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Mendeleevite-(Nd), $(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca)_{30}(Si_{70}O_{175})(OH,H_2O,F)_{35}$, a new mineral from the Darai-Pioz alkaline massif, Tajikistan

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ABSTRACT

Mendeleevite-(Nd), $(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca)_{30}(Si_{70}O_{175})(OH,H_2O,F)_{35}$ is a new mineral from the Darai-Pioz alkaline massif, Tajikistan. Mendeleevite-(Nd) was found in a pectolite aggregate in silexites (quartz-rich rocks) which consist of fine to medium pectolite grains, quartz, aegirine and fluorite, with minor khvorovite, mendeleevite-(Ce), sokolovaite, hyalotekite, orlovite, kirchhoffite, pekovite, neptunite, zeravshanite, senkevichite, nordite-(Ce), alamosite, pyrochlore-group minerals and baratovite. Mendeleevite-(Nd) forms colourless cubic crystals 10–40 μm in size; it has a vitreous lustre and a Mohs hardness of 5–5.5; $D_{meas.} = 3.20(2)$ g/cm^3, $D_{calc.} = 3.155$ g/cm^3. Mendeleevite-(Nd) is optically isotropic, with the refractive index $n = 1.582(2)$. Mendeleevite-(Nd) is cubic, space group $Pm\bar{3}$, $a = 21.9106(4)$ Å; $Z = 2$. The six strongest reflections in the powder X-ray diffraction pattern are [d (Å), I (%), ($h\ k\ l$)] are: 11.01, 100, (0 0 2); 15.63, 55, (0 1 1); 3.47, 42, (2 0 6); 3.099, 42, (3 4 5); 2.192, 42, (0 0 10); 1.819, 41, (3 6 10). Chemical analysis by electron microprobe gave SiO_2 42.30, Ce_2O_3 10.12, La_2O_3 3.60, Nd_2O_3 16.19, Pr_2O_3 2.79, Sm_2O_3 4.19, Gd_2O_3 1.69, Eu_2O_3 0.47, SrO 2.99, CaO 2.20, Cs_2O 8.50, K_2O 0.85, H_2O 3.85, F 1.25, $-O = F_2$ –0.53, sum 100.46 wt.%, with H_2O calculated by analogy with mendeleevite-(Ce). The empirical formula based on 210 (O + F) apfu, with F + OH + H_2O = 35 pfu, is $Cs_6(\square_{4.20}K_{1.80})_{\Sigma 6}\{[(Nd_{9.57}Ce_{6.13}Sm_{2.39}La_{2.20}Pr_{1.68}Gd_{0.93}Eu_{0.27})_{\Sigma 23.17}(Ca_{3.90}Sr_{2.87})_{\Sigma 6.77}]_{\Sigma 29.94}\square_{0.06}\}_{\Sigma 30}(Si_{70.03}O_{175})(OH_{14.47}F_{6.54})_{\Sigma 21.01}(H_2O)_{14}$, $Z = 2$. The simplified and ideal formulae are $(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca)_{30}(Si_{70}O_{175})(OH,H_2O,F)_{35}$ and $Cs_6(REE_{23}Ca_7)(Si_{70}O_{175})(OH,F)_{19}(H_2O)_{16}$, respectively. The compatibility index (from measured density) = –0.039 (excellent). Mendeleevite-(Nd) is a Nd analogue of mendeleevite-(Ce), $(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca,\square)_{30}(Si_{70}O_{175})(H_2O,OH,F,\square)_{35}$. Both minerals are named after Dmitri Mendeleev (1834–1907), the great Russian chemist, author of the periodic table of chemical elements, who has had a significant impact on the development of natural sciences and industry, both in Russia and around the world.

Keywords: mendeleevite-(Nd), new mineral species, mendeleevite-(Ce), alkaline rocks, Darai-Pioz massif, Tajikistan, electron microprobe analysis.

