Research Note

Drying of samples may alter foraminiferal isotopic ratios and faunistic composition

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ABSTRACT: Drying of marine sediment samples is required to determine the number of foraminifers per g as an indication for paleoenvironmental changes. Our results show that oven-drying may lead to alteration of the stable oxygen isotope signal. The $\delta^{18}O$ values of *Turborotalita quinqueloba* (Natland) from dried samples are as much as 2.8‰ lighter than their equivalent from samples which were not dried before preparing. Differences in the isotopic composition of *Bulimina aculeata* (d`Orbigny) were less dramatic (<0.5‰). The drying as well altered the composition of benthic assemblages, thus oven-drying should be generally avoided.

INTRODUCTION

Foraminifers and their stable isotope compositions are widely used as paleoenvironmental proxies because of their wide distribution in most marine settings and their sensitivity to environmental changes. Particularly the oxygen isotope ratios of planktic and benthic foraminifers have become one of the most important tools in paleoclimatology. Concerns about the validity of our stable isotope data were raised after it became evident that many of the observed fossil foraminifers from the study area displayed poor preservation. We hypothesized that drying of samples could be connected to this phenomenon. Drying of bulk sediment samples in an oven is a common method to determine the dry weight, necessary to calculate the number of foraminifers per g. A different approach, described below, was thus applied to the second set of samples. The goal was to determine the influence of oven-drying on the faunistic and isotopic composition of foraminifers.

MATERIAL AND METHODS

Core GeoTü KL 71 was recovered during the Meteor cruise M44/1 in December 1999 in the Sea of Marmara from 560m water depth. The core was kept in cold storage to prevent desiccation. An organic-rich interval corresponds to Holocene Sapropel S1 (Sperling et al. 2001). The first set of samples was taken in 5cm intervals and dried in an oven at 50°C for several days (dried samples in the following). The dry weight was noted, the samples washed through a 63µm sieve, and picked of all benthic foraminifers. Samples were also picked for specimens of the planktic species *Turborotalita quinqueloba* and the benthic species *Bulimina aculeata* to measure oxygen and carbon isotope ratios. The tests were ultrasonically cleaned in distilled water, and measured following the standard procedures at the Leibniz-Laboratory for Stable Isotope Research, Kiel. The results are reported as per mil deviation with respect to the international standard V-PDB, with a reproducibility of less than 0.1%. The second row of samples was taken in 1-2cm intervals. The volume of the sediment was noted, the samples split, and one set washed immediately through a 63µm sieve without allowing the sediment to dry (wet samples in the following). Samples were picked for foraminifers and stable isotope analysis accordingly. The determination of the dry weight, necessary to calculate "Foraminifers per g", was conducted by the weighing of dried split samples of known volume.

RESULTS

Stable oxygen isotopes

Stable oxygen isotope records of core GeoTÜ KL 71, plotted against the sediment-depth, are presented in text-figure 1. The $\delta^{18}O_{wet}$ values ($\delta^{18}O$ of wet samples) of *T. quinqueloba* vary from –0.3 to 2.32‰, whereas dried specimens ($\delta^{18}O_{dry}$) showed considerable depleted ratios, ranging from –1.82 to 1.39‰. The benthic species *B. aculeata* depicts depleted $\delta^{18}O_{dry}$ values as well ($\delta^{18}O_{wet}$: 1.7 to 3.16 vs. $\delta^{18}O_{dry}$: 1.15 to 2.83‰). In addition to this offset, dried and wet oxygen isotope ratios of *T. quinqueloba* show markedly different down-core trends. The wet curve is comparatively smooth, with the most depleted $\delta^{18}O_{wet}$ values occurring after the end of sapropel deposition. The $\delta^{18}O_{dry}$ values show large down-core fluctuations, and the most depleted values occur within the sapropel.

