

Accumulation of ferromanganese crusts derived from carrier-free $^{10}\text{Be}/^{9}\text{Be}$

Lachner, J.; Ploner, M.; Steier, P.; Sakaguchi, A.; Usui, A.;

Originally published:

March 2020

Nuclear Instruments and Methods in Physics Research B 467(2020), 146-151

DOI: <https://doi.org/10.1016/j.nimb.2019.11.047>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-31927>

Release of the secondary publication
on the basis of the German Copyright Law § 38 Section 4.

CC BY-NC-ND

Accumulation of ferromanganese crusts derived from carrier-free $^{10}\text{Be}/^9\text{Be}$

Johannes Lachner, Marco Ploner, Peter Steier

University of Vienna, Isotope Research and Nuclear Physics, Währinger Str. 17, 1090 Wien, Austria

Aya Sakaguchi

University of Tsukuba, Tsukuba, 305-8577, Japan

Akira Usui

Kochi University, B200 Monobe, Nankoku, Kochi 783-8502, Japan

Abstract

1 The occurrence of ^{10}Be in natural archives is commonly used to date their formation and growth on time scales of
2 million years. Accelerator Mass Spectrometry (AMS) can perform a direct measurement of the $^{10}\text{Be}/^9\text{Be}$ ratio. The
3 carrier-free method, in which no ^9Be carrier is added to the original sample, is especially suitable for $^{10}\text{Be}/^9\text{Be}$ ratio
4 determination in the marine environment. By normalizing the ^{10}Be content to ^9Be , temporal variations of Be uptake
5 processes into the archive are eliminated.

6 Here, we present a simple method for the chemical extraction of beryllium from ferromanganese (FeMn) crusts
7 or nodules, the measurement procedure, and the first carrier-free $^{10}\text{Be}/^9\text{Be}$ measurements at the 3 MV AMS facility
8 VERA. Several tests of chemical methods are discussed including different options to short-cut and accelerate the
9 procedure for special cases. Results from FeMn crust 237KD from cruise VA13/2 in the Pacific ocean show the
10 known $^{10}\text{Be}/^9\text{Be}$ distribution with depth that is commonly related to a changing growth rate of the archive. In this
11 context we discuss the potential influence of diffusion and adsorption processes on the age models of FeMn crusts that
12 are based on radioactive nuclides such as ^{10}Be and ^{230}Th . Including an open-system behavior for these isotopes in the
13 description of their profiles allows interpreting the accumulation of crusts with a constant growth rate over millions of
14 years and does not require the assumption of abrupt growth changes.

Key words: ^{10}Be , carrier-free $^{10}\text{Be}/^9\text{Be}$, 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 ^{10}Be ($T_{1/2}=1.39$ Myr, Korschinek et al. (2010); Chmeleff et al. (2010)). The use of the $^{10}\text{Be}/^9\text{Be}$ ratio in
18 dating assumes that ^{10}Be 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 ^{10}Be is primarily
20 produced in the atmosphere by spallation reactions of cosmic rays, ^9Be is abundant in the lithosphere and from there

21 is transferred into aqueous media via erosion. In the ocean water no variations of ^9Be due to changing weathering
22 input are detected over the last 10 Myr (Willenbring and von Blanckenburg, 2010), i.e. ^9Be is suitable to compensate
23 for any effects caused by a potential temporal variability in the Be uptake process into an archive. Therefore, the
24 $^{10}\text{Be}/^9\text{Be}$ ratio can be assumed to be more robust than the ^{10}Be concentration alone.

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

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

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

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

49 2. Materials and AMS setup

50 2.1. Target materials and chemical preparation

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

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

The applied chemical procedure (Fig. 1) consisted of dissolution of the original material with subsequent column chemistry and a final coprecipitation in an Fe_2O_3 matrix, following previously described routines for the extraction 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 $\leq 1 \mu\text{g}$ Be in 2 mg Fe_2O_3 . Chemistry blanks to study the entry of either ^9Be or ^{10}Be into the procedure were produced by using all chemicals required for the Be extraction without an original sample.

