Chapter 8

Pore Water Geochemistry as a Tool for Identifying and Dating Recent Mass-Transport Deposits

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Abstract Several previous studies have shown that submarine mass-movements can profoundly impact the shape of pore water profiles. Therefore, pore water geochemistry and diffusion models were proposed as tools for identifying and dating recent (max. several thousands of years old) mass-transport deposits (MTDs). In particular, sulfate (SO_4^{2-}) profiles evidentially indicate transient pore water conditions generated by submarine landslides. After mass-movements that

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result in the deposition of sediment packages with distinct pore water signatures, the SO_4^{2-} profiles can be kink-shaped and evolve into the concave and linear shape with time due to molecular diffusion. Here we present data from the RV METEOR cruise M78/3 along the continental margin off Uruguay and Argentina. SO_4^{2-} profiles of 15 gravity cores are compared with the respective acoustic facies recorded by a sediment echosounder system. Our results show that in this very dynamic depositional setting, non-steady state profiles occur often, but are not exclusively associated with mass-movements. Three sites that show acoustic indications for recent MTDs are presented in detail. Where recent MTDs are identified, a geochemical transport/reaction model is used to estimate the time that has elapsed since the perturbation of the pore water system and, thus, the timing of the MTD emplacement. We conclude that geochemical analyses are a powerful complementary tool in the identification of recent MTDs and provide a simple and accurate way of dating such deposits.

Keywords Mass-movement • Pore water profiles • Non-steady state • Seismo-acoustic facies • Geochemical modeling

8.1 Introduction

Seismo-acoustic approaches provide the means to estimate dimensions of MTDs, but for absolute dating and identifying small-scale internal structures they need to be complemented by sediment data. However, based on visual core descriptions, MTDs are often hard to distinguish from homogeneous hemipelagic sediments, as both might lack clear stratification. Pore water profiles can be used to close this gap as was demonstrated first by De Lange (1983), who identified a “fresh-to-brackish sediment ‘slab’, with preservation of structural and pore water composition” underlying marine sediments in the Norwegian Sea.

With respect to pore water, sediments are classified into steady state and non-steady state systems (Schulz 2006). Simplified, steady state systems are in equilibrium and show a linear SO_4^{2-} decrease with depth towards the sulfate-methane transition zone (SMTZ) where the process of anaerobic oxidation of methane (AOM; e.g., Barnes and Goldberg 1976) occurs. Zabel and Schulz (2001) and Hensen et al. (2003) presented non-steady state SO_4^{2-} profiles from the Zaire deep-sea fan and the continental margin off Uruguay and suggested that kink, concave-up, and s-type SO_4^{2-} profiles can be explained by submarine landslides that carry their initial pore water signals downslope. The base of an MTD can, according to the authors, be indicated by a kink of the pore water profile, which evolves into a concave and finally a linear shape due to molecular diffusion. The re-equilibration of the SO_4^{2-} pore water profile was modeled to estimate the timing of the mass-movement.

With this review paper, we expand on the previous approaches and give a regional compilation showing the pervasiveness of non-steady state SO_4^{2-} profiles at the continental margin off Uruguay and Argentina and their relation to MTDs as indicated

