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An empirical calibration for ^{4}He quantification in minerals and rocks by laser fusion and noble gas mass spectrometry using Cerro de Mercado (Durango, Mexico) fluorapatite as a standard

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Abstract

An empirical calibration with a natural mineral standard (fluorapatite from Cerro de Mercado, Mexico) is proposed as a method to determine the ^{4}He concentration of mineral and rock samples. The procedure is based on the fusion of several aliquots of the fluorapatite standard with a well-spaced weight distribution in order to obtain a good correlation in coordinates of ^{4}He peak height versus fluorapatite weight. The weight is then converted to moles using the accepted mineral age (31.4 Ma) and appropriate formula. Experimental peak height of ^{4}He for the unknown samples are converted to moles with the regression determined for fluorapatite. The procedure is fast and inexpensive, and both precision and accuracy are always below 10% and usually about 3–5%.

Keywords: Geochemistry; Geochronology; (U–Th)/He; Apatite

1. Introduction

The determination of helium (^{4}He) concentration in minerals and rocks is an important issue for (U–Th)/He geochronology [1] and also for geochemical modelling [2]. Helium is a noble gas that can be separated conveniently by high vacuum procedures or gas chromatography. Although the latter method has been used extensively for gas and water analyses, the concentration of He in solid matter is generally too low for quantification or even detection without sensitive mass spectrometry. During the last few years, ^{4}He has been measured extensively in several minerals used in geochronology [1]. The usual method of quantification is isotope dilution, using a pure ^{3}He spike [3]. This is a good and accurate method and can be used to make absolute quantifications, but the delivery tank and pipette must be well calibrated. Moreover, the determination of the ^{3}He/^{4}He isotopic ratio suffers from the great mass discrimination, which is found in electron bombardment sources at such low masses. Nevertheless, well established laboratories are now using a modified isotope dilution method that uses both ^{4}He and ^{3}He. With this combined calibration the main problems cited above are reduced, specially the mass discrimination [4]. Accuracies and/or precisions of about 1–2% using isotope dilution for helium are reported [4,5].

We applied an alternative method, based on an empirical calibration with a known standard. This method proved to be reliable and simple. It is based on the measurement of the He released by fusion of several small fragments of the fluorapatite from Cerro de Mercado (Durango, Mexico). The ^{4}He peak height is plotted against the weight of each standard aliquot and a regression is made. The weight is converted to an absolute amount of He and the same regression is used for the unknowns. The accuracy of our method is about 5%, which is not as good as isotope dilution but nonetheless convenient due to its simplicity.

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2. Theory

The concentration of ^{4}He in any natural sample is related to four factors: (a) the initial ^{4}He that was acquired during mineral or rock formation; (b) the amount of radioactive elements that produce alpha particles (i.e. ^{4}He nucleus); (c) the time elapsed since mineral or rock formation and (d) the thermal history of the rock.

The initial concentration of ^{4}He can be measured in any mineral or rock that not has enough time to generate ^{4}He by radioactive decay or whose radiogenic helium contribution can be accounted for. This value can be used in conjunction with the ^{3}He/^{4}He isotopic ratio for geochemical studies [2]. The amount of radioactive nuclides is of fundamental importance because the He production is proportional to it. The most important producers are U and Th. U produces the greater number of alpha particles. The time elapsed since mineral formation is an important factor of influence, because radioactivity obeys an exponential law. Finally, the thermal history of the rock is also critical because diffusion of atoms is a thermally activated process that follows the Arrhenius law in minerals. Complete retention, partial retention or complete loss was all possible in different thermal scenarios [6].

The general production equation taking into account U and Th contributions and time is (in atoms):

$$\begin{aligned} {}^4\mathrm{He} = {} & 8\,{}^{238}\mathrm{U}(e^{\lambda_{238}t} - 1) + 7\,{}^{235}\mathrm{U}(e^{\lambda_{235}t} - 1) \\ & + 6\,{}^{232}\mathrm{Th}(e^{\lambda_{232}t} - 1) \end{aligned} \tag{1}$$

Decay constants for λ_{238}, λ_{235} and λ_{232} are 1.551×10^{-10}, 9.849×10^{-10} and $4.948 \times 10^{-11}\ \mathrm{yr}^{-1}$, respectively [5].

