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Article in *The Canadian Mineralogist* · May 2015

DOI: 10.3749/canmin.1400091

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CHEMICAL EVOLUTION AND LATE-STAGE RE-EQUILIBRATION OF Zr-Hf-U-BEARING COLUMBITE-GROUP MINERALS IN THE KOKTOKAY NO. 1 GRANITIC PEGMATITE, ALTAI, NORTHWESTERN CHINA

RONG YIN, RU CHENG WANG[§], AI-CHENG ZHANG, HUAN HU, AND JIN CHU ZHU

State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210046, China

CAN RAO

Department of Earth Sciences, Zhejiang University, Hangzhou 310027, China

HUI ZHANG

Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002, China

ABSTRACT

The Koktokay No. 1 pegmatite in northwestern China is a highly fractionated Li-Cs-Ta (LCT)-type granitic pegmatite. As main Nb-Ta oxides in this pegmatite, columbite-group minerals (CGMs) not only display variations in Nb/Ta and Fe/Mn, but also are typified by noticeable Zr, Hf, and U contents. Here, we report on the chemical evolution and late-stage re-equilibration of CGMs in the processes of crystallization and evolution of this pegmatite. Columbite-group minerals record large variations in Ta/(Nb + Ta) values (0.06–0.98) and moderate variations in Mn/(Fe + Mn) values (0.58–0.99), which could be a result of fractional crystallization of pegmatite magma. The concentrations of ZrO₂, HfO₂, and UO₂ in CGMs from the contact zone inwards to zone II of this pegmatite are uniformly less than 0.35 wt.%. However, primary tantalite-(Mn) with Ta/(Nb + Ta) and Mn/(Fe + Mn) values of 0.63–0.98 and 0.86–0.99, respectively, show relatively high contents of ZrO₂, HfO₂, and UO₂, up to 1.68, 0.73, and 1.25 wt.%, respectively. The contents of ZrO₂, HfO₂, and UO₂ are positively correlated with variations in Ta/(Nb + Ta) values within different grains and single grains of primary tantalite-(Mn). Crystal-chemical considerations suggest that Zr, Hf, and U are possibly present in the tantalite-(Mn) structure due to the substitution $3(\text{Zr,Hf,U})^{4+} = 2(\text{Nb,Ta})^{5+} + (\text{Fe,Mn})^{2+}$. In some areas within the primary tantalite-(Mn) crystals in zone III, specific tantalite-(Mn) has been identified with sharp but irregular contacts with the host tantalite. Such tantalite-(Mn) is chemically depleted in Zr, Hf, and U, but contains many small inclusions of zircon, the MnZrTa₂O₈ phase, uraninite, and U-rich member of the microlite group of minerals. In a similar way, the primary Zr-Hf-U-bearing tantalite-(Mn) experienced late-stage local re-equilibration, giving rise to the formation of secondary Zr-Hf-U-depleted tantalite-(Mn) and other Zr- or U-rich mineral inclusions in an open fluid-mediated system. The behaviors of Zr, Hf, and U in CGMs in the Koktokay No. 1 pegmatite are indicative of Zr, Hf, and U enrichment during fractional crystallization of a highly fractionated pegmatite magma on one hand and imply late-stage activities of fluids on the other. Considerable enrichment of U and Hf in CGMs indicates that this type of mineral may act as a target for *in situ* LA-ICP-MS U-Pb dating and Lu-Hf isotope measurements, which may provide key information for understanding the source of the magma and the evolution mechanism of the Nb-Ta mineralization.

Keywords: Koktokay No. 1 pegmatite, columbite-group minerals, Zr-Hf-U bearing, MnZrTa₂O₈ phase, zircon, evolution, chemical re-equilibration.

INTRODUCTION

Niobium-tantalum and zirconium-hafnium are two important rare element pairs that are often used in mineral chemistry-based research to unravel the processes and extents of magmatic-hydrothermal frac-

tional crystallization in highly evolved granitic rocks. The chemical evolution of columbite-group minerals (CGMs) is traditionally characterized by the ratios of Ta/(Nb + Ta) and Mn/(Fe + Mn), which usually increase with fractional crystallization of granites or granitic pegmatites (*e.g.*, Černý & Ercit 1985). The majority of such

[§] Corresponding author e-mail address: rcwang@nju.edu.cn

research focuses on variations in major element concentrations in CGMs and zircon–hafnon series minerals (e.g., Correia Neves *et al.* 1974, Černý *et al.* 1985, Lahti 1987, Wang *et al.* 1997, Novák *et al.* 2003, Zhang *et al.* 2004). On the other hand, CGMs may closely coexist with zircon and evolve simultaneously with the latter in rare-element granites and pegmatites (Fontan *et al.* 1980, Wang *et al.* 1996). Recently, Van Lichtervelde *et al.* (2009, 2011) studied the behavior of zircon with respect to Ta mineralization in the Tanco pegmatite of southern Manitoba, Canada. They found that zircon can contain up to 4.7 wt.% Ta₂O₅, and that Ta concentrations in zircon vary in accordance with the stages of Ta mineralization recorded in the pegmatite. In contrast, the behaviors of trace and minor elements (Zr, Hf, and U) in CGMs remain poorly constrained, despite the fact that the maximum concentrations and behaviors of these elements in CGMs are not only important for improving our understanding of Nb-Ta-Zr-Hf mineralogy (Černý *et al.* 2007), but also critical for the further development of columbite U-Pb geochronology and Hf isotope analysis (Romer & Wright 1992, Romer & Smeds 1994, Che *et al.* 2015).

Romer *et al.* (1996) determined the UO₂ concentrations in CGMs from different granites and granitic pegmatites and found that the majority of the CGMs contain <500 ppm UO₂, but a few CGMs may have up to 5700 ppm UO₂. Černý *et al.* (2007) studied the behaviors of Zr and Hf in CGMs from a few moderately to highly fractionated granitic pegmatites. They determined that the contents of ZrO₂ and HfO₂ in CGMs can attain 1.26 wt.% and 0.12 wt.%, respectively. However, no systematic variations were observed between zones within individual pegmatites (Černý *et al.* 2007). Melcher *et al.* (2015) reported trace elements (including Zr, Hf, and U) and U-Pb isotopic systematics in Ta-Nb oxide minerals from abundant African pegmatites and rare metal granites. They observed that the content of ZrO₂ in columbite-group minerals in these pegmatites could be up to 1.8 wt.%, while the concentrations of Hf and U could attain 4308 ppm and ~1 wt.%, respectively (Melcher *et al.* 2015). However, no obvious correlation between Zr and the Fe-Mn and Nb-Ta fractionation indices for CGMs was observed (Melcher *et al.* 2015). The Koktokay No. 1 pegmatite, located in the Altai region of northwestern China, is an extremely fractionated granitic pegmatite, as evidenced by the presence of very rare zirconian hafnon (Yin *et al.* 2013). It is possible that ZrO₂, HfO₂, and UO₂ concentrations in CGMs systematically vary among different zones in this highly fractionated granitic pegmatite. Recent research has revealed that CGMs in the Koktokay No. 1 pegmatite contain up to 1.68 wt.% ZrO₂, 0.73 wt.% HfO₂, and 1.25 wt.% UO₂. Here, we report the different mineralogical habits and petrographic textures involving CGMs from the Koktokay No.1 granitic pegmatite, as well as the major and minor element chemical evolution, describe the chemical re-equilibration of Zr-Hf-U-bearing CGMs with fine-grained Zr- or U-rich minerals such as zircon, MnZrTa₂O₈ phase, uraninite, and a U-rich

microlite group mineral, and discuss the origins of these minerals, as well as implications for our understanding of these pegmatitic systems.

INTERNAL ZONING OF THE KOKTOKAY NO. 1 PEGMATITE

The Altai Mountains lie in the contiguous areas of China, Mongolia, Russia, and Kazakhstan. The Chinese Altai is distributed on the southwestern slope of the Altai Mountains (Zhu *et al.* 2006). Tectonically, the Chinese Altai Mountains belong to the Altai Paleozoic active continental margin, which is located in the SW part of the Siberian Plate and can be subdivided into three geotectonic units. From NE to SW these units are: the Nolt late Paleozoic volcanic belt, the Qinhe-Halong Paleozoic magmatic belt, and the Kelan River late Paleozoic volcanic belt. The Koktokay rare metals and gem minerals ore field lies in the Qinhe-Halong Paleozoic magmatic belt (Yang 1994). The Koktokay No. 1 pegmatite was discovered in 1935 and was initially exploited for beryl, spodumene, Nb-Ta oxides, and pollucite. It is a highly fractionated Li-Cs-Ta (LCT)-type granitic pegmatite (Yin *et al.* 2013). This pegmatite is located in the Koktokay district of the Altai region of northwestern China, near the No. 3 pegmatite, which is aged approximately 218 ± 2 Ma, determined by U-Pb isotopic dating of columbite-tantalite (Che *et al.* 2015) (Fig. 1a). The Koktokay No. 1 pegmatite was intruded into a surrounding metagabbro body and is also one of the longest pegmatites in this district (1400 m long and 1–7 m thick). Field observations show that its internal structure is asymmetrically zoned (Fig. 1b). From the thin contact zone between the pegmatite and surrounding metagabbro upwards, five zones have been identified on the basis of their macroscopic textures and different mineral assemblages: an aplitic zone (zone I), a quartz-muscovite zone (zone II), a cleavelandite-quartz-spodumene zone (zone III), a blocky quartz zone (zone IV), and a blocky microcline zone (zone V). Zone I is characterized by fine-grained minerals and a layered aplitic texture. Zones II and III are composed of coarse-grained to large rock-forming minerals. Zones IV and V are mainly composed of monominerals and exhibit typical blocky texture. Distributions of rock-forming and accessory minerals in the different texture zones of the Koktokay No. 1 pegmatite are listed in Table 1. The detailed characteristics of the Koktokay No. 1 pegmatite are discussed in a previous publication (Yin *et al.* 2013).