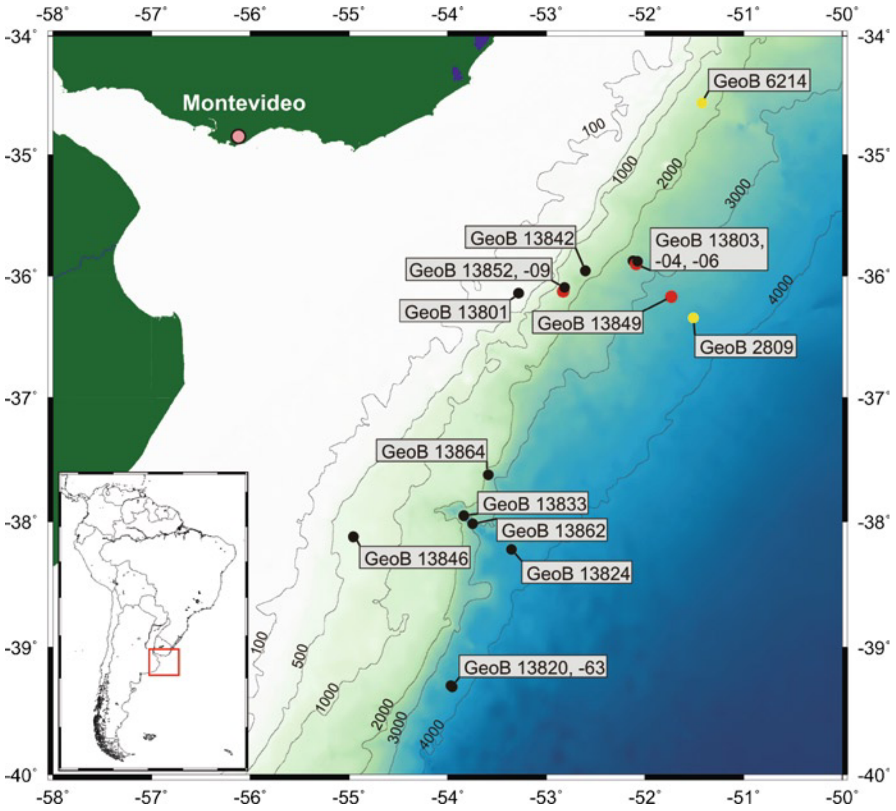

Fig. 8.1 Study area off Uruguay and Argentina and core locations. The sites marked in *red* are discussed in this study. The *yellow dots* mark the sites that are discussed in detail by Hensen et al. (2003)

by sediment echosounder data. The integration of geochemical, sedimentological, and geophysical data allows a better understanding of the dynamic interactions of pore water, sediments, and physical processes and offers a unique approach to date recent MTDs.

8.2 Study Area

The study area (Fig. 8.1) is characterized by dynamic oceanographic conditions including the Brazil-Malvinas Confluence near 38°S and the interaction of Antarctic water masses with the North Atlantic Deep Water at different depths (Piola and Matano 2001). The sedimentary processes along the margin were described in detail by Krastel et al. (2011). Mass movements occur within canyons and on the lower slope (Krastel et al. 2011).

8.3 Material and Methods

Sediment echosounder data were obtained with the Atlas Hydrographic PARASOUND system, which gives a dm-scale vertical resolution and a horizontal resolution of 7% of the water depth. Gravity cores were retrieved from various water depths (Table 8.1). Methane (CH_4) and pore water samples were gained as described in Henkel et al. (2011).

We performed transport/reaction modeling using the software CoTReM (Adler et al. 2001) and following the method of Hensen et al. (2003). We consider AOM (Eq. 8.1) as the most important process for SO_4^{2-} reduction at depth.

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \tag{8.1}$$

Borowski et al. (1996) proposed that the upward flux of CH_4 can be quantitatively estimated from the downward flux of SO_4^{2-}. Measured CH_4 data were not used for the simulation because of the known inaccuracy related to degassing during core retrieval (e.g., Dickens et al. 1997). Except for bioirrigation and sedimentation rate (SR) that are considered in the model as advective terms, we simulated exclusively diffusive transport of pore water species. The reaction-specific change in concentration at a specific sediment depth ($\Delta C_{\mathrm{s,d}}$) was calculated as follows:

$$\Delta C_{\mathrm{s,d}} = R_{\mathrm{s,d}} \times dt_{\mathrm{num}} \times SC_{\mathrm{s,d}} \tag{8.2}$$

Where $R_{\mathrm{s,d}}$ is the reaction rate, $\mathrm{dt}_{\mathrm{num}}$ is the time step used in the model run, and $SC_{\mathrm{s,d}}$ is a stoichiometric factor (see Hensen et al. 2003). Details to $R_{\mathrm{s,d}}$ are given in Sect. 8.4.

8.4 Results and Discussion

Identification of submarine landslides by SO_4^{2-} profiles is restricted to MTDs that are only a few meters thick. A thicker MTD that is not completely penetrated by the gravity corer may show a linear SO_4^{2-} profile in the cored interval. In such a case, the change in gradient (the kink) occurs below the cored depth and the MTD could thus not be identified on the basis of the SO_4^{2-} profile. Fifteen of the investigated cores penetrated the SMTZ and therefore provided the required information for an appropriate description of the SO_4^{2-} profile (Table 8.1, Fig. 8.1). The SO_4^{2-} profiles are classified into the types linear, concave-up, and kink shape (Table 8.1). The acoustic facies with special emphasis on reflection configuration and amplitude are included as well in Table 8.1. Nine of the investigated cores reveal non-linear profiles. Three of these nine cores (GeoB 13801, −03, −42) are not related to MTDs as indicated by PARASOUND data (Table 8.1). We therefore consider that the non-linearity of these SO_4^{2-} profiles can be attributed to alternative processes, such as CH_4 gas ebullition (Haeckel et al. 2007) or a sudden increase in the upward flux of CH_4 (Kasten et al. 2003) possibly due to gas hydrate dissociation.

