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The age of the Donghai rock crystals (clear quartz), eastern China: Constraint from biotite Ar-Ar geochronology

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Abstract: The paper presents the newest age information of the rock crystals (clear quartz crystals) in Donghai County of eastern China, and discusses the evolution of the rock crystal-bearing quartz veins with respect to the exhumation history of the Su-Lu ultra-high pressure (UHP) metamorphic belt. Biotite samples were collected from the alteration zone of the quartz veins and Ar-Ar method was used to date the biotite in an attempt to decipher the age of the rock crystals based on the relation between the biotite and the quartz veins. The dating yields biotite Ar-Ar plateau age, isochron age, and inverse-isochron age of 239.8±2.6 Ma, 241.0±2.6 Ma, and 241.1±2.7 Ma respectively. The ages are close to the peak metamorphism age (at 240-245 Ma) of the Su-Lu UHP belt, indicating that the rock crystals of the quartz veins were crystallized in the early stage of exhumation of the Su-Lu UHP metamorphic belt.

Keywords:rock crystal, biotite, Ar-Ar geochronology, ultra-high pressure metamorphism, Donghai

1. Introduction

Donghai County of Jiangsu Province in eastern China is well-known for its huge reserve and production of top-quality rock crystals (i.e. clear quartz crystals). The area is tectonically located within the Su-Lu ultra-high pressure (UHP) metamorphic belt (Fig. 1). The rock crystals have been mined for over hundred years. However, their genesis, age of crystallization, and their relation to the ultra-high pressure metamorphism remain unclear even though there have been several publications that deal with the relevant issues (Fan *et al*., 1998; Wang *et al*., 2003; Li *et al*., 2005, 2006). The Fifth Geological Team of Jiangsu Geological Bureau (1976) suggested that the rock crystal were produced by migmatization and metamorphism associated with biotite-bearing pegmatite in Precambrian time. Fan *et al*. (1998) suggested that they were the products of meso-hydrothermal activities during the Yanshanian orogeny (middle-late Mesozoic Era). Wang *et al*. (2003) recently proposed that they were crystallized at 208 Ma based on Rb-Sr dating of fluid inclusions obtained from some rock crystals, and that the age was correspondent to the transition time from the exhumation of the UHP metamorphic belt to subsequent extensional tectonic regime.

Our early publication (Li *et al*., 2006) indicates that there were multiple hydrothermal activities/events that were closely related to the rock crystal-bearing quartz veins, and that there were several types of fluid inclusions contained in rock crystals. The Rb-Sr dating is therefore problematic. In this paper, we present an Ar-Ar date on carefully selected biotite that was synchronologic to the rock crystals. We believe that a reliable dating of the rock crystals would significantly help understanding their crystallization process and their relation to other geologic processes such as the UHP metamorphism and the retrograde metamorphism during the exhumation of the UHP belt.

2. Geologic setting

Donghai rock crystal deposits are located in the Su-Lu ultra-high pressure metamorphic belt (Fig. 1a). The host rock includes Precambrian gneiss, feldspar-migmatite, amphibole-schist, and eclogite. The deposits occur along northeast-trending faults, and the rock crystal-bearing quartz veins mostly strike northeast as well. Two types of primary rock crystal quartz veins exist in the area: one with biotite and the other without biotite.

The former occurs as biotite quartz pegmatite dikes/veins. The second type of quartz veins is mainly com-

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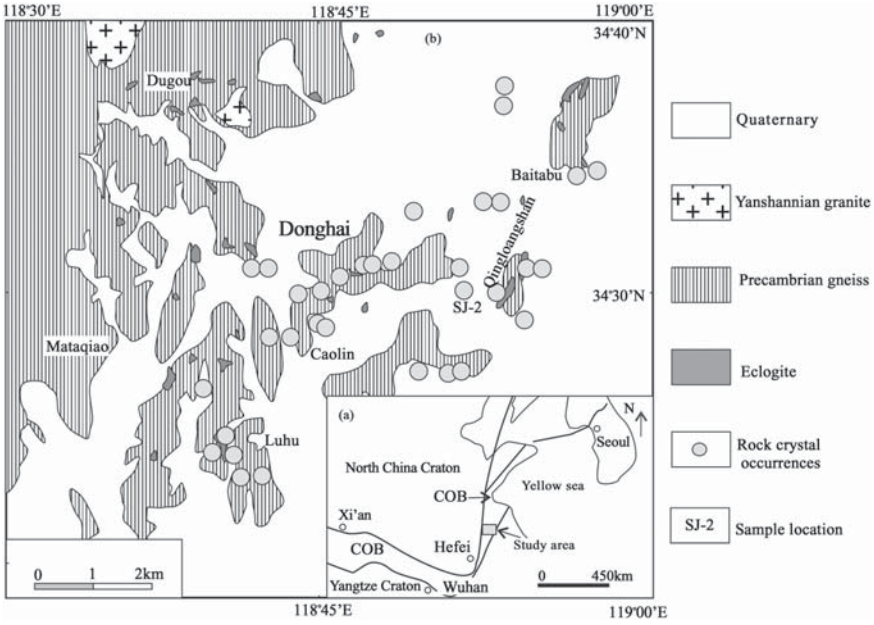