Introduction

Mendeleevite-(Nd), $(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca)_{30}(Si_{70}O_{175})(OH,H_2O,F)_{35}$ [REE = rare-earth elements and $\square$ = vacancy] occurs in the moraine of the Darai-Pioz glacier in the upper reaches of the

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TABLE 1. Comparison of mendeleevite-(Nd) and mendeleevite-(Ce).

	mendeleevite-(Nd)	mendeleevite-(Ce)
Simplified formula	$(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca)_{30}$ $(Si_{70}O_{175})(OH,H_2O,F)_{35}$ $REE = (Nd_{9.57}Ce_{6.13}Sm_{2.39}La_{2.20}$ $Pr_{1.68}Gd_{0.93}Eu_{0.27})_{\Sigma 23.17}$	$(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca,\square)_{30}$ $(Si_{70}O_{175})(H_2O,OH,F,\square)_{35}$ $REE = (Ce_{11.33}La_{5.86}Nd_{3.23}Pr_{1.54}$ $Sm_{0.32}Gd_{0.20})_{\Sigma 22.48}$
System	cubic	cubic
Space group	$Pm\bar{3}$	$Pm\bar{3}$
a (Å)	21.9106(4)	21.9148(4)
Z	2	2
Strongest refl. in the powder diffr. data: $d_{obs.}$ (Å) (*I*)	11.01 (100), 15.63 (55), 3.47 (42), 3.099 (42), 2.192 (42), 1.819 (41)	10.95 (100), 3.097 (50), 3.46 (40), 15.53 (30), 12.62 (30), 2.190 (30)
Colour	colourless with a pale brown hue	colourless with a slight brown tint
Lustre	vitreous	vitreous
$D_{meas.}$, g/cm^3	3.20(2)	3.12(2)
$D_{calc.}$, g/cm^3	3.155	3.062
Hardness (Mohs)	5–5.5	5–5.5
N	1.582(2)	1.578(2)
Reference	This work	Sokolova *et al*. (2011); Pautov *et al*. (2013)

Darai-Pioz River, the Alaisky mountain ridge, Tien-Shan Mountains, Tajikistan. The mineral is named after Dmitri Mendeleev (1834–1907), the great Russian chemist, author of the periodic table of chemical elements, who has had a significant impact on the development of natural sciences and industry, both in Russia and around the world. Mendeleevite-(Nd) is a Nd analogue of mendeleevite-(Ce), $(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca,\square)_{30}(Si_{70}O_{175})(H_2O,OH,F,\square)_{35}$ (Table 1). The new mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2015-031). The holotype specimen has been deposited in the mineral collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, registration # 4707/1.

The crystal structure of mendeleevite-(Ce) (Sokolova *et al*., 2011) is extremely complex. It is listed as the fourth most complex mineral structure out of 20 most complex mineral structures (Krivovichev, 2013). Refining such a structure is not a trivial process, so as mendeleevite-(Nd) is just substitution of one rare-earth for another, with a slight change in the amount of *REE* and Ca(+Sr) accompanied by change in the OH:H_2O ratio, there is little value in investigating the structure. Here, we report the description of mendeleevite-(Nd) as a new mineral.

Occurrence and mineral association

Mendeleevite-(Nd) was found in the upper part of the Darai-Pioz alkaline massif, which is located at the juncture of Turkestan, Alaisky and Zeravshan ranges in the upper reaches of the Darai-Pioz river (which is a left tributary of the Yarhych river). The majority of its outcrops are covered by glaciers and are very difficult to access. The massif is a ring structure slightly extended in the northwest direction. It occupies the core of a large synclinal fold of terrigenous rocks and schists. The Darai-Pioz massif is composed mainly of biotite granites, aegirine-bearing and quartz-bearing syenites. Rocks of the massif have been intruded by alkaline pegmatites, fenites and carbonatites, with rich rare-metal mineralization. In the north-eastern part of the massif, there is a stock of cancrinite-foyaites. Geology and mineralogy of the Darai-Pioz alkaline massif was considered by Dusmatov (1968, 1971), Belakovskiy (1991) and others. The characteristic feature of the mineralogy of the massif is a wide variety of Cs minerals: kupletskite-(Cs) (Yefimov *et al*., 1971; Cámara *et al*., 2010), sokolovaite (Pautov *et al*., 2006), telyushenkoite (Sokolova *et al*., 2002; Agakhanov *et al*., 2003), zeravshanite (Pautov *et al*., 2004; Uvarova *et al*., 2004), kirchhoffite (Agakhanov *et al*., 2012), mendeleevite-(Ce) (Sokolova *et al*., 2011; Pautov *et al*.,

