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Evgeny GALUSKIN[1], Irina GALUSKINA[1], Piotr DZIERŻANOWSKI[2]

NEW NATURAL PHASE $MnTi_2O_4(OH)_2 \times H_2O$(?) WITH UNCERTAIN STRUCTURE – INDICATOR OF SEA FLOOR METASOMATISM

Abstract: A new natural mineral phase $MnTi_2O_4(OH)_2 \times H_2O$(?) was discovered in serpentinites of Wiluy deposit. It was originated due to metasomatism of skarnoids at sea floor condition in the continental rift zone.

Keywords: $MnTi_2O_4(OH)_2 \times H_2O$, kassite, cafetite, metasomatism, Wiluy River.

INTRODUCTION

In aposkarn achtarandite rocks of the Wiluy deposit, Yakutia, which is known as the type locality of grossular and wiluite, a new natural water-containing Ti-Mn-hydroxide with ratio Ti:Mn=2:1 was discovered. Minerals with the similar Ti:R^{2+} ratio belong to a pseudobrookite group, which includes armalcolite $MgFeTi_4O_{10}$ and pseudobrookite $FeTi_2O_5$ (Bowles 1998). In metamorphic rocks of Priol'hkon'e (Baikal Lake) a new phase $MnTi_2O_5$ was discovered. This mineral probably belongs to the pseudobrookite group also, but it was not investigated up to now (Konev et al. 2001). This new Ti-Mn-phase is more similar in composition to water-OH-containing Ca-Ti-oxides discovered in alkaline rocks of Afrikanda massif, Kola peninsula called cafetite $Ca[Ti_2O_5](H_2O)$ (Krivovichev et al. 2003) and kassite $Ca[Ti_2O_4(OH)_2]$ (Grey et al. 2003). In this paper authors present data concerning only morphology, composition and origin of the new phase, which we have conditionally named "Mn-kassite", it was found as a small up to 7-8 μm crystals being in tight intergrowth with chlorite and serpentine.

GEOLOGY

Outcrops of achtarandite rocks are located among the Siberian traps, on the shores of Wiluy River near Chernyshevsky town, Yakutia. "Mn-kassite" was found in serpentinites, forming layered series of metasomatic rocks together with rodingite-like rocks. The protolith of metasomatic rocks of Wiluy deposit was a ksenolite of Ordovician sedimentary rocks, captured by Erbeyeksky trap intrusion, which was placed in the Achtaranda tectonic zone belonging to the East part of the volcano-tectonic Tungus megastructure of the Siberian platform. The three main stages can be distinguished in the history of formation of achtarandite

[1] *University of Silesia, Będzińska Street 60, 41-200 Sosnowiec, Poland; galuskin@us.edu.pl*
[2] *Warsaw University, Żwirki i Wigury Street 93, 02-089 Warszawa, Poland; p.dzierzanowski@uw.edu.pl*

rocks: skarnation, serpentinization, and late hydrothermal alteration (Galuskina et al. 2001).

METHODS OF INVESTIGATION

Morphology, internal structure and composition of "Mn-kassite" were investigated by electron microscope FEI/Philips ESEM XL30 with EDS detector (University of Silesia) and by microprobe CAMECA SX100 (Warsaw University). Microprobe measurements, included of oxygen measuring, were carried out at conditions: 15 kV and 20 nA. Natural and synthetic standards were used.

ASSOCIATION, MORPHOLOGY AND COMPOSITION OF "Mn-KASSITE"

"Mn-kassite" in serpentinites was detected within chlorite pseudomorphs after relic skarn Ti-Al-diopside (Table 1). Crystals of Ti-Al-diopside were substituted by sponge agreggate of chlorite, on which crystals of "Mn-kassite" (Table 1), titanite (Table 1), and anatase grew. Relics of perovskite (Table 1), kimzeyite and schorlomite were also noted. Sponge pseudomorph was usually filled by minerals of serpentine group, oxides-hydroxides of manganese (asbolane, corandite-hollandite, manganite and others) or calcite. Kassite-like mineral (Table 1) was detected in rodingite-like rocks with abundant relics of fassaitic pyroxene and ilmenite. The „Mn-kassite" forms crystals of different habit with hexagonal cross-section: discus-like, pinacoidal, prismatic, rombohedral (Fig. 1a). Twins and split crystals are noted, as well (Fig. 1b).

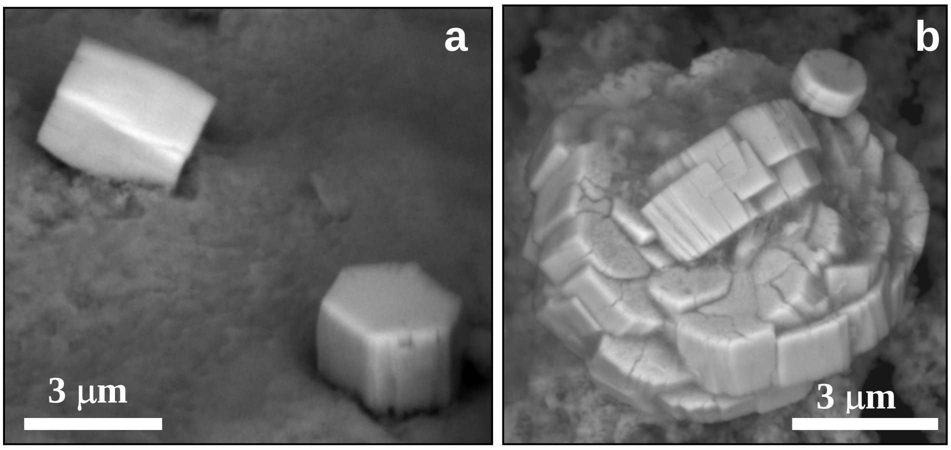

Fig.1. Morphology of "Mn-kassite", BSE, low vacuum, 0.3 Torr: a – prismatic crystals, b – split aggregate of crystals.

