Fluids in Convergent Margins: What do We Know about their Composition, Origin, Role in Diagenesis and Importance for Oceanic Chemical Fluxes?

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Fluids in convergent margins: what do we know about their composition, origin, role in diagenesis and importance for oceanic chemical fluxes?

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The nature and origin of fluids in convergent margins can be inferred from geochemical and isotopic studies of the venting and pore fluids, and is attempted here for the Barbados Ridge, Nankai Trough and the convergent margin off Peru. Venting and pore fluids with lower than seawater Cl^- concentrations characterize all these margins. Fluids have two types of source: internal and external. The three most important internal sources are: (1) porosity reduction; (2) diagenetic and metamorphic dehydration; and (3) the breakdown of hydrous minerals. Gas hydrate formation and dissociation, authigenesis of hydrous minerals and the alteration of volcanic ash and/or the upper oceanic crust lead to a redistribution of the internal fluids and gases in vertical and lateral directions. The maximum amount of expelled water calculated can be *ca.* 7 $m^3\,a^{-1}\,m^{-1}$, which is much less than the tens to more than 100 $m^3\,a^{-1}\,m^{-1}$ of fluid expulsion which has been observed. The difference between these figures must be attributed to external fluid sources, mainly by transport of meteoric water enhanced by mixing with seawater.

The most important diagenetic reactions which modify the fluid compositions, and concurrently the physical and even the thermal properties of the solids through which they flow are: (1) carbonate recrystallization, and more importantly precipitation; (2) bacterial and thermal degradation of organic matter; (3) formation and dissociation of gas hydrates; (4) dehydration and transformation of hydrous minerals, especially of clay minerals and opal-A; and (5) alteration, principally zeolitization and clay mineral formation, of volcanic ash and the upper oceanic crust.

1. Introduction

Fluids play a central role in the deformational, thermal and geochemical evolutions of active convergent plate margins (von Huene 1984). Here, considerable fluid–solid diagenetic and metamorphic reactions take place and significant fluid volumes are expelled which may play an important role in global geochemical budgets. The most important internal fluid sources are: (1) pore fluids of the sediment and oceanic crust, present at all depths, and expelled by porosity reduction processes (Carson 1977; Bray & Karig 1985; Fowler *et al.* 1985; Bangs *et al.* 1990; Davis *et al.* 1990); (2) fluids derived from diagenetic and metamorphic dehydration; and (3) fluids from breakdown reactions of hydrous minerals. Additional sources are decarbonation of calcareous phases, and biogenic or thermogenic decomposition of organic matter

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(Powers 1967; Perry & Hower 1972; Claypool & Kaplan 1974; Kastner *et al.* 1990; Peacock 1990; Vrolijk *et al.* 1990; Taira *et al.* 1991).

The most important external fluid sources probably are meteoric water transport and seawater mixing through seismic pumping or density inversion induced convection (Kastner *et al.* 1990; Le Pichon *et al.* 1990*a*, *b*). Widespread venting, supporting extensive benthic biological communities (Kulm *et al.* 1986; Boulegue *et al.* 1987), mud volcanoes and diapirs, carbonate chimneys (Westbrook & Smith 1983; Ritger *et al.* 1987; Brown & Westbrook 1988; Langseth *et al.* 1988; Carson *et al.* 1990) and heat flow anomalies (Fisher & Hounslow 1990; Foucher *et al.* 1990) are the important direct manifestations of localized fluid expulsion in accretionary complexes and seaward of the deformation front. In addition, indirect information about both localized and dispersed fluid expulsion is provided by means of seismic studies, e.g. of arcward thinning of the underthrusted sediments (Bray & Karig 1985; Fowler *et al.* 1985; Bangs *et al.* 1990), mineralized veins, carbonate crusts and cements (Kemp 1990; Lindsley-Griffin *et al.* 1990; Kulm *et al.* 1990; Sample 1990; Vrolijk 1987), and the presence of thermogenic methane at shallow depths, such as in the Barbados Ridge decollement (Vrolijk *et al.* 1990).

One of the striking observations central to the problem of the role of fluids in convergent plate margins is the marked discrepancy between the fluid flow rates of tens to over 100 m a^{-1}, obtained at some of the sites of localized fluid discharge or deduced from heat flow measurements, and the calculated maximum rates of fluid discharge, of the order of millimetres per year, assuming steady-state compactive dewatering (Carson *et al.* 1990; Foucher *et al.* 1990; Le Pichon *et al.* 1990*a*, *b*). Even the addition of all other internal fluid sources, particularly from hydrous minerals dehydration and/or breakdown reactions, does not significantly diminish this discrepancy. Hence the need to invoke external sources for the observed 'excess' fluid seems inescapable. In the Cascadia accretionary complex, geochemical evidence suggests a shallow source (less than 100–750 MBSF) for this 'excess' fluid (Carson *et al.* 1990). Discerning fluid sources and budgets, even in such complex systems where original geochemical and isotopic characteristics are modified by fluid–solid exchange reactions and pervasive fluid mixing, hence decoupling of signatures, should be possible with a proper mix of geochemical and isotopic tracers.

2. Background of Barbados, Nankai and Peru convergent margin sites

The summaries of the main geophysical, sedimentological and of some geochemical features, characterizing each of these margins, provided in tables 1 and 2, clearly indicate their large diversity. Notwithstanding, surface manifestations of fluid venting exist at each. In the Nankai Trough, however, they seem to be confined to the eastern, and not to the western region that was drilled. The drill sites at these margins are marked in figure 1. At the Barbados Ridge, Ocean Drilling Project (ODP) Site 671 is located *ca.* 4 km arcward of the toe of the accretionary complex. The decollement was penetrated at *ca.* 500 MBSF and comprises a zone *ca.* 40 m thick (Moore *et al.* 1988). At the western Nankai Trough, ODP Site 808 was penetrated through the accretionary prism, frontal thrust and decollement to basaltic basement. The decollement was encountered at *ca.* 960 MBSF and it comprises a zone *ca.* 20 m thick (Taira *et al.* 1991). In the Peru margin Sites 685 and 688, the sites closest to the trench were chosen because their pore fluid isotopic composition suggests the presence of two distinct fluid régimes in this margin. Site 685 (*ca.* 9° S) is the only

