Submarine weathering of silicate minerals and the extent of pore water freshening at active continental margins

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Abstract

In order to investigate how submarine weathering processes may affect the water balance of sediments at convergent plate margins, six sediment cores were retrieved off Central Chile at water depth between ~800 and 4000 m. The sediment solid phase was analyzed for its major element composition and the pore fluids were analyzed for dissolved sulfate, sulfide, total alkalinity, major cations, chloride, bromide, iodide, hydrocarbons as well as the carbon isotopic composition of methane. Because of negligible weathering on land, surface sediments off Central Chile are rich in reactive silicate minerals and have a bulk composition similar to volcanic rocks in the adjacent Andes. Deep-sourced fluxes of alkalinity, cations and chloride indicate that silicate minerals are subject to weathering in the forearc during burial. Comparison of deep-sourced signals with data from nearby Ocean Drilling Program Sites reveals two different types of weathering processes: In shallow (tens of meters), methanic sediments of slope basins with high organic carbon burial rates, reactive silicate minerals undergo incongruent dissolution through reaction with CO₂ from methanogenesis. At greater burial depth (hundreds of meters), silicate weathering is dominated by authigenic smectite formation. This process is accompanied by uptake of water into the clay interlayers thus leading to elevated salinities in the surrounding pore water. Deep-seated smectite formation is more widespread than shallow silicate dissolution, as it is independent from the availability of CO₂ from methanogenesis. Although solute transport is not focused enough to form cold seeps in the proper sense, tectonically induced, diffuse fluid flow transfers the deep-seated signal of smectite formation into the shallow sediments.

The temperature-controlled conversion of smectite to illite is considered the most important dehydration process in marine forearc environments (depth of kilometers). However, in agreement with other studies at active margins (e.g. Aleutians, Cascadia, Nankai Trough) and despite ubiquitous evidence for smectite formation, little evidence for seafloor seepage of dehydration fluids could be found off Central Chile. We argue that the circular process of pore water uptake during smectite formation and release upon illitization implies a balanced freshwater budget and therefore a rather limited potential for net pore water freshening on a margin-wide scale. According to this rationale, pore water freshening at seafloor seeps preferentially occurs at lower latitudes (Central America, Barbados, Mediterranean Ridge) where terrestrial weathering is more intense thus leading to external (i.e. detrital) smectite and thus freshwater inputs to the subduction system.

1. INTRODUCTION

The movement and alteration of fluids within forearc sediments of convergent plate margins plays a pivotal role in the cycling of chemical substances between the ocean, the earth’s crust and the mantle (Moore and Vrolijk, 1992): During subduction of underthrust sediments, pore water solutes may be trapped within newly formed,
authigenic minerals (e.g. smectite formation from volcanic detritus) (Martin et al., 1995; Masuda et al., 1996) and thus effectively removed from the earth’s surface hydrological cycle. Conversely, mineral transformation processes at higher temperatures (e.g. transition from smectite to illite at 60–150 °C; Kastner et al., 1991) within both the overriding and the subducting plate are accompanied by the liberation of water and chemical elements (Kastner et al., 1993; Bekins et al., 1994; Hensen et al., 2004; Torres et al., 2004). Provided that hydraulic pathways such as faults or permeable sediment strata are available, the hereby evolving freshened fluids (i.e. pore fluids with a chlorinity < seawater) may become recycled into the ocean though submarine fluid escape structures like cold seeps or mud volcanoes (Moore and Vrolijk, 1992; Kopf, 2002; Ranero et al., 2008; Saffer and Tobin, 2011). Despite the general agreement on this hydro-geological model, the actual number of known deep-sourced fluid escape structures (i.e. those discharging freshened pore fluids from clay dehydration rather than hydrocarbon gases alone) at convergent plate margins is rather limited. A prominent example is the Central American margin off Nicaragua and Costa Rica where numerous deep-rooted cold seeps, so-called mud mounds, have been discovered over the last two decades (Hensen et al., 2004; Ranero et al., 2008; Sahling et al., 2008). By contrast, at many other convergent plate boundaries (e.g. Aleutians, Cascadia margin, Nankai Trough), little evidence for seepage of dehydration fluids from the seafloor has been found. A commonly held concept is that distal fluid flow and the occurrence of cold seeps is tied to the presence of extensional normal faults that typically occur in non-accretionary or erosive convergent margins such as the one of Central America (Ranero et al., 2008). In contrast, compressional thrust faults, that are typical for accretionary convergent margins, are thought to be less effective in channeling dehydration fluids, thus giving rise to diffuse rather than focused fluid flow (Moore and Vrolijk, 1992; Carson and Sercat, 1998).

In order to study subduction-related diagenetic processes in an accretionary convergent margin setting, we conducted a research cruise off Central Chile in September and October 2010 (RV SONNE cruise SO210, ‘CHIFLUX’). The Central Chilean continental margin is characterized by frontal sediment accretion as well as the presence of thrust and splay faults cutting through the marine forearc. In agreement with other studies in accretionary convergent margins and despite extensive seafloor surveying and sampling, no seepage structures with focused discharge of freshened fluids were discovered during the CHIFLUX cruise. However, pore fluids recovered from sediments on the accretionary prism revealed ubiquitous evidence for submarine weathering processes, as evidenced by deep-sourced alkalinity and calcium fluxes as well as elevated pore water salinities. In the present article, we will discuss the controlling factors of submarine silicate weathering off Central Chile and in other continental margin environments. Furthermore, we will evaluate how submarine (instead of terrestrial) weathering may affect deep-sourced freshening signals from clay dehydration upon upward advection to the seafloor. Implications for the current understanding of forearc dewatering will be briefly discussed.

2. GEOLOGICAL SETTING

The Central Chilean continental margin north of the Chile Triple Junction is shaped by the subduction of the oceanic Nazca Plate beneath the South American Plate. In the study area at ~36°S (Fig. 1A), the incoming plate has an age of about 30 Ma (Tebbens and Cande, 1997) and the trench fill has an approximate thickness of 1.5–2 km (Völker et al., 2006). During the process of plate collision, the upper part of the sedimentary trench fill is frontally accreted to the overriding plate forming the active accretionary prism, whereas the lower sediment section (about 1 km) is underthrust beneath the marine forearc in a subduction channel (Bangs and Cande, 1997; Geersen et al., 2011). Sediment accretion in the study area is likely active since late Miocene or early Pliocene following a period of non-accretion or subduction erosion (Kukowski and Oncken, 2006; Melnick and Echtler, 2006). The switch from subduction erosion to sediment accretion may have been triggered by the expansion of the Patagonian ice sheet at ~6 Ma resulting in an increased supply of sediments to the trench (e.g. Bangs and Cande, 1997; Melnick and Echtler, 2006). The active accretionary prism extends for about 25 km from the deformation front (~4800 to 2500 m water depth). Ongoing plate collision and the associated adding of trench sediment to the lower forearc results in the development of a sequence of landward dipping thrust faults that separate individual thrust sheets (Fig. 1B). A paleo-accretionary prism (hereafter referred to as framework rock; Von Huene et al., 1997), that presumably consists of Cretaceous elastic sedimentary rocks and Paleozoic metamorphic rocks (González, 1989), is located landward of the active accretionary prism (Fig. 1B). The paleo-accretionary prism is covered with 0.5–2 km of Cenozoic slope and shelf sediments (Contreras-Reyes et al., 2010). At roughly 2200 and 1350 m water depth, two landward dipping thrust faults, that likely splay away from the main plate boundary, crop out at the seafloor (Geersen et al., 2011). The transition from the paleo-accretionary prism to the continental basement is located roughly beneath the Chilean coast (not covered by Fig. 1B).

