

Laser Ablation ICP-MS Analysis of Marine Sediments from the Oxfordian (Late Jurassic): A Comparison of Three Preparation Techniques

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Abstract: Trace element analyses of marine sediments provide important information on past oceanographic and climatic changes. Five samples consisting of grey to black marls with layers of carbonate nodules (so called “Terre Noires” from a 102 m long profile from Oze, Southern France) were prepared in three different ways to find the most appropriate preparation technique for major, minor and trace elements by LA-ICP-MS analysis:

1. Powder pills were dry pressed after milling 30 g of a sample down to fine powder (around 1 µm in size).
2. Cubes of marl were cut out of the hand specimens and analyzed directly after polishing.
3. Fused glasses were prepared by mixing a 5:1 ratio of flux (Li₂B₄O₇) to finely ground samples.

The LA ICP-MS analysis was performed using a pulsed 193 nm ArF Excimer laser (with a homogenized beam profile) in combination with an ELAN 6100 DRC ICP-MS. Samples were measured for the following elements: Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Sn, Cs, Ba, La, Ce, W, Tl, Pb, Bi, U. Analytical precision based on replicate analyses depends strongly on the preparation method. Typical RSDs (relative standard deviations) from analyses of the mentioned elements in powder pills range between 5 % (Mn, Sr) and 50 % (Zn). For the cubes generally higher RSDs were found than in the powder pills, between 5 % (Sc) and 90 % (Cu). Generally, RSDs from fused glass pills were lower than 6 %. Heterogeneous element distribution in the cubes leads to non-representative sampling by the laser and these data can therefore not be considered for interpretation of the results. From the statistics it can be seen that the analyses of powder pills are better but the RSDs are still unacceptably high. Statistically the best analytical results are obtained from the homogeneous glass pills. Therefore lithium borate fused glasses is the preferred method of preparation for sediment analysis.

Keywords: Laser ablation, marine sediments, oxfordian, sample preparation.

INTRODUCTION

The distribution of trace elements in marine sediments provides essential information about the seawater chemistry in the past, redox state of bottom water, weathering and erosion processes, as well as about sudden changes in oceanic circulation. Changes in biogeochemical cycles, biological productivity, tectonic activity, wind strength and volcanic, hydrothermal, hydrogenous, eolian and fluvial sources can also be deduced from the knowledge about the repartition of trace elements. Elements like Fe, K, Mg, Ti and Co are mainly of terrestrial origin. Ba, P, Zn are seen as nutrient related elements [1]. Calvert and Pedersen [2] state that the concentrations of trace and minor elements in marine sediments reflects the range of chemical, oceanographic and sedimentary controls on their supply to, their distribution in and their removal from the ocean. Some minor and trace elements are precipitated where free dissolved sulphide is present (Cu, Cd, Ni, Zn) without undergoing a valency change, whereas others undergo a change in valency and are

either more efficiently adsorbed onto solid surfaces under oxic (iodine) or anoxic (vanadium) conditions or are precipitated under anoxic conditions (Cr, Mn, Mo, Re, U, V) [2, 3]. Hence, the enrichment of these minor and trace elements relative to their crustal abundances indicates that the host sediments accumulated under anoxic conditions. Enrichment of Fe occurs mainly in terrestrial, platform and shelf regions.

Fig. (1) indicates the location in France from which the samples were collected. The samples consist of the so called Terres Noires from Oze, France (grey to black marlstone with carbonate nodules parallel to the bedding). These nodules are circular to oval in cross section, and about three to twenty cm in diameter. These nodules become more abundant in the upper part of the section. The section from which the examined samples were taken was deposited in the Tethyan Subalpine Basin, a deep epeiric basin influenced by tectonics related to the opening of the Alpine Tethys and the Atlantic. The “Terres Noires” facies deposited in the Early Oxfordian during the cordatum-antecedens (ammonite) subzones consists of dark marlstones with carbonate contents commonly between 30 and 40 wt-%. Organic carbon content is in average 1 % [4-6]. Organic matter is a mixture of mainly marine and sparse terrestrial material based on bio-marker evidence. Detrital minerals include clay minerals and