SAMPLES AND ANALYTICAL METHODS

The samples analyzed in this study were collected from four prospects during three different field trips; they cover all textural zones in the Koktokay No. 1 pegmatite. Polished thin sections of these samples were prepared for petrographic analysis and quantitative determination of

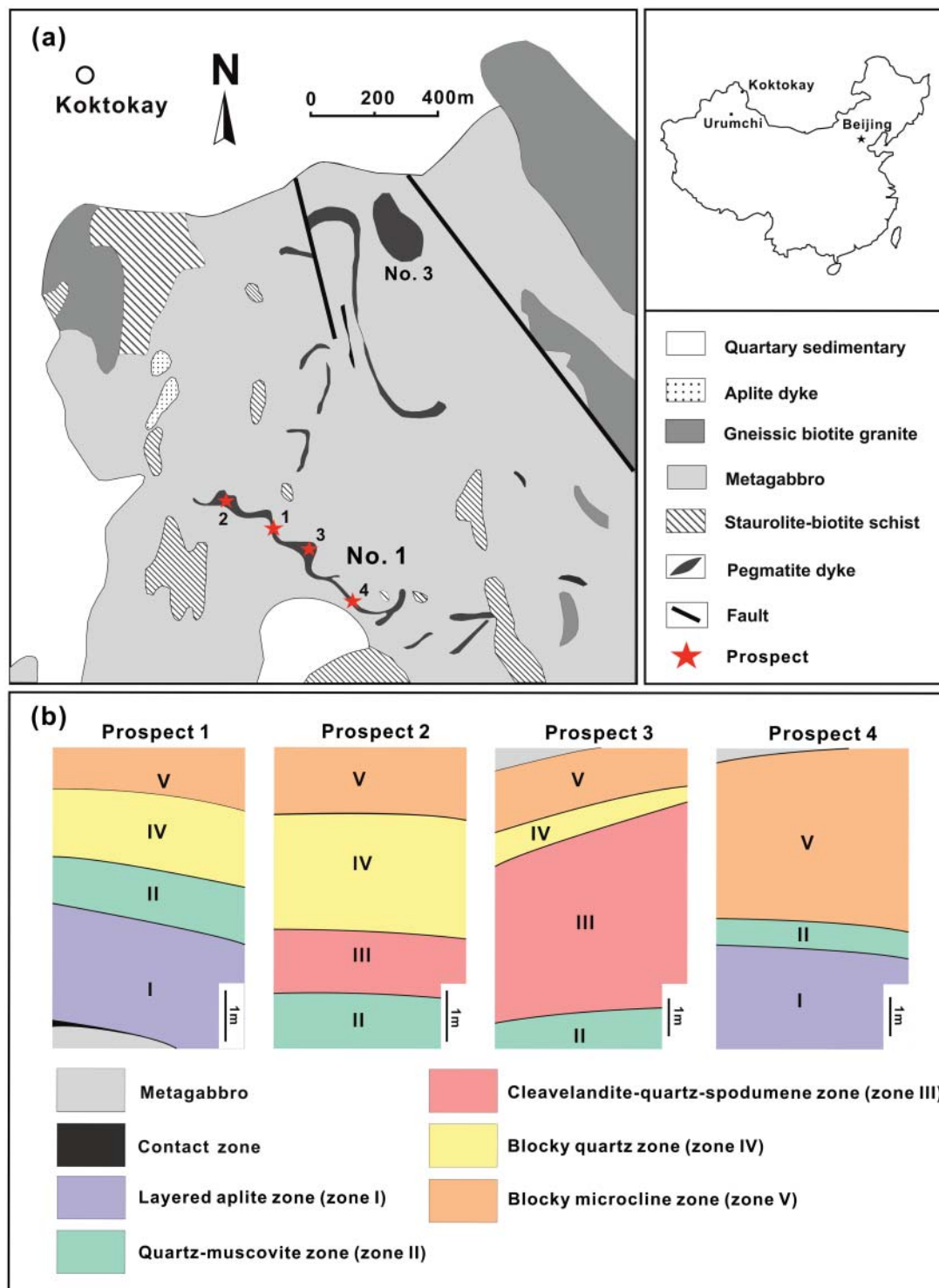


FIG. 1. (a) Geological map showing the location of the Kокtokay pegmatite district of northwestern China (modified from Zhang *et al.* 2004) and the prospects that were sampled for this study. (b) Schematic textural zones of the Kокtokay No. 1 pegmatite at the four prospects sampled for this study. See Yin *et al.* (2013) for a detailed description of each textural zone.

TABLE 1. DISTRIBUTION OF ROCK-FORMING AND ACCESSORY MINERALS IN TEXTURE ZONES OF THE KOKTOKAY NO. 1 PEGMATITE

	contact zone	zone I	zone II	zone III	zone IV	zone V
quartz	42	40	32	47	99	1
albite	28	47	45	32		1
muscovite	17	17	20	20	1	
microcline						98
spodumene				4		
lepidolite				+++		
apatite	+++	+++	+++	+++		
beryl		++	+++	++		
garnet		+++		++		
tourmaline	8			+		
pollucite				++		
zircon	++	+++	+	+++		
Nb-Ta oxide	++	+++	+++	+++		
microlite				++		
stibiotantalite				+		
brockite		+	+			
gahnite				+		
reddingite				+		
uraninite	+	+	+			
kyanite	+					
glaucofanite	+					
lithiophilite				+++		

Note: Rock-forming minerals were estimated in vol.%. Rock-forming minerals proportions of zone III, zone IV, and zone V were estimated from field observation; others were estimated from thin sections observation. The symbols +++, ++, and + represent abundant, present, and rare, respectively.

Nb-Ta oxide mineral chemistry. Petrographic textures were observed using backscatter electron (BSE) imaging and a JEOL 8100 electron probe micro-analyzer (EPMA) at Nanjing University, China, a Hitachi 3400N II Scanning Electron Microscope (SEM) with an Energy Dispersive Spectrometer (EDS) at Purple Mountain Observatory, Nanjing, China, and a LEO1530VP Field Emission-Scanning Electron Microscope (FE-SEM) at the Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing, China.

Mineral compositions were measured using wavelength-dispersion spectroscopic (WDS) EPMA and a focused (~1 µm in diameter) 20 nA beam current accelerated at a voltage of 15 kV. These analyses were quantitatively calibrated using the following natural and synthetic standards: Nb metal (Nb, *Lα*), Ta metal (Ta, *Lα*), fayalite (Fe, *Kα*), MnO₂ (Mn, *Kα*), ZrO₂ (Zr, *Lα*), Hf metal (Hf, *Mα*), MnTiO₃ (Ti, *Kα*), SnO₂ (Sn, *Lα*), CaWO₄ (W, *Lα*), Sc metal (Sc, *Kα*), UO₂ (U, *Mα*), apatite (Ca, *Kα*), and zircon (Si, *Kα*). Peak and background counting times for most elements were 20 s and 10 s, respectively. Zirconium and hafnium concentrations were measured using counting times of 60 s and 30 s for peaks and 30 s and 15 s for backgrounds, respectively. The detection limits for ZrO₂, HfO₂, and UO₂ during this EPMA

analysis are approximately 160, 180, and 230 ppm, respectively. The ZAF routine was used for all data reduction. X-ray elemental mapping was used to identify the spatial distribution of elements and chemical heterogeneities in small areas of single crystals; this mapping used accelerating voltages of 20 or 15 kV and a beam current of 20 or 100 nA.

RESULTS

Columbite-group minerals are the dominant Nb-Ta oxides in the Koktokay No. 1 granitic pegmatite. They are common in zones I and III, but are much less common in the contact zone and in zone II, and are totally absent in zones IV and V. The majority of the CGMs in the Koktokay No. 1 pegmatite are subhedral to euhedral.

Columbite-group minerals in the contact zone

The CGMs in the contact zone are 15 to ~100 µm in length (Fig. 2a) and are generally present as inclusions within or as interstitial fills between tourmaline and muscovite. A few CGMs are also associated with zircon (Fig. 3a in Yin *et al.* 2013). The CGMs in this zone are columbite-(Mn) (Fig. 3) with Ta/(Nb + Ta)

and Mn/(Fe + Mn) values of 0.06–0.19 and 0.58–0.77, respectively (Table 2). Chemical variations are present both within and between single CGM crystals, and inter-mineral variations are much more significant than intra-mineral variations. The majority of CGMs in this zone have ZrO₂, HfO₂, and UO₂ concentrations below detection limits (Table 2; Fig. 4), with the exception of one CGM grain that contains up to 0.35 wt.% ZrO₂, 0.09 wt.% HfO₂, and 0.39 wt.% UO₂.