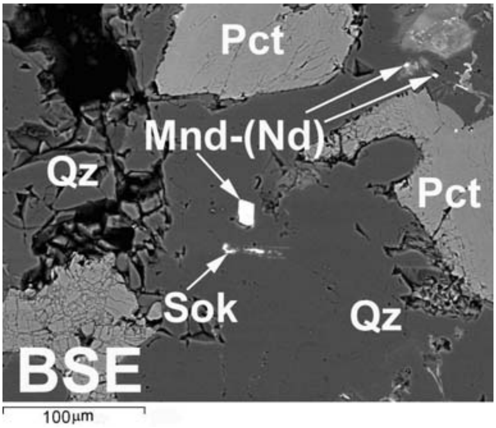

FIG. 1. Back-scattered electron image of mendeleevite-(Nd) [Mnd-(Nd)] and associated minerals: pectolite (Pct), quartz (Qz) and sokolovaite (Sok).

2013), senkevichite (Agakhanov *et al*., 2005; Uvarova *et al*., 2006) and odigitriaite (Agakhanov *et al*., 2015).

Mendeleevite-(Nd) was found in a pectolite aggregate in quartz-rich rocks which consist mainly of medium-coarse to granular quartz (Fig. 1). These rocks have a very characteristic appearance: in an aggregate of colourless, transparent quartz, there are chaotic purple-pink plates of sogdianite, large plates of polylithionite, reddish-brown translucent lenticular crystals of stillwellite-(Ce), grass-green crystals of leucosphenite, irregular grains or poorly terminated crystals of pink or light-orange reedmergnerite, white or pale green microcline, dark green turkestanite crystals, yellow-orange baratovite plates and black aegirine crystals. Brownish-grey nest-like clusters of pectolite aggregate (1 to 30 cm wide) mainly consist of fine to medium pectolite grains, quartz, aegirine and fluorite, with minor khvorovite, mendeleevite-(Ce), sokolovaite, hyalotekite, orlovite, kirchhoffite, pekovite, neptunite, zeravshanite, senkevichite, nordite-(Ce), alamosite, pyrochlore-group minerals and baratovite.

Physical properties

Mendeleevite-(Nd) occurs as transparent, colourless, sometimes with a pale brown hue, crystals 10–40 µm in size. It is brittle, with conchoidal fracture. Streak is white, lustre is vitreous, cleavage and parting have not been observed. The Mohs hardness is 5–5.5. Microhardness VHN, measured with PMT-3, calibrated with NaCl, is 621 kg/mm^2 (average of 10 measurements ranging from 491 to 672 kg/mm^2, loading is 50 g). The mineral is not soluble either in water, or in HCl (1 : 1). It does not luminesce under ultraviolet light. The density, determined by flotation in methylene-bromoform solution, is 3.20(2) g/cm^3, the calculated density is 3.155 g/cm^3. The mineral is optically isotropic, with the refractive index $n = 1.582(2)$. An infrared (IR) spectrum of mendeleevite-(Nd) was collected from a KBr pellet with Specord 75 IR. The IR spectrum of mendeleevite-(Nd) is similar to that of mendeleevite-(Ce). However due to lack of sufficient material, only a poor-resolution IR spectrum has been obtained. The absorption bands in the mendeleevite-(Nd) IR spectrum are as follows (cm^{-1}): 3408, 1612, 1011, 980, 695(shoulder), 547(shoulder).

The compatibility index (1–Kp/Kc) is –0.039 (excellent, using measured density) and –0.056 (good, using calculated density) (Mandarino, 1981).