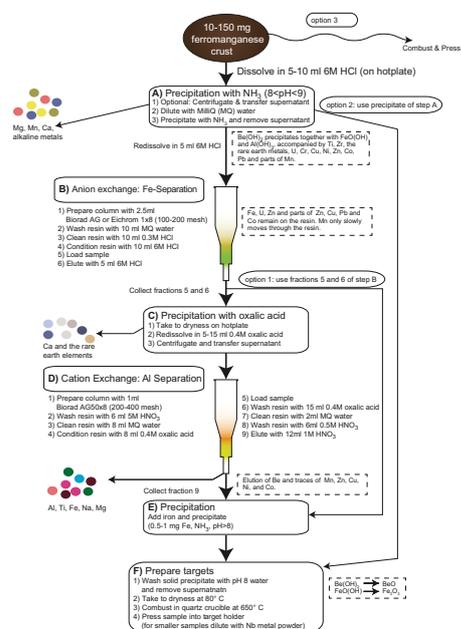


Figure 1: Schematic of the chemical procedure including options to short-cut the multi-step column chemistry.

The main component of the final carrier-free Be target is the Fe_2O_3 matrix, which dilutes the concentrated ^9Be so that the targets last long enough during the measurement. As an alternative to the strong chemical pre-concentration followed by a controlled dilution we tested several options to reduce the chemical efforts or even to use the FeMn crust directly. Previous experiments on the extraction of Be from natural samples indicated that there are no negative influences of remainders of Al or Ti above a simple dilution effect (Merchel et al., 2008). For this reason, various steps of the chemical procedure were omitted and three different options of a reduced chemistry were studied. In this project thirteen samples were prepared from the crust 237KD retrieved by the cruise VA13/2. Four samples underwent short

72 versions of the chemical procedure. Several samples were from material with an independently determined $^{10}\text{Be}/^9\text{Be}$
73 ratio (Usui et al., 2007, 2017).

74 2.2. AMS setup

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

81 2.3. Beam transport

82 The BeO^- extraction from the Fe_2O_3 target matrix is very efficient: In combination with the good transmission
83 from the low energy side into the ionization chamber it enables us to detect more than 0.1% of the total material during
84 the first hour of sputtering a target. Test samples containing a known amount of BeO show an output corresponding
85 to a BeO^- formation efficiency of 2% over a sputtering time of 2.5 h. Charge exchange in the stripper has been tested
86 for Ar and He resulting in optimal conditions (55%) for Ar stripping to the Be^{2+} state at a terminal voltage of 3 MV
87 and a lower maximum value (42%) for stripping with He gas. In contrast to the conventional ^{10}Be measurements it is
88 not required to raise the stripper gas pressure in order to suppress surviving $^9\text{BeH}^{2+}$ molecules. The lower intensity of
89 $^9\text{BeH}^{2+}$ from the carrier-free samples allows for operation at the pressure with optimum yield for the 2+ charge state.
90 This slightly improves the measurement yield for the carrier-free method. For a stable measurement of the pA-nA ^9Be
91 currents a longer integration time is required and takes up $\approx 6\%$ of the measurement time. By positioning the detector
92 after a magnetic quadrupole allowing for optimal focusing of the beam through the 5 mm-5 mm absorber foil stack the
93 $^{10}\text{Be}^{2+}/^9\text{Be}^{2+}$ ratio of the standards is measured at 80% of the nominal value. The losses of ^{10}Be relative to ^9Be are
94 partially explained by the tight counting bin, while additional processes are still under discussion (Steier et al., 2019).

95 Within 2.5 hours an overall efficiency of 0.8% for ^{10}Be detection can be reached. On the whole, there is no major
96 difference in efficiency for ^{10}Be detection from carrier-free samples compared to a conventional determination.

