Archimer
http://archimer.ifremer.fr

Determination of rare earth elements and other trace elements (Y, Mn, Co, Cr) in seawater using Tm addition and Mg(OH)$_2$ co-precipitation

Nicolas Freslon[a, b, c], Germain Bayon[a, *], Dominique Birot[a], Claire Bollinger[b, c], Jean Alix Barrat[b, c]

[a] Département Géosciences Marines, IFREMER, 29280 Plouzané, France
[b] Université Européenne de Bretagne, 35000 Rennes, France
[c] CNRS UMR6538, IUEM, Université de Brest, 29280 Plouzané, France

[*] Corresponding author : G. Bayon, Tel.: +33 2 98 22 46 30; fax: +33 2 98 22 45 70, email address: gbayon@ifremer.fr

Abstract:

This paper reports on a novel procedure for determining trace element abundances (REE and Y, Cr, Mn, Co) in seawater by inductively coupled plasma sector field mass spectrometry (ICP-SFMS). The procedure uses a combination of pre-concentration using co-precipitation onto magnesium hydroxides and addition of thulium spike. The validity of the method was assessed onto 25 ml volumes of certified reference materials (NASS- and CASS-4) and in house seawater standard. Procedural blanks were determined by applying the same procedure to aliquots of seawater previously depleted in trace elements by successive Mg(OH)$_2$ co-precipitations, yielding estimated contributions to the studied samples better than 1.1% for all elements, with the exception of Cr (<3.3%) and Co (up to 8%). The reproducibility of the method over the six month duration of the study was smaller than 11% RSD for all the studied elements. Results obtained for NASS-5 and CASS-4 agree well with published working values for trace elements.

Keywords: Trace elements; Rare earth elements (REE); Seawater; Mg(OH)2 co-precipitation; ICP-MS; Thulium

1. Introduction

During the last decade, there has been increased interest in determining the global distribution of dissolved trace elements in the ocean and understanding the processes that control their concentrations in seawater. This major community effort, which recently led to the establishment of an ambitious international sampling program (GEOTRACES), requires the use of accurate and rapid analytical techniques for the measurement of key trace elements in seawater.

In recent years, inductively coupled plasma mass spectrometry (ICP-MS) has become the method of choice for determining trace element abundances in the ocean. ICP-MS techniques are rapid, highly sensitive and exhibit very low detection limits, thereby allowing simultaneous multi-element determination of seawater samples over a wide range of concentration (down to sub $ng.kg^{-1}$ levels) with high sample throughput. Due to the presence of salts (around $35g.kg^{-1}$) and to the relatively very low trace element contents in the ocean, the analysis of seawater samples by ICP-MS typically requires an initial step of preconcentration/matrix reduction. A number of methods have been successfully developed in the past for preconcentrating trace elements and separating the salt matrix prior to ICP-MS analysis (e.g. separation using chromatography [1], solid phase extraction [2], liquid-liquid extraction [3, 4], ion exchange resins [5-7], electrochemical deposition [8], or co-precipitation). For instance, co-precipitation techniques involve the precipitation of solid-phases (typically hydroxides), which act as selective scavengers for a number of dissolved species naturally present in seawater, thereby leading to significant trace element preconcentration from the seawater matrix. Various examples of co-precipitation methods can be found in the literature, including co-precipitation onto gallium hydroxides [9], iron hydroxides [10-12], magnesium hydroxides [13-17], or onto other mineral phases [18].

Trace element concentrations in seawater can be determined by ICP-MS through external calibration, using certified reference materials or multi-elemental reference standard solutions. Isotope-dilution (ID) ICP-MS techniques are also particularly well suited for measuring high-precision trace element concentrations in seawater. Although ID-ICP-MS has been mainly applied to the measurement of single elements in seawater [19-21], a few studies have also reported applications for multi-element determination [13,17,22]. For example, Shaw et al (2003) [13] used a mixed spike cocktail (^{142}Ce, ^{145}Nd, ^{161}Dy, ^{171}Yb) to determine REE concentrations in seawater samples after $Mg(OH)_2$ co-precipitation. Saito and Schneider (2006) [17] also investigated the suitability of the Mg co-precipitation method for determining Fe, Mn and Co abundances in seawater by ID-ICP-MS. In addition to providing precise results, one major advantage of using ID techniques for quantifying trace element abundances in seawater is that they do not require quantitative recovery during sample preparation.

Recently, a novel method was developed at IFREMER for quantifying trace element abundances in seawater by ICP-MS, which involved pre-concentration using Fe co-precipitation and addition of a Tm spike [10]. The addition of Tm spike in the samples prior to co-precipitation produces a Tm anomaly in the resulting chondrite-normalized REE patterns, which can be used to determine the Tm concentration in the sample solutions and serves as internal standard for the remaining elements [23,24]. This method was shown to be well suited for the determination of precise and accurate concentrations for REE, Y, V, Hf, Zr and Th in seawater. However, the presence of relatively high blank levels (e.g. up to 7 pg for light REEs), due to the addition of Fe for co-precipitation, required analysis of large volume samples (100 ml) and prevented accurate determination of key trace elements (e.g. Mn, Co, Cr, Ni, Cu, Sc).

