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# Dating pyrite by radiogenic helium: new approach to determine the age of hydrothermal processes

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**Abstract.** In this study, the possibility of U-Th-He dating of pyrite is explained and then substantiated by isotope geochemistry. The first U-Th-He age obtained for 9 pyrite samples from the VMS type Uzelga deposit, Urals ( $377 \pm 8$  Ma; MSWD 1.2) is in good agreement with independent biostratigraphic age estimations (380-390 Ma). This leads to the conclusion that pyrite can be used as a U-Th-He mineral geochronometer. Based on the results of step-heating experiments and U-Th-He age estimations it is shown that chalcopyrite, bornite and pyrrhotite are unlikely to be used in geochronology. The relative ease of U-Th-He dating in comparison with other geochronological methods makes this approach interesting for further application.

## 1 Introduction

Historically, isotope systems using radiogenic helium were found to be unsuitable in terms of geochronology. Retention of this element in crystalline structures is too low for use as a geochronometer, but use as a thermochronometer is well known. However, recent studies have shown that containment of helium in metals is possible even over geological timescales. High retentivity of He was found in gold and native minerals of platinum (Shukolyukov et al. 2012). Afterwards high migration parameters of helium were observed in non-native mineral sperrylite,  $\text{PtAs}_2$  (Yakubovich et al. 2015). Sperrylite is chemically and crystallographically similar to some of the sulphides. Thus by analogous reasoning, we suggest that high migration parameters of helium can be expected in sulphides as well.

The purpose of this study is to test the possibility of U-Th-He dating of some of the sulphides including pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), pyrrhotite ( $\text{Fe}_n\text{S}_{n+1}$ ) and bornite ( $\text{Cu}_5\text{FeS}_4$ ) from a number of deposits in the Ural region of Russia.

The Gai, Uzelga, and Molodezhnoe deposits are classic, well-studied volcanogenic massive sulphide deposits (VMS), located in the South Urals (Magnitogorsk paleovolcanic arc). Gai is considered the world's largest VMS deposit. Formation of this mineralization is closely related to andesite-dacite-rhyolite Early-Middle Devonian submarine volcanism

and hydrothermal alteration of rocks (Herrington et al. 2005; Vikentyev et al. 2017).

## 2 Identifying the source of helium

We propose that the main sources of helium in the studied minerals are from inclusions of U-Th-containing minerals. There is evidence (Melekestseva et al. 2014) of U concentrations up to 11 ppm in sulphides of "black smokers" (which are the predecessors of modern VMS deposits). Nevertheless, the possibility of captured helium during crystallisation still remains. Helium concentrations found in chalcopyrite of modern "black smokers" are  $1.1 \times 10^{-10}$  –  $1.3 \times 10^{-8}$   $\text{cm}^3/\text{g}$  (Luders and Niedermann 2010). In our samples from the volcanogenic massive sulphide deposits, these concentrations are higher by orders of magnitude: up to  $1.22 \times 10^{-4}$   $\text{cm}^3/\text{g}$  in pyrite,  $3.65 \times 10^{-5}$   $\text{cm}^3/\text{g}$  in chalcopyrite and  $2.93 \times 10^{-4}$   $\text{cm}^3/\text{g}$  in pyrrhotite. This allows us to conclude that helium in the analyzed sulphides is mostly radiogenic and that trapped helium may be considered insignificant.

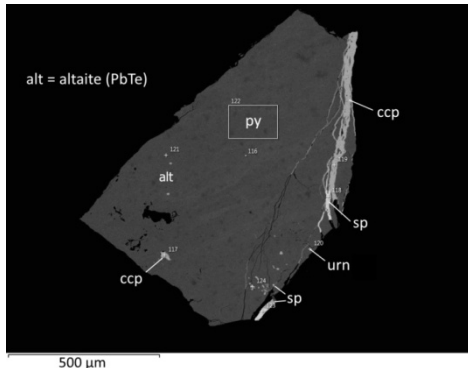
It should be noted that concentrations of helium may vary (sometimes 10 times or more) from sample to sample. This fact probably indicates unevenness of distribution of U and Th inclusions in mineral grains of the studied sulphides (cf., Ayupova et al. 2018). It can be used as an argument for submicron inclusions of radioactive minerals as the source of U and Th instead of isomorphic admixture in the crystalline structure.