Table 1. *Comparison of data for the Barbados, Nankai and Peru subduction zones*

	Barbados	Nankai	Peru
age of subducting plate/Ma	*ca.* 90	*ca.* 15–17	*ca.* 30 north of 10° S *ca.* 40 south of 10° S
convergence rate/ (mm a^{-1})	slow, *ca.* 20	slow, *ca.* 25	fast, *ca.* 90
geothermal gradient/ (°C km^{-1})	28 at site 674, at 92–434 mbsf[a] 36 at Site 671, at 36–168 mbsf	*ca.* 110 at Site 808[b]	47–50 at four sites[c] (683, 685, 682, 688)
sediment type	fine-grained hemipelagic clays and muds	ashy silt-sand turbidites hemipelagic muds	organic-rich diatomaceous muds and silts
organic C content (%)	<0.2	0.1–0.6	3–4
fate of incoming sediments	much accreted, some subducted or subcreted	much accreted, some subducted or subcreted	much subducted or subcreted, some accreted
manifestations of venting			
(*a*) at sites drilled	mineralized veins and faults	none[b]	mineralized veins; fluid escape structures[d]
(*b*) in and seaward of the accretionary complex	thermal regime, mud volcanoes and diapirs[e]	benthic communities, thermal régime, carbonate cements and chimneys and mud volcanoes[b]	dredged clams[f]
gas hydrates	no seismic evidence for bsr, but indirect geochemical evidence for possible presence of gas hydrates in region drilled; further south present at 600–800 mbsf[g]	present; bsr is very shallow, at *ca.* 200 mbsf[b]	ubiquitous, bsr at *ca.* 470 mbsf near site 682 to *ca.* 610 mbsf near site 688[h]

[a] Fisher & Hounslow 1990. [b] Taira *et al.* 1991. [c] Yamano & Uyeda 1990. [d] Kemp 1990; Lindsley-Griffin *et al.* 1990. [e] Langseth *et al.* 1988; Foucher *et al.* 1990; Le Pichon *et al.* 1990*b*. [f] Kulm *et al.* 1986. [g] Bangs *et al.* 1990; Gieskes *et al.* 1990. [h] Kvenvolden & Kastner 1990.

accretionary complex site drilled, and Site 688 (*ca.* 11° S) exhibits non-steady state geochemical profiles, resembling those obtained at the Barbados Ridge Site 671 (Suess *et al.* 1988; Elderfield *et al.* 1990; Kastner *et al.* 1990).

3. The chloride problem

Despite the large disparity in the overall geologic characteristics of these convergent margins, the majority of the interstitial and discharged fluids analysed to date are characterized by lower than seawater chloride concentrations. Lower than seawater Cl^- pore fluids are ubiquitous in convergent margin sediments; seawater Cl^- dilutions of 10 to over 50 % have been reported. The lowest Cl^- values, shown in figures 2 and 3, are given in table 3. Another conspicuous characteristic of most Cl^- depth profiles, illustrated in figure 2, is their distinctly non-steady-state nature. Many of the Cl^- minima are situated at unconformities, faults, particularly

Table 2. *Synthesis of characteristics of pore fluid* Cl^-, $\delta^{18}O$ *and* $^{87}Sr/^{86}Sr$ *depth profiles for the Barbados, Nankai and Peru accretionary complexes*

	Barbados Ridge site 671	Nankai Trough site 808	Peru Margin site 688	Peru Margin site 685
Cl^- concentrations	decrease with depth; non-steady-state profile	increase in the trench-fill turbidite section; then decrease toward decollement; below, increase again toward oceanic basement	decrease with depth; non-steady-state profile	decrease with depth
$\delta^{18}O$ values	decrease with depth; non-steady-state profile	not available	decrease with depth; non-steady-state profile	decrease with depth; non-steady-state profile
$^{87}Sr/^{86}Sr$ ratios	non-steady-state profile	decrease with depth to 'proto-decollement', then increase at decollement	decrease with depth	more radiogenic than seawater; non-steady-state depth profile
	Cl^- and $^{87}Sr/^{86}Sr$ depth profiles may be coupled Cl^- and $\delta^{18}O$ depth profiles are decoupled	Cl^- and $^{87}Sr/^{86}Sr$ depth profiles are decoupled	Cl^- and $^{87}Sr/^{86}Sr$ depth profiles are decoupled the profiles of $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ appear to be coupled at depths >300 m	Cl^- and $^{87}Sr/^{86}Sr$ depth profiles are decoupled the profiles of $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ appear to be coupled, inversely correlated, at depths >80 m

in the decollement, and are associated with methane and other geochemical and isotopic anomalies as summarized in table 4 (Gieskes *et al.* 1990; Kvenvolden & Kastner 1990; Kastner *et al.* 1990; Le Pichon *et al.* 1990*a*; Taira *et al.* 1991). Some are also associated with thermal anomalies (Fisher & Hounslow 1990; Foucher *et al.* 1990). The occurrence of anomalies at high permeability horizons, at lithological and structural discontinuities, and the coincidence of the geochemical and thermal minima and maxima, indicate lateral fluid flow. Diffusion–advection calculations imply that the important Cl^- minima horizons at Sites 671, 672, 674, 683, and 688 (figure 2) cannot be older than several to tens of thousands of years. For fluid flow along the decollement horizon at Site 671, Barbados Ridge, a thermal model by Fisher & Hounslow (1990) suggests fluid flow velocity of 10^{-7} m s^{-1}. Because this velocity is 100 times faster than predicted by steady-state models, they concluded that fluid flow is transient. The question of transient against steady-state fluid flow in convergent margins directly hinges upon the major problem of the large disparity between observed rates of fluid discharge and those calculated, assuming steady-state flow. Preliminary modelling of the Cl^- concentrations depth profile at Site 808, western Nankai Trough (figure 2*b*) supports transient fluid flow also along this decollement zone. Simple diffusion–advection calculations suggest that a pulse of low

