

## Dissolved Iron in the Arctic and Antarctic Oceans

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Iron (Fe) is an essential trace element for all biota but the dissolved Fe in ocean waters is extremely low and limiting for phytoplankton growth in over 40% of world ocean surface waters. Indeed in the Southern Ocean extremely low dissolved Fe was found in surface waters along the Greenwich meridian, both in the Antarctic Circumpolar Current and in the most southerly Weddell Gyre adjacent to the ice-covered Antarctic continent [1]. The low dissolved Fe is maintained in solution by organic complexation [2]. The extending continental ice-sheet floating over the continental shelf is unique in largely preventing biological processes and cycling. As a consequence Antarctica is the only continent that does not supply Fe [1] and Mn [3] from shelf sediment sources into adjacent surface and intermediate waters. In contrast the shelves at both sides of the Antarctic Peninsula are a source for dissolved Fe, Mn and Al into the western Weddell Sea and southern Drake Passage, respectively. Otherwise dissolved Fe concentrations are extremely low in the entire water column of the Weddell Sea and Drake Passage. In West Antarctica the local Pine Island Glacier is a source of dissolved Fe [4] fueling intensive phytoplankton blooms [5] in the Amundsen Sea where organic complexation [6] of Fe plays a key role. In deep waters there is a significant hydrothermal plume of Fe and Mn over the Bouvet Triple Junction region. One water mass in Drake Passage also shows hydrothermal Fe and Mn associated with  $\delta^3\text{He}$  anomalies originating from the Pacific Ocean [7]. In the Arctic Ocean a very strong hydrothermal Fe and Mn plume was found over the Gakkel Ridge [8, 9]. The large spatial extent of Fe of hydrothermal origin is ascribed to its stabilization in solution by organic complexation [10]. Surface waters in the central Arctic Ocean have fairly high dissolved Fe concentrations due to the Transpolar Drift bringing along coastal waters, mainly of Siberian riverine origin with high dissolved Fe contents [11]. As a result the Arctic Ocean has fairly adequate Fe abundance for phytoplankton growth, this in contrast to the very low and bio-limiting dissolved Fe in large areas of the Antarctic Ocean.

[1] Klunder et al. (2011) *Deep-Sea Res. II*, 56, 2678. [2] Thuroczy et al. (2011) *Deep-Sea Res. II*, 56, 2695. [3] Middag et al. (2011) *Deep-Sea Res. II*, 56, 2661. [4] Gerringa et al. (2012) *Deep-Sea Res. II*, in press. [5] Alderkamp et al. (2012) *Deep-Sea Res. II*, in press. [6] Thuroczy et al. (2012) *Deep-Sea Res. II*, in press. [7] Middag et al. (2012) *J. Geophys. Res. Oceans*, in press. [8] Middag et al. (2011) *Geochim. Cosmochim. Acta*, 75, 2393. [9] Klunder et al. (2012a) *J. Geophys. Res. Oceans*, in press. [10] Thuroczy et al. (2011) *J. Geophys. Res. Oceans*, 116, C10009, doi:10.1029/2010JC006835. [11] Klunder et al. (2012b) *J. Geophys. Res. Oceans*, in press.

## Atmospheric gases: the archaeological glasses memory

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The atmospheric components of past climatic changes are often constrained from ice records of polar ice sheets. In temperate areas, this kind of study is more difficult to apply due to the low spatial and temporal resolution of the iced records.

In this study, we propose an alternative method based on analyses of atmospheric gases trapped in bubbles of archaeological glasses from the Western Europe and dated between the 1<sup>st</sup> century BC to the present. Indeed, during the shaping of ancient glasses, bubbles are created in glass paste, from the melting of raw materials inside furnace and glass-paste degassing, or from the step of glass working in open air. In this second case, the surrounding atmosphere could be trapped, particularly during the glass-making of ancient and medieval stained windows.

While the study of Vesicle Size Distribution (VSD) [1] of archaeological flat glasses show a bimodal size bubbles distribution in flat glasses, the distribution of the other kind of glasses (blown cup or vessel, and raw glasses) are unimodal. Geochemical analyses of major gases included in bubbles in flat glasses, show a chemical dichotomy between two groups of bubbles, independent of chemical composition of glass paste. The smallest bubbles ( $\text{Ø} < 100\text{-}500\ \mu\text{m}$ ) are exclusively composed of  $\text{CO}_2$ . In contrast, the largest bubbles ( $\text{Ø} > 250\text{-}500\ \mu\text{m}$ ) are  $\text{N}_2$  rich (~80%),  $\text{CO}_2$  poor and contained Ar (~1%), and sometimes  $\text{O}_2$ . So, the origins of the two populations of bubbles are obviously different and the largest vesicles seem to have an atmospheric origin (the Ar/ $\text{N}_2$  ratios of these large bubbles are closed to the modern atmosphere).

Despite these gases look like an atmospheric composition, the  $\text{CO}_2$  contents are too high and the oxygen contents are too low. The carbon excess could have different origins (mixing between atmosphere and furnace/combustion gases, and/or chemical reactions between trapped gases and particular soots). SEM analyses have shown some deposits in the inner wall of the largest bubbles (graphite, carbon oxides etc.), supporting the idea of a catch of elements as alien to glass and in-situ chemical reactions.

We need to take care of these soot-reactions and the gases diffusion rates through the glass, to estimate the initial compositions of gases included in vesicles, and to extract the atmospheric contribution from the bubbles gases set using mixing models. Finally, we suggest that the archaeological glasses could appear like a new but complex source of archeo-climatic recording.

[1] Sarda & Graham (1990), *EPSL* 97, 268-289.