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Accumulation of ferromanganese crusts derived from carrier-free ¹⁰Be/⁹Be

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Abstract

The occurrence of ¹⁰Be in natural archives is commonly used to date their formation and growth on time scales of million years. Accelerator Mass Spectrometry (AMS) can perform a direct measurement of the ¹⁰Be/⁹Be ratio. The carrier-free method, in which no ⁹Be carrier is added to the original sample, is especially suitable for ¹⁰Be/⁹Be ratio determination in the marine environment. By normalizing the ¹⁰Be content to ⁹Be, temporal variations of Be uptake ocesses into the archive are eliminated. Here, we present a simple method for the chemical extraction of beryllium from ferromanganese (FeMn) crusts or nodules, the measurement procedure, and the first carrier-free ¹⁰Be/⁹Be measurements at the 3 MV AMS facility VERA. Several tests of chemical methods are discussed including different options to short-cut and accelerate the procedure for special cases. Results from FeMn crust 237KD from cruise VA13/2 in the Pacific ocean show the 9 known ¹⁰Be/⁹Be distribution with depth that is commonly related to a changing growth rate of the archive. In this 10 context we discuss the potential influence of diffusion and adsorption processes on the age models of FeMn crusts that 11 are based on radioactive nuclides such as ¹⁰Be and ²³⁰Th. Including an open-system behavior for these isotopes in the 12 description of their profiles allows interpreting the accumulation of crusts with a constant growth rate over millions of 13 years and does not require the assumption of abrupt growth changes. 14

Key words: ¹⁰Be, carrier-free ¹⁰Be/⁹Be, AMS, VERA, ferromanganese crusts

15 1. Introduction

¹⁶ Dating environmental archives on the time-scale of several million years can be accomplished using the long-lived ¹⁷ radioisotope ¹⁰Be ($T_{1/2}$ =1.39 Myr, Korschinek et al. (2010); Chmeleff et al. (2010)). The use of the ¹⁰Be/⁹Be ratio in ¹⁸ dating assumes that ¹⁰Be follows ⁹Be during incorporation into an archive and that there has been a constant initial ¹⁹ isotopic concentration over the time of formation without subsequent isotopic exchange. While ¹⁰Be is primarily ²⁰ produced in the atmosphere by spallation reactions of cosmic rays, ⁹Be is abundant in the lithosphere and from there ²⁰ *Preprint submitted to Elsevier September 20, 2019*

is transferred into aqueous media via erosion. In the ocean water no variations of ⁹Be due to changing weathering 21 input are detected over the last 10 Myr (Willenbring and von Blanckenburg, 2010), i.e. ⁹Be is suitable to compensate 22

for any effects caused by a potential temporal variability in the Be uptake process into an archive. Therefore, the 23

 ${}^{10}\text{Be}/{}^9\text{Be}$ ratio can be assumed to be more robust than the ${}^{10}\text{Be}$ concentration alone. 24

In order to measure ¹⁰Be/⁹Be ratios it is crucial to determine minute amounts of the long-lived ¹⁰Be and the sta-25 ble ⁹Be without introducing any contamination for either of the two isotopes. There are few carrier-free approaches, 26 measuring ¹⁰Be/⁹Be with SIMS (von Blanckenburg et al., 1996a) or AMS (Maden et al., 2004). Alternatively, the 27 ¹⁰Be/⁹Be ratio is determined by combination of an AMS measurement and a suitable mass-spectrometric determina-28 tion of ⁹Be concentration. In that case a conventional AMS measurement is conducted using several $100 \,\mu g$ of ⁹Be 29 carrier and diluting the natural ${}^{10}\text{Be}/{}^{9}\text{Be}$ ratios that typically range from 10^{-7} to 10^{-11} by ≈ 3 orders of magnitude. 30 The additional measurement of the natural ⁹Be content in the sample is typically carried out with ICP-OES (Graham 31 et al., 2004), AAS (Ménabréaz et al., 2012) or ICP-MS (Feige et al., 2013). 32

Disadvantages of the carrier-free method comprise the necessity to determine very low ⁹Be currents and that direct 33 information on the ¹⁰Be concentration of the sample is not available without a further independent determination of 34 the ⁹Be concentration in the sample.