Morphology of crystals, character of twins and split crystals allow to assume a $\bar{3}m$ point group (?).

Totals of microprobe analyses obtained for the „Mn-kassite" vary in the range

Table 1. Composition of Ti-minerals from achtarandite serpentinite, wt. %.

	Ti-Al diopside	perovskite	titanite	kassite		„Mn-kassite“	
SiO_2	38.30	0.25	30.23	0.28	0.18	0.50	0.43
TiO_2	4.84	56.04	36.68	63.33	64.25	55.54	56.51
ZrO_2	n.d.	0.46	0.29	0.34	0.24	0.10	0.07
HfO_2	n.d.	0.06	0.03	0.06	0.65	n.d.	n.d.
Al_2O_3	16.30	n.d.	0.13	n.d.	n.d.	0.58	0.11
Cr_2O_3	0.06	0.06	n.d.	0.08	0.05	n.d.	n.d.
Ce_2O_3*	n.d.	0.33	0.20	0.40	0.39	n.m.	n.m.
Fe_2O_3	5.17	1.72	2.74	1.37	1.26	3.72	4.23
FeO^X		0.51					
MgO	10.33	n.d.	n.d.	n.d.	n.d.	0.35	0.48
MnO	0.02	0.03	n.d.	1.08	0.61	24.13	24.82
MnO_2						1.96	3.40
CaO	25.24	39.14	27.19	21.74	22.14	n.d.	0.17
Na_2O	0.02	n.d.	0.03	n.d.	n.d.	n.d.	n.d.
F	n.d.	0.03	0.05	0.05	0.45	n.m.	n.m.
H_2O^X			0.22	10.91	10.60	13.68	10.46
-O=F		0.01	0.02	0.02	0.19		
Total	100.28	98.62	97.77	99.60	100.63	100.57	100.68$^{\triangle}$
			calculated on:				
	4 cations	2 cations			3 cations		
Ca	1.01	0.97	0.98	0.95	0.96		0.01
Mn^{2+}				0.04	0.02	0.90	0.89
Fe^{+2}		0.01					
Mg						0.02	0.03
Fe^{3+}		0.02	0.02	0.01	0.02	0.08	0.07
X	**1.01**	**1**	**1**	**1**	**1**	**1**	**1**
Mg	0.57						
Fe^{3+}	0.15	0.01	0.05	0.03	0.02	0.04	0.06
Al	0.13						
Ti^{4+}	0.14	0.97	0.92	1.95	1.96	1.85	1.81
Mn^{4+}						0.06	0.10
Zr		0.01	0.01	0.01			
Hf					0.01		
Si		0.01	0.01	0.01	0.01	0.02	0.02
Al			0.01			0.03	0.01
Y	**1.99**	**1**	**1**	**2**	**2**	**2**	**2**
Si	1.42		1.00				
Al	0.58						
Z	**2**		**1**				
F			0.01	0.01	0.06		
OH			0.06	2.99	2.87	4	3

* - $Ce_2O_3+La_2O_3+Y_2O_3$, ^{X} - calculated on charge balance, $^{\triangle}$- in sum calculated O = 40.63 wt.% (measured O = 40.21 wt.%).

86-87 wt. % for analyses with calculated oxygen and from 97.5 to 100 wt. % for analyses with measured oxygen. This fact points out high hydrogen content in the mineral. Analyses of “Mn-kassite” obtained at without-oxygen series of measurements were calculated for 7 oxygen and 4 hydrogen atoms – $MnTi_2O_4(OH)_2{\times}H_2O$ or $MnTi_2O_5{\times}2H_2O$ (Tab. 1), while these with measured oxygen were better calculated for 6.5 oxygen and 3 hydrogen atoms (Tab. 1) - $MnTi_2O_4(OH)_2 \times 0.5H_2O$ or $MnTi_2O_5 \times 1.5H_2O$. Iron is a main impurity in the "Mn-kassite" and is incorporated to the structure as the end-member $Fe^{3+}{}_2TiO_4(OH)_2$.

DISCUSSION

Formation of „Mn-kassite" was connected to the stage of mass hydration of achtarandite skarnoids. During this process Mg-enriched rocks were turned into serpentinites and Ca-enriched ones – into rodingite-like rocks (Galuskina et al. 2001). Relatively high mobility of Ti, realized from the Ti-Al-diopside, perovskite and ilmenite decomposition, possible due to the increased alkalinity of solutions caused serpentinization and rodingitization of achtarandite rocks. High water content in "Mn-kassite" and abudance of hydrogarnets and "hydrovesuvianites" in rodingite-like rocks point out their formation as a result of metasomatism of sea floor in the rift zone at the conditions from prehnite-pumpellyite to zeolite facies, what is characteristic for typical rodingites (Dubińska et al. 2004). Low-temperature hydroterms connected to volcanic activity of Achtaranda rift zone were, probably, the source of manganese. Thus, "Mn-kassite" could be an indicator of metasomatism of rocks being at condition of the sea floor in the continental rift zone. The role of sea water during metasomatic processes (serpentinization and rodingitization) is supported by the presence of increased Cl-content in "hydrovesuvianites" (Galuskin et al. 2003).

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