Chemical composition

The chemical composition of mendeleevite-(Nd) was determined using a JEOL Superprobe JCXA-733 electron microprobe equipped with energy-dispersive (EDS) and wavelength-dispersive spectrometers (WDS). Twelve points were analysed on two grains. For all elements except F, measurements were carried out using (Si–Li) EDS with an INCA analysis system, with an accelerating voltage of 20 kV, a probe current of 2 nA and a probe diameter of 1 µm. Fluorine was analysed by WDS with an accelerating voltage of 10 kV, a probe current of 50 nA and a probe diameter of 5 µm. The following standards were used: microcline USNM 143966 (Si, K), $CePO_4$ (Ce), $LaPO_4$ (La), $NdPO_4$ (Nd), $PrPO_4$ (Pr), $SmPO_4$ (Sm), $GdPO_4$ (Gd), $EuPO_4$ (Eu), anorthite USNM 137041 (Ca), MgF_2 (F). Content of H_2O was calculated by analogy with mendeleevite-(Ce) (Sokolova *et al*., 2011) (for details, see below). The data were reduced and corrected by the *PAP* method for F (Pouchou and Pichoir, 1985) and by *XPP* correction for other elements. The chemical composition of mendeleevite-(Ce) is given in Table 2 and is an average of 12 analyses.

Chemical formula

Here we explain how we write the chemical formula for mendeleevite-(Nd) by analogy with

TABLE 2 . Chemical analysis and unit formula for mendeleevite–(Nd).

Constituent	Average	Range (wt.%)	Esd.		Unit formula (apfu)
SiO_2	42.30	41.65 – 43.22	0.53	Si	70.03
Gd_2O_3	1.69	1.41 – 2.07	0.34	Gd	0.93
Eu_2O_3	0.47	0.18 – 1.06	0.27	Eu	0.27
Sm_2O_3	4.19	3.57 – 4.56	0.33	Sm	2.39
Nd_2O_3	16.19	15.25 – 16.85	0.27	Nd	9.57
Pr_2O_3	2.79	2.28 – 3.53	0.56	Pr	1.68
Ce_2O_3	10.12	9.72 – 10.78	0.47	Ce	6.13
La_2O_3	3.60	3.23 – 4.11	0.45	La	2.20
SrO	2.99	2.15 – 3.60	0.14	Sr	2.87
CaO	2.20	1.93 – 2.65	0.30	Ca	3.90
Cs_2O	8.50	7.18 – 9.55	0.47	Cs	6.00
K_2O	0.85	0.12 – 1.73	0.70	K	1.80
F	1.25		0.47	F	6.54
H_2O**	3.85			H_2O	14.00
				OH	14.47
$–O = F_2$	–0.53				
Total	100.46				

Esd–Estimated standard deviation
* empirical formula calculated on the basis of 210 (O + F) apfu, with $F + OH + H_2O = 35$ pfu, $Z = 2$
** calculated by analogy with mendeleevite-(Ce) (Sokolova *et al*., 2011)

mendeleevite-(Ce). Table 3 reports assigned site-populations for specific groups of cations and anions in the crystal structures of mendeleevite-(Ce) (Sokolova *et al*., 2011) and mendeleevite-(Nd).

In mendeleevite-(Ce), (*REE* + Ca + Sr) occur at the *M* sites, Cs at the *A* sites, K at the *B* sites (□ > K) and Si at the *Si* sites, with a total charge of 367.02^+. There are 210 (anions + H_2O groups) per

TABLE 3. Assigned site-populations for mendeleevite-(Nd) and mendeleevite-(Ce)*.

