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ESR-dating of the Arctic sediment core PS1535 dose-response and thermal behaviour of the CO_2^--signal in foraminifera☆

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Abstract

ESR-spectra of foraminifera in arctic sediment cores display the CO_2^--signal ($g = 2.0006$). Research on the thermal behaviour of the CO_2^--signal shows that both natural and artificial irradiation generates a precursor and a thermal unstable component of the CO_2^--signal. The precursor can be transfered to the stable radical, and unstable radicals can be removed by heating. The signal-change by heating depends on the irradiation dose. Because of the varying response on thermal treatment, the dose-response curves show systematic differences depending on the applied procedure (single- or multi-aliquot method with or without heating). A model for the description of the CO_2^--signal-change is presented. The combination of two exponential saturation functions seems to be an adequate analytical description of the dose-response curve of the CO_2^--signal in foraminifera. Due to the limited thermal stability this signal can be used for dating foraminifera with ages up to about 190 ka. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The possibility of dating deep-sea sediments using the ESR-signals in foraminifera has been reported in several studies (Sato, 1982; Mangini et al., 1983; Siegele and Mangini, 1985; Barabas et al., 1988; Mudelsee et al., 1992).

Mudelsee et al. (1992) showed that dating of pacific foraminifera with the CO_2^--signal ($g = 2.0006$) is possible up to about a D_E of 250 Gy, corresponding to an age of 100 ka. Because of its longer lifetime, dating with the SO_3^--signal ($g = 2.0036$) seems possible up to 800 ka.

To investigate whether the ESR-method delivers reliable ages for arctic foraminifera we chose the sediment core PS1535-8/-10, where an independent $\delta^{18}O$-stratigraphy is available. This is of interest because in the majority of cases the $\delta^{18}O$-stratigraphy cannot be used for dating arctic sediments due to a lack of a continuous record of biogenic carbonate and to meltwater events influencing the $^{16}O/^{18}O$-ratio.

We concentrate our research on the CO_2^--signal, because as a result of this study, the SO_3^--signal appears only sporadically in arctic foraminifera. In foraminifera irradiation produces an interfering short-living signal (Barabas et al., 1992a) and the measurement of the CO_2^--signal requires heating after the irradiation. Here we also examine the effect of the heating procedure on the CO_2^--signal.

2. Sample material

The material for our study are selected planktonic foraminifera *Neogloboquadrina Pachyderma* (sieve fraction 125–250 μm) which is the most frequent species in sediments of the central Arctic Ocean. The sediment core PS1535-8/-10 is located in the Fram Strait at the southern boundary of the Arctic Ocean (78°44.8′N, 1°52.8′E; water depth: 2557 m). For the core PS1535-8/-10 a reliable $\delta^{18}O$-stratigraphy that could be used for dating ("$\delta^{18}O$-ages") as well as the water content of PS1535-8 are available (Köhler and Spielhagen, 1990; Spielhagen, pers. comm.).

3. Experimental

We created signal growth curves on irradition and studied the thermal behaviour on aliquots of 70–100 mg of foraminifera.

At most depths the content of foraminifera is so small that the single-aliquot method has to be used. Three depths (315, 379 and 463 cm) of the sediment core contained enough foraminifera enabling the multi-

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aliquot method. In detail we performed the following experiments:

1. The CO_2^--signal growth curves of six single-aliquots were measured using a heating procedure (1 h at 120°C) after each irradiation step. The maximum dose was 8000 Gy.

2. Three natural aliquots (depth 76 cm, corresponding to a δ^{18}O-age of 30 ka) were heated 200 min at 100, 120 and 140°C, respectively. The ESR-signals were measured every 20 min.

3. After irradiation the three multi-aliquot samples were stored at room temperature for four months. Then all aliquots were measured, heated for 60 min at 120°C and measured again.

ESR-measurements were done with a Bruker EMS104 spectrometer (X-band). Standard parameters used for the CO_2^--signal are: a microwave power of 50 mW, a modulation amplitude of 1.01 G and a field sweep of 40 G. All aliquots were normalized to weight and the signal intensity of an internal foraminifera-standard (pacific foraminifera of core RNDB 75P) that was always measured before and after a series of measurements. A ^{137}Cs γ-source (Deutsches Krebsforschungszentrum (DKFZ), Heidelberg) with a dose rate of 11 Gy/min was used for γ-irradiation . The contents of U, Th and K were measured via α- and γ-spectrometry.

4. Natural signals

The natural CO_2^--signal shows the expected development and grows with increasing core depth (Fig. 1), whereas the signals of the SO_2^- ($g = 2.0057$) and SO_3^--radicals show no significant increase with depth and have a similar development. Only at three depths (37, 77 and 628 cm) these signals are pronounced, and SO_3^- grows with irradiation. At all other depths the signal is in saturation.