In an application such as the dating of a marine archive, however, where the ¹⁰Be/⁹Be ratio is the quantity of 36 interest, the great advantage of the carrier-free method is that only one measurement, i.e. the AMS measurement, is 37 required. This advantage is reinforced by the fact that the determination of the stable ⁹Be concentration in a sample 38 aliquot is challenging and seems to be easily affected e.g. by matrix effects (Merchel et al., 2013). 39

FeMn crusts are compact archives spanning periods of several half-lives of ¹⁰Be and thus are a suitable material to 40 apply the carrier-free Be method. They exist only in oxidizing environments without sedimentation and accumulate 41 material by precipitation from ocean water which results in slow growth rates of few mm/Myr. They reach total 42 thicknesses of some centimeter. For dating these archives on short periods (< 1 Myr)²³⁰Th_{exc} is used (Eisenhauer 43 et al., 1992); on longer time ranges than quantifiable with ¹⁰Be this can be performed with Os isotopes (Klemm et al., 44 2005). Alternatively, a magnetostratigraphic technique also shows results consistent with ¹⁰Be/⁹Be dating (Oda et al., 45 2011; Noguchi et al., 2017). In any case, the closed-system conditions for the element used to establish an age model 46 are a fundamental requirement and highly mobile species such as uranium, for which open-system conditions in FeMn 47 crusts have been documented (Neff et al., 1999), are not qualified.

2. Materials and AMS setup 49

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2.1. Target materials and chemical preparation 50

FeMn crusts are mainly composed of oxides of Fe and Mn (for 237KD from cruise VA13/2 $C_{Fe} = 17.5\%$ and 51 C_{Mn} =23.9%, Eisenhauer et al. (1992)) with abundances of Na, Mg, Al, Ca in the range of a few percent. In contrast 52 to those rather abundant elements the Be concentration usually amounts to several $\mu g/g$. With sample amounts of 53

10-150 mg this leaves us with some 10 to some 100 ng of 9 Be for the analysis. During the cruise VA13/2 the crust 54 sample 237KD was recovered at 09°25' N, 146°03' W from 4830 m water depth. It has a thickness of up to 40 cm 55 and has been previously dated using ¹⁰Be (Segl et al., 1984; Segl et al., 1984) and ²³⁰Th (Eisenhauer et al., 1992). 56 Furthermore, it has been used to derive the interstellar/Supernova ⁶⁰Fe signal (Knie et al., 2004). For this crust a 57 change in elemental composition is reported at an age of 13 Myr (Frank et al., 1999). 58

The applied chemical procedure (Fig. 1) consisted of dissolution of the original material with subsequent column 59 chemistry and a final coprecipitation in an Fe₂O₃ matrix, following previously described routines for the extraction 60 of the authigenic Be from FeMn crusts or marine sediments (von Blanckenburg et al., 1996a; Lachner et al., 2013).

The obtained material was pressed into Al cathodes. Targets used for tuning the machine consist of $\leq 1 \mu g$ Be in 2 mg

Fe₂O₃. Chemistry blanks to study the entry of either ⁹Be or ¹⁰Be into the procedure were produced by using all 63

chemicals required for the Be extraction without an original sample. 64

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Figure 1: Schematic of the chemical procedure including options to short-cut the multi-step column chemistry.

The main component of the final carrier-free Be target is the Fe₂O₃ matrix, which dilutes the concentrated ⁹Be so 65 that the targets last long enough during the measurement. As an alternative to the strong chemical pre-concentration 66 followed by a controlled dilution we tested several options to reduce the chemical efforts or even to use the FeMn 67 crust directly. Previous experiments on the extraction of Be from natural samples indicated that there are no negative 68 influences of remainders of Al or Ti above a simple dilution effect (Merchel et al., 2008). For this reason, various steps 69 of the chemical procedure were omitted and three different options of a reduced chemistry were studied. In this project 70 thirteen samples were prepared from the crust 237KD retrieved by the cruise VA13/2. Four samples underwent short 71

versions of the chemical procedure. Several samples were from material with an independently determined ¹⁰Be/⁹Be
 ratio (Usui et al., 2007, 2017).