97 3. Results

98 3.1. Chemical yield

99 After a full chemical procedure the currents of real samples range from 0.5 to 15 nA $^9\text{Be}^{16}\text{O}^-$. At the same time
100 the level of blanks for ^9Be currents amounts to 10-25 pA with a ^{10}Be counting rate 0.01-0.1 s^{-1} . This introduction of
101 ^9Be into the sample, which is monitored via the chemistry blanks, corresponds to additional 5 pg Be in the original
102 material. Typically, traditional carrier-added targets exhibit $^9\text{Be}^{16}\text{O}^-$ currents of 1 μA (Steier et al., 2019).

103 Previous $^{10}\text{Be}/^9\text{Be}$ measurements of the same material with conventional AMS (Fig. 2) and double preparations of
 104 the same material and measurement in different carrier-free beam times produce $^{10}\text{Be}/^9\text{Be}$ results that are consistent
 within 5% for $^{10}\text{Be}/^9\text{Be}$ ratios $\geq 10^{-9}$.

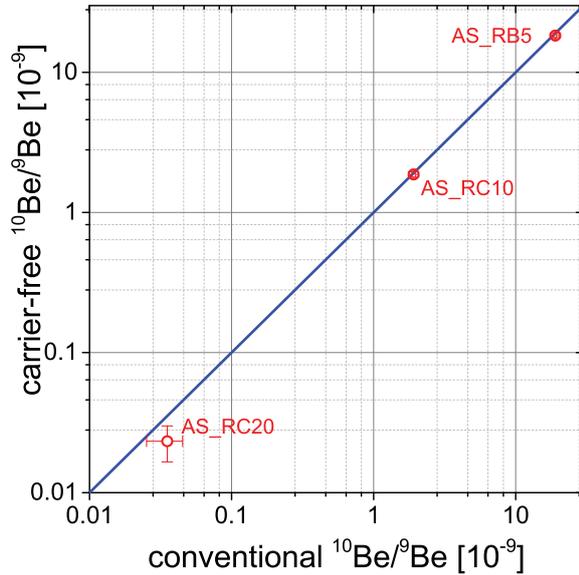


Figure 2: Comparison between $^{10}\text{Be}/^9\text{Be}$ ratios determined with the carrier-free method at VERA and previous results (Usui et al., 2007, 2017) on the same material.

105
 106 Relative to a direct use of the raw FeMn crust material after combusting it at 650°C an improvement of the output
 107 by a factor ≈ 5 (Fig. 3) can be accomplished by performing at least option 2 of the chemical separation (Fig. 1), i.e. the
 108 dissolution of FeMn material with a subsequent Fe hydroxide coprecipitation. Using option 1 a further factor ≈ 3
 109 be gained by including the steps with the first column and the subsequent coprecipitation with added Fe solution. Still,
 110 relative to the full chemistry another factor ≥ 4 is missing. These differences are related to the greater concentration of
 111 the samples if the full chemistry is performed. Furthermore, better purification of the material changes the composition
 112 of the AMS target, e.g. removing compounds with poor electric and thermal conductivity, and may increase the yield
 113 of the BeO^- current. The different options show no major effect on the ^{10}B intensity, which was measured for the
 114 different targets as the $^{10}\text{B}^{2+}$ current in a Faraday cup directly in front of the detector at 5-50 pA.

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

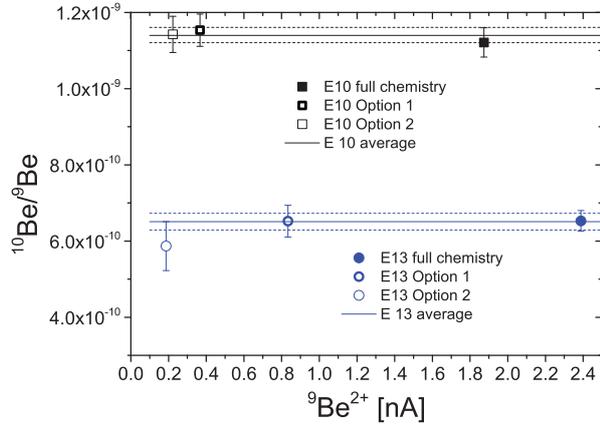


Figure 3: Short-cutting the chemical procedure results in lower ${}^9\text{Be}$ currents but gives consistent results for the ${}^{10}\text{Be}/{}^9\text{Be}$ ratio.

