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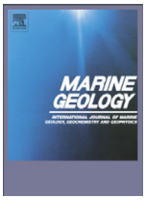

When deep diagenesis in Arctic Ocean sediments compromises manganese-based geochronology

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ABSTRACT

We used a diagenetic model to test the hypothesis that manganese-rich layers in gas hydrate-bearing Arctic Ocean sediments are reliable time markers for interglacial periods. In the model, diagenesis is fuelled by two sources of reactive carbon: particulate organic carbon settling to the sediment surface, and methane diffusing up from deep gas hydrate deposits. The model includes oxidation of organic carbon and soluble reduced manganese by oxygen supplied continuously from an invariant bottom-water oxygen reservoir; reduction of particulate manganese by hydrogen sulfide generated through anaerobic methane oxidation; transport of dissolved oxygen and manganese by diffusion; and advective transport of particulate components by burial. Particulate organic matter and particulate manganese are only supplied to the sediment during interglacials. Sulfate reduction is not modeled explicitly; instead, the effect of anaerobic methane oxidation on Mn reduction is simulated at the lower boundary of the model by prescribing that particulate manganese is reduced there to soluble Mn(II). The soluble reduced Mn then diffuses upward and is oxidatively precipitated to Mn(IV) by downward diffusing oxygen. The upward flux of soluble Mn(II) is thus a function of the rate at which particulate manganese is advected into the Mn-reduction layer at the bottom of the model; it is not synchronous with events at the sediment–water interface. Model runs reveal that, under idealized but realistic conditions for the Arctic Ocean, oxidation of upward-diffusing Mn(II) generates post-depositional manganese enrichments that cannot readily be distinguished from the manganese-rich sediment layers that accumulate during interglacials. This compromises the use of manganese-rich layers as proxies for interglacial periods. In contrast, manganese-rich layers may be used as first-order markers of interglacial periods in sediments where gas hydrates or other forms of reactive carbon are absent.

1. Introduction

Poor preservation of microfossil records in Arctic Ocean sediments has spurred the search for alternative proxies for the Quaternary chronology of these sediments (Jakobsson et al., 2000; and references therein). Manganese-rich interbedded layers, found in numerous long cores recovered from the Central Arctic Ocean (März et al., 2011; Löwemark et al., 2014; Macdonald and Gobeil, 2012) are strong candidates as proxies of interglacial periods. A time scale based on manganese content and sediment color in a core from the Lomonosov Ridge correlates closely with an independent paleomagnetic chronology of the same core, based on Brunhes-age estimates of geomagnetic excursions (Jakobsson et al., 2000; Löwemark et al., 2008). Recent geochemical work has shown that the manganese-rich layers are also rich in several trace metals as well as in biogenic and ice-rafted carbonate and contain preserved traces of bioturbation (März et al., 2011; Löwemark et al., 2014).

There are few measurements of dissolved manganese in long cores from the Arctic. Dickens et al. (2007) measured manganese in a long core from about 1200 m depth on the Lomonosov Ridge and found increasing concentrations of dissolved Mn in the pore water beginning a few m below the sea floor and reaching maximum values at 20 m depth. In a more detailed study, März et al. (2011) working with a long core from 1200 m depth on the Mendeleev Ridge, found an upward directed gradient of dissolved manganese between 6 and 3 m, suggesting possible overprinting of diagenetically mobilized manganese on existing Mn-rich layers.

A scenario whereby the fluxes of particulate organic carbon and manganese to the sea floor in the Arctic Ocean varied dramatically during the glacial cycles of the Quaternary is consistent with observations. During glaciations, the absence of primary production virtually shuts

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off the flux of organic carbon, and the ice cover on the continents slows down the delivery of manganese-rich sedimentary material to the sea floor. During interglacials, primary production is turned on and delivers fresh organic carbon to the sea floor while rivers and the expanded continental shelves deliver terrigenous organic carbon and manganese-bearing particulate matter (Macdonald and Gobeil, 2012). Upon burial, manganese-rich interglacial sediments enter the geological record sandwiched between layers of manganese-poor glacial sediment. If the manganese-rich layers remain intact, they mimic the glaciation-interglaciation cyclicity. Several plausible mechanisms for delivering manganese-rich sediment to the sea floor during interglacials have been proposed (e.g. Macdonald and Gobeil, 2012).

The hypothesis that Mn-rich sediment layers enter the geological record intact rests on the assumption that diagenetic remobilization and redistribution of manganese is fuelled exclusively by organic carbon settling from the water column and that manganese diagenesis stops when this carbon has been consumed. The objective of the present study is to test this hypothesis and verify if manganese-rich layers in deep Arctic Ocean sediments can be used as a proxy for interglacial periods. It is not our intention to reconstruct the past. Specifically, we test this hypothesis for sediments that host gas hydrates. Such sediments are abundant in the Arctic Ocean where vast amounts of methane hydrates are believed to be stored (Buffett and Archer, 2004; Klauda and Sandler, 2005). The actual amounts are uncertain (Milkov, 2004).

