ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA
VOL. LXIX SECTIO AAA 2014

CRYOGENIC SEPARATION OF GLAUCONITE AND FORAMINIFERA FROM THE CRETACEOUS/PALEOGENE BOUNDARY INTERVAL AT NASIŁÓW, POLAND, FOR RADIOMETRIC DATING AND STRATIGRAPHY

Artur Wójtowicz[1*], Tomasz Pieńkos[1], Stanisław Hałas[1], Danuta Peryt[2]
Tomasz Durakiewicz[3], Agnieszka Młynek[4]

[1] Mass Spectrometry Laboratory, Institute of Physics, UMCS, 20-031 Lublin, Poland
[2] Institute of Paleobiology, Polish Academy of Sciences, 00-818 Warsaw, Poland
[3] Los Alamos National Laboratory, Condensed Matter and Thermal Physics
Los Alamos, NM 87545, USA
[4] Chair and Department of Biophysics, Medical University of Lublin
20-074 Lublin, Poland
[*]Corresponding author. E-mail address: artur.wojtowicz@umcs.pl

ABSTRACT

We have demonstrated that cryogenic separation of glauconite and foraminifera from the host rock allows to preserve the integrity of extracted specimens, assures minimal damage and causes no artificial fractionation. The K/Ar dating of two glauconite samples from Cretaceous/Paleogene boundary in the Nasiłów outcrop yields 62.0 and 66.3 Ma. The discrepancy in these dates, much larger than expected from analytical precision, may result from too low %K, which was 5.91 and 5.73, respectively.

Keywords: foraminifera, glauconite, cryogenic separation, K-Ar dating

1. INTRODUCTION

Mineral or specimen separation from the host rock is a crucial part of the sample preparation process. Commonly used methods include acid etching and/or dissolution, mechanical grinding and subsequent use of heavy liquids as well as magnetic separation. Successful separation must be performed in a way ensuring:

(i) mechanical integrity of separated specimens,

(ii) lack of contamination,

(iii) minimal chemical damage,

(iv) lack of weight or size-derived fractionation of the separate.

By "mechanical integrity" one would understand lack of cracks, breaks and fractures either on the surface or penetrating through the bulk of separated specimens. Such mechanical damage is common, e.g. in calcite crystals separated by grinding the host rock. Also, a grain should be well-separated in a sense of not being contaminated by other minerals. Chemical damage occurs when acids are used to dissolve the host rock, e.g. in the case of specimen extraction from limestone. Weight or size–derived fractionation becomes a serious problem when a given fraction of the separate, e.g. the smallest grains or the largest shells, are more damaged than other fractions of the separate, or even destroyed in the process.

Cryogenic separation is a method that meets all the above requirements. Series of freezing-thawing cycles, with each cycle lasting only tens of minutes, allows water to penetrate the grain boundaries even in rocks as hard as granite. Below $4^{o}C$ water expands, and subsequently becomes ice below $0^{o}C$. Ice crystals continue to expand when temperature drops, therefore increasing the distance between grains. The convenient desktop apparatus of our construction was described in [1], including schematic diagrams. It should be noted, that our design is based on the use of Peltier effect, contains no movable parts and it is environmentally friendly.

For testing purposes we have chosen a well-known Cretaceous/Paleogene boundary section at Nasiłów. Up to 0.5 m thick layer of glauconitic sandstone is deposited directly on the uppermost Maastrichtian hard limestone (see Fig. 1). Description of the profile and our previous stable isotope and radiogenic dating results were published before in [2]. In Fig. 2 a concentrate of glauconite grains is presented. Figures 3 and 4 show examples of foraminifera. Both glauconites and foraminifera were separated from the host rock (sandstone) by the use of approximately 48 hours of repetitive freezing-thawing cycles in our cryogenic separation apparatus.

FIG. 1. The Cretaceous/Paleogene boundary profile in the Nasiłów quarry. Glauconitic sandstone overlies an intensively burrowed hard limestone terminating the uppermost Maastrichtian siliceous limestone.