120 3.2. Cross contamination

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

127 3.3. FeMn crust samples

128 The typical surface samples of FeMn crusts or nodules show values of ${}^{10}\text{Be}/{}^9\text{Be} \approx 10^{-7}$ and exhibit present-day
 129 ratios of ocean bottom water (von Blanckenburg et al., 1996b). The lowest crust sample in our study yielded a ratio
 130 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
 131 or 17 Myr. Even with a 30% measurement uncertainty for the lowest ratio this results in a relatively small dating
 132 uncertainty of 5% (≈ 1 Myr) if one can assume a strict abidance by the decay law. The assumption of a constant initial
 133 ${}^{10}\text{Be}/{}^9\text{Be}$ ratio has to be tested over those timescales with an independent dating method.

134 4. Modeling ${}^{10}\text{Be}/{}^9\text{Be}$ ratios in FeMn crusts

135 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
 136 growth rate G of the FeMn crust. Assuming a closed-system behavior of Be in the crust one can derive growth rates
 137 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
 138 from the presented data of crust 237KD. This estimation of the growth rates does not include the slightly lowered
 139 surface data point measured with the carrier free method. Such an inversion (Kusakabe and Ku, 1984) or a flattening
 140 (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,

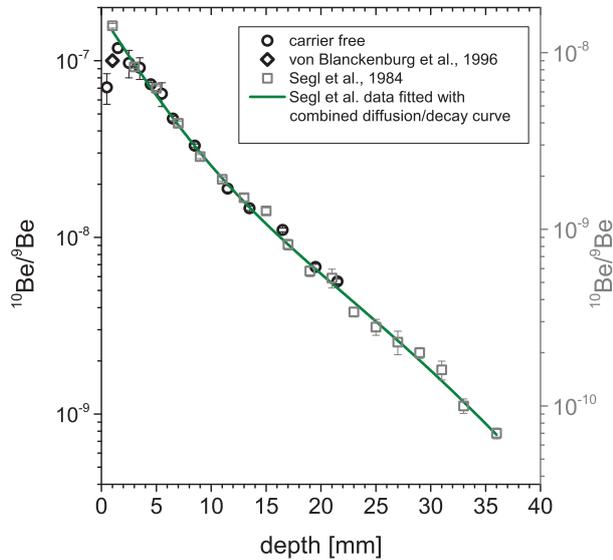


Figure 4: Carrier-free $^{10}\text{Be}/^9\text{Be}$ results (left axis) for crust 237KD VA13/2 from the central Pacific are compared with literature data (left axis: von Blanckenburg et al. (1996b), right axis: Segl et al. (1984)). The right axis is shifted by a constant factor (1/9) relative to the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

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

151 If one relaxes the requirement of a closed-system behavior of Be in the crust, an alternative explanation of the kink
 152 in the $^{10}\text{Be}/^9\text{Be}$ ratio over depth is conceivable: Crusts exhibit a porous structure with mean porosity of 60% (Hein
 153 et al., 2003). These pores are filled with seawater so that the deeper layers in the crusts are presumably connected to
 154 the surface. Therefore, any chemical exchange between the crust and the pore fluid leads to a mobile behavior, e.g.
 155 diffusion of ions and subsequent adsorption to the crust, effectively removing ions from the pore fluid. An additional
 156 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 ^{10}Be in FeMn crusts (Ku et al., 1979). A mobile and open-system behavior inside FeMn crusts was observed

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

Incorporation of ^{10}Be 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:

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

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

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

176 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
 177 is fitted to the depth profile shown in Fig. 4, it yields a (constant) growth rate $G=2.0\pm 0.1$ mm/Myr. In this case, the
 178 contribution from post-depositional addition of ^{10}Be (2nd and 3rd terms in eqn. 2 with parameter p_0) is found to
 179 exceed the original component (1st term with parameter N_0) for depths greater than 10 mm.

