Bulletin of the Geological Survey of Japan, vol. 65 (1/2), p. 17 - 22, 2014

Short Article

Zircon U-Pb age of the Triassic granitoids at Nui Phao, northern Viet Nam

Shunso Ishihara[1,*] and Yuji Orihashi[2]

Shunso Ishihara and Yuji Orihashi (2014) Zircon U-Pb age of the Triassic granitoids at Nui Phao, northern Viet Nam. *Bull. Geol. Surv. Japan*, vol. 65 (1/2), p. 17-22, 3 igures, 1 table, 1 photograph.

Abstract: Rock-forming zircon was separated from so-called Triassic granitoids at Nui Phao in the northern Viet Nam, and the contained zircons were dated by LA-ICPMS U-Pb method, as the earliest Triassic of ca. 250 Ma. These new results are suggestive to identify the formation ages of Sn-W and REE ore deposits hosted in the granitoids.

Keywords: North Viet Nam, granitoid, Triassic, Permian, Ion-absorption REE deposit, tin, tungsten, Nui Phao

1. Introduction

Both calc-alkaline and alkaline granitoids of the Phanerozoic age are distributed in the northernmost part of Viet Nam. The calc-alkaline granitoids occur in sedimentary terrains in the northeastern part of the Red River (Song Hong) Fault (Chu ed., 2006), while the alkaline granitoids with younger ages (Hayashi *et al*., 2009; Trung *et al*., 2007) predominate in the southwestern part from the Red River fault (Fig. 1). In the Nui Phao Tam Dao tin-tungsten mineralized district of the sheet map F-48-XXII "Tuyen Quang" in North Vietnam (Long ed., 2001), three stages of Phanerozoic granitoids are described, namely Devonian, Triassic and Cretaceous. Yet, there is no age dating on these granitoids.

Recently, scheelite-fluorite mineralized ores were discovered at Nui Phao of the sheet map (Richards *et al*., 2003), and the ore deposits were identified to be a zoned skarn type around the Da Lien granite (Someya, 2012). Mica minerals are abundant in this ore body and were dated by Ar-Ar method to have Cretaceous in age (81.5-83.7 Ma, Sanematsu and Ishihara, 2011). Yet no age dating has been performed on the other "Triassic" Nui Phao granitoids. This paper describes the U-Pb age determination on zircon separated from the Nui Phao granitoids.

2. Geologic Outline

In the studied region, the oldest rock unit is Precambrian gneisses and intrusive rocks, which are distributed in the western part of the studied area (Fig. 2). The other wider part of the area is essentially Paleozoic-Mesozoic sedimentary terrain, which are composed of Cambrian crystalline schist, phyllite and limestone, Ordovician sandstone-bearing chert, limestone and shale, and Devonian calcareous sandstone and shale. Two

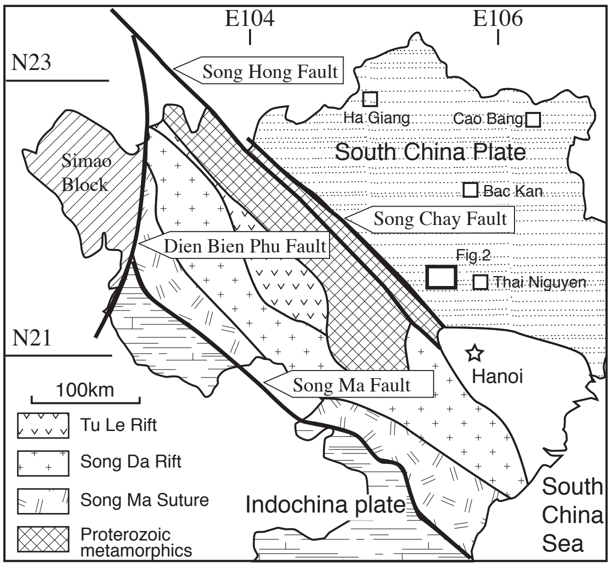


Fig. 1 Geological setting of the northern Viet Nam.