Modern (i.e. surficial) slope and trench sediments at 36°S have a similar bulk composition as the Cretaceous to Holocene magmatic arc in the adjacent Southern Chilean Volcanic Zone (SVZ) (Lucassen et al., 2011). Bulk mineral assemblages are characterized by a low grade of maturity and consist predominantly of plagioclase, pyroxene, amphiboles and variable amounts of mostly unaltered volcanic ash. Chlorite is the dominant clay mineral at 36°S, followed by illite and only minor amounts of detrital smectite (Lamy et al., 1998). The low degree of weathering documented by the bulk geochemistry and mineralogy of the sediments has been ascribed to the steep relief on land causing rapid erosion as well as seasonal precipitation (i.e. maximum rainfall in winter coincides with lowest temperatures) resulting in low weathering rates (Baba, 1986; Lamy et al., 1998). Because of efficient offshore transport with distal turbidity currents, bulk and clay mineral assemblages on the incoming plate west of the Peru–Chile trench do not significantly differ from those on the adjacent continental slope (Lamy et al., 1998).
Comparably little information is available about fluid seepage on the Central Chilean forearc. Grevemeyer et al. (2006) detected elevated heat flow values ($142 \text{ mW m}^{-2}$ compared to a background of $35-40 \text{ mW m}^{-2}$) in the vicinity of a thrust ridge on the upper slope (1435 m water depth) and attributed this to the ascent of deep-sourced fluids. Moreover, seafloor sampling further upslope revealed the occurrence of gas-charged sediments and methane-related chemosynthetic organisms in the so-called Concepción Methane Seepage Area (Coffin et al., 2007; Sellanes et al., 2008). Widespread backscatter anomalies related to the presence of authigenic carbonates as well as locally disrupted bottom simulating reflectors indicate that methane seepage occurs over vast seafloor areas between 36 and 37°S at water depth between 600 and 1000 m (Klaucke et al., 2012).

3. MATERIAL AND METHODS

3.1. Sampling strategy

Most of the sampling stations during the CHIFLUX cruise were visually inspected using a deep-towed camera sled prior to coring. Gravity cores (GCs, 6 m length) were retrieved at most of the structural seafloor features described in the previous section (Fig. 1 and Table 1). GC18 was taken on the upper slope in the Concepción Methane Seepage Area. Gas bubbles were observed escaping from the core pipe during recovery of this core. In addition to GC18, a number of video-guided short cores were taken within the Concepción Methane Seepage Area. Since the pore water chemistry of these cores is largely similar to the topmost sediment section of GC18 (Linke and Ship-
board Scientific Party, 2012), they will not be considered in this article. GC17 was taken at the outcrop of the upper splay fault, north of the main transect, where Greve Meyer et al. (2006) had recorded the elevated heat flow. The coring location of GC23 is located in the outcrop area of the lower splay fault and GC21, GC20 and GC24 where taken in the vicinity of thrust faults on the active accretionary prism. With exception of GC18, where visual seafloor inspection had revealed the presence of bacterial mats, no indication for active seepage (bacterial mats, chemosynthetic fauna, authigenic carbonates) was observed at any of the above sites. Sediments of GC18 consisted of dark green to gray compacted clay with fragments of authigenic carbonates. The remaining sediment cores predominantly consisted of gray to dark gray silty clay with abundant black ash and few sand layers.

3.2. Pore water recovery and chemical analyses

Upon recovery GCs were cut into 1 m segments and split lengthwise into an archive half for visual description and a work half for subsampling and geochemical analysis. Subsampling and pore water recovery were carried out in a cool room at the approximate seafloor temperature of 6 °C. Pore waters were separated from the sediment matrix by the aid of a squeezing device operated with argon gas at pressures between 3 and 5 bar. Upon squeezing, pore waters were filtered through 0.2 μm cellulose acetate membrane filters. A small sediment aliquot was stored in pre-weighed and air-tight plastic cups for shore-based analyses of cations (concentrated HNO₃, supra pure) were stored in pre-cleaned LDPE vials for shore-based analyses of cations by inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN 720-ES). Iodide (I⁻) concentrations were also determined onshore by IC (METROHM 881 Compact, UV detection mode). In order to obtain the composition of local bottom water, the supernatant water of a multi core (86-MUC04, 36°28.24′S, 73°44.07′W, 1006 m water depth) was treated the same way as described for pore waters. The IAPSO salinity standard was used to check the reproducibility and accuracy of all chemical analyses (Gieskes et al., 1991). A detailed description of all analytical methods applied routinely during research cruises and in shore-based laboratories at GEOMAR may be obtained from the following webpage: http://www.geomar.de/en/research/fb2/fb2-mg/benthic-biogeochemistry/mg-analytik/.

The hydrocarbon composition of head space gas was determined using a CE 8000 TOP gas chromatograph equipped with a 30 m capillary column (Restek Q-PLOT, 0.32 mm) and a flame ionization detector (FID). A precision of 1–3% was achieved by replicate measurements of standard hydrocarbon mixtures. Stable carbon isotope ratio measurements of methane were performed by continuous flow isotope ratio mass spectrometry (cf-IRMS). Up to 1 ml of head space gas was injected on a ShinCarbon ST100/120 packed gas chromatography column for separation of light hydrocarbon gases in a Thermo TRACE gas chromatograph. Subsequent combustion of the separated gases to CO₂ was conducted in a Pt/Ni combustion furnace at 980 °C. The δ¹³C value of the CO₂ produced was determined downstream by using a Thermo MAT253 mass spectrometer equipped with split inlet and Nafion dryer. The reproducibility of the δ¹³C values is about ±0.3‰ (2 SD).

The total carbon (TC) and total organic carbon (TOC) content of freeze-dried and ground sediment samples was determined by flash combustion in a Carbo Erba Elemental Analyzer (NA1500) with a reproducibility of about 1% relative SD. The carbonate carbon was removed by adding 1 M HCl prior to TOC analyses and total inorganic carbon (TIC) was calculated by subtracting TOC from TC. For major element analyses of the solid phase by X-ray fluorescence spectroscopy (PANalytical MagixPro with Rh anode), sediments were ground to <63 μm grain size and converted to melt tablets with lithium tetraborate. The reproducibility of the XRF measurements, based on repeated analyses of standard reference materials, is about 1% relative SD. The Ca bound to silicates (Ca²⁺ or CaO³⁻) was approximated by subtracting Ca bound to carbonates (CaCO₃ = 8.33 · TIC) from total Ca. The Chemical Index of Alteration (CIA), a measure of the degree to which primary minerals have undergone alteration through weathering.

### Table 1

<table>
<thead>
<tr>
<th>Station</th>
<th>Core</th>
<th>Longitude W</th>
<th>Latitude S</th>
<th>Water depth (m)</th>
<th>Recovery (cm)</th>
<th>Mean TOC (wt.%)</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>GC18</td>
<td>73°43.28′</td>
<td>36°21.86′</td>
<td>859</td>
<td>580</td>
<td>0.84 ±0.28</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>GC17</td>
<td>73°32.37′</td>
<td>35°54.23′</td>
<td>1417</td>
<td>560</td>
<td>1.30 ±0.74</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>GC23</td>
<td>73°52.14′</td>
<td>36°21.95′</td>
<td>2199</td>
<td>570</td>
<td>2.68 ±0.16</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>GC21</td>
<td>73°39.96′</td>
<td>36°20.83′</td>
<td>3192</td>
<td>583</td>
<td>2.63 ±0.24</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>GC20</td>
<td>74°03.17′</td>
<td>36°20.60′</td>
<td>3544</td>
<td>570</td>
<td>0.79 ±0.79</td>
<td></td>
</tr>
<tr>
<td>97</td>
<td>GC24</td>
<td>74°06.45′</td>
<td>36°20.22′</td>
<td>3842</td>
<td>573</td>
<td>0.77 ±0.77</td>
<td></td>
</tr>
</tbody>
</table>

*Uppermost ~200 cm were lost during recovery.*
ing, was calculated as follows: CIA = \( \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}} \times 100 \) (Nesbitt and Young, 1982).