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

184 Sensitive measurements of other natural or anthropogenic radioactive isotopes with different half-lives could be of
185 eminent help to explain the behavior of the $^{10}\text{Be}/^9\text{Be}$ ratio:

186 Highly-resolved ^{230}Th ($T_{1/2} = 75$ 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
188 set of data was interpreted as an exponential decay curve showing a growth rate of ≈ 6 mm/Myr for the investigated
189 region, i.e. the recent 200 kyr, which disagreed with the lower growth rates derived from ^{10}Be 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,
191 discordant $^{230}\text{Th}_{exc}$ and ^{10}Be data for a number of FeMn nodules have also been interpreted as recent changes in
192 growth rate (Krishnaswami et al., 1982).

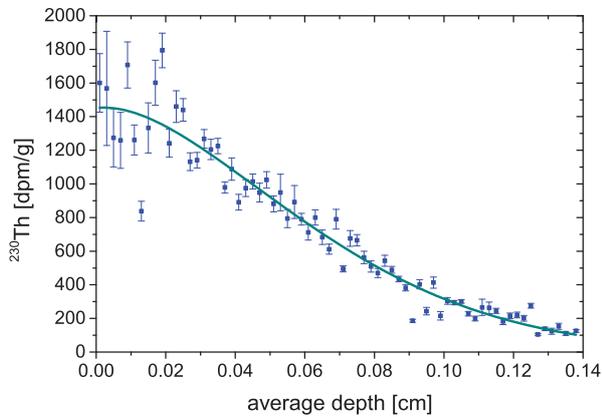


Figure 5: ^{230}Th concentrations as a function of depth for the same crust as studied in the present work (237KD from cruise VA13/2) from the central Pacific over depth (Eisenhauer et al., 1992). The solid line is a fit based on equation 2 using the growth rate $G=2.0$ mm/Myr that was derived from ^{10}Be 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 ^{10}Be derived growth rate and a dominant additional input of ^{230}Th via incorporation of
196 dissolved Th into the crust (Fig. 5). This would mean that in this case the ^{230}Th concentration does not give direct
197 information on the age. Thereby, the disagreement of the ^{10}Be and ^{230}Th 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 ^{53}Mn ($T_{1/2}=3.7$ Myr, Honda and Imamura (1971)) measurements. Data
200 from the same crust 237KD (Poutitsev, 2007) are available but the uncertainties are too high to distinguish between
201 different growth scenarios of the crust. The ^{53}Mn data were described by a constant growth of the crust at a rate of
202 $\approx 2.5 \pm 0.2$ mm/Myr over the first 3 cm, which could mean a mobile behavior of ^{10}Be in the crust. However, a changing
203 growth rate at a depth of 10-12 mm was also compatible with the same data set (Poutitsev, 2007).

204 In the case of ^{26}Al , a similar mobility of Al and Be would result in a stronger influence on the distribution. Due
205 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

206 thus may create an impact already at shallower depths than for ^{10}Be . However, in the case of ^{26}Al one also has to
207 consider the additional production via the reaction $^{23}\text{Na}(\alpha,n)^{26}\text{Al}$, depending on the α flux from $^{230,232}\text{Th}$ and ^{238}U
208 decay (Feige, 2014), which also depends on depth in the crust.

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

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

224 5. Conclusion

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

233 Conventional radiometric dating of FeMn crusts uses a closed system behavior and changes in the $^{10}\text{Be}/^9\text{Be}$ 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 $^{10}\text{Be}/^9\text{Be}$ data.

237 High-resolution isotopic data of different systems such as the discussed $^{10}\text{Be}/^9\text{Be}$, $^{53}\text{Mn}/^{55}\text{Mn}$, $^{187}\text{Os}/^{188}\text{Os}$, $^{230}\text{Th}_{\text{exc}}$
238 or of anthropogenic nuclides are required to assess the growth of FeMn crusts, to investigate a potential mobile be-

239 havior 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.