Fig. 1 Simplified geological map of rock crystal deposits in Donghai County, eastern China. COB=Central Orogenic Belt.

posed of quartz. Trace amount of tiny minerals such as chlorite, epidote, specularite, rutile, and tourmaline are observed in these quartz veins. Both types of quartz veins occur along fractures, fissures, and contacts between different rock units. Most of them are irregular in shape, 20 meters long, and several centimeters to several meters thick. They all have a massive texture. Close to geode cavities found within quartz veins, they change their color from white to light yellow, and colorless, and become transparent or translucent.

The host rocks near the contact with quartz veins are hydrothermally altered. The alteration next to the biotite-free type of quartz veins includes vermiculitation, epidotization, and chloritization, while biotitization and epidotization have been found next to the biotite-bearing quartz veins, the biotite quartz pegmatite.

Placer rock crystals are the important reversers, and mined from Quaternary surface deposits. They are usually as big as several meters in diameter, and are better quality in terms of crystal clearness.

3. Sampling and analysis method

3.1 Sample location and description

The sample (SJ-2) used for Ar-Ar dating was collected from Qinglongshan Mountain (Fig. 1b). In the area, the quartz veins have a steep dip angle; they are 20 meters long and 1-2 meters thick (Fig. 2a, b). The locality produces normally small size and top-quality rock crystals with a single crystal weight of 0.1-0.5 kilograms. Exceptionally, in 1965, a huge rock crystal weighted more than 3,500 kilograms was excavated at the locality. The rock crystal which have embayed boundary, are consists of sub-grain (Fig.2c, d), which have different extinction position under microscope. Top-quality rock crystal quartz is conspicuous in the growth zone.

Several alteration zones were determined from the quartz vein to eclogite, such as scale-like biotite zone, epidote-biotite zone, epidote-amphibole zone and amphibole zone (Fig. 2c, d). The scale-like biotite zones are 0-0.3 m wide in general, and the others usually 0.2-2 m thick. The sample SJ-2 was taken from the scale-like biotite zone next to a rock crystal quartz vein, and the biotite is in platy with brownish in color.

3.2 Analysis methods

The biotite sample is purified by using magnetic separator and then cleaned by using ultrasonic treatment under ethanol. The purity of mineral grains (0.08-0.15 mm) is more than 99 percent. Samples are wrapped by aluminum foil and loaded into a tube of Al foil. Each tube contains 2-3 monitor samples. The tubes are sealed into quartz bottle. The bottle is irradiated for 3,064 minutes in the nuclear reactor (A Swimming Pool Reactor at Chinese Institute of Atomic Energy in Beijing). The reactor delivers a neutron flux of ~ 6.0 x 10^{12} n cm^{-2} s^{-1} and the integrated neutron flux is about 1.10 x 10^{18} n cm^{-2}. After irradiation, the samples and monitors are removed from the quartz bottle and then loaded into the vacuum extraction system. They are baked out for 48 hours at 120-150 °C.

The Ar extraction system comprises an electron bombardment heated furnace in which the samples are