4. RESULTS

4.1. Pore water chemistry

Pore water profiles of \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{Ca}^{2+} \) and TA are shown for all cores in Fig. 2A and examples for pore water profiles of \( \text{Mg}^{2+}/\text{Cl}^- \), \( \text{Ca}^{2+}/\text{Cl}^- \) and \( \text{Na}^+/\text{Cl}^- \) ratios are given for GC20 and GC21 in Fig. 3. GC23 at 2199 m water depth is the only site where \( \text{Cl}^- \) concentrations are equal to local bottom water values (550 mM) throughout the cored depth interval. GCs from greater water depth (i.e., those from the accretionary prism) show downcore increasing \( \text{Cl}^- \) concentrations (up to 617 mM of \( \text{Cl}^- \) at the bottom of GC20) whereas GCs from shallower water depth are characterized by downcore deceasing \( \text{Cl}^- \) concentrations (up to 527 mM of \( \text{Cl}^- \) at the bottom of GC17). The \( \text{Cl}^- \) profile of GC18 is somewhat scattered showing a spike at 422 cm below seafloor (cmbsf) (523 mM of \( \text{Cl}^- \)). The depth

![Fig. 2. (A) Pore water profiles of \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{Ca}^{2+} \) and TA along the transect depicted in Fig. 1. Vertical dashed lines and vertical arrows represent local bottom water concentrations of \( \text{Cl}^- \), \( \text{SO}_4^{2-} \) and \( \text{Ca}^{2+} \). The uppermost 200 cm of GC21 were lost during core recovery because of over penetration. (B) Cross plots of carbonate alkalinity (CA) and \( \text{Ca}^{2+} \) versus \( \text{SO}_4^{2-} \). 'D' means concentrations or CA values are relative to local bottom water values. Only data from above the depth of sulfate depletion were considered in the linear regressions. The slope of the regression lines and the stoichiometric ratios calculated according to Eq. (3) are listed in Table 2.](image-url)
of sulfate depletion increases in the order GC18 < GC23 < GC21 < GC17 < GC20 < GC24, i.e. there is no clear relationship between sulfate penetration depth, water depth and/or pore water salinity. In general, Ca\(^{2+}\) concentrations decrease and TA values increase with depth. In most cores, TA reaches near constant values at the depth of sulfate depletion. Exceptions are GC21 and GC23 where TA continues to increase below the depth of sulfate depletion.

The concentrations of methane and higher hydrocarbons as well as the stable carbon isotope composition of methane were determined for GC17, GC18, GC20 and GC21. The \(\delta^{13}\)C-CH\(_{4}\) is plotted versus CH\(_4\)/(C\(_2\)H\(_6\) + C\(_3\)H\(_8\)) in Fig. 4 (‘Bernard diagram’ after Bernard et al. (1978) and Faber and Stahl (1984)). The hydrocarbon composition of samples from above the sulfate penetration depth is likely to represent shallow degradation of hydrocarbons rather than their origin or original mode of formation (Stadnitskaia et al., 2006). Therefore, only samples from below the sulfate penetration depth are shown in Fig. 4. All of the data plot within the field of microbial hydrocarbon gases. Among the samples measured, those of GC21 show the purest microbial signature whereas those of GC20, GC17 and particularly GC18 contain more higher hydrocarbons and are thus shifted towards lower CH\(_4\)/(C\(_2\)H\(_6\) + C\(_3\)H\(_8\)) ratios. Samples of GC18 are characterized by heavier \(\delta^{13}\)C-CH\(_{4}\) values as compared to samples from the other cores. A compilation of pore water data (Cl\(^{-}\), SO\(_4^{2-}\), TA, TH\(_2\)S, Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), I\(^{-}\), Br\(^{-}\), CH\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), CH\(_4\)/(C\(_2\)H\(_6\) + C\(_3\)H\(_8\)), \(\delta^{13}\)C-CH\(_4\)) is given in Table EA-1 in the Electronic Annex.

### 4.2. Major element composition of the solid phase

The average TOC concentrations of all cores are listed in Table 1. The highest TOC values were observed at intermediate water depth in GC21 and GC23 (~2.6% TOC). Se-
lected cores (GC20, GC21 and GC23) were analyzed for their major element composition. The results are illustrated in ternary diagrams in Fig. 6. All samples plot within a narrow range close to the average composition of andesite rocks and volcanic rocks in the SVZ of Chile. A compilation of solid phase data is given in Table EA-2 (Al2O3, MgO, CaO, Na2O, K2O) and Table EA-3 (TOC, TIC) in the Electronic Annex.

5. DISCUSSION

In Section 5.1, we will examine the stoichiometry of sulfate consumption and bicarbonate production across the continental margin with the aim of identifying deep-sourced fluxes of alkalinity and Ca2+ at specific sites. By combining continental margin with the aim of identifying deep-sourced fate consumption and bicarbonate production across the margin scale may be affected by submarine weathering.

5.1. Identification of deep-sourced alkalinity and calcium fluxes

Deep-sourced fluxes of alkalinity and Ca2+ may be modified in the surface sediments by early diagenesis of organic matter and associated precipitation of authigenic carbonates. Separating deep-sourced from shallow pore water geochemical signals is, therefore, the aim of the following section.

The early diagenetic breakdown of organic matter in marine sediments generally results in a release of bicarbonate ions into the pore water and thus in increasing alkalinity values with depth. Oxid degradiation and denitrification produce CO2 rather than bicarbonate with no net effect on alkalinity and iron and manganese reduction yield only a few milliequivalents of alkalinity per liter. By far the most important process of alkalinity production during early diagenesis in marine systems is sulfate reduction, either coupled to the oxidation of organic matter (Eq. (1)) or to the oxidation of methane (anaerobic oxidation of methane, AOM) and other hydrocarbons (Eq. (2)), respectively (Niewöhner et al., 1998; D’Hondt et al., 2002):

\[
2\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- \quad (1)
\]

\[
\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O} \quad (2)
\]

Organiclastic sulfate reduction yields two moles of bicarbonate per mole of sulfate whereas AOM yields one mole of bicarbonate and one mole of bisulfide per mole of sulfate. Taking into account a few meq L\(^{-1}\) from manganese and iron reduction and a seawater sulfate concentration of ~28 mM, the maximum TA value that may produced during early diagenesis of organic matter is thus <60 meq L\(^{-1}\).

