A Study of Determination of Geological Age by Thermal Analysis Method

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Absract :-(U-Th)/He geological dating method is a rapidly developed dating method in recent years. The key of the (U-Th)/He dating is the determination of 4He content. However the measurement of the 4He content is very complicated because 4He is gas. This paper suggest an approach to determine 4He content by thermal analysis method based on previous studies，thus a new geological dating method is proposed.

Measuring the annealing heat of the α ion nuclear tracks, then comparing the annealing heat of the to-be-determined samples with standard sample, the geological age of the to-be-dertermined samples can be calculated. This paper select Durango apatite as the standard sample, and the geological age of apatite from Maanshan, Anhui, China is measured by the proposed method. The applicable scope and condition of the proposed method is also discussed in this paper.

Keywords: (U-Th)/He geological dating; Solid state nuclear track detector; Thermal analysis method; DSC curve; Annealing heat; Apatite.

1 INTRODUCTION

Fission track method, devised in 1965[1-4] soon got widespread use[5-8] , and up to now it is still one of basic techniques for nuclear science dating [9-17]. Nonetheless, this technique has a drawback. In the basic dating formula,

$$t = \frac{1}{\lambda_D}\ln(\frac{\lambda_D N_F}{\lambda_F N_{238}} + 1) \quad (1)$$

^{238}U total decay constant λ_D=1.551×10^{-10}a^{-1}. The number of ^{238}U nuclei in spontaneous fission and that of existing N_{238} (number of existing ^{238}U nuclei) can be both accurately measured. Instead, no unified value of ^{238}U spontaneous fission constant λ_F had not been got till now[18], that is, λ_F values obtained by various laboratories via different methods, deviate greatly from one another. Now the three λ_F values used are indicated respectively: (7.03±0.11)×10^{-17}a^{-1}; 6.9×10^{-17}a^{-1}; 8.46×10^{-17}a^{-1}. The difference between the max and min values was large as 18.4%. When these two were inserted into equation (1) to calculate the age (order of 10^{6}a), they showed a difference of 18% or so. As a very complicated process, measuring N_F i.e. number of ^{238}U nuclei via chemical etching led to a high degree of uncertainty.

(U-Th)/He geochronology is a dating method that developed rapidly in recent years[19-21] . Now this method has been widely used in crustal denudation research, near-surface substance dating and low-temperature geothermal history [19,22,23]. One of most important works in this technique is how to accurately determine ^{238}U, ^{232}Th, ^{147}Sm and ^{4}He contents in the mineral. Of all, neutron activation analysis (NAA) for ^{238}U, ^{232}Th, ^{147}Sm is a very advanced one. Instead, helium isotope, as a gas, makes itself difficult to measure. Hence, how to accurately measure ^{4}He content is the key to (U-Th)/He dating. Based on the determination of solid state nuclear track in apatite via thermal analysis method [24-26], the same method was employed to determine ^{4}He in apatite. This trial determination of the geological age got initial results. Here we expected this could give a reference for other scholars or inspire them.

2 Evidence for detetmination of geological age of apatiteby thermal analysis method

Durango apatite, from Mexico, showing roughly the same geological age via different methods, is often taken as the standard sample for (U-Th)/He dating across the international scientific community[27]. The suggested age of this sample is about 31Ma. For example, ^{40}Ar/^{39}Ar dating indicates its age is 31.44 ± 0.18Ma [27]; K-Ar dating shows the result is 31.0 ± 0.5Ma [27]. If (U-Th)/He dating is employed, ^{4}He content should be obtained even by theoretical calculation. The basic formula for (U-Th)/He dating is

$$\begin{aligned} N_{^4He} = {} & 8N_{^{238}U}(e^{\lambda_{238}t} - 1) + 7N_{^{235}U}(e^{\lambda_{235}t} - 1) \\ & + 6N_{^{232}Th}(e^{\lambda_{232}t} - 1) + 1N_{^{147}S_m}(e^{\lambda_{147}t} - 1) \end{aligned} \quad (2)$$

where, $N_{^4He}$, $N_{^{238}U}$, $N_{^{235}U}$, $N_{^{232}Th}$ and $N_{^{147}S}$ denote the numbers of ^{238}U、^{235}U、^{232}Th and ^{147}S$_m$ nuclei respectively; λ_{238}, λ_{235}, λ_{232} and λ_{147} are their respective α radioactive decay constants; t denotes the geological age of (U-Th)/He.