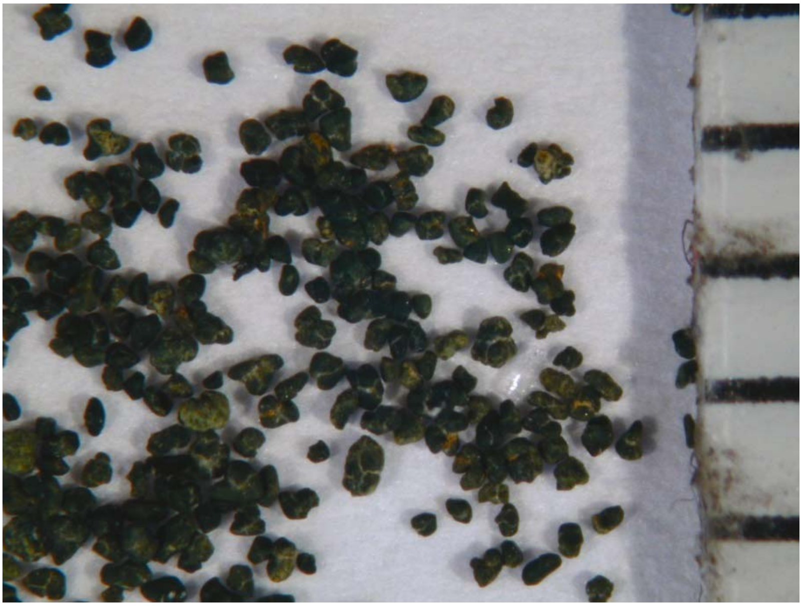

FIG. 2. Cryogenic separate of glauconites from the Nasiłów quarry, 1mm scale on the right.

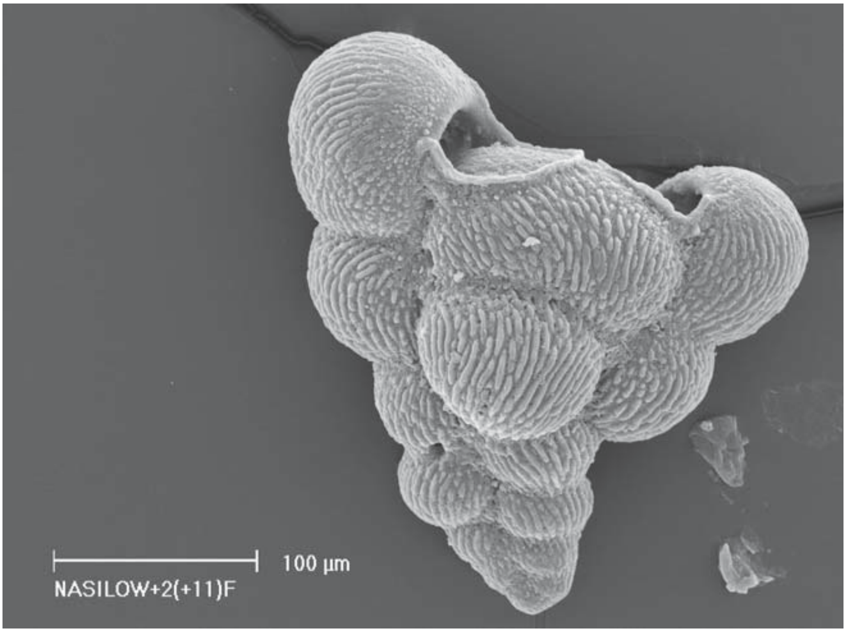

FIG. 3. *Planoglobulina carseyae* (Plummer).