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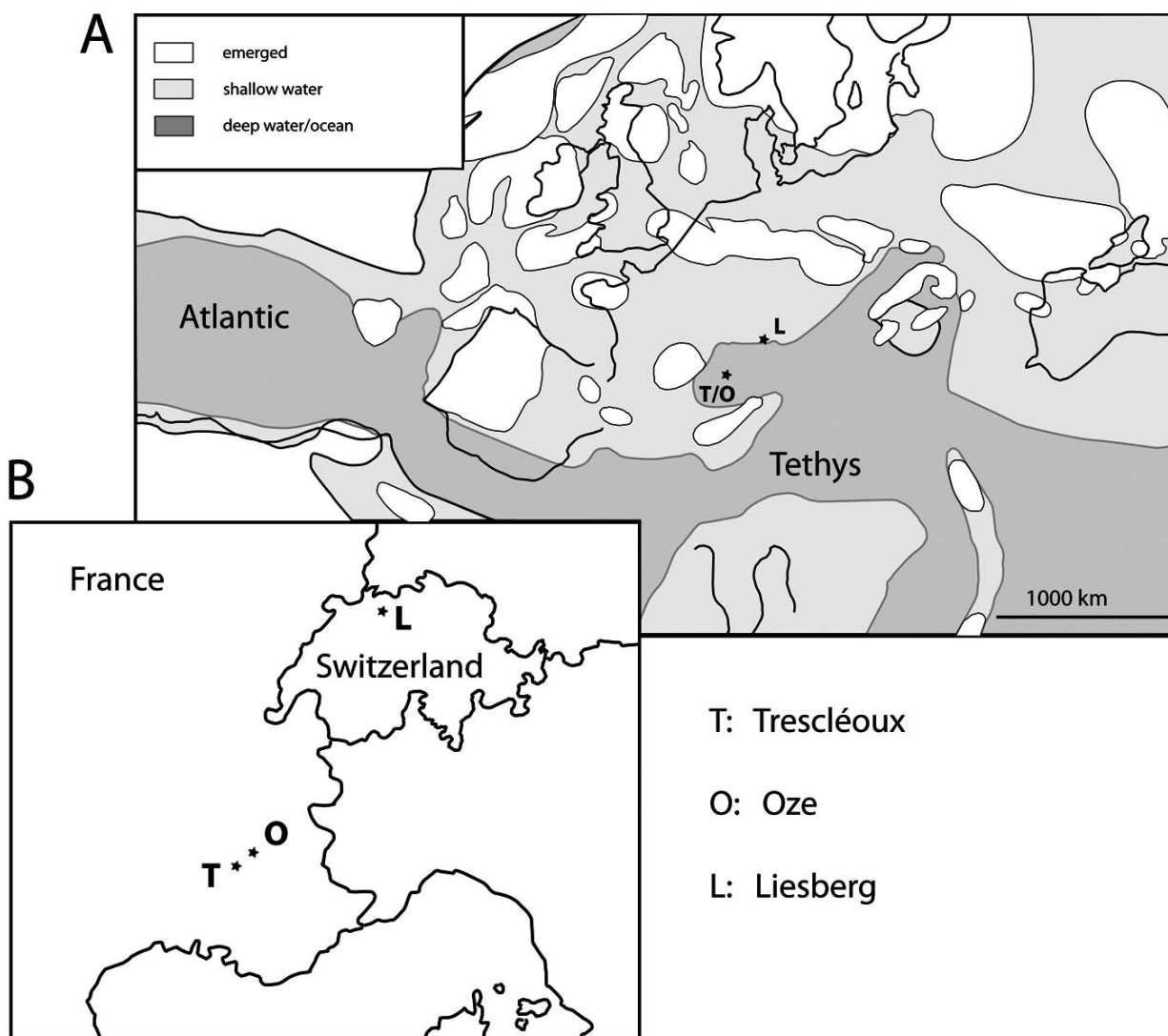


Fig. (1). Location map (A) and paleogeography (B) of the studied sections. T = Trescléoux, O = Oze. Black lines represent modern coast lines and state borders. Paleomap modified after Ziegler (1988). Location map from [4].

quartz, carbonate include micrite, coccoliths and foraminifera: macrofossils are rare and consist mainly of ammonites and belemnites. The marlstones are bedded at decimeter- to meter-scale [4-6].

Analyses of trace elements in marine sediments are usually carried out by X-ray fluorescence (XRF, see e.g. [7-9]) or solution nebulisation ICP-MS (e.g. [10, 11]). In comparison to XRF, ICP-MS analysis can provide improved detection limits and an expanded list of elements, but the conventional approach using solution nebulization requires the sample to be completely dissolved. Sample dissolution is a laborious process that may be complicated by incomplete sample digestion, volatile element escape, contamination, and other issues (see [12]). An alternative approach is to determine major, minor and trace elements by laser ablation ICP-MS. LA-ICP-MS is a well-established, powerful tool for the analysis of major, minor and trace elements requiring minimal or minor sample preparation [13-20].

This paper is aimed at the development of an accurate and precise LA-ICP-MS technique for the whole rock analysis of marine sediments. We evaluate the following analytical approaches:

1. Powder pills were dry pressed after milling 30 g of a sample down to fine powder (around 1 μm in size).
2. Cubes of marl were cut out of the hand specimens and analyzed directly after polishing.
3. Fused glasses were prepared by mixing a 5:1 ratio of flux ($\text{Li}_2\text{B}_4\text{O}_7$) to finely ground samples.

Concerning the first approach, Sylvester [17] mentions some studies (see references therein) in the late 1980s and early 1990s where the suitability of pressed powder pellets for whole rock chemical analysis were evaluated. The main finding of these early studies was that quantitative data (accurate to 5 % or better) could be achieved only if calibration standards and unknowns were closely matched in terms of composition and mineralogy.

The second approach was also used by Jackson *et al.* [21] and Pearce and Mann [22]. Jackson *et al.* [21] concluded that LA-ICP-MS is capable of rapid, precise and accurate determination of concentrations of trace elements in sediments and the limit of detection is typically less than 1 ppm for many elements.

