A test of reproducibility of authigenic beryllium extraction from clay sediment in the facility of the Dept. of Geology and Palaeontology, Comenius University in Bratislava (Slovakia)

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Abstract: The purpose of the study was to investigate, whether the newly developed laboratory at the Dept. of Geology and Palaeontology (Comenius University in Bratislava, Slovakia) is suitable for processing of samples for authigenic $^{10}Be/^9Be$ dating method. The approach was validated on reprocessing of four samples, which were previously analysed at CEREGE (Aix-en-Provence, France). The samples underwent leaching and resin chemistry. Each sample was triplicated with the preparation of a blank sample. Processed samples were sent to CEREGE for isotopic measurements, which provided 15 values of $^{10}Be/^9Be$ ratio. The obtained values showed a good consistency for each sample, although two subsamples appeared as outliers (one of which was original). Analytical uncertainties are comparable to the original measurements, difference is below 1.5 %. Processing blanks yielded stable values at least three orders of magnitude lower than measured subsample $^{10}Be/^9Be$ ratios, what imply a good workflow conditions. These tests revealed that the new laboratory is suitable for processing samples for authigenic $^{10}Be/^9Be$ dating method.

Key words: authigenic $^{10}Be/^9Be$, cosmogenic nuclide, chemical treatment test, reproducibility evaluation, radiometric dating

1. INTRODUCTION

The authigenic $^{10}Be/^9Be$ dating method provides a strong geochronological tool for the late Cenozoic deposits, with possibility to date the event of sedimentation of clay particles (Bourlés et al., 1989; Lebatard et al., 2008; Šujan et al., 2016). The age calculation is based on the difference of sample $^{10}Be/^9Be$ ratio from initial isotopic ratio, which appeared during deposition. The initial ratio is used as a starting point, from which $^{10}Be/^9Be$ decreases with the half-life of ^{10}Be (1.387 ± 0.012 Ma; Chmeleff et al., 2010; Korschinek et al., 2010), providing a chemically closed system. The ratio is formed during adsorption of beryllium to surface of clay particles in a water column. The source of both isotopes differs, ^{10}Be being formed in the atmosphere by interaction of nitrogen with cosmic rays, while ^9Be is derived from chemical weathering of rock massifs in a drainage basin.

The high potential of the dating method is related to possibility of timing the deposition of continental sequences, which commonly lack biostratigraphically significant fossils or contain highly endemic fauna. The Carpathian-Pannonian area is a region with dominance of such a deposition in the late Miocene to Quaternary period (e.g., Magyar et al., 2013; Kováč et al., 2017). Due to this, a laboratory focused on processing of authigenic $^{10}Be/^9Be$ samples was developed at the Dept. of Geology and Palaeontology (Comenius University in Bratislava, Slovakia), to satisfy the need of the geochronological tool in question.

This contribution is focused on verification of the quality of sample processing in the new laboratory. It is based on reprocessing of samples, previously analysed in laboratory at CEREGE (Aix-en-Provence, France), together with processing blanks. The resulting isotopic ratios should demonstrate the reproducibility and effectivity of the laboratory workflow.

2. METHODOLOGY

Four samples (A–D) were selected from the study of Šujan et al. (2016), with $^{10}Be/^9Be$ ratio varying from 6.255 ± 0.212 × 10^{-11} to 6.89 ± 0.12 × 10^{-09}. The samples originate from boreholes and outcrops, with calculated ages 10.60 ± 0.66 Ma (A, originally W-Rip-3), 9.36 ± 0.40 Ma (C, resp. W-Bal-1), 5.80 ± 0.31 Ma (B, resp. W-Di-3) and recent or Holocene, respectively (D, resp. R14). The purpose of a wide range of used isotopic ratios is to identify possible cross-contamination. Batches of four samples A–D plus one processing blank underwent preparation in three runs, using 1.5 g of powdered clay in each.