Organiclastic sulfate reduction rates are known to be highest at the sediment surface whereas sulfate reduction driven by AOM is most intense at the depth of sulfate depletion, also referred to as the sulfate-methane transition zone (SMTZ) (e.g. Fossing et al., 2000; Treude et al., 2005). The linear shape of most pore water sulfate profiles in Fig. 2A suggests that AOM is the principle process of net sulfate consumption in central Chilean slope sediments. If organiclastic sulfate reduction contributed more to sulfate depletion, pore water profiles would be non-linear, i.e. display a concave down gradient at the top (Borowski et al., 1996; Hensen et al., 2003). A more rigorous distinction between organiclastic sulfate reduction and AOM may be achieved by examining the stoichiometry of sulfate consumption to bicarbonate production using cross plots of bicarbonate (or carbonate alkalinity at typical pore water pH values) versus sulfate (Fig. 2B). It follows from Berner (1977) and Fick’s first law of diffusion that the relation between bicarbonate produced and sulfate consumed (R\(_{\text{HCO}_3^-/\text{SO}_4^{2-}}\)) is given by the product of the slope of the regression line (dHCO\(_3^-\)/dSO\(_4^{2-}\)) and the ratio between the diffusion coefficients (D) of the two solutes (see also Burdige and Komada, 2011):

\[
R_{\text{HCO}_3^-/\text{SO}_4^{2-}} = -\frac{D_{\text{HCO}_3^-}}{D_{\text{SO}_4^{2-}}} \cdot \frac{d\text{HCO}_3^-}{d\text{SO}_4^{2-}} \quad (3)
\]

The pore waters of GC18, GC21 and GC23 contain variable amounts of sulfide (see EA-Table 1 in the Electronic Annex), which has to be considered when using titration alkalinity as an estimate of bicarbonate concentrations or carbonate alkalinity (hereafter referred to as CA). As H\(_2\)S is only detectable in the SMTZ where AOM predominates, it is reasonable to assume that HS\(^-\) is the principle sulfide species in pore water (cf. Eq. (2)). As a consequence, CA may be calculated by subtracting TH\(_2\)S from TA. The regression slopes (dCA/dSO\(_4^{2-}\)) of cross plots in Fig. 2B and the stoichiometric ratios (R\(_{\text{Ca}^{2+}/\text{SO}_4^{2-}}\)) calculated according to Eq. (3) are listed in Table 2.

Provided that organiclastic sulfate reduction and AOM are the only processes affecting sulfate and bicarbonate concentrations, values of R\(_{\text{Ca}^{2+}/\text{SO}_4^{2-}}\) should vary between end members of 1.0 and 2.0. However, many of the stoichiometric ratios in Table 2 are lower than the anticipated range, which indicates that bicarbonate has been lost through precipitation of authigenic carbonate minerals:

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (4)
\]

Carbonate precipitation is also reflected by the pore water Ca\(^{2+}\) profiles decreasing from seawater values at the top to variable degrees of Ca\(^{2+}\) depletion in the SMTZ. The extent of bicarbonate removal with authigenic carbonates can be approximated from cross plots of pore water Ca\(^{2+}\) versus sulfate following a similar approach as described above (Fig. 2B; see Table 2 for d\text{Ca}/dSO\(_4^{2-}\)) and R\(_{\text{Ca}^{2+}/\text{SO}_4^{2-}}\) values). As two moles of bicarbonate are lost per mole of Ca\(^{2+}\) during carbonate precipitation (Eq. (4)), the R\(_{\text{Ca}^{2+}/\text{SO}_4^{2-}}\) has to be considered twice when correcting stoichiometric ratios:

\[
R_{\text{CA}^{2+}/2\text{SO}_4^{2-}} = R_{\text{CA}^{2+}/\text{SO}_4^{2-}} + 2 \cdot R_{\text{Ca}^{2+}/\text{SO}_4^{2-}} \quad (5)
\]
The $R_{\text{Ca}^2+:\text{SO}_4}$ ratios for GCs on the central Chilean slope range from 0.9 to 1.9 (Table 2). Burdige and Komada (2011) demonstrated that $R_{\text{Ca}^2+:\text{SO}_4}$ deviating from 2 are typically the result of advective methane supply from deeper sediment strata. According to this concept, a higher deep-sourced methane flux should result in a lower $R_{\text{Ca}^2+:\text{SO}_4}$ with 1.0 being the end member where sulfate reduction is solely mediated by AOM. This is corroborated by the $R_{\text{Ca}^2+:\text{SO}_4}$ of 1.0 of Site GC18 in the Concepcion Methane Seepage Area. Gas bubbling was observed during recovery of this core and pore waters of GC18 contain a comparably higher proportion of thermogenic gas (Fig. 4). Both of these observations are in agreement with a deep-sourced methane flux fueling AOM in shallow sediments. GC17 and GC24 display $R_{\text{Ca}^2+:\text{SO}_4}$ values between the two end member values, which is common for continental margin sediments where typically both organoclastic sulfate reduction and AOM occur (Fossing et al., 2000; Treude et al., 2005; Burdige and Komada, 2011). By contrast, the $R_{\text{Ca}^2+:\text{SO}_4}$ of GC20 as well as GC21 and GC23 are somewhat surprising as they are particularly high or low (n.b. $R_{\text{Ca}^2+:\text{SO}_4}$ < 1.0 at GC20) suggesting that sulfate reduction at these sites is solely mediated by organoclastic sulfate reduction and AOM, respectively. Such an end member situation is in clear contradiction with previous work off Central Chile by Treude et al. (2005) who found significant microbial rates of both processes in sediments from 800 to 3000 m water depths.

Numerous studies have shown that the depth of the SMTZ is insensitive to organoclastic sulfate reduction but solely controlled by methane as well as sulfate fluxes and AOM intensity, respectively (Borowski et al., 1996; Nießwöhner et al., 1998; Treude et al., 2005). Consequently, if the relative intensities of organoclastic sulfate reduction and AOM were the only processes affecting $R_{\text{Ca}^2+:\text{SO}_4}$, one should anticipate a positive correlation with sulfate penetration depth. GC17, GC18 and GC24 do indeed plot on such a relationship (Fig. 6), while GC20, GC21 and GC23 are shifted towards lower and higher $R_{\text{Ca}^2+:\text{SO}_4}$, respectively. This deviation from the projected trend clearly shows that additional $\text{Ca}^{2+}$ or bicarbonate fluxes from below the cored depth interval have to be considered in order to explain the $R_{\text{Ca}^2+:\text{SO}_4}$ observed (Fig. 6). GC21 and GC23 reveal downcore increasing TA values below the SMTZ (Fig. 2A) indicating a deep-seated source of CA other than organic matter diagenesis. The deep-sourced $\text{Ca}^{2+}$ flux at GC20 is more difficult to discern from pore water profiles. Nonetheless, $\text{Ca}^{2+}$ depletion in the SMTZ of GC20 is less pronounced compared to the other sites (Fig. 2B; 53% with respect to local bottom water compared to $\approx 75\%$ at the other sites) which is likely due to an additional source of $\text{Ca}^{2+}$ at greater depth.

5.2. Controls on submarine weathering: silicate dissolution versus smectite formation

All sediment cores from the accretionary prism (GC20, GC21 and GC24) reveal downcore increasing pore water chlorinities indicating a deep-sourced flux of $\text{Cl}^-$ into the cored sediment section (Fig. 2A). The most pronounced chlorinity anomaly is observed at GC20 in the central area of the accretionary prism. In principle, pore waters with $\text{Cl}^-$ concentrations in excess over contemporary seawater, also referred to as brines, may be generated by one of the following processes: The dissolution of evaporite minerals and admixing of evaporated and buried seawater, the sequestration of pore water by hydrous minerals (e.g. smectite forming from volcanic detritus during burial) (e.g. Martin et al., 1995) and the formation of gas hydrates (e.g. Haeckel et al., 2004; Torres et al., 2004b). Sediments in the active prism off Central Chile are younger than 6 Ma and have been deposited in a deep-sea environment (cf. Section 2). Any relationship between sub-aerial evaporation and the elevated pore water salinities observed can thus be clearly ruled out. Furthermore, GC18 in the Concepcion Methane Seepage Area is the only site where appreciable methane fluxes could be identified. Although it is likely that gas hydrates are present in the deeper subsurface at the other sites, increases in pore water chlorinity related to hydrate formation could so far only be shown in areas with high gas emission rates (e.g. Hydrate Ridge; Haeckel et al., 2004; Torres et al., 2004b). Moreover, if gas hydrate formation was the reason for elevated pore water salinities, we should observe a positive correlation between $\text{Cl}^-$ concentration and sulfate penetration depth (i.e. methane flux; see previous section), which is not the case. Therefore, sequestration of pore water by gas hydrates can also be excluded as a possible reason for brine formation in the accretionary prism.

