



## One-million year Rare Earth Element stratigraphies along an Antarctic marine sediment core



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### ABSTRACT

An integrated system, based on Inductively Coupled Plasma-Sector Field Mass Spectrometry (ICP-SFMS) and Inductively Coupled Plasma-Atomic Emission Spectrophotometry (ICP-AES) techniques, was optimised for the geochemical characterisation of soils and marine sediments. Sample mineralization was carried out with HF, HNO<sub>3</sub> and HClO<sub>4</sub>. Operative blanks were at least two orders of magnitude lower than the lowest concentration measured in real samples. For ICP-SFMS, the detection power of the method in high resolution mode was sufficient for an accurate quantification of metals, yet avoiding REEs' (Rare Earth Elements) isobaric interferences. Once tested the accuracy on six certified materials, the methods were applied to the analysis of 39 major and trace metals on the top 90 m of sediments from the ANDRILL AND-1B core, covering the last million years. Stratigraphies of REEs and of normalised markers from this core clearly highlight a discontinuity at about 660,000 years before present. This pattern is well shown by the results of a PMF (Positive Matrix Factorization) statistical analysis, revealing two different sources for the sedimentary material, whose relative contribution changed around that time. Such a result is consistent with previous studies and confirms the net change in the provenance of glacial fluxes in the McMurdo region (Ross Ice Shelf, Antarctica) in the last million years.

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### 1. Introduction

REEs have been widely used as excellent proxies for several geochemical processes in cosmogenic chemistry, igneous petrology, and sedimentology. Indeed, REEs are fractionated in the environment because the progressive increase of the charge/radius ratio with the atomic number (the so-called lanthanide contraction) causes small but systematic differences in their chemical properties. Besides, due to their low solubility and scarce mobility in the terrestrial crust, REEs display a conservative behaviour in the environment [7]. As a consequence, REEs' abundance varies in weathering products, and their relative changes are used as a marker of source rocks [16,31].

The Antarctic cryosphere (the complex system composed by the continental ice cap, coastal ice shelves, sea-ice, and marine sediments) is considered one of the most precious archives of paleo-environmental and paleo-climatic information (EPICA—European Project for Ice Coring in Antarctica [5]; EPICA [6,23]). Indeed, the surface and volume changes of the Antarctic ice cap, as a consequence of climate forcings, play a

critical role in the climatic system and constitute complex feedbacks with hydrosphere, atmosphere, lithosphere, and biosphere. In particular, changes in ice-volume affect the global sea level, Earth albedo, atmospheric and oceanic circulation, marine productivity, and greenhouse gas emissions and uptake processes. Such environmental changes, in turn, affect the solar irradiance budget and the global transport and distribution of matter and energy [1,12].

In this context, one of the main goals of the ANTARCTIC DRILLING Program (ANDRILL) was to gather information on past changes in the Antarctic climate and on the dynamics of the Antarctic ice cap over the last 35 millions of years (Ma), by a geochemical, mineralogical, and palaeontological characterisation of two deep sediment cores drilled in the Ross Sea region, which is close to the current margin of the Ross Sea Ice Shelf [9]. In particular, detailed palaeo-climatic and palaeo-environmental information can be obtained from sedimentological, geochemical, and geophysical stratigraphies of the ANDRILL-MIS (McMurdo Ice Shelf) B1 sediment core (AND-B1, 1260 m deep, covering the Plio-Pleistocene period: 0–15 Ma ago), composed by glaciomarine, terrigenous, volcanic, and biogenic sediment that has accumulated in the Windless Bight region of a flexural moat basin surrounding Ross Island.

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In this paper, we report the first results on the geochemical stratigraphy of the uppermost 90 m of the AND-B1 core, roughly covering the last one million years, by an analytical set-up developed for the sample mineralisation and the determination of 39 major and trace elements, including REEs.

The element quantification was carried out by an integrated system with Inductively Coupled Plasma (ICP) Atomic and Emission Spectrophotometry (ICP-AES) or High-Resolution Sector-Field Mass Spectrometry (ICP-SFMS) detectors, depending on element concentrations and interferences.

A multi-element internal standard method was used to correct matrix effects. An accurate quantification of the residuals after internal standard correction allowed identifying signal temporal drifts which are different element by element. The correction of such drifts, by periodical repetitions of a multi-standard and of a certified material solution, significantly improved reproducibility and accuracy. The improved detection limits for all the REEs allowed using the high resolution technique (10,000 m/ $\Delta m$ ) in their determination by ICP-MS, hence avoiding possible isobaric interferences.

