2.369	- O(1)B	2.363
-O(2)A x2	2.698	- O(2)A x2	2.672
-O(2)C x2	2.657	- O(2)C x2	2.671
-O(2)D x2	2.416	- O(2)D x2	2.380
Nb-O(1)x2	1.987	Ti - O(1) x2	1.953
-O(2)Ax2	1.996	- O(2)A x2	1.959
-O(2)Cx2	1.972	- O(2)C x2	1.958
Bond Angles			
Nb-O(1)-Nb	= 155.0°	Ti-O(1)-Ti	= 156.9°
Nb-O(2)A-Nb	= 155.8°	Ti-O(2)A-Ti	= 155.8°
O(2)A-Nb-O(2)C	= 89.7°	O(2)A-Ti-O(2)C	= 89.4°
O(1)-Nb-O(2)C	= 88.5°	O(1)-Ti-O(2)C	= 89.3°
O(1)-Nb-O(2)A	= 89.8°	O(1)-Nb-O(2)A	= 89.6°
Tilt Angles			
[001] =	6.7°	[001] =	5.4°
[010] =	9.6°	[010] =	8.4°
[111] =	11.7°	[111] =	10.0°

Latrappite (this work) ; $CaTiO_3$ perovskite (Buttner & Maslen 1992)
Estimated standard deviations of bond lengths ±0.002

of latrappite with up to 40 mol.% $Ca_2Nb_2O_7$; in all cases, the electron-diffraction patterns correspond to a simple orthorhombic lattice with no extra diffraction maxima present (Fig. 4). The high-resolution images did not reveal a layered structure for any of the grains examined (Fig. 4). Either these samples of latrappite do not contain sufficient amounts of the $Ca_2Nb_2O_7$ component to permit formation of discrete layers analogous to those observed in the synthetic compounds, or such layers occur in an orientation that was not visible in the high-resolution images collected in this study. Although latrappite contains up to 48 wt.% Nb_2O_5, the majority of the Nb is probably associated with solid solutions involving the "normal" perovskites, $NaNbO_3$ and Ca_2NbFeO_6. Consequently, any excess oxygen contributed to the overall structure by the $Ca_2Nb_2O_7$ component must be accommodated in the perovskite framework without the formation of the discrete oxygen-rich regions observed by Nanot *et al.* (1975).

CONCLUSIONS

This study has shown that latrappite is a Nb-rich member of a continuous solid-solution series that exists among $CaTiO_3$, $NaNbO_3$, $Ca_2NbFe^{3+}O_3$, and $Ca_2Nb_2O_7$. Mössbauer spectrometry has demonstrated that only ferric iron is present in the mineral. The crystal structure of latrappite is similar that of $CaTiO_3$ perovskite, but differs in exhibiting greater distortion and tilting of the perovskite framework polyhedra arising from the entry of the larger cations Nb and Fe into the TiO_6 polyhedra.

ACKNOWLEDGEMENTS

RHM and FCH were supported by Equipment and Operating Grants of the Natural Sciences and Engineering Research Council of Canada (NSERC). PCB was supported by a Post-Doctoral Fellowship from NSERC. The HRTEM work was done at the Electron Microbeam Analysis Facility at the Department of Earth and Planetary Sciences, University of New Mexico. Fred Wicks, Tony Mariano and Jörg Keller are thanked for providing samples of perovskite from the Oka and Kaiserstuhl complexes. Dr. Anton Chakhmouradian is thanked for analyzing Nb-rich perovskite from Oka and Magnet Cove. Dr. E.H. Nickel and an anonymous reviewer provided useful comments on an initial draft of this work. Bob Martin is thanked for his usual attention to editorial matters in the preparation of the final text.