74 2.2. AMS setup

For ¹⁰Be measurements the AMS system VERA (e.g. Steier et al. (2004)) is operated at a terminal voltage of the pelletron accelerator of 3 MV along with stripping to the 2+ charge state. High transmission through the accelerator and sufficient energy for isobar suppression (E = 7.18 MeV) can be combined. The detection of ¹⁰Be²⁺ is carried out in a gas ionization chamber with a passive absorber consisting of a foil stack of SiN foils to stop the isobar ¹⁰B (Steier et al., 2019). Due to the lower ⁹Be content in the sample the interference from ⁹BeH²⁺ molecules in the detector is largely reduced compared to conventional measurements.

81 2.3. Beam transport

The BeO⁻ extraction from the Fe₂O₃ target matrix is very efficient: In combination with the good transmission 82 from the low energy side into the ionization chamber it enables us to detect more than 0.1% of the total material during 83 the first hour of sputtering a target. Test samples containing a known amount of BeO show an output corresponding 84 to a BeO⁻ formation efficiency of 2% over a sputtering time of 2.5 h. Charge exchange in the stripper has been tested 85 for Ar and He resulting in optimal conditions (55%) for Ar stripping to the Be²⁺ state at a terminal voltage of 3 MV 86 and a lower maximum value (42%) for stripping with He gas. In contrast to the conventional ¹⁰Be measurements it is 87 not required to raise the stripper gas pressure in order to suppress surviving ⁹BeH²⁺ molecules. The lower intensity of 88 ⁹BeH²⁺ from the carrier-free samples allows for operation at the pressure with optimum yield for the 2+ charge state. 89 This slightly improves the measurement yield for the carrier-free method. For a stable measurement of the pA-nA ⁹Be 90 currents a longer integration time is required and takes up $\approx 6\%$ of the measurement time. By positioning the detector 91 after a magnetic quadrupole allowing for optimal focusing of the beam through the 5 mm-5 mm absorber foil stack the 92 ${}^{10}\text{Be}^{2+}/{}^9\text{Be}^{2+}$ ratio of the standards is measured at 80% of the nominal value. The losses of ${}^{10}\text{Be}$ relative to ${}^9\text{Be}$ are 93 partially explained by the tight counting bin, while additional processes are still under discussion (Steier et al., 2019). 94 Within 2.5 hours an overall efficiency of 0.8% for ¹⁰Be detection can be reached. On the whole, there is no major 95 difference in efficiency for ¹⁰Be detection from carrier-free samples compared to a conventional determination. 96

97 3. Results

98 3.1. Chemical yield

After a full chemical procedure the currents of real samples range from 0.5 to $15 \text{ nA} {}^{9}\text{Be}{}^{16}\text{O}^{-}$. At the same time the level of blanks for ${}^{9}\text{Be}$ currents amounts to 10-25 pA with a ${}^{10}\text{Be}$ counting rate 0.01-0.1 s^{-1} . This introduction of ${}^{9}\text{Be}$ into the sample, which is monitored via the chemistry blanks, corresponds to additional 5 pg Be in the original material. Typically, traditional carrier-added targets exhibit ${}^{9}\text{Be}{}^{16}\text{O}^{-}$ currents of 1 μ A (Steier et al., 2019). Previous ¹⁰Be/⁹Be measurements of the same material with conventional AMS (Fig. 2) and double preparations of the same material and measurement in different carrier-free beam times produce ¹⁰Be/⁹Be results that are consistent within 5% for ¹⁰Be/⁹Be ratios $\geq 10^{-9}$.



Figure 2: Comparison between ${}^{10}\text{Be}/{}^{9}\text{Be}$ ratios determined with the carrier-free method at VERA and previous results (Usui et al., 2007, 2017) on the same material.

