Silicate weathering in anoxic marine sediments

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Introduction

Two sediment cores retrieved at the northern slope of Sakhalin Island, Sea of Okhotsk, were analysed for biogenic opal, organic carbon, carbonate, sulphur, major element concentrations, mineral contents and dissolved substances including nutrients, sulphate, methane, major cations, humic substances and total alkalinity. Down-core trends in mineral abundance suggest that plagioclase feldspars and other reactive silicate phases (olivine, pyroxene, volcanic ash) are transformed into smectite in the methanogenic sediment sections. The element ratios Na/Al, Mg/Al and Ca/Al in the solid phase decrease with sediment depth indicating a loss of mobile cations with depth and producing a significant down-core increase in the chemical index of alteration. Pore waters separated from the sediment cores are highly enriched in dissolved Mg, total alkalinity, humic substances and boron. The large contents of dissolved organic carbon in the deeper methanogenic sediment sections ($50-150$ mg dm^{-3}) may promote the dissolution of silicate phases through complexation of Al^{3+} and other structure-building cations. A non-steady state transport-reaction model was developed and applied to evaluate the down-core trends observed in the solid and dissolved phases. Dissolved Mg and total alkalinity were used to track the in-situ rates of marine silicate weathering since thermodynamic equilibrium calculations showed that these tracers are not affected by ion exchange processes with sediment surfaces. The modelling showed that silicate weathering is limited to the deeper methanogenic sediment section whereas reverse weathering was the dominant process in the overlying surface sediments. Depth-integrated rates of marine silicate weathering in methanogenic sediments derived from the model ($81.4-99.2$ mmol CO$_2$ m^{-2} yr^{-1}) are smaller than the marine weathering rates calculated from the solid phase data ($198-245$ mmol CO$_2$ m^{-2} yr^{-1}) suggesting a decrease in marine weathering over time. The production of CO$_2$ through reverse weathering in surface sediments ($4.22-15.0$ mmol CO$_2$ m^{-2} yr^{-1}) is approximately one order of magnitude smaller than the weathering-induced CO$_2$ consumption in the underlying sediments. The evaluation of pore water data from other continental margin sites shows that silicate weathering is a common process in methanogenic sediments. The global rate of CO$_2$ consumption through marine silicate weathering estimated here as $5-20$ Tmol CO$_2$ yr^{-1} is as large as the global rate of continental silicate weathering. Details of the present work can be found in (Wallmann *et al.*, 2008).

Methods

Sediments were taken by piston coring at the northern continental slope of Sakhalin Island during cruise SO178 with RV SONNE in July−September 2004. Core KL-13-6 was retrieved at a water depth of 713 m (position: 52º43.88′N; 144º42.65′E) while core KL-29-2 was taken further north (53º50.00′N; 144º14.23′E) at 771 m water depth. Pore fluids were processed and analysed as previously described (Wallmann *et al.*, 2006). Solids were characterized by polarization microscopy, XRD and XRF. A numerical transport-reaction model was applied to the pore water data set to calculate

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rates of organic matter degradation, sulphate reduction, methane production, anaerobic oxidation of methane, carbonate precipitation and dissolution, and silicate weathering. Within this modelling framework, down-core changes in the rate of silicate weathering were traced and tracked applying the concentration profiles of dissolved Mg and total alkalinity (Wallmann *et al.*, 2008).

Results and discussion

Rapidly accumulating sediments composed of biogenic opal, organic matter, plagioclase feldspars, olivine, pyroxene, volcanic glass, clay minerals and other products of continental weathering are deposited at the Sakhalin slope. Reverse weathering occurring in the upper section of the studied sediment cores induces the fixation of dissolved cations (Mg^{2+}, Na^+, K^+, Li^+) in authigenic clays and the consumption of carbonate alkalinity. Ammonium released during the breakdown of organic matter is adsorbed at sediment surfaces replacing adsorbed Ca^{2+} and Na^+ ions that are released into the pore water via cation exchange. Reactive silicates (plagioclase feldspars, olivine, pyroxene, volcanic glass) are partly dissolved and transformed into cation-depleted silicate phases in the deeper methanogenic sediment sections (Fig. 1).

The marine weathering of these silicates induces the release of Mg^{2+}, Ca^{2+} and Na^+ as well as the formation of authigenic carbonates (Fig. 2). The CO_2 which formed during carbonate precipitation and breakdown of organic matter in methanogenic sediments is completely neutralized during silicate weathering. Rates of marine silicate weathering are one order of magnitude greater than the rates of reverse weathering and cation exchange in Sakhalin slope sediments and significantly larger than the rates of continental silicate weathering in the hinterland drained by the Amur River.