Table 8.1 M78/3 core locations complemented by the shape of SO_4^{2-} profile and the acoustic facies

GeoB #	Latitude	Longitude	Depth [mbsf]	SO_4^{2-} profile	Acoustic facies
13801–2	36° 08.49′ S	53° 17.16′ W	243	Concave-up	Parallel layered; low to high amplitudes
13803–2	35° 52.65′ S	52° 07.19′ W	2,462	Concave-up	Parallel layered; medium to high amplitudes
13804–1	35° 54.30′ S	52° 05.42′ W	2,593	Kink	Chaotic, hummocky
13806–1	35° 52.82′ S	52° 04.61′ W	2,586	Concave-up	Transparent sheet-like layer; parallel layered sediment below
13809–1	36° 07.67′ S	52° 49.90′ W	1,400	Linear	Transparent sheet-like layer; parallel layered sediment below
13820–1	39° 18.06′ S	53° 58.03′ W	3,613	Linear	Parallel layered; low to high amplitudes
13824–1	38° 13.14′ S	53° 21.29′ W	3,821	Linear	Parallel layered; low to high amplitudes
13833–2	37° 57.45′ S	53° 50.21′ W	3,404	Concave-up	No data
13842–1	35° 57.57′ S	52° 36.30′ W	1,555	Kink	Parallel-subparallel layered; low to high amplitudes
13846–2	38° 07.19′ S	54° 57.46′ W	637	Linear	Parallel layered; low to high amplitudes
13849–1	36° 10.41′ S	51° 43.96′ W	3,278	Concave-up	Lens-shaped transparent unit; parallel layered below
13852–1	36° 05.70′ S	52° 48.98′ W	1,320	Concave-up	Transparent sheet-like layer; parallel layered below
13862–1	38° 01.11′ S	53° 44.70′ W	3,588	Kink	No data
13863–1	39° 18.70′ S	53° 57.16′ W	3,687	Linear	Parallel layered; low to high amplitudes
13864–2	37° 37.47′ S	53° 35.33′ W	2,757	Linear	Parallel layered; medium to high amplitudes

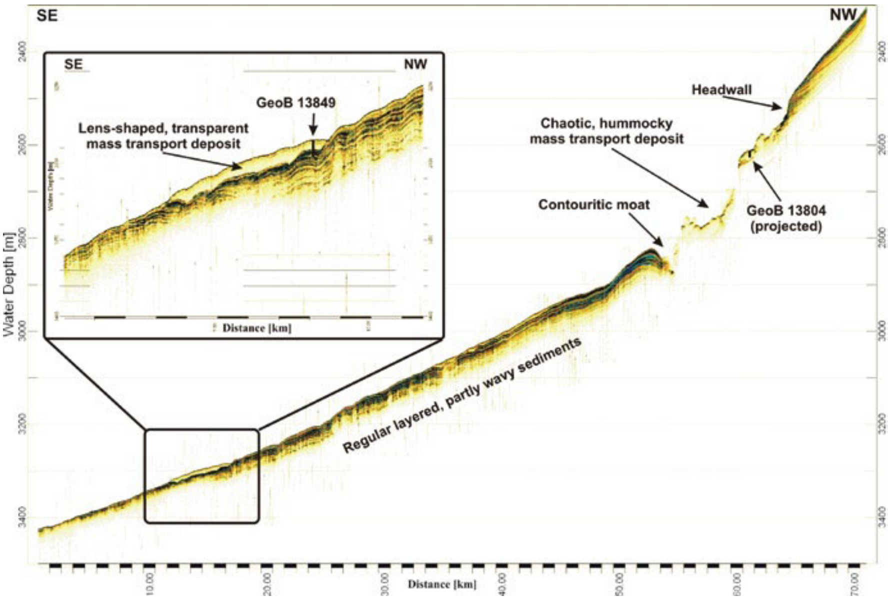

Fig. 8.2 PARASOUND profile obtained during RV METEOR cruise M78/3 crossing the continental slope in SE-NW direction. The profile shows the position of core GeoB 13804 (projected) at a hummocky surface interpreted as mass-transport deposit. Site GeoB 13849 is shown in the close-up at the rim of a lens-shaped transparent unit overlying parallel layered sediments. At the core location, the transparent unit interpreted as a gravity flow deposit is ~6 m thick

At several sites (GeoB 13806, −09, −49, −52), acoustically transparent deposits overlay parallel layered sediments (Table 8.1, Figs. 8.2 and 8.3). In general, such transparent units represent either homogeneous or extremely heterogeneous sediments with loss of internal bedding (Kuehl et al. 2005). Transparent acoustic facies often represent MTDs, which may also show a hummocky surface and an erosional base (Hampton et al. 1996).