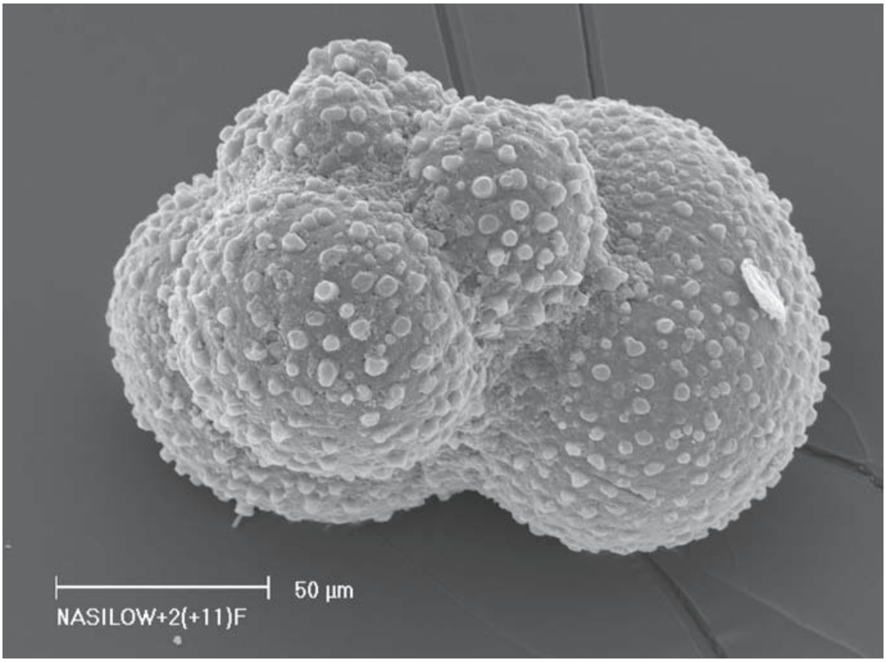

FIG. 4. *Globoconusa daubjergensis* (Brönnimann).

2. RESULTS AND DISCUSSION

As it can be seen in Fig. 2, glauconite grains are very well separated, without traces of etching or contamination. Results of potassium content determination are given in Table 1, whereas the K/Ar dating results are presented in Table 2. Sample D was taken from a burrow filled with glauconitic sandstone located 5 cm below the hardground, whereas sample F was taken from the glauconitic sandstone 11 cm above the Maastrichtian hard limestone surface. Cautious reader will immediately note that age in Table 2 is apparently reversed: sample D appears to be younger than sample F.

This result is not surprising if one considers the complex sedimentological history of the K/P boundary at Nasiłów as well as the geochemistry of glauconite.

Faunal condensation and mixing of Danian and Maastrichtian fossils in the glaucontic sandstone, overlying the Maastrichtian hard limestone, are interpreted as being the result of the erosion of part of the section including the uppermost Maastrichtian and lowermost Danian (e.g. [3-6]). The unit itself has been included either in Maastrichtian (e.g. [7], [8]) or in Danian (e.g. [3], [6], [9], [10]). During the deposition of the glauconitic sands the topmost surface of the Maastrichtian rock has been intensively burrowed and filled with that sediment.

Existence of multiple burrows penetrating the glauconitic sandstone and the Maastrichtian chalk, together with possible multiple bioturbation in the fresh sediment, where the reworked Maastrichtian material was also present, points to a vertical mixing as one possible source of age reversal in K/Ar dating. Another, perhaps even more convincing explanation comes from the geochemical point of view. Glauconite is a complex geochemical system, which attains maturity over an extended period of burial time. Mature glauconite is closed to isotope exchange with its environment. One of the geochemical signatures of mature glauconite is the potassium content [11].

For low potassium contents, the radiometric age of glauconite is artificially increased. As it was shown before [2] glauconite from the Nasiłów section may be considered mature at potassium contents larger than 6.3%. Samples analyzed here revealed potassium content below 6% and therefore are located on the slope of maturity curve. Entire 4.3 Ma age difference between our samples may therefore be considered as artificial.

At the present stage of investigation, the conclusion is, that the 62Ma is an approximate age of the oldest Paleocene sediments in this profile. More detailed study, involving stable isotopes and grain size separates is needed in order to finally resolve the Nasiłów puzzle.

Table 1. Results of potassium content determination of two samples of glauconite.

Sample	Total weight [mg]	Analysed weight [mg]		$\left(\frac{^{39}K}{^{41}K}\right)_{mix}$	% K	Average % K	Relative standard error [%]
		sample	spike				
Nasiłów D	94.78	4.20	4131.02	2.57	5.97	5.91	0.34
				2.53	5.86		
				2.47	5.70		
				2.58	6.01		
				2.50	5.79		
				2.55	5.92		
				2.57	5.98		
				2.54	5.90		
				2.59	6.04		
Nasiłów F	71.47	4.91	5587.17	2.21	5.75	5.73	0.35
				2.23	5.84		
				2.21	5.75		
				2.25	5.89		
				2.18	5.67		
				2.18	5.67		
				2.19	5.69		
				2.17	5.59		

TABLE 2. Results of the radiometric dating of glauconite samples.