In this study, we have investigated the suitability of combining the Tm addition method with $Mg(OH)_2$ co-precipitation for determining trace element abundances in seawater. The recommended procedure reported in this study allows simultaneous determination of the REEs + Y and a few other trace elements (Cr, Co, Mn) in small volume (25ml) seawater samples.

2. Experimental

2.1. Reagents

All sample preparations were conducted in a Class 1000 (ISO 6) clean laboratory. Upon opening, chemical solutions were stored within a Class 100 laminar flow bench (ISO 5). Deionized water purified with a Milli-Q system (Millipore®) at 18.2 MΩ (herein referred to as MQ-H$_2$O) was used for material cleaning and acid dilutions. Polypropylene centrifuge tubes and disposable pipette tips were pre-cleaned thoroughly using diluted HNO$_3$ acid solutions and MQ-H$_2$O. Nitric acid solutions (commercial grade, Merck) were distilled three times using a sub-boiling system. Optima ammonia solution (20-22%) from Fisher Scientific® (Loughborough, UK) and a thulium mono-elementary solution (custom grade, CGTM1-1, Inorganic Ventures Inc.) were used for co-precipitation experiments. Others mono-elementary solutions (custom grade, CG*xx*1-1, Inorganic Ventures Inc., where *xx* stands for: Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Hf, Th, U, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn or Cd) were also used for recovery calculations.

2.1. Seawater samples

An in house seawater standard (Dellec SW) was used for method development and blank preparation. Dellec SW is a coastal surface seawater collected off Brittany (NO France) in acid-cleaned 15-L polyethylene jerry-can like containers, filtered through 0.45µm cellulose membrane filters (Whatman®, Dassel, Germany) and acidified to ~ pH 1.5 using sub-boiled concentrated HNO$_3$. Two certified reference materials (CRMs) purchased from the National Research Council of Canada (NRCC) were analyzed to validate our procedure: CASS-4 (nearshore seawater) and NASS-5 (seawater). These reference materials are certified for a wide range of trace elements (e.g. As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, U, V, Zn), and are now relatively well characterized for the REEs [5,10,25,26]. In addition to these two CRMS, a certified rock standard (basalt BHVO-2, USGS) was also used to correct for instrumental drift and calibration purpose.

2.3. Procedural blanks

For blank determination, a known weight of Dellec SW (about 25 g) was transferred into a cleaned 50 ml polypropylene centrifuge tube. A volume of 600 µl of 20-22% NH$_3$ solution (aqueous NH$_3$) was added to the tube to increase the pH to ~ pH 9.5, which led to precipitation of magnesium hydroxides. The tube was shaken and allowed to rest for 2-3 minutes, before centrifugation during 5 minutes at 3800 rpm. The supernatant was then transferred into a cleaned 50 ml tube, prior to addition of 100µl of aqueous NH$_3$ and centrifugation (5 minutes / 3800 rpm). This step was repeated three times using 80, 60 and 50µl of aqueous NH$_3$ solution, respectively, to form successive Mg(OH)$_2$ precipitates. A final (sixth) step of co-precipitation was attempted, but with no success (i.e. no formation of Mg(OH)$_2$ precipitate). At this stage, however, it is very likely that most of the magnesium initially present in the sample had been already removed during the first five co-precipitations. Prior to measurement by ICP-SFMS, the five successive residues of Mg(OH)$_2$ precipitate were dissolved in 300µl of 20% (v/v) sub-boiled HNO$_3$ solution, quantitatively transferred into a 15 ml cleaned polypropylene tube and diluted with 2,700µl MQ-H$_2$O. The efficiency of successive co-precipitations in scavenging trace elements from a seawater

sample was assessed by analysing replicate series of these five residues of $Mg(OH)_2$ precipitate (see Fig. 1).

2.4. Sample preparation

A known weight of sample (about 25 g) was transferred into a pre-cleaned 50 ml polypropylene centrifuge tube, spiked with a known weight (about 50 mg) of Tm solution (957.3 $ng.kg^{-1}$) and shaken. The mixture was then allowed to equilibrate for 15 minutes. Magnesium hydroxides were formed by increasing the pH of the solution to ~ pH 9.5, through stepwise addition of aqueous NH_3. For each sample, an initial 25-ml aliquot was first used to determine the minimum volume of ammonia required to form $Mg(OH)_2$ precipitates. For these 'test' samples, 250µl of aqueous NH_3 solution was first added to the sample, followed by 10µl successive increments until a precipitate was detected. Then, considering v - the volume of aquaeous NH_3 added to any sample to obtain $Mg(OH)_2$ precipitates, a volume v – 20 µl of aqueous NH_3 solution was added into a 50 ml polypropylene tube containing another 25 ml aliquot of the same sample. The tube was shaken and left 2-3 minutes to equilibrate before centrifugation (5 minutes / 3800 rpm). The supernatants were discarded and, prior to ICP-SFMS analysis, the $Mg(OH)_2$ residues were dissolved in ultra-pure diluted HNO_3 solutions (see section Procedural blanks).