Columbite-group minerals in zone I

Columbite-group minerals in zone I are generally present as interstitial phases between rock-forming minerals such as albite, quartz, and muscovite, although a few CGM crystals are also observed as inclusions within apatite and spessartine. The CGMs in this zone are generally >100 µm long and the majority have complex zoning textures with brighter rims visible in BSE

images (Fig. 2b). This complex internal texture is consistent with the significant compositional variations present within single CGMs (Table 2), where, for example, the darker cores of these CGMs usually have Ta/(Nb + Ta) values <0.5 (e.g., analysis No. 20) and the brighter rims usually have Ta/(Nb + Ta) values >0.5 (e.g., analysis No. 16) (Figs. 2–3; Table 2). There is no systematic correlation between Mn/(Fe + Mn) values (0.58–0.84) and the brightness of these CGMs. This zone is dominated by columbite-(Mn) with minor tantalite-(Mn) (Fig. 3). The CGMs in this zone usually have low ZrO₂, HfO₂, and UO₂ contents, mostly below detection limits, and rarely show values up to 0.19, 0.18, and 0.60 wt.%, respectively (Table 2; Fig. 4).

Columbite-group minerals in zone II

Columbite-group minerals in zone II, 100–250 µm in length, are texturally and chemically similar to the CGMs in zone I. They are usually associated with

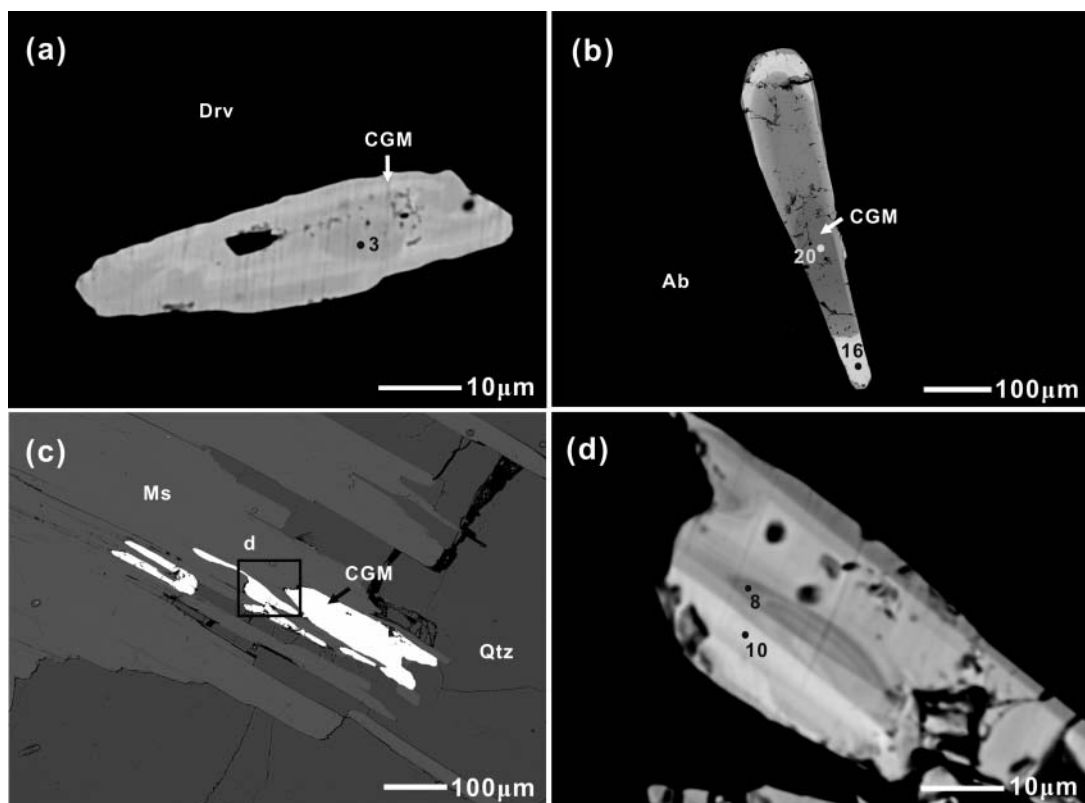


Fig. 2. Backscattered electron (BSE) images of CGMs from Koktokay No. 1 pegmatite. (a) Columbite-(Mn) from the contact zone; (b) columbite-(Mn) with a Ta-rich rim from zone I; (c) columbite-(Mn) at the grain boundary between muscovite and quartz from zone II; (d) magnified image of (c). The numbers in (a, b) correspond to representative compositions given in Table 2. Abbreviations: CGM = columbite-group mineral, Drv = dravite, Ab = albite, Ms = muscovite, Qtz = quartz.

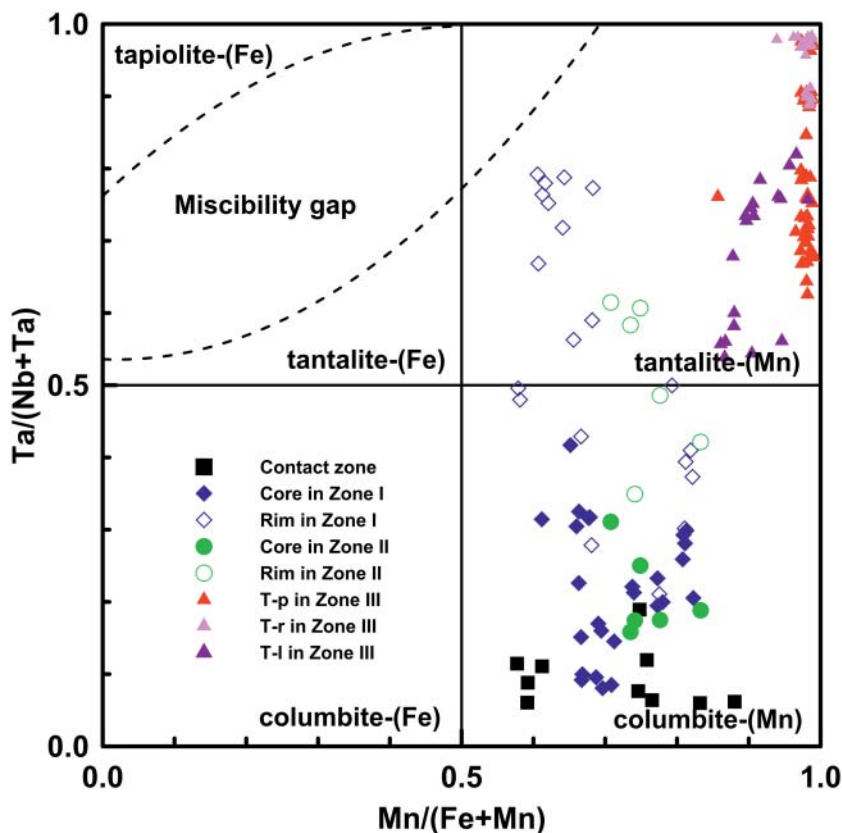


FIG. 3. Columbite-tantalite quadrilateral diagram for the classification of columbite-group minerals from the Koktokay No. 1 granitic pegmatite. Abbreviations for tantalite in zone III: T-p = primary tantalite-(Mn), T-r = re-equilibrated tantalite-(Mn), T-l = late tantalite-(Mn).

quartz, muscovite, and albite (Fig. 2c), with a few CGMs present as inclusions in apatite. These CGM crystals also have complex zoning textures (Fig. 2d) that are related to variations in chemical compositions. The dark cores show an increase in Nb compared to the bright border zone, which is relatively enriched in Ta (e.g., analyses No. 8 and No. 10). Although these CGMs have a limited range in Mn/(Fe + Mn) values (0.71–0.84), they have more varying Ta/(Nb + Ta) values (0.15–0.61; Fig. 3). The ZrO₂, HfO₂, and UO₂ contents in CGMs from zone II are also mostly below detection limits, with a few points attaining approximately 0.56 wt.% ZrO₂, 0.16 wt.% HfO₂, and 0.14 wt.% UO₂, respectively (Table 2; Fig. 4).