In equation (2), λ_{238}, λ_{235}, λ_{232} and λ_{147} are known quantities of fixed values. If $N_{^{238}U}$, $N_{^{235}U}$, $N_{^{232}Th}$ and $N_{^{147}S}$ contents in apatite were experimentally measured, then the number of ^{4}He nuclei per g sample can be obtained upon inserting of 31Ma, the

geological age, into equation (2)[27]. determined that, average ^{238}U, ^{232}Th和$^{147}S_m$ contents in Durango apatite sample were 13.612μg/g, 265.555μg/g and 30.99μg/g respectively. This allowed us to calculate N_{238_U} =3.443025×10^{16}n/g, N_{235_U} =2.494953×10^{14}n/g (^{235}U content equal to 1/138 of ^{238}U), $N_{232_{Th}}$ =6.890694×10^{17}n/g and N_{147_S} =1.269114×10^{17}n/g. When these values and t=31Ma were substituted into equation (2), we got that $N_{4_{He}}$ =7.753670×10^{15}n/g, theoretical value of $N_{4_{He}}$, calculated from suggested geological age of Dorango apatite. The measured value $N_{4_{He}}$ =7.508144×10^{15}n/g (this value obtained by [27]who conducted conversion of the measured helium content 1.2472×10^{-8}mol/g).

Comparing theoretical with measured values, we got the difference is in the region of 3%. This told us two points: First, during the period of 31Ma, most ^4He isotopes produced by uranium, thorium and samarium remained in Durango apatite, that is, few were lost over the period. Second, we got reliable results by means of (U-Th)He dating applicable to Durango apatite. In apatite, each ^4He ion corresponds to the number of its nuclear tracks. Having measured the number of tracks via thermal analysis method, we discovered it a feasible method in (U-Th) He dating. It was worth trying so.

3 Thermal analysis method for Geological Dating

In preliminary researches, we successfully measured the number of nuclear tracks in apatite samples[24]. We argued that annealing heat of radiated samples correspond to the number of nuclear tracks, thus proving the feasibility of detecting solid-state nuclear tracks via thermal analysis method [25]. This principle enabled us to determine the correspondence between Durango standard apatite sample's annealing heat and number of tracks. By use of US-based TA Q2000 differential scanning calorimeter, we plotted DSC curve (scam rate 5℃/min,Mass=5.7300mg, as shown in Fig. 1) of standard Durango apatite sample and determined the above annealing heat. The measured heat was Q_B=1.964J/g.

$$q = \frac{Q_B}{{}_B N_{4_{He}}} = \frac{1.964 J / g}{7.753670 \times 10^{15} n / g} \tag{3}$$

The significance of Q value denotes the average heat released by all α ion nuclear tracks during thermal annealing while α decay occurred to uranium, thorium and samarium.

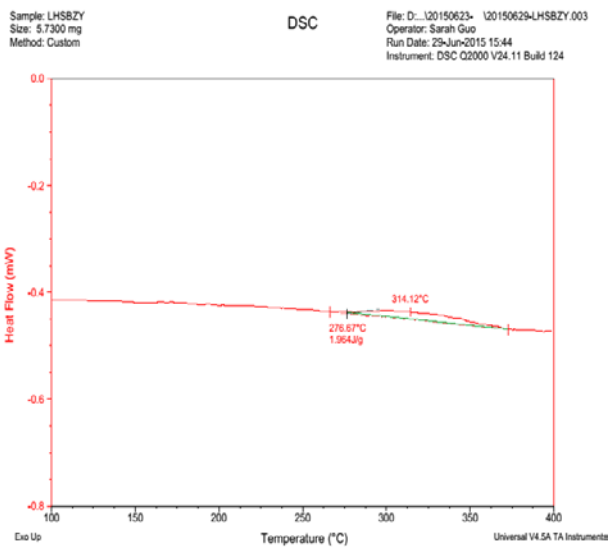

Fig 1. The DSC curve of Durango reference sample.

By performing neutron activation analysis of the three to-be-determined geological samples, China Institute of Atomic Energy got the data about uranium and thorium in Tab 1:

Tab 1. Results of different samples by Neutron Activation Analysis method

Sample name	Mass (mg)	U content	Th content
Apatite from Ma An Shan, Anhui	100.5	26.2± 2.9%ppm	189.6± 2.2%ppm
Epidote from Geology Museum of .Hebei Xingtai	100.6	2.12± 4%ppm	2.26± 3.6%ppm
Baddeleyite from Germany	101.2	0.4039% ± 2% (content percentage)	541.2± 2.6%ppm