On other cores from high latitudes we obtained similar results. This means that the SO_3^--signal cannot be routinely used for dating arctic foraminifera. The reason for this phenomenon will be examined in further studies.

5. Thermal behaviour of the CO_2^--signal

In foraminifera artificial irradiation produces a short-living signal with probably orthorhombic symmetry, (g-factors 2.0027/2.0020/2.0009) which interferes with the CO_2^--signal (Barabas et al., 1992a). To remove the short-living signal a heating procedure after irradiation is necessary. We analysed the effect of heating on the CO_2^--signal.

5.1. Natural signals

The natural signal of 30 ka old foraminifera shows an increase after the first 20-minute heating step ($T = 120$°C) (Fig. 2). Then the signal remains constant up to 200 min heating time. The peak-to-peak intensity of the CO_2^--signal after heating is about 10% bigger than before. The same result is obtained applying temperatures of 100 and 140°C. Fig. 3 shows the increase, denoted by Δ, determined in six other samples with different δ^{18}O-ages. In the natural spectra of foraminifera we did not detect the short-living signal produced by artificial irradiation. So the increase, Δ, cannot be explained by a signal overlapping with the short-living signal, as this signal is not present in natural samples (Barabas et al., 1992a).

Apparently, the natural CO_2^--signals grow significantly due to the heating treatment. The magnitude of the increase seems to depend on the age of the sample.

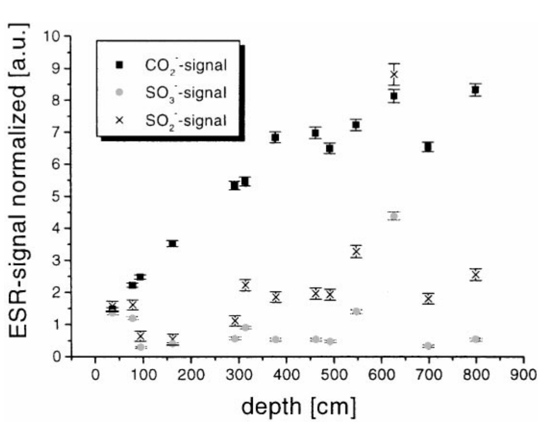

Fig. 1. Natural signals of 13 aliquots of PS1535.

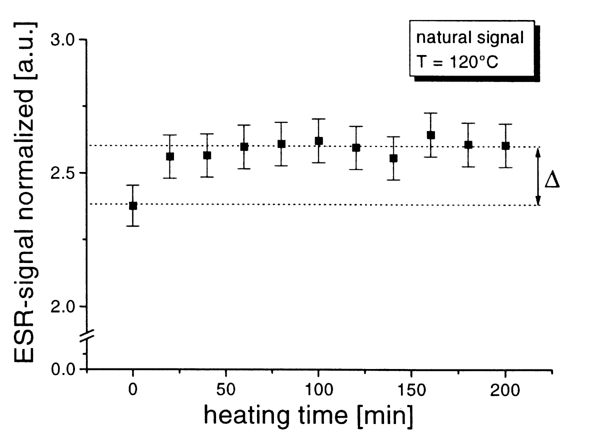

Fig. 2. CO_2^--signal-development of a natural aliquot (depth 77 cm, age 30 ka) due to heating at 120°C.

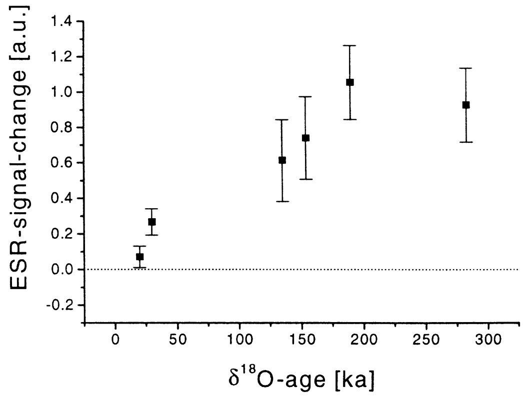

Fig. 3. CO_2^--signal-change Δ of natural aliquots by heating (1 h, 120°C), stratigraphic δ^{18}O-ages according to Köhler et al., 1990 and Spielhagen, pers. comm.