Columbite-group minerals in zone III

Columbite-group minerals in zone III are highly variable in size, ranging from several millimeters to tens of microns. They are present mainly as interstitial fills

between albite, quartz, muscovite, and spodumene, and rarely as inclusions in muscovite and apatite. The majority of CGMs in zone III are tantalite-(Mn) with limited variations in Mn/(Fe + Mn) values (0.86–0.99) and more significant variations in Ta/(Nb + Ta) values (0.54–0.98) (Fig. 3). Unlike the CGMs in other zones, the tantalite-(Mn) grains in zone III often contain elevated concentrations of Zr, Hf, and U, with highest contents of 1.68 wt.% ZrO₂, 0.73 wt.% HfO₂, and 1.25 wt.% UO₂ (Table 3). The tantalite-(Mn) in this zone can be divided into three subgroups depending on petrographic textures and chemical features:

(1) Primary tantalite-(Mn) (T-p): The majority of the CGMs in zone III appear to be homogeneous or simply zoned in BSE images; as such, these minerals are here termed primary tantalite-(Mn), abbreviated as T-p. These tantalite-(Mn) grains typically approach the Mn-dominant tantalite endmember with Mn/(Fe + Mn) values of 0.98–0.99 (Fig. 3), but they have highly variable inter- and intra-mineral Ta/(Nb + Ta) values. Again different from those in the above zones, the primary tantalite-(Mn)

TABLE 2. EPMA COMPOSITIONS OF COLUMBITE-GROUP MINERALS IN DIFFERENT TEXTURAL ZONES IN THE KOKTOKAY NO. 1 PEGMATITE

	Contact zone			Zone I			Zone II		
	Average (n = 10)			Average (n = 46)			Average (n = 18)		
Nb ₂ O ₅	66.36 (4.09)	70.45	65.07	42.56 (17.41)	53.22	13.22	45.24 (12.66)	58.40	43.82
Ta ₂ O ₅	11.42 (4.67)	7.53	13.48	36.96 (18.32)	25.84	66.62	35.76 (12.96)	20.58	39.07
FeO	5.72 (2.18)	7.87	7.79	5.28 (1.33)	6.92	6.49	4.29 (0.56)	4.77	4.53
MnO	13.87 (2.18)	11.27	12.14	12.45 (1.73)	13.48	10.50	14.16 (1.23)	14.15	12.84
ZrO ₂	0.09 (0.12)	0.04	0.17	0.06 (0.08)	bdl	0.07	0.04 (0.08)	bdl	0.02
HfO ₂	0.04 (0.03)	bdl	0.07	0.05 (0.05)	bdl	0.13	0.07 (0.03)	0.04	0.09
TiO ₂	0.79 (0.40)	1.47	0.55	0.54 (0.46)	0.60	1.06	0.15 (0.25)	0.04	0.04
UO ₂	0.06 (0.12)	bdl	bdl	0.10 (0.13)	0.08	0.43	0.07 (0.05)	bdl	bdl
SnO ₂	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
WO ₃	0.58 (0.18)	0.72	0.35	0.49 (0.19)	0.53	0.77	0.31 (0.24)	0.51	0.34
Sc ₂ O ₃	0.01 (0.00)	bdl	bdl	0.06 (0.04)	bdl	0.08	0.05 (0.04)	0.01	0.03
Total	98.94	99.35	99.62	98.56	100.60	99.38	100.14	98.5	100.78
Calculated based on 6 O									
Nb	1.781	1.843	1.750	1.288	1.499	0.464	1.339	1.642	1.303
Ta	0.184	0.119	0.218	0.673	0.438	1.409	0.637	0.348	0.699
Fe	0.284	0.380	0.387	0.295	0.360	0.421	0.234	0.248	0.249
Mn	0.697	0.552	0.612	0.706	0.711	0.691	0.785	0.745	0.715
Zr	0.003	0.001	0.005	0.002	bdl	0.003	0.001	bdl	0.001
Hf	0.001	bdl	0.001	0.001	bdl	0.003	0.001	0.001	0.002
Ti	0.035	0.064	0.025	0.027	0.028	0.062	0.007	0.002	0.002
U	0.001	bdl	bdl	0.001	0.001	0.007	0.001	bdl	bdl
Sn	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
W	0.009	0.011	0.005	0.009	0.009	0.016	0.005	0.008	0.006
Sc	0.001	bdl	bdl	0.004	bdl	0.005	0.003	0.001	0.002
Ta/(Nb+ Ta)	0.09	0.06	0.11	0.34	0.23	0.75	0.32	0.17	0.35
Mn/(Fe+ Mn)	0.71	0.59	0.61	0.71	0.66	0.62	0.77	0.75	0.74

Notes: Numbers in parentheses are standard deviations. Numbers 20, 16, 8, and 10 are representative analyses shown in Figure 2. bdl = below detection limit.

grains in zone III are clearly enriched in Zr, Hf, and U (e.g., compositions No. 17 and No. 12 in Table 3). Their highest contents are 1.68 wt.% ZrO₂, 0.73 wt.% HfO₂, and 1.25 wt.% UO₂. The values of Zr + Hf and U in these minerals positively correlate with variations in Ta/(Nb + Ta), but have no clear correlation with Mn/(Fe + Mn) (Fig. 4).

(2) Re-equilibrated tantalite-(Mn) (T-r): Some large primary tantalite-(Mn) grains contain turbid porous regions that appear darker than the clean regions in the BSE images; the boundaries between the two regions are sharp and irregular (Fig. 5). The EPMA results indicate that tantalite from the turbid regions (termed as T-r) has Ta/(Nb + Ta) and Mn/(Fe + Mn) ratios generally similar to those of the clean region (T-p), and are close to the tantalite-(Mn) endmember (Table 3, Fig. 3). However, the T-r phases are much depleted in Zr, Hf, and U (e.g.,

analyses No. 18 and No. 24 in Table 3). Mean values of ZrO₂, HfO₂, and UO₂ contents are 0.25, 0.08, and 0.05 wt.%, respectively (Table 3). The differences in Zr, Hf, and U concentrations between the T-p and T-r are clearly evident in X-ray elemental maps (Fig. 6). Moreover, the turbid regions (T-r) are characterized by the presence of a few fine-grained inclusions (from submicron to ~20 µm in size), which were identified as zircon, a MnZrTa₂O₈ phase, uraninite, and a U-rich member of the microlite group of minerals. Muscovite is occasionally present at the contact between T-r and T-p phases.

Zircon inclusions in T-r are always anhedral and uniformly <10 µm in size (generally 1–2 µm). Several measurable zircon inclusions within these T-r minerals yielded EPMA analyses indicating that they are HfO₂-rich (16–19 wt.%, Table 4); these analyses also yielded Ta₂O₅ concentrations of ~2 wt.%.

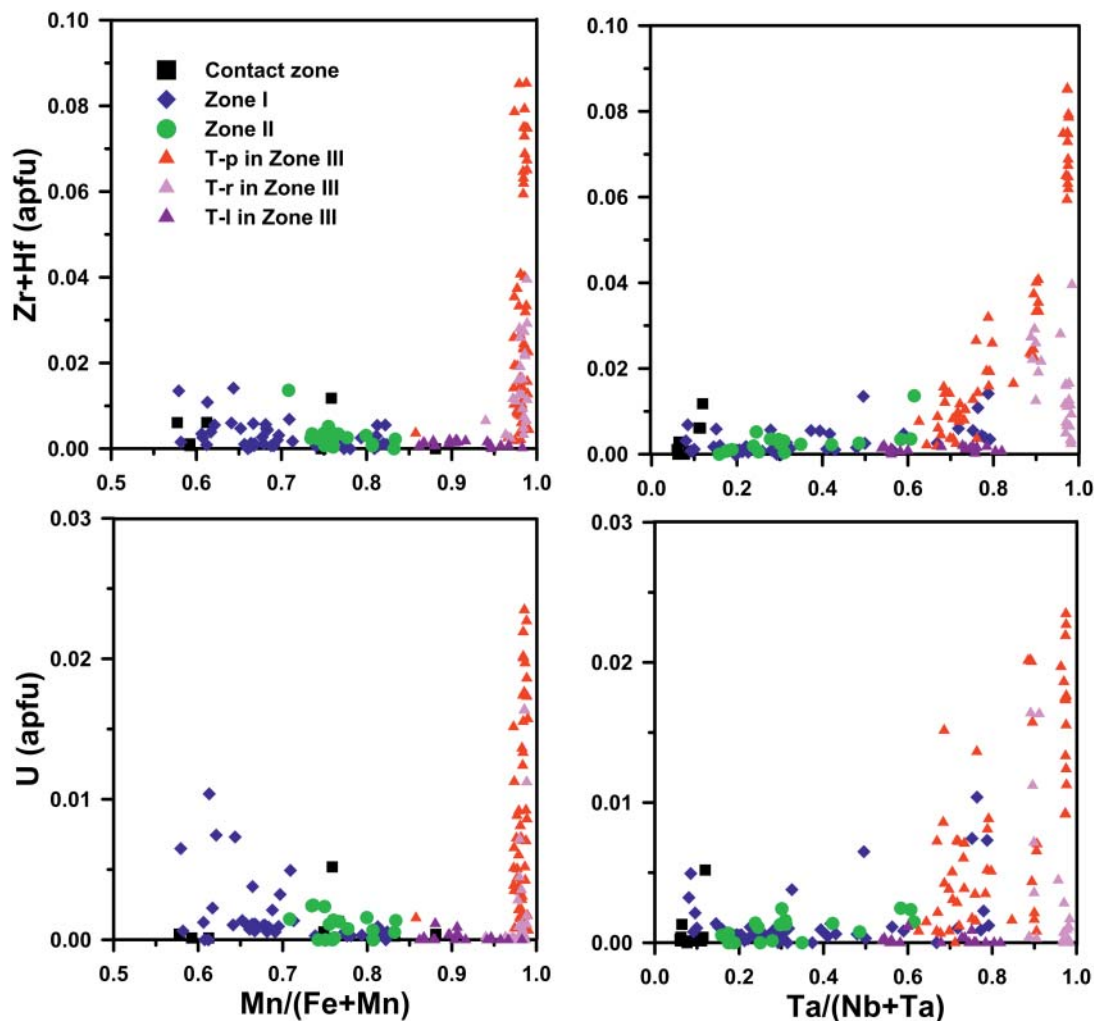


FIG. 4. Diagram showing variations in Zr + Hf and U versus Ta/(Nb + Ta) and Mn/(Fe + Mn) for CGMs from different textural zones in the Koktokay No. 1 pegmatite. Abbreviations are as in Figure 3.