Electron microprobe analysis made in the SPBU resource center "Geomodel" confirmed this hypothesis. We observed inclusions of uraninite and monazite in a number of grains, which record high helium concentrations (Fig. 1).

## 3 Methods

Experimental studies were performed in the isotope geology laboratory of IPGG RAS (St. Petersburg, Russia) with a MSU-G-01-M mass-spectrometer (made by CJSC "Spektron-Analit"). This instrument can detect  $^4\text{He}$  in quantities as small as  $2.3 \times 10^{-12}$   $\text{cm}^3$ . Helium

extraction is performed by electric heating of the sample in a rhenium cuvette up to 1400°C. Details of the helium measurement technique and the design of the instrument are described in Shukolyukov et al. (2012).



**Figure 1.** SEM image of a pyrite grain from Uzelga deposit. Py – pyrite, ccp – chalcopyrite, sp – sphalerite, urn – uraninite.

Analysis of each sample can be made by two different methods: a more precise destructive way, when we simply drop the mineral grain inside the cuvette; or non-destructively, when the grain is kept inside a vacuum-sealed quartz tube and placed into or out of the extractor using a tantalum cylinder. This second possibility allowed us to use the same grain we measured helium content in, to measure U and Th concentrations in, thus getting data necessary for U-Th-He isotope dating. Concentrations of radioactive isotopes were measured in dissolved grains by an isotope dilution method on an ICP-MS NexION 300D (Perkin Elmer) in IGS RAS and on an ELEMENT XR in IPGG RAS.

We also immersed samples in acids (HCl for pyrite and chalcopyrite, H<sub>2</sub>SO<sub>4</sub> for pyrrhotite) for 24–48 hours to get rid of superficial impurities that might affect helium extraction. However, samples measured after acid etching showed no difference in extraction kinetics, compared to regular ones.

#### 4 Identifying migration parameters

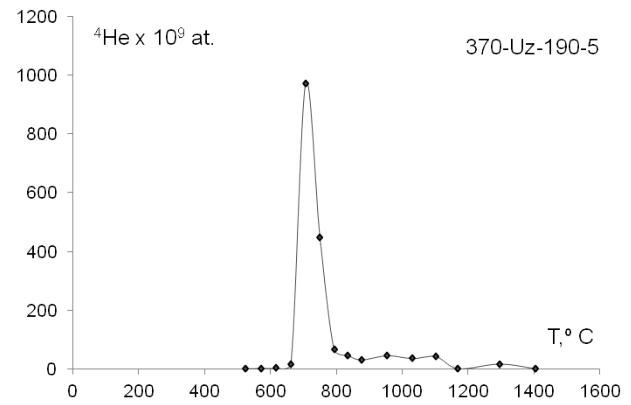
Migration parameters of different minerals were determined by destructive step-heating of samples (each step lasting 2–6 minutes, up to 20 stages from 440°C to 1400°C). During the experiments, we acquired quantities of helium, extracted at each stage. Using this data, we produce kinetics graphs (Fig. 2 and 4), allowing us to characterize extraction, and compose Arrhenius plots (Fig. 3 and 5). Activation energy [kcal/mol] then was determined by the slope of the line; while the y-intercept corresponds to the natural the frequency factor  $k_0$  [s<sup>-1</sup>] as described in Yakubovich et al. (2019).

For most minerals the desorption kinetics remained rather simple (Fig. 2), single-staged; pyrrhotite shows complex two-staged desorption with peaks at ≈900°C and ≈1300°C (Fig. 4).

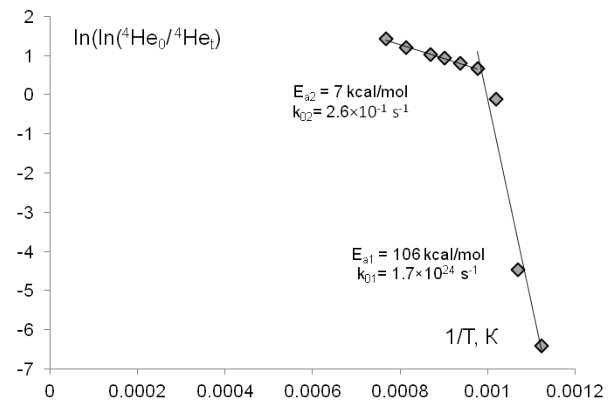
In spite of the inclusions in some of the pyrite samples, none of them have shown multi-staged helium desorption. Considering average track depth of the α-

particles as 10 μm (SRIM; Ziegler et al. 2010) and size of such inclusions (1–5 μm), this can be evidence of the prior implantation of <sup>4</sup>He from radioactive minerals (monazite, zircon) into the sulphide matrix and its subsequent extraction from a single mineral, rather than from all of them in a grain, providing different migration parameters.