In previous studies at the Izu Bonin and New Hebrides margins, Martin et al. (1995) identified sequestration of pore water by authigenic smectite as the reason for elevated pore water salinities ($\text{Cl}^- \leq 1240$ mM). Other convergent margins where saline pore fluids have been found in association with authigenic smectite formation are the accretionary prism of the Nankai Trough (ODP Site 808,
Cl⁻ < 590 mM) (Kastner et al., 1993; Masuda et al., 1996) as well as the one off Southern Chile (ODP Sites 859-861, see Fig. 1A for location, Cl⁻ < 650 mM) (Behrmann et al., 1992; Zheng et al., 1995). Authigenic smectite formation in marine sediments requires the availability of fresh siliciclastic material such as volcanic ash or reactive silicate minerals like olivine, pyroxene and plagioclase all of which are abundant on the Central Chilean margin (Lamy et al., 1998). In fact, sediments off Central Chile have a relatively uniform composition that is similar to that of intermediate volcanic rocks in the SVZ (Fig. 5A and Lucassen et al., 2011). Furthermore, surface sediments contain negligible amounts of detrital smectite (Lamy et al., 1998) and have a low chemical index of alteration (CIA of 60–65% compared to 58% of SVZ rocks; Fig. 5B) indicating that they are almost unweathered when arriving at the forearc. For comparison, surficial forearc sediments off Costa Rica have a CIA of 75% and consist almost exclusively of detrital smectite that has formed on land prior to erosion and transport into the ocean (Fig. 5B; Spinelli and Underwood, 2004). Mg-rich Smectite formation from volcanic detritus and reactive silicate minerals may be expressed with the following generalized chemical equation (Appelo and Postma, 2004).

\[
\left[ (K, Na)_2O \cdot MgO \cdot CaO \cdot Al_2O_3 \cdot SiO_2 + 7H_2SiO_4 \right] + Mg^{2+} + nH_2O \rightarrow 2(K, Na)_{0.5}(Mg, Al)Si_2O_10(OH)_2 \cdot (n + 12)H_2O + Ca^{2+}
\]  

(6)

The molecule in square brackets represents a volcanicogenic mineral assemblage consisting of silica, aluminum, Ca, Mg and alkaline metal ions (Fig. 5A). The silicon stoichiometry of Eq. (6) is not well constrained as both silica from primary minerals and additional silicic acid from dissolving diatoms (Michalopoulos et al., 2000) may contribute to smectite formation. However, the net effect on pore water chemistry of smectite formation according to Eq. (6) would be Mg²⁺ depletion, Ca²⁺ enrichment and elevated salinities related to the large-scale uptake of pore water into the interlayer of the authigenic smectite (Gieskes and Lawrence, 1981; Kastner et al., 1991). Taking into account the deep-sourced Ca²⁺ flux identified in the previous section, this pore water geochemical signature is in striking agreement with the relative enrichments of solutes in pore waters of GC20 (Fig. 3A). Furthermore, uniform Na⁺/Cl⁻ ratios suggest that the loss of water from the pore space is related to smectite rather than zeolite formation as the latter is accompanied by a discrimination of Na⁺ against Cl⁻ (Martin et al., 1995).

Although less pronounced than at Site GC20, the positive chlorinity anomaly of GC21 (Fig. 2A) is still indicative of hydrous mineral formation at depth. In contrast to GC20, however, pore waters of GC21 are enriched in Mg²⁺ (Fig. 3A) and a deep-sourced flux of alkalinity rather than Ca²⁺ was identified in the previous section. This pore water chemical signature requires alternative or additional reactions besides the one described by Eq. (6). Fermentation and methanogenesis (e.g. Eq. (7)), the microbial degradation pathway following sulfate reduction, produce CO₂ rather than bicarbonate with no net effect on TA or CA:

\[
CH_3CH_2COO^- + 2H_2O \rightarrow CH_3COO^- + CO_2 + 3H_2 \rightarrow CH_2COO^- + H^+ \rightarrow CH_4 + CO_2
\]  

(7)

As a consequence, CA fluxes from below the SMTZ cannot be directly linked to the decomposition of organic mat-

---

**Fig. 5.** (A) Ternary diagram illustrating the bulk composition of sediments on the Central Chilean marine forearc as compared to the average composition of basalt, andesite, rhyolite (De la Roche et al., 1980) and magmatic rocks in the Southern Volcanic Zone (SVZ) of Chile (Lucassen et al., 2011 and references therein). (B) Ternary diagram illustrating the extent to which primary minerals have undergone weathering during transport and after deposition on the forearc. The axis on the right-hand side indicates the Chemical Index of Alteration (CIA) (Nesbitt and Young, 1982). The gray arrow represents a predicted weathering trend as magmatic rocks in the SVZ are progressively weathered to smectite (CIA = 75%), kaolinite and gibbsite (CIA = 100%) (Nesbitt and Young, 1989). The composition and CIA of surficial forearc sediments off Costa Rica on the Central American margin are shown for comparison (ODP Site 1040; data from Kimura et al., 1997).
ter in the deep subsurface. An alternative source of alkalinity is the transformation of \( CO_2 \) into bicarbonate through submarine weathering of silicate minerals (Aloisi et al., 2004; Wallmann et al., 2008):

\[
[[K, Na]O, MgO, CaO, Al_2O_3, SiO_2] + H_2SO_4 + 6CO_2 + 3H_2O \\
\rightarrow Al_2Si_2O_5(OH)_4 + K^+ + Na^+ + Mg^{2+} + Ca^{2+} + 6HCO_3^-
\]

(8)

\[
[[K, Na]O, MgO, CaO, Al_2O_3, SiO_2] + 6CO_2 + 8H_2O \\
\rightarrow 2Al(OH)_3 + K^+ + Na^+ + Mg^{2+} + Ca^{2+} + H_2SO_4 + 6HCO_3^-
\]

(9)

Eqs. (8) and (9) describe the incongruent dissolution of the volcanicogenic mineral assemblage described above resulting in the formation of kaolinite or gibbsite and the release of bicarbonate and dissolved cations into the pore water. The pore water geochemical signature resulting from Eqs. (8) and (9) is in agreement with the deep-sourced CA flux and the relative \( Mg^{2+} \) enrichments (Fig. 3A) observed at Site GC21. Any enrichiment in pore water \( Ca^{2+} \) resulting from Eqs. (8) and (9) is likely to be masked by precipitation of authigenic carbonates (Eq. (4)) as several meq L\(^{-1}\) of CA are released per mole of \( Ca^{2+} \) (cp. Wallmann et al., 2008).