The authigenic phase was leached from a powdered sample according to Bourlés et al. (1989) and Carcaillet et al. (2004). The original procedure comprises leaching machine with sand bath heating in individual bins and magnetic stirring. In the presented concept, a hot plate with magnetic stirring was used (model Nahita^{TM} blue 692/1), because of much lower costs of the equipment

(Fig. 1). The stable temperature of leaching was provided by a sand bath in a glass crystallization bowl. A built-in probe thermometer was used to establish a stable temperature, which was checked by a second probe thermometer. The leaching temperature varied between 85°C and 95°C due to the equipment properties, what corresponded to ca. 335°C of the hotplate temperature. The room temperature was stable during the experiment, attaining ~20°C. The target temperature was reached after ~105 min of preheating, what was the reason for decrease of the leaching duration to six hours comparing to seven hours within the original procedure (Bourlés et al., 1989). The purpose of changing the leaching duration was to prevent contamination of the authigenic phase by extraction of beryllium from the mineral lattice of clay particles. The suitable temperature of the hotplate was settled after a set of initial experiments, comprising observation of the temperature of the solution in tubes and its variability. Position of build-in and independent probe thermometers was alternated during the initial experiments, showing stable temperature in the central part of the crystallisation bowl (90 ± 5°C), where were then located samples during the extraction experiments. The leaching temperature of the solution was slightly decreased comparing to the original experiment (95 ± 5°C; Bourlés et al., 1989) with aim to prevent

boiling of the solution and loss of a sample, considering variability of the temperature observed during initial experiments. The stirring speed was set on 300 rpm. One litre of the leaching solution comprised demineralised water (740 ml), acetic acid (260 ml; 96 % concentration) and hydroxilamonium hydrochloride (2.78 g). All samples underwent leaching in the same temperature and stirring conditions, with the same duration of the process.

The tubes with samples were centrifuged immediately after the leaching and the solution was transferred to bottles and weighted. An aliquot of 2 ml for AAS measurement was taken and 300 mg of beryllium carrier was added – the Scharlau standard 1000 mg.L^{-1} for ICP. The ^{10}Be/^{9}Be ratio of this specific standard solution was measured at AMS ASTER (CEREGE) with resulting value of 7.80×10^{-15}. The anion and cation exchange using Dowex 1x8 and 50wx8 resins was then applied (Merchel et al., 1999), to separate the beryllium from authigenic phase from iron, magnesium, boron and aluminium. Resulting samples were transferred to crucibles in few drops of nitric acid and oxidised to BeO in an oven. Finally, the crucibles were sent to the CEREGE laboratory (Aix-en-Provence, France) together with the tubes containing aliquot for ^{9}Be measurements using AAS. The samples represented by beryllium powder were mixed with niobium and put into cathodes for measurements by the 5 MV ASTER AMS facility.

3. RESULTS AND DISCUSSION

Table 1 summarises the measured isotopic concentrations and ^{10}Be/^{9}Be ratios. To compare the different ^{10}Be/^{9}Be ratios, the method proposed by Ward & Wilson (1978) was applied. This method is based on chi-square (χ^2) analysis. To compare n values, the 0.05 critical value for a chi-square with (n-1) degrees of freedom is calculated and compared with the theoretical value given by chi-square table. If the calculated value is lower than the theoretical one, then all ^{10}Be/^{9}Be ratios are statistically reproducible and could be used to calculate mean ^{10}Be/^{9}Be ratios; otherwise outliers are rejected until the distribution passes the test. In our case, the 3 values will be comparable if the deduced χ^2 value is lower than the theoretical one of 5.99 for n=3 (see Table 1).

As could be seen on Fig. 2, the subsample B3 reveals an outlier value, differing significantly from the original and two latter subsamples. This subsample was excluded also using χ^2 test. Another value deviating from remaining subsamples represent D-orig, what implies that our newly gained results provide a reliable value more likely. The remaining data indicate a good replicability of authigenic phase extraction, confirmed by the results of χ^2 test.

The outlier values might represent a result of sample inhomogeneity, although each sample consisted of well mixed several tens of grams of crushed clays. As could be seen from the gained results (Fig. 2), processing several subsamples can provide an efficient tool to overcome the possible effect of sample inhomogeneity.

Absolute values of isotopic concentrations are relatively stable and consistent with original values. Percentual

Fig. 1. Experimental setup of leaching of the authigenic phase from powdered clay sediment. Each sample tube contains 1.5 g of powdered sediment, 30 ml of leaching solution and a stirring magnet.