The $\text{MnZrTa}_2\text{O}_8$ phase is a Zr-Mn-Ta oxide mineral. It is irregular in shape and is generally $<10\ \mu\text{m}$ in size, but some of the grains attain $20\ \mu\text{m}$ in size. It may be associated with zircon, uraninite, and/or a U-rich member of the microlite group minerals (Figs. 5–6). The representative EPMA analyses are given in Table 4. This mineral contains 73.1 wt.% Ta_2O_5 , 11.2 wt.% MnO, 10.4 wt.% ZrO_2 , 3.57 wt.% HfO_2 , 0.51 wt.% Nb_2O_5 , and 0.25 wt.% FeO on average (Table 4). This yields a calculated average chemical formula of $(\text{Mn}_{1.04}\text{Fe}_{0.02})(\text{Zr}_{0.56}\text{Ta}_{0.21}\text{Hf}_{0.11}\text{Sn}_{0.02}\text{Ti}_{0.01})(\text{Ta}_{1.97}\text{Nb}_{0.03})\text{O}_8$. The ideal endmember could be $\text{MnZrTa}_2\text{O}_8$, as proposed by Černý *et al.* (2007). The $\text{MnZrTa}_2\text{O}_8$ phase in this study has a very high Ta content at “the Sn- (or Zr-) site”, which is not the case for Černý *et al.* (2007) and the ideal endmember (Table 3).

Uraninite inclusions in T-r have only been identified using X-ray elemental mapping results (*e.g.*, Fig. 6); these grains appear as small bright spots in porous T-r in BSE images.

The U-rich microlite group mineral inclusions in T-r are tiny and irregular, but a few U-rich microlites attain $20\ \mu\text{m}$ in size. They have maximum UO_2 contents of 20.6 wt.% (Table 4).

Muscovite inclusions are generally present in T-r regions along the boundaries with T-p regions (Fig. 5d). These inclusions were identified by the presence of anomalously high Si, Al, and K concentrations based on SEM-EDS data.

(3) Late tantalite-(Mn) (T-l): The tantalite-(Mn) grain shown in Figure 5a contains dark patches and overgrowth

TABLE 3. EPMA COMPOSITIONS OF THREE TYPES OF TANTALITE-(Mn) IN ZONE III OF THE KOKTOKAY NO. 1 PEGMATITE

	T-p			T-r			T-l		
	Average (n = 56)	17	12	Average (n = 24)	18	24	Average (n = 19)		
Nb ₂ O ₅	10.02 (6.94)	1.24	1.20	2.50 (1.90)	1.49	1.04	18.26 (6.53)	18.43	24.71
Ta ₂ O ₅	73.42 (6.59)	81.47	80.15	82.60 (2.77)	84.55	83.88	64.58 (6.93)	64.61	57.14
FeO	0.31 (0.28)	0.13	0.21	0.29 (0.15)	0.21	0.23	1.42 (0.60)	1.84	1.95
MnO	14.45 (0.91)	13.50	14.04	13.96 (0.49)	13.65	14.45	14.22 (0.80)	13.09	14.09
ZrO ₂	0.62 (0.54)	1.64	1.61	0.30 (0.19)	0.16	0.08	bdl	bdl	bdl
HfO ₂	0.26 (0.18)	0.64	0.51	0.12 (0.12)	0.09	bdl	0.05 (0.03)	0.08	0.03
TiO ₂	0.23 (0.14)	0.08	0.06	0.09 (0.06)	0.13	0.05	0.15 (0.05)	0.23	0.05
UO ₂	0.48 (0.38)	1.18	0.93	0.16 (0.27)	bdl	bdl	0.01 (0.02)	bdl	bdl
SnO ₂	0.01 (0.02)	bdl	bdl	0.02 (0.02)	bdl	bdl	0.02 (0.03)	0.03	0.11
WO ₃	0.31 (0.21)	0.35	0.28	0.48 (0.17)	0.53	0.30	0.53 (0.11)	0.54	0.61
Sc ₂ O ₃	0.09 (0.11)	bdl	bdl	bdl	bdl	bdl	0.02 (0.03)	bdl	0.07
Total	100.20	100.23	99.00	100.52	100.81	100.03	99.26	98.85	98.76
Calculated based on 6 O									
Nb	0.360	0.047	0.046	0.094	0.056	0.040	0.562	0.639	0.826
Ta	1.589	1.867	1.855	1.872	1.924	1.927	1.406	1.348	1.15
Fe	0.021	0.009	0.015	0.02	0.015	0.016	0.08	0.118	0.12
Mn	0.973	0.963	1.011	0.985	0.967	1.033	0.949	0.85	0.883
Zr	0.024	0.068	0.067	0.012	0.007	0.003	bdl	bdl	bdl
Hf	0.006	0.015	0.012	0.003	0.002	bdl	0.001	0.002	0.001
Ti	0.014	0.005	0.004	0.006	0.008	0.003	0.008	0.013	0.003
U	0.009	0.022	0.018	0.003	bdl	bdl	0.000	bdl	bdl
Sn	0.000	bdl	bdl	0.001	bdl	bdl	0.000	0.001	0.003
W	0.006	0.008	0.006	0.010	0.011	0.007	0.01	0.011	0.012
Sc	0.006	bdl	bdl	bdl	bdl	bdl	0.001	bdl	0.005
Ta/(Nb+ Ta)	0.82	0.98	0.98	0.95	0.97	0.98	0.71	0.68	0.58
Mn/(Fe+ Mn)	0.98	0.99	0.99	0.98	0.99	0.98	0.92	0.88	0.88

Notes: Numbers in parentheses are standard deviations. Numbers 17, 12, 18, and 24 are representative analyses shown in Figure 6. bdl = below detection limit.

rims (Fig. 5c), which are here termed as late stage tantalite-(Mn) (abbreviated to T-l). They differ from the above-described T-p and T-r by their relatively high concentrations of Nb and Fe. They have relatively low Ta/(Nb + Ta) and Mn/(Fe + Mn) values (0.54–0.84 and 0.86–0.98, respectively; Fig. 3). The concentrations of Zr, Hf, and U in these regions are mostly close to or below detection limits (Fig. 4; Table 3).

DISCUSSION

Evolution of columbite-group minerals in the Koptokay No. 1 pegmatite

Variations in chemical compositions of columbite-group minerals are an important indicator of fractionation processes of granitic pegmatites (e.g., Černý *et al.* 1985, 1986, Novák & Diviš 1996, Novák & Černý 2001,

Novák *et al.* 2003, Zhang *et al.* 2004, Rao *et al.* 2009, Tindle & Breaks 2000, Chudík *et al.* 2011). As such, variations in the concentrations of major and minor elements in CGMs might be used to trace the evolution of the Koptokay No. 1 pegmatite. The Ta/(Nb + Ta) values of CGMs gradually increase from the contact zone through zone I to zone II, although their Mn/(Fe + Mn) values are almost invariant. The primary CGMs (T-p) in zone III are highly enriched in Ta and Mn compared with the CGMs in zones I and II, and the change in CGM composition between zones I and II to zone III is discontinuous. The values of Ta/(Nb + Ta) and Mn/(Fe + Mn) in CGMs of zone III are high, up to 0.98 and 0.99 respectively. The presence of nearly tantalite-(Mn) endmember and Zr-rich hafnon in zone III (Yin *et al.* 2013) indicates that zone III is extremely fractionated compared with zones I and II (Fig. 3). Linnen & Keppler (1997) demonstrated that the different solubilities of columbite and tantalite in

