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Dissolved rare earth elements in the central-western sector of the Ross Sea, Southern Ocean: Geochemical tracing of seawater masses

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HIGHLIGHTS

- Rare earth element composition as fingerprint of new formation water masses is proposed.
- REEs pattern coming from catchment area and hydrothermal activity of western Ross Sea.
- Tb and Nd peaks are recognized as particular fingerprint of HSSW waters.

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ABSTRACT

The present essay contributes to the existing literature on rare earth elements (REEs) in the southern hemisphere by presenting the first data, to our knowledge, on the vertical profiles of dissolved REEs in 71 samples collected in the central-western sector of the Ross Sea (Southern Ocean-SO). The REEs were measured in the water samples collected during the 2002–2003 and 2005–2006 austral summers. 4 samples were collected and analysed in the framework of a test experiment, as part of the WISSARD Project (Whillans Ice Stream Subglacial Access Research Drilling). Our results show significant differences between the REE patterns of the main water masses present in the SO: we could observe specific signature in the High Salinity Shelf Water (HSSW), Ice Shelf Water (ISW) and Low Salinity Shelf Water (LSSW). A significant increase in Terbium (Tb) concentration was observed in the HSSW and ISW, the two principal water masses contributing to the formation of Antarctic Bottom Water (AABW) in the Ross Sea area, and in LSSW. Some of the HSSW samples show enrichment in Neodymium (Nd). Dissolved REE could therefore be used as tracers to understand the deep circulation of the SO (Pacific sector).

We hypothesize that: (I) the characteristic dissolved REE pattern may derive from the composition of source area and from the hydrothermal activity of the central-western area of the Ross Sea; (II) the Tb anomaly observed in the AABW on the South Australian platform could be partially explained by the contribution of AABW generated in the Ross Sea region.

1. Introduction

The Ross Sea is a key area for the formation of new waters and plays for the ventilation of ocean bottom waters worldwide. It comprises the waters covering the continental shelf and is limited to the north by the ideal line running between Cape Colbeck and Cape Adare and to the south by the Ross Ice Shelf (RIS) (Dinniman et al., 2003; Cincinelli et al., 2008). The only water of external origin influencing the Ross Sea mass waters is the warm, nutrient-rich and salty Circumpolar Deep Water (CDW), carried around the Antarctic continent by the Antarctic Circumpolar Current (ACC) (Catalano et al., 2000; Orsi and Wiederwohl, 2009). By mixing with the surface and shelf waters of the Ross Sea, the CDW generates the so-called MCDW. The most characteristic water of the Ross Sea is the HSSW, which, by flowing beneath the RIS contributes to the formation of ISW. Our knowledge about trace element distribution in the waters of the Ross Sea is partial and limited to specific elements such as heavy metals (Fe, Cd, Cu, Pb, Mn, Zn, etc.) (Capodaglio et al., 1989; Gragnani and Torcini, 1992; Abollino et al., 1995; Scarponi

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et al., 1995, 1997; Capodaglio et al., 1998; Fitzwater et al., 2000; Frache et al., 2001; Grotti et al., 2001; Coale et al., 2005; Corami et al., 2005; Turetta et al., 2010; Rivaro et al., 2011).

The distribution of trace elements in ocean waters is controlled by two principal factors: the origin and the processes affecting the dissolved/particulate partition. The characteristic profile of the vertical concentration of trace elements therefore reflects their origin and geochemical reactivity (Bruland, 1983). There is also evidence that their interaction with dissolved organic matter may also play an important role in the distribution of reactive elements that are not involved in biological cycles (Capodaglio et al., 1990). On the one hand, the complexity of the cycles that control trace element distribution makes it quite difficult to define the concentration levels in specific water masses. On the other hand, the elemental composition could be a good means to identify specific water masses. Therefore, it is particularly important to be able to identify the markers of specific water masses in order to follow their contribution to the overall oceanic circulation.

REEs in the ocean are of lithogenic origin (Goldstein and Hemming, 2003), with contributions from aerosol particles and dissolved river loads (Sholkovitz et al., 1999; Dubinin, 2004). Other studies suggest that the dominant source of REEs in the ocean is the dissolution of sediments from continental shelves (Zhang et al., 2008), while in ice-covered oceans the major source of REEs is probably particulate matter rafted by sea ice and glacial ice (Winter et al., 1997). Due to their consistent geochemical behaviour, REEs may be useful to trace the different seawater masses and to recognize their provenance and fate; and due to their relatively short mean oceanic residence time, they can also be used to characterize water masses in terms of ocean circulation and geochemical behaviour (Piepgras and Jacobsen, 1992; Byrne and Sholkovitz, 1996; Alibo and Nozaki, 2004). In particular, as reported by Nozaki and Alibo, "the vertical profiles of light REEs (LREEs) and some medium REEs (MREEs) are variable from basin to basin" and "the heavy REEs (HREEs) are largely governed by the horizontal processes of ocean circulation" (Nozaki and Alibo, 2003).