2.5. Instrumentation

The analyses were performed at the Pôle Spectrométrie Océan (Brest, France) on a Element2 ICP-SFMS (Thermo Electron, Bremen, Germany) equipped with an ASX 100 auto-sampler (CETAC Technologies, Omaha, NE, USA). The operating conditions and measurement parameters are given in Table 1. Solutions were introduced via a Teflon® 100 µl nebulizer and a quartz dual cyclonic spray chamber (ESI). A quartz injector and a set of nickel sampler and skimmer cones were used during the course of this study. The Element2 was operated in low (LRM, m/Δm approx. 300) and medium (MRM, m/Δm=4500) resolution modes, depending on the required sensitivity and potential interferences for each element. Measured isotopes in LRM were ^{89}Y, ^{90}Zr, ^{91}Zr, ^{97}Mo, ^{135}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{146}Nd, ^{147}Sm, ^{149}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu, ^{177}Hf, ^{178}Hf, ^{232}Th and ^{238}U. In MRM, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{110}Cd, ^{111}Cd isotopes were measured. Masses were scanned in the E-scan and bi-scan modes.

2.6. Interference corrections

Polyatomic oxide and hydroxide interferences on the rare earth elements (REE) were corrected using oxide formation rates determined by analyzing solutions of MQ-H_2O, Ba+Ce, Pr+Nd and Sm+Eu+Gd+Tb at the beginning of each measurement session [23,24]. Oxide formation rates during the course of this study were generally ~0.1% for BaO^+/Ba^+, <0.1% for $CeOH^+/Ce^+$ and ~3% for PrO^+/Pr^+. Barium ($^{135}Ba^{16}O^+$) and $^{141}Pr^{16}O^+$ interferences on ^{151}Eu and ^{157}Gd, respectively, were always lower than 20% for all the studied samples. Neodymium oxide ($^{143}Nd^{16}O^+$) interference accounted for less than 10% of the measured ^{159}Tb signals. All other interferences were negligible (less than 3%).

2.7. Calculation

Elemental concentrations were calculated using the Tm addition method [10,24]. Details on the calculations can be found in Bayon et al. (2009) [23]. Briefly, for each sample, elemental concentrations can be calculated using the sample mass, the amount of Tm added, and by calibrating the raw data acquired during the measurement session against an unspiked (no added Tm) BHVO-2 reference solution (diluted ~ 10,000 times), run after every three samples to correct for the instrumental drift. The BHVO-2 values used for the calculations are given in Bayon et al. (2011) [10].

3. Results and discussion

3.1. Effect of successive Mg(OH)$_2$ co-precipitations on trace element scavenging

The efficiency of successive co-precipitations in scavenging trace elements from a seawater sample (Dellec SW) is illustrated in a graph representing measured ICP-MS intensities (cps) versus the number n of successive co-precipitations (Fig. 1). The measured intensities in the residual Mg hydroxide precipitates decrease significantly during the first four co-precipitations (e.g. down to ~ 1000 cps for Y and Zr, to ~ 100 cps for La, Ce, Th, Cr and Mn, and to ~ 10 cps for all other elements), clearly showing that the studied trace elements were efficiently removed from the initial solutions. With the exception of a few elements (Th, Co, Y, Zr), the intensity levels measured after four successive co-precipitations for each element are 1) very similar to those obtained for the fourth Mg-precipitates, and 2) comparable to background levels (measured intensities for 2% (v/v) ultra pure HNO$_3$ solution). Taken together, this indicates that the supernatant left after four successive co-precipitations has been quantitatively depleted in most of the trace elements of interest here, and hence can be considered as suitable for providing an estimate of the total procedural blank in this study.

3.2. Limits of detection and method blanks

Our best estimates for the method blanks and the detection limits for our procedure are listed in Table 2. Detection limits were calculated as three times the standard deviation of a series of 24 procedural blanks. The blank levels were < 1 pg for all REE, Hf and Th, and < 6 pg for Y and Zr. Average blanks were higher for Co (20 pg), Mn (26 pg) and Cr (92 pg). Average blank contributions to the studied seawater standards were negligible for Tm and Mn (<0.1%), and always below 1% for Y+REE, with the exception of Eu (1.1% for CASS-4 and Dellec SW) and Ho (1.4% for CASS-4; 1.2% in Dellec SW). Average blank contributions were slightly higher for Hf, Zr, and Th (< 3%), for Cr (< 4%), and for Co (<8%).

3.3. Co-precipitation yields

An important requirement prior to using the Tm addition method for calculating elemental abundances in seawater samples is that the elements under interest must be scavenged at levels similar to Tm during Mg co-precipitation (i.e. similar extraction yields). To estimate the co-precipitation yields of our procedure, we calculated elemental concentrations for a series

of CRM samples (n = 11) using external calibration, and compared the obtained data to certified values (for Mn, Cr and Co), or recently published high quality values [5,10,13,25,26]. The calibration curve used for calculating concentrations in the studied solutions was derived from the analysis of $Mg(OH)_2$ residues, co-precipitated from aliquots of seawater samples previously depleted in trace elements by successive co-precipitations (see procedure described in section 2.3) and spiked with various amounts of a multi-element homemade stock solution.