243 **Acknowledgements**

244 We are very grateful to Kosuke Goto for helpful discussions on the Os isotopic signature and to Marcus Christl
245 for bringing to our notice the past works on U mobility in FeMn crusts. The comments of an anonymous reviewer are
246 also gratefully acknowledged.

247 **References**

- 248 G. Korschinek, A. Bergmaier, T. Faestermann, U. Gerstmann, K. Knie, G. Rugel, A. Wallner, I. Dillmann, G. Dollinger, C. L. von Gostomski,
249 K. Kossert, M. Maiti, M. Poutivtsev, A. Remmert, A new value for the half-life of ^{10}Be by Heavy-Ion Elastic Recoil Detection and liquid
250 scintillation counting, *Nucl. Instrum. Meth. B* 268 (2) (2010) 187 – 191.
- 251 J. Chmeleff, F. von Blanckenburg, K. Kossert, D. Jakob, Determination of the ^{10}Be half-life by multicollector ICP-MS and liquid scintillation
252 counting, *Nucl. Instrum. Meth. B* 268 (2) (2010) 192–199.
- 253 J. Willenbring, F. von Blanckenburg, Long-term stability of global erosion rates and weathering during late-Cenozoic cooling, *Nature* 465 (2010)
254 211 – 214.
- 255 F. von Blanckenburg, N. Belshaw, R. O’Nions, Separation of ^9Be and cosmogenic ^{10}Be from environmental materials and SIMS isotope dilution
256 analysis, *Chem. Geology* 129 (1-2) (1996a) 93 – 99.
- 257 C. Maden, M. Döbeli, P. W. Kubik, M. Frank, M. Suter, Measurement of carrier-free ^{10}Be samples with AMS: the method and its potential, *Nucl.*
258 *Instrum. Meth. B* 223-224 (2004) 247–252.
- 259 I. Graham, R. Carter, R. Ditchburn, A. Zondervan, Chronostratigraphy of ODP 181, Site 1121 sediment core (Southwest Pacific Ocean), using
260 $^{10}\text{Be}/^9\text{Be}$ dating of entrapped ferromanganese nodules, *Marine Geology* 205 (1-4) (2004) 227 – 247.
- 261 L. Ménabréaz, D. L. Bourlès, N. Thouveny, Amplitude and timing of the Laschamp geomagnetic dipole low from the global atmospheric ^{10}Be
262 overproduction: Contribution of authigenic $^{10}\text{Be}/^9\text{Be}$ ratios in west equatorial Pacific sediments, *J. Geophys. Res.: Solid Earth* 117 (2012)
263 B11101.
- 264 J. Feige, A. Wallner, L. Fifield, Korschinek, G., Merchel, S., Rugel, G., Steier, P., Winkler, S.R., Golser, R., AMS measurements of cosmogenic
265 and supernova-ejected radionuclides in deep-sea sediment cores, *EPJ Web of Conferences* 63 (2013) 03003.
- 266 S. Merchel, W. Bremsler, D. L. Bourlès, U. Czeslik, J. Erzinger, N.-A. Kummer, L. Leanni, B. Merkel, S. Recknagel, U. Schaefer, Accuracy of
267 ^9Be -data and its influence on ^{10}Be cosmogenic nuclide data, *J. Radioanal. Nucl. Chem.* 298 (2013) 1871 – 1878.
- 268 A. Eisenhauer, K. Gögen, E. Pernicka, A. Mangini, Climatic influences on the growth rates of Mn crusts during the Late Quaternary, *Earth Planet.*
269 *Sci. Lett* 109 (1) (1992) 25 – 36.
- 270 V. Klemm, S. Lévassieur, M. Frank, J. R. Hein, A. N. Halliday, Osmium isotope stratigraphy of a marine ferromanganese crust, *Earth Planet. Sc.*
271 *Lett.* 238 (1) (2005) 42 – 48.
- 272 H. Oda, A. Usui, I. Miyagi, M. Joshima, B. P. Weiss, C. Shantz, L. E. Fong, K. K. McBride, R. Harder, F. J. Baudenbacher, Ultrafine-scale
273 magnetostratigraphy of marine ferromanganese crust, *Geology* 39 (2011) 227–230.
- 274 A. Noguchi, H. Oda, Y. Yamamoto, A. Usui, M. Sato, J. Kawai, Scanning SQUID microscopy of a ferromanganese crust from the northwestern
275 Pacific: Submillimeter scale magnetostratigraphy as a new tool for age determination and mapping of environmental magnetic parameters,
276 *Geophys. Res. Lett.* 44 (2017) 5360–5367.