Triassic sedimentary units, (a) coal-bearing sandstone, shale and conglomerate, and (2) shale and sandstone alternation, are present in the eastern part of the studied area (Fig. 2).

Granitoids are classified as Devonian, Triassic and Cretaceous, among which the Triassic one is most widely exposed in

[1] AIST, Geological Survey of Japan
[2] Earthquake Research Institute, The University of Tokyo
*Corresponding author: S.Ishihara,Central 7,1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan. Email: s-ishihara@aist.go.jp

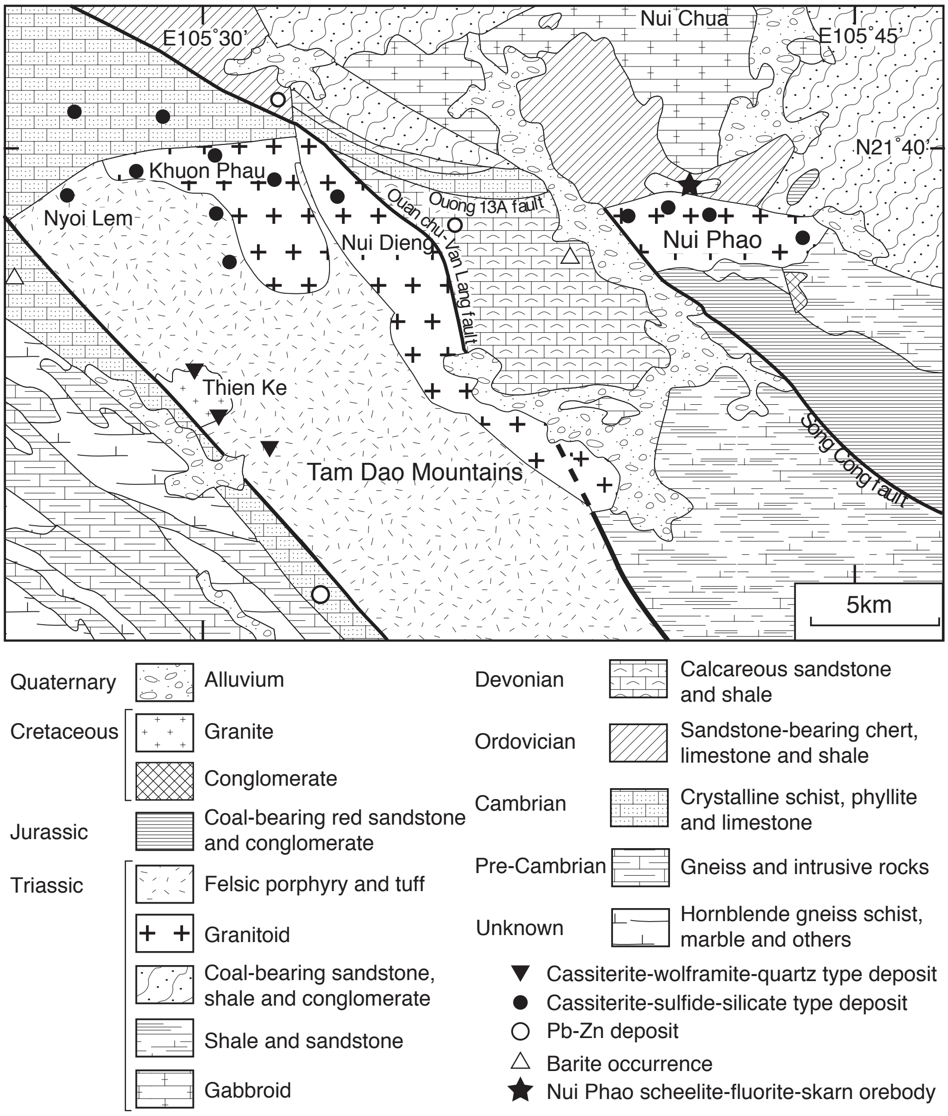


Fig. 2 General geology of the Tam Dao Sn-mineralized district (after Kiem and Luyen, 1991).

the studied area (Long ed., 2001), as Nui Dieng, Khuon Phau and Nui Phao plutons (Fig. 2). Coeval Triassic volcanic unit of felsic porphyry and tuffs occurs together with the Nui Dieng and Khuon Phau granitoids in the middle southern part of the area (e.g., Tam Dao Mtn., Fig. 2). Thus, they can be considered as a volcano-plutonic complex. The Nui Phao granitic complex is associated with no volcanic equivalent and is intruded by Cretaceous Da Lien granitoids.