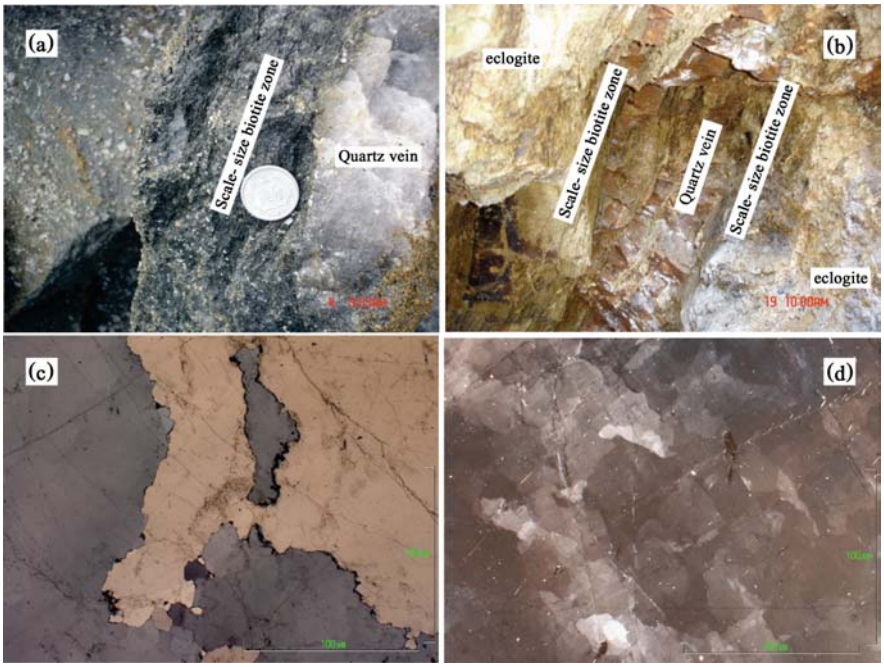

Fig. 2 The rock-crystal-bearing quartz vein and its relationship with eclogite. (a) Quartz vein hosted in the eclogite. (b) Quartz vein is surrounded by hydrothermal biotite zone. (c) Embayed boundary of rock crystal quartz. (d) sub-grains-like quartz in the rock crystal quartz.

heated under vacuum. The thermocouple is used to monitor and control the temperature of the furnace. The furnace is automatically attained the set temperature and remains within a few degrees from it. The released gases are admitted to a purification system. There are 30 minutes duration for heating-extraction for each temperature increment, and 30 minutes for purification as well. The purification system uses a U-tube cooled with a mixture of acetone and dry-ice, a titanium sublimation pump at 38A filament current and a titanium sponge furnace at 800 °C. The gases are purified by two Sorb-AC pumps at room temperature in the last step. The Argon purified is trapped in an activated charcoal finger at liquid-nitrogen temperature, and then released into the MM-1200B Mass Spectrometer for analyzing Ar isotope.

Measured isotopic ratios are corrected for the mass discrimination, atmospheric Ar component, blanks and irradiation induced mass interference. The correction factors of interfering isotopes produced during irradiation are determined by analysis of irradiated K_2SO_4 and CaF_4 pure salts and their values are: $(^{36}Ar/^{37}Ar)Ca$ =0.000240; $(^{40}Ar/^{39}Ar)k$ =0.004782; $(^{39}Ar/^{37}Ar)Ca$ = 0.000806. The blanks of the m/e = 40, m/e = 39, m/e = 37, m/e = 36 and are less than 6 x 10^{-15} mol, 4 x 10^{-16} mol, 8 x 10^{-17} mol and 2 x 10^{-17} mol, respectively. The decay constant used is λ = 5.543 x 10^{-10} a^{-1} (Steiger and Jäger, 1977). All ^{37}Ar were corrected for radiogenic decay (half-life 35.1 days). Uncertainty in each apparent age is given at 2σ. The monitor used in this work is an internal standard: Fangshan biotite (ZBH-25), which accepted age is 132.8±1.3 Ma (Sang *et al.*, 2006) .The J-values of these monitors are placed on the Table 1. Detailed analyses techniques are described in Chen *et al.* (1994, 2002).

4. Results

The ages and 2σ uncertainties are plotted against the cumulative released ^{39}Ar fraction to establish the age spectra (Fig. 3). The argon isotope ratios are presented graphically on classic isotope correlation plots using program ISOPLOT of Ludwig (2001). The ^{40}Ar-^{39}Ar data are summarized in Table 1, which incorporates the apparent age spectra and the atmospheric argon and Ca: K ratios for each heating.

The sample shows the plateau age of 239.8±1.6 Ma, calculated from steps 3 to 13, representing 92.59 percent of the total argon release (Fig. 3a). The isochron age of 241.0±2.6 Ma (MSWD=1.08, initial $^{40}Ar/^{36}Ar$=292.4±2.6) is concordant with the plateau age (Fig. 3b). The inverse-isochron age of 241.1±2.7 Ma (MSWD=2.8, initial $^{40}Ar/^{36}Ar$=291.1±3.9) is also concordant with the plateau age (Fig. 3c).

5. Discussions and Conclusions

By far there have been three references regarding the

Table 1 The $^{40}Ar/^{36}Ar$ stepwise heating data of biotite.

