Relationship of pore water freshening to accretionary processes in the Cascadia margin: Fluid sources and gas hydrate abundance

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[1] Drilling in the Cascadia accretionary complex enable us to evaluate the contribution of dehydration reactions and gas hydrate dissociation to pore water freshening. The observed freshening with depth and distance from the prism toe is consistent with enhanced conversion of smectite to illite, driven by increase in temperature and age of accreted sediments. Although they contain gas hydrate -as evidenced by discrete low chloride spikes- the westernmost sites drilled on Hydrate Ridge show no freshening trend with depth. Strontium data reveal that all the mélange samples contain deep fluids modified by reaction with the subducting oceanic crust. Thus we infer that, at the westernmost sites, accretion is too recent for the sediments to have undergone significant illitization. Our data demonstrate that a smooth decrease in dissolved chloride with depth cannot generally be used to infer the presence or to estimate the amount of gas hydrate in accretionary margins. INDEX TERMS: 1040 Geochemistry: Isotopic composition/chemistry; 4809 Oceanography: Biological and Chemical: Colloids; 4825 Oceanography: Biological and Chemical: Geochemistry; 8150 Tectonophysics: Plate boundary—general (3040). Citation: Torres, M. E., B. M. A. Teichert, A. M. Tréhu, W. Borowski, and H. Tomaru (2004), Relationship of pore water freshening to accretionary processes in the Cascadia margin: Fluid sources and gas hydrate abundance, Geophys. Res. Lett., 31, L22305, doi:10.1029/2004GL021219.

1. Introduction

[2] Fluids play a critical role at accretionary margins, as they impact the geochemical budgets and geomechanical properties of the prism. Dissolved chloride in pore fluids has been used to quantify processes that release water and to identify migration pathways and transience of fluid flow in these active margin settings [e.g., *Bekins et al.*, 1995]. Many convergent margins have fluids with Cl^- concentrations lower than seawater [e.g., *Kastner et al.*, 1991]. Processes responsible for such freshening include smectite dehydration and gas hydrate dissociation. At depth, diagenetic conversion of smectite to illite is primarily controlled by temperature and time [*Bekins et al.*, 1994], and methane is generated by microbial and thermal decomposition of organic matter. Advection of methane-bearing fluids into shallow sediments in which pressure and temperature conditions lie within the gas hydrate stability zone (GHSZ) leads to formation of gas hydrates [e.g., *Sloan*, 1998]. During this process salts are excluded and removed over time by advection or diffusion. Gas hydrate dissociation upon core recovery releases fresh water to the sediment [e.g., *Ussler and Paull*, 2001].

[3] Here we use data collected during Ocean Drilling Program (ODP) Legs 146 and 204 to evaluate fluid sources and freshening processes along the Cascadia accretionary wedge (Figure 1). Comparison of these data with those collected by drilling 100 km east of the Juan de Fuca Ridge during Leg 168 [*Fisher and Davis*, 2000], indicate that all fluids sampled within the accreted mélange on Hydrate Ridge have a component altered by exchange with oceanic crust. Increased freshening of pore waters with distance from the prism toe correlates with an increase in clay dehydration and not with hydrate abundance [*Tréhu et al.*, 2004].

2. Fluid Sources in Hydrate Ridge

[4] The Cascadia margin evolved in response to subduction of the Juan de Fuca plate beneath North America (Figure 1). The subducting oceanic plate is overlaid by a thick sediment package, whose upper portion is accreted to the margin to form an accretionary wedge. The deeper incoming sediment is underthrusted and underplated beneath a poorly imaged mélange complex, generating a series of ridges within the wedge [e.g., *McKay et al.*, 1992]. The accreted complex is covered with a hemipelagic slope drape of varying thickness.

[5] Sediment and fluid samples have been recovered from the Cascadia accretionary complex offshore Vancouver (Site 889), at Site 892 on the northern summit of Hydrate Ridge, and at six sites near its southern summit [*Westbrook et al.*, 1994; *Tréhu et al.*, 2003] (Figure 1). Pore water from sediment and basement prior to subduction are available from Sites 888 [*Westbrook et al.*, 1994] and 1027 [*Fisher and Davis*, 2000]. The Cl^- and Sr^{+2} concentration is illustrated in Figure 2, showing their relative distance (not to scale) from the prism toe. Sediment penetration at each of these sites, and depth to basement or accreted mélange are listed in Table 1.