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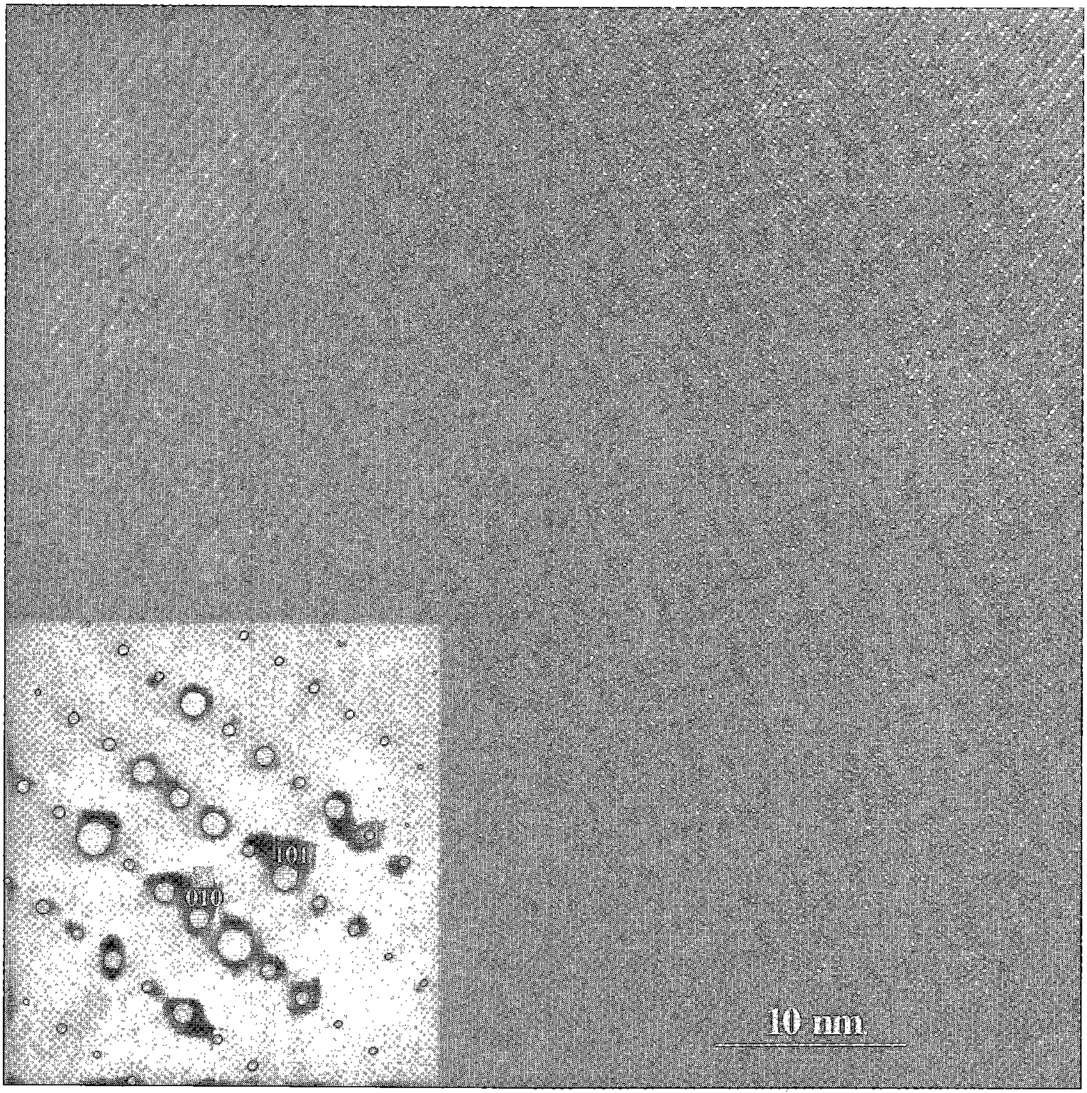

FIG. 4. HRTEM image and selected-area electron-diffraction pattern of latrappite.

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Received June 20, 1997, revised manuscript accepted November 15, 1997.