- 277 U. Neff, A. Bollhöfer, N. Frank, A. Mangini, Explaining discrepant depth profiles of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}_{\text{ex}}$ in Mn-crusts, *Geochim. et Cosmochim.*
278 *Acta* 63 (15) (1999) 2211 – 2218.
- 279 M. Segl, A. Mangini, G. Bonani, H. Hofmann, M. Nessi, M. Suter, W. Wölfli, G. Friedrich, W. Plünger, A. Wiechowski, J. Beer, ^{10}Be -dating of a
280 manganese crust from Central North Pacific and implications for ocean palaeocirculation, *Nature* 309 (7) (1984) 540 – 543.
- 281 M. Segl, A. Mangini, G. Bonani, H. Hofmann, E. Morenzoni, M. Nessi, M. Suter, W. Wölfli, ^{10}Be dating of the inner structure of Mn-encrustations
282 applying the Zürich tandem accelerator, *Nucl. Instrum. Meth. B* 5 (2) (1984) 359 – 364.
- 283 K. Knie, G. Korschinek, T. Faestermann, E. A. Dorfi, G. Rugel, A. Wallner, ^{60}Fe Anomaly in a Deep-Sea Manganese Crust and Implications for a
284 Nearby Supernova Source, *Phys. Rev. Lett.* 93 (17) (2004) 171103.
- 285 M. Frank, R. O’Nions, J. Hein, V. Banakar, 60 Myr records of major elements and Pb-Nd isotopes from hydrogenous ferromanganese crusts:
286 reconstruction of seawater paleochemistry, *Geochim. Cosmochim. Acta* 63 (11) (1999) 1689 – 1708.
- 287 J. Lachner, M. Christl, H.-A. Synal, M. Frank, M. Jakobsson, Carrier free $^{10}\text{Be}/^{9}\text{Be}$ measurements with low-energy AMS: Determination of
288 sedimentation rates in the Arctic Ocean, *Nucl. Instrum. Meth. B* 294 (0) (2013) 67 – 71.
- 289 S. Merchel, M. Arnold, G. Aumaitre, L. Benedetti, D. Bourles, R. Braucher, V. Alfimov, S. Freeman, P. Steier, A. Wallner, Towards more precise
290 ^{10}Be and ^{36}Cl data from measurements at the 10^{-14} level: Influence of sample preparation, *Nucl. Instrum. Meth. B* 266 (22) (2008) 4921 –
291 4926.
- 292 A. Usui, I. J. Graham, R. G. Ditchburn, A. Zondervan, H. Shibasaki, H. Hishida, Growth history and formation environments of ferromanganese
293 deposits on the Philippine Sea Plate, northwest Pacific Ocean, *Island Arc* 16 (2007) 420–430.
- 294 A. Usui, K. Nishi, H. Sato, Y. Nakasato, B. Thornton, T. Kashiwabara, A. Tokumaru, A. Sakaguchi, K. Yamaoka, S. Kato, S. Nitahara, K. Suzuki,
295 K. Iijima, T. Urabe, Continuous growth of hydrogenetic ferromanganese crusts since 17Myr ago on Takuyo-Daigo Seamount, NW Pacific, at
296 water depths of 800-5500m, *Ore Geology Reviews* 87 (2017) 71–87.
- 297 P. Steier, R. Golser, W. Kutschera, A. Priller, C. Vockenhuber, S. Winkler, VERA, an AMS facility for all isotopes, *Nucl. Instrum. Meth. B* 223-224
298 (2004) 67–71.
- 299 P. Steier, M. Martschini, J. Buchriegler, J. Feige, J. Lachner, S. Merchel, L. Michlmayr, A. Priller, G. R. E. Schmidt, A. Wallner, E. M. Wild,
300 R. Golser, Comparison of methods for the detection of ^{10}Be with AMS and a new approach based on a silicon nitride foil stack, *Int. J. Mass*