In principle, all of the reactions expressed by Eqs. (6), (8), and (9) may be referred to as weathering, as they involve the transformation of identical, cation-rich primary silicate minerals to secondary minerals and dissolved cations. However, in contrast to smectite formation (Eq. (6)), silicate dissolution according to Eqs. (8) and (9) requires the availability of \( CO_2 \) (Appelo and Postma, 2005). The major \( CO_2 \) source for weathering reactions in marine sediments is methanogenesis and fermentation (Eq. (7)) (Wallmann et al., 2008). Silicate dissolution should thus be dependent on the intensity of methanogenesis, or in other words, on the amount of organic matter that is buried beyond the SMTZ. In agreement with this hypothesis, high CA values and deep-sourced CA fluxes in GC21 and GC23 coincide with the highest organic carbon concentrations throughout the transect (Table 1). Moreover, in contrast to all other GCs, GC21 and GC23 show little downcore variability in TOC (Fig. 7) indicating high organic carbon burial rates. These are unlikely the result of elevated biological productivity in the overlying water column since primary production off Central Chile generally decreases from the coastal upwelling cells into the deep-sea (Hebbeln et al., 2000). Instead, elevated TOC concentrations are most likely the result of lateral sediment supply from further upslope. The coring sites GC21 and GC23 are situated within small forearc basins whereas GC20 and GC24 are located in steeper slope environments (see bathymetry in Fig. 1B). Trapping of laterally displaced fine-grained material at Sites GC21 and GC23 is likely related to the terraced seafloor morphology of the Central Chilean continental slope. Further evidence for higher sedimentation rates and enhanced carbon burial at Sites GC21 and GC23 is provided by the relative enrichments of pore water \( I^- \) and \( Br^- \) across the margin (Fig. 8). In general, both \( I^- \) and \( Br^- \) are released from decaying organic matter during diagenesis (Price and Calvert, 1977; Martin et al., 1993). Once released into the pore water, \( Br^- \) behaves conservatively
and may become recycled into the water column though molecular diffusion or upward fluid advection. By contrast, \( I^- \) is oxidized to molecular iodine (I\(_2\)) and subsequently scavenged by organic phases in the oxic surface layer of the sediment (Price and Calvert, 1977; Kennedy and Elderfield, 1987). This contrasting behavior of \( I^- \) and Br\(^-\) during early diagenesis results in a continuous discrimination of the two elements against each other and therefore to an increase of the pore water I\(^-/Br^-\) ratios with sediment depth (see data in EA-Table 1 of the Electronic Annex) and increasing organic carbon burial rates, respectively (Martin et al., 1993). On the Central Chilean margin, CA values and I\(^-/Br^-\) ratios are well correlated and show coincident maxima at Sites GC21 and GC23 (Fig. 8). This observation substantiates that submarine weathering according to Eqs. (8) and (9) is enabled by enhanced organic carbon burial driving intense CO\(_2\) production in the subsurface.

Although incongruent dissolution of reactive silicates (Eqs. (8) and (9)) is a reasonable explanation for the pore water cation and CA anomalies at Site GC21, it cannot account for the Cl\(^-\) enrichment as no hydrous minerals are formed during this process. A solution to this apparent contradiction can be identified from the pore water geochemical profiles of ODP Site 861 (Fig. 3B) which was drilled off Southern Chile at 45°51.0’S (Fig. 1A; Behrmann et al., 1992). Like GC21, ODP Site 861 is located in a small forearc basin (1652 m water depth) with elevated sedimentation rates as compared to the surrounding slope environment. Moreover, much like at 36°S, surface sediments of Southern Chile are rich in reactive silicate minerals and contain negligible amounts of detrital smectite (Kurnosov et al., 1995).

Pore water profiles of ODP Site 861 feature essentially the same weathering-related diagenetic signatures like those observed or inferred for GC21 (Fig. 3): Deep-sourced Ca\(^{2+}\), Mg\(^{2+}\) and alkalinity fluxes below the SMTZ; Ca\(^{2+}\), Mg\(^{2+}\) and alkalinity (>60 meq L\(^{-1}\)) maxima at 55 mbsf; Cl\(^-\) (650 mM) and Ca\(^{2+}\) (> bottom water) maxima at the lower end of the core (500 mbsf). This vertical secession of diagenetic signatures indicates that silicate dissolution (Eqs. (8) and (9)) and smectite formation (Eq. (6)) are spatially decoupled processes with the latter occurring at much greater depth than the former. A comparably shallow reaction zone (i.e. at tens of mbsf) of silicate dissolution driven by CO\(_2\) from methanogenesis (Eqs. (8) and (9)) is consistent with a purely microbial hydrocarbon signature in pore fluids of GC21 (Fig. 4). A deep-seated zone of smectite formation (i.e. at several hundred mbsf) is in agreement with earlier studies reporting positive Cl\(^-\) anomalies related to smectite authigenesis (e.g. Martin et al., 1995; Masuda et al., 1996). Smectite formation is favored by the elevated temperatures prevailing in the deep subsurface (≥~20°C, Nankai Trough accretionary prims; Masuda et al., 1996).

Moreover, the lower porosity at greater burial depth implies that weathering takes place at lower water–rock ratios. As a consequence, relatively more cations and silica are released into a smaller volume of pore water, which facilitates oversaturation with respect to smectite.

At ODP Site 861, the SMTZ as well as the shallow and deep reaction zone are connected to each other by molecular diffusion or advection of solutes and authigenic carbonates seem to precipitate in diagenetic fronts where weathering-related TA and Ca\(^{2+}\) fluxes meet each other (horizontal arrows in Fig. 3B). This is indicated by positive excursions in the CaCO\(_3\) profile where alkalinity from AOM and weathering meets bottom water Ca\(^{2+}\) (~20 mbsf) and where alkalinity from weathering meets deep-sourced Ca\(^{2+}\) from smectite formation (~185 mbsf). A potential third weathering-related CaCO\(_3\) peak is present at the lower end of the core where Ca\(^{2+}\) is released during smectite formation in the deep-seated reaction zone.

### 5.3. Transport of deep-seated weathering signals into the shallow sediments

At ODP Site 861, pore water Cl\(^-\) does not significantly deviate from seawater values in the uppermost 50 m of the sediment column. This is in sharp contrast to GC21 and particularly GC20 where significant deviations from seawater values were detected within the uppermost 10 mbsf. Difusive transport is unlikely efficient enough as to transfer the deep-seated chlorinity signal from smectite formation into the shallow sediments. In order to strengthen this hypothesis (i.e. that active fluid flow does occur in the accretionary prism), we applied a simple, one-dimensional transport model simulating diffusive and advective transport of Cl\(^-\) from the deep-seated reaction zone of smectite formation to the seafloor. The transport model is based on well-established differential equations (Berner, 1980; Boudreau, 1997) and computes concentration-depth profiles by considering the decrease in porosity with depth, molecular diffusion as well as advective transport of Cl\(^-\) via sediment burial, steady state compaction and pressure-driven flow (see Table EA-4 in the Electronic Annex for equations). Boundary conditions as well as the burial and upward fluid velocities applied in the model runs are summarized in Table 3.

In order to obtain reasonable scenarios for solute transport at Site GC20, we first tested the model with well constrained boundary conditions, sedimentation rates and porosity profiles (see Table EA-4) of ODP Sites 859 and 861. These were drilled on an E-W transect off Southern Chile at 45.9°S (Fig. 1A; Behrmann et al., 1992). ODP Site 859 is located seaward of Site 861 in a similar slope setting like GC20 (45°53.8’S, 2741 m water depth). Pore water Cl\(^-\) at ODP Site 859 increases in the uppermost 50 mbsf and scatters around values of 605 mM below 50 mbsf (Fig. 9A). A major excursion towards lower Cl\(^-\) concentrations at 50–60 mbsf has been attributed to gas hydrate dissolution during core recovery (Froelich et al., 1995). No attempt was made to consider this ex-situ process in the modeling. The concave down shape of the pore water Cl\(^-\) profile of Site 859 can only be modeled when applying an upward advection velocity that exceeds pore water burial. Pore water advection at Site 859 is likely sustained by lateral compression due to plate convergence and frontal sediment accretion at the deformation front of the prism. By contrast, modeling the linear and concave up shape of the pore water Cl\(^-\) profile at Site 861 requires that upward pore water advection is equal to or slower than pore water burial. This does not necessarily point to a lack of advective
flow but could also be related to the high sedimentation rates prevailing in the forearc basin of Site 861. Given the similarity of the depositional environments, pore water Cl\(^-\)/C\(^0\) profiles for GC20 were modeled adopting the sedimentation rate of ODP Site 859. A first set of profiles was modeled under the assumption that solute transport is mediated by diffusion only. To this end, upward fluid velocities were chosen such that the profiles become linear over the entire modeled domain (i.e. upward advection and pore water burial cancel out each other). The only way by which this approach yields reasonable fits to the measured data is when unrealistically high Cl\(^-\)/C\(^0\) concentrations at the lower boundary are assumed. Table 3 shows the properties and boundary conditions applied in the model runs. All equations and porosity profiles are summarized in EA-Table 4 in the Electronic Annex. Burial velocities and porosity data for ODP cores were taken from Behrmann et al. (1992) for Sites 859 and 861 and Mix et al. (2003) for Site 1235.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ODP Site 859</th>
<th>ODP Site 861</th>
<th>GC20</th>
<th>ODP Site 1235</th>
<th>GC17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length (m)</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Sediment burial velocity at the lower boundary(a), (v_{\text{Bottom}}) (cm yr(^{-1}))</td>
<td>0.004</td>
<td>0.026</td>
<td>0.004</td>
<td>0.070</td>
<td>0.070</td>
</tr>
<tr>
<td>([\text{Cl}^-]/C^0) ((\text{mM}))</td>
<td>550</td>
<td>560</td>
<td>550</td>
<td>555</td>
<td>545</td>
</tr>
</tbody>
</table>