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Relative to a direct use of the raw FeMn crust material after combusting it at 650°C an improvement of the output 106 by a factor ≈ 5 (Fig. 3) can be accomplished by performing at least option 2 of the chemical separation (Fig. 1), i.e. the 107 dissolution of FeMn material with a subsequent Fe hydroxide coprecipitation. Using option 1 a further factor \approx 3 can 108 be gained by including the steps with the first column and the subsequent coprecipitation with added Fe solution. Still, 109 relative to the full chemistry another factor ≥ 4 is missing. These differences are related to the greater concentration of 110 the samples if the full chemistry is performed. Furthermore, better purification of the material changes the composition 111 of the AMS target, e.g. removing compounds with poor electric and thermal conductivity, and may increase the yield 112 of the BeO⁻ current. The different options show no major effect on the ¹⁰B intensity, which was measured for the 113 different targets as the ${}^{10}B^{2+}$ current in a Faraday cup directly in front of the detector at 5-50 pA. 114

While the relative uncertainty for the ¹⁰Be/⁹Be ratio increased for the targets with reduced chemical treatment because of the lower ¹⁰Be counting rate, the ratios are in good agreement (Fig. 3). Short-cutting the chemical procedure thus is an alternative for a quick screening of a large number of samples where precision dating is not required. With the reduced Be content in the AMS target and the lower Be output of the sample uncertainties are higher by a factor of two due to the lower counting statistics.



Figure 3: Short-cutting the chemical procedure results in lower ⁹Be currents but gives consistent results for the ¹⁰Be/⁹Be ratio.

120 3.2. Cross contamination

In a measurement sequence of blanks and high standards we also determined the cross-contamination for ¹⁰Be in our ion source (type MC-SNICS, NEC, Middleton, USA). The cross-contamination for Be in the ion source is modeled depending on the rate and measurement time of standards and on the period between standard and blank measurement. For measurement parameters and sample run times during routine operation this results in a typical cross-contamination $\frac{10Be/9Be_{blank}}{10Be/9Be_{standard}} \approx 5 \cdot 10^{-5}$. While continuously sputtering a sample the cross-contamination decreases roughly exponentially with a half-life of ≈ 35 minutes.

127 3.3. FeMn crust samples

The typical surface samples of FeMn crusts or nodules show values of ${}^{10}\text{Be}/{}^9\text{Be}\approx10^{-7}$ and exhibit present-day ratios of ocean bottom water (von Blanckenburg et al., 1996b). The lowest crust sample in our study yielded a ratio of ${}^{10}\text{Be}/{}^9\text{Be}\approx(2.3 \pm 0.7) \cdot 10^{-11}$. From the decay law one may thus derive a dating range of at least ≈12 half-lives or 17 Myr. Even with a 30% measurement uncertainty for the lowest ratio this results in a relatively small dating uncertainty of 5% (≈1 Myr) if one can assume a strict abidance by the decay law. The assumption of a constant initial ${}^{10}\text{Be}/{}^9\text{Be}$ ratio has to be tested over those timescales with an independent dating method.

¹³⁴ 4. Modeling ¹⁰Be/⁹Be ratios in FeMn crusts

The common interpretation for a kink in the ${}^{10}\text{Be}/{}^9\text{Be}$ ratio over depth (e.g. at ca. 15 mm in Fig. 4) is a changing growth rate *G* of the FeMn crust. Assuming a closed-system behavior of Be in the crust one can derive growth rates of 2.62±0.08 mm/Ma for the top 12 mm of the crust and 4.08±0.24 mm/Ma deeper than 12 mm or before 4.5 Myr from the presented data of crust 237KD. This estimation of the growth rates does not include the slightly lowered surface data point measured with the carrier free method. Such an inversion (Kusakabe and Ku, 1984) or a flattening (Mangini et al., 1986) has been previously reported for the ${}^{10}\text{Be}/{}^9\text{Be}$ ratio in the top mm of FeMn crusts. However,



Figure 4: Carrier-free ${}^{10}\text{Be}/{}^9\text{Be}$ results (left axis) for crust 237KD VA13/2 from the central Pacific are compared with literature data (left axis: von Blanckenburg et al. (1996b), right axis: Segl et al. (1984)). The right axis is shifted by a constant factor (1/9) relative to the right axis. Both data sets show a decrease over depth that cannot be explained with a simple exponential decay of ${}^{10}\text{Be}$ at constant growth rate. Model predictions for a constant growth rate with Be mobility according to equation 2.