	Mendeleevite-(Nd)		Mendeleevite-(Ce)	
Site	Site population (apfu)	Charge	Site population (apfu)	Charge
Cations				
M(1–3)	23.17 *REE* + +3.90 Ca + 2.87 Sr + 0.06 □	83.05^+	22.50 *REE* + +4.68 Ca + 1.00 Sr + 1.82 □	78.86^+
A(1,2)	6.00 Cs + 6.00 □	6.00^+	4.65 Cs + 1.35 □; 4.71 □ + 1.29 Cs	5.94^+
B(1,2)	1.80 K + 4.20 □	1.80^+	3.89 □ + 2.11 K; 5.89 □ + 0.11 K	2.22^+
Si(1–7)	70 Si	280.00^+	70 Si	280.00^+
Σ		370.85^+		367.02^+
Anions and H_2O groups				
O(1–19)	175 O	350.00^-	175 O	350.00^-
O(20–27)	14.00 H_2O + (14.46 OH + 2.54 F)	17.00^-	17.79 H_2O + (10.17 OH + 2.83 F)	13.00^-
F	4 F	4.00^-	4 F	4.00^-
Σ		371.00^-	Σ	367.00^-

*from Sokolova *et al*. (2011)

TABLE 4. X-ray powder diffraction data for mendeleevite–(Nd).

$I_{obs.}$	$d_{obs.}$(Å)	$d_{calc.}$(Å)	*h k l*	$I_{obs.}$	$d_{obs.}$(Å)	$d_{calc.}$(Å)	*h k l*
55	15.63	15.51	0 1 1	6	2.432	2.434	0 0 9
40	12.73	12.64	1 1 1	8	2.374	2.375	2 0 9
100	11.01	10.96	0 0 2				0 2 9
22	7.76	7.75	0 2 2	9	2.365	2.367	5 5 6
14	6.94	6.93	1 0 3	14	2.323	2.323	2 2 9
8	6.63	6.61	1 1 3				6 2 7
11	4.91	4.90	0 2 4				5 0 8
12	4.26	4.22	1 1 5	42	2.192	2.190	0 0 10
30	4.07	4.07	2 3 4				6 0 8
			2 0 5	27	2.129	2.127	0 5 9
			3 2 4				5 0 9
26	3.88	3.872	0 0 4	14	2.094	2.090	3 1 10
3	3.75	3.757	3 3 4				5 2 9
11	3.66	3.650	2 4 4				5 6 7
			0 0 6	17	2.03	2.028	4 1 10
30	3.56	3.556	1 1 6				7 2 8
			3 2 5				2 7 8
			2 3 5	16	1.925	1.924	7 0 9
42	3.47	3.463	2 0 6				0 7 9
			0 2 6	11	1.896	1.893	7 2 9
6	3.341	3.342	3 3 5				5 3 10
15	3.304	3.305	2 2 6	41	1.819	1.821	3 6 10
5	3.271	3.271	0 3 6	24	1.795	1.795	0 7 10
			3 0 6				7 0 10
42	3.099	3.099	3 4 5	11	1.727	1.725	5 6 10
			4 3 5				6 5 10
			0 5 5				4 8 9
22	3.040	3.072	1 5 5	30	1.676	1.679	5 1 12
10	2.984	2.982	1 2 7				1 5 12
			2 1 7				5 8 9
			3 3 6				8 5 9
			2 5 5	8	1.646	1.642	5 3 12
17	2.856	2.854	1 3 7				3 5 12
			3 5 5	12	1.611	1.610	4 5 12
12	2.804	2.805	3 4 6	28	1.546	1.548	8 6 10
			4 3 6				0 2 14
8	2.714	2.716	5 2 6				0 10 10
			4 0 7	8	1.538	1.540	7 3 12
9	2.7	2.698	1 4 7				
			4 1 7				
21	2.548	2.547	3 1 8				
			5 0 7				
			0 5 7				

formula unit in the crystal structure of mendeleevite-(Ce). The positive charge of 367.02^+ is compensated by the negative aggregate charge of 367.00^- provided by three groups of anions: (1) 350^- from 175 O atoms which belong to Si tetrahedra; (2) 4^- from 4 F atoms; and (3) 13.00^- from 13.00 monovalent anions (10.17 OH + 2.83 F) (Table 3). Hence the latter aggregate negative charge is provided by 192 anions per formula unit (pfu) and there are also ~18 H_2O groups in mendeleevite-(Ce).

