Old iodine in fluids venting along the Central American convergent margin

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[1] Focused fluid expulsion at cold vents is a common feature of subduction zones, serving as an important backflux of water and volatile elements to the oceanic reservoir. The strong enrichment of iodine in fluids collected from mounds along the Central American convergent Margin allowed the determination of $^{129}I/I$ ratios for age calculations in order to determine potential source formations in this active, erosional margin. The majority of the determined iodine ages are between 40 and 20 Ma. Because these ages are older than the age of host sediments and underthrust sediments on the oceanic plate (<18 Ma), a major contribution of iodine must come from old, organic rich sources in the upper plate. Both the iodine concentrations and ages determined for the mounds in this study are similar to reported values for hydrate fields at accretionary margins, indicating that iodine and associated organic carbon cycling at both erosional and accretionary margins may occur on similar time scales. **Citation:** Lu, Z., C. Hensen, U. Fehn, and K. Wallman (2007), Old iodine in fluids venting along the Central American convergent margin, *Geophys. Res. Lett.*, *34*, L22604, doi:10.1029/2007GL031864.

1. Introduction

[2] Fluid expulsion and gas emission are often-observed features along continental margins, surface expressions of which include cold seeps, gas hydrates, mud diapirs, and mud volcanoes. The origin of fluids and mud usually can be traced to depths of several kilometers [*Hensen et al.*, 2004; *Kopf*, 2002], but the exact source regions are still under investigation at many margins. Fluid flow from these deep-seated sources returning to shallow marine reservoirs is an efficient recycling mechanism to maintain the global geochemical balance, including the carbon cycle. Both mud volcanoes and gas hydrates have been suggested to be a potentially significant but poorly constrained input of hydrocarbon gas to the oceanic and atmospheric system [*Dickens et al.*, 1995; *Kopf*, 2002; *Milkov et al.*, 2003]. Tracing the source of methane rich fluids might help pinpoint the source location and unravel these recycling processes at active margins. The Central American margin (CAM) is a well-studied example of an erosional margin with many mud diapirs and cold seeps present, where we applied the iodine isotopic system to locate potential source formations responsible for the release of organic species.

[3] Marine organisms usually concentrate iodine and the subsequent release during the degradation of organic materials causes pore fluids associated with hydrocarbons to be considerably enriched in iodine compared to seawater (0.4 μM). Once released by organic matter, iodine is rarely involved in diagenetic reactions and only transported in aquatic fluids, making it an excellent tracer for the origin of fluids and methane. Iodine has one stable isotope (^{127}I) and one long-lived radioisotope (^{129}I; $T_{1/2}$ = 15.7 Myr), a product of Xe isotope spallation in the atmosphere and spontaneous fission of ^{238}U in the crust, which allows the age determination of organic sources responsible for the release of iodine and, by association, of methane. Due to the long residence time of iodine in the ocean ($\sim$300 kyr [*Broecker and Peng*, 1982]), the marine system reached an uniform pre-anthropogenic input ratio of $^{129}I/I = 1500 \pm 150 \times 10^{-15}$ [*Fehn et al.*, 2007a]. Anthropogenic ^{129}I released from nuclear tests and reprocessing has significantly increased the ratio in surface reservoirs, but does not affect deep sediments [*Moran et al.*, 1998; *Snyder and Fehn*, 2004]. The pore water ^{129}I system has been successfully applied for the dating in several oil fields and gas hydrate fields [*Fehn et al.*, 1990, 2000, 2003, 2006; *Tomaru et al.*, 2007a]. The purpose of this study is to determine the age of iodine in fluids collected from a number of dewatering sites (mounds) in the Central American convergent margin and to identify the organic source for iodine within the tectonic setting of this region.

2. Geological Background

[4] The CAM along the coasts of Costa Rica and Nicaragua is formed by the subduction of the Cocos plate beneath the Caribbean plate (Figure 1a). There are three morphologically different segments on the oceanic plate characterizing the forearc area in this region. The relatively smooth East Pacific Rise crust is subducted off Costa Rica and southern Nicaragua. South to the end of Nicoya Peninsula is a rough section of seamount covered oceanic crust. A thick oceanic ridge segment (Cocos Ridge) is subducted beneath the southern continental slope of Costa Rica. The entire study section is dominated by subduction erosion, a process removing mass from the underside of the upper plate [*Ranero and von Huene*, 2000], resulting in a frontal sediment prism much smaller than is typical for accretionary margins (Figure 1b). Rapid subsidence starting in Miocene indicates that basal tectonic erosion associated with crustal thinning has been active since that time [*Vannucchi et al.*, 2004]. Landward from the prism, the forearc wedge is covered by 1–2 km of hemipelagic sediments. Anoxic diagenesis driven by the degradation of high amounts of