The third approach was studied intensively by Becker and Dietze [16], Sylvester [17], Günther *et al.* [18], Nesbitt *et al.* [23], Ødegård and Hamester [24], Yu *et al.* [25] and Eggins [26]. Nesbitt *et al.* [23] demonstrated that standard X-ray fluorescence glass discs are a useful tool in determining REE patterns whereas Ødegård and Hamester [24] conclude that their method (high resolution double-focusing, magnetic sector inductively coupled plasma-mass spectrometer with a ultraviolet laser ablation) is a valuable supplement to XRF for low level element concentration measurements. Becker and Dietze [16] mention the simple, fast, cheap and easy-to-handle sample preparation for the production of homogeneous targets for LA-ICP-MS from inhomogeneous geological powder samples by lithium-borate fusion. Sylvester [17] used a similar method of sample preparation as Becker and Dietze [16] and found that within-session reproducibility for most elements greater than 1 to 5 ppm in concentration was better than 5 % RSD. Below 1 ppm, RSDs tended to be > 5 % – with the low RSDs reflecting the homogeneity of lithium-borate glasses and the higher RSDs reflecting larger analytical error at these low concentration level. Günther *et al.* [18] used geological samples fused with $\text{Li}_2\text{B}_4\text{O}_7$ and calibrated them successfully without matrix-matched standards. Yu *et al.* [25] mentioned a combined XRF and laser ablation ICP-MS technique on glasses prepared by fusing the sample with a lithium borate flux. Advantages of this technique include the ability to measure major and trace element abundances on a single sample using a quick and simple preparation that attacks resistant phases such as zircon without the need for acid dissolution. Yu *et al.* [25] moreover mentioned that by using a matrix-matched calibration, agreement of the LA-ICP-MS results with published reference values or those obtained by solution ICP-MS is ≤ 10 % relative. Analytical precision based on replicate analyses is typically ≤ 5 % RSD. Eggins [26] mentioned the following advantages of preparing fused lithium-borate discs: (1) robust sample digestion and reduced analyte recovery problems, (2) potential integration with XRF analysis and (3) greater spectral simplicity compared to SN-ICP-MS. According to Eggins [26], 90 % of determinations of twenty-five trace elements are indistinguishable from published reference values at the 95 % confidence level.

This work was carried out to determine unambiguously the best sample preparation method for the analysis for major, minor and trace element contents of the aforementioned marine sediments. 1. Powder pills were dry pressed. 2. Cubes of marl were cut out from the hand specimens and analyzed directly. 3. Fused glasses were prepared with a suitable flux. So far no studies using LA-ICP-MS in connection with any of the above mentioned preparation methods were ever published in the scientific literature.

Our goal was to establish the most appropriate sample preparation and analytical method for the analysis of major, minor and trace element contents of the above mentioned

marine sediments, the so called Terres Noires from Oze, France (grey to black marlstone with clearly visible carbonate nodules parallel to the bedding). For the locations see Fig. (1).

2. EXPERIMENTAL

2.1. Sample Preparation

Five samples consisting of the Terres Noires from Oze were prepared in three different ways:

1. Powder pills (one centimeter in diameter) were dry pressed after crushing and milling 30 g of a sample down to very fine grains (around 1 μm in size) for five minutes in a micronising mill (MacCrone). This mill is used for sample preparation for XRD analyses as well.
2. Cubes of marl (one on two centimeters) were cut out of the hand specimens and analyzed directly after polishing.
3. Fused glasses were prepared by mixing a 5:1 ratio of flux to the finely ground samples (appr. 1.5 g, same procedure of grinding as for powder pills). After determination of the loss of ignition and careful homogenization the samples were transferred to Pt crucibles and melted at 1100°C in a top loading furnace (Claisse M4 Fluxer from Corporation Scientifique Claisse, Sainte-Foy, Québec, Canada) for 15 min. Automatic agitation ensured a good homogeneity of the melt. The melt was automatically poured onto Pt plates and air cooled before further use. XRF analyses of the fused glasses to determine major elements to be used as internal standards were carried out at the institute for mineralogy and petrography at ETH Zurich using a wave-length dispersive X-ray fluorescence spectrometer (WD-XRF, Axios, PANalytical). For reference see [18]. The glasses were broken into small pieces manually and ablation was performed on the places of fracture.

2.2. Laser Ablation Analysis

The LA ICP-MS analyses of major, minor and trace elements were performed using a pulsed 193 nm ArF Excimer laser (Lambda Physik, Germany) with a homogeneous beam delivery prototype system similar to a Geolas system (Microlas, Germany, see [14]) in combination with an ELAN 6100 DRC (Perkin Elmer, Canada) ICP-MS. Typical instrumental settings are summarized in Table 1. A laterally homogeneous energy distribution is characteristic for the laser system used. The optical setup of the beam allows the use of crater diameters between 4 and 100 μm at constant energy density on the sample by using different apertures for shaping the laser. A CCD camera permits the observation of the sample during ablation. The differently prepared samples were loaded along with the glass reference standards in a 15 cm^3 ablation cell and put on the stage of a modified petrographic microscope. To the laser ablation carrier gas, helium, the make up gas argon was admixed after the ablation cell and the aerosole carried to ICP-MS. The linear dynamic range of about 9 orders of magnitude in dual detector mode could be achieved by dual detector calibration.

Analyses were performed in sequence and every ablation was stored individually as a transient signal. 230 readings were measured per replicate. The elements measured are

listed in Table 2 and cover all elements of interest in marine sediment samples accessible by ICP-MS. Five randomly

selected spots per sample were ablated in order to detect potential heterogeneities within the sample.