no similar surface behavior was observed in the previous ¹⁰Be/⁹Be determination of the same crust (Fig. 4, Segl et al. 141 (1984)). Therefore, a surface contamination of our FeMn crust sample with ⁹Be could also be an explanation. In the 142 comparison with Segl et al. (1984) a factor of ≈ 9 difference between the two ${}^{10}\text{Be}/{}^{9}\text{Be}$ data sets is striking. A third 143 independent measurement of a top crust sample from cruise VA13/2 (von Blanckenburg et al., 1996b) gives a ¹⁰Be/⁹Be ratio of $1.0 \cdot 10^{-7}$ and thus is compatible with the carrier-free data set rather than with the conventional measurement. 145 Therefore, we presume that the factor might come from a systematic offset in the ⁹Be determination of Segl et al. 146 (1984). Apart from this, the presented growth rates are in agreement with the previously derived values for the same 147 crust if one corrects for the updated value of the ¹⁰Be half-life (Korschinek et al., 2010; Chmeleff et al., 2010). Segl 148 et al. (1984) related the change of growth rate to a change in ocean circulation patterns transporting less Fe and Mn to 149 the growth site of the crust and thus leading to slower accumulation. 150

If one relaxes the requirement of a closed-system behavior of Be in the crust, an alternative explanation of the kink in the ¹⁰Be/⁹Be ratio over depth is conceivable: Crusts exhibit a porous structure with mean porosity of 60% (Hein et al., 2003). These pores are filled with seawater so that the deeper layers in the crusts are presumably connected to the surface. Therefore, any chemical exchange between the crust and the pore fluid leads to a mobile behavior, e.g. diffusion of ions and subsequent adsorption to the crust, effectively removing ions from the pore fluid. An additional input of the radioactive isotope creates the appearance of a younger age for deeper material.

¹⁵⁷ Models taking into account both diffusion and radioactive decay exist since the earliest studies of U isotopes ¹⁵⁸ and ¹⁰Be in FeMn crusts (Ku et al., 1979). A mobile and open-system behavior inside FeMn crusts was observed

for soluble species such as U (Neff et al., 1999; Henderson and Burton, 1999). The diffusion in the pore water and 159 mobility between the fluid and solid phase of the crust is documented for depths up to 6 mm. Processes including Be 160 exchange between the fluid and the solid phase are not sufficient to explain the effects observed in FeMn crusts if one 161 exclusively considers Be that is primarily incorporated into the crust's top layer and later remobilized into the liquid 162 phase: Based on the estimations of Be mobility deduced from U mobility by Henderson and Burton (1999) the ¹⁰Be 163 decay curve should be disturbed by < 1% on timescales of 30 Myr. Instead of only redistributing incorporated Be by 164 diffusion, processes of adsorption from the fluid to the solid phase in the highly porous crust material may have to be 165 considered for the incorporation together with continuous input from the ocean bottom water to the pore water of the 166 crust (Kusakabe and Ku, 1984). In such post-depositional diagenesis some of the Be dissolved in the ocean water is 167 directly transported via the pore water into greater depth of the crust and incorporated there. 168

Incorporation of ¹⁰Be from the pore water into the FeMn crust (growth rate $G = 1/\mu\tau$, τ as the radionuclide's mean lifetime) can be included by the addition of a depth-dependent production term p to the normal decay equation:

$$dN(x)/dx = -\mu \cdot N(x) + p(x) \tag{1}$$

In general, diffusion processes will produce a depth and time dependent production term p = p(x, t). We assume a constant growth rate and introduction from the surface to depth with a function $p(x) = p_0 \cdot (1 - erf(x/x_D))$, which is derived from the solution of the differential diffusion equation. The diffusion length x_D states to which depth the radionuclide diffused during time t and is connected with the effective diffusivity D_{eff} by $x_D = 2\sqrt{D_{eff}t}$. The surface boundary condition is $N(0) = N_0 + p_0/\mu$, where the first term describes the contribution by direct fixation of Be at the boundary and the second term gives the input of the mobile component to the top layer. Then, the differential equation 1 is solved by

$$N(x) = N_0 \cdot e^{-\mu x} + \frac{p_0}{\mu} \cdot (1 - erf(x/x_D)) + \frac{p_0}{\mu} \cdot e^{-\mu x} \cdot \left(e^{\mu^2 x_D^2/4} \cdot (erf(\mu x_D/2) - erf(\mu x_D/2 - x/x_D))\right).$$
(2)