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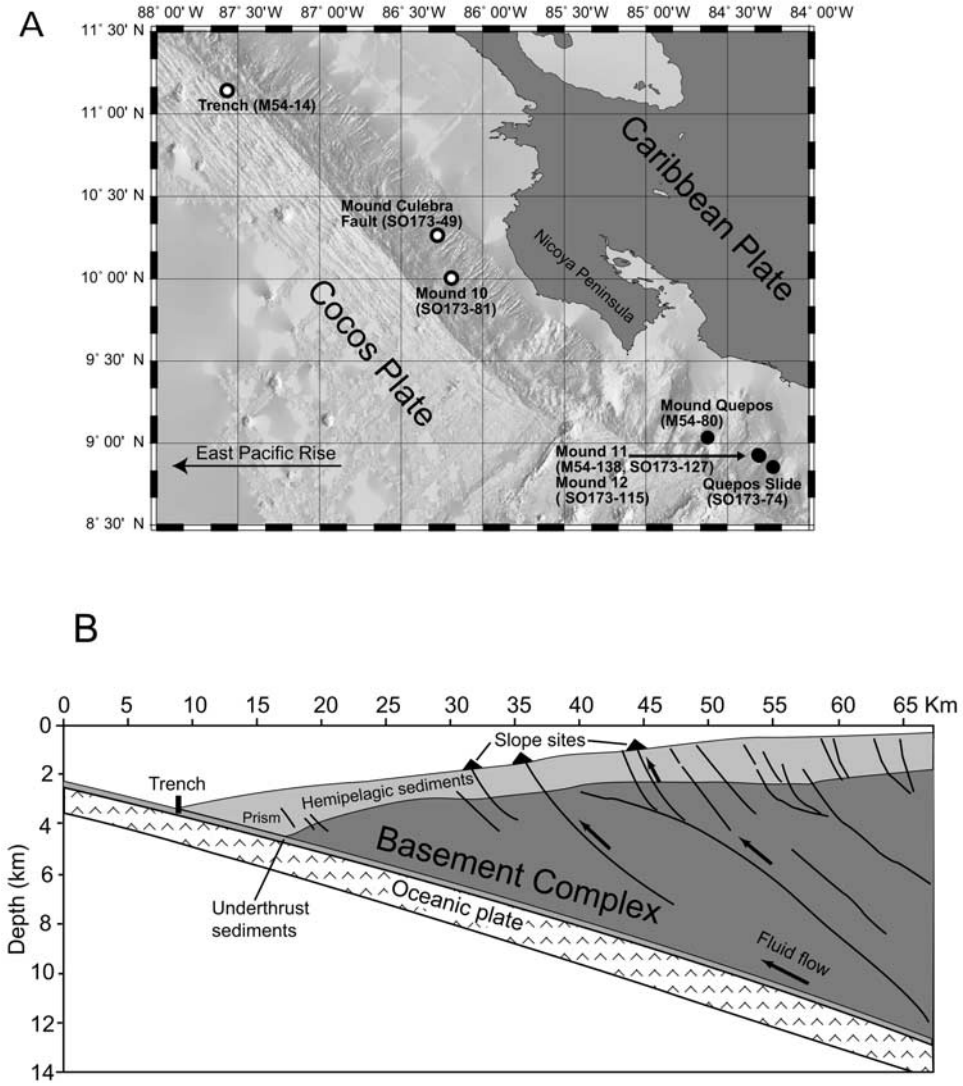

Figure 1. (a) Map of the study area at the Central American convergent margin. The sites are subdivided into a northern group (open circles) and a southern group (closed circles); (b) A schematic cross-section of the subduction zone modified from seismic profiles after *Hensen et al.* [2004].

organic material is responsible for the accumulation of biogenic methane and gas hydrates in these sediments [*Hensen and Wallmann*, 2005; *Luckge et al.*, 2002].