Table 1. LA-ICP-MS Device and Operating Conditions

Excimer 193 nm ArF Laser Compex 1101	
Output energy	50 mJ
Energy density on sample	17 J/cm ²
Pulse duration	15 ns
Repetition rate	10 Hz
Pit sizes	40 / 90 µm
Ablation cell	Plexiglass with anti-reflection coated silica glass window
Cell He gas flow	1.05 l min ⁻¹
ELAN 6100 quadrupole ICP-MS	
Nebulizer gas flow	0.95 l min ⁻¹
Auxiliary gas flow	0.8 l min ⁻¹
Cool gas flow	15 l min ⁻¹
Rf power	1400 kV
Detector mode	Dual, 9 orders of magnitude linear dynamic range
Quadrupole settling time	3 ms
Data acquisition parameters	
Sweeps per reading	1
Reading per replicate	230
Replicates	1
Dwell time per isotope	10 ms
Oxide production rate	< 0.5 %

Table 2. Element Concentrations and Standard Deviations (in ppm) as Measured by LA-ICP-MS (Three Analyses Per Average)

	OZ15						OZ265					
	Cube		Powder Pill		Fusion		Cube		Powder Pill		Fusion	
	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.
Na	1500	1100	2200	1000	2350	30	1600	1400	2500	900	2431	15
Mg	3600	900	6000	800	5970	80	5000	2000	7100	600	7350	60
Al	15000	5000	38000	9000	36800	200	30000	20000	56000	7000	58800	500
Si	45000	13000	160000	40000	146100	1100	160000	100000	210000	20000	195100	1700
P	41000	11000	19000	3000	16700	200	120	70	170	30	288	20
K	2600	1300	9000	3000	7650	60	8000	6000	14000	2000	13130	50
Sc	3.4	0.6	6.4	1	8.66	0.13	10	4	8.4	1	10.8	0.7
Ti	500	200	1600	300	2218	17	2100	1900	2800	400	3481	10
V	30	11	65	13	70.5	0.3	60	40	91	11	98.2	1
Cr	12	7	41	10	57	5	50	30	80	20	80	6
Mn	340	130	440	30	410	3	160	60	220	20	213.8	1.2
Fe	17000	4000	24000	6000	22700	200	21000	9000	26000	2000	27350	180
Co	1.3	0.3	5	2	4.4	0.4	4	3	6.3	0.6	6.72	0.19
Ni	23	6	42	13	34	9	35	17	51	5	49	8
Cu	3	3	15	7	12.3	1.5	15	9	18	2	15.9	0.7
Zn	26	11	130	60	71	5	60	30	78	9	55.1	1.2
As	2.1	0.6	5.2	1	4.4	0.4	8	5	7.6	0.9	5	0.8
Rb	14	7	57	17	40.6	0.6	50	30	86	13	73.7	1.6
Sr	820	50	660	20	654	5	350	40	327	18	337.7	0.7

(Table 2) Contd.....

	OZ15						OZ265					
	Cube		Powder Pill		Fusion		Cube		Powder Pill		Fusion	
	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.
Y	210	50	113	19	111.8	1.7	11	5	13	3	18.2	0.4
Zr	23	6	37	8	130	3	50	40	48	7	146.6	1.2
Nb	3.3	2	7.9	1.7	11.1	0.3	11	10	13	2	18.6	0.4
Sn	0.84	0.18	2.5	1.3	3.3	0.5	1.6	0.9	2.7	0.4	3.8	0.6
Cs	1	0.5	4.5	1.2	3.01	0.15	4	3	6.7	1	5.9	0.3
Ba	24	11	77	18	77.6	1.7	80	60	119	17	127.3	1.2
La	230	60	130	20	121.9	1.4	20	9	24	3	26.4	0.4
Ce	500	140	310	50	279	3	36	15	46	9	46.1	0.4
W	0.27	0.11	0.7	0.2	0.77	0.1	0.7	0.6	1.3	0.3	1.28	0.18
Pb	2.5	0.5	13	11	5.7	0.3	13	10	14	2	10.4	0.3
U	1.6	0.5	1.7	0.3	1.86	0.05	0.9	0.8	1.3	0.4	1.59	0.07