The calculated co-precipitation yields are displayed in Fig. 2. Note that co-precipitation recoveries were not determined for Cr. The calculated recoveries of the REEs range from ~ 72 % (for Tb) to 93 % (for Yb). All REE+Y exhibit reproducible co-precipitation yields (mean recovery of 83 ± 14%), which are within error, or close (for Tb, Yb and Lu), to those calculated for Tm (82 ± 5%). In agreement with Shaw et al. (2003) [13], this suggests that Mg co-precipitation does not lead to any significant fractionation amongst the REEs. Importantly, this also validates the use of our Tm addition method for determining REE+Y abundances in seawater samples after Mg co-precipitation.

In contrast to the REEs, co-precipitation recoveries calculated for all other studied elements differed from those for Tm. Zirconium and Hf were removed almost quantitatively during co-precipitation (i.e. ~ 100% recovery), whereas Th was less efficiently scavenged from the initial seawater solutions (~ 60%). Importantly, the co-precipitation recoveries of these elements were not reproducible (standard deviation 1s > 15%), showing clearly that our procedure is not well suited for accurate determination of Zr, Hf and Th abundances in seawater. In contrast, co-precipitation yields for Co and Mn, were higher than Tm (i.e. average recovery of 106% and 96%, respectively), but relatively reproducible (respectively 7% and 5% RSD). While the high scavenging efficiency of Mn during $Mg(OH)_2$ co-precipitation had already been reported previously by Saito and Schneider [17], the co-precipitation yields calculated for Co in our study were significantly higher than those estimated in this earlier work. One possible explanation accounting for the observed differences in cobalt scavenging could be that the apparent recovery efficiencies were calculated using different approaches in the two studies: i.e. direct analyses of certified reference materials (our study), and additions of a mixed (Fe, Mn, Co) standard solution to dissolved $Mg(OH)_2$ samples [17].

3.4. Precision and accuracy – Application to the analysis of NASS-5 and CASS-4

The analytical results for the natural water CRMs used in this study (NASS-5 and CASS-4) and our in house seawater (Dellec SW) are listed in Table 2, together with certified values (for Mn, Co and Cr) and selected literature data (for REE+Y). For each of the three seawater standards, the data presented in Table 2 correspond to the mean values ± 1 standard deviation, acquired over a period of about 6 months. The precision on our series of replicate measurements (n = 17 for NASS-5; n = 11 for CASS-4; n = 20 for Dellec SW) is also expressed as the relative standard deviation (RSD). Note that the elements reported in Table 2 correspond to those that were analysed successfully during our co-precipitation experiments. Other elements that were measured but not reported (Mo, Ba, U, Sc, Ti, V, Ni, Cu, Zn, Cd), presented a bad reproducibility (RSD>15%) and/or error compare to reference value were superior to 15%.

For the REEs, the accuracy of our procedure can be assessed by comparing the obtained Post-Archean Australian shale (PAAS)-normalized values to recently published high quality reference data (Fig. 3). Our measured concentrations for REE + Y are in agreement with values obtained after other pre-concentration methods prior to analysis (e.g. iron co-precipitation [10], solvent extraction [25], chelating resin [5,26]). With few exceptions (i.e. La and Eu), our data agree within 10% error with those obtained using the Tm addition method

and iron co-precipitation [10], and liquid-liquid extraction [25]. Our data for La and Eu were slightly lower (11.8% for NASS-5) and higher (11.9% for CASS-4) than those reported after Fe-coprecipitation by Bayon et al. (2011) [10], respectively. One possible explanation for these higher Eu values would be that we under-corrected the contribution of the $^{135}Ba^{16}O$ isobaric interfence to the ^{151}Eu signal. However, the efficiency of the Ba separation from the precipitate was significantly improved during $Mg(OH)_2$ precipitation compared to the Fe-coprecipitation procedure, as already discussed by Shaw et al. (2003) [13]. This is shown clearly by the much lower Ba/REE ratios in CASS-4 and NASS-5 (i.e. Ba/Eu cps ratios of ~ 8 after Mg-coprecipitation and ~ 100 after Fe-coprecipitation; results not shown here), which suggests that our new Eu values for these reference materials may be more accurate than those obtained by Bayon et al. (2011) [10]. Over the 6-month period of measurement, the precision for the REEs was always better than 10% for the three studied seawater standards (Table 2), with the exception of Eu (14% RSD) and Tb (11% RSD) in CASS-4.