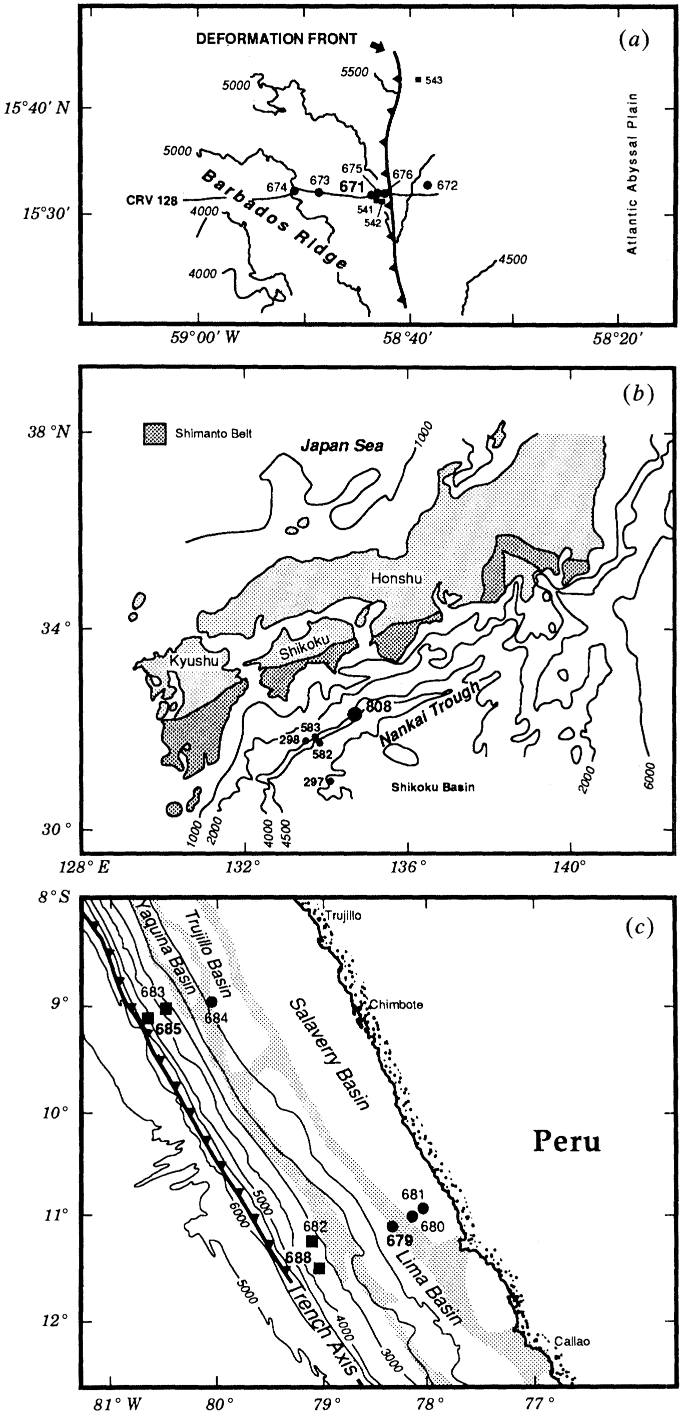

Figure 1. Schematic maps of study areas. Bathymetry is in metres. Closed circles and squares identify sites drilled. Bold numbers designate sites emphasized in this study. (*a*) At the Barbados Ridge, CVR-128 is a multichannel seismic line. (Modified from Moore *et al.* 1988.) (*b*) At the Nankai Trough. (Modified from Leg 131 ODP preliminary report no. 31, 1990, Ocean Drilling Program.) (*c*) At the Peru margin. (Modified from Kastner *et al.* 1990.)

Table 3. *The lowest* Cl^- *values as shown in figures 2 and 3*

location	Cl^-/mM	approx. dilution of seawater (%)	reference
Barbados Ridge, site 671, at decollement	505	10	Gieskes *et al.* (1990)
Barbados Ridge, site 674, 17 km arcward from deformation front, at 448 mbsf	394	30	Gieskes *et al.* (1990)
Mud Pie, 12 km seaward of Barbados accretionary complex	250	55	Le Pichon *et al.* (1990*a*)
Nankai Trough, site 808, at 1110 mbsf	447	20	Taira *et al.* (1991); Gamo *et al.* (1991); Gieskes *et al.* (1991); Kastner *et al.* (1991)
Peru Margin, site 683, at 452 mbsf	454	20	Kastner *et al.* (1990)
Peru Margin, site 688, at Plio-Pleistocene unconformity at 365 mbsf	471	16	Kastner *et al.* (1990)
Peru Margin, site 679 at eastern edge of mid-to-upper slope, Lima Basin, 320 mbsf	339	40	Kastner *et al.* (1990)

Cl^- fluid along the decollement, may have occurred over 3×10^5 years ago. This is the minimum time needed to establish the long, greater than 250 m, diffusion profile observed (between 820 and 560 mbsf) in figure 2*b* (Gieskes *et al.* 1990; Gamo *et al.* 1991; Kastner *et al.* 1991; Taira *et al.* 1991).

It is worthwhile noting that, except for the high Cl^- fluids in the forearc basins of the Peru margin (Kastner *et al.* 1990), in the trench-fill turbidites at Nankai (Taira *et al.* 1991) and in Vanuatu, fluids with significantly higher than seawater Cl^- concentrations, widespread in fluid inclusions within mineralized veins (Vrolijk 1987), have not been encountered in accretionary complex sediment pore fluids as yet. Even these fluids are not as concentrated as observed in many fluid inclusions.