	OZ279						OZ300					
	Cube		Powder Pill		Fusion		Cube		Powder Pill		Fusion	
	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.
Na	3000	1800	2400	400	2430	50	2000	900	2100	300	2170	20
Mg	9000	5000	9400	1500	9630	140	5700	1300	5800	1300	5790	60
Al	44000	8000	51000	6000	54800	600	50000	30000	44000	13000	45300	400
Si	139000	18000	155000	18000	159000	5000	220000	70000	210000	70000	178000	4000
P	250	40	350	30	352	15	240	40	310	60	304	16
K	11000	2000	13700	1600	12700	200	13000	3000	12000	4000	10460	90
Sc	10	3	9.9	1.3	11.3	0.7	10	2	8.3	1.4	8.7	0.9
Ti	2200	600	2900	1000	3291	10	2700	1200	2300	600	2810	20
V	78	14	90	10	96.2	1.8	100	50	90	30	89.3	1.6
Cr	56	11	68	8	82	5	80	50	64	16	67.7	1.9
Mn	280	150	270	40	252	4	190	110	143	9	138.7	1.9
Fe	22000	6000	26000	3000	27100	500	16000	4000	20000	4000	21800	200
Co	5.2	1.1	7.8	0.9	8.27	0.13	4	2	7.6	1.5	7.6	0.2
Ni	33	7	41	8	42	5	33	7	42	9	41	2
Cu	10	6	9.8	1.9	14.9	0.9	10	3	14	3	12.7	0.5
Zn	55	10	72	13	51.2	1.4	54	9	72	14	51	2
As	1.3	0.2	4.1	1.4	2.88	0.11	5	4	6.1	1	4.9	0.6
Rb	65	13	78	10	72.8	1.7	70	20	67	18	59.4	1.5
Sr	420	40	420	20	445.8	1.4	320	40	350	30	353	1.8
Y	15	3	15.4	1.5	21.5	0.8	16	6	14	3	17.8	0.6
Zr	80	50	70	30	152	3	51	14	60	30	122	3
Nb	10	3	14	4	14.62	0.05	12	4	13	5	13.6	0.4
Sn	2.1	0.3	2.6	0.4	4.2	0.6	2.9	1.9	2.1	0.6	3.6	0.4
Cs	5.5	1.2	6.3	0.9	5.63	0.19	7	2	5.4	1.2	4.75	0.07
Ba	97	10	121	13	142	3	110	40	310	130	604	5
La	26	4	26	3	30.4	0.3	25	5	24	4	24.1	0.6
Ce	42	6	47	4	51.7	1.2	43	11	41	7	41.2	0.8
W	0.87	0.19	1.3	0.4	1.21	0.15	1	0.3	1	0.3	1.1	0.17
Pb	8.1	1.8	11.1	0.7	9	0.2	14	10	11	3	7.7	0.2
U	1.1	0.3	1.3	0.3	1.66	0.03	1.3	0.3	1.1	0.2	1.36	0.08

(Table 2) Contd.....

	OZ301					
	Cube		Powder Pill		Fusion	
	Mean	Std.	Mean	Std.	Mean	Std.
Na	550	100	2200	1600	2004	18
Mg	3500	300	6100	900	6170	90
Al	3200	400	37000	9000	39200	200
Si	21000	6000	170000	50000	154000	3000
P	6100	1400	170	30	207	7
K	1000	190	10000	2000	9170	90
Sc	1.24	0.04	7.2	1	7.3	0.5
Ti	220	80	2100	800	2319	7
V	7.4	0.6	69	14	75.4	1.7
Cr	5.4	0.6	50	9	60.9	1.6
Mn	200	20	210	30	204	2
Fe	2100	400	20000	2000	20800	300
Co	0.9	0.5	4.9	1.2	5	0.3
Ni	3.2	0.7	33	5	32	9
Cu	1.31	0.19	11	2	11.1	0.8
Zn	6.6	0.6	63	11	40	2
As	0.32	0.04	3.7	1.1	3.18	0.06
Rb	6.5	1.1	59	14	51.4	0.9
Sr	200	40	420	40	402	4
Y	27	5	15.5	1.6	16.5	0.3
Zr	7.7	1.1	80	40	106.1	1.4
Nb	1.2	0.2	10	4	11.43	0.05
Sn	0.43	0.06	1.9	0.3	3.5	0.3
Cs	0.62	0.16	4.6	1	4	0.3
Ba	13	2	99	14	122.9	1.7
La	19	3	21	3	23.3	0.4
Ce	37	6	34	4	37.2	0.7
W	0.12	0.02	0.8	0.3	0.84	0.13
Pb	1	0.2	12	5	7	3
U	0.51	0.06	1.2	0.3	1	4

Two measurements of each of the two external standards were performed at the beginning and at the end of each set. These analyses of the external standards enclosed up to 16 analyses of unknowns and are indispensable for the calibration of analytical sensitivities and to correct for drift correction. The instrument was optimized for multielement analysis.

Data reduction for concentration and limit of detection calculation was undertaken using the software LAMTRACE and in-house spreadsheets following methods as described by Heinrich *et al.* [19] and Longerich *et al.* [27]. NIST 610 [15] and GSE 1G [28, 29] were used as external standards.

3. RESULTS

Some typical LA-ICP-MS signals showing the intensity as a function of time for some representative elements (P, Ti, Mn, Fe, Sr, Zr) of sample OZ265 (prepared as powder pill, cube and glass pill) are presented in Fig. (2). The transient signals vary considerably according the preparation method used. All signals were visually examined during data acquisition, the signals from the cubes had the highest variation in comparison to the signals obtained from the powder and glass pills (Fig. 2). This visual observation is particularly important for heterogeneous or multi-phase samples. The laser was usually started after 30 seconds of background signal acquisition. Selected signal intervals were then inte-