The depth profile can be described by equation 2, which has four free parameters N_0 , μ , p_0 , and x_D . If this equation is fitted to the depth profile shown in Fig. 4, it yields a (constant) growth rate G=2.0±0.1 mm/Myr. In this case, the contribution from post-depositional addition of ¹⁰Be (2nd and 3rd terms in eqn. 2 with parameter p_0) is found to exceed the original component (1st term with parameter N_0) for depths greater than 10 mm.

With the presented scenario of continuous adsorption of Be into the crust at a constant ⁹Be concentration in the seawater one has to expect also an increased ⁹Be concentration with depth. At least for the crust 237KD the ⁹Be concentration data (Segl et al., 1984) shows such a trend and thus is in agreement with an additional input of dissolved ions into the crust over time.

- Sensitive measurements of other natural or anthropogenic radioactive isotopes with different half-lives could be of
 eminent help to explain the behavior of the ¹⁰Be/⁹Be ratio:
- Highly-resolved ²³⁰Th ($T_{1/2}$ =75 kyr) data in the top 1.4 mm of the same crust 237KD VA13/2 (Eisenhauer et al.,
- 187 1992) show a decrease of the concentration only after a rather flat behavior in the top ≈ 0.2 mm as shown in Fig. 5. This
- set of data was interpreted as an exponential decay curve showing a growth rate of $\approx 6 \text{ mm/Myr}$ for the investigated
- ¹⁸⁹ region, i.e. the recent 200 kyr, which disagreed with the lower growth rates derived from ¹⁰Be at greater depths in the
- ¹⁹⁰ crust. This disagreement was explained in terms of a recent change in the accumulation rate of the crust. Similarly,

discordant ²³⁰Th_{exc} and ¹⁰Be data for a number of FeMn nodules have also been interpreted as recent changes in growth rate (Krishnaswami et al., 1982).



Figure 5: 230 Th concentrations as a function of depth for the same crust as studied in the present work (237KD from cruise VA13/2) from the central Pacific over depth (Eisenhauer et al., 1992). The solid line is a fit based on equation 2 using the growth rate G=2.0 mm/Myr that was derived from 10 Be to define the parameter μ .

¹⁹³ If, on the other hand, we use the model of a combined exponential decay and a diffusional input with post-¹⁹⁴ depositional fixation (eq. 2) the data for crust 237KD from cruise VA13/2 (Eisenhauer et al., 1992) can be equally ¹⁹⁵ well described assuming the ¹⁰Be derived growth rate and a dominant additional input of ²³⁰Th via incorporation of ¹⁹⁶ dissolved Th into the crust (Fig. 5). This would mean that in this case the ²³⁰Th concentration does not give direct ¹⁹⁷ information on the age. Thereby, the disagreement of the ¹⁰Be and ²³⁰Th data can be resolved so that the recent change ¹⁹⁸ of the growth rates may be unnecessary in order to bring both data sets into accordance.

¹⁹⁹ The age model might be expanded using ⁵³Mn ($T_{1/2}=3.7$ Myr, Honda and Imamura (1971)) measurements. Data ²⁰⁰ from the same crust 237KD (Poutivtsev, 2007) are available but the uncertainties are too high to distinguish between ²⁰¹ different growth scenarios of the crust. The ⁵³Mn data were described by a constant growth of the crust at a rate of ²⁰² $\approx 2.5\pm0.2$ mm/Myr over the first 3 cm, which could mean a mobile behavior of ¹⁰Be in the crust. However, a changing ²⁰³ growth rate at a depth of 10-12 mm was also compatible with the same data set (Poutivtsev, 2007).