Sample:	Nasiłów D	Nasiłów F
Weight [mg]	48.55	47.41
Potassium content [%]	5.91	5.73
^{38}Ar dose [pmol]	71.21	71.21
^{40}Ar/^{38}Ar ratio	0.5666	0.5602
^{40}Ar/^{36}Ar ratio	1330	1457
Radiogenic ^{40}Ar [pmol/g]	646.5	670.9
% of radiogenic Ar	77.8	79.7
Radiometric age [Ma]	62.0	66.3

Cryogenic method used in extracting foraminifers from the glauconitic sandstone works as well as for glauconites. Obtained from that rock minute, thin-shelled and fragile Danian (and Maastrichtian) planktonic foraminifera are clean and very well preserved (see Figs 3 and 4). Planktonic foraminifera are the minor component of the foraminiferal assemblage. Danian species are represented by *Globoconusa daubjergensis* (Brönnimann), *Parasubbotina pseudobulloides* (Plummer), *Globanomalina* sp., *Chiloguembelina* sp., *Globotruncanella caravacaensis* (Smit).

3. CONCLUSIONS

In this study we have demonstrated that cryogenic separation of glauconite and foraminifera from the host rock is a simple and convenient method. Use of cryogenic separation allows to preserve the integrity of extracted sample, assures minimal damage and no artificial fractionation. Its applicability was shown in the previously published paper [1] also for the granite-forming minerals and other host rocks like tufas.

REFERENCES

1. Nowak J., Durakiewicz T., Hałas, S. (2002) *Separation of single-mineral grains by means of cryogenic disintegrator and the LST heavy liquid for radiometric dating*, Materials of the "6th Session on Dating of Minerals and Rocks", Warsaw, Poland, 2002, 40-47.
2. Durakiewicz T., Wójtowicz A., Banaś M., Kalicka L., (1997) *Isotopic composition of oxygen in Tertiary glauconites dated by K/Ar method*, Materials of the "4th Session on Dating of Minerals and Rocks", 11-12 December 1997, Lublin, 27-40.
3. Pożaryska K. (1965) *Foraminifera and biostratigraphy of the Danian and Montian in Poland*, Palaeontologia Polonica **14**, 1-156.
4. Machalski M., Walaszczyk I. (1987) *Faunal condensation and mixing in the uppermost Maastrichtian/Danian Greensand (Middle Vistula Valley, Central Poland)*, Acta Geologica Polonica **37**, 1-2, 75-91.
5. Hansen H.J., Rasmussen K.L., Gwóźdź, R., Hansen, J.M., Radwański, A. (1989) *The Cretaceous/Tertiary boundary in Central Poland*, Acta Geologica Polonica **39**, 1-4, 1-12.
6. Machalski M. (1998) *Granica kreda-trzeciorzęd w przełomie Wisły*, Przegl. Geol. **46**, 11, 1153-1161.
7. Pożaryski W. (1938) *Stratygrafia senonu w przełomie Wisły między Rachowem i Puławami. Senonstratigraphie im Durchbruch der Weichsel zwischen Rachów und Puławy in Mittelpolen*, Bull. Geol. Surv. Poland **6**, 1-94.
8. Abdel-Gawad G. I. (1986) *Maastrichtian non-cephalopod mollusks* (*Scaphopoda, Gastropoda and Bivalvia*) *of the Middle Vistula Valley*, *Central Poland*, Acta Geologica Polonica **36**, 1-3, 69-224.
9. Peryt D. (1988) *Maastrichtian extinctions of planktonic Foraminifera in Central and Eastern Poland*, Revista Española de Paleontologia **3**, 105-114.
10. Żarski M., Jakubowski G., Gawor-Biedowa E. (1998) *The first Polish find of a Lower Paleocene crocodile Thoracosaurus Leidy, 1852: geological and palaeontological description*, Geological Quarterly **42**, 2, 121-130.
11. Odin G.S., Dodson M.M., *Zero isotopic age of glauconites*, in: G.S. Odin (ed.), *Numerical Dating in Stratigraphy*, Wiley (1982) 277-305.