Three sites (GeoB 13804, −49, and −09) will be discussed, that represent the three different categories of SO_4^{2-} profiles and which have all been recovered from sites that show acoustic indication of potential MTDs (Fig. 8.4). Core GeoB 13804 was retrieved from an acoustically chaotic facies with a hummocky surface. Core GeoB 13849 was recovered from a lens-shaped transparent unit (Fig. 8.2) and core GeoB 13809 was taken from an acoustically-transparent, sheet-like deposit downslope of a prominent scar (Krastel et al. 2011). This 5–6 m thick sedimentary body is characterized by parallel upper and lower boundaries and shows no termination within the surveyed area (Fig. 8.3). The interpretation of this feature from PARASOUND data is therefore not unambiguous. It may result either from downslope sediment-transport processes or from sheeted-contouritic deposition of homogeneous material (see discussion below).

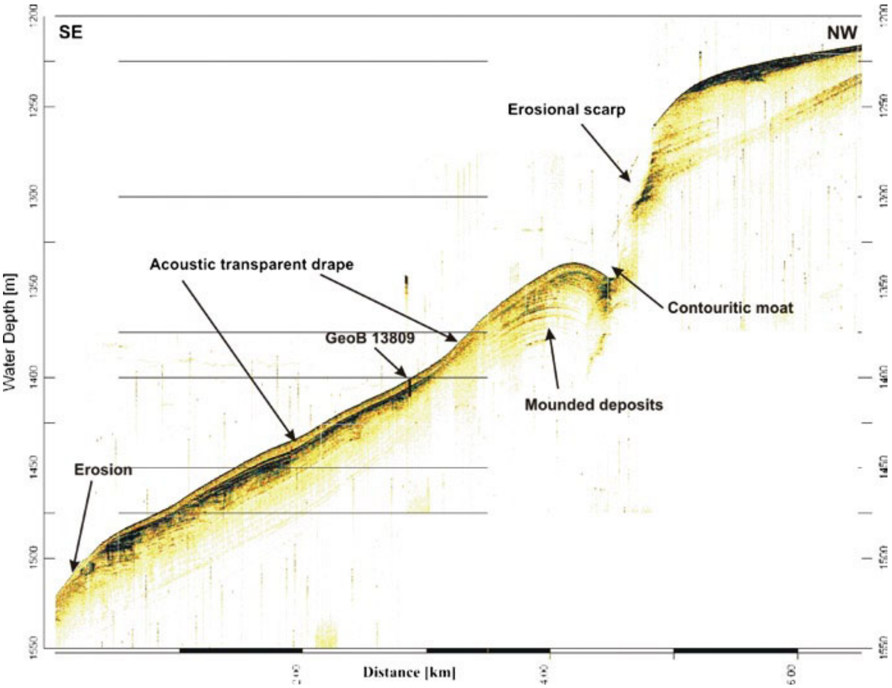

Fig. 8.3 PARASOUND profile obtained during RV METEOR cruise M78/3 crossing the continental slope in SE-NW direction. Station GeoB 13809 is located to the SE of a contouritic moat. The profile at the core location shows parallel layered sediments and a strong reflector in 5–6 depth that has an erosive character and is overlain by a sheet-like transparent unit

8.4.1 Pore Water Profiles at Potential MTD Sites

The SO_4^{2-} profile at site GeoB 13804 has a kink shape with a gradient change at ~2.8 m (Fig. 8.4). A sedimentological boundary between gray and very dark gray mud occurs at 2.43 m, thus ~0.35 m above the gradient change of the SO_4^{2-} profile (Fig. 8.4). Above this sedimentological contact, which is also reflected by a significant downcore increase in undrained shear strength (Henkel et al. 2011), the core shows a stack of undisturbed sand/silt layers (Fig. 8.4). Bioturbation structures are present between 0 and 2.79 m depth. Bioirrigation and vertical gas or fluid migration in the whole ~2.8 m thick package can be excluded (Henkel et al. 2011). Therefore, we conclude that the kink shaped SO_4^{2-} profile is the result of the combination of bioirrigation to a paleo-depth of 0.35 m and a ~2.4 m thick slide mass. In accordance with the studies of Zabel and Schulz (2001) and Hensen et al. (2003) at other locations, the most recent mass-transport event at site GeoB 13804 must have happened in the form of a coherent slide mass carrying its initial SO_4^{2-} profile downward, because the internal structure of this package was not destroyed. It is known from previous expeditions that sites with nearly constant SO_4^{2-} concentrations over the length of a

