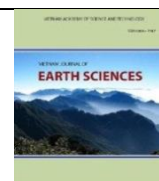




Vietnam Academy of Science and Technology

Vietnam Journal of Earth Sciences

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Formation pressure-temperature (P-T) of Ye Yen Sun granite

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Received 25 October 2018; Received in revised form 3 March 2019; Accepted 8 March 2019

ABSTRACT

Ye Yen Sun Cenozoic granitoid formations include biotite granite, fine- to medium-grained amphibol-biotite granite, and mostly undeformed fine- grained granite porphyry. Temperature calculation by the zircon saturation method gives the formation temperature ranging from about 680°C to 850°C; the pressure, determined on the basis of the major element composition, varies between 10 and 1 kbar (about 33 to 3.3 km deep). The granites viewed as "hot" or "intermediate" magmas were formed at the site of extension or transformation tectonics. Thus, the ability to form these granites due to the melting of the lower crust under the stretching region along the two wings of the Red River shear zone is a mechanism to be considered.

Keywords: Cenozoic granitoid; Ye Yen Sun; Phan Si Pan; Zr-saturation temperature.

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1. Introduction

On the structural plan of Northern Vietnam (NVN), the Phan Si Pan uplift block is located in the Northwest, which is a 200 km long zone running in the northwestern-southeastern direction, from the northernmost point of Lao Cai Province to Song Da of Hoa Binh province. In the southwest, it borders the Song Da-Tu Le rift (Tran Van Tri, Vu Khuc (co-editor), 2009) by the Than Uyen-Nam Xe faults, while the northeast borders the Red River shear zone.

Within the Phan Si Pan uplifting block, magmatic activity is very diverse in composition and ages from pre-Cambrian to Cenozoic. The oldest rocks are classified into

the Ca Vinh complex (Archean) comprised of diorite-granodiorite (tonalite-plagiogranite), Xom Giau (Paleoproterozoic), composed of biotite granite, Bao Ha Paleoproterozoic metagabbro, and Po Sen Neoproterozoic high-potassic (-K) calc-alkaline I-type granitoids.

In addition to the pre-Cambrian granitoids as mentioned above, Phan Si Pan uplift block is also home to the Permian sub-alkaline and alkaline granitoids (Muong Hum, Phu Sa Phinand Phan Si Pantype) and Cenozoic granitoids. Geological and geochemical features, and age of Phanerozoic granitoids have been mentioned in various works (Pham Trung Hieu et al., 2009; Pham Thi Dung, 2013; Tran et al., 2015; Usuki et al., 2015).

The Ye Yen Sun complex was formerly established by E.P. Izokh as reported in Dovjikov et al. (1965), which consisted of the entire block of the same name, trending in the

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northwest-southeast. The block is comprised of two clearly distinct components: The southeastern part of the block is mainly composed of strongly deformed biotite granites called Phan Si Pan granite, while the northwest part is mainly composed of almost undeformed, bright-colored, fine-medium-grained biotite granites and termed as Ye Yen Sun granite. These granitic rocks are observed cutting through severely Phan Si Pan deformed biotite granite. The age of the highly deformed biotite granite is determined as Permo-Triassic (262–249 Ma), while the age of the little or barely deformed biotite granite is as Late Eocene - Oligocene (35-30 Ma) (e.g. Pham et al., 2009; Pham, 2013; Tran et al., 2015; Usuki et al., 2015). The boundaries between the two types of granites have not been clearly defined and needed separate mapping projects. Thus, the northwestern part of the Ye Yen Sun batholith, as perceived by E.P. Izokh, is called Ye Yen Sun Cenozoic granitoids.

So far, crystallization pressure-temperature (P-T) conditions of Ye Yen Sun granitoids has not been mentioned in any work. Therefore, in this paper, we focus on the determination of forming temperature (T) - pressure (P) of the Ye Yen Sun non-deformed Cenozoic granites, in order to contribute to the understanding of their origin and formation environment.