Our measured concentrations for Mn and Co agree well (within 10%) with the CRM certified values: 954 ± 51 ng.kg^{-1} and 2587 ± 192 ng.kg^{-1} for Mn in NASS-5 and CASS-4 (certified values: 897 ± 57 ng.kg^{-1} and 2715 ± 190 ng.kg^{-1}, respectively); 10 ± 1 ng.kg^{-1} and 23 ± 2 ng.kg^{-1} for Co in NASS-5 and CASS-4 (certified values: 10 ± 3 ng.kg^{-1} and 25 ± 3 ng.kg^{-1}, respectively). The precisions for these three elements were better than 10% (RSD), with the exception of Co in CASS-4 (11%). This provides assurance that these two elements can be successfully measured in seawater samples using our recommended procedure, despite the fact that they exhibit co-precipitation yields slightly different than those for the REEs.

Similarly, our measured concentration for Cr in NASS-5 (110 ± 7 ng.kg^{-1}) is in agreement with the certified value (107 ± 15 ng.kg^{-1}) and other published high-quality Cr data [27, 28]. Additional analyses would be needed to further validate whether total Cr in seawater can be routinely measured using our recommended procedure (e.g. determination of coprecipitation yields, analyses of other CRMs). However, the evidence that the long-term reproducibility obtained on our Cr measurements (~6 % RSD for NASS-5) is similar to the precision achieved using ID- ICP-SFMS (~ 5 % RSD; [28]) suggests that our method is well-suited for determination of Cr abundances in seawater.

Conclusions

To summarize, we showed that the Mg coprecipitation technique combined with addition of a Tm spike allows simultaneous determination of the REEs and other trace elements (Y, Mn, Co, Cr) in seawater by ICP-SFMS. Our recommended procedure provides low blanks (mostly < 1% for the REEs, Y and Mn, and < 5% for Cr and Co) and achieves a good reproducibily for 25-mL samples (typically lower than 10% over the six-month duration of the experiments, with the exception of Eu 14%). In addition, its short preparation time (about 10 minutes) makes it particularly well-suited for high sample throughput and routine measurements of seawater samples.

Acknowledgements

References

[1]   S.P. Verma, E. Santoyo, Geostand. Geoanal. Res. 31 (2007) 161-184

[2]   M.L. Firdaus, K. Norisuye, T. Sato, S. Urushihara, Y.Nakagawa, S. Umetani, Y. Sohrin, Anal. Chim. Acta. 583 (2007) 296-302

[3]   M.B. Shabani, T. Akagi, H. Shimizu, A. Masuda, Anal. Chem. 62 (1990) 2709-2714

[4]   G.J. Batterham, N.C. Munksgaard, D.L. Parry, J. Anal. At. Spectrom. 12 (1997) 1277-1280

[5]   Y. Zhu, A. Itoh, E. Fujimori, T. Umemura, H. Haraguchi, Bull. Chem. Soc. Jpn. 78 (2005) 659-667

[6]   T. Yabutani, S. Ji, F. Mouri, H. Sawatari, A. Itoh, K. Chiba, H. Haraguchi, Bull. Chem. Soc. Jpn. 72 (1999) 2253-2260

[7] R.K. Katarina, T. Takayanagi, K. Oshita, M. Oshima, S. Motomizu, Bull. Chem. Soc. Jpn. 24 (2008) 1537-1544

[8] W.J. Clark, S.H. Park, D.A. Bostick, D.C. Duckworth, G.J. van Berkel, Anal. Chem. 78 (2006) 8535-8542

[9]   T. Akagi, K. Fuwa, H. Haraguchi, Anal. Chim. Acta. 177 (1985) 139-151

[10] G. Bayon, D. Birot, C. Bollinger, J. A. Barrat, Geostand. Geoanal. Res. 35 (2011) 145-153

[11] C.L. Chou, J.D. Moffatt, J. Fresenius, Anal. Chem. 368 (2000) 59-61

[12]   Y. Zhu, K. Inagaki, H. Haraguchi, K. Chiba, J. Anal. At. Spectrom. 25 (2010) 364-369

[13] T.J. Shaw, T. Duncan, B. Schnetger, Anal. Chem. 75 (2003) 3396-3403

[14] J. Wu, E.A. Boyle, Anal. Chem. 69 (1997) 2464-2470

[15]   M. Grotti, F. Soggia, F. Ardini, R. J. Frache, Anal. Spectrom. 24 (2009) 522-527

[16]   J. Wu, Mar. Chem. 103 (2007) 370-381

[17]   M.A. Saito, D.L. Schneider, Anal. Chim. Acata 565 (2006) 222-233

[18]   P. Grindberg, S. Willie, R.E. Sturgeon, J. Anal. At. Spectrom. 20 (2005) 717-723

[19]   B.A. Mc Kelvey, K.J. Orians, Mar. Chem. 60 (1998) 245-255

[20]   J. Wu, E.A. Boyle, Anal. Cim. Acta.(1998) 183-191

[21]   Y. Zhu, K. Inakagi, K. Chiba, J. Anal. At. Spectrom. 24 (2009) 1179-1183

[22]   M.P. Field, R.M. Sherrell, Anal. Chem. 70 (1998) 4480–4486

[23]   G. Bayon, J.A. Barrat, J. Etoubleau, M. Benoit, S. Révillon, C. Bollinger, Geostand. Geoanal. Res. 32 (2009) 51-62.