[5] Along the middle to upper continental slope more than 100 dewatering sites are unambiguously identified at present. Growth of carbonate capped mounds is ascribed to the long-term escape of CH_4-rich fluids associated with carbonate precipitation and is amplified by mud extrusions. Structural analysis of the deep subsurface indicates that the mounds are located on top of the hemipelagic sediment cover, which is underlain by a thick and intensely faulted ophiolithic basement making up the major part of the overriding plate (Figure 1b). Some of the faults actually penetrate the entire overriding plate down to the décollement [*Hensen et al.*, 2004; *Ranero and von Huene*, 2000]. Dewatering of subducted sediments has been considered to be a driving source of fluid and mud expulsion on the continental slope [*Hensen et al.*, 2004], with source formations perhaps deeper than 10 km [*Kastner et al.*, 2006].

3. Samples and Methods

[6] During cruises M54 of R/V Meteor in 2002 and SO173 of R/V Sonne in 2003, a large number of dewatering sites have been sampled by a gravity-corer (GC) or multicorer (MC). For the present study we used samples obtained from 6 GC and 2 TV-guided MC deployments. Six sites are on the continental slope off Costa Rica at water depths between 1000 and 2500 m, and one site is located in the trench offshore Nicaragua (5400 m) (Figure 1a). Mound 11 was sampled twice during the two cruises.

[7] Pore water was retrieved from sediment samples by pressure filtration in a cooled laboratory at about 4°C, as described earlier [*Wallmann et al.*, 2006]. Iodide and chloride concentrations of pore waters were determined by

ion chromatography at IFM-GEOMAR. Standard deviations were about 1% for chloride and 5% for iodide. Pore waters with relatively high iodide concentrations were then selected for ^{129}I measurement; in a few cases adjoining samples were combined for ^{129}I determinations. The extraction of iodine, sample preparation and determination of ^{129}I/I ratios on AMS followed established methods [*Fehn et al.*, 1992; *Sharma et al.*, 2000], with the actual isotope determination carried out at PrimeLab, Purdue University.

4. Results and Discussions

4.1. Iodine Concentrations

[8] Iodine concentrations were determined in the fluid samples from seven different sites, with one site (Mound 11) sampled twice (Figure 2). The measured concentrations are between 0.45 and 644 μM, with concentrations starting close to seawater values (0.4 μM) at the sediment-seawater interface and reaching considerably higher concentrations with depth. The depth profiles present three different depth trends (Figure 3a): At sites SO 173/49, 173/74 and 173/81, iodine shows a gradual increase in the concentrations towards deep layers, similar to pore water profiles observed in other marine sediments [*Martin et al.*, 1993; *Moran et al.*, 1998]. The relatively few data from Site 54/14 and 54/80 suggest that these profiles follow a similar trend. A much faster increase is found in Mound 11 (site SO173/127 and M54/138), where the concentrations increased to $\sim$250 μM within the upper 20 cm of the core indicating very strong upward advection of deep fluids. By contrast, iodine concentrations increased slowly from 2 to $\sim$3 μM in the upper half of Site 173/115, and reached only 40 μM at the bottom of the core. This shape probably is the result of downward mixing of seawater [*Schmidt et al.*, 2005] and goes along with a clearly biogenic, hence, shallow source of methane at Mound 12 (C. Hensen unpublished data). Because the concentration in this site is too low for iodine dating, we exclude this site from the discussion of deep fluid sources.

[9] Clearly, all fluids associated with these mud volcanoes are enriched in iodine compared to seawater, but the enrichment varies significantly between sites. For the convenience of discussion, we divide the sites into a northern and a southern group, following the tectonic boundary between the smooth and rough slabs. Comparing the deepest samples from each core, the northern sites (M54/14; SO173/49, 81) reach relatively higher iodine concentrations of up to $\sim$600 μM, whereas, the southern group is less enriched in iodine, with concentrations of $\sim$200 μM, due to the pronounced dilution effect indicated by Cl concentrations (Figure 2).

4.2. Iodine Ages

[10] Results of 25 ^{129}I/I determinations are listed in Figure 2, together with individual errors (1 σ). Ages were calculated using the standard decay equation:

$$R_{SA} = R_0 e^{-\lambda_{129} t} \quad (1)$$

where R_{SA} and R_0 are ^{129}I/I ratios of samples and initial seawater (1500×10^{-15}) and λ_{129} is the decay constant of ^{129}I (4.41×10^{-8} yr^{-1}). The resulting ages are minimum values, because neither the potential presence of anthropogenic ^{129}I or fissiogenic ^{129}I were taken into account. None of the ratios is above the pre-anthropogenic input ratio, indicating the absence of major contamination from anthropogenic ^{129}I, and corrections for fissiogenic ^{129}I in marine sediments typically are within the error limits of the calculations