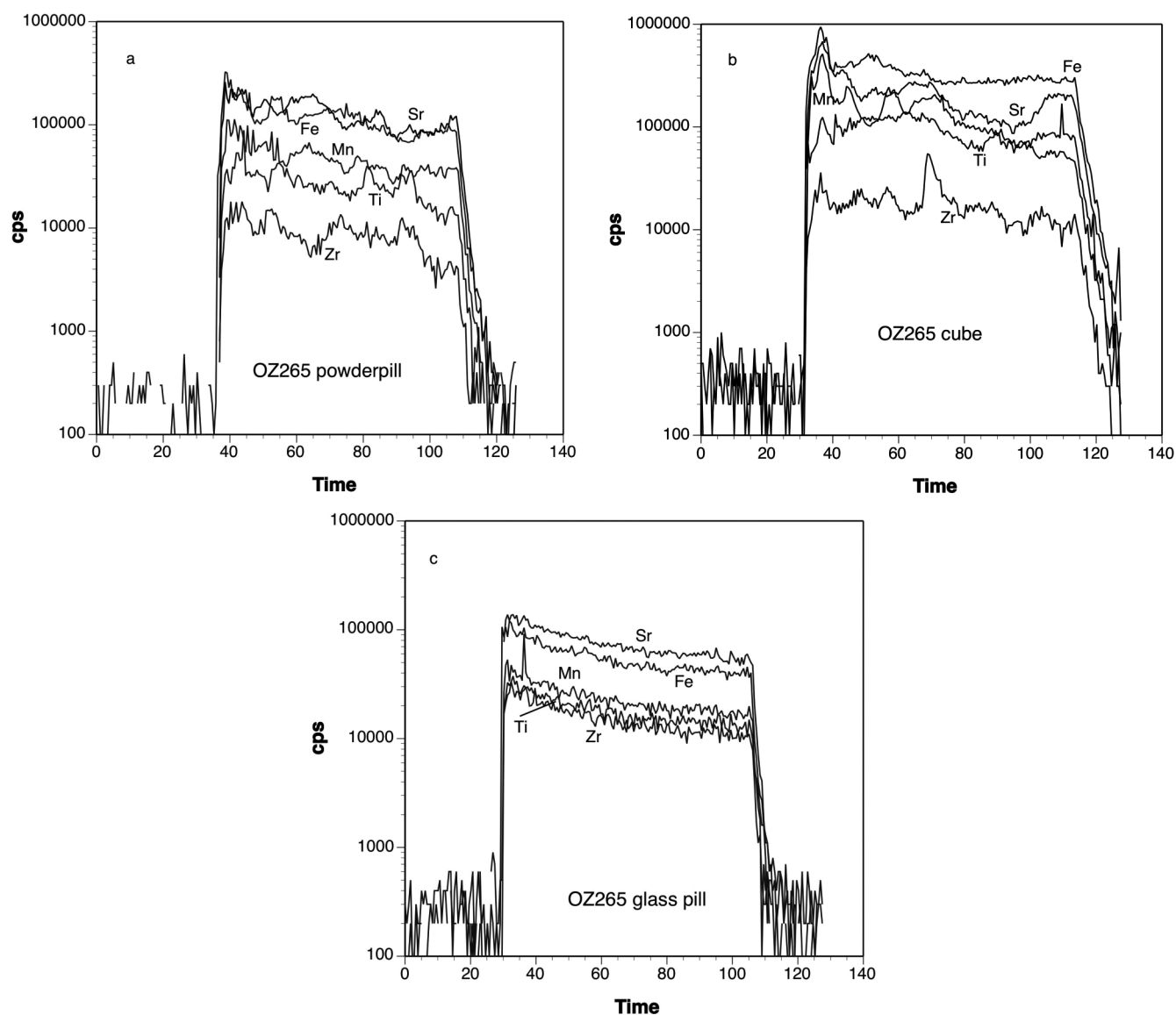


Fig. (2). Some typical transient signals (intensity *versus* time for LA) for a few representative elements (Ti49, Mn55, Fe56, Sr88, Zr40) of sample OZ265. **a)** powder pill, **b)** cube, **c)** glass pill.

grated and net count rates for each element were obtained from background count rates and gross ablation count rates.

The measured concentrations and one standard deviation of thirty analyte elements, five samples and three different preparation methods are reported in Table 2. A few representative analyzed elements (P, Ti, Mn, Fe, Sr, Zr) with their respective error bars (standard deviation) are shown in Fig. (3).

Ca was used as an internal standard (concentration determined by XRF in the glass beads) ahead of the analysis by LA-ICP-MS. Ca was chosen as an internal standard as it provides the best accuracy for REE trace elements analyzed (La, Ce) due to the similar chemical behavior. All major elements (Na, Mg, Al, Si, P, K, Ca) were determined by XRF prior to laser ablation analysis. The difference in concentration for the major elements between XRF and LA-ICP-MS analysis of the fused samples did not exceed 10 % which is in the same range as previously reported for fused

samples and comparison between XRF data and LA-ICP-MS data [16, 24].

The precision (relative standard deviation RSD for 5 replicates for elements analyzed) within the cubes was in the range of 40 % to 90 %. The highest RSDs were found for elements having a concentration close to the detection limit, e.g. Cu. From these high RSDs and the high variability of intensities during ablation (Fig. 2b) it can be concluded that the cubes have a heterogeneous composition in the range of the analysis (90 μm laser beam). Best precision was found for glass pills with RSDs generally lower than 6 %. This does not hold for some element concentrations close to the detection limit. As described previously, fused glass pills are homogeneous. The RSDs of the element concentrations as measured in the powder pills are in general lower than 50 % RSD, but higher than for the glass pills.