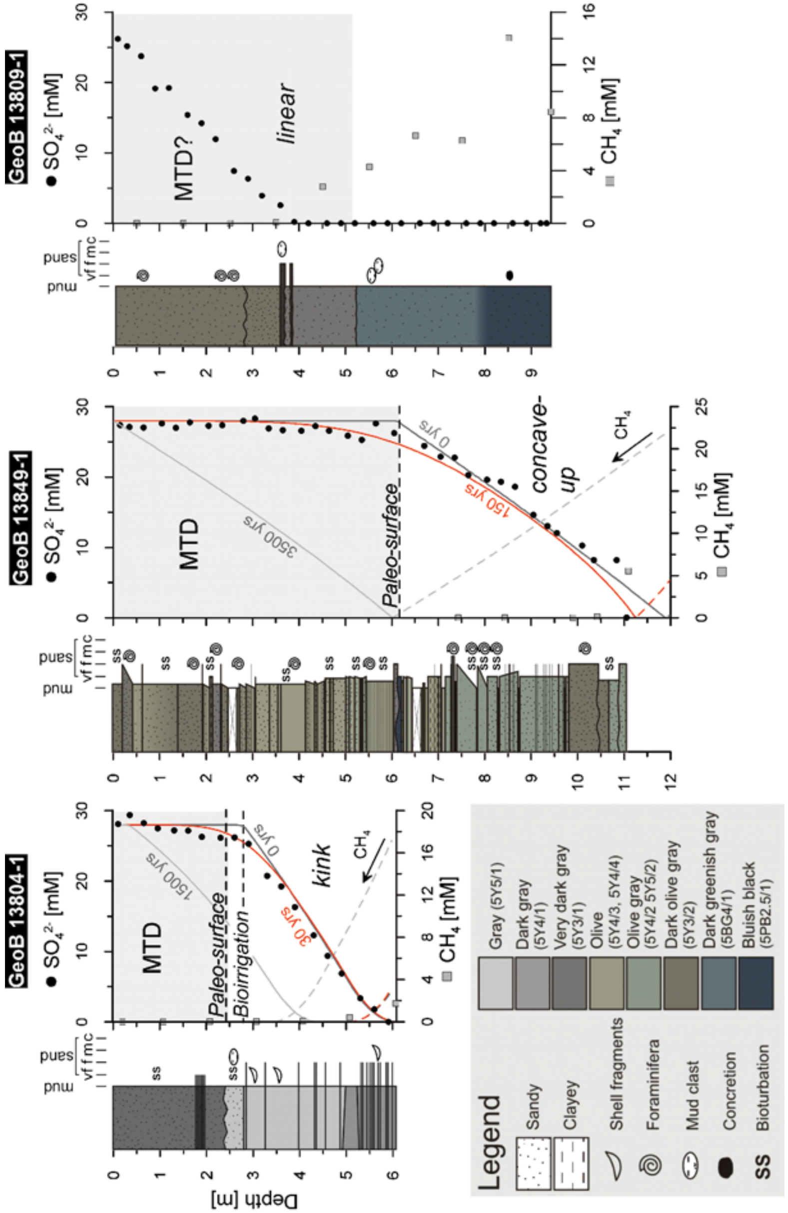

Fig. 8.4 Lithology, SO_4^{2-}, and CH_4 profiles of gravity cores. The non-steady state SO_4^{2-} profiles at sites GeoB 13804 and GeoB 13849 are related to recent MTDs (*gray shaded*). The *gray* lines labeled with "0 years" in the graphs of GeoB 13804 and −49 show the starting conditions for the models that were set up to estimate the timing of the mass-transport deposition. Data of site GeoB 13804 including the geochemical simulation are described in detail in Henkel et al. (2011). The values in *brackets* (legend) represent the Munsell color code

Table 8.2 Parameterization for transport and reaction modeling for sites GeoB 13804 and –49