The Triassic granitoids here are stock in size (<100 km^2), intruding into the Cambrian to Devonian strata (Fig. 2). Around the Nui Phao body, it is said that the granitoid intrudes into middle Triassic Na Khuat Formation and is covered by basal conglomerate of Jurassic Ha Choi Formation (Long ed., 2001, p. 66). This field observation implies that the examined granitoids should be dated younger than the middle Triassic in age.

In the Nui Phao area, the Triassic granitoids are generally called Nui Phao Granite by mining geologists. This is composed of coarse-grained porphyritic biotite granite with relatively high color index as granite, but with low magnetic susceptibilities (i.e., ilmenite series). Intruding into the Ordovician calcareous sediments and Triassic granite, very small Cretaceous granitic body, called as Da Lien Granite, occurs together with cassiterite-quartz greisen, cassiterite-dissemination and scheelite skarnization at the northern margin of the Triassic Nui Phao granitoids (Fig. 2). This Cretaceous granite is a muscovite and/or biotite granitic body containing tourmaline and fluorite in highly leucocratic phases.

A total of 88 million tons of the ores containing 0.19 % WO_3, 0.18 % Cu, 0.09 % Bi, 0.19 g/t Au and 7.95 % CaF_2, are known in the skarn ore deposit (Richards *et al*., 2003). Someya (2012) studied the skarn orebody and clarified zoning of the skarn minerals; i.e., garnet, clinopyroxene, and amphibole skarns, formed from the granite to the wall rock side, and the formation temperature of the ore minerals under the strongly reducing conditions around 400˚C.

As Quaternary ore deposits, cassiterite placer has been mined in many places by local people. The Nui Phao granitoids are heavily weathered to thick saprolite in the Nui Phao area (Photo. 1A). Thus, it may contain the ion-absorption-type REE deposits in the saprolite, and its possibility was studied in details by Omura (2008) and Mentani (2011). This kind of the ore deposits are common in the Early Yanshanian granite region in the southern China (Murakami and Ishihara, 2008), and similar weathering condition is expected in the northern Viet Nam during the past geologic time.

3. The Nui Phao Granitoids and Analyzed Samples

In the studied area, the Nui Phao Triassic granite is a coarse-grained biotite granitic stock with many cassiterite and wolframite anomalies (Fig. 2), and with no radiometric age data. The Cretaceous Da Lien granite is tourmaline-bearing two-mica variety, occurring as small cupola genetically related to the tungsten skarn mineralization.

Biotite and muscovite of the altered and mineralized granite were dated by $^{40}Ar/^{39}Ar$ method (Sanematsu and Ishihara, 2011). All the four biotite and muscovite samples showed Cretaceous ages between 81.5 and 83.7 Ma, even including one Triassic-looking coarse-grained granite sample. Thus, the Cretaceous age for the mineralization was confirmed, but the age of the Nui Phao granite remained unknown.