**Upward fluid velocity \(\leq\) burial velocity (**'Diffusion 1' in Fig. 9 and dashed lines in Fig. 11)\)**

<table>
<thead>
<tr>
<th>Upward fluid velocity, (v_{\text{Top}}) (cm yr(^{-1}))</th>
<th>([\text{Cl}^-]/C^0) ((\text{mM}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>660</td>
</tr>
</tbody>
</table>

**Upward fluid velocity \(\leq\) burial velocity (**'Diffusion 2' in Fig. 9)\)**

<table>
<thead>
<tr>
<th>Upward fluid velocity, (v_{\text{Top}}) (cm yr(^{-1}))</th>
<th>([\text{Cl}^-]/C^0) ((\text{mM}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>660</td>
</tr>
</tbody>
</table>

**Upward fluid velocity \(\geq\) burial velocity (**'Net advection' in Fig. 9 and solid lines in Fig. 11)\)**

<table>
<thead>
<tr>
<th>Upward fluid velocity, (v_{\text{Top}}) (cm yr(^{-1}))</th>
<th>([\text{Cl}^-]/C^0) ((\text{mM}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>605</td>
</tr>
</tbody>
</table>

\(a\) Sediment burial velocity at the lower boundary equals sedimentation rate.

---

**Fig. 9.** Measured and modeled pore water Cl\(^-\) profiles of (A) ODP Sites 859 and 861 (pore water data and burial velocities from Behrmann et al., 1992) and (b–d) GC20. (B) Measured data and modeled profiles within the sediment section sampled (1–6 mbsf). (C–D) Whole length of the modeled profiles (0–500 mbsf). Note differing concentration and depth scales. Dashed lines were computed assuming that pore water burial and upward pore water advection cancel out each other (i.e. net transport of Cl\(^-\) ions is mediated by diffusion only). Solid lines were computed assuming that upward pore water advection exceeds pore water burial (i.e. net transport of Cl\(^-\) ions is mediated by both diffusion and upward pore water advection). The gray area in (B) indicates supersaturation with respect to halite (saturation index, SI\(_{\text{NaCl}}\) > 0). Input parameters for the different model runs are summarized in Table 3.
boundary are chosen (Table 3 and ‘Diffusion 1’ in Fig. 9B and C). In this modeling scenario, pore fluids reach saturation with respect to halite at 200 mbsf (i.e. implying halite dissolution/precipitation), which can be excluded based on the overall tectonic setting of the Central Chilean accretionary prism (see section 5.2). Another set of model runs was performed where upward solute transport is mediated by both diffusion and compaction-driven fluid advection (i.e. upward advection exceeds pore water burial). An accurate fit to the measured data was achieved by applying a Cl^{-} concentration at the lower boundary similar to that of ODP Site 861 and an upward fluid velocity of 0.03 cm yr^{-1} (‘Net advection’ in Fig. 9B and D). For comparison, a diffusive profile with the same lower boundary conditions yields seawater-like Cl^{-} concentration in the shallow sediments, which is consistent with the pore water data of ODP Site 861 (‘Diffusion 2’ in Fig. 9B and C).

Our simple modeling experiment clearly shows that the presence of deep-sourced Cl^{-} anomalies in shallow sediments of the Central Chilean accretionary prism requires active upward fluid flow. Positive Cl^{-} anomalies occur over large horizontal distances (Figs. 1 and 2) and none of the coring sites revealed typical seep characteristics. This observation is in agreement with the general assumption that fluid flow through sediments in accretionary prisms is widespread and diffuse rather than localized and focused (Moore and Vrolijk, 1992; Carson and Screaton, 1998).

5.4. Evidence for pore water freshening and relation to submarine weathering

Deep-sourced pore waters in the accretionary prism off Central Chile reveal ubiquitous evidence for authigenic smectite formation. Given that sediments on the incoming plate have essentially the same composition like those on the adjacent slope (Lamy et al., 1998), they are likely to undergo authigenic smectite formation as well. Upon heating during deep burial and ongoing subduction (to a depth of kmbsf), smectite within the prism and underthrust sediments will become unstable and its diagenetic conversion to illite or smectite-illite mixed layer minerals will start at about 60 °C (Kastner et al., 1991). During this process, water that has been sequestered prior to deposition (detrital smectite) or during submarine weathering (authigenic smectite) will be liberated again thus causing pore water freshening (Bekins et al., 1994; Hensen et al., 2004; Torres et al., 2004a). The spatial range where this process can theoretically occur may be constrained by comparing the thermal properties of the Central Chilean marine forearc with the temperature window of the smectite to illite transition (60–150 °C; Kastner et al., 1991) (Fig. 10). Sediment temperatures at the plate interface were computed by adapting a thermal model for the Chilean subduction zone to the plate age and sediment thickness at 36°S (Völker et al., 2011). From these décollement temperatures, isotherms were obtained through linear interpolation to the sediment surface assuming a uniform bottom water temperature of 5 °C. According to Fig. 10, smectite to illite conversion is possible throughout the marine forearc at sediment depths >2–5 kmbsf. During the CHIFLUX cruise, weakly freshened pore fluids were only encountered on the upper slope at Site GC17 and, to a lesser extent, at Site GC18 in the Concepción Methane Seepage Area (Fig. 2A). Moreover, downcore chlorinity decreases up to 483 mM at 177 mbsf (Mix et al., 2003) were detected during ODP Leg 202 at ODP Sites 1233 (41°0.0’S, 838 m water depth) and 1235 (36°9.6’S, 489 m water depth; Fig. 1) both of which are located landward of and at shallower water depth than GC17 and GC18.