301 *Spectrom.* 444 (2019) 116175.
- 302 F. von Blanckenburg, R. O’Nions, N. Belshaw, A. Gibb, J. Hein, Global distribution of beryllium isotopes in deep ocean water as derived from
303 Fe-Mn crusts, *Earth and Planetary Science Letters* 141 (1-4) (1996b) 213 – 226.
- 304 M. Kusakabe, T.-L. Ku, Incorporation of Be isotopes and other trace metals into marine ferromanganese deposits, *Geochim. Cosmochim. Acta*
305 48 (11) (1984) 2187–2193.
- 306 A. Mangini, M. Segl, H. Kudrass, M. Wiedicke, G. Bonani, H. Hofmann, E. Morenzoni, M. Nessi, M. Suter, W. Wölfli, Diffusion and supply
307 rates of ^{10}Be and ^{230}Th radioisotopes in two manganese encrustations from the South China Sea, *Geochim. Cosmochim. Acta* 50 (1) (1986)
308 149–156.
- 309 J. Hein, A. Koschinsky, M. Bau, F. Manheim, J.-K. Kang, L. Roberts, Cobalt-rich ferromanganese crusts in the Pacific, in: D. Cronan (Ed.),
310 *Handbook of Marine Mineral Deposits*, CRC Press, Boca Raton, Florida, 239–279, 2003.
- 311 T. Ku, A. Omura, P. Chen, ^{10}Be and U-Series Isotopes in Manganese Nodules from the Central North Pacific, *Marine Geology and Oceanography*
312 *of the Pacific Manganese Nodule Province. Marine Science* 9 (1979) 791–814.
- 313 G. M. Henderson, K. W. Burton, Using ($^{234}\text{U}/^{238}\text{U}$) to assess diffusion rates of isotope tracers in ferromanganese crusts, *Earth Planet. Sc. Lett.*
314 170 (3) (1999) 169 – 179.
- 315 S. Krishnaswami, A. Mangini, J. Thomas, P. Sharma, J. Cochran, K. Turekian, P. Parker, ^{10}Be and Th isotopes in manganese nodules and adjacent
316 sediments: Nodule growth histories and nuclide behavior, *Earth Planet. Sci. Lett.* 59 (2) (1982) 217–234.
- 317 M. Honda, M. Imamura, Half-life of ^{53}Mn , *Phys. Rev. C* 4 (1971) 1182–1188.
- 318 M. Poutivtsev, Extraterrestrisches ^{53}Mn in hydrogenetischen Mangankrusten, Ph.D. thesis, TU München, 2007.
- 319 J. Feige, Supernova-Produced Radionuclides in Deep-Sea Sediments Measured with AMS, Ph.D. thesis, Dissertation University Vienna, 2014.

- 320 M. Sharma, D. Papanastassiou, G. Wasserburg, The concentration and isotopic composition of osmium in the oceans, *Geochimica et Cosmochimica*
321 *Acta* 61 (1997) 3287–3299.
- 322 W. J. Pegram, K. K. Turekian, The osmium isotopic composition change of Cenozoic sea water as inferred from a deep-sea core corrected for
323 meteoritic contributions, *Geochimica et Cosmochimica Acta* 63 (1999) 4053–4058.
- 324 K. T. Goto, T. Nozaki, T. Toyofuku, A. H. Augustin, G. Shimoda, Q. Chang, J. Kimura, K. Kameo, H. Kitazato, K. Suzuki, Paleocceanographic
325 conditions on the São Paulo Ridge, SW Atlantic Ocean, for the past 30 million years inferred from Os and Pb isotopes of a hydrogenous
326 ferromanganese crust, *Deep Sea Research Part II: Topical Studies in Oceanography* 146 (2017) 82–92.