The Southern Ocean is considered as one of the most important feeders of bottom waters worldwide. By comparing our data to those found in the literature, we may hypothesize the contribution of newly formed waters from the Ross Sea to the water masses of the South Pacific Ocean. Taking into account the behaviour of Tb and Nd in the new waters HSSW, ISW, LSSW, as well as in MCDW we can characterize the AABW generated from the new waters of the Ross Sea (Orsi et al., 1999; Corami et al., 2005; Orsi and Wiederwohl, 2009) and recognize this water mass in the South Australian platform. To this aim, we normalized REE concentrations against the composition of North Pacific Deep Water (NPDW) (Nozaki, 2001).

The aim of this paper is to propose a new data set of dissolved REEs from the Ross Sea, Southern Ocean, in order to contribute to the knowledge of inter-basin circulation. The REE pattern is used as a tracer of seawater masses and to recognize possible sources of REEs in the Ross Sea. Total dissolved REE concentrations were measured along the vertical profile at various sites in the Ross Sea (Antarctica) in order to emphasize characteristic anomalies of water masses contributing to the formation of AABW.

2. Methodology and characteristics of the research area

2.1. Material and methods

In the framework of the Italian expeditions in Antarctica on board of the R.V. Italica, during the austral summer 2002–2003 and 2005–2006, 71 seawater samples from 10 depth profiles were collected in the western sector of the Ross Sea (Southern Ocean, Antarctica). Fig. 1 shows the location of the sampling sites while Table 1 summarises the spatial coordinates and maximum depth of each profile, and the year of the campaign; the sites were chosen in order to evaluate some of the relevant water masses present in the area. The sampling strategy was based on *in situ* measurements of salinity, temperature and dissolved oxygen along the water column (sampling depth was decided in order to include waters with different characteristic in the studied profile). After sampling, the hydrological bottles were immediately transferred into a mobile clean-laboratory (Class 100) installed on board, the samples were filtered and immediately frozen at −20 °C for transport to Italy without any additional treatment. Sampling strategy, filtration and storage on board, as well as the sample handling and analysis procedure were described in previous papers (Turetta et al., 2004, 2010).

Details regarding the samples from the WISSARD project are

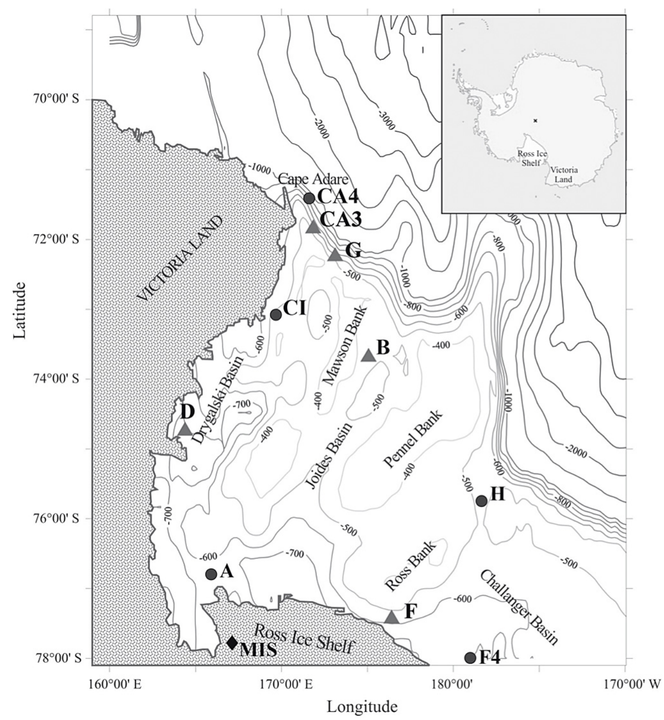

Fig. 1. Sampling sites; simplified map of the western sector of the Ross sea (bottom topography in meters). Triangles represent the 2002–2003 campaign; dots represent the 2005–2006 campaign; diamonds represent the boreholes of the Wissard project samples (Turetta et al., 2010, modified). Each depth profile is indicated as a single point.

Table 1
Geographical coordinates of the profiles. The depth column indicates the floor depth.

Profile	Latitude S	Longitude E/W	Depth (m)
2002–2003			
B	74°01.10′ S	175°04.60′ E	581
CA3	71°56.00′ S	171°52.00′E	630
D	75° 07.00′ S	164° 28.00′ E	1050
F	77°32.30′ S	176°02.00′ E	700
G	72°20.00′S	173°03.00′ E	510
2005–2006			
A	76°41.00′ S	169°04.00′ E	790
CA4	71°32.32′ S	172°17.16′ E	1688
CI	73°13.58′ S	171° 13,44′ E	537
F4	77°56.34′ S	177°53.09′ W	654
H	75°57.06′ S	177°23.11′ W	615