Basic parameters GeoB 13804/–49		Boundary conditions GeoB 13804/–49	
Model length [m]	8/15	Sedimentation rate [cm kyear^{-1}]	80–180[a]/5[b]
Cell discretisation [cm]	5	Upper boundary SO_4^{2-} [mmol l^{-1}]	28[c]
Time step [year]	0.05	Upper boundary CH_4 [mmol l^{-1}]	0[c]
Porosity φ	0.6/0.7[d]	Lower boundary SO_4^{2-} [mmol l^{-1}]	0
Temperature [°C]	3.5	Lower boundary CH_4 [mmol l^{-1}]	40/35
Diffusion coefficients[e]	D_0	D_{sed}	
SO_4^{2-} [cm^2 year^{-1}]	179.5	88.79	
CH_4 [cm^2 year^{-1}]	293.6	145.2	

[a] Exceptionally high sedimentation rate derives from unsupported ^{210}Pb. For details see Henkel et al. (2011)

[b] According to Ewing et al. (1971) and Hensen et al. (2003)

[c] Bottom water concentrations

[d] Average porosity as measured on board

[e] Diffusion coefficient in free solution (D_0) calculated for a temperature of 3.5°C and corrected for tortuosity (θ) after Boudreau (1997); $D_{sed} = D_0/\theta^2$, while $\theta^2 = 1 - \ln(\varphi^2)$

gravity core (as it is expected for the source area of the slide) occur in the study area (Bleil et al. 1994).

Site GeoB 13849 is characterized by a concave-up shaped SO_4^{2-} profile (Fig. 8.4). Based on PARASOUND data, the thickness of the surficial MTD unit is estimated to be ~6 m (Fig. 8.2), which fits well to the SO_4^{2-} profile showing a change in gradient at the same depth. The lithology displays a sharp contact between bluish black fine sand interbedded with olive muddy fine sand below and dark gray muddy fine sand above 6.10 m. Based on the geochemical and PARASOUND data this boundary is interpreted as the base of the MTD.

The visual description of core GeoB 13809 reveals a sharp, irregular contact at 5.12 m. Since this boundary correlates to the base of the acoustically transparent layer imaged in PARASOUND data, it possibly represents the base of an MTD (Fig. 8.4). Core GeoB 13809 displays a linear SO_4^{2-} profile. The inferred mass-movement thus took place several hundreds to thousands of years ago, so that the SO_4^{2-} profile could diffusively re-equilibrate into a linear shape.

8.4.2 Geochemical Transport/Reaction Modeling

The diffusive re-equilibration of the SO_4^{2-} profile over time was simulated for sites GeoB 13804 and –49 (parameterization in Table 8.2). A maximum reaction rate $R_{s,d}$ of 0.1 mol dm^{-3} year^{-1} was defined to produce a broad SMTZ with overlapping CH_4 and SO_4^{2-} profiles at site GeoB 13804 (Fig. 8.4). That rate was used as long as the reactants were available in sufficient amounts (0th order kinetics). For lower concentrations of the reactants and for site GeoB 13849, where the SMTZ is restricted to a distinct depth, the AOM reaction rate was determined based on second order kinetics. The starting conditions for the model runs are shown as gray lines in Fig. 8.4: Each sediment package (the MTD and the sediment below) still hosts its initial pore water characteristic. For site GeoB 13804, the model results reveal that the proposed mass-movement took place less than 30 years ago (Fig. 8.4, Henkel et al. 2011). The event could therefore have been associated with a weak (5.2 m_b) earthquake in 1988 (Henkel et al. 2011). The epicenter was ~70 km away from the core location (Assumpção 1998; Benavídez Sosa 1998).

According to the best fit between measured SO_4^{2-} concentrations and the simulation (red line in Fig. 8.4), the MTD at site GeoB 13849 occurred approximately 150 years ago. The age of the MTD roughly corresponds to an earthquake in 1848 (intensity in Montevideo IV-V based on the Mercalli scale) with an epicenter ~200 km west of the study site (Benavídez Sosa 1998). Complete re-equilibration of the SO_4^{2-} profile is reached after ~3,500 years (Fig. 8.4).

8.5 Conclusions

This study demonstrates that integrating geophysical, sedimentological, and pore water data provides a scientifically valid approach to constrain the ages of recent MTDs. Pore water geochemical analyses are cost-efficient, easily accessible compared to other methods, and can provide information regarding paleosurfaces or erosive contacts that are not apparent from visual core inspection. Applying a comprehensive, multi-disciplinary approach as presented in this study over a larger region could provide a historical record of the frequencies of mass-transport events. Such a record may be compared to documented earthquakes and in this way shed light on the dynamic and complex links between various geological processes.

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