The origin of the ubiquitous low-Cl^- fluids is of great importance to the understanding of the hydrogeochemistry of convergent margins. The migration of fluids expelled by tectonic compaction, by porosity reduction processes, could not be the source for the low-Cl^-, methane-rich, fluids that are discharging at the sea floor and supporting prolific benthic communities (Kulm *et al.* 1986, 1990; Boulègue *et al.* 1987; Ritger *et al.* 1987; Carson *et al.* 1990; Le Pichon *et al.* 1990*b*) unless they are modified by mixing with a more dilute fluid. The possible internal processes that may provide H_2O for the formation of the low-Cl^- fluids are: (1) dehydration or breakdown of hydrous minerals, particularly of clay minerals and opal-A; (2) dissociation of primarily methane gas hydrates (clathrates); (3) clay membrane ion filtration. Similarly, the possible sources for the associated elevated methane concentrations are: (1) biogenic or thermogenic combustion of organic matter; (2) gas hydrates dissociation; (3) decarbonation reactions plus CO_2 reduction.

The most important diagenetic dehydration reactions, the stepwise dehydration of smectite and its transformation to illite, are dependent on temperature, pore pressure and precursor composition, as well as on the availability of K^+ and Al^{3+} from other phases and on the disposability of silica by quartz precipitation, for example as a cement, or by transport in solution away from the reaction site, as indicated in the following reaction:

$$\text{smectite} + K^+ + Al^{3+} = \text{illite} + \text{silica} + H_2O$$

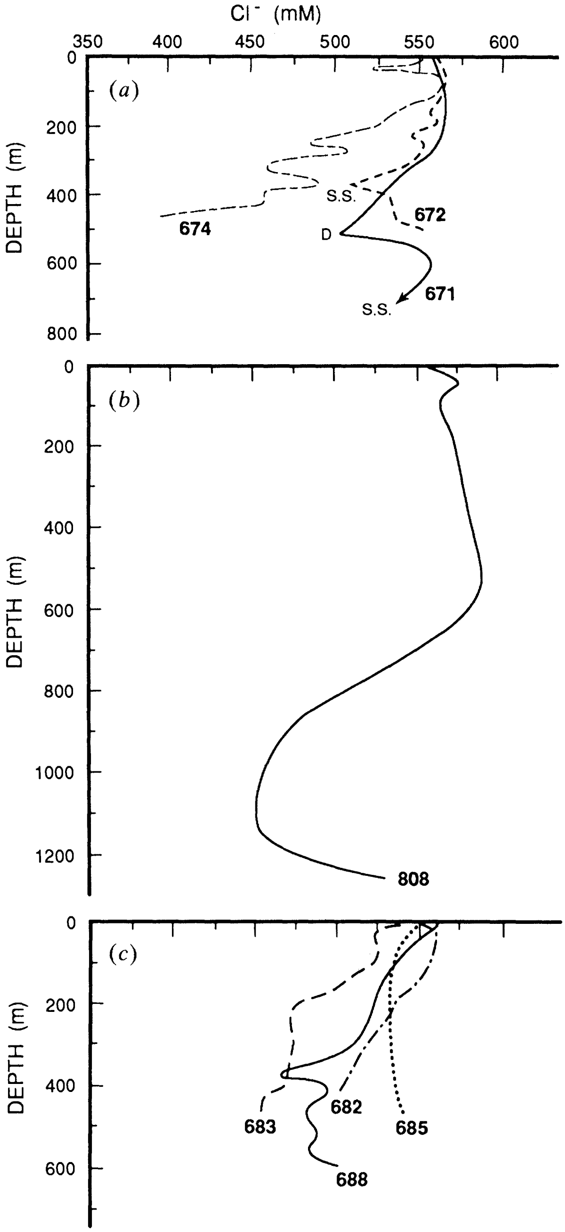

Figure 2. Depth profiles of chloride concentrations in pore fluids from the (*a*) Barbados Ridge Sites 671, 672, 674 (data from Gieskes *et al.* 1990); (*b*) Nankai Trough Site 808 (data from Taira, Hill *et al.* 1991); (*c*) Peru margin Sites 682, 683, 685, 688 (data from Kastner *et al.* 1990).

(Powers 1967; Perry & Hower 1972).

The optimal temperature range for this reaction is *ca.* 60–160 °C. These margins have geothermal gradients ranging from over 30° to 110 °C km^{-1} which correspond to a depth range of 550 m to several kilometres. Therefore, the non-steady-state features of the Cl^- pore fluid profiles observed at shallower than 550 m depth in the Barbados and Peru margins (figure 2) cannot be formed in this way and must either

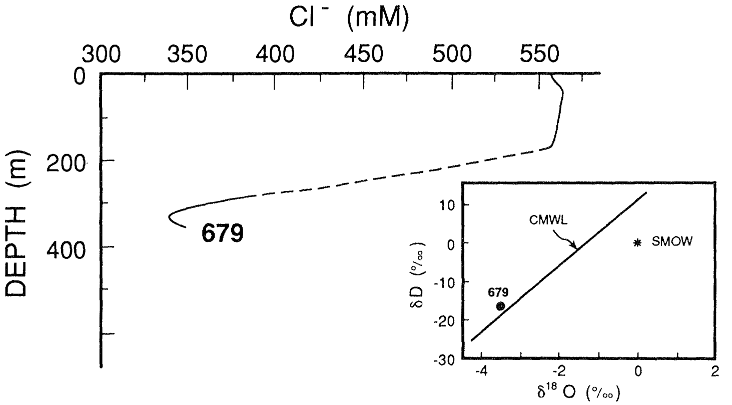

Figure 3. Depth profile of chloride concentrations in pore fluids from the Peru Margin Site 679 (data from Kastner *et al.* 1990) and a plot of the $\delta^{18}O$ and δD values of the Cl minimum fluid (339 mM) at 320 MBSF.