[6] Pore fluids recovered from the accreted mélange at Hydrate Ridge are enriched in dissolved Li^{+1} and contain heavy hydrocarbons, indicating that the fluids have experienced temperatures higher than 70°C. Given the regional geothermal gradient of $0.055 \pm 0.005°C$ m^{-1}, these data reflect migration from depths >1 km [*Whiticar et al.*, 1995; *Kastner et al.*, 1995; *Tréhu et al.*, 2003; *Milkov et al.*, 2003].

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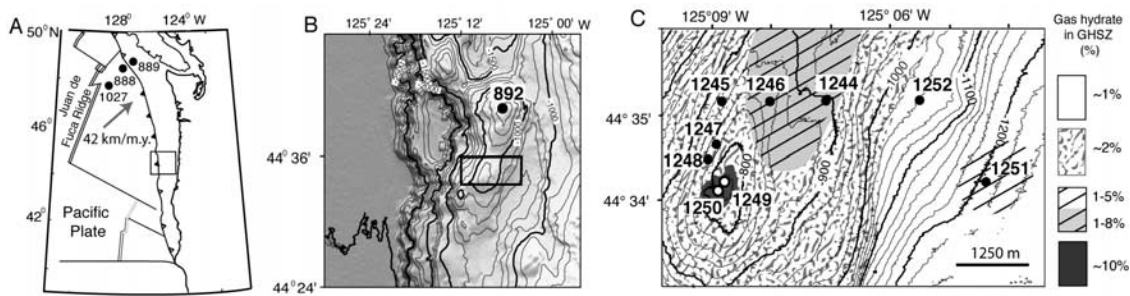[5]Now at Department of Earth and Environmental Sciences, University of Rochester, Rochester, New York, USA.

Figure 1. a. Tectonic setting of the Cascadia subduction zone and locations of ODP sites 888, 889 and 1027; box demarks area shown in Figure 1b. b. Hydrate Ridge bathymetry; box demarks area detailed in Figure 1c. c. Area targeted during Leg 204, showing location of drilled sites and gas hydrate abundance estimated by *Tréhu et al.* [2004].

The dissolved strontium concentration and isotope data further expand this inference by indicating fluid-rock interactions with oceanic basement. An increase in Sr^{+2} concentration by exchange with the underlying crust was documented at Site 1027 [*Elderfield et al.*, 1999]. No increase is apparent at Site 888 since penetration here is 200 meters above basement (Table 1). Pore fluid recovered from the accreted wedge show an increase in Sr^{+2} with distance from the toe (Figure 2). These data suggest an incremental contribution of fluids from the deep accreted sequences resulting from a progressive arcward increase in pore pressure [*Bekins et al.*, 1995; *Saffer and Bekins*, 1998]. Strontium concentration is also modified by carbonate diagenesis within the sediments, which is the likely cause for concentrations lower than in seawater at Site 889 [*Kastner et al.*, 1995]. Details of the strontium isotope fractionation and inferred fluid-rock interactions within the drilled sequences are discussed elsewhere [*Kastner et al.*, 1995; B. Teichert, unpublished data, 2004]. Here we use the $^{87}Sr/^{86}Sr$ ratio of pore water samples collected within the accreted mélange to show that these fluids all have a deep-sourced component, which has been influenced by isotopic
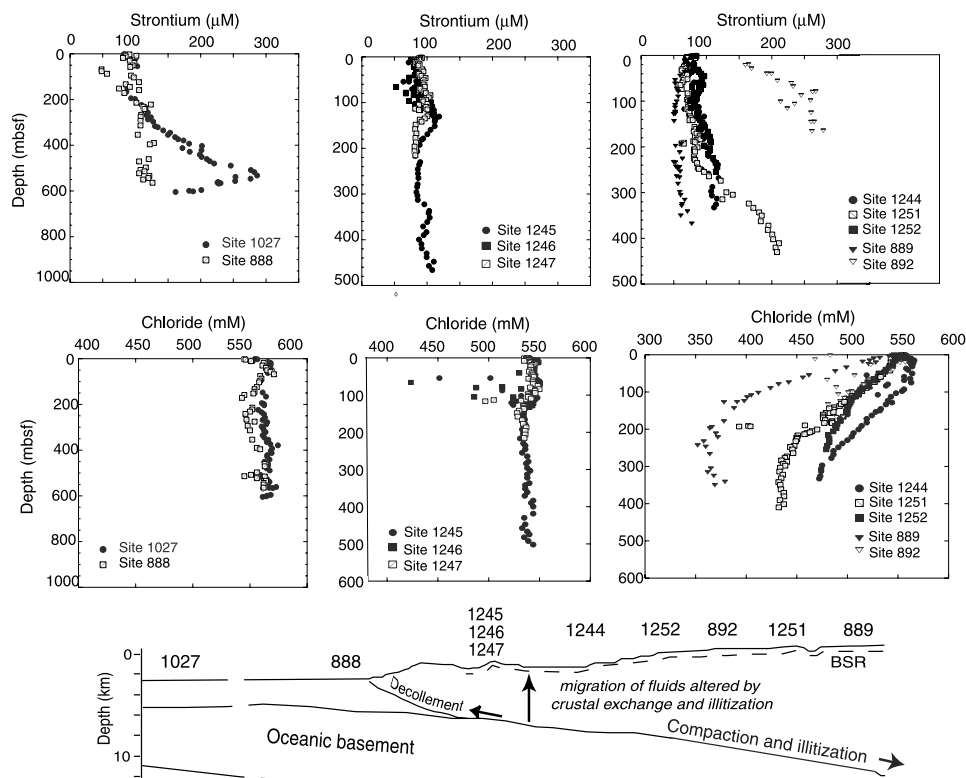