3.1 Examined samples

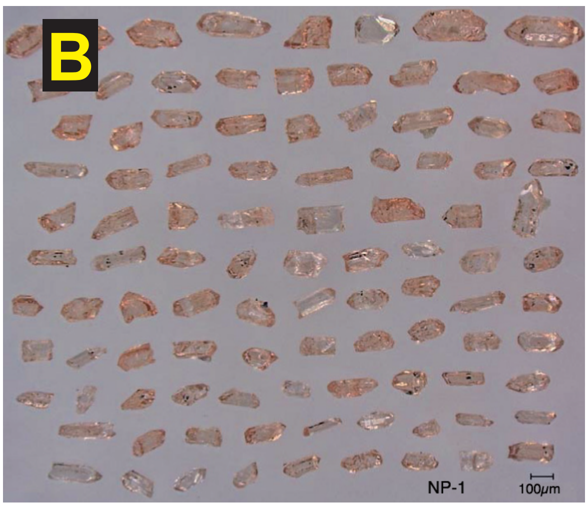
Two samples were selected; one from the largest outcrop of the Nui Phao granitoids at the community of Nui Phao (Photo. 1A), while the other from nearby abandoned drill core for the construction of the mine facility. The analyzed sample of NP-1 was taken from the fresh block remaining in the huge reddish outcrop (Photo. 1A), and NP-2 was taken from abandoned drill cores for the mine construction. Both granite samples have a high color index as granite, containing no hornblende but biotite. Mafic enclaves are rare but some sedimentary enclaves are present. The magnetic susceptibility is measured in field is low, below 3.0 x 10^{-3} SI unit, which means that the rock belongs to the ilmenite-series granitoid of Ishihara (1977).

Under the microscope, the rock is coarse-grained, relatively unaltered. Quartz is most abundant, often rounded in form and sometimes occurring as microveinlets. It shows weak wavy extinction, meaning local stress effect during high temperature stage, and the following substages. Plagioclase is dusty and alkali feldspar contains rarely perthite flakes. Biotite has two modes of occurrence: one euhedral crystals having clear cleavage and greenish brown in the Z-axis, while the other is irregular in shape with reddish brown in color. The latter could be recrystallized variety.

Separated zircon crystals are shown in Photograph 1B. They are mostly euhedral forms, and are considered magmatic in origin.

3.2 Analytical results and age of mineralization

U-Pb ages for the obtained zircons are analyzed by LA-ICPMS set in the Earthquake Research Institute, the University of Tokyo. The analytical method is the same as those described in Orihashi *et al*. (2008). The results on the two samples are listed in Table 1, The Tera-Wasserburg Concordia diagrams are shown in Fig. 3. Both the examined rocks showed the earliest Triassic age around 250 Ma, in assuming that the Permian and



Photograph. 1A Weathered outcrop of the Triassic granite at Nui Phao. The weathered crusts often exceed 10 meters in thickness.

Photograph. 1B Separated zircon grains used for the age dating (Sample NP-1).

Table. 1 U-Pb isotopic data for zircon crystals from the samples NP-1 and NP-2, determined by LA-ICP-MS.