[24]   J.A. Barrat, F. Keller, J. Amossé, R.N. Taylor, R.W. Nesbitt, T. Hirata, Geostand. Newsl. 20 (1996) 133-139

[25]   M.G. Lawrence, B.S. Kamber, Geostand. Geoanal. Res. 31 (2007) 95-103

[26]   D. Rahmi, Y.B. Zhu, E. Fujimori, T. Umemura, H. Haraguchi, Talanta 612 (2007) 600-606

[27]   L. Yang, S. Willie, R.E. Sturgeon, J. Anal. At. Spectrom. 24 (2009) 958-963

[28] I. Sánchez Trujillo, E. Vereda Alonso, M.T. Siles Cordero, J.M. Cano Pavón, A. García de Torres, J. Anal. At. Spectrom. 25 (2010) 1063-1071

[29] S.R. Taylor, S.M. McCLennan, The Continental Crust: its Composition and Evolution. Blackwell, Oxford, 1985.

Tables

Table 1. ICP–MS operating conditions and measurement parameters.

RF power	1200 W
Coolant argon flow rates	16.11 l/min
Auxiliary argon flow rates	0.61 l/min
Nebulizer argon flow rates	0.88 l/min
Torch	Quartz thermo fisher
Nebulizer	Teflon® 100 µl
Spray chamber	ESI Quartz dual cyclonic
Cones	Nickel
Acquisition mode	E-scan + bi-scan
No. of scans	2 (LRM) + 2 (MRM)
Ion lens settings	Adjusted daily to obtain maximum signal intensity
Wash time	150 s (5% v/v HNO_3)

Table 2. Total procedural blanks, limits of detection and results for NASS-5, CASS-4 and Dellec SW.

Elements	Method blank (pg)	Limit of detection (ng kg⁻¹)	NASS-5					CASS-4					Dellec SW		
			This report (n = 17)			Reference		This report (n = 11)			Reference		This report (n = 20)		
			Mean (ng kg⁻¹)	s	RSD (%)	Mean (ng kg⁻¹)	s	Mean (ng kg⁻¹)	s	RSD (%)	Mean (ng kg⁻¹)	s	Mean	s	RSD (%)
Cr	92	1.03	110	7	6.2	107[a]	15	—	—	—	141[a]	29	131	14	11
Mn	26	0.49	954	51	5.4	897[a]	57	2587	192	7.4	2715[a]	190	2027	68	3.3
Co	20	0.23	10	1	10	10[a]	3	23	2	11	25[a]	3	18.1	0.9	5.1
Y	4	0.11	25	1	6.1	25.4	0.5	20.5	0.9	4.5	20.5	0.1	21.0	0.6	2.7
La	0.3	0.012	11.2	0.9	8.4	12.7	0.2	9.0	0.7	7.6	9.1	0.1	3.3	0.1	4.4
Ce	0.4	0.020	5.4	0.2	4.2	5.4	0.6	3.8	0.1	3.1	3.76	0.02	4.9	0.1	2.0
Pr	0.1	0.007	1.98	0.07	3.4	2.06	0.03	1.27	0.06	4.9	1.280	0.003	0.78	0.04	5.0
Nd	0.4	0.029	8.4	0.2	2.8	8.6	0.2	5.6	0.4	7.2	5.38	0.03	3.6	0.2	4.4
Sm	0.2	0.015	4.7	0.2	3.3	4.7	0.6	5.6	0.3	4.6	5.60	0.02	0.92	0.04	4.3
Eu	0.06	0.006	0.32	0.02	5.9	0.30	0.05	0.23	0.03	14	0.21	0.01	0.22	0.02	6.9
Gd	0.1	0.016	1.8	0.1	6.2	1.86	0.04	1.31	0.09	7.2	1.31	0.03	1.36	0.08	5.9
Tb	0.05	0.004	0.27	0.01	5.1	0.276	0.003	0.19	0.02	11	0.185	0.004	0.20	0.02	8.1
Dy	0.1	0.005	1.86	0.05	2.9	1.88	0.04	1.4	0.1	9.4	1.36	0.02	1.50	0.06	3.9
Ho	0.1	0.005	0.47	0.04	7.4	0.469	0.009	0.36	0.03	9.3	0.359	0.004	0.46	0.03	5.5
Er	0.2	0.006	1.47	0.04	2.8	1.46	0.01	1.18	0.06	5.1	1.174	0.005	1.20	0.03	2.7
Yb	0.06	0.008	1.26	0.06	4.6	1.27	0.02	1.09	0.07	6.2	1.12	0.01	1.06	0.04	3.3
Lu	0.03	0.001	0.20	0.01	4.9	0.199	0.004	0.185	0.009	5.0	0.180	0.001	0.17	0.01	6.0