Table 4. *Chemical and isotopic shifts at the Barbados Ridge and Nankai Trough decollements and at the Plio-Pleistocene unconformity at* ODP *Site 688, Peru Margin*

	Barbados[a] at decollement, ODP Site 671	Nankai[b] at decollement, ODP Site 808	Peru[c] at distinct Cl^- minimum spike, ODP Site 688
Cl^-	decreases	decreases	decreases
$^{87}Sr/^{86}Sr$	decreases	increases (or no change ?)	no change
Sr^{2+}	decreases	increases	decreases
$\delta^{18}O$	increases	not available	decreases
CH_4	increases	decreases	increases
silica	increases	increases	increases
Ca^{2+}	decreases	decreases	decreases
Mg^{2+}/Ca^{2+}	increases	no change	increases

[a] Gieskes *et al.* (1990); Vrolijk *et al.* (1990).
[b] Leg 131 Shipboard Scientific Party (1990).
[c] Kastner *et al.* (1990); Elderfield *et al.* (1990).

originate from a different low Cl^- local source or be advected and/or laterally transported from other regions. Volatiles, mainly H_2O, CO_2 and CH_4 from the breakdown of clay minerals and organic matter in the subducting sediments and from hydrous silicates in the altered downgoing oceanic slab, must be migrating up and returned to the surface (Ernst 1990; Peacock 1990). Advective and/or lateral fluid flow is similarly supported by the opal-A dehydration and transformation to quartz reactions, which occur between about 30 and 40 and 80 and 100 °C (Keene 1975; Hein *et al.* 1978; Kastner 1981).

The common observation that pore fluids become progressively dilute with depth has been attributed largely to sampling artefacts or to drilling-induced pressure release that causes gas hydrate dissociation (Hesse & Harrison 1981). Indeed, gas hydrates are widespread in this environment as shown by the presence of a bottom simulating reflector (BSR) which delineates the base of the gas hydrate stability field (Kvenvolden & McMenamin 1980). Their dissociation would release both fresh water

Table 5. *Changes in oxygen and hydrogen isotopic compositions resulting from fluid–rock interactions*[a]

reaction	pore fluid isotopic shifts $\delta^{18}O$	 δD
oceanic basalt alteration		
(*a*) at <200 °C, low water/rock	−	+
(*b*) at >200 °C, low water/rock	+	+
hydration reactions	−	+
dehydration reactions	+	−
hydrous minerals recrystallization		
(*a*) lower temperature than precursor	−	+
(*b*) higher temperature than precursor	+	− or +[b]
clay minerals authigenesis	−	+
clay membrane ion filtration		
(*a*) filtrate	−	−
(*b*) residual fluid	+	+
meteoric water mixing	−	−
gas hydrate		
(*a*) formation	−	−
(*b*) dissociation	+	+
fluid–gas exchange reactions, with		
(*a*) CO_2	−	
(*b*) H_2S		+

[a] The table was compiled mainly from the following references: Savin & Epstein (1970); Coplen & Hanshaw (1973); Schoell (1980); Yeh (1980); Hesse & Harrison (1981); Phillips & Bentley (1987); Kvenvolden & Kastner (1990); Peacock (1990).

[b] Depending on temperature of recrystallization.

and methane. At the Peru margin, methane gas hydrates are ubiquitous and the methane source is mostly biogenic (Kvenvolden & Kastner 1990). The calculated depths of the BSRs, of 612 MBSF at Site 685 and 473 MBSF at Site 688, suggest that except for the deepest portion of the Cl^- profile at Site 688, gas hydrate dissociation could account for most of the pore fluids' Cl^- dilution seen in the figure 2*c* depth profiles. However, gas hydrates have not been observed at the Barbados drill sites nor has a BSR been identified in their vicinity although gas hydrates exist at a distance southward of the drilling region. At Site 671, the calculated BSR is at *ca*. 500 MBSF (R. Hyndman, personal communication). As seen in figure 2, low Cl^- fluids also exist below this depth and the $\delta^{13}C$ value of the methane in and below the decollement indicates a thermogenic source, implying advection from greater depths (Vrolijk *et al*. 1990). Similarly, in the Nankai Trough, at Site 808, where gas hydrates were recovered, the calculated BSR is at a considerably shallower depth, of just *ca*. 200 MBSF, than the depth range of the low Cl^- pore fluids, shown in figure 2*b* (Taira *et al*. 1991). Several additional geochemical tracers, such as oxygen and hydrogen isotopes of the pore fluids, are needed to establish the quantitative importance of gas hydrates as sources of low Cl^- fluids. The oxygen isotope profiles of figure 4*c* do not support a sole gas hydrate dissociation source, as indicated in table 5 (Hesse & Harrison 1981; Kvenvolden & Kastner 1990).

As yet the quantitative importance of the clay membrane ion filtration process in thick clay-rich sediments, originally suggested by Coplen & Hanshaw (1973), has not been evaluated. Experimental work (Haydon & Graf 1986; Phillips & Bentley 1987) indicates that the efficiency of the process is greatly pressure dependent, suggesting that in the compressional régimes of active convergent margins clay membrane ion filtration may be a more important process of low Cl^- fluid production than previously assumed.

It is important to note that the residual fluids, produced by two of the above low Cl^- fluid production processes (gas hydrate formation and clay membrane ion filtration) are 'brines', fluids of high solute concentrations and of high density. In addition, $CaCl_2$ brines form from volcanic ash and upper oceanic crust hydration reactions. Because the quantitative importance of these three processes to the overall fluid budgets in convergent margins is as yet unknown, it seems premature to evaluate the role of the residual brines in the overall hydrogeochemistry of this environment.

4. Fluid budgets

The budget of H_2O will be considered further here, the important internal sources of H_2O being: (1) porosity reduction, and (2) mineral dehydration and breakdown reactions.

Source 1. *Loss of water by porosity reduction.* If a 15% porosity reduction from 50 to 35% is assumed, in accordance with the porosity loss in the subducted sediments of the Nankai Trough (Bray & Karig 1985), 2.3×10^8 m^3 H_2O would be expelled from 1 km^3 sediment, or 230 m^3 H_2O m^{-2}. The length of time over which this water is expelled differs at various margins. Assuming a 2 cm a^{-1} subduction rate, and expulsion of water along the toe of the accretionary complex, the expected production of H_2O is 4.6 m^3 a^{-1} m^{-1} (m^3 per year per metre length of decollement or other tectonic features); 4.6 m^3 H_2O a^{-1} m^{-1} would be expelled to the ocean. At a faster subduction rate, of 5 cm a^{-1}, 11.5 m^3 H_2O a^{-1} m^{-1} would be expelled.

