The Open University CEPSAR

Thermo Fisher Determination of Cr isotopic composition in low-level carbonates SCIENTIFIC by MC-ICP-MS: a sensitive proxy for redox changes?

Pierre Bonnand¹ (p.bonnand@open.ac.uk), Ian Parkinson¹, Rachael James², Manuela Fehr¹, Nick Rogers¹, Anne-Mari Karjalainen¹, Ian Fairchild³

1-Introduction

Chromium has four isotopes (⁵⁰Cr, ⁵²Cr, ⁵³Cr and ⁵⁴Cr) with relative abundances of 4.31%, 83.789%, 9.501%, and 2.365% respectively. Mass dependent fractionation of chromium isotopes has the potential to provide new information on a number of environmental processes but, until recently, accurate and precise measurements of Cr isotopes in low-concentration natural samples has not been possible. In this study, we present new methodology for the separation of low levels of Cr from the sample matrix, together with new protocols for the accurate and precise measurement of Cr isotopes using a double-spike technique combined with the Thermo Fisher Neptune MC-ICP-MS (in medium resolution mode) and an Aridus II sample introduction system.

We then apply our technique to the analysis of carbonate material from the Neoproterozoic and the Phanerozoic. It is now widely accepted that levels of atmospheric oxygen increased in two major steps: the Great Oxidation Event, at ~2.4 Ga, and during the Neoproterozoic (~1 Ga to ~545 Ma). As Cr isotopes are strongly fractionated by redox processes, our aim is to test whether the Cr isotope composition of marine carbonate tracks the evolution of atmospheric oxygen.









to the daily mean of the standard measurements. Errors bars represent the internal error (2SD) during the measurement and the grey bands represent the 2SD of the mean.

addresses:

1: Dept. of Earth and Env. Sciences The Open University, Walton Hall, Milton Keynes, MK76AA, UK 2: National Oceanography Centre Southampton, European Way, Southampton, SO14 3ZH, UK 3: University of Birmingham, School of Geography, Earth and Env. Sciences, Birmingham, UK

2-Analytical methods

• A simple 1-step cation exchange column separates Cr from the sample matrix (Fig. 1). Note that there are two Cr peaks.

• The yield from the column is 70-80%.

• The total procedural blanks is 0.12-0.2ng which is negligible relative to the amount of sample processed (~300ng of Cr).

• In order to test the separation of the matrix from the Cr fraction, we analysed a standard-spike mixture doped with a carbonate matrix and we treated as a sample. When analysed by MC-ICP-MS these mixtures gave the same result as the normal standard-spike analysis (Fig. 2).

AC-ICP-MS operating conditions							
Therm Aediu Aridus (-con Sweej	nofisher m Reso s II es o gas an	Neptune lution d lens s	e MC-ICF	P-MS	for maxi	mum intensity	
Cup C .3	Configura L2	ation L1	С	H1	H2	H3	
⁹ Ti	⁵⁰ Cr	⁵¹ V	⁵² Cr	⁵³ Cr	⁵⁴ Cr	⁵⁶ Fe	
Resolution Sensitivity Integration Time Jumber of cycles Jumber of blocks			~5000 ~9V fo 8.389 10 10	~5000 ~9V for ⁵² Cr 8.389 10 10			

• During the course of this study, different operational settings were used (Fig. 3) and there is no difference between Cr measurements in high resolution (200ppb Cr) and medium resolution (50ppb Cr)

 The external reproducibility on the standard solution is ±0.028‰ on $\delta^{53/52}$ Cr_{SRM979} and ±0.055‰ on $\delta^{54/52}$ Cr_{SRM979} (Fig 3).

• We analysed a dolomitic standard (JDo-1) and the reproducibility on $\delta^{53/52}$ Cr_{SRM979} is ±0.075‰ (n=8). Thus, the external reproducibility of our technique is $\pm 0.075\%$.

• We tried to assess the influence on $\delta^{53/52}Cr_{SRM979}$ induced by the isobaric interference correction. Fe has potentially the greatest interference effect (up to 0.4%; Fig. 4), especially if the isotopic composition of iron is not natural. However, our separation technique reduces this effect to trivial amounts.

 Samples were spiked with a mixed ⁵⁰Cr-⁵⁴Cr double spike to correct for isotope fractionation during sample purification and analysis.

• A ⁵⁰Cr/⁵²Cr_{mix} of 0.5074 was targeted in order to reduce the error amplification induced by the addition of the spike (Fig. 5)





-0.0005

-0.0010

-0.0015

0.008 -

0.004 -

-0.004

-0.008

3- Results Continental crust [1] 626 Phanerozoic carbonates Neoproterozoic carbonates



Figure 6: $\delta^{53/52}$ Cr_{SRM 979} for carbonate samples from the Neoproterozoic (orange) and form the Phanerozoic (green). Errors are within the symbol.

 The Cr isotopic composition of Phanerozoic carbonates is heavier than that of the continental crust. This suggests either: (i) that Cr isotopes are fractionation as they are incorporated into carbonates, or (ii) that seawater has a $\delta^{53/52}$ Cr value that is higher than the continental crust.

• A plot of $\delta^{54/52}$ Cr versus $\delta^{53/52}$ Cr indicates that all of our samples lie on a mass dependent fractionation line (Fig. 7).

4- Discussion and Summary

Chromatography procedure

• Our column chemistry is characterised by a double Cr peak [2]. • As recovery of Cr is not 100%, a double spike technique is used to correct for isotope fractionation during the column chemistry.

MC-ICP-MS measurements

• Our MC-ICP-MS technique utilises a Thermo Fisher Neptune MC-ICP-MS, an Aridus II sample introduction system, and a 50 ppb solution of Cr. Thus, this technique can be used to analyse low concentration natural samples, such as carbonates.

Cr isotopic composition in carbonates and redox condition in the oceans.

• The Cr isotopic composition of carbonates from the Neoproterozoic are different from those of Phanerozoic carbonates.

- +1.9‰)
- are similar to those recorded in banded iron formations [3].

• The Cr isotopic composition of the Neoproterozoic samples seem to indicate that during the Neoproterozoic the oceans were not fully oxidized.



• The isotopic composition of the carbonates from the Neoproterozoic and the Phanerozoic are different (Fig. 6).

• Neoproterozoic carbonates have $\delta^{53/52}$ Cr values that vary from -0.5 to +0.2% (mean = -0.107%)

• Phanerozoic and modern carbonates have $\delta^{53/52}$ Cr values of +0.5 - +1.9% (mean = +1.371%)

• The Cr isotopic composition of the Neoproterozoic carbonates is similar to that of the continental crust (Fig. 6). This may suggest that in the Neoproterozoic, all seawater Cr was in a single oxidation state.



Figure 7: Cr isotopic compositions for 21 carbonates samples.

• Carbonates precipitating from oxic seawater have relatively high $\delta^{53/52}$ Cr values (+0.5 to

• Carbonates precipitating under (putative) low-oxygen conditions have $\delta^{53/52}$ Cr values that

References: 1. R. Schoenberg, S. Zink, M. Staubwasser and F. von Blanckenburg, *Chemical Geology*, 2008, **249**, 294-306. 2. A. Trinquier, J. L. Birck and C. J. Allegre, *Journal of Analytical Atomic Spectrometry*, 2008, 23, 1565-1574. 3. R. Frei, C. Gaucher, S. W. Poulton and D. E. Canfield, *Nature*, 2009, **461**, 250-U125.