The relative intensity of pore water freshening and/or fluid advection at Site GC17 and nearby ODP Site 1235 may be evaluated using the one-dimensional diffusion–advection model introduced in the previous section. Pore water Cl^{-} profiles for both cores were modeled by applying the sedimentation rate, lower boundary condition and porosity profile of Site 1235 (Table 3 and Table EA-4 in the Electronic Annex). A reasonable fit to the pore water Cl^{-} data of Site 1235 could be achieved with an upward advection velocity of 0.08 cm yr^{-1} (Fig. 11). Using the same

Fig. 10. Thermal cross section across the Central Chilean marine forearc at 36°S (after Völker et al., 2011). The gray area represents the theoretical temperature range of the diagenetic smectite to illite transition (60–150 °C; Kastner et al., 1991). Coring locations and major splay faults are shown for orientation.
lower boundary condition for GC17 requires a higher fluid advection velocity (0.18 cm yr\(^{-1}\)) in order to fit the measured data (Fig. 11). Alternatively, the data of GC17 could be fitted by applying a lower Cl\(^-\) concentration at the lower boundary. Besides a scatter at 422 cmbsf, that is likely related to hydrate dissolution during core recovery, pore water Cl\(^-\) concentrations of GC18 range between the modeled lines of GC17 and Site 1235 (Fig. 11). We thus observe a succession of increasing advection velocities and/or pore water freshening intensities (Site1235 < GC18 < GC17) towards the outcrop of the upper splay fault depicted in Fig. 1B. A deep-seated fluid source at the splay fault beneath Site GC17 is consistent with a high heat flow observed in this area in a previous study (Grevemeyer et al., 2006). In a recent article, Lauer and Saffer (2012) highlighted the role of splay faults in channeling heat and solutes through the upper plate of convergent margins. The advection velocity modeled for GC17 is in good agreement with the range of advection velocities reported for splay faults by these authors (0.08–2.6 cm yr\(^{-1}\); Lauer and Saffer, 2012).

Assuming that splay faults mediate the ascent of freshened fluids in slope sediments off Central Chile, appropriate temperatures for smectite dehydration are solely met within the framework rock of the upper plate (Fig. 10). At the lower end of the splay faults, decoulement temperatures range between 160 and 200 °C suggesting that smectite dehydration within the underthrust sediments is completed further seaward. According to the thermal cross section in Fig. 10, appropriate temperatures for smectite dehydration within the underthrust sediments are met between 5 and 45 km from the deformation front. However, despite unequivocal evidence for deep-sourced fluid flow (see previous section) and despite extensive sediment coring and visual as well as acoustic seafloor survey (Geersen et al., 2011; Linke and Shipboard Scientific Party, 2012), no indication for seepage of freshened fluids could be found in this area.

To explain the lack of shallow pore water freshening in sediments of the Central Chilean accretionary prism, we have to consider the ubiquity of saline fluids from submarine weathering processes. Because of mixing with saline fluids, any freshening signal originating from deeper within the subduction system is unlikely to survive transport into the shallow sediments. This is in sharp contrast to the Central American margin where no fluids with elevated salinity from submarine weathering have been encountered. The accretionary versus erosive character of the Central Chilean and Central American convergent margins may be important for the availability of fluid pathways. According to our results, however, an even more important difference between the two subduction systems is related to the differing weathering regimes prevailing in the sediment source areas on land. Volcanogenic sediments are abundant in both Central America and Central Chile (Fig. 6A). However, in tropical Central America weathering is almost completed on land and therefore forearc sediments consist almost entirely of detrital smectite (Fig. 6B; Spinelli and Underwood, 2004). The interlayer water of the detrital smectite was sequestered outside of the subduction system and may therefore produce a pronounced signal of pore water freshening upon smectite dehydration. By contrast, in Central Chile weathering intensities on land are minor (Lamy et al., 1998; Lucassen et al., 2011) and smectite formation from volcanic detritus occurs chiefly after transport to the forearc and during burial. The circular process of pore water uptake during formation of smectite and release upon its conversion to illite implies a balanced freshwater budget and therefore a rather limited potential for net pore water freshening on a continental margin scale. This whole model of weathering- or climate/relief-controlled forearc dehydration is consistent with the upper plate origin assumed for freshened fluids at Sites GC17 and 1235. Dehydration reactions within the Mesozoic sedimentary rocks of the continental framework are unlikely to reflect current subduction zone inputs or modern climate but rather those of the Mesozoic when average climate was likely to be more favorable for terrestrial weathering (Sellwood and Valdes, 2006).

6. SUMMARY AND IMPLICATIONS

Owing to a low intensity of terrestrial weathering, surface sediments off Central Chile are rich in reactive silicate minerals and have a similar bulk composition like volcanic rocks in the adjacent Andes. Deep-sourced fluxes of alkalinity and cations into the shallow sediments as well as elevated pore water salinities indicate that weathering reactions occur after deposition and during different stages of diagenesis during burial. In shallow (tens of meters) methanogenic sediments of slope basins with high sedimentation and organic carbon burial rates, reactive silicate minerals are incongruently dissolved through reaction with CO\(_2\) from methanogenesis. This process is accompanied by release of bicarbonate, Ca\(^{2+}\) and Mg\(^{2+}\) into the pore water. At greater burial depth (hundreds of meters) or higher temperatures and lower water–rock ratios, reactive silicate minerals are converted to authigenic smectite. During this process, water is taken up into the interlayers of the smectite thus leading to elevated pore water salinities. Deep-seated smectite formation is more widespread than silicate...
dissolution, as it is independent from organic carbon burial and methanogenesis. Although pore water advection is not focused enough to form cold seeps in the proper sense, tectonically induced fluid flow transfers the deep-seated signal of smectite formation into the shallow sediments. The following general conclusions are drawn from these findings:

(1) Wallmann et al. (2008) were the first to emphasize the importance of incongruent silicate dissolution in methaneic sediments as an oceanic net sink of CO$_2$. According to our findings, submarine weathering may occur if both organic matter and reactive silicate minerals are available below the depth of sulfate depletion. As reactive silicate minerals are abundant throughout the Central Chilean margin, organic matter is the limiting factor for silicate dissolution. Below a certain threshold of organic carbon burial and at greater burial depth, silicate dissolution is replaced by, apparently CO$_2$-neutral, smectite formation. On passive continental margins and in areas where terrestrial weathering is more intense (i.e. those with a warm and humid climate and/or little morphology), submarine weathering is likely limited by the availability of reactive silicate minerals. Accurate global estimates of the CO$_2$ sink through submarine weathering require a better understanding of the threshold values (e.g. CIA of surface sediments and organic carbon burial rates) beyond which submarine silicate weathering does occur.

(2) The temperature-controlled transformation of smectite to illite is considered the most important dehydration process in marine forearc environments (Saffer and Tobin, 2011). On the Central Chilean margin, most of the smectite available for dehydration has not formed on land but in the subduction system. The consecutive uptake of pore water during smectite formation and release during illitization implies a balanced freshwater budget when averaged over the entire forearc. Differences in porosity during water uptake and release as well as differential fluid pathways of hydration and dehydration fluids (e.g. drainage along the décollement versus diffuse flow in the prism) might leave some room for seabed seepage of freshened pore fluids. However, when comparing Central Chile to other convergent margins where most of the smectite is formed on land (e.g. Central American margin (Spinelli and Underwood, 2004); Barbados (Capet et al., 1990); Mediterranean Ridge (Ryan et al., 1973)), the overall potential for net pore water freshening is rather limited. According to this rationale, significant pore water freshening in seabed seeps is primarily to be expected at low latitudes where terrestrially derived, detrital smectite may provide an external freshwater input to the subduction system. The Central and Southern Chilean margin is likely to be an end member regarding the relationship between submarine versus terrestrial weathering. However, there are numerous other convergent margins where ubiquitous seabed seepage of hydrocarbon gases but none of freshened pore fluids from clay dehydration has been observed (e.g. Aleutians, Cascadia margin, Nankai Trough). Similar to Central and Southern Chile, at the Nankai Trough saline pore fluids in sediments on both the upper (Kastner et al., 1993) and the incoming plate (Expedition 333 Scientists, 2011) indicate that submarine weathering does take place. In such settings, the relationship between terrestrial and submarine weathering (or terrigenous and authigenic smectite) is likely to be critical for the extent to which deep-sourced freshening signals from smectite dehydration reach the seafloor. This should be considered in future studies on the recycling of water at convergent plate margins.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.09.043.

REFERENCES