Pore water data obtained at other productive continental margin sites demonstrate that silicate weathering is a common process in methanogenic sediments with high metabolic activity. Most of the CO_2 formed during the anaerobic breakdown of organic matter is converted into alkalinity and authigenic carbonates (Wallmann *et al.*, 2008). Thus, silicate weathering in methanogenic marine sediments constitutes a significant sink for CO_2 and a source for carbonate alkalinity that needs to be included in future budgets of the global and marine carbon cycles. The global rate of marine silicate weathering estimated as $5-20$ Tmol CO_2 yr^{-1} may be as high as the global CO_2 consumption through continental weathering.

Conclusions and perspectives

Marine sediments have previously been regarded as important CO_2 sinks since large amounts of organic carbon formed though photosynthesis are ultimately buried at the seafloor. It has, however, been ignored that the degradation of organic matter in anoxic sediments works in a fundamentally different way than aerobic degradation. While aerobic respiration recycles CO_2 into the oceans and atmosphere, anaerobic degradation, coupled to marine silicate weathering, produces large amounts of carbonate alkalinity and authigenic carbonates. Thus, CO_2 fixed in organic matter during primary production is not recycled but transformed into other carbon
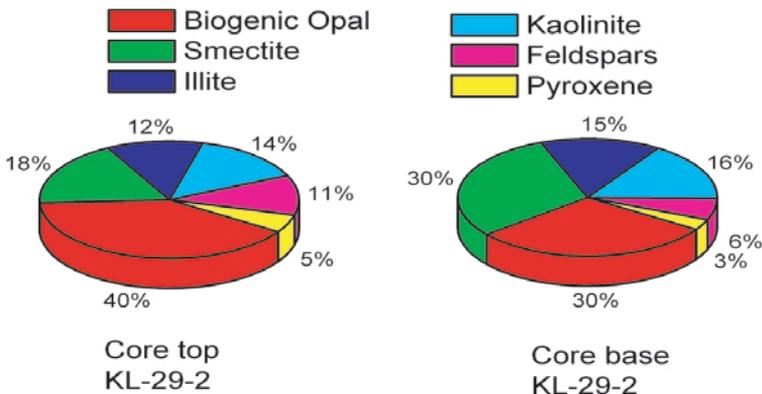
FIG. 1. Composition of surface sediments and core base sediments retrieved at the northern Sakhalin slope (KL-29-2).
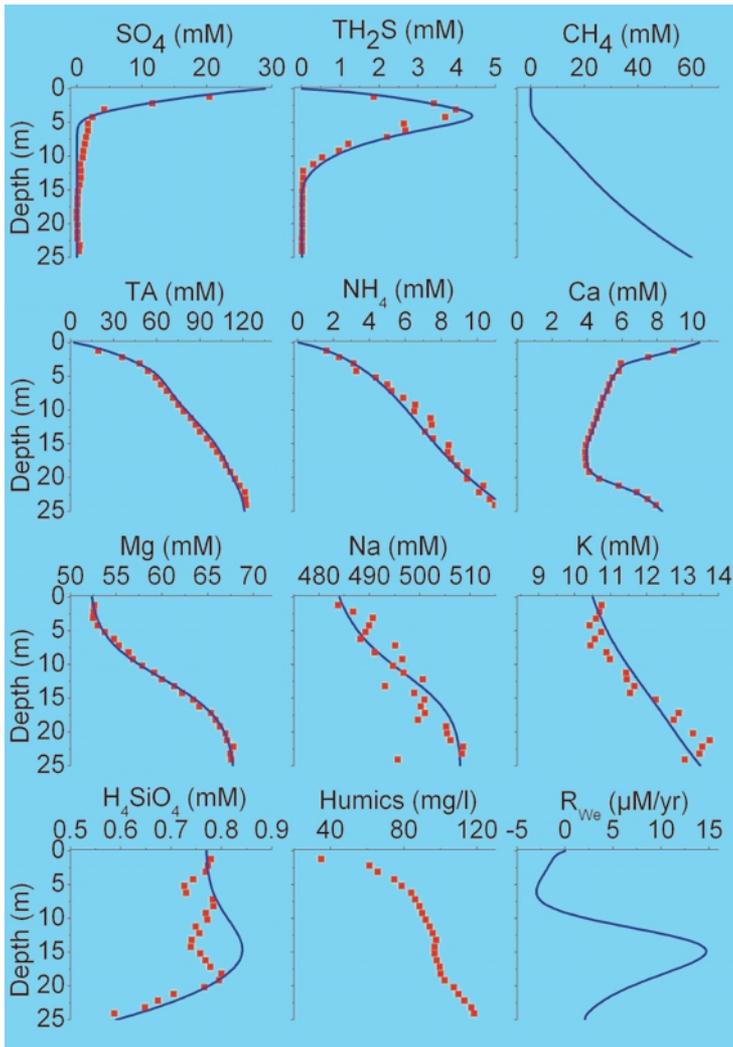
FIG. 2. Composition of pore fluids in sediments retrieved at the northern Sakhalin slope (KL-29-2). Red squares indicate data and blue curves represent the model results. TA is total alkalinity and R_{WE} gives the rate of CO_2 consumption via silicate weathering.