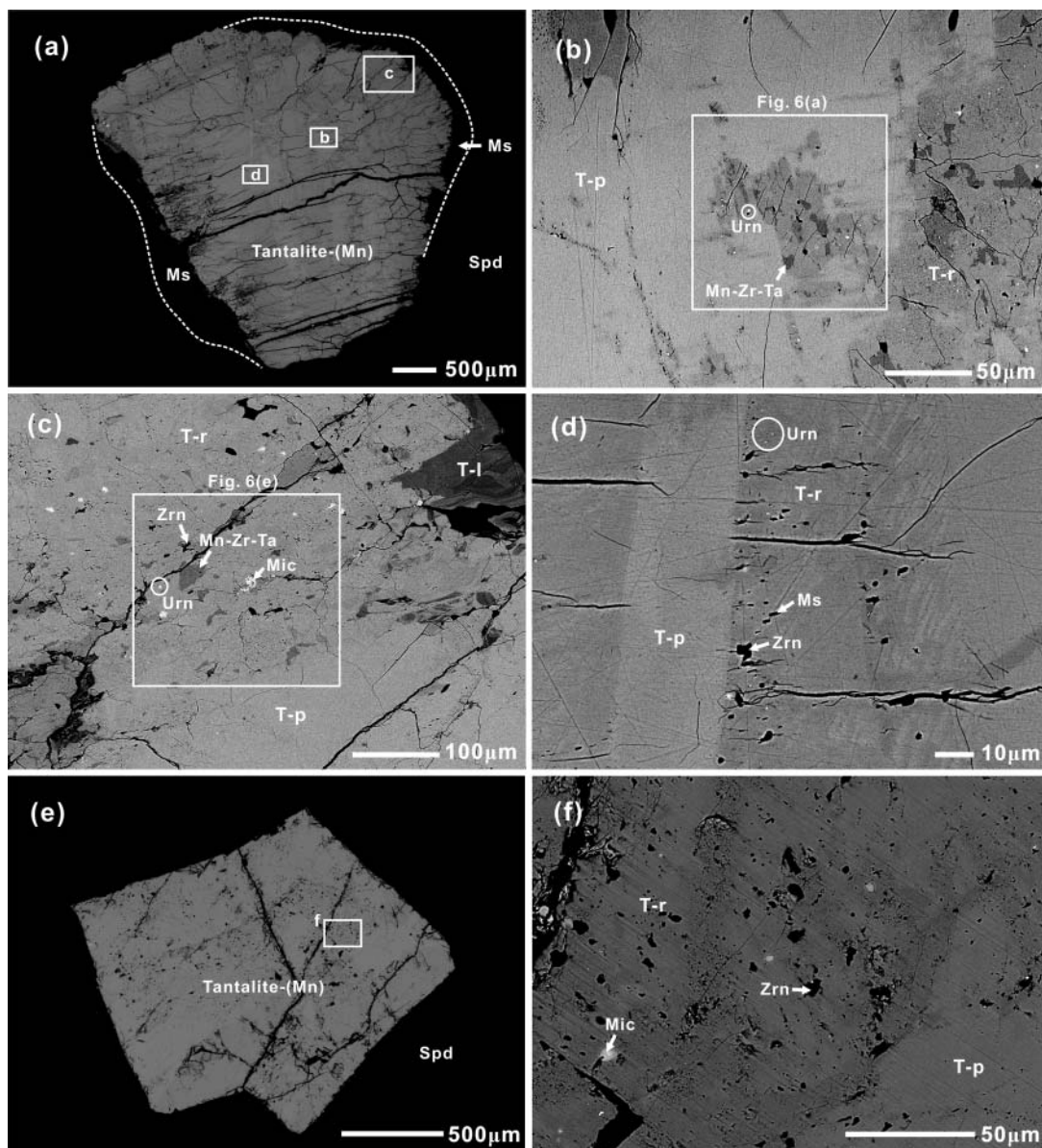


FIG. 5. BSE images of tantalite-(Mn) minerals with complex internal textures from zone III of the Kottokay No. 1 pegmatite. (a), (e) Tantalite-(Mn) crystals associated with muscovite and spodumene exhibit complex textures. (b), (c), (d), (f) show detail textures of (a) and (e). Three regions could be distinguished inside tantalite-(Mn) grains: primary tantalite-(Mn) abbreviated as T-p, re-equilibrated tantalite-(Mn) abbreviated as T-r, and late tantalite-(Mn) abbreviated as T-l. T-p regions are homogeneous and have no inclusions and micron-sized holes. T-r regions show large amounts of inclusions and exhibit a porous appearance. The two regions have a sharp and irregular boundary. The bright inclusions in T-r are uraninite and a uranium-rich member of the microlite group of minerals, whereas dark inclusions are identified as zircon and a $\text{MnZrTa}_2\text{O}_8$ phase. There are also small amounts of muscovite inclusions in T-r. T-l is darker than T-p and T-r and looks like an overgrowth rim of tantalite-(Mn). Abbreviations are as in Figure 3 with Urn = uraninite, Mn-Zr-Ta = $\text{MnZrTa}_2\text{O}_8$ phase, Mic = U-rich microlite, Zrn = zircon, Ms = muscovite, Ab = albite, Spd = spodumene.

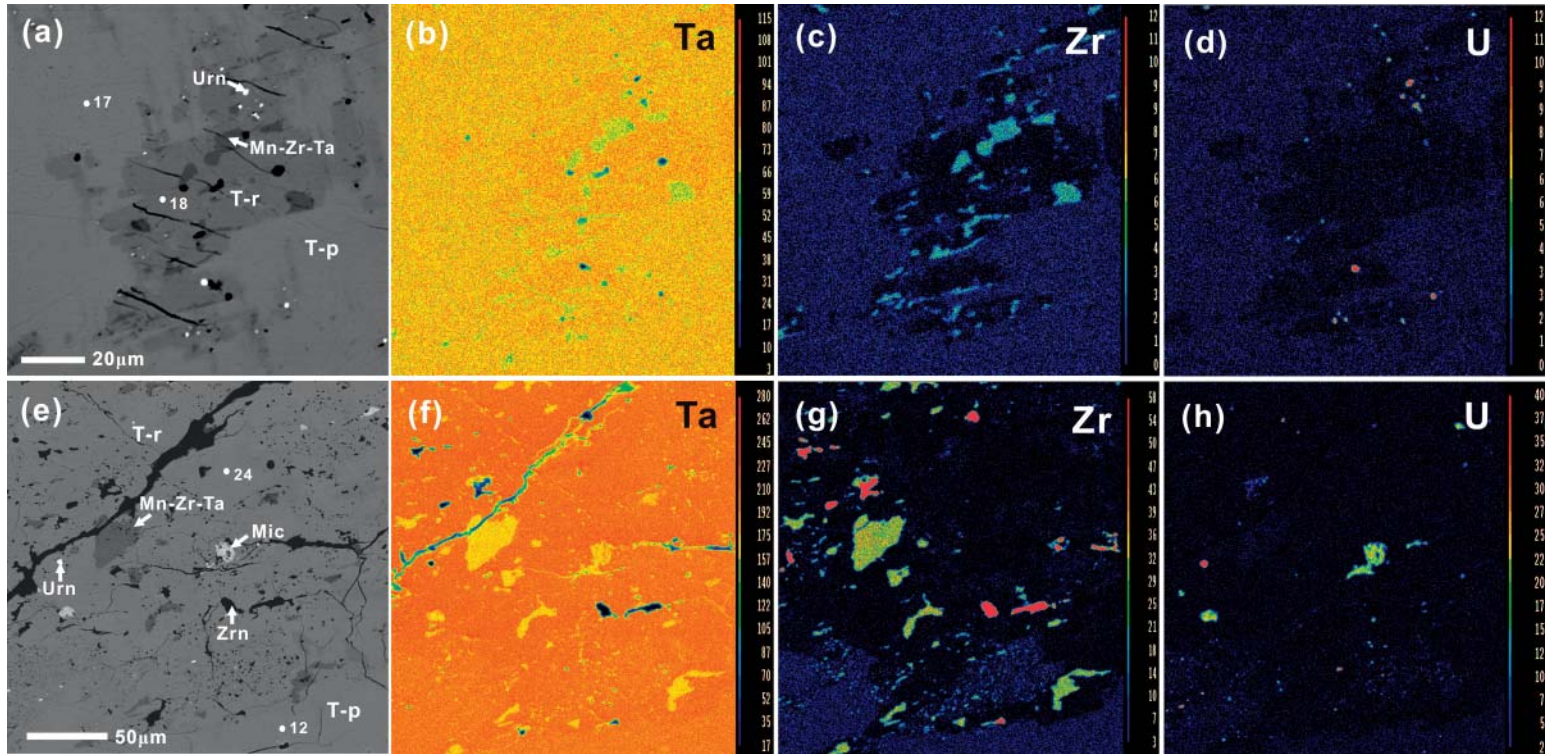


FIG. 6. BSE images and X-ray elemental mappings of two selected areas in Figure 5. (a, e) BSE image, (b–d, f–h) X-ray mappings of Ta, Zr, and U, respectively. The numbers in (a, e) correspond to representative compositions given in Table 2. Abbreviations are as in Figures 3 and 5.