T(°C)	$(^{40}Ar/^{39}Ar)_m$	$(^{36}Ar/^{39}Ar)_m$	$(^{37}Ar/^{39}Ar)_m$	$(^{38}Ar/^{39}Ar)_m$	$*^{40}Ar/^{39}Ar$	^{39}Ar ($\times10^{-14}$mol)	^{39}Ar (Cum.)(%)	Age(Ma)	±1σ (Ma)	Ca/K	$^{40}Ar/^{39}Ar$
400	142.3258	0.4605	0.0874	0.1472	6.2475	353.67	1.29	123.6	5.4	0.1687	309
500	58.4930	0.1649	0.0142	0.0467	9.7702	1674.59	7.38	189.7	9.5	0.0274	355
600	46.1735	0.1147	0.0170	0.0406	12.2817	1088.81	11.34	235.4	3.4	0.0329	403
700	18.6585	0.0213	0.0037	0.0167	12.3476	6805.57	36.09	236.6	2.6	0.0071	876
780	14.6787	0.0075	0.0040	0.0142	12.4688	4296.45	51.72	238.7	2.5	0.0077	1957
860	14.3502	0.0058	0.0072	0.0139	12.6234	3225.24	63.45	241.5	2.4	0.014	2474
910	14.6065	0.0068	0.0082	0.0139	12.5944	1953.78	70.55	241.0	2.4	0.0157	2148
960	14.3202	0.0059	0.0066	0.0146	12.5611	3563.07	83.51	240.4	2.5	0.0128	2427
1010	15.1540	0.0086	0.0090	0.0154	12.6211	1311.39	88.28	241.5	2.4	0.0174	1762
1060	15.5024	0.0101	0.0110	0.0148	12.5120	1038.52	92.06	239.5	2.6	0.0212	1534
1110	17.2343	0.0156	0.0116	0.0182	12.6081	1472.41	97.41	241.2	2.5	0.0224	1104
1180	19.2563	0.0224	0.0144	0.0204	12.6417	647.37	99.77	241.8	3.4	0.0279	859
1280	21.1478	0.0310	0.3166	0.0267	11.9968	53.83	99.97	230.3	5.7	0.6112	682
1400	31.1770	0.0796	1.0859	0.0811	7.7433	9.56	100.00	152	18	2.0963	391

W=60.00mg J=0.011348

Total age =234.6Ma

crystallization age of the rock crystals. The first, also the earliest suggests it was in Precambrian, according to age of migmatization and metamorphism of biotite quartz pegmatite (Fifth Geological Team of Jiangsu Geological Bureau, 1976). The second proposes that it was in the Yanshanian (i.e. middle-late Mesozoic; Fan *et al.* 1998). And the third, also the newer argues that it was in Jurassic based on a 208 Ma age of fluid inclusions with Rb-Sr dating (Wang *et al.*, 2003), and it pinpointed a transition from the exhumation of the ultra-high pressure metamorphic belt to an extensional tectonic regime. However, the fluid inclusions in rock crystal have several stages (Li *et al.*, 2006), which make it difficult to determine the exact timing of rock crystal.

Our biotite Ar-Ar dating, as indicated above, yields the age about 240 Ma of closure temperature of argon diffusion of biotite, which can be regarded as the age of biotite crystallization, because the biotite is the product of a short-lived hydrothermal activity. The close association between biotite and the quartz vein indicates that biotite is synchronological to the emplacement of the quartz vein and also to the crystallization of the rock crystals, the clear quartz crystals. The result suggests the age of the quartz veins further back to the Triassic time.

Intensive research in recent years has been focused on the topics related to Su-Lu ultra-high pressure metamorphic belt, such as its collision model and exhumation history. Attention has also been paid to the fluids involved during its exhumation and retrograde metamorphic process (Suo *et al.*, 2005; Li *et al.*, 2004; You *et al.*, 2005). For example, Zheng *et al.* (2003) suggested the time for peak metamorphism, quartz-eclogite-facies recrystallization, granulite-facies recrystallization, and amphibolite-facies recrystallization was 245-240 Ma, 230 Ma, 220 Ma, and 200 Ma, respectively. You *et al.* (2005) revealed a three-stage UHP metamorphic history: the first stage, the peak metamorphism, was between 240 and 230 Ma; the second was characterized by a retrograde metamorphism that took place between 226 Ma and 219 Ma; and the third, also the last, was coeval with the late uplifting/exhumation that was accompanied by brittle deformation during 180-170 Ma. What happened in between 219 Ma and 180 Ma was the UHP belt was trapped in the middle crust. Zhang *et al.* (2005) however proposed an eight-stage model in which the belt experienced the peak metamorphism in between 245-240 Ma which is in agreement with Hacker *et al.* (1998) and Webb *et al.* (1999), and later in between 240-230 Ma was uplifted from the lower mantle to the middle crust. The belt was recrystallized in 230-205 Ma when it was trapped in the middle crust, and later was exhumed to be exposed in about 190 Ma.

