## Reg. No: 2020/37/B/ST10/01697; Principal Investigator: dr hab. in . Marek Stanisław Szczerba

The isotopic dating of rock samples provides information on the age of a given rock, and thus enables the identification of its location in Earth's history. One of many methods of isotopic dating is potassium-argon (K-Ar) dating. This method is based on the radioactive decay of the potassium-40 isotope to the argon-40:  ${}^{40}$ K  $\rightarrow$   ${}^{40}$ Ar. If the mineral contains potassium, then with increasing age,  ${}^{40}$ Ar accumulates in its structure. Therefore, by testing the ratio of  ${}^{40}$ Ar to  ${}^{40}$ K, it is possible to determine the age of a given mineral (to an accuracy of about 1-2%). This calculation assumes that  ${}^{40}$ Ar has not escaped from the mineral structure during geologic time. There is agreement in the scientific community that, for minerals with large crystals and below a certain temperature,  ${}^{40}$ Ar remains trapped inside the mineral structure. However, in the case of clay minerals (less than 2 micrometers in size), many researchers suggested that  ${}^{40}$ Ar can escape from their structure by a diffusion mechanism.

Clay minerals are invisible under optical microscopes. They are recognizable only under the best electron microscopes. Because of their small size, K-Ar dating is not used for studying single crystals, but material consisting of billions of crystals. Such material can have various origins: it can be brought by rivers to the place of rock formation, as well as, formed inside the rock after it has been slightly heated (approx. 75-150 °C). Determination of the age of clay minerals, despite many complications in determining their origin is, however, very important: the temperature range of their formation in the rock corresponds to that in which oil is formed in the rocks. Therefore, their dating enables the age of oil production to be indirectly determined.

The aim of the project is to introduce a new method for determining the origin of clay minerals in the rock, based on the study of oxygen and hydrogen isotopes, and to verify two very important problems related to the dating of K-Ar clay minerals.

The first problem results from the fact that after the  ${}^{40}$ K  $\rightarrow {}^{40}$ Ar transformation, the newly formed argon-40 atom gains a speed of about 11.8 km/s. Computer simulations have shown that for such small minerals as clay minerals, a certain percentage of  ${}^{40}$ Ar can escape from the structure into the surrounding micropores. This results in a decrease of the measured age compared to the actual age of these minerals. Experimental verification of this fact has never been confirmed and is the first goal of this project.

The second goal results from the observation that, as a result of heating of clay minerals in laboratory experiments, <sup>40</sup>Ar escapes from the structure simultaneously with water molecules formed from the merging of two structural OH groups:

 $OH + OH \rightarrow H_2O\uparrow + O_{in mineral structure}$ 

It has not been studied how precisely <sup>40</sup>Ar loss correlates with water loss, and whether <sup>40</sup>Ar cannot escape sufficiently due to diffusion. Addressing this problem will allow the two processes to be separated accurately. This is important because the models defining the "closure temperature", i.e. the temperature below which <sup>40</sup>Ar can no longer escape from the mineral structure, may be incorrect for micaceous minerals. Until now <sup>40</sup>Ar escape, which correlates with water escape (observed in laboratory experiments) have been used in the "closing temperature" calculations. <sup>40</sup>Ar escape as a result of diffusion is more difficult to be observed in the laboratory due to the overlap with the first process, but it is more likely to occur in the nature.

The above studies will be supported by isotopic methods that will facilitate verification of whether the minerals in the sample are of homogenous origin. The fractions of clay minerals separated from rocks (e.g. 0.02-0.05, 0.05-0.2 or 0.2-2 micrometers) may contain minerals from various sources, i.e. of different ages. This would not enable the investigation of the processes described above, and would return the incorrect age, depending on the size of the separated fraction. The verification of homogeneity will consist of testing the isotopic ratios of hydrogen and oxygen in water released from minerals, as a result of gradual heating. The lack of variability of isotope ratios at different temperatures will indicate the homogeneous origin of the studied minerals.

Project results will produce a better understanding of the K-Ar dating of clay minerals. A significant step is the introduction of a method for recognizing the diverse origin of clay minerals by isotopic methods, which until now, were carried out by other methods (e.g. X-ray diffraction), and often were not included in the dating of these ultra-fine minerals.