Single-metal recovery and accuracy were evaluated by using a set of marine sediments (NIST 2702, GBW 07313, CRM-MURST-ISS-A1) and soil (Basalt, Hawaiian Volcanic Observatory BHVO-1, Japanese andesite JA-2, Montana soil NIST 2711) certified materials; the results are reported in Tables 1 and 2 in the Supplementary material.

## 2. Materials and methods

Sample mineralisation was carried out with a mixture of ultrapure  $\text{HNO}_3$  (69.5% reagent grade, purified by sub-boiling distillation – s-b d.), HF 40% (Suprapur grade), and  $\text{HClO}_4$  70% (Suprapur grade).

Three internal standards were used for ICP-SFMS analyses (In, Re and Ge at 12, 30, and 60  $\mu\text{g L}^{-1}$ , respectively) and a mono-element internal standard (Ge, 5  $\text{mg L}^{-1}$ ) was used for ICP-AES analyses.

Detailed information about reagents and standard solutions are reported in the Supplementary material.

### 2.1. Instrumentation

Analytical measurements were carried out using a Sector-Field ICP mass spectrometer and an ICP-AES spectrophotometer. The instrumental set-up conditions are reported in Table 3 in the Supplementary material.

Analytical performances obtained in this paper allowed performing ICP-MS measurements in the high resolution mode for analysing trace metals and REEs in all the AND-B1 samples. In this way, isobaric interferences were minimised. The main interferences occurring in low- and high- resolution (LR: 1000 m/ $\Delta m$ ; HR: 10,000 m/ $\Delta m$ ) modes are listed in Table 4 in the Supplementary material. Although a few elements or molecular species interfere on the determination of some analytes also in the HR mode, they are present in soils and marine sediments at very low concentrations and their contribution to the analytical signal is negligible (at least, two orders of magnitude lower than the background levels).

### 2.2. Method setup

#### 2.2.1. Sample mineralisation

A mineralization procedure with  $\text{HNO}_3 + \text{HF} + \text{HClO}_4$ , slightly modified with respect to the methods reported in literature [3,19,20,27,29,33,34] was used. The formation of poorly soluble fluorides, especially with Zr, Hf, and REEs, was minimised by removing HF after mineralization [33]. Samples were freeze-dried, coarsely (2 mm) sieved and milled up to size homogenization by an agate ball mill. An aliquot of about 100 mg (accurately weighed) was placed into a pre-washed 15-mL PFA Savillex vial and 2 mL of s-b d.  $\text{HNO}_3$ , 3 mL of s.p. HF and 3 mL of s.p.  $\text{HClO}_4$  were added. The sealed vials were mineralised following the procedure in detail reported in the Supplementary

material. Mineralised solutions were stored at +4 °C and analysed within 48 h after dissolution.

Although micro-wave digesters were available, the hot-plate technique was chosen in order to standardize the mineralization procedure inside the ANDRILL geochemistry consortium. Mineralization recovery, accuracy and reproducibility were successfully tested on certificated materials.

#### 2.2.2. Reproducibility, detection limits and reagent blank

Reproducibility (RSD), Limits of Quantification (L.O.Q.) and blank values are shown in Table 1. Single-element reproducibility was evaluated by 10 repetitions of multi-element standard solutions. The ICP-MS (HR mode) RSD was better than 3% at 1  $\mu\text{g/L}$  level. For ICP-AES, RSD was better than 1.5% at 10  $\mu\text{g/L}$  level, with few exceptions: Fe (2.3%), K (4.3%) and Ca (8.8%). The relatively poor RSD for Ca is due to the high blank contribution, but it does not affect the real sample measurements, where Ca concentrations are as high as 1  $\text{mg/L}$  (see below).

L.O.Q. values were calculated as  $10\sigma$  of 10 repetitions of one standard solution containing 40  $\text{ng L}^{-1}$  (ICP-SFMS) or 2  $\mu\text{g L}^{-1}$  (ICP-AES) of each element.

**Table 1**

Basic analytical performances of ICP-SFMS and ICP-AES techniques. ICP-SFMS: analytical masses, detection limits, blank levels, RSD%, and internal standards applied. ICP-AES: Wavelengths, detection limits, blank levels, RSD%, and internal standards applied.