Figure 2. Dissolved Cl^- and Sr^{+2} concentrations at sites drilled on the Cascadia margin. The bottom panel illustrates the location of the sites relative to a schematic transect arcward from the incoming plate, but the relative site locations are not to scale. The depth to the accreted mélange and BSR, and distance to the prism toe are listed in Table 1.

Table 1. Depth to Basement, Accreted Melange, BSR and Sediment Penetration in Meters Below Seafloor. Distance to the prism toe in kilometers ±1.

Site	Basement	Melange	BSR	Penetration	Distance to Prism Toe
1027	608	not present	not present	608	
888	850	not present	not present	566	
1245		470	134	540	12.5
1246		280	114	180	13.5
1247			121	270	12.5
1244		240	124	380	15.0
1252		115		260	17.0
892		∼70	74	178	18.0
1251		300	193	445	19.0
889		160	225	386	20.0

exchange with oceanic crust (Figure 3a). The Mg/Sr ratio of mélange fluids is consistent with a two-end mixing curve between seawater and basal fluids (Figure 3b). These data provide geochemical support to hydrological models of the Cascadia margin, which show that flow here is predominantly driven by compaction of the accreted sediments as they are subjected to increased burial [*Saffer and Bekins*, 1998].

3. Fluid Freshening in Accretionary Margins

[7] Coincident with the Sr^{+2} increase due to crustal exchange reactions, there is an eastward decrease in the dissolved Cl^- content of the mélange fluids (Figure 2). Fluids sampled west of the deformation front at Sites 888 and 1027 reflect Cl^- variations that correlate with contemporaneous seawater changes [*Kastner et al.*, 1995; *Elderfield et al.*, 1999]. Similarly, Sites 1245, 1246 and 1247, which were drilled less than 14 km away from the prism toe, do not show significant freshening with depth. East of these sites the dissolved Cl^- in the mélange decreases markedly to values as low as 440 mM at Site 1251 located at ∼19 km from the toe (Table 1). The Cl^- decrease is even more pronounced at Site 889, on northern Hydrate Ridge, where mélange fluids have a Cl^- concentration of 350 mM [*Kastner et al.*, 1995; *Tréhu et al.*, 2003].

[8] The pattern of enhanced deep freshening in the Cascadia margin is consistent with progressive illitization with distance from the toe (Figure 3c). This mechanism is analogous to that modeled by *Bekins et al.* [1994] for the Barbados margin. They showed that fresh water release due to illitization increases arcward as the subducted sediment is exposed to higher temperatures for increasingly longer times.

4. Gas Hydrate Concentration Based on Dissolved Chloride Data

[9] Drilling in hydrate-bearing slope sediment of the Middle America margin, generated a data set that shows pervasive fluid freshening with depth, which has been interpreted to be a diagnostic pattern for gas hydrate presence [*Hesse*, 2003]. The freshening effect is most pronounced at Sites 497, 498 [*Harrison and Curiale*, 1982] and 568 [*Hesse et al.*, 1985] drilled more than 40 km landward from the trench axis during Deep Sea Drilling Program Legs 67 and 84. Is this effect due to gas hydrate dissociation or clay dehydration?

[10] A smooth decrease in Cl^- with depth is observed in Cascadia at Sites 889, 892, 1244, 1251, 1252, but not at Sites 1245 to 1247 (Figure 2). Because of Cascadia's low geothermal gradient, and the drilling strategy used on Hydrate Ridge, we now have a unique data set with which to test the reliability of the "diagnostic" Cl^- pattern for gas hydrate abundance.