Concerning the elemental concentrations and their uncertainties (error bars in Fig. 3) it is important to note that the uncertainties of samples OZ15 and OZ301 (cubes only) are

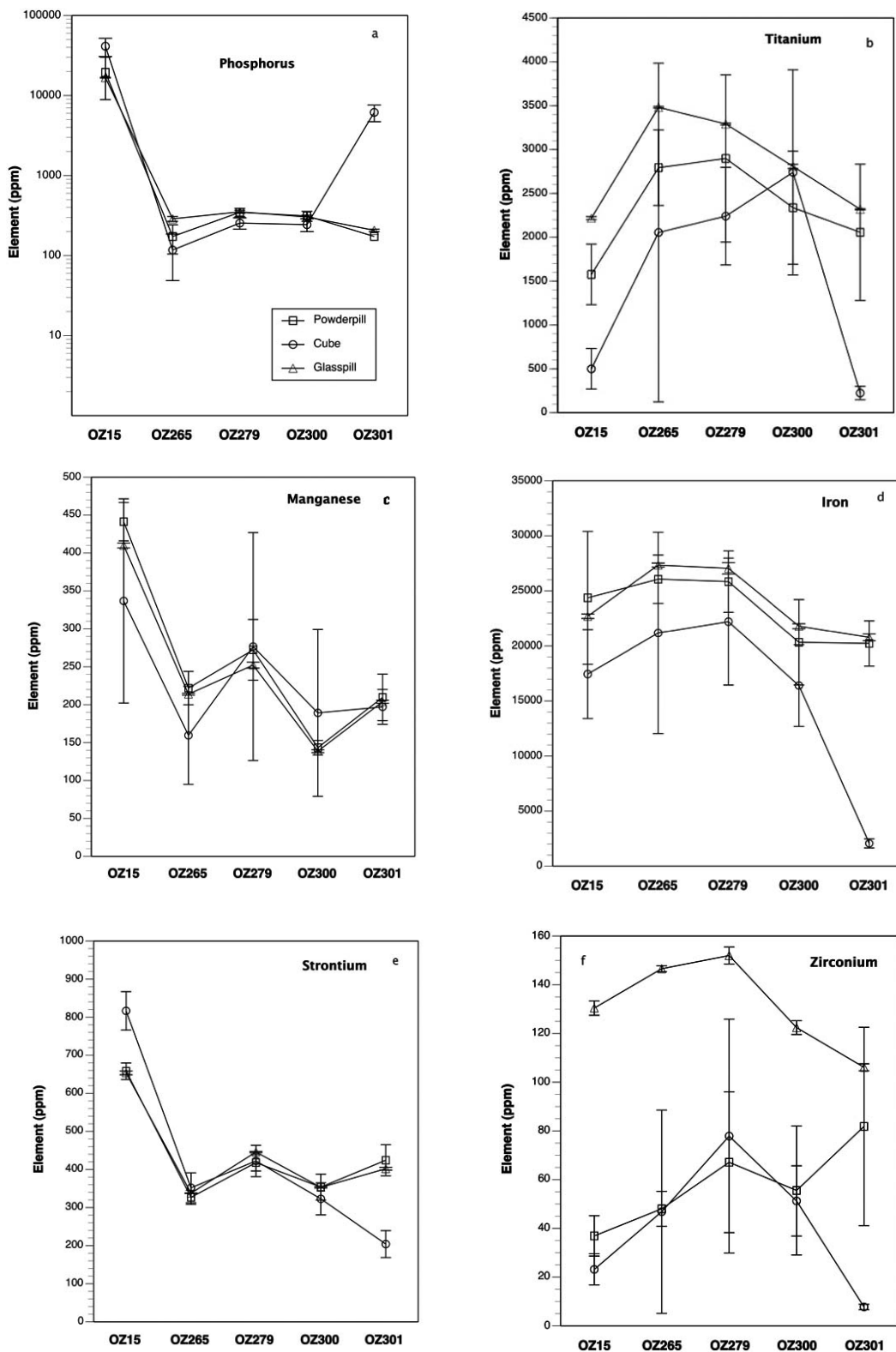


Fig. (3). (a, b, c, d, e, f). Some representative elements (P, Ti, Mn, Fe, Sr, Zr; n = 3) with their respective error bars (proportional to one standard deviation) for all of the samples analyzed.

usually lower (in the range of 6 % to 54 %) than the uncertainties of the other samples. The absolute concentrations for the cubes OZ15 and OZ301 are often low and significantly lower than the concentrations for the powder- and glass pills of the same sample (see Fig. 3). Mn is the sole exception of

this observation. Normally (as shown for Ti of samples OZ265, OZ279 and OZ300 in Fig. 3), the error bars for the analysis of the cubes are distinct, and higher than for the analysis of the powder and glass pills and should therefore overlap the error bars of the powder and glass pills.

4. DISCUSSION AND CONCLUSIONS

The unsteadiness of an individual signal is directly proportional to sample heterogeneity. The geological material of the cubes (cut, as is, from hand specimens) accounts for the inhomogeneous sampling by the laser. Even though the ablation spots were selected carefully to coincide with homogeneous parts of the sample and the pit size did not exceed 90 μm , this preparation method is not suitable for marine sediments. Moreover, the internal standard element (Ca) is not homogeneously distributed and this has an effect on all element concentrations. Calculation to 100 % oxide of the elements is not possible due to the presence of carbonates, sulfates, phosphates, water, chlorides and others. The measurements of the cubes can therefore not be taken as representative due to the heterogeneous element distribution within the samples or much more replicates than the 5 used are necessary to get accurate means. This heterogeneity leads to results which are in some cases too low or too high as compared with the analyses of the powder and glass pills (samples OZ15 and OZ301). The error bars of samples OZ15 and OZ301 (cubes) are by far too small as expected from the low concentration of the various trace elements. Mn and Ce were the only elements that could be analyzed representatively within the cubes as the concentration of Mn and Ce is close to the concentration of the powder pills and the glass pills (OZ15 and OZ301) and the error bars overlap the others. Mn was either adequately present at the ablation spot or Mn is homogeneously distributed between the minerals (the minerals were not determined e.g. by XRD). RSDs up to 90 % for some elements as measured within the cubes are not standard in laser ablation and these results have therefore to be rejected.