2. Geological and geochemical characteristics

Ye Yen Sun Cenozoic granites were studied through the sections in the northwestern part of the Ye Yen Sun batholith, including: (i) from Quy Ho Lake to Binh Lu (along the QL4D road); (ii) from Si Lo Lau to Tung Qua Lin; (iii) from Nam Xe to Sin Suoi Ho (along Ye Yen Sun stream); and (iv) in Chung Leng Ho (Fig. 1). The granitoids here are exposed in block or in the form of dykes, mainly composed of biotite granite, small grained amphibole-biotite-granite and medium-grained porphyritic granite. The distinctive feature of these rocks

as compared to Permian granite in Southeastern Ye Yen Sun block (also called Phan Si Pan) is that they are not deformed or weakly deformed. Mineralogical composition of the Ye Yen Sun granite is of (1) quartz, K-feldspar, plagioclase, biotite, sphene, zircon ± apatite ± fluorite. The K-feldspar is orthoclase in composition with $K_2O=16.13-16.96wt\%$, $Na_2O=0.32-0.63wt\%$, $Al_2O_3=17.43-17.95wt\%$, $SiO_2=64.78-65.18wt\%$. The biotite has very low titanium content ($TiO_2=0.83-1.10wt\%$), relatively low aluminum ($Al_2O_3=13.71-14.92wt\%$) and high magnesium ($MgO=11.83-13.1wt\%$) (Pham, 2013). Muscovite is occasionally found among the mineral assemblages, usually as secondary.

Geochemically, Cenozoic granitoids in the northwest of Ye Yen Sun block, as compared with Permian granitoids in southeastern Ye Yen Sun, have higher $Al_2O_3(14.57-16.56wt\%)$ and $CaO(0.52-1.85wt\%)$, lower $TiO_2(0.08-0.42wt\%)$, $Fe_2O_3(0.35-2.47wt\%)$, $MnO(0-0.04wt\%)$ and $K_2O(3.51-4.72wt\%)$ contents; total alkaline ($Na_2O + K_2O(8.07-10.18wt\%)$). Their Lacroix index (K_2O/Na_2O) is generally greater than 0.6, indicating that they are relatively close to the high-K alkaline granite of calc-alkaline series.

The trace element composition shows that the granites depleted in high field strength elements such as Ta (0.45–3.62 ppm), Nb (6.62–28.1 ppm), Zr (45.6–181 ppm), Y (3.62–26.4 ppm) and Hf (2.63–6.98 ppm), but relatively enriched in large ionic lithophile elements such as Sr (216–1289 ppm) and Ba (481–2513 ppm), and light rare earth elements (total REE = 42.3–250.71 ppm). The K/Rb, Rb/Sr and Rb/Ba ratios range from 121–253, 0.09–1.08, and 0.04–0.42, respectively (Table 1 and Pham et al., 2013; Tran et al., 2015), making them intermediate granite between I- and S-type granite. The geochemical composition of Cenozoic Ye Yen Sun granitoids is aluminum saturated (Fig. 2). Mineralogical and geochemical characteristics reflecting the I- type granite of Ye Yen Sun

granitoids include: (i) the presence of high-Mg biotite and amphibole, usually associated with sphene (ii) medium to high alkalinity, in which the K_2O/Na_2O ratios ranging from medium to high; (iii) the content of rare earth elements and Nb, Ta, Zr is medium or low. In addition to the characteristic features of I-type granite, the studied magmas also show the S-type characteristics most clearly expressed in

high aluminum, rich in Sr, Ba, and high in $^{87}Sr/^{86}Sr$. Thus, geochemical characteristics of Cenozoic Ye Yen Sun granites show that they are intermediate granite between I- and S-type. Aluminum saturation characteristics of studied granitoids allow for applying their forming temperature and pressure calculation based on the Zr saturation and the major elemental compositions mentioned below.