By transforming the number of ^{238}U and ^{232}Th atoms to μg/g and He to moles/g we obtain:

$$\begin{aligned} {}^4\mathrm{He} = {} & 0.0336\,{}^{238}\mathrm{U}(e^{\lambda_{238}t} - 1) \\ & + 0.0298({}^{238}\mathrm{U}/137.88)(e^{\lambda_{235}t} - 1) \\ & + 0.0258\,{}^{232}\mathrm{Th}(e^{\lambda_{232}t} - 1) \end{aligned} \tag{2}$$

This equation gives the He production if the age of the sample and U and Th concentrations are known. In a real geological case it is much more common to solve the equation for the age rather than the He, since the latter is measured analytically. In this case the equation must be solved by iteration or numerical approximation. In our experiments we need to determine the He concentration of the standard used, so Eq. (2) fits well if the right side variables are known.

3. Experimental

3.1. Standard selection

The selection of the standard is very important, because the final accuracy and precision of the method will be related to the homogeneity of the material used. We choose fluorapatite from Cerro de Mercado, Durango (Mexico). This mineral is available in beautiful transparent yellow crystals up to 2–3 cm long that are abundant and can be acquired easily from collectors. They are found in a volcanogenic iron deposit associated with volcanic rocks dated by K/Ar at 31.4 ± 0.5 (2σ) Ma [7], recalculated by Green [8] using Steiger and Jäger decay constants [9]. This is the maximum age of the fluorapatite. A recent measurement using a corrected fission track method with external calibration gives 29.7 ± 1.1 Ma [10], which is equivalent within error to the above age. In conclusion, and taking into account that a detailed petrogenetic study of the iron deposit has not been done yet, it is safe to assume an age of 31.4 ± 0.5 Ma for these fluorapatites.

3.2. Sample preparation

The fluorapatite crystals, chosen as large as possible so as to diminish He recoil losses, are first painted externally with ink and then broken up into small fragments of 100–1000 μm in diameter and sieved to the 200–400 μm fraction. The painted fragments, corresponding to the external parts of the crystal, are rejected (the outer part is the most affected by He diffusion or recoil). This procedure ensures a homogeneous sample, although occasionally a fragment is out of regression.

Fluorapatite fragments were weighed with a well-calibrated microgram balance and loaded in the holes of a 5 cm diameter copper plate. The samples weigh from ∼0.2 to ∼8 mg, and consist of one or two fluorapatite fragments. The copper plate is covered with a ZnSe window to avoid grain loss by thermal ejection and placed in a stainless steel UHV chamber with a CLEARTRAN® viewport.

3.3. He measurement

The vacuum chamber is evacuated with a turbomolecular pump. Final pressure of the extraction line after 4–5 days of pumping is $<4 \times 10^{-9}$ Torr. The samples were fused with a 50 W CO_2 laser with a 1–3 mm beam diameter. Apatites fuse very easily and homogeneously with the CO_2 laser. Evolved gases were cleaned with a cold finger, a charcoal trap with liquid N_2 and two solid state SAES® getters maintained at room temperature and at 400 °C. After 12 min of fusion and cleaning, He(+Ne) were equilibrated in a MM1200 noble gas mass spectrometer operated in static vacuum mode. In all measured fluorapatite samples Ne was negligible. The signal was acquired with both a Faraday collector and a secondary electron multiplier (Balzers® 218) operated in analogue mode, with variable gain in different experiments. Maximum sensitivity is $\sim 2 \times 10^{-17}$ moles of ^{4}He and procedural blanks are $\sim 6 \times 10^{-15}$ moles. From these data it is derived that the limit of detection (3σ) with our instrumentation is about 2×10^{-14} moles ($\sim 5 \times 10^{-10}$ cc STP).