A striking feature of the analyses of powder and glass pills is the almost parallel concentration curves in Fig. (3). This holds for all the elements not shown in Fig. (3), too. This agreement is a good indicator for representative sampling of both powder and glass pills.

Zirconium is the only element which concentration as defined within the glass pills is much higher than within the cubes and the powder pills. An explanation for this behavior is the fact that heavy minerals can sediment within the powder or the glass pills and therefore representative sampling is difficult.

From analytical statistics (SD, RSD, confidence interval), the preparation method with glass pills is preferred for LA-ICP-MS. Due to heterogeneity of the samples prepared either as rock cubes or powder pills and the unacceptable high RSD of those samples these two preparation techniques are not suitable for the analysis of marine sediments by LA-ICP-MS.

XRF (used to determine the internal standard) is a routine technique and the major element composition can be obtained with best precision and accuracy whereas LA-ICP-MS is more suitable for trace element analysis than XRF. Moreover, LA-ICP-MS provides much lower LOD for trace elements than XRF [26]. Therefore a combination of both methods is the most suitable for the marine sediments presented in this study. To ensure maximum accuracy, XRF was done on the same glass pellet before crushing prior to LA-ICP-MS. However, assessment of the accuracy of the

LA-ICP-MS method, by comparing the measured values with known values, is difficult due to the poor precision and accuracy to which many element concentrations are known in published reference material compilation [26]. This holds especially true for marine sediments of the kind used in the present study. Nevertheless, preparation of the glass pills is preferred to the conventional solution ICP-MS due to (see also [18, 24-26]).

- the preparation of solutions is as laborious (HF!) as the preparation of lithium borate glass pills
- constituent phases (e.g. zircon) of certain rocks and accessory minerals are resistant to acid attack and are therefore not completely dissolved. This effect is less likely for the fusion of glass pills.
- contamination of solutions by acids
- preparation of a solution array in order to be analyzed for major, minor and trace elements
- matrix effects in solution as a consequence of the high major element concentrations
- solutions containing high concentrations of Cl^- cause interferences by Cl^- species
- volatile elements can easily escape from solution (a minor problem by glass fusion as well)

Therefore the analysis of minor and trace elements in the mentioned marine sediments is most conveniently carried out on fused glass pills using LA-ICP-MS.

5. GEOLOGICAL IMPLICATIONS

The concentrations of trace and minor elements in marine sediments reflects the range of chemical, oceanographic and sedimentary controls on their supply to, their distribution in and their removal from the ocean [2]. Such controls include the composition of sedimentary detritus delivered to the ocean, the partitioning of individual elements between solid and solution phases, the biogeochemical cycling of the elements in the ocean and the manner in which they are delivered to the sea floor, and the post-depositional conditions in bottom sediments that may lead to diagenetic element recycling or precipitation.

For a detailed description of the samples see [4]. According to Kuhn *et al.* [30], the enrichments in manganese and iron in carbonates of Valanginian (Cretaceous) age deposited in the Tethys and Atlantic Oceans correlate to a positive $\delta^{13}\text{C}$ excursion. The correlation of the $\delta^{13}\text{C}$ excursion with trends in Mn and Fe contents seems to reflect changes in Valanginian paleoceanography and climate.

Louis-Schmid *et al.* [4] report about a $\delta^{13}\text{C}$ excursion in the Argovien facies (marls with marly limestone) in Trescléoux upper part just above the samples taken for this study. The high concentration of the nutrient related element P in the lowermost part of the Oze section (sample OZ15, Fig. 3) suggests a more oligotrophic setting with an elevated biological productivity (Brumsack, 1986). The high content of Sr (Fig. 3), which shows a strong correlation with Ca (due to its primary fixation in the lattice of calcareous skeletal material) supports the thesis of a more oligotrophic setting [31] Manganese is as well more concentrated in the

lowermost part of the Oze section (Fig. 3). Mn is a good indicator of an oxic environment as it forms highly insoluble oxides under these conditions [2, 9]. Elements like Ti, Fe, Y, Zr, La and Ce are mainly of detrital origin. The concentrations of Y, La and Ce are much higher in the lower than in the upper part of the Oze section suggesting detrital input [1]. Zr shows a rather irregular pattern concerning concentrations due to sample preparation difficulties concerning this element. Enhanced bio-productivity finally is the main switch turning an oxygenated into an anoxic environment [32] leading to lower Mn concentrations in samples OZ2656, OZ279, OZ300, and OZ301.

This work was mainly undertaken as a base study to evaluate the method of choice for the analysis of trace elements in marine sediments. In a further study we will determine the trace elements at the full length of the same profiles in order to monitor the correlation between $\delta^{13}\text{C}$ -values from the sections and to gain more insight on past oceanographic and climatic changes.

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