Stable carbon isotopes

The $\delta^{13}C_{dry}$ values of *T. quinqueloba* are slightly depleted, as compared with their wet counterparts ($\delta^{13}C_{wet}$: -3.23 to –1.92 vs. $\delta^{13}C_{dry}$: -3.22 to –2.03‰). Minor differences are also shown by *B. aculeata* ($\delta^{13}C_{wet}$: -2.15 to –0.9 vs. $\delta^{13}C_{dry}$: -1.93 to –0.89‰). Both species show similar down-core trends of dried and wet samples.

Benthic foraminiferal assemblages

The down-core distribution of three of the most abundant benthic species in core GeoTü KL 71 is shown in text-figure 2. *Chilostomella oolina* (Natland) is present in variable numbers in almost every wet sample above 1.20m core depth; whereas

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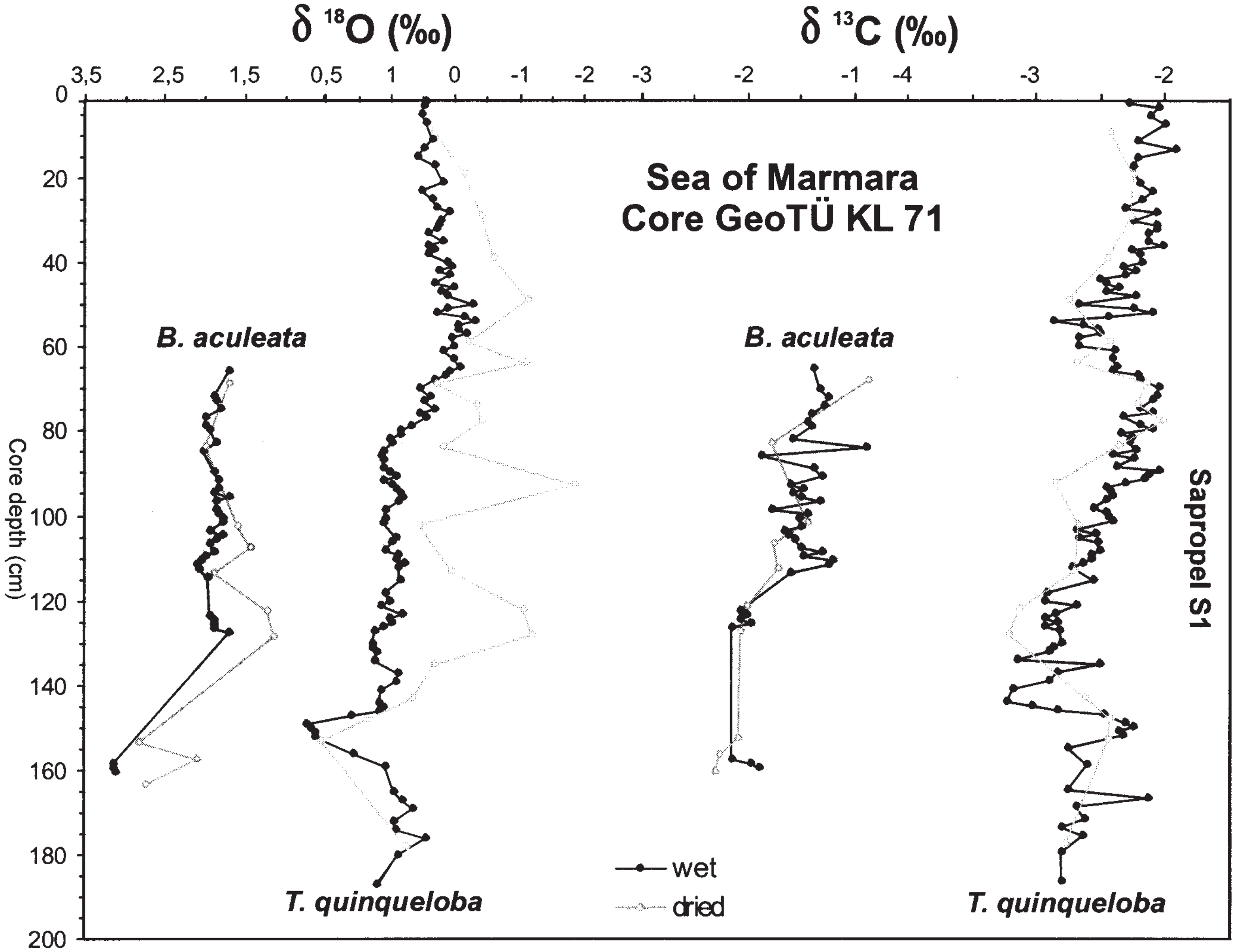

TEXT-FIGURE 1
Stable isotope records of *B. aculeata* and *T. quinqueloba* in core GeoTü KL 71.