a   The reference data correspond to certified values. Other reference data correspond to the concentrations determined after iron co-precipitation and Tm addition (Bayon et al. [10]).
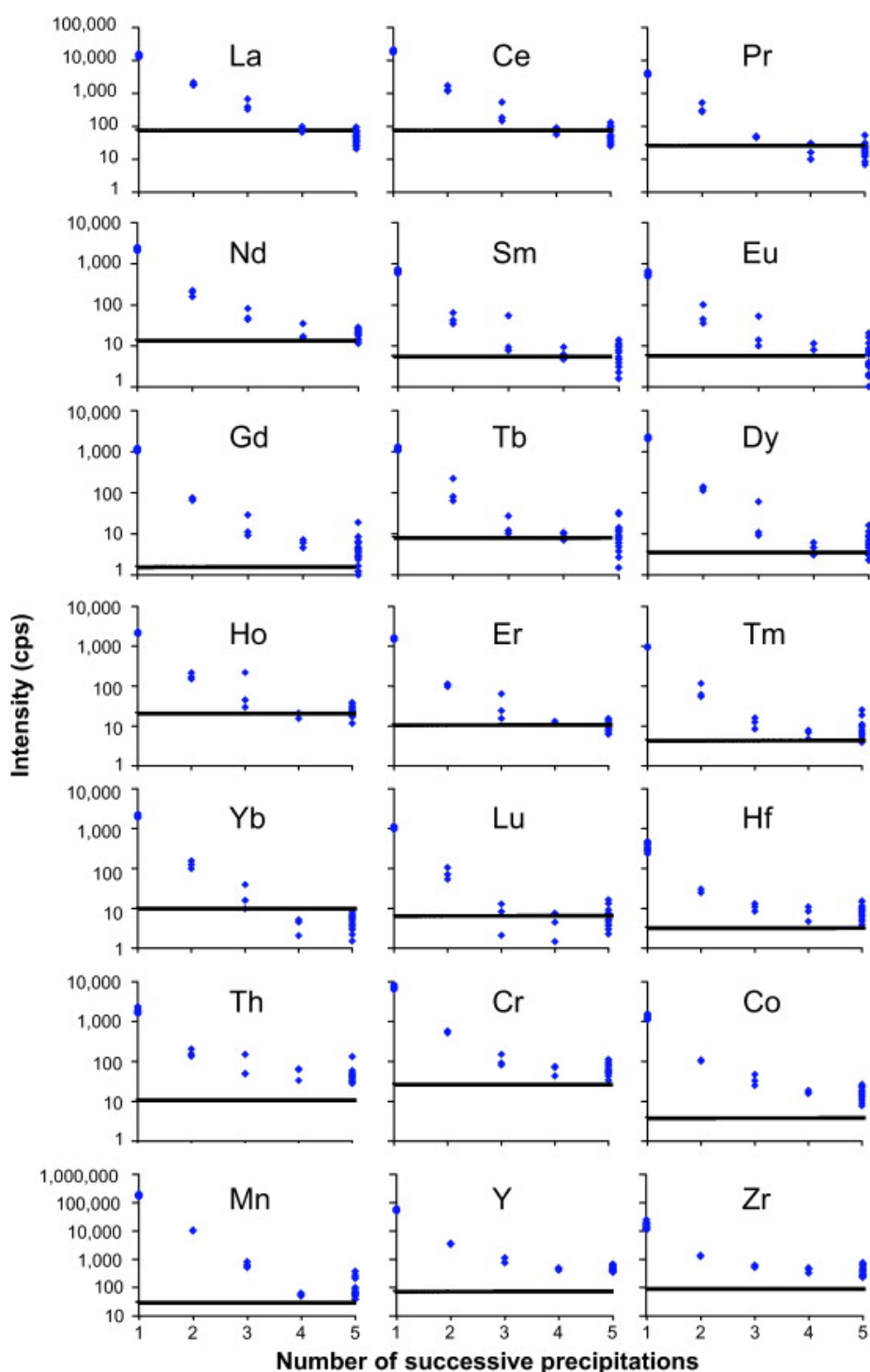
Figures