In the case of 26 Al, a similar mobility of Al and Be would result in a stronger influence on the distribution. Due to the shorter half-life of 0.7 Myr the 26 Al concentration decays faster over depth and a transport of 26 Al from surface thus may create an impact already at shallower depths than for ¹⁰Be. However, in the case of ²⁶Al one also has to consider the additional production via the reaction ²³Na(α ,n)²⁶Al, depending on the α flux from ^{230,232}Th and ²³⁸U decay (Feige, 2014), which also depends on depth in the crust.

Profiles of anthropogenic fission products, e.g. ⁹⁰Sr, with a depth dependance that can be explained by input via diffusion would serve as a fingerprint for a non-closed system behavior. Similarly, the detection of radionuclides that are of unambiguous anthropogenic origin, e.g. ²³⁸Pu or ²⁴⁰Pu, in greater depths of FeMn crusts would indicate post-depositional addition of material.

In contrast to the radionuclides discussed above, the ¹⁸⁷Os/¹⁸⁸Os isotope system is not primarily governed by 213 radioactive decay. ¹⁸⁷Os is a daughter of the long-lived ¹⁸⁷Re with a half-life of 46 Gyr and thus is continuously 214 produced. However, the input of ¹⁸⁷Os to the ocean, which is mainly by continental weathering (Sharma et al., 1997), 215 has found to be not continuous (Pegram and Turekian, 1999). Therefore, relative dating up to 80 Myr can be performed 216 by identifying a common pattern of ¹⁸⁷Os/¹⁸⁸Os in archives. The measured ¹⁸⁷Os/¹⁸⁸Os in the archive is adjusted to 217 the known seawater curve over time in order to get a depth-age relationship. This can help in the identification of 218 growth-rate changes or hiatuses (Klemm et al., 2005; Goto et al., 2017). It is advantageous for this method that it 219 is not based on a strong gradient in the isotopic ratio: Os mobility would wash out the original signature but may 220 not necessarily shift the age model towards younger ages. For all radionuclides, a mobile behavior leads to apparent 221 younger ages of the crust in greater depths. The determination of the Os isotopic ratio therefore may give valuable 222 complementary information on the age model of old FeMn crusts. 223

224 5. Conclusion

Measuring ¹⁰Be/⁹Be ratios is a powerful tool to date marine deposits in the time range of million years. The 225 method is applicable for marine sediments but also for ferromanganese (FeMn) crusts with growth rates of only few 22 mm/Myr, which are of special interest for geochemical and even astrophysical studies. The low abundance of Be 227 in natural materials poses challenges to the preparation of samples and to very sensitive measurements of both ¹⁰Be 228 and ⁹Be: The presented procedure to separate Be from the matrix works for sample sizes of 10-100 mg FeMn crust 229 containing less than 1 μg^{9} Be and results in Be currents in the range of several 100 pA to few nA. Options of shortening 230 and simplifying the carrier-free method make it suitable for both quick large-scale surveys with many samples and 231 highly sensitive determination of low natural ¹⁰Be/⁹Be ratios. 232

²³³ Conventional radiometric dating of FeMn crusts uses a closed system behavior and changes in the ¹⁰Be/⁹Be curve ²³⁴ then can be attributed to a change in the growth rate. The model introduced in this work shows an alternative inter-²³⁵ pretation of the depth profile of radioactive nuclei in a crust on the basic assumption of a constant growth rate but ²³⁶ including a depth dependent input. Still, age information can be obtained from the ¹⁰Be/⁹Be data.

High-resolution isotopic data of different systems such as the discussed ${}^{10}\text{Be}/{}^{9}\text{Be}$, ${}^{53}\text{Mn}/{}^{55}\text{Mn}$, ${}^{187}\text{Os}/{}^{188}\text{Os}$, ${}^{230}\text{Th}_{exc}$ or of anthropogenic nuclides are required to assess the growth of FeMn crusts, to investigate a potential mobile behavior of Be in the FeMn crust, and to put stronger limits on models describing post-depositional diagenesis. For a

²⁴⁰ better understanding of the pore water interaction with the solid phase of the FeMn crust and of effects from diffusion

²⁴¹ or accretion of elements the evaluation of multiple isotopic systems in crusts with different porosities and growth

²⁴² histories will be very helpful.

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