TABLE 4. REPRESENTATIVE EMPA COMPOSITIONS OF MINERAL INCLUSIONS IN RE-EQUILIBRATED AREAS OF TANTALITE-(Mn) (T-r) IN THE KOKTOKAY NO. 1 PEGMATITE

	MnZrTa ₂ O ₈ phase							
	This study		Černý <i>et al.</i> (2007)	Ideal	zircon		U-rich microlite	
Na ₂ O							0.41	0.16
Nb ₂ O ₅	0.65	0.40	14.66		bdl	0.05	0.42	0.19
Ta ₂ O ₅	73.95	72.37	50.57	69.50	2.50	2.15	71.39	71.60
FeO	0.25	0.23	bdl		0.19	0.32	0.20	0.28
MnO	11.0	11.1	12.48	11.16	0.35	0.23	0.16	0.21
CaO							1.66	1.67
PbO							0.49	1.14
ZrO ₂	9.32	11.47	9.59	19.34	48.89	45.12		
HfO ₂	3.30	3.82	1.15		16.31	19.31		
TiO ₂	0.10	0.05	0.19		bdl	0.02	bdl	bdl
UO ₂	0.20	0.32	bdl		0.23	0.12	20.06	19.59
SiO ₂					31.18	30.83		
SnO ₂	0.66	0.52	9.84		bdl	bdl		
WO ₃	0.03	bdl	0.57		bdl	bdl	bdl	bdl
Sc ₂ O ₃	bdl	bdl	bdl		bdl	bdl	0.86	1.10
Total	99.43	100.27	99.05	100.00	99.65	98.15	95.24	95.78
			O = 8		O = 4		Nb + Ta + W + Ti = 2	
Na							0.081	0.032
Nb	0.033	0.020	0.662		bdl	0.001	0.023	0.010
Ta	2.225	2.149	1.374	2.000	0.022	0.020	1.977	1.990
Fe	0.023	0.021	bdl		0.005	0.009	0.017	0.024
Mn	1.028	1.025	1.055	1.000	0.010	0.007	0.014	0.018
Ca							0.181	0.183
Pb							0.013	0.031
Zr	0.504	0.612	0.468	1.000	0.784	0.741		
Hf	0.104	0.119	0.033		0.152	0.185		
Ti	0.008	0.004	0.014		bdl	0.001	bdl	bdl
U	0.005	0.008	bdl		0.002	0.001	0.455	0.446
Si					1.025	1.038		
Sn	0.029	0.023	0.392		bdl	bdl		
W	0.001	bdl	0.015		bdl	bdl	bdl	bdl
Sc	bdl	bdl	bdl		bdl	bdl	0.038	0.049
Ta/(Nb+Ta)	0.99	0.99	0.67		1.00	0.96	0.989	0.995
Mn/(Fe+Mn)	0.98	0.98	1.00		0.65	0.42	0.45	0.43

Note: bdl = below detection limit.

peraluminous melt is the cause of the increase of Ta/(Nb+Ta). Compared with the ASI [molar Al/(Na+K) ratio] of the melt, the contents of fluxing elements, especially fluorine, show almost no effect on the solubility of columbite-(Mn) and tantalite-(Mn) (Aseri *et al.* 2015, Fiege *et al.* 2011). Thus, it can be inferred with petrography and with experimental results that the chemical variation of CGMs from the contact zone to zone III with Ta/(Nb + Ta) and Mn/(Fe + Mn) is probably due to fractional crystallization of pegmatite magma. Yin *et al.* (2013) classified the zircon (*sl*) in zone III into two groups. Zircon grains with Hf/(Zr + Hf) values of 0.12–0.19 are typical magmatic zircon, whereas those with high Hf/(Zr + Hf) values (0.15–0.75) are related to coupled Li-F fluxing effects in

pegmatite magma. Thus, it can be deduced that fractional crystallization of the same pegmatite magma may result in stronger fractionation for Nb-Ta than for Zr-Hf. However, the presence of Nb-Fe-rich tantalite-(Mn) (T-1) within some CGMs (*e.g.*, Fig. 5c) is indicative of a chemical reversal prior to the final solidification of zone III. This reversal implies that the system underwent at least a local addition of external Nb-Fe-rich material that resulted in development of Nb-Fe-rich tantalite-(Mn) overgrowths on early-formed Nb-Fe-poor tantalite-(Mn).

Zirconium, Hf, and U are somewhat trace elements found in columbite-group minerals. Černý *et al.* (2007) described variations in the concentrations of

Zr and a few other minor elements in CGMs from a few moderately to highly fractionated granitic pegmatites. Their data show that CGMs with low Ta/(Nb + Ta) and Mn/(Fe + Mn) values also usually contain low concentrations of Zr; in addition, CGMs with high Ta/(Nb + Ta) and Mn/(Fe + Mn) values (~0.3–0.6 and ~1.0, respectively) are usually Zr-enriched (Černý *et al.* 2007). The general trends of Zr + Hf values versus Ta/(Nb + Ta) and Mn/(Fe + Mn) values for the Koktokay No. 1 pegmatite are similar to those observed by Černý *et al.* (2007). However, the Zr + Hf enrichments in this study are associated with CGMs in zone III that have Ta/(Nb + Ta) values >0.6 (Fig. 4). Combining the data of Černý *et al.* (2007) with our observations suggests that the ZrO₂ + HfO₂ contents of CGMs are not controlled by substitution between Nb and Ta, but in fact more realistically by the concentrations of these elements in pegmatite magmas. This inference is supported by the fact that a few tantalite-(Mn) crystals in zone III (*e.g.*, T-1) have similar Ta/(Nb + Ta) values but distinctly different ZrO₂ + HfO₂ contents (Fig. 4). Additionally, the positive correlation between Zr, Hf, U, and Ta/(Nb + Ta) is exhibited both within a single zoned primary tantalite-(Mn) grain and between different crystals (Figs. 4, 7). The presence of a positive correlation between Zr + Hf and Ta/(Nb + Ta) in primary CGMs in zone III may be a function of variations in the extent of fractional crystallization of the CGMs in this zone. In addition, Mn-Fe substitution in CGMs may also affect the partition coefficients of Zr and Hf in these grains, since all of the high Zr + Hf CGMs analyzed during this study and by Černý *et al.* (2007) are extremely Mn-enriched [Mn/(Fe + Mn) ≈ 1]. The same correlation also exists for U versus Ta/(Nb + Ta) and Mn/(Fe + Mn) in the CGMs analyzed during

this study (Fig. 4). This similarity suggests that the content of UO₂ in CGMs is most likely controlled by the same factors that control the content of ZrO₂ + HfO₂ in CGMs. This inference is partially supported by differences in the ionic radii of the cations in CGMs. The ionic radii of ^{VI}Nb⁵⁺, ^{VI}Ta⁵⁺, ^{VI}Fe²⁺, and ^{VI}Mn²⁺ are 0.64, 0.64, 0.78, and 0.83 Å, respectively (Shannon 1976, Ercit *et al.* 1995). Of these cations, the radius of ^{VI}Fe²⁺ is closer to the ionic radii of ^{VI}Zr⁴⁺, ^{VI}Hf⁴⁺, and ^{VI}U⁶⁺ (0.72, 0.71, and 0.73 Å, respectively). This indicates that Zr, Hf, and U ideally substitute at the Fe²⁺ octahedral site. Because the content of FeO in primary tantalite-(Mn) is generally less than 1 wt.%, it is difficult to estimate the correlation between Fe and Zr, Hf, and U. However, the data for primary tantalite-(Mn) plot along the (Fe,Mn)(Nb,Ta)₂O₆–(Zr,Hf,U)O₂ join (Fig. 8), which indicates that Zr, Hf, and U may be incorporated into the crystal structure of CGMs by the following substitution: 3(Zr, Hf, U)⁴⁺ = 2(Nb, Ta)⁵⁺ + (Fe, Mn)²⁺. Therefore, Zr⁴⁺, Hf⁴⁺, and U⁴⁺ are not only incorporated at the Fe²⁺, Mn²⁺ sites, but also at the Nb⁵⁺, Ta⁵⁺ sites. Thus, significant contents of Zr, Hf, and U in the crystal structure of tantalite-(Mn) in zone III probably involved a cation disordering (Ercit 1994; and references therein), since these cations are located at two different crystallographic sites. The following minor elements are also found in CGMs, with their ionic radii in six-fold coordination: W⁶⁺ 0.58 Å, Sn⁴⁺ 0.69 Å, Sc³⁺ 0.745 Å, and Ti²⁺ 0.605 Å (Shannon 1976). Contents of Sc, except for the data near or below the detection limit, shows positive correlation with Zr+Hf+U due to the similar ionic radius. Černý *et al.* (2007) mentioned the positive correlation between Sn and Zr+Hf in CGM, however, the concentration of Sn in T-p is mostly below or close to its detection limit.