Spot no.	Th/U	$^{207}Pb/^{206}Pb$	Error 2σ	$^{206}Pb/^{238}U$	Error 2σ	$^{207}Pb/^{235}U$	Error 2σ	Disc** (%)	^{238}U-^{206}Pb age (Ma)	Error 2σ	^{235}U-^{207}Pb age (Ma)	Error 2σ
1) Sample: NP-1												
1	0.23	0.0499 ±	0.0023	0.0408 ±	0.0015	0.281 ±	0.017		258 ±	10	251 ±	15
2	0.39	0.0513 ±	0.0025	0.0411 ±	0.0016	0.291 ±	0.018		260 ±	10	259 ±	16
3 *	0.23	0.0522 ±	0.0023	0.0432 ±	0.0016	0.311 ±	0.018		273 ±	10	275 ±	16
4	0.31	0.0528 ±	0.0024	0.0403 ±	0.0015	0.293 ±	0.017		254 ±	10	261 ±	15
5	0.32	0.0507 ±	0.0024	0.0401 ±	0.0015	0.280 ±	0.017		253 ±	10	251 ±	15
6	0.28	0.0518 ±	0.0024	0.0401 ±	0.0015	0.287 ±	0.017		254 ±	10	256 ±	15
7 *	0.26	0.0518 ±	0.0024	0.0466 ±	0.0018	0.333 ±	0.020		294 ±	11	292 ±	17
8	0.29	0.0506 ±	0.0023	0.0410 ±	0.0016	0.286 ±	0.017		259 ±	10	255 ±	15
9	0.33	0.0526 ±	0.0025	0.0405 ±	0.0015	0.294 ±	0.018		256 ±	10	261 ±	16
10 *	0.17	0.1184 ±	0.0066	0.1067 ±	0.0043	1.74 ±	0.12	-42	654 ±	26	1,024 ±	71
11 *	0.30	0.0620 ±	0.0038	0.0375 ±	0.0015	0.321 ±	0.024	-6.1	237 ±	10	282 ±	21
12	0.27	0.0575 ±	0.0036	0.0421 ±	0.0017	0.334 ±	0.025		266 ±	11	293 ±	22
13	0.13	0.0498 ±	0.0030	0.0410 ±	0.0017	0.282 ±	0.020		259 ±	11	252 ±	18
14	0.29	0.0496 ±	0.0031	0.0399 ±	0.0016	0.273 ±	0.021		252 ±	10	245 ±	18
15 *	0.11	0.0786 ±	0.0044	0.1680 ±	0.0068	1.82 ±	0.13		1,001 ±	41	1,053 ±	73
16	0.25	0.0522 ±	0.0033	0.0401 ±	0.0016	0.289 ±	0.022		254 ±	10	258 ±	19
17	0.25	0.0535 ±	0.0033	0.0377 ±	0.0015	0.278 ±	0.021		239 ±	10	249 ±	19
18	0.20	0.0520 ±	0.0032	0.0409 ±	0.0017	0.293 ±	0.021		258 ±	11	261 ±	19
19	0.14	0.0523 ±	0.0019	0.0395 ±	0.0010	0.285 ±	0.013		249.9 ±	6.4	255 ±	11
20 *	0.50	0.0566 ±	0.0020	0.0400 ±	0.0010	0.312 ±	0.014	-1.6	253.0 ±	6.5	276 ±	12
21	0.23	0.0514 ±	0.0019	0.0402 ±	0.0010	0.285 ±	0.013		253.9 ±	6.5	254 ±	11
22	0.25	0.0519 ±	0.0018	0.0382 ±	0.0010	0.273 ±	0.012		241.9 ±	6.2	245 ±	11
23	0.33	0.0539 ±	0.0021	0.0394 ±	0.0010	0.293 ±	0.014		248.9 ±	6.4	261 ±	12
24	0.29	0.0535 ±	0.0017	0.0394 ±	0.0010	0.291 ±	0.012		249.3 ±	6.4	259 ±	11
25	0.26	0.0532 ±	0.0019	0.0388 ±	0.0010	0.285 ±	0.012		245.3 ±	6.3	254 ±	11
26	0.28	0.0529 ±	0.0018	0.0383 ±	0.0010	0.279 ±	0.012		242.2 ±	6.2	250 ±	11
27 *	0.34	0.0642 ±	0.0019	0.0668 ±	0.0017	0.591 ±	0.023	-6.2	417 ±	11	472 ±	18