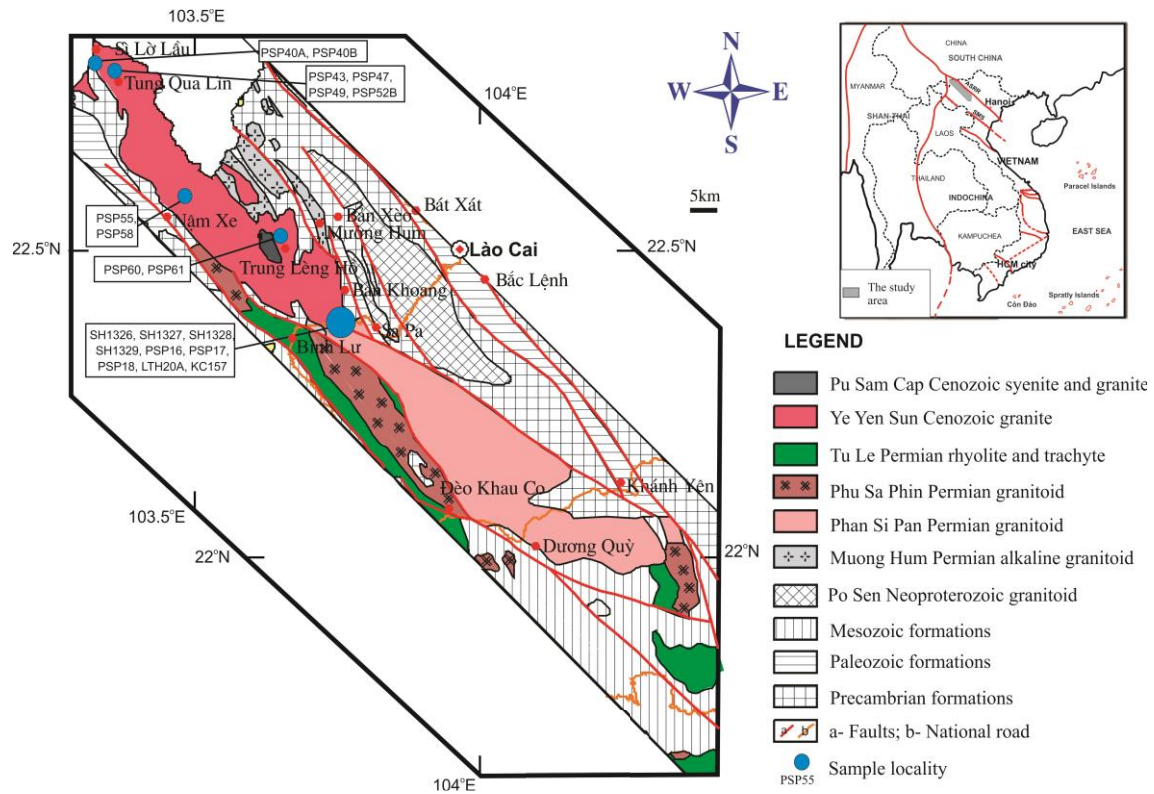


Figure 1. Geological scheme and survey locations of Cenozoic granite in the Phan Si Phan Uplift block

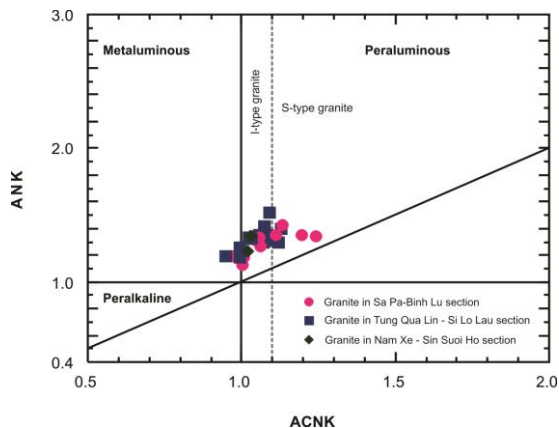


Figure 2. Plots of ANK versus ACNK of Ye Yen Sun Cenozoic granitoids (after Maniar and Piccoli, 1989), where $ACNK = Al_2O_3 / (CaO + Na_2O + K_2O)$; $ANK = Al_2O_3 / (Na_2O + K_2O)$

3. Methods of formation temperature and pressure calculation of Ye Yen Sun Cenozoic granitoids and results

To determine the formation temperature and pressure conditions of the studied granitoids we applied the calculation methods based on the Zr saturation and the graph

method based on the composition of the major elements. These are the methods used by many granitoid researchers to confirm their practicality.

3.1. Calculation based on melt Zr-saturation

This method is derived from the experiments of Watson and Harrison (1983), Harrison and Watson (1983), Watson (1996), Baker et al. (2002), Miller et al. (2003), Hanchar and Watson (2003), and Chemiak and Watson (2003). Experimental results of the above authors have provided the basis for the modeling of granitoid formation temperature based on Zr saturation in the melt.