Q2000 differential scanning calorimeter scanned apatite from Ma An Shan, Anhui, plotting an DSC curve as shown in Fig. 2 (scam rate 5℃/min, Mass=6.8100mg). As measured annealing heat Q_D=2.102J/g, the number of nuclear tracks in per gram sample(s) to be determined

$$
\begin{aligned}
{}_D N_{^4He} &= \frac{Q_D}{q} = \frac{Q_D}{Q_B}\,{}_B N_{^4He} \\
&= \frac{2.102 J/g}{1.964 J/g} \times 7.753670 \times 10^{15} n/g \\
&= 8.298480 \times 10^{15} n/g
\end{aligned} \tag{4}
$$

As per U (apatite) and Th contents in Tab 1, we made calculations: $N_{^{238}U} = 6.62700 \times 10^{16} n/g$

$N_{^{235}U} = 4.80000 \times 10^{14} n/g$ and

$N_{^{232}Th} = 4.91979 \times 10^{17} n/g$; no ^{147}S was detected.

Having inserted these Values into equation (1), we got that the geological age of sample(s) to be determined t=3.56875×10^{7}a.

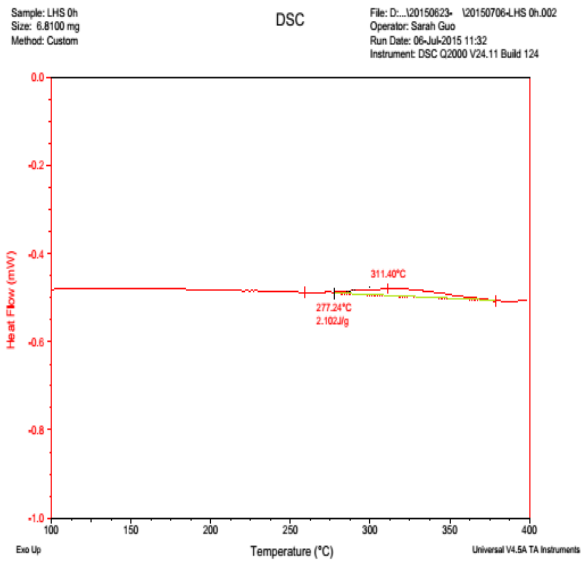

Fig 2. The DSC curve of apatite collected in Ma An Shan.

The same method allowed us to calculate the geological age of epidote from Geology Museum of Hebei Xingtai, China, is 6.049994×10^{8}a; that of baddeleyite from Germany is 4.879925×10^{5}a.

In the entire dating process, heat instead of helium content was measured. This avoided those difficulties

such as complicated experiment and demanding precision due to the fact that helium is a gas.

4 DISCUSSION

4.1 Comparison between routine (U-Th)/He method and thermal analysis (U-Th) /He dating method

The key to determination of apatite ^{4}He content via thermal analysis method is the thermal annealing heat of α ion nuclear tracks. Experimental research in this aspect indicated, fission tracks fell off gradually with increasing temperature and time [18,21]. Given a certain annealing rate (which means the ratio of subsiding tracks to those prior to annealing), the relation between heating time (t) and temperature (T, absolute temperature) is written as below [18]:

$$\ln t = \ln a + E / kT \qquad (5)$$

In the above equation, a is constant, E activation energy for annealing and k Boltzmann constant (k=1.38042×10^{-23}Jk^{-1}). Annealing temperature-time graph (Arrhenius' plot) for fission track in apatite from some place is as shown in Fig. 3 [18]. In the graph, logarithmic coordinates were taken along time-axis; annealing rates were taken at 0%, 50% and 100% respectively. Each a ion's nuclear track showed a much lesser density of damage to mineral samples than fission track did. Nuclear track density of the former was 6-7 orders of magnitude greater than the latter. The law of how ion nuclear track subsided with growing temperature and time is similar to that of fission track, but different from it[21] , but its mathematical expression and graph should be similar to equation (5) and Arrhenius plot respectively.

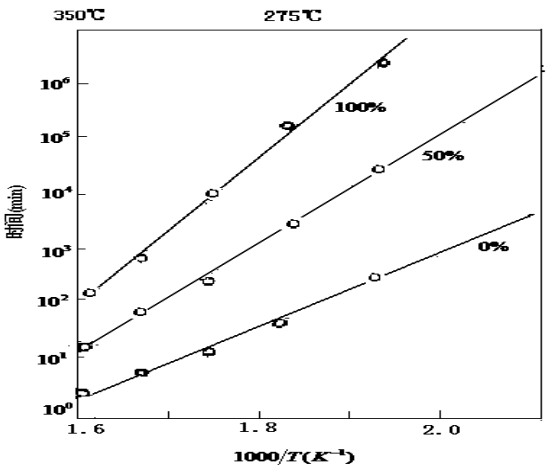

Fig 3. The Arrhenius 'Plot of fission track in some apatite sample.