				Weighted average of ^{238}U - ^{206}Pb age (N =20)					***250.7 ±***	***3.1***	***(95% conf.; MSWD = 2.6)***	
2) Sample: NP-2												
1	0.19	0.0538 ±	0.0034	0.0398 ±	0.0015	0.296 ±	0.022		251.8 ±	9.3	263 ±	19
2	0.29	0.0518 ±	0.0030	0.0392 ±	0.0014	0.279 ±	0.019		247.6 ±	9.1	250 ±	17
3 *	0.75	0.1220 ±	0.0066	0.0435 ±	0.0016	0.732 ±	0.048	-86	275 ±	10	558 ±	36
4	0.32	0.0541 ±	0.0033	0.0393 ±	0.0015	0.293 ±	0.021		248.3 ±	9.2	261 ±	19
5 *	0.24	0.0546 ±	0.0033	0.0374 ±	0.0014	0.282 ±	0.020		236.7 ±	8.7	252 ±	18
6 *	0.27	0.0711 ±	0.0038	0.0579 ±	0.0021	0.568 ±	0.037	-14	363 ±	13	457 ±	30
7 *	0.10	0.0760 ±	0.0042	0.0710 ±	0.0026	0.743 ±	0.050	-15	442 ±	16	564 ±	38
8	0.32	0.0528 ±	0.0034	0.0394 ±	0.0015	0.287 ±	0.021		249.4 ±	9.3	256 ±	19
9 *	0.58	0.0571 ±	0.0034	0.0589 ±	0.0021	0.464 ±	0.032		369 ±	13	387 ±	26
10 *	0.19	0.0538 ±	0.0027	0.0457 ±	0.0016	0.339 ±	0.021		288 ±	10	296 ±	18
11	0.24	0.0525 ±	0.0027	0.0401 ±	0.0014	0.291 ±	0.018		253.7 ±	8.8	259 ±	16
12	0.27	0.0504 ±	0.0027	0.0391 ±	0.0014	0.272 ±	0.017		247.2 ±	8.6	244 ±	16
13	0.25	0.0488 ±	0.0028	0.0396 ±	0.0014	0.266 ±	0.018		250.5 ±	8.7	240 ±	16
14	0.27	0.0506 ±	0.0028	0.0392 ±	0.0014	0.273 ±	0.018		247.9 ±	8.6	245 ±	16
15 *	0.02	0.1164 ±	0.0049	0.2232 ±	0.0076	3.584 ±	0.194	-9.2	1,299 ±	44	1,546 ±	84
16	0.28	0.0503 ±	0.0029	0.0385 ±	0.0013	0.267 ±	0.018		243.2 ±	8.5	240 ±	16
17	0.29	0.0502 ±	0.0027	0.0390 ±	0.0014	0.270 ±	0.018		246.9 ±	8.6	243 ±	16
18	0.11	0.0540 ±	0.0022	0.0397 ±	0.0012	0.296 ±	0.015		251.1 ±	7.5	263 ±	13
19	0.16	0.0508 ±	0.0022	0.0390 ±	0.0012	0.273 ±	0.014		246.7 ±	7.4	245 ±	13
20	0.30	0.0548 ±	0.0024	0.0407 ±	0.0012	0.308 ±	0.016		257.3 ±	7.7	272 ±	14
21 *	1.20	0.1463 ±	0.0057	0.0427 ±	0.0013	0.861 ±	0.042	-120	269.3 ±	8.0	631 ±	31
22 *	0.18	0.0608 ±	0.0024	0.0540 ±	0.0016	0.452 ±	0.023	-3.3	339 ±	10	379 ±	19
23 *	0.42	0.0724 ±	0.0029	0.1064 ±	0.0032	1.063 ±	0.053	-4.2	652 ±	19	735 ±	36
24 *	0.35	0.0540 ±	0.0022	0.0502 ±	0.0015	0.374 ±	0.019		315.9 ±	9.4	322 ±	16
25	0.27	0.0542 ±	0.0024	0.0396 ±	0.0012	0.295 ±	0.016		250.1 ±	7.5	263 ±	14
26 *	0.33	0.0524 ±	0.0024	0.0412 ±	0.0012	0.298 ±	0.016		260.2 ±	7.8	265 ±	15
				Weighted average of ^{238}U - ^{206}Pb age (N =14)					***249.5 ±***	***2.2***	***(95% conf.; MSWD = 0.72)***	