Watson and Harrison (1983) determined the relationship between the Zr- saturation and temperature and major element composition of the melt by the following equation:

$$\ln D_{Zr}^{Zircon/melt} = \{-3.18 - [0.85 (M-1)]\} + 12,900/T$$

Inferred from the above equation:

$$T_{Zr}(K) = 12,900 / [2.95 + 0.85M + \ln(496,000/Zr^{melt})]$$

Where:

$D_{Zr}^{Zircon/melt}$ is Zr distribution coefficient between zircon (approximately 496,000 ppm) and melt

- M is cation ratio calculated as:

$$M = (Na + K + 2 \times Ca)/(Al \times Si)$$

M is a compositional factor that accounts for dependence of zircon solubility on SiO₂ and peraluminosity of the melt [(Na + K + 2 × Ca)/(Al × Si), all in cation fraction].

- T (K) is in Kelvin, converted to Celciusas
 $T (^{\circ}C) = T (K) - 273,15$.

Applying the above temperature calculation formula, formation temperatures of Ye Yen Sun Cenozoic granitoids can be calculated that show ranging from 680°C to 850°C, average 763°C (Table 1). The correlation between the Zr content and the saturation temperature is shown in Fig. 3.

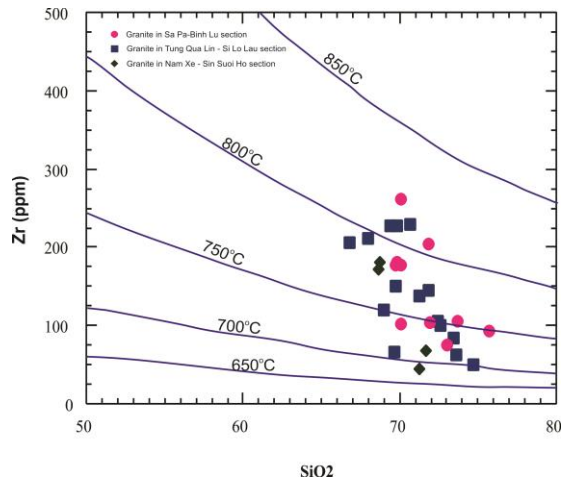


Figure 3. Plots of Zr (ppm) vs. Zr-saturation temperature (T_{Zr}) of Ye Yen Sun Cenozoic granites

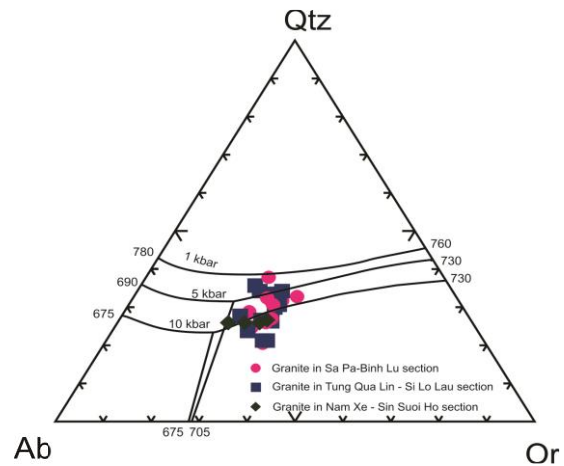


Figure 4. Formation temperature-pressure correlation of Ye Yen Sun Cenozoic granites in Qtz-Ab-Or diagram (after Johannes and Holtz, 1996)

3.2. Calculation based on the major element composition

This method is based on the empirical results of several authors, such as Tuttle and Bowen (1958), Luth et al. (1964), Merrill et al. (1970), Huang and Wyllie (1975), Ebadi and Johannes (1991), Holtz et al. (1992), and Holtz et al. (1995). Experiments on the crystallization temperature and pressure of the Qtz-Ab-Or system (Haplogranite) were conducted under saturated conditions and at pressure levels of 0.5, 1, 2, 5, 10, 15, 20 and

30 kbar. This synthesis of experimental results allowed for Johannes and Holtz (1996) constructing physicochemical charts (Fig. 4). Assuming Ye Yen Sun Cenozoic granitoids were formed from water saturated melts (this is expressed by the presence of significant amounts of OH-bearing mineral groups such as biotite and hornblende in the composition),

the major element composition is converted to the normative quartz (Qtz) - albite (Ab) - orthoclase (Or) using CIPW method. Calculate results are shown in Table 1. The results illustrated in Fig. 4 show that the studied granitoids may be formed at the temperature range of about 670 to 780°C, with pressure varying from >1 to over 10 kbar.