By analogy with mendeleevite-(Ce), we assign available cations in the structure of mendeleevite-(Nd): (*REE* + Ca + Sr) to the *M* sites; Cs to the *A* sites; K to the *B* sites (□ > K) and Si to the *Si* sites, with a total aggregate charge of 370.85^+(Table 3). Considering mendeleevite-(Nd) and mendeleevite-

(Ce) being isostructural, we assume that there are 210 (anions + H_2O groups) per formula unit in the crystal structure of mendeleevite-(Nd). The positive charge of 370.85^+ must be compensated by the negative aggregate charge. There are two anion groups which sum to 179 apfu (atoms per formula unit) and they contribute the following charge: (1) 350^- from 175 O atoms which belong to Si tetrahedra + (2) 4^- from 4 F atoms, i.e. 354^-. The positive charge of 370.85 – 354 = 16.85^+ must be compensated by monovalent anions. The chemical analyses gives 6.54 F apfu. (Table 2), we have already counted a contribution from 4 F apfu (see above) and hence we must have 17 monovalent anions, (14.46 OH + 2.54 F), with an aggregate charge of 17.00^- to compensate the positive charge of 16.85^+. So far we have considered 196 anions [175 O + 4 F + (14.46 OH + 2.54 F)] and hence we need 14 H_2O groups to achieve 210 (anions plus H_2O groups) pfu as in mendeleevite-(Ce) (Table 3).

The empirical formula for mendeleevite-(Nd) was calculated on 210 (O + F) apfu by analogy with mendeleevite-(Ce), with H_2O also calculated by analogy with mendeleevite-(Ce), i.e. with F + OH + H_2O = 35 pfu: $Cs_6(\square_{4.20}K_{1.80})_{\Sigma 6}\{[(Nd_{9.57}Ce_{6.13}Sm_{2.39}La_{2.20}Pr_{1.68}Gd_{0.93}Eu_{0.27})_{\Sigma 23.17}(Ca_{3.90}Sr_{2.87})_{\Sigma 6.77}]_{\Sigma 29.94}\square_{0.06}\}_{\Sigma 30}(Si_{70.03}O_{175})(OH_{14.47}F_{6.54})_{\Sigma 21.01}(H_2O)_{14}$, $Z = 2$. The simplified and the ideal formulae are written by analogy with mendeleevite-(Ce) (Sokolova *et al.*, 2011; Pautov *et al.*, 2013): $(Cs,\square)_6(\square,Cs)_6(\square,K)_6(REE,Ca)_{30}(Si_{70}O_{175})(OH,H_2O,F)_{35}$ and $Cs_6(REE_{23}Ca_7)(Si_{70}O_{175})(OH,F)_{19}(H_2O)_{16}$, respectively.

X-ray data

Powder X-ray diffraction data were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer (Co*K*α) equipped with cylindrical image plate detector using Debye-Scherrer geometry (*d* = 127.4 mm). The powder X-ray diffraction data of mendeleevite-(Nd) are given in Table 4. The *a* unit-cell parameter refined from the powder data is 21.9106(4) Å; V = 10518.7(9) Å^3. The extinction laws in the powder X-ray data (Table 4) are in accord with the space group $Pm\bar{3}$, as in mendeleevite-(Ce) (Sokolova *et al.*, 2011) and we assign this space group to the mendeleevite-(Nd) structure.

Summary

Mendeleevite-(Nd) is a Nd-analogue of mendeleevite-(Ce). Mendeleevite-(Nd) and mendeleevite-(Ce) differ in the dominant *REE* element, Nd and Ce, respectively, with a slight change in amounts of *REE* and Ca(+ Sr): $REE_{23}Ca_7$ [mendeleevite-(Nd)] and $REE_{22}Ca_6$ [mendeleevite-(Ce)] accompanied by change in the OH:H_2O ratio: 14.46:14.00 [mendeleevite-(Nd)] and 10.17:17.75 [mendeleevite-(Ce)] (Table 3).

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