PLATE 1
SEM images of foraminiferal specimens from core GeoTü KL 71.

1-4 *Turborotalita quinqueloba* (Natland), 1: wet sample from 91cm core depth, 2: detail from 1, 3: dried sample from 91cm core depth, 4: detail of 3.

5-8 *Globobulimina affinis* (d`Orbigny), 5: wet sample from 101cm core depth, 6: detail of 5, 7: dried sample from 101cm core depth, 8: detail of 7.

9 *Sigmoilinita* sp., partly dissolved with filling of framboidal pyrite, dried sample from 91cm core depth.

10 Pyrite framboids in *Turborotalita quinqueloba* (Natland), wet sample from 91cm core depth.

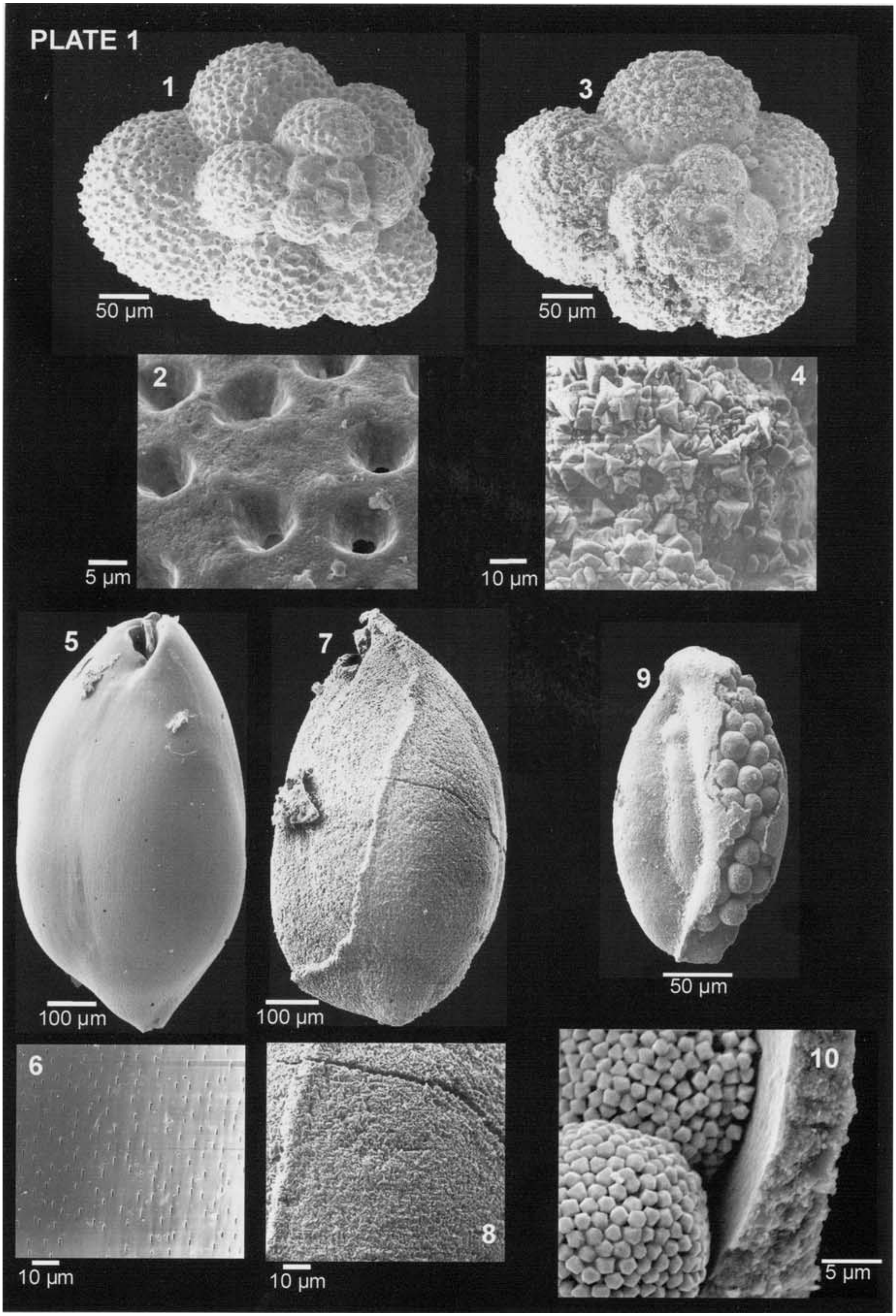
PLATE 1
1
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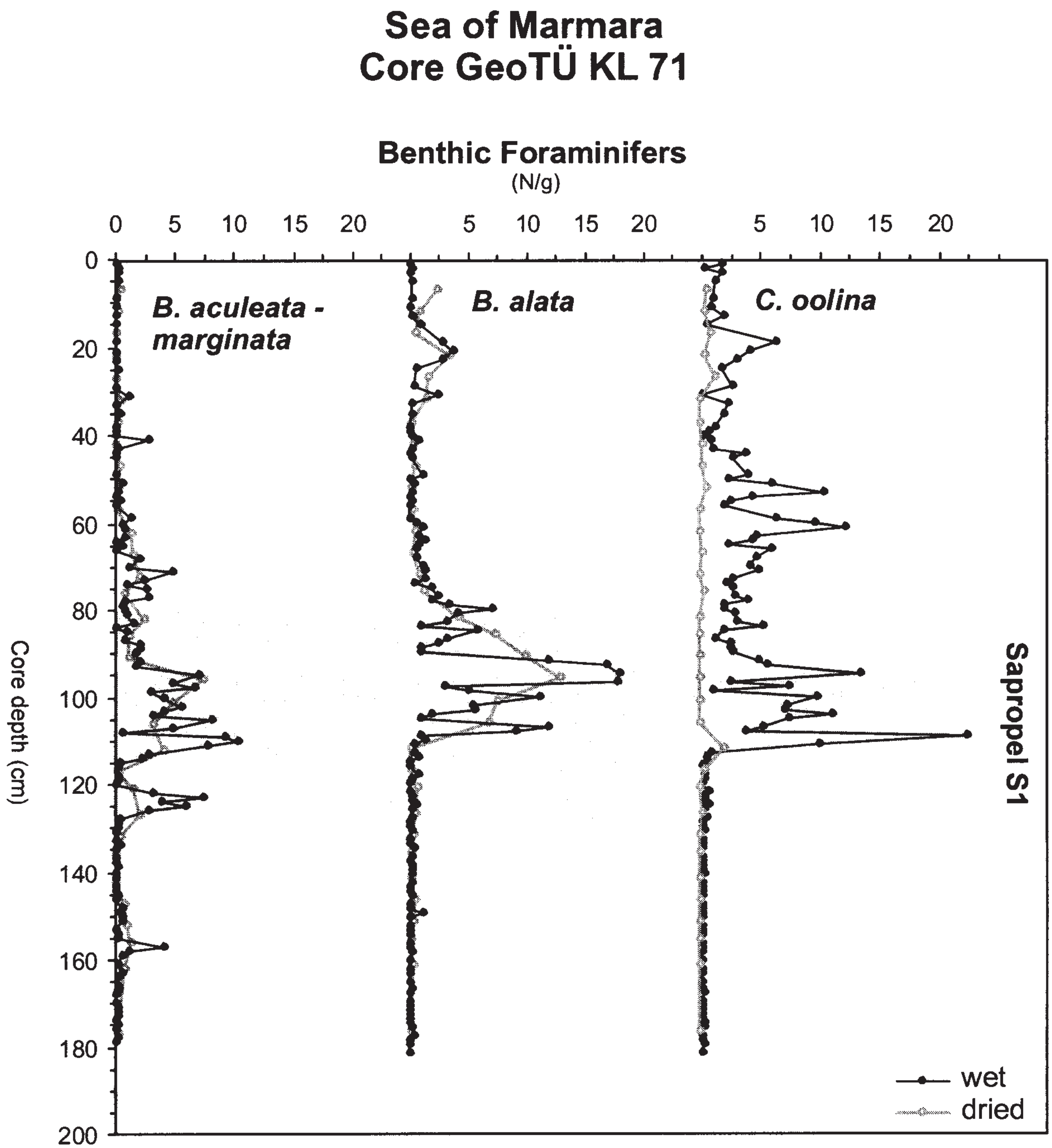