Table 1. Major element compositions (wt%) and Zr concentrations (ppm) of Ye Yen Sun Cenozoic granites

Sample	SH-1326	SH-1327	SH-1328	SH-1329	PSP16	PSP16/3	PSP17	KC157	PSP 18	LTH 20A
	1	2	3	4	5	6	7	8	9	10
SiO ₂	75.74	69.75	70.10	71.99	73.69	69.88	73.06	71.84	70.10	70.11
TiO ₂	0.08	0.22	0.20	0.17	0.09	0.17	0.11	0.25	0.15	0.34
Al ₂ O ₃	14.89	16.27	16.56	16.10	14.81	15.66	15.11	14.88	15.08	15.05
Fe ₂ O ₃ T	0.35	1.33	1.19	0.80	0.95	2.04	0.77	1.68	0.91	2.12
MnO	0.00	0.04	0.02	0.02	0.02	0.04	0.02	0.04	0.04	0.03
MgO	0.00	0.13	0.00	0.07	0.10	0.19	0.20	0.41	0.25	0.53
CaO	0.81	1.75	1.45	1.60	1.22	0.97	1.26	1.59	1.57	0.52
Na ₂ O	4.04	4.44	4.34	4.12	4.92	5.06	4.20	3.81	4.86	3.46
K ₂ O	4.03	4.56	4.72	4.17	4.07	5.12	4.64	4.70	4.28	5.07
P ₂ O ₅	0.01	0.07	0.03	0.04	0.02	0.11	0.03	0.07	0.05	0.12
LOI	0.21	0.77	1.35	1.03	0.24	0.74	0.81	1.08	1.12	1.51
TOTAL	100.16	99.31	99.95	100.12	100.13	99.98	100.21	100.35	98.41	98.86
Zr (ppm)	92.89	177.2	178.3	103.6	106	181	76	205	103.00	261.80
TZr (°C)	755.27	791.37	797.94	755.70	747.37	786.45	726.19	806.43	738.99	847.03
M	1.19	1.45	1.37	1.31	1.46	1.54	1.38	1.42	1.55	1.20
Qtz	37.74	26.06	26.92	32.52	29.00	20.47	30.78	31.72	24.94	32.87
Or	25.60	30.92	31.58	27.98	26.03	32.97	30.18	31.63	28.62	33.98
Ab	36.66	43.01	41.50	39.50	44.97	46.55	39.04	36.65	46.44	33.15

To be continued

Sample	PSP 40A	PSP 40B	PSP43	PSP47	PSP49	PSP52B	PSP 52C	PSP55	PSP58	PSP 60	PSP 61
	11	12	13	14	15	16	17	18	19	20	21
SiO ₂	72.59	72.42	71.31	69.01	69.79	69.67	68.00	68.71	68.76	71.70	71.26
TiO ₂	0.14	0.14	0.22	0.25	0.24	0.23	0.42	0.31	0.34	0.15	0.15
Al ₂ O ₃	14.91	14.57	15.23	15.56	15.88	15.81	16.22	15.77	15.90	15.67	15.31
Fe ₂ O ₃ T	1.03	1.05	1.63	1.76	1.42	1.50	2.47	1.96	2.18	1.26	1.16
MnO	0.02	0.01	0.02	0.03	0.01	0.02	0.03	0.02	0.03	0.03	0.02
MgO	0.30	0.29	0.55	0.46	0.54	0.32	0.90	0.71	0.74	0.31	0.28
CaO	1.35	1.29	1.78	1.85	1.87	1.40	2.05	1.99	1.96	1.46	1.50
Na ₂ O	4.05	3.82	4.92	4.78	4.45	4.79	4.75	4.25	4.44	5.06	5.38
K ₂ O	4.40	4.42	3.67	4.83	4.32	5.09	3.99	4.38	4.22	4.06	3.51
P ₂ O ₅	0.05	0.05	0.08	0.12	0.09	0.08	0.18	0.15	0.17	0.05	0.05
LOI	0.38	0.98	0.49	0.33	0.62	0.27	0.64	0.46	0.27	0.74	0.46
TOTAL	99.22	99.04	99.90	98.98	99.23	99.18	99.65	98.71	99.01	100.49	99.08
Zr	101.40	106.70	137.70	121.00	150.20	66.60	211.50	171.60	182.00	68.50	45.60
TZr (°C)	750.19	756.11	764.75	745.53	774.49	705.09	799.91	784.43	789.32	711.79	680.31
M	1.37	1.34	1.52	1.64	1.48	1.55	1.54	1.50	1.51	1.48	1.51
Qtz	32.50	34.11	27.70	21.41	26.54	21.29	23.74	26.52	25.99	25.87	25.83
Or	29.16	29.48	24.80	32.55	29.72	33.57	28.23	30.79	29.57	26.66	23.25
Ab	38.35	36.41	47.50	46.03	43.74	45.14	48.02	42.69	44.44	47.48	50.92