ICP-SFMS Finnigan MAT Element2					
Element	Analytical mass	D.L. ( $\text{ng L}^{-1}$ )	Blank ( $\text{ng L}^{-1}$ )	RSD % ( $1 \mu\text{g L}^{-1}$ )	Internal standard
Ce	$^{140}\text{Ce}$	8.4	d.l.	0.8	$^{115}\text{In}$
Cr	$^{52}\text{Cr}$	9.1	127.9	1.1	$^{115}\text{In}$
Cs	$^{133}\text{Cs}$	3.6	d.l.	1.1	$^{115}\text{In}$
Dy	$^{163}\text{Dy}$	10	d.l.	2.0	$^{185}\text{Re}$
Er	$^{166}\text{Er}$	9.9	d.l.	2.2	$^{185}\text{Re}$
Eu	$^{151}\text{Eu}$	11.2	d.l.	1.7	$^{115}\text{In}$
Gd	$^{157}\text{Gd}$	15.6	d.l.	1.6	$^{115}\text{In}$
Hf	$^{178}\text{Hf}$	13.8	38	2.3	$^{185}\text{Re}$
Ho	$^{65}\text{Ho}$	7	d.l.	1.1	$^{185}\text{Re}$
La	$^{139}\text{La}$	10.4	d.l.	1.3	$^{115}\text{In}$
Lu	$^{175}\text{Lu}$	5.4	d.l.	1.5	$^{185}\text{Re}$
Nb	$^{93}\text{Nb}$	6.7	27.8	0.8	$^{72}\text{Ge}$
Nd	$^{146}\text{Nd}$	13.9	d.l.	2.7	$^{115}\text{In}$
Ni	$^{60}\text{Ni}$	15	133.6	2.5	$^{72}\text{Ge}$
Pr	$^{141}\text{Pr}$	5.9	d.l.	0.8	$^{115}\text{In}$
Rb	$^{85}\text{Rb}$	12	20.9	1.3	$^{72}\text{Ge}$
Sc	$^{45}\text{Sc}$	9	11.3	1.3	$^{72}\text{Ge}$
Sm	$^{147}\text{Sm}$	14.2	d.l.	2.0	$^{115}\text{In}$
Ta	$^{181}\text{Ta}$	6.4	38	1.4	$^{185}\text{Re}$
Tb	$^{159}\text{Tb}$	5.8	d.l.	1.4	$^{185}\text{Re}$
Th	$^{232}\text{Th}$	11	d.l.	1.3	$^{185}\text{Re}$
Tm	$^{169}\text{Tm}$	6.9	d.l.	1.3	$^{185}\text{Re}$
U	$^{238}\text{U}$	4	d.l.	1.3	$^{185}\text{Re}$
Y	$^{89}\text{Y}$	7	d.l.	1.2	$^{72}\text{Ge}$
Yb	$^{172}\text{Yb}$	8.9	d.l.	1.4	$^{185}\text{Re}$
Zr	$^{90}\text{Zr}$	18.9	254.1	1.6	$^{72}\text{Ge}$

  

ICP-AES Varian 720-ES					
Element	Wavelength (nm)	D.L. ( $\mu\text{g L}^{-1}$ )	Blank ( $\mu\text{g L}^{-1}$ )	RSD % ( $10 \mu\text{g L}^{-1}$ )	Internal standard (nm)
Al	396.152	0.46	1.8	0.8	Ge 209.426
Ba	455.403	0.023	0.11	0.1	Ge 209.426
Be	313.107	0.016	0.019	0.1	Ge 209.426
Ca	317.933	0.68	7.1	8.8	Ge 209.426
Co	230.786	0.28	0.38	0.6	Ge 209.426
Fe	238.204	0.14	1.3	2.3	Ge 209.426
K	766.491	0.51	1.8	4.3	Ge 209.426
Li	670.783	0.034	0.39	0.3	Ge 209.426
Mg	285.213	0.13	0.9	0.6	Ge 209.426
Mn	257.61	0.029	0.1	0.2	Ge 209.426
Na	588.995	0.25	2.1	1.5	Ge 209.426
Sr	407.771	0.019	0.089	0.2	Ge 209.426
Ti	336.122	0.079	0.28	0.4	Ge 209.426

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