A similar calculation for 20% porosity reduction from 55 to 35% would produce 360 m^3 m^{-2} from 1 km^3 of sediment which translates to 7.2 m^3 H_2O a^{-1} m^{-1} for a subduction rate of 2 cm a^{-1}, and 18 m^3 H_2O a^{-1} m^{-1} for a subduction rate of 5 cm a^{-1}.

Source 2. *Mineral dehydration and breakdown reactions.* Complete dehydration of a low porosity (30%) smectite-rich (20 wt%) sediment, with 15 wt% interlayer water in the smectite ($\rho = 2.5$ g cm^{-3}), would produce 2.1×10^7 m^3 H_2O from 1 km^3 sediment equal to 2.1×10^{10} kg H_2O. An equivalent volume of H_2O would also be produced from a same low porosity (30%) but opal-A rich (30 wt%) sediment, with 10% water in the opal-A. This is an order of magnitude less than the 2.3×10^{11} kg H_2O produced from source 1. At a subduction rate of 2 cm a^{-1}, 4.2×10^2 kg H_2O a^{-1} could be expelled to the ocean. The complete breakdown of the smectite to an anhydrous phase would provide an additional 0.7×10^{10} kg H_2O. In addition, based on data from the ODP on upper oceanic crust alteration and its porosity in the uppermost 1 km (Alt *et al.* 1986; Becker *et al.* 1989), a conservative value of 3 wt% volatiles, all H_2O, is assumed instead of the 2 wt% assumed by Peacock (1990). Thus a 1 km^3 oceanic crust ($\rho = 3$ g cm^{-3}) which contains 9×10^7 m^3 H_2O could provide 9×10^{10} kg H_2O, the same order of magnitude as from smectite dehydration. At a subduction rate of 2 cm a^{-1}, 1.8 m^3 H_2O a^{-1} m^{-1} could be expelled from an oceanic crust column of 0.02 m × 1 m × 1000 m. Similar calculations for a 5 m a^{-1} subduction rate would provide 4.5 m^3 H_2O a^{-1} m^{-1}.

These calculations demonstrate that expulsion of water by porosity reduction is the most important internal source of volatiles in accretionary complexes. Complete smectite dehydration and oceanic crust dehydration provide an order of magnitude less volatiles.

Fluid discharge velocities of tens to over 100 $m^3\ a^{-1}\ m^{-1}$ in the eastern Nankai Trough, Barbados Ridge and Cascadia (Carson *et al.* 1990; Foucher *et al.* 1990; Le Pichon *et al.* 1990*b*) are one to two orders of magnitude greater than possible from the above internal fluid sources. Because dispersed flow is pervasive, particularly in clastic-sediment dominated margins, as manifested by the widespread occurrence of carbonate cements in Cascadia (Carson *et al.* 1990; Sample 1990), or implied by the absence of localized flow in the western Nankai Trough, Site 808 (Gieskes *et al.* 1990; Taira *et al.* 1990), this discrepancy is even larger. Localized discharge of fluids derived from large regions by non-steady-state, transient fluid flow or by the addition of large volumes of fluids from external sources, as suggested by Le Pichon *et al.* (1990*b*), of which the most important is meteoric water, may partly explain this major discrepancy. However, hydrologic flow tends to be shallow, mostly above 1 km (Cathles 1990). The only rather clear case of long distance lateral migration of meteoric water in convergent margins is the extreme low Cl^- fluid observed at Site 679, Peru margin (figure 3). This site is, however, situated at just *ca.* 450 m water depth, and the Andes could have easily provided the required head. The oxygen and hydrogen isotopes of this low Cl^- fluid suggest a meteoric water source. The slight shift from the meteoric water line must have been caused by water–gas exchange reactions indicated in table 5. Another interesting possible solution to the problem of disparity between observed fluid fluxes and the internally available fluid, suggested by Le Pichon *et al.* (1990*b*), is seawater mixing with a low-Cl^- fluid by seismic pumping or density inversion induced convection.

5. A hypothesis on the origin of the fluids

In addition to the differences in the Cl^- concentration depth profiles discussed already, the most distinctive features seen in the chemical and isotopic pore fluid profiles of figure 4 are: (1) the low methane concentrations in the Barbados and Nankai margins and the very high concentration in the Peru margin. This difference positively correlates with the organic C contents given in table 1; (2) the positive methane anomalies both at the Barbados decollement horizon and at the Cl^- minimum horizons of Peru Site 688, and the small negative anomaly at the Nankai decollement horizon; (3) a non-radiogenic low Sr concentration source, probably oceanic crust, associated with both the Barbados decollement and the distinct Cl^- minimum at Site 688, horizons, and a radiogenic and high Sr concentration source, most probably from clay minerals dehydration, transformation and/or breakdown at the decollement horizon at Nankai; and (4) the higher than seawater $^{87}Sr/^{86}Sr$ ratios of the pore fluids at Site 685, Peru margin, indicating linkage with continental crust (Elderfield *et al.* 1990; Kastner *et al.* 1990), and the apparent lack of communication between the pore fluids of adjacent thrust sheets, clearly indicated by the $^{87}Sr/^{86}Sr$ ratios against 1/Sr plot of Site 685 pore fluids (figure 4*c*).

These, plus additional complexities in the pore fluids geochemical and isotopic profiles displayed in figure 4 and summarized in tables 2 and 4, together with the marked disparity between field observations of fluid flow rates at fluid discharge sites and the calculated maximum possible rates of fluid discharge from all internal sources, may be explained by the following working hypothesis.