Remark: 1-10: granite along Sa Pa-Binh Lu section; 11-17: granite along Tung Qua Lin-Si Lo Lau section; 18-21: granite of Nam Xe-Sin Suoi Ho route, data for 1-21 are from Pham Thi Dung (2013); M=(K+Na+2Ca)/(Al*Si)

4. Discussions

4.1. Pressure and temperature of magma crystallization

The results of determination of the formation temperature based on the zirconium (Zr) saturation level (Table 1, Fig. 3) show that the crystallization process of Ye Yen Sun Cenozoic granite occurs in the temperature range of 850°C to about 680°C. The crystallization temperature is lower than the liquidus temperature of about 150°C, while the solidification temperature is substantially similar to the solidus temperature.

Recently, research has revealed that very few cases of zircon begin to crystallize near the liquidus temperature during crystallization of granite magma. In most cases, the zircon is formed in the temperature range of the granite crystallization sequence (about 100–200°C, Harrison et al., 2007) and close to the solidus temperature. According to Moecher et al. (2014), zircon crystallizes near liquidus temperature (~ 1000°C) in granite magmas containing high Zr content (830–1201 ppm), while granite magmas containing low Zr content, around 100–300 ppm, the temperature of zircon crystallization may be as low as about 700–800°C (200–300°C lower). Thus, the zircon crystallization temperature does not necessarily coincide with any Zr saturation temperature, which means that zircon can crystallize at any temperature during the crystallization of granite magma, from the liquidus to the solidus. The results zircon saturation-based temperature in the Ye Yen Sun Cenozoic granite indicates that the magma crystallized at different temperatures with the majority of Zr contents varying within 100–200 ppm, which is consistent with temperature of zircon crystallization may be as low as about 700–800°C (Moecher et al., 2014).

Another issue is how does the hydrostatic pressure and water content in the magmatic melt affect the Zr saturation? Boehnke et al.

(2013) show that the pressure <25 kbar does not affect the Zr saturation in magma, i.e. the T_{Zr} temperature is independent of the pressure of <25 kbar. Additionally, the authors have also stated that the water content in the melt does not significantly affect the Zr saturation. Formation pressure of Ye Yen Sun Cenozoic granite is lower than 10 kbar, suggesting that it did not affect the Zr saturation temperature. From the above statements it can be assumed that the studied magma may start crystallizing at ~ 850°C and end at ~ 680°C.

4.2. Hot and cold granite

Watson and Harrison (1983) proposed the concept of "hot" granite and "cold" granite. Hot granite has a Zr-saturation temperature (T_{Zr}) $\geq 800^\circ\text{C}$, while cold granite has a temperature $\leq 700^\circ\text{C}$. These two types of granites have different characteristics: hot granite in general does not contain inherited zircon (because the temperature is large enough to dissolve it) and is similar to mantle-derived magma, e.g. granites formed at the extensional tectonic or transformation setting (Miller et al., 2003). In contrast, cold magma usually contains zircon (mineral) that is inherited from the source because the low temperature does not dissolve the residual zircon and this magma is usually formed at extensional tectonic setting (crustal thinning). These authors, however, also emphasized that both types of magma can contain inherited zircon crystals. Thus, the possibility of zircon crystallization from magma is main component, while zircon inheritance may present in limited quantity. This should be considered when using zircon for age determination or, using thermometers based on Ti content in zircon. The Ye Yen Sun granites have Zr saturation temperatures (T_{Zr}) ranging from 680 to 850°C, which is regarded as "hot" granite type. This suggests that Ye Yen Sun granites were formed at the extensional tectonic or transformation settings. The above conclusions are also consistent with the formation ages and high-K calc-alkaline