[11] The gas hydrate content at sites drilled on southern Hydrate Ridge (Figure 1c) was estimated by integrating data from pressure core samples, discrete Cl^- anomalies, and continuous infrared imaging of cores [*Tréhu et al.*, 2004; *Milkov et al.*, 2004]. These data show that gas hydrate content is independent of the magnitude of the overall pore water freshening with depth, and is only apparent as discrete excursions to low values that overlay the overall Cl^- distribution above the bottom simulating reflector (BSR, Table 1). For example, Sites 1244 and 1245 both have very similar hydrate contents, averaging 2–4% within GHSZ, but have very different dissolved Cl^- profiles. Site 1252 bears very little hydrate, but the trend to low Cl^- values at depth is well defined at this site (Figure 2).

[12] Site 889, drilled offshore Vancouver during Leg 146, has the most marked decrease in the dissolved Cl^- content of all sites in the Cascadia margin. We believe that this decrease is due to illitization and fluid migration from the deep accreted sequences. Such a mechanism was originally recognized as a possible explanation for fluid freshening at this site [*Westbrook et al.*, 1994]. However, a more recent interpretation of these data assume that the observed Cl^- decrease with depth is due entirely to gas hydrate dissociation, yielding gas hydrate estimates of 25–30% [*Hyndman et al.*, 2001]. *Ussler and Paull* [2001] show that when estimates are based on the magnitude of discrete deviations from a smoothly decreasing Cl^- baseline, gas hydrate at Site 889 appears to be concentrated in discrete layers that contain 2–5% gas hydrate. We concur with the lower estimate based on our postulate that the trend to low Cl^-
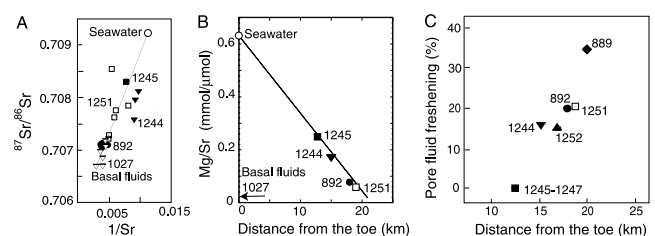

Figure 3. a. Mixing relationship between $^{87}Sr/^{86}Sr$ ratios and the 1/Sr concentration of mélange fluids in the Cascadia prism (samples deeper than mélange depth, Table 1) points to an end member enriched in dissolved strontium with the non-radiogenic isotope ratio of the basal fluids sampled at Site 1027. b. Mg/Sr ratios in mélange fluids show a progressive decrease with distance from the prism toe away from bottom seawater values and towards those measured at the base of Site 1027. b. Increase in pore fluid freshening of mélange samples with distance from the prism toe, consistent with progressive illitization as mélange sequences are exposed to higher temperatures over longer time periods. Data are from *Kastner et al.* [1995], *Elderfield et al.* [1999], *Tréhu et al.* [2003], and B. Teichert (unpublished data, 2004).

values reflects illitization at depth. The lower estimate is also consistent with our calculations of gas hydrate concentration on southern Hydrate Ridge based on multiple proxies [*Tréhu et al.*, 2004].

5. Summary

[13] Mg/Sr ratios and strontium isotope data in fluids sampled within the accreted mélange of Hydrate Ridge reveal a progressively larger component of fluids modified by reaction with the subducting oceanic crust as distance from the prism toe increases. This is likely the result of upward advection of fluids in response to increased pore pressure at depth. Dehydration of smectite as the sediments are transported beneath the accreted mélange releases water to the sediment, which is apparent as a smooth decrease in dissolved Cl^- with depth. Strontium data reveal that the lack of freshening at Sites 1245, 1246 and 1247 is not due to an absence of deep fluids at this site. Rather, it delineates the easternmost location at which no significant clay dehydration has occurred. Site 1244, drilled 2.5 km east of Site 1245, shows a measurable freshening effect, which gets more pronounced with distance from the toe.

[14] Data generated by drilling along an east-west transect in the southern Hydrate Ridge region allowed us to separate the effects of clay dehydration reactions from those of gas hydrate dissociation on the dissolved Cl^- distribution. Whereas discrete negative anomalies within the GHSZ are indeed the result of gas hydrate dissociation during core recovery (Figure 2), the smooth decrease with depth is independent of gas hydrate processes, and instead reflects the degree of illitization at depth. These results indicate that the smooth decrease with depth, commonly observed at sites drilled over accreted mélanges, should not be used to estimate gas hydrate abundance.

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