Tab. 1. Isotopic concentrations of ^{9}Be and ^{10}Be (at.g^{-1}) and their ratios extracted from the authigenic phase of original samples (orig) from Šujan et al. (2016) and of their replicates (1–3) processed in this study. * – ^{10}Be/^{9}Be ratio in the case of processing blanks is not natural but includes 300 mg of beryllium standard carrier. The χ^2 test compares the three values measured for each sample to the theoretical one of 5.99 for 3 samples. If the χ^2 test is lower than the three samples are statistically comparable. Weighted average values are shown with standard deviations.

ID	Original ID	Genesis	^{9}Be (at.g^{-1}) × 10^{16}	^{10}Be (at.g^{-1}) × 10^5	Natural ^{10}Be/^{9}Be × 10^{-9}	^{10}Be/^{9}Be uncertainty (σ_1 in %)	Weighted average	χ^2 for n=3
A-orig		floodplain	6.31 ± 0.12	11.56 ± 0.48	1.833 ± 0.085	4.64		n
A1	W-Rip-3	floodplain	5.86 ± 0.09	11.15 ± 0.63	1.973 ± 0.115	5.74	1.970 ± 0.067	0.87
A2		floodplain	4.98 ± 0.08	9.88 ± 0.58	2.058 ± 0.126	6.14		
A3		floodplain	5.58 ± 0.08	10.24 ± 0.57	1.902 ± 0.109	5.74		
B-orig		floodplain	5.14 ± 0.05	115.6 ± 3.61	22.512 ± 0.734	3.26		n
B1	W-Di-3	floodplain	5.84 ± 0.03	122.16 ± 4.65	21.671 ± 0.834	3.85		
B2		floodplain	4.67 ± 0.07	96.77 ± 3.57	21.494 ± 0.863	4.1	22.423 ± 0.539	10.17 (B3 outlier)
B3		floodplain	5.15 ± 0.15	128.94 ± 4.8	25.943 ± 1.23	4.74		
C-orig		lacustrine	6.19 ± 0.07	38.7 ± 1.23	6.255 ± 0.212	3.39		n
C1	W-Bal-1	lacustrine	6.32 ± 0.05	36.42 ± 1.53	5.97 ± 0.255	4.27		
C2		lacustrine	6.35 ± 0.01	38.9 ± 1.70	6.329 ± 0.277	4.37	6.269 ± 0.154	2.49
C3		lacustrine	6.13 ± 0.09	38.68 ± 1.50	6.548 ± 0.27	4.12		
D-orig		lacustrine	2.24 ± 0.02	1542.54 ± 24.23	689.120 ± 12.006	1.74		n
D1	R14	lacustrine	3.13 ± 0.02	1537.59 ± 46.41	508.578 ± 15.768	3.10		
D2		lacustrine	3.07 ± 0.02	1525.62 ± 38.50	514.737 ± 13.381	2.60	524.092 ± 8.519	4.61
D3		lacustrine	2.91 ± 0.02	1548.67 ± 41.52	551.576 ± 15.483	2.80		
Blank 1	n	n	n	n	0.00105 ± 0.00030*	28.96		n
Blank 2	n	n	n	n	0.00099 ± 0.00017*	17.56		
Blank 3	n	n	n	n	0.00106 ± 0.00024*	22.31		