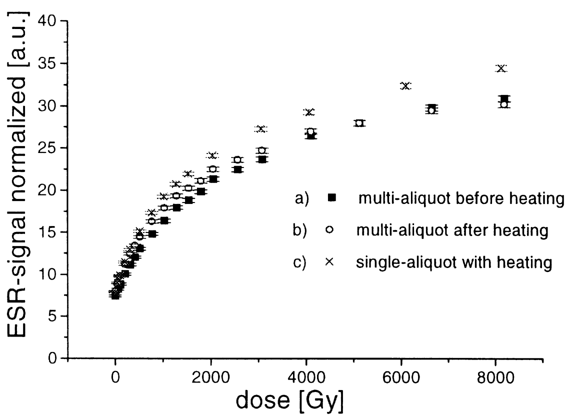

Fig. 4. CO_2^--signal growth curves of one depth (379 cm) obtained for the multi-aliquot (a, b) and single-aliquot (c).

5.2. Signals of irradiated aliquots

The dependence of the increase Δ on the irradiation-dose was studied using multi-aliquot samples of three depths (315, 379 and 463 cm). Six weeks after irradiation the short-living signal has no more influence on the peak-to-peak intensity of the CO_2^--signal. Four months after irradiation this short-living signal cannot be detected anymore. In Fig. 4 the signal growth curves four months after irradiation (depth 379 cm) before (a) and after (b) the heating treatment are plotted.

The difference between curves (b) and (a) corresponds to the change Δ of the peak-to-peak intensity due to heating (1 h, 120°C). Fig. 6a shows that this change of the ESR-signal, Δ, is dependent on the γ-dose. Below 5000 Gy the difference, Δ, is positive and has a maximum at about 1000 Gy. But in aliquots irradiated with more than 6000 Gy the signals decrease by heating. The same behaviour is observed at depths 463 and 315 cm (Fig. 6b).

The single-aliquot growth curve in Fig. 4, curve (c), reveals a large systematic difference between single- and multi-aliquot. The effect on the D_E is discussed below.

6. A model for the signal-change Δ as a function of dose

From the results above, we assume that irradiation produces a non-measurable precursor that can be transferred into a radical by heating. Recently, Idrissi et al. (1999) described an initial increase of the CO_2^-- (and CO_3^--) signal in irradiated monohydrocalcite. This was explained by the presence of a precursor feeding the radical by heating. The phenomenon is thought to be caused by anisotropic radicals which become isotropic. However, they did not have any evidence for increase of the signal in fossil samples. In contrast, we observe an increase of the natural CO_2^--signal in fossil foraminifera and the older samples display the larger increase of natural signals due to heating (Fig. 3).

To describe our observations, we assume the following simple model for the CO_2^--signal (Fig. 5):

1. Irradiation produces a precursor of the CO_2^--signal. We assume an exponential saturation function P(D) for the precursor production.
2. In addition to the known stable CO_2^--signal, irradiation produces a thermal unstable CO_2^--component. It can be removed by a short heating treatment. We assume an exponential saturating behaviour $S_U(D)$ for this production.
3. Both components are present in the natural sample.
4. Heating removes the unstable CO_2^--component and transfers the precursor to the (stable) CO_2^--radical ($S_P(D)$) instantaneously (within 20–60 min).

On the basis of our model, the measured CO_2^--signals are:

1. Before heating $S_1(D) = S_0(D) + S_U(D)$,
2. After heating $S_2(D) = S_0(D) + S_P(D)$,

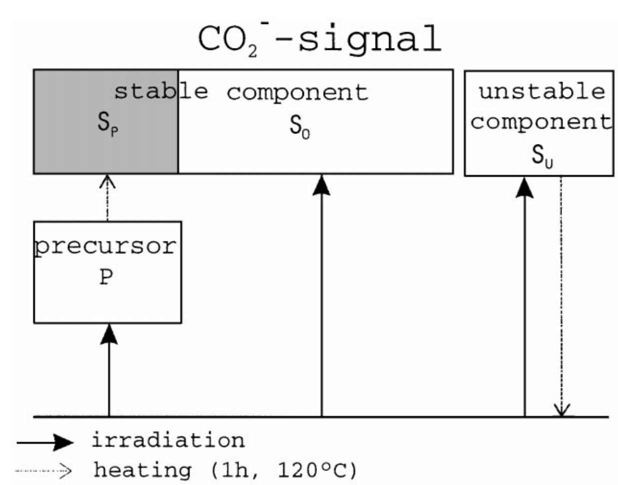

Fig. 5. Qualitative model for signal-change Δ.

where $S_0(D)$ denotes the stable CO_2^--component. The difference between these two signal growth curves is

$$\Delta(D) = S_2(D) - S_1(D) = S_P(D) - S_U(D)$$
$$= K_P\left[1 - \exp\left(-\frac{D + D_0}{D_P}\right)\right]$$
$$- K_U\left[1 - \exp\left(-\frac{D + D_0}{D_U}\right)\right] \quad (1)$$

D_0 is the natural irradiation dose, D_P, D_U are saturation dose for precursor and unstable CO_2^--component, respectively, and K_P, K_U are saturation level of precursor, unstable component.