* Because the data are either statistically rejected or discordant, the data are not included calculating the weighted average of ^{238}U-^{206}Pb age.
** Degree of discordance (%); negative numbers and blanks show normal discordant and concordanct within 2σ of the analytical error, respectively.

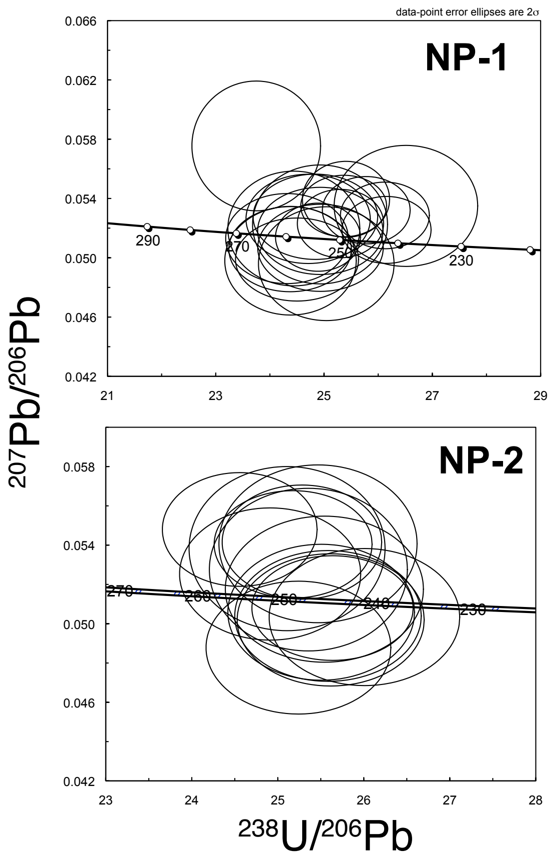


Fig. 3 Tera-Wasserburg concordia diagrams of U-Pb SHRIMP zircon data.

Triassic (P-T) boundary is 252.2 Ma (The Geologic Time Scale 2012, Gradstein *et al*. eds., 2012).

There are many Sn and W showings described in the studied region (Fig. 2). Age of the showings is yet unknown except for the Nui Phao W-Cu-F deposits, which were identified genetically related to the nearby Cretaceous granite. A coarse-grained granite looking similar to the Triassic granite (NP161), showed no plateau but the total fusion age of a Cretaceous as 78.8 Ma (Sanematsu and Ishihara, 2011). This granite must have been originally the Triassic in age, but re-equilibrated when it was captured as a xenolith by the Cretaceous granite magma. It is interesting to know if the other Sn and W showings are associated with Triassic or Cretaceous granites.

4. Correlation to Other Region

In the sedimentary terranes of northern Vietnam, there are a few sporadic intrusive bodies of granitic composition described in the same age group (i.e., Chu Bien ed., 2006). About 100 km north of our studied area, similar ages were reported recently by Roger *et al*. (2012), as Triassic Phia Bioc Granite as 245 Ma, whose intrusion was considered related to the nappe tectonism of the sedimentary rocks. This age is very close but slightly younger than our result of 250 Ma.

Roger *et al*. (2012) also reported 87.3 Ma for the Cretaceous Phia Oac Granite. We have only ^{40}Ar-^{39}Ar ages of 81.5-83.7 Ma on mica minerals related to W-F mineralization. Zircon age needs to be examined on the Cretaceous granite, hosting the W-F skarn deposits.

5. Concluding Remarks

Tin and tungsten deposits in northern Viet Nam are generally known to have Cretaceous age (Anh *et al*., 2010; Sanematsu and Ishihara, 2011), and are related often to leucogranites (e.g., Nui Phao and Thien Ke, Fig. 2). Within the earliest Triassic granite in question, many occurrences of the cassiterite- silicate-sulfide association are described in Fig. 2 by Kiem and Luyen (1991) and Long ed. (2001). It is interesting to know whether or not these mineralizations are related to the host Triassic granitoids or Cretaceous leucogranites still hidden close to the cassiterite-sulfide ore deposits.

There are questionable subject on saprolite REE deposits. The best host rock for the ion-adsorption-type REE deposit seems to be two-mica granite, as seen in the Longnan area in southern China (Wu *et al*., 1990). This type of granite has not been reported widely in the studied area. However, detailed petrographical studies are necessary for the Triassic granite in order to evaluate a resource potentiality of REE saprolite, as well as cassiterite and/or tungsten ore deposits.

References

Anh, P. L., Vladimirov, A. G. and Kruk, N. N. (2010) Stanniferous granites of Vietnam: Rb-Sr and Ar-Ar isotope age, composition, sources, and geodynamic formation conditions. Doklady Earth Sci., **432**, 839-845.

Chu Bien, ed. (2006) Mineral resources map of Viet Nam. 1/1,000,000 scale, Dept. Geology & Minerals, Ministry Industry, Hanoi.

Gradstein, F. M., Ogg, J. G., Schmitz, M. and Ogg, G. M. eds. (2012) The Geologic Time Table 2012, Elsevier, 1144 p.