In principle, we employed the method of comparing the ages of to-be-determined samples with standard sample. If holding the view that measured for both samples with thermochronological analysis instrument operating at the same conditions, we will get the same ages no matter what method we could use. Thorough annealing of the tracks was not necessary. But, measuring some annealing heat was also feasible. For example ,scam rate 5°C/min , In this case, the amount of heat of apatite from Ma An Shan, Anhui, in Tab 1, Mass=15.6310mg ,Q_D=0.6597J/g , with reference to sample Durango apatite's annealing heat (Mass=14.5700mg,Q_B=0.6721J/g,); we calculated 3.27343 ×10^{7}a, the age of apatite from Ma An Shan using the same method, though the heat obtained via this method was about 1/3 of the previous one (see Q_D and Q_B values in equation (4)). We almost got the same result because we held fast to measuring the heats of standard and to-be-determined samples under the same conditions of thermal analyzer . As introduced by analyzer manufacturer, the heat amount that the instrument can collect accounts for 20-97% of the total. Obviously, annealing heat varies with different methods or instruments for the same geological sample. So, the same age should be got if both samples are measured by the analyzer operating at the same conditions. Durango apatite and that

from Ma An Shan Anhui, China have the same law for annealing. The age of apatite from Ma An Shan measured in this paper may be close to the actual age. Geological data has shown that ,Ma An Shan region had four 3-stage volcanic eruptions in the Cretaceous Period (135 million years - 70 million years) of Mesozoic Era; and eruption also happened in the late Tertiary period (around 22 million years from now) of Cenozoic era, thus making apatite widely present in almost all igneous rocks[18] . Though there was no other dating method's result comparable with our results, these geological data told us the age of the isotopes in the samples collected in this paper is possible to be 30 million years old.

The experiments indicated, both tracks will completely subside at 350°C and 720°C respectively after 1-hr heating of apatite and zircon undergo by the same spontaneous fission fragments [18], showing annealing law varies with samples. Epidote from Geology Museum of Hebei Xingtai, baddeleyite from Germany and standard Durango apatite sample are very different minerals. So, the geological age of these samples using this method may differ greatly from the actual age.

Geological samples have closure temperatures. Closure temperature points to a certain temperature when nuclear tracks in sample(s) will be partially annealed and subside. It is suggested here, to-be-determined samples and reference samples which undergo similar geological environments should be selected as much as possible, thus enabling closure temperature to affect both samples, so that the impact of low closure temperature on the results is minimized.

4.2 Novelties and problems of thermal analysis (U-Th) /He dating method

(1) Fission-track dating measures the number of spontaneous tracks; on the other hand, (U-Th)/He thermochronology measures the number of α decay tracks. The measuring object for thermal analysis method is 6-7 orders of magnitude greater than that for fission-track method. Damage density is directly proportional to the square of charged ions' effective charge[18] . As a result, the measuring object was still 3-4 orders of magnitude greater than the other method, although each spontaneous fission track produced much greater damage density than α decay track did when effective charge of α ions was taken at Z*=2 and spontaneous fission Z* at 40-50. So, dating precision can be improved significantly. (2) This solved the dating error caused by no unified value taken for spontaneous fission constant λ_F. (3) This method has the following basic process: Grind collected samples, measure the annealing heat using thermal analyzer to work out the geological age, which appear much easier than fission-track method [18]. (4) Compared with direct (U-Th) /He dating method with ^{4}He, the thermal analysis method needs no complex instrumentation or precision operation techniques in ^{4}He measurement[27], thus facilitating widespread use of thermal analysis (U-Th) /He dating method. Judging from the current experimental results, nuclear tracks in the minerals undergo the slow process of heat release, which affects the precision of annealing heat measurement. It is considered this will grow better step by step with improving measurement method and instrument.

5 CONCLUSIONS

We have presented a thermal analysis method to determine geologic age. This work is not mature, and it needs to further improve. In future, based on the characteristics of the slow heat release of geological sample, we would pay attention to find a suitable instrument to measure the quantity of annealing heat,

To research on the laws of the alpha ion nuclear track annealing .

Apatite, sphene and zircon all have different closure temperatures. Now many applied researches have combined apatite (U-Th)/He method with apatite fission track method, or apatite (U-Th)/He with zircon (U-Th)/He, etc. to investigate in detail how geological time or body evolved during low-temperature period. If thermal analysis (U-Th) /He dating method could succeed, then it will be a new method comparable with the above. Geological thermal historical data about periods lower than 150°C is of great importance to petroleum resources assessment and petroleum exploration technique [18]. If going further, this research will also play a positive role in both petroleum resources assessment and petroleum exploration technique.

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