TEXT-FIGURE 2
Down-core distributions of some abundant benthic foraminifers in core GeoTü KL 71.

dried samples yield few or none. Other benthic species such as *Bolivina alata* (Reuss), *B. aculeata*, and *Bulimina marginata* (d'Orbigny) show few apparent differences between dried and wet samples.

DISCUSSION

The stable isotope composition of planktic, and to a lesser extent, of benthic foraminifers differs considerably depending on the method chosen for preparation. The highest offset occurs within the TOC-rich sapropel, where *T. quinqueloba* shows as much as 2.8‰ artificial $\delta^{18}O$ depletion. The deviation of $\delta^{13}C$ is less pronounced and rarely exceeds 0.5‰ artificial depletion. Specimens of *T. quinqueloba* have been investigated under light microscope and SEM to determine possible causes of the artificial depletion. Tests of *T. quinqueloba* from wet samples are translucent with a glassy appearance when observed under the light microscope, whereas dried tests often display a dull white color. The investigation under the SEM reveals that inorganic calcite crystals have been grown inside and outside dried tests (pl. 1, figs. 3-4). In some instances, crystals grew big enough to be recognized under the light microscope, but more often the size is less than 1µm. Benthic species such as *Globobulimia affinis* (d'Orbigny) display smooth surfaces when unaltered but signs of dissolution and precipitation of inorganic calcite as well (pl. 1, figs. 5-8). We attribute the change in color and the isotopic depletion to the precipitation of inorganic calcite on the foraminiferal tests.

Ultrasonic cleaning of the tests could not remove the overgrowths, thus only exceptionally well preserved specimens with a glassy appearance should be used for stable isotope analysis.

Since this type of preservation was rather rare in dried samples from the study area, we recommend that oven-drying is generally avoided. Freeze-drying as applied by some laboratories as an alternative preparing method (Abelmann 1988) may overcome this problem.

A possible explanation for the dissolution of calcareous foraminifers may be the oxidation of pyrite during desiccation. Pyrite is a common feature in organic rich sediments and often occurs inside foraminiferal tests as framboidal (raspberry-like) crystals (pl. 1, figs. 9-10). The results of a soil drainage experiment (Ritsema and Groenenberg 1993) indicate that after air enters the sample, O_2 oxidizes pyrite, thus producing H_2SO_4 (equation 1).

$$4FeS_{2(s)} + 15O_{2(g)} + 14\,H_2O \rightarrow 4Fe(OH)_{3(s)} + 16\,H^+_{(aq)} + 8SO_{4\,(aq)}^{2-} \quad (1)$$

The decrease in pH results in the dissolution of carbonate.

$$CaCO_{3(s)} + 2\,H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2O + CO_{2\,(foraminiferal)} \quad (2)$$

This process may explain the almost complete absence of *C. oolina*, an important oxygen depletion indicator (Sen Gupta and Machain-Castillo 1993), in dried samples. Other species are not notably influenced, which points to differential dissolution resistance. Differential *in situ* resistance of benthic species was noted before (e.g. Boltovskoy and Totah 1992), our results indicate that differential dissolution may also occur as a result of sample preparation.

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