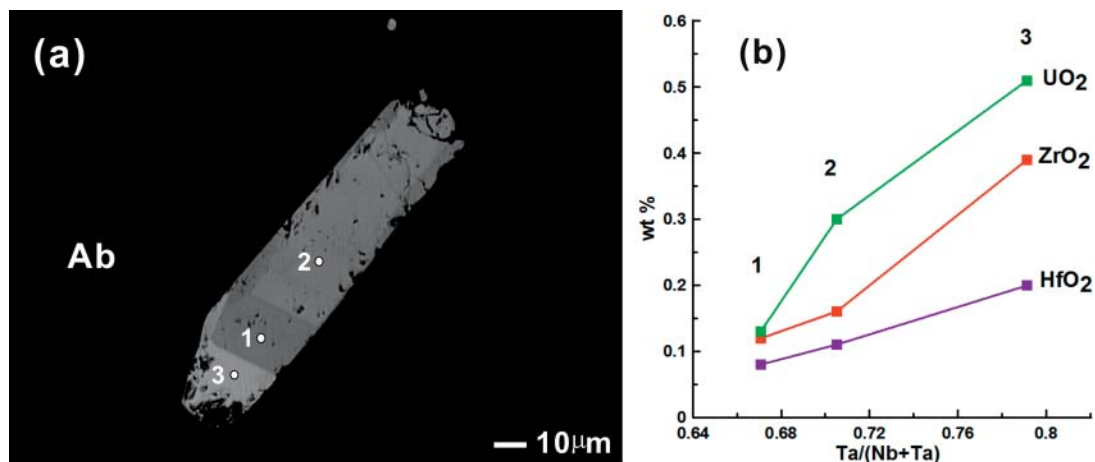


FIG. 7. Tantalite-(Mn) from zone III with zonation (a) and the correlation (b) between ZrO₂-HfO₂-UO₂ contents and Ta/(Nb + Ta) in the crystal shown in (a).

The following substitution could also be incorporated into the crystal structure as noted by Johan & Johan (1994): $W^{6+} + (Zr, Hf, U)^{4+} = 2(Nb, Ta)^{5+}$, $6(Zr, Hf, U)^{4+} + 3Sc^{3+} = 4Fe^{2+} + 5(Nb, Ta)^{5+}$.

Chemical re-equilibration of Zr-Hf-U-bearing tantalite-(Mn)

The last magmatic stage of the granitic pegmatite evolution is generally coupled with a hydrothermal stage (Jahns & Burnham 1969, Burnham & Nekvasil 1986, London 1986, 1992). Determining the stability of CGMs during the transition between magmatic and hydrothermal processes and during hydrothermal activity is important for our understanding of the possible conditions and processes during Nb and Ta mineralization within granitic pegmatites (e.g., Rao *et al.* 2009, Van Lichtervelde *et al.* 2009). In contrast to the primary tantalite-(Mn) in zone III, re-equilibrated tantalite-(Mn) grains (T-r) exhibit deficits of Zr, Hf, and U and contain abundant fine-grained inclusions and micron-sized holes. These features provide a significant opportunity to further our understanding of the role of fluids during the formation of Ta mineralization.

The T-r regions shown in Figures 5 and 6 are always enclosed in the T-p regions, and are clearly

depleted in Zr, Hf, and U compared with the T-p regions distinctly enriched in these elements. In addition, the former is always closely spatially related to a fine-grained mineral assemblage of Zr and U, including zircon, the $MnZrTa_2O_8$ phase, uraninite, and a U-rich member of the microlite group of minerals (Figs. 6a, 6e). The above features establish both spatial and chemical relationships between the primary tantalite-(Mn) and re-equilibrated tantalite-(Mn). A hypothesis that Zr-Hf-U-bearing tantalite-(Mn) minerals became unstable and underwent local chemical re-equilibration with hydrothermal fluids may be envisaged. Activity of fluids during the formation of such secondary assemblages is supported by the porous texture of the T-r phases and the presence of coexisting muscovite. The occurrence of zircon and microlite also suggests that Si and Ca should be present in the fluid and that this primary tantalite-(Mn) consequently evolved in an open system. Similar textures are often described for zircon (e.g., Xie *et al.* 2005, Geisler *et al.* 2007) and cassiterite (e.g., Masau *et al.* 2000), which favors the mechanism of so-called dissolution-reprecipitation proposed by Putnis (2009). Therefore, the primary tantalite-(Mn) might have experienced an open-system re-equilibration which is responsible for the formation of secondary tantalite-

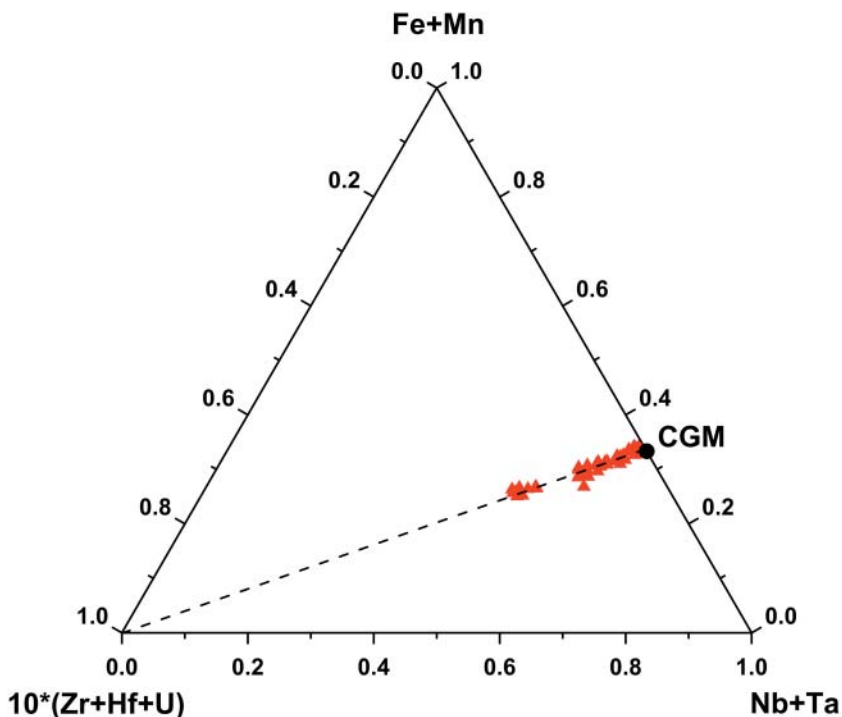


FIG. 8. $(Nb^{5+} + Ta^{5+}) - (Mn^{2+} + Fe^{2+}) - 10 \times (Zr^{4+} + Hf^{4+} + U^{4+})$ diagram for primary tantalite-(Mn) from zone III in the Koktokay No. 1 pegmatite. Abbreviations: CGM = columbite-group mineral.

(Mn) and other Zr- or U-rich minerals, as described below:

Zr-Hf-U-bearing tantalite-(Mn)
 + Si, Ca-bearing fluid → tantalite-(Mn) + zircon
 + MnZrTa₂O₈ phase + uraninite
 + U-rich member of the microlite group of minerals
 ± (muscovite).

Potential implications for Zr-Hf-U-bearing columbite-group minerals

As an extremely fractionated granitic pegmatite as deduced by the presence of hafnon (Yin *et al.* 2013), the Koktokay No.1 pegmatite also displays particular features in terms of evolution of the columbite-group minerals, notably marked by variations in Zr, Hf, and U concentrations.

The data presented in this paper indicate that the CGMs in the Koktokay No. 1 pegmatite contain UO₂ up to 1.28 wt.%; the presence of this amount of U has potential implications for the U-Pb dating of columbite-group minerals. Columbite-group minerals have been used for U-Pb dating for about 20 years (*e.g.*, Romer & Wright 1992, Romer & Smeds 1994) and the ages derived from this type of analysis can not only constrain the age of Nb-Ta mineralization, but also the formation age of the host rocks for this mineralization. The composition of primary tantalite-(Mn) from zone III indicates that tantalite-(Mn) can contain significant concentrations of UO₂, which is a positive result for *in situ* U-Pb dating by laser-ablation ICP-MS. However, interaction between U-bearing tantalite-(Mn) and hydrothermal fluids can cause disassociation into pure tantalite-(Mn) and U-rich mineral(s). The presence of these fine-grained U-rich mineral(s) as inclusions in the pure tantalite-(Mn) implies that the latter may not be suitable for U-Pb dating. Therefore, we suggest checking very carefully if CGMs are clean and free of inclusions before using these minerals for U-Pb dating, especially if their host rocks were affected by hydrothermal fluids.

Columbite-group minerals from the Koktokay No. 1 pegmatite also contain a small amount of hafnium. The HfO₂ content may reach 0.73 wt.%. Such considerable Hf concentration indicates the possibility of columbite-group minerals as a potential target for *in situ* LA-ICP-MS Lu-Hf isotope measurement. There is almost no detailed research about Lu-Hf isotopes of columbite-group minerals. Lu-Hf isotopes of CGMs could be used to characterize the source of magma and evaluate the contribution of depleted mantle or continental crust to Nb-Ta mineralization. Additionally, the variation of Hf isotope composition in CGMs from different localities or different texture zones in a single pegmatite, even if determined from an individual grain, may provide an opportunity to gain more information about the origin

or evolution of Nb, Ta-bearing magma (Marko *et al.* 2014).

ACKNOWLEDGMENTS

We would like to thank Prof. Wen-Lan Zhang, Prof. Xiao-Ming Chen, and Mr. Bin Wu for assistance during EPMA analysis and Dr. Lei Xie for assistance during fieldwork. We are grateful to Dr. Pietro Vignola, Dr. Pavel Uher, and an anonymous reviewer for their helpful comments on an early version. This work was supported by the Natural Science Foundation of China (Grant No. 41230315).

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Received November 11, 2014, revised manuscript accepted May 1, 2015.