compounds (HCO_3^-, $CaCO_3$) during anoxic diagenesis. The global rate of carbon transformation in anoxic sediments is estimated here to be 7.6–28.8 Tmol C yr^{-1}. This value is at least as large as the global rate of organic carbon burial in marine sediments (13 Tmol C yr^{-1}; (Hedges and Keil, 1995) and therefore this previously ignored CO_2 sink has to be considered in future budgets of global carbon cycling.

The total alkalinity (TA) inventory of the oceans is believed to be controlled by riverine HCO_3^- inputs and through carbonate burial at the seafloor. The alkalinity budget of the Holocene ocean seems to be out of balance since TA removal through carbonate burial (48 Tmol yr^{-1}; Berner and Berner, 1996) is larger than the riverine TA flux (38 Tmol yr^{-1}; Berner and Berner, 1996). Part of this imbalance is caused by glacial to interglacial sea-level changes affecting carbonate burial on the continental shelves. The TA generated in anoxic marine sediments through silicate weathering and sulphur burial

$(4.3-15.5$ Tmol $yr^{-1})$ has, however, never been considered and may in fact account for a major portion of the apparent TA imbalance.

Marginal seas are known to act as CO_2 pumps taking up atmospheric CO_2 and exporting carbonate alkalinity into the open ocean (Tsunogai *et al*., 1999). This continental-shelf pump operating in the Sea of Okhotsk (Otsuki *et al*., 2003) and in other marginal seas (Thomas *et al*., 2004) may remove large quantities of anthropogenic CO_2 from the atmosphere. Anoxic sediments that are preferentially deposited at productive continental margins may contribute to the CO_2 uptake through marine silicate weathering and sulphur burial.

The global rate of authigenic carbonate burial in anoxic marine sediments estimated here as $3.3-13.3$ Tmol $CaCO_3$ yr^{-1} approaches the modern rate of pelagic carbonate burial (10 Tmol $CaCO_3$ yr^{-1}; (Archer, 1996). Productive continental margins with high rates of terrigenous sedimentation are thus important and previously ignored sites of carbonate accumulation. Approximately 50% of the Ca buried in authigenic carbonates originates from seawater such that the Ca balance of the ocean is also affected by anoxic diagenesis.

In contrast to continental weathering, marine weathering is not directly coupled to average global surface temperature and atmospheric pCO_2. Carbon transformations in anoxic sediments are rather fueled by the deposition of particulate organic matter and reactive silicate phases. As a result the consumption of CO_2 in these sediments is controlled by continental erosion and marine productivity. The negative climate feedback established by the temperature- and pCO_2-dependent rate of continental weathering (Berner, 2004) is weakened by marine weathering processes since reactive silicate phases which are not consumed on land may be weathered in methanogenic sediments. Marine weathering might, thus, amplify climate change on geological time scales and could, for example, contribute to the draw-down of atmospheric CO_2 observed during the late Cenozoic and glacial periods of the Quaternary.

The results presented in this study also have major implications for the applied geosciences. Natural gas hydrates and gas reservoirs formed in marine sediments contain large amounts of CH_4 but usually much less CO_2 even though both gases are produced at equi-molar rates during the break-down of organic matter. Small CO_2 contents in natural gas and gas hydrates may be caused by marine weathering processes. Hence, the CO_2 consumption via marine silicate weathering should be considered in basin modelling to better predict the CO_2 contents of economically important natural gas and gas hydrate reservoirs. Moreover, marine sediments are increasingly used for the disposal of CO_2 separated from natural gas and in coal power plants (House *et al*., 2006). The results presented in this study imply that terrigenous sediments with large contents of reactive silicate phases might be well-suited for sites of CO_2 disposal since CO_2 may be rapidly neutralized by marine silicate weathering.

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