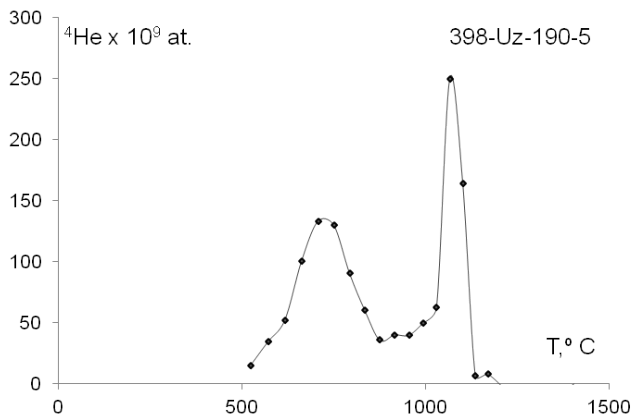
Summarizing the results of conducted step-heating experiments (Yakubovich et al. 2019), we can see greatest potential for usage of pyrite for rock ages determination, as it showed the highest activation energies (>80 kcal/mol). Chalcopyrite and bornite may have some possibilities to be used as geothermochronometers, as their  $E_a$  looks comparable to apatite (20–40 kcal/mol). Complex release of He from pyrrhotite makes it unlikely to be used in geochronology.



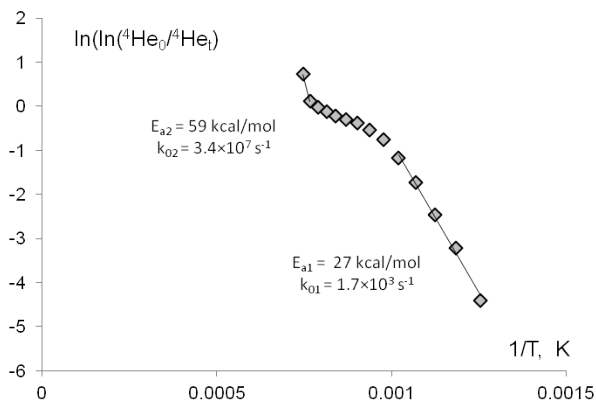
**Figure 2.** The character of helium migration kinetics from pyrite of the Uzelga deposit. Representative example.



**Figure 3.** Arrhenius plot, acquired from the same pyrite sample (Fig. 2) of the Uzelga deposit.  $E_a$  – activation energy,  $k_0$  – frequency factor.



**Figure 4.** The character of helium migration kinetics from pyrrhotite of the Uzelga deposit. Representative example.



**Figure 5.** Arrhenius plot, acquired from the same pyrrhotite sample of the Uzelga deposit (Fig. 4)  $E_a$  – activation energy,  $k_0$  – frequency factor.

## 5 U-Th-He dating attempts

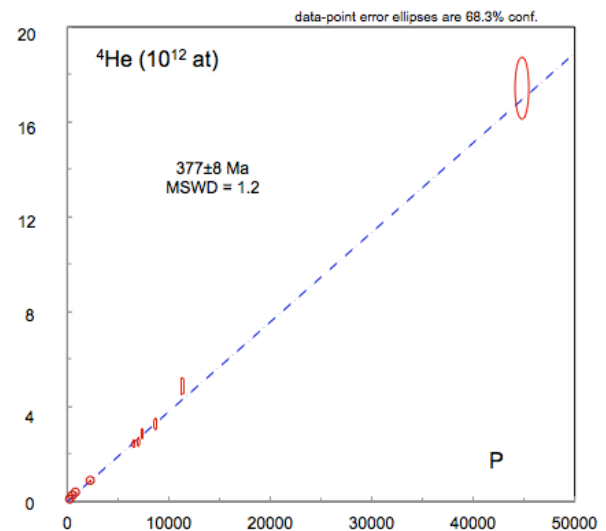
To test the possibility of U-Th-He dating of pyrite we conducted measurements of U, Th and He in  $FeS_2$  grains from the Uzelga deposit with conodont-based age of mineralization (380-390 Ma; Artyushkova and Maslov 2008; Chernyshev et al. 2008). Also we determined U-Th-He ages of pyrrhotite and chalcopyrite from the Uzelga and Gai deposits.