7. Discussion

7.1. The signal-change Δ

The model was applied to the difference curve $\Delta(D)$ (Fig. 6a and b), using a least-squares fit. All three data sets can be described by function (1) using nearly identical parameters ($D_P \approx 400$ Gy, $K_P \approx 2.2$ a.u., $D_U \approx 18000$ Gy, $K_U \approx 8$ a.u. $D_0 \approx 200$ Gy). Because of the good concordance for the three different samples, we conclude that our assumptions are reasonable. The large error bars of Δ (the difference of two signals of similar magnitude) are the limiting factor of the fitting procedure, resulting in a large uncertainty for the parameters. Obviously, further work is necessary to confirm our conclusions.

7.2. The difference between single- and multi-aliquot

Multi-aliquots are heated only once, single-aliquots are heated after each irradiation step. As heating changes the peak-to-peak intensity of the CO_2^--signal because of the transfer of precursors to radicals, there is a difference between the signal growth curves of the single- and multi-aliquot methods (curves (c) and (b) in Fig. 4). It is of interest which of both procedures comes closer to the natural development of the signals. One could guess that natural storing conditions are better represented by the single-aliquot procedure. But still it has to be examined which method is the better approximation. The difference in the equivalent dose D_E derived from the two different methods amounts to between 5% (sample 379 cm) and 19% (sample 463 cm) (Table 1). Generally, for arctic samples the single-aliquot method is applied due to small amounts of foraminifera available.

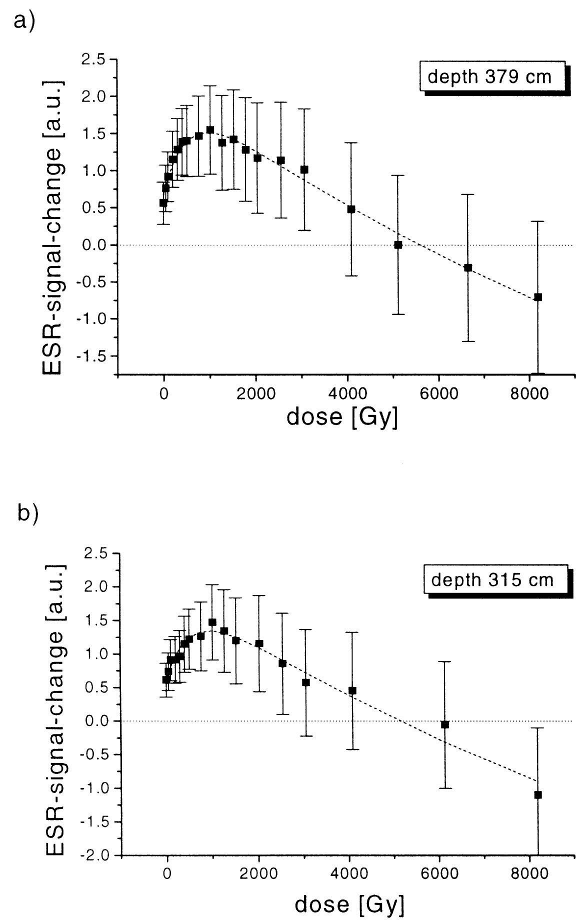

Fig. 6. a and b: Signal-change Δ of irradiated aliquots by heating (1 h, 120°C). The dashed lines were derived from Eq. (1) (parameters: see text).

7.3. Dating of core PS1535

According to Barabas et al. (1992b) the stable CO_2^--signal has two components of which one is more stable than the other. Supposing that these two components have different irradiation-sensitivities, the signal growth curve will have two components as well. In this case the CO_2^--signal growth curve should be a sum of two exponential saturation functions:

$$S(D) = K_1\left[1 - \exp\left(-\frac{D + D_E}{D_1}\right)\right] + K_2\left[1 - \exp\left(-\frac{D + D_E}{D_2}\right)\right].$$

With this function a good fit of the signal growth curves of all foraminifera studied could be achieved. Neither the single exponential saturation function nor the single exponential saturation function with an additional exponent γ (Grün and MacDonald, 1989) (γ-function, here $\gamma = 0.86$) were able to fit the measured data satisfyingly over the dose range of 8000 Gy applied for the foramini-