The central fluid system consists of internally produced fluids, originally pore fluids of seawater origin. The geochemical and isotopic characteristics of this fluid system are determined by dilution through mineral dehydration reactions and by

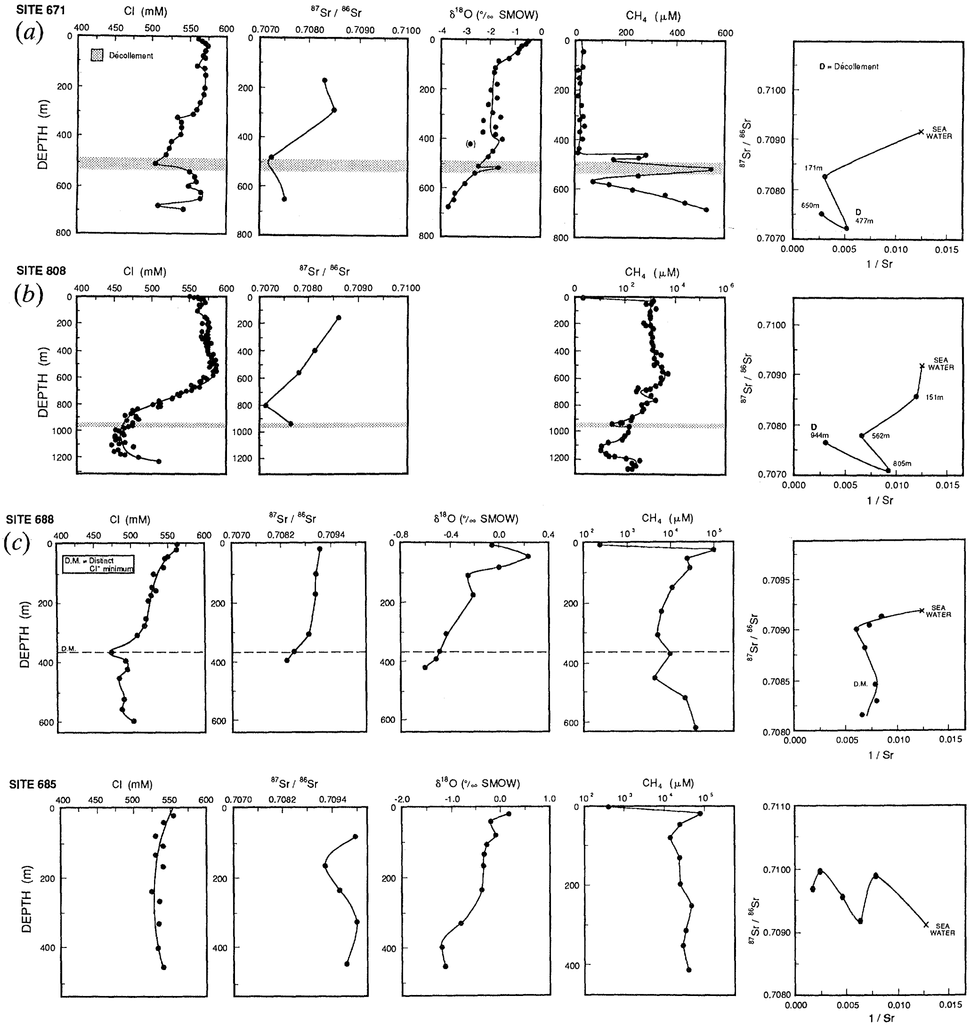

Figure 4. Depth profile of chloride and methane concentrations of ^{87}Sr/^{86}Sr ratios and of δ^{18}O values, and mixing relationships between ^{87}Sr/^{86}Sr ratios and $1/\mathrm{Sr}^{2+}$ concentrations for (*a*) Site 671, Barbados Ridge (data from Gieskes *et al.* 1990; Vrolijk *et al.* 1990); (*b*) Site 808, Nankai Trough (data for Cl^- and CH_4 from Taira *et al.* 1991); (*c*) Sites 688 and 685, Peru margin (data from Kastner *et al.* 1990; Elderfield *et al.* 1990).

fluid–mineral exchange reactions plus diffusion–advection. The central fluid system is modified locally by mixing with fluids from: (1) *external sources*, e.g. meteoric water through short- or long-distance transport and possibly seawater through density inversion induced convection or seismic pumping (Le Pichon *et al.* 1990*b*). These sources may play an important role primarily in the shallower levels, within the uppermost tens to hundreds of metres, of accretionary complexes) and (2) *internal sources*, e.g. from deeper or overpressured regions of the convergent margin, transported vertically and laterally along tectonic and sedimentologic conduits, such as the decollement, faults or sand horizons. These sources may be important at all depths.

The extent of mixing with either source, whether transient or steady state, determines the intensity and nature of the geochemical and isotopic compositions at the minima and maxima horizons, observed in figure 4. The depth profiles between these 'anomalous' horizons are also affected through diffusion–advection. The minima and maxima horizons of figure 4 coincide with decollements, faults, unconformities and zones of high intergranular permeability (Gieskes *et al.* 1990; Kastner *et al.* 1990). They carry key information about the distinctive hydrology at each margin. Thus, to identify the origin of these and similar complex fluids, unique combinations of diagnostic geochemical and isotopic parameters need to be established. Clearly, as indicated in table 5, this cannot be accomplished solely by the oxygen and hydrogen isotopic compositions of the waters.