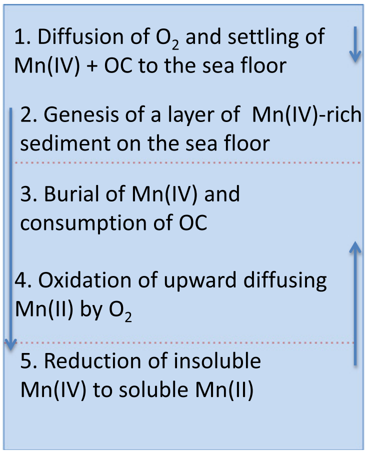
2. Model description

2.1. The conceptual model

The choice of diagenetic model for this study was dictated by our objective, which was to test the hypothesis that manganese-rich layers in deep Arctic Ocean sediments can be used as a proxy for interglacial periods. To this end, we chose the simplest possible model that would help us meet this objective and left out reactions that could give a more complete description of diagenesis such as oxidation of Fe(II) and ammonia by oxygen and reduction of Fe(III) by hydrogen sulfide. The sedimenting reactive organic matter is assumed to be mineralized entirely through oxic respiration (the mineralization process is carbon limited), so a more complex model that includes the products of anaerobic mineralization pathways would not be expected to change our conclusions.

The model we used is a one-dimensional non-steady state diagenetic transport-reaction model that captures the essential features of manganese diagenesis, i.e. reduction of Mn(IV) to Mn(II) (dissolution), reoxidation of Mn(II) to Mn(IV) (precipitation), transport of dissolved manganese by diffusion, and transport of precipitated manganese by advection. Fig. 1 shows the conceptual version of the model. It includes two sources of reactive organic carbon: fresh organic matter settling through the water column and methane released from gas hydrates deep in the sediment column. The reactive organic carbon deposited on the sediment surface is consumed in reactions with dissolved oxygen as it is buried and advected downward. Oxygen diffuses into the sediment from a permanently oxygenated water column. The second source of carbon, methane, is oxidized by micro-organisms that use sulfate as a terminal electron acceptor. This process, anaerobic methane oxidation (AMO), is known to take place in the sulfate-methane transition layer (SMT) where upward diffusing methane and downward diffusing sulfate are consumed and become depleted. AMO produces sulfide, which reduces oxidized particulate Mn(IV) to soluble Mn(II) (Aller and Rude, 1988). Methane may also reduce oxidized manganese directly (Beal et al., 2009). The model domain is bounded at the top by the sediment surface and at the bottom by a depth that remains at a fixed distance from the upper boundary. Thus, both boundaries move upwards at the rate with which sediment accumulates, set at 1 cm Ky^{-1} in the model. One may reasonably expect that the sediment accumulation rate is higher during interglacials than during glacials and, therefore, that the assumption of constant sedimentation rate may not be realistic. Nonetheless, since the differential rates are not known, and given that the spatial scale of Mn redistribution (~2 m) is greater than the thickness of the sediment layer deposited during one cycle, making this assumption is not expected to change the conclusions.

The reactions in the SMT that produce hydrogen sulfide are not included explicitly in the model, nor is the reduction of Mn(IV) to Mn(II) by hydrogen sulfide. Instead, reducing conditions are prescribed near the bottom of the model domain. There, particulate oxidized manganese, advected downward by burial, is reduced to soluble Mn(II), which diffuses upwards until reoxidized by downward diffusing oxygen. The thickness of the prescribed reduction layer (a few cm in the numerical model implementation) is not critical because the production rate of dissolved Mn(II) is transport controlled, i.e. the rate of reductive dissolution overwhelms the rate of supply of reducible manganese. The choice of a 5-m thick model domain was inspired by the data of März et al. (2011),



① Bottom water $[O_2]$ is constant; settling fluxes of Mn(IV) and OC are constant during interglacials and zero during glacials.

② Accumulation of Mn(IV)-rich settling particulate matter through the water column forms a Mn(IV)-rich layer on the sea floor

③ During burial, OC becomes exhausted and the Mn(IV)-rich layer generated during an interglacial is preserved until it reaches the reduction zone.

④ Mn(II) is reoxidized and precipitated as Mn(IV) when it encounters downward diffusing O_2. The O_2 penetration depth depends on the oxygen demand of OM and Mn(II) oxidation.

⑤ Anaerobic methane oxidation creates a reducing environment where insoluble Mn(IV) is reduced to soluble Mn(II). The upward flux of Mn(II) from this layer equals the flux of Mn(IV) into the layer. The fluxes depend on the distribution of Mn(IV) in the sediment column and the burial rate.

Fig. 1. Spatial representation of the conceptual model. In the time evolution of this system, the processes associated with step 4 only take place once step 5 has occurred for the first time.