Hayashi, T., Machida, S., Fukasawa, H., Takahashi, K., Nguyen, B. M., Ninh, Q. T., Tran, V. M. and Nguyen, D. T. (2009) Age of carbonatite and alkaline magmatism in North Vietnam and its rare earth mineralization. Abstract with Programs, Annual Mtg. Sym.: Geology and Mineral Resources of Vietnam and Surrounding Region, 21p.

Ishihara, S. (1977) The magnetite-series and ilmenite-series granitic rocks. Mining Geol., **27**, 293-305.

Kiem, D. D. and Luyen, P. V. (1991) Geology of tin deposits in Vietnam.117 p., Hanoi.

Long, P. D. ed. (2001) Geology and mineral resources map and text of Vietnam: Tuyen Quang sheet. Scale 1:200,000, Dept. Geol. Miner. Res., Hanoi, 47-88.

Mentani, T. (2011) So-called “Ion-adsorption type” REE deposits found in weathered crust of ilmenite-series granite in northern Vietnam. M.S. Thesis, Univ. Tokyo, 107p.

Murakami, H. and Ishihara, S. (2008) REE mineralization of weathered crust and clay sediment on granitic rocks in the Sanyo Belt, SW Japan, and the southern Jiangxi Province, China. Resource Geol., **58**, 373-401.

Omura, T. (2008) Enrichment of rare earth elements in weathered granites of northern Vietnam. Graduation Thesis, Univ. Tokyo, Text 2 p., Figs. 12, Tables 2 (in Japanese).

Orihashi, Y., Nakai, S. and Hirata, T. (2008) U-Pb age determination for seven standard zircons using inductively coupled plasmas-mass spectrometry coupled with frequency quintupled Nd-YAG (λ = 213 nm) laser ablation system: Comparison with LA-ICO-MS zircon analyses with a NIST glass reference material. Resource Geol., **58**, 101-123.

Richards, J. P., Dang, G., Dudka, S. F. and Wong, M. L. (2003) The Nui Phao tungsten-fluorite-copper gold-bismuth deposit, northern Vietnam: An opportunity for sustainable development. Explor. Mining Geol., **12**, 61-70.

Roger, F., Maluski, H., Lepvier. C., Van, T. V. and Paquette, J. -L. (2012) LA-ICPMS zircons U/Pb dating of Permo-Triassic and Cretaceous magmatisms in Northern Vietnam – Geodynamical implications. Jour. Asian Earth Sci., **48**, 72-82.

Sanematsu, K. and Ishihara, S. (2011) $^{40}Ar/^{39}Ar$ ages of the Da Lien granite related to the Nui Phao W mineralization in northern Vietnam. Resource Geol., **61**, 304-310.

Someya, N. (2012) Geology and genesis of the Nui Phao W-skarn deposit, northern Viet Nam. M.S. Thesis. Univ. Tokyo, 54p.

Trung, N. M., Nuong, N. D. and Itaya, T. (2007) Rb-Sr isochron and K-Ar ages of igneous rocks from the Samnua Depression Zone in northern Vietnam. Jour. Miner. Petrol. Sci., **102**, 86-92.

Wu, C-Y., Huang, D-H. and Guo, Z. X. (1990) REE geochemistry in the weathered crust of granites, Longnan area, Jiangxi Province. Acta Geol. Sinica, **3**, 193-210.

Received December 2, 2013
Accepted March 25, 2014

ベトナム北部，ヌイパオにおける三畳紀花崗岩類のジルコン U-Pb 年代

石原舜三・折橋裕二

要　旨

ベトナム北部のレッドリバー断層以東には“三畳紀”花崗岩が古生層中に広域的には南北方向に貫入する. ヌイパオ産試料から造岩鉱物のジルコンを分離し, U-Pb法で年代測定を試み, 250 Ma前後の三畳紀最早期の年代であることを確認した. この花崗岩には錫･タングステン鉱徴地が多数記載されており, また最近, その風化部にイオン吸着REE鉱床が発見されているので, 今後はそれぞれの鉱化年代を明らかにする必要がある.