geochemical characteristics of the granitoids, formed by hybrid between mantle and crustal sources (Pham, 2013). This type of magma usually occurs during the transition from compression to extension mode (Lameyre, 1988; Bonin, 1990). The formation age of these granites is 35–30 Ma (Pham, 2013; Tran et al., 2013), apparently coinciding with the period of continental lithosphere extension in western Yangtze River craton 34–17 Ma (Anczkiewicz et al., 2007; Nguyen et al., 2009) leading to the formation of different magma complexes, including potassic and ultra-potassic alkaline magmas in the Song Da rift zone and in other structures in south China. Thus, the possibility of granite melt generation in a stretching region along the two walls of a shear zone should be also a mechanism to consider. In this case, it may be agreeable with the assumption of their synchronous shearing relationship with the shear motion along the Red River zone as exemplified by Jinping granite in Chinese territory (Zhang et al., 1999).

Formation pressure of Ye Yen Sun Cenozoic granitoids is determined to be between 10 and 1 kbar, equal to 33–3 km deep (Fig. 4). The results imply that the magma started to crystallize from deep levels (~ 33 km), and probably corresponds to the Zr saturation temperature (T_{Zr}) at about 800 to 850°C. The crystallization process would continue with the elevation of magma until reaching the depth of 3.3 km. During this process, the magma composition continues to change in more acidic direction with the corresponding Qtz/Or/Ab components from 25/23/50 to 43/28/27 (Table 1). There was no significant difference in the forming pressure between the three sampling areas of Sa Pa - Binh Lu, Tung Qua Lin-Si Lo Lau and Nam Xe-Sin Suoi Ho. However, with the Zr saturation temperature (see Fig. 3), the highest T_{Zr} (about 730 to 850°C) is distributed in the Sa Pa-Binh Lu area, medium T_{Zr} (700-830°C) is in the area Tung Qua Lin Si Lo Lau. The

lowest T_{Zr} (680–800°C) is in the area in Nam Xe- Sin Suoi Ho area; this trend occurs with the decrease in the Zr content in the direction of decreasing T_{Zr} . Thereby, it is possible that Sapa-Binh Lu granite crystallized the earliest, followed by Tung Qua Lin-Si Lo Lau, and finally Nam Xe-Sin Suoi Ho. The above results show that the formation temperature and pressure is unevenly distributed over the whole structure of the block, with the trend of crystallization temperature decreasing gradually from Sa Pa-Binh Lu to Tung Qua Lin-Si Lo Lau area, and finally Nam Xe-Sin Suoi Ho, reflecting the sequence of the evolution of magmatic crystallization of the study area.

In summary, the process of magma crystallization occurs with the simultaneous change of temperature-pressure (change with the rise of magma) and the composition. The crystallization starts early, at high temperatures and pressures ($T \sim 850^\circ\text{C}$, $P \sim 10$ kbar). During elevation, the magma continues to crystallize. In the first stage, the ratio between the solid phase and the liquid phase is very low, the mobility of magma is high so that they move easily. The later the ratio grows, at a time when solid phase becomes dominant, the mobility decreases, and magma stops at a depth of ~ 3.3 km until fully frozen.

5. Conclusions

Study of P-T condition of Ye Yen Sun Cenozoic granitoids may lead to the following conclusions:

The crystallization temperature of Ye Yen Sun Cenozoic granite formations may start at about 850°C and ends at about 680°C. Their formation pressure is about 10 to 1kbar, at 33–3.3 km deep.

The study showed that the temperature and pressure were unequally distributed on the structural plane of Ye Yen Sun Cenozoic granitoids.

Studies show that Ye Yen Sun Cenozoic granitoid is a "hot" or "intermediate" granite formed at extensional tectonic or transitional tectonic settings and might be related to the Cenozoic left lateral movement of the Red River Fault zone.

Acknowledgements

This study was funded by (Vietnam) National Foundation of Science and Technology Development (NAFOSTED) under the project code 105.01-2016.07. The authors would like to thank Dr. Nguyen Hoang for important suggestions in completing the article.

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