Table 1
Data of PS1535-8/-10

Depth (cm)	δ^{18}O-age (ka)	Method	D_E (Gy)	^{232}Th (dpm/g)	^{230}Th (dpm/g)	^{238}U (dpm/g)	^{234}U/^{238}U	K (%)	Water (%)	ESR-ages (ka)
37	19.6	Single-aliquot	42.9 ± 0.8	2.77 ± 0.11	3.66 ± 0.13	1.66 ± 0.10	0.94 ± 0.09	2.90 ± 0.20	69.50 ± 6.0	21.8 ± 2
77	29.7	Single-aliquot	70.7 ± 1.4	2.63 ± 0.12	4.63 ± 0.14	1.59 ± 0.11	0.96 ± 0.10	2.69 ± 0.20	65.61 ± 6.5	30.8 ± 2
315	123	Multi-aliquot	318.5 ± 25.1	2.79 ± 0.12	3.52 ± 0.14	1.82 ± 0.08	0.89 ± 0.06	2.72 ± 0.20	59.98 ± 5.5	130.6 ± 10
379	135	Single-aliquot	306.8 ± 18.3	2.64 ± 0.10	3.35 ± 0.12	3.19 ± 0.15	1.02 ± 0.07	2.62 ± 0.20	48.04 ± 5.0	137 ± 11
379	135	Multi-aliquot	323.0 ± 29.5	2.64 ± 0.10	3.35 ± 0.12	3.19 ± 0.15	1.02 ± 0.07	2.62 ± 0.20	48.04 ± 5.0	148 ± 17
463	154	Single-aliquot	301.7 ± 17.6	2.44 ± 0.10	2.86 ± 0.10	1.85 ± 0.11	1.07 ± 0.06	2.59 ± 0.20	41.48 ± 4.6	130 ± 10
463	154	Multi-aliquot	370.8 ± 30.5	2.44 ± 0.10	2.86 ± 0.10	1.85 ± 0.11	1.07 ± 0.06	2.59 ± 0.20	41.48 ± 4.6	154 ± 14
548	190	Single-aliquot	387.8 ± 28.5	2.93 ± 0.20	2.23 ± 0.20	1.77 ± 0.10	0.94 ± 0.10	2.70 ± 0.20	50.00 ± 5.0[a]	191 ± 20
700	282	Single-aliquot	416.6 ± 31.8	2.35 ± 0.20	1.61 ± 0.12	1.50 ± 0.10	1.01 ± 0.10	2.25 ± 0.20	50.00 ± 5.0[a]	243 ± 30

[a] Assumption (watercontent of PS1535-10 was not measured).

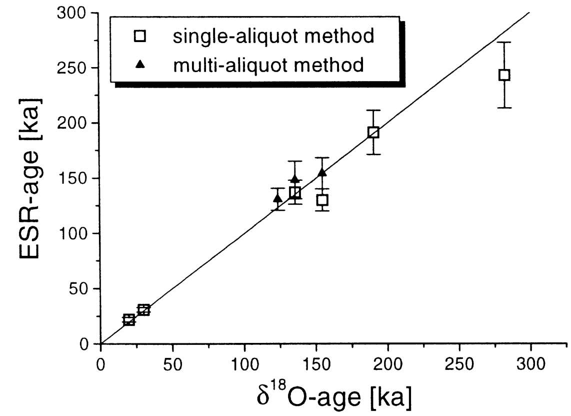

Fig. 7. ESR-ages of PS1535 compared to δ^{18}O-ages (Köhler et al., 1990; Spielhagen, pers. comm.).

fera in this work (Hoffmann et al., in preparation). The normalized χ^2-values for the above function, the γ-function and the single exponential saturation function were (0.2–0.7), (1.8–9) and (3–12), respectively.

Table 1 lists the equivalent-doses D_E and the contents of U, Th and K of the sediment. We calculated the ESR-ages using a recently developed program (ESRA) that takes into account the radioactive disequilibria due to Thorium-excess and authigenic Uranium (Hoffmann et al., in preparation). Fig. 7 shows the ESR-ages compared to δ^{18}O-ages. Both, single- and multi-aliquot method yield good results and agree with the δ^{18}O-ages up to 190 ka.

8. Conclusions

The heating procedure (1 h, 120°C) which is commonly applied for removing the short-living signal that interferes with the CO_2^--signal, transfers precursor to the CO_2^--signal. Also it removes the unstable component of the CO_2^--signal. The presented model explains the signal-change by heating and it qualitatively explains the difference between the signal growth curves of single- and multi-aliquot methods.

The analytical description of the CO_2^--signal growth curves of foraminifera as the sum of two single exponential saturation functions yields best results. Dating of arctic foraminifera with CO_2^--signal is possible up to 190 ka.

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