6. Diagenesis

Diagenetic reactions which are widespread in accretionary complex sediments are intimately involved in the fluid budget and fluid distribution, particularly within the central fluid system. Diagenesis significantly modifies the geochemistry and isotopic composition of the fluids as well as the porosity and permeability of the sediments and, hence, the hydrology of the complex. It also changes the mechanical properties of the sediments and even affects the thermal properties (Carson 1977; Hesse & Harrison 1981; Kulm *et al.* 1986; Ritger *et al.* 1987; Vrolijk 1987; Kastner *et al.* 1990; Kvenvolden & Kastner 1990; Sample 1990). In such rapid sedimentation régimes, diffusional communication with seawater ceases at shallow burial depths, of a maximum a few tens of metres. Therefore, the composition and reactivity of the sediments and fluid flow assume major roles in controlling the availability of solutes and consequently the nature and extent of diagenesis. The important diagenetic reactions are:

I. *Carbonate recrystallization and more importantly precipitation.* The latter reaction, which influences the physical properties of the sediments, is more likely to be limited by the availability of Ca^{2+} and/or Mg^{2+} rather than of bicarbonate, especially in margins of sediments rich in organic matter. The overall vertical distribution of the diagenetic carbonate phases is: calcite (plus Mg-calcite) kinetically precedes dolomite (or ankerite) formation. The rate of dolomite formation markedly increases with depth, with increasing Mg^{2+}/Ca^{2+} (or $Mg^{2+}+Fe^{2+}/Ca^{2+}$) ratios and bicarbonate concentrations and with decreasing sulphate concentrations. At even greater depths, coformation of dolomite and calcite or formation of only calcite may ensue. The formation of the Fe^{2+} and Mn^{2+} carbonates siderite and rhodochrosite, respectively, which depends on the availability of Fe^{2+} and Mn^{2+} relative to Ca^{2+} and Mg^{2+}, is of minor importance in most convergent margin sediments and occurs mostly at intermediate or greater depths. When dissolved (e.g. by organic or other acids) or decomposed via decarbonation, the carbonates become an important source of CO_2.

II. *Bacterial and thermal degradation of organic matter*. This is an important source of the volatiles CO_2 and CH_4 (Claypool & Kaplan 1974) as well as of some H_2O. These and the above mentioned carbonate reactions are interrelated. Furthermore, mainly CH_4, but also CO_2 and other organic volatiles, are essential for gas hydrate formation.

III. *Gas hydrate formation and dissociation.* Occurring within the uppermost 1 km of the sediment section (Kvenvolden & McMenamin 1980), gas hydrates not only modify the chemistry and oxygen and hydrogen isotopic compositions of the pore fluids (Claypool & Kaplan 1974; Hesse & Harrison 1981; Kvenvolden & Kastner 1990) but they also lead to a redistribution of the fluids involved in these reactions, in reducing the porosity and permeability of the host sediments and influencing their thermal properties. Undoubtedly, at least some of the fluids discharging at the seafloor supporting dense benthic communities originate from gas hydrate dissociation (Kulm *et al.* 1986; Boulegue *et al.* 1987; Carson *et al.* 1990). As yet little is understood about the state of the residual 'brine' and its involvement in diagenesis and hydrology of these margins.

IV. *The dehydration and transformation of hydrous minerals, especially of clay minerals and opal-A*. The smectite to illite transformation, is one of the important reactions responsible for the evolution of low Cl^- fluids observed in all the margins studied. The physical properties of the sediments are also altered by this reaction. Based on its optimal temperature range, of *ca.* 60 to 160 °C, and dependent on the geothermal gradient, this reaction may span over a depth interval of several kilometres, starting at a burial depth of greater than 500 m. An important byproduct is dissolved silica, which is a major source of quartz cement (Perry & Hower 1972). The opal-A through opal-CT to quartz dehydration and transformation occurs between over 30 and less than 100 °C (Keene 1975; Kastner 1981) and may also, as with the clay reaction, contribute H_2O to the formation of low Cl^- fluids, over a depth interval between over 100 m and less than 2.5 km, dependent on the geothermal gradient.

These carbonate and quartz cements, forming by reactions I and IV, are extremely important phases. They include key geochemical and isotopic tracers, which could provide invaluable information about the transport of solutes and heat, by dispersed flow, during diagenesis (and metamorphism) (Bickle & McKenzie 1987).

V. *Hydrous minerals breakdown*, especially during deeper burial diagenesis and metamorphism.

VI. *Volcanic ash* (*and upper oceanic crust*) *hydration alteration to zeolites and clay minerals*. Because of the abundance of volcanic ash in convergent margin sediments these are quantitatively important hydration reactions, consuming water (plus mostly Mg^{2+} and alkalies) at low to medium temperatures and releasing it at depth, at higher temperatures, from dehydration and breakdown reactions of the authigenic zeolites and clay minerals. Dependent on the mass balance between these hydration reactions and the dehydration and transformation reactions described in IV, higher than seawater Cl^- fluids may evolve. The pore fluids of Site 808 (figure 2*b*), at under 560 m and at over 1200 m are probably good examples of such fluids.

Ion-exchange, adsorption–desorption and oxidation–reduction, and other diagenetic reactions are of lesser importance to the fluid and geochemical budgets at convergent margins.

7. Geochemical fluxes

The volume of fluid expelled from ocean margins by subduction on a global basis has been estimated at about 1 $km^3\ a^{-1}$ (COSOD II 1987). This is similar to the values obtained in §4, considering the factor of 3 error of the COSOD II estimate. Thus, for a 30550 km global length of subduction system, the maximum internal fluid source of 10 $m^3\ a^{-1}\ m^{-1}$ is equivalent to 0.3 $km^3\ a^{-1}$. These values are very much lower than the hydrologic flow rate at margins of 100 $km^3\ a^{-1}$ estimated by COSOD II (1987). The use of values of this order taken together with data for Sr isotopic compositions and Li concentrations gives fluxes of the same order as river and hydrothermal input rates if hydrological flow is considered but of the order of 1% of these rates for internally derived fluids (Elderfield *et al.* 1990; Martin *et al.* 1991). These estimates are typical of fluxes for several elements. This would seem to suggest that the geochemical fluxes to seawater associated with subduction processes are of minor importance to the ocean geochemical cycle but it should be remembered that the high observed fluid discharge rates have been attributed to externally derived fluids and there is, as yet, no realistic estimate of a global average flux from this source (the observed fluid discharge rates of over 100 $m^3\ a^{-1}\ m^{-1}$ are equivalent to over 3 $km^3\ a^{-1}$). The high volume transport associated with such fluid sources makes them extremely important to geochemical fluxes and a detailed documentation of the hydrology of the uppermost tens to hundreds of metres of accretionary complexes is a vital prerequisite to a better definition of their importance to the oceanic budget of elements and isotopes.

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