Figure 1. Effect of successive $Mg(OH)_2$ co-precipitations on trace element scavenging.
The efficiency of successive co-precipitations in scavenging rare earth and other trace elements (Hf, Th, Cr, Co, Mn, Y and Zr) from our in house coastal seawater standard (Dellec SW) is illustrated as measured ICP-MS intensities (cps) versus the number N of successive co-precipitations. There were 24 replicate samples (n=24) analysed for the first coprecipitation experiment (N1); n=6 for N2; n=6 for N3; n=6 for N4 and n=24 for the last series of successive coprecipitation experiments (N5). In each panel, the thick line indicates the mean background intensity obtained during the course of our experiments for a 2% sub-boiled HNO_3 solution.
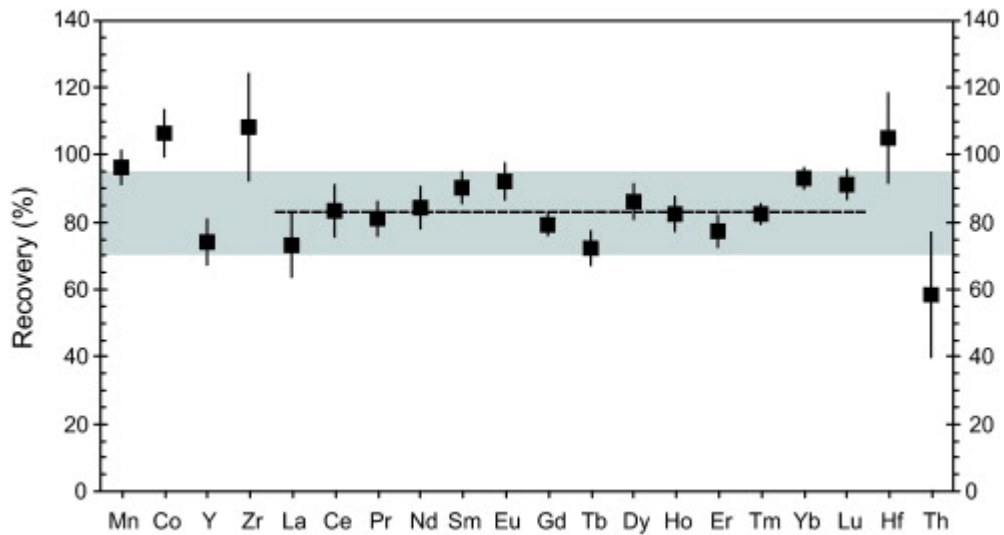
Figure 2. Co-precipitation yields during Mg co-precipitation.

The average percent recoveries were calculated using both NASS-5 (n=7) and CASS-4 (n=4) after one Mg co-precipitation experiment. The shaded area corresponds to the range of yields calculated for the REEs, from ~ 72 % for Tb to 93 % for Yb, with a mean recovery of 83 ± 14% (dashed line). Error bars represent 1 standard deviation.
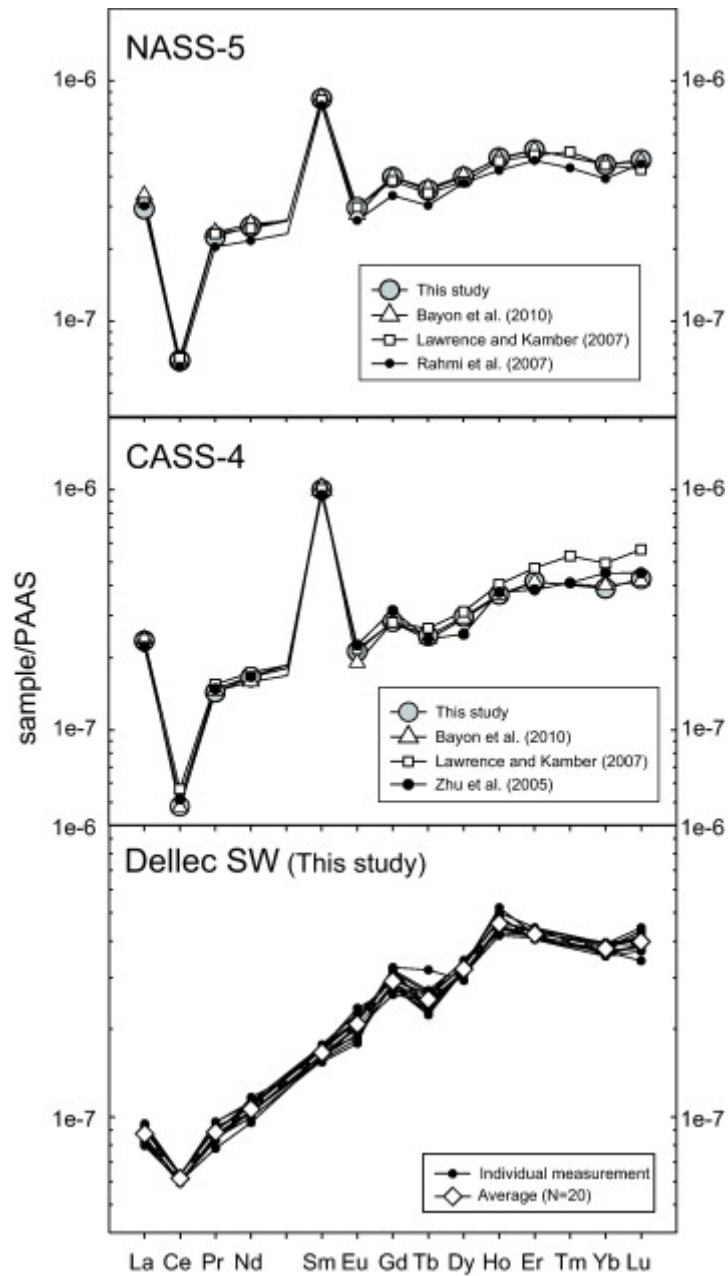
Figure 3. Post-Archean Australian Shales (PAAS)-normalized (Taylor and McClennan, 1985 [29]) REE patterns for NRCC water reference materials (NASS-5, CASS-4) and in house coastal seawater Dellec SW. Note that the Sm anomaly observed in NASS-5 and CASS-4 does not correspond to a natural oceanic feature, but reflects instead contamination during reference material preparation [25].