Zheng *et al.* (2004) dated zircon grains collected from kyanite-quartz veins hosted in Zhujiachong LT/UHP eclogite, and got two group ages, one was about 223-216 Ma, and the other between 182 - 181 Ma. The first group age was interpreted to be response to the fluids released during exhumation and the second associated with the later rapid exhumation. As mentioned above, the peak metamorphism for Su-Lu ultra-high pressure metamorphic belt is no later than 240 Ma, and after 240 Ma, the areas mainly experienced exhumation and

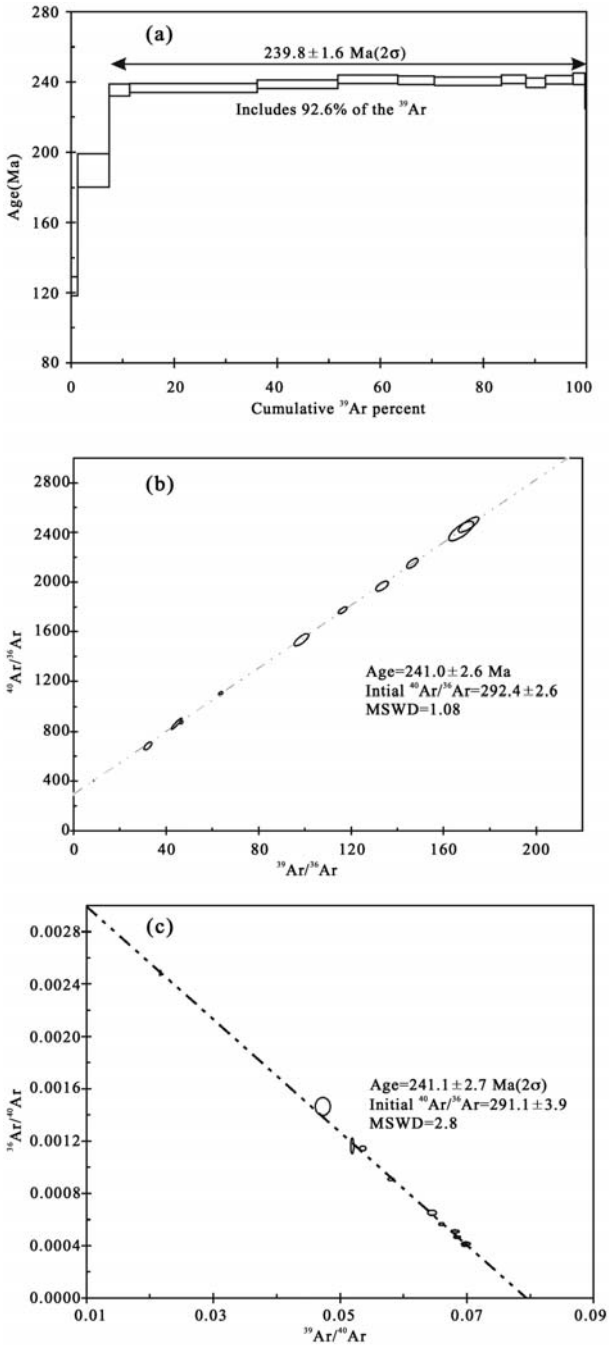

Fig. 3 Biotite $^{40}Ar/^{39}Ar$ plateau age (a), the isochron age (b) and inverse-isochron age (c).

retrograde metamorphism. Therefore the biotite age of 240 Ma from this study suggests that the rock crystals in Donghai region were crystallized in the early stage of exhumation of the Su-Lu ultra-high pressure metamorphic belt.

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東中国ドンハイ水晶の年代：黒雲母の Ar-Ar 年代による制約

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要　旨

本論文は，中国東部，江蘇省東海県の水晶の年代を報告し，水晶を含有する石英脈の形成史と蘇魯超高圧変成帯の上昇侵食史との関係を議論したものである．年代測定に用いた黒雲母試料は石英脈に伴う変質帯から採取され，Ar-Ar法を用いて年代測定を行った．黒雲母と石英脈との関係から得られた年代は水晶の形成年代を表すものと解釈される．分析により，Ar-Arプラトー年代，アイソクロン年代，逆アイソクロン年代として，それぞれ239.8±2.6 Ma, 241.0 ± 2.6 Ma, 241.1 ± 2.7 Maの結果を得た．これらの年代は蘇魯超高圧変成帯における変成作用の頂点の年代（240～245 Ma）と近接しており，石英脈中の水晶は，蘇魯超高圧変成帯の上昇侵食初期に形成されたことを示す．