As presented in Table 1, all pyrite measurements except sample 437 lie within the expected Devonian age of the Uzelga deposit within the 2-sigma error range. Six of the studied grains lie within the expected age within 1-sigma age error. Sample 437 has the lowest concentration of  $^4He$  ( $6.6 \times 10^{-6} \text{ cm}^3/\text{g}$ ). Thus it might be some influence of trapped or implanted  $^4He$  that led to the increase of the age. Overdispersion for a number of grains may be due to the relative long alpha-stopping distances that may affect the U-Th-He ages especially in case of the inhomogeneous distribution of parent nuclides (Farley et al. 1996; Vermeesch 2010). The obtained data was used to build an U-Th-He isochron (Fig. 6). Calculated by the slope “average” U-Th-He age is  $377 \pm 8 \text{ Ma}$  (MSWD 1.2) is in a good agreement with existing geochronological data (380-390 Ma).

**Table 1.** U-Th-He ages of pyrite, chalcopyrite and pyrrhotite from the Uzelga and Gai deposits (calculated in HeliPlot software;

Vermeesch 2010); pooled – combined multi-grain estimation as if several grains were measured together as one sample (method proposed by Vermeesch 2008). All data are blank corrected. All uncertainties are in 1-sigma range.

#	Weight, mg	$^4He$ , ncc	$\sigma$	U, ng	$\sigma$	Th, ng	$\sigma$	Age, Ma	$\pm$
Pyrite of Uzelga deposit									
599	0,841	91,2	0,5	2,018	0,02	b.d.l.	–	356	19
600	0,347	13,1	0,2	0,273	0,003	b.d.l.	–	382	20
601	0,807	121,9	0,5	2,69	0,027	b.d.l.	–	367	19
602	0,486	93,9	0,5	2,173	0,022	b.d.l.	–	345	18
603	0,282	31,6	0,3	0,703	0,007	b.d.l.	–	362	19
604	0,692	106,5	0,5	2,28	0,023	b.d.l.	–	379	19
433	~ 1	181	1,2	3,50	0,04	0,05	0,001	415	21
435	~ 1	7,4	0,1	0,150	0,001	0,04	0,0004	375	19
437	0,6	3,7	0,0	0,060	0,001	0,02	0,0002	464	24
Pooled sample		651	4	13,8	0,14	0,106	0,001	376	19
Pyrrhotite of Uzelga deposit									
383	~ 1	13,4	0,7	13,9	0,14	19,3	0,19	6	1
396	~ 1	5,4	0,3	0,642	0,006	0,281	0,003	61	3
Chalcopyrite of Gai deposit									
436	~ 1	1,4	0,1	0,196	0,002	3,63	0,04	11	1
408	~ 1	27,2	1,4	3,14	0,03	b.d.l.	–	72	4
380	~ 1	10,8	0,5	2,15	0,022	0,49	0,01	39	2
384	~ 1	8,2	0,4	0,120	0,001	0,212	0,002	388	20
blank									
Qu	–	1,3	0,1	0,004	0,001	0,002	0,001	–	–



**Figure 6.** U-Th-He isochron for pyrite from Uzelga deposit calculated via method described in Vermeesch (2008) (constructed in Isoplot software; Ludwig 1999).

The data confirms the results of step-heating experiments and predicts that pyrite may be used as a

geochronometer.

Pyrrhotite samples showed systematically younger ages that indicates loss of radiogenic helium during their geological history. Younger ages are also common for chalcopyrite. Only one of four studied grains from the Gai deposit gave an Devonian age closely corresponding to the biostratigraphic age of the deposit. This agrees with results of step-heating experiments that predicted relatively low retention of helium in these sulphides. Thus it is unlikely that pyrrhotite or chalcopyrite may be used as geochronometers.

## 6 Conclusion

The results of step-heating experiments show the possibility of U-Th-He dating of pyrite. The first U-Th-He ages obtained for pyrite samples from Uzelga deposit (377±8 Ma) are in a good agreement with independent biostratigraphic age estimations (380-390 Ma). This leads to the conclusion that pyrite can be used as a U-Th-He mineral geochronometer. The relative ease of U-Th-He dating in comparison with other geochronological methods makes this approach interesting for further application.

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