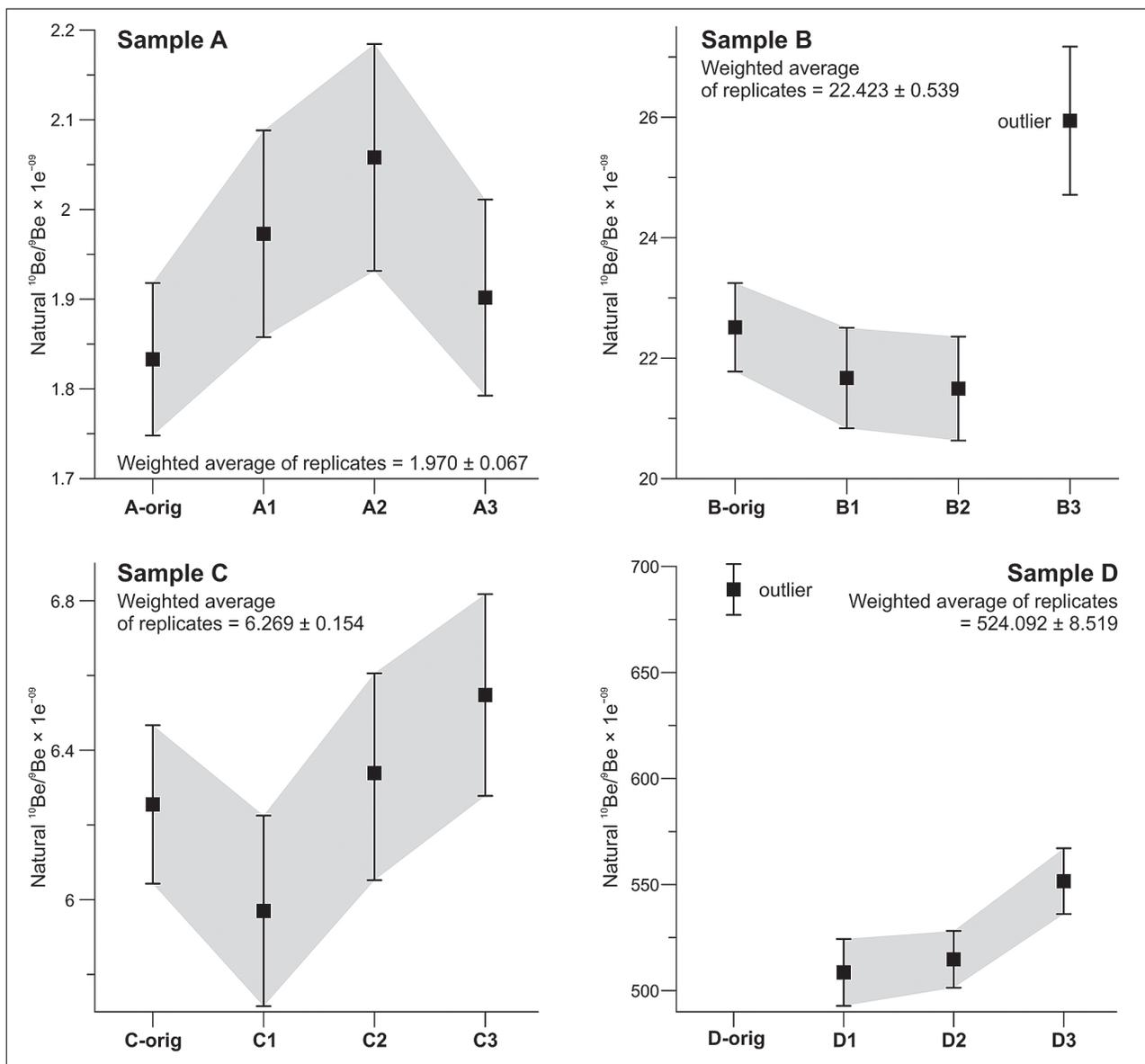**Fig. 2.** Plots with natural $^{10}Be/^9Be$ ratios for each sample represented by an original subsample (orig) and three replicate subsamples (1–3). Note a good fit between subsamples with exceptions of B3 and D-orig. Means are shown with standard deviations.

uncertainties of newly processed subsamples are systematically higher comparing to original subsamples, but differences are below 1.5%. Mentioned values indicate, that effectivity of the extraction is slightly lower than the processing employed originally at the CEREGE institute but having low effect on age calculation.

Processing blanks yielded stable isotopic ratios at least three orders of magnitude lower comparing to the processed samples, what implies a low level of background contamination. Variation of isotopic ratio through the three replicate runs reveals no systematic change (Fig. 2), what also points to no notable change in background contamination during the test. The fact that isotopic ratios of subsamples do not differ systematically from original values (with an exception of the sample D) also indicate negligible cross-contamination difference from original conditions.

4. CONCLUSION

The laboratory test aimed to reveal, whether is the workflow in the facility in question suitable for processing samples for authigenic $^{10}Be/^9Be$ dating. Three replicate runs of four samples with known isotopic ratios yielded consistent values, thus implying effective leaching of the authigenic phase. Analytical uncertainties showed comparable values as the original ones. Two outlier subsample values are expected to be a result of sample inhomogeneity. Processing blanks revealed a low level of contamination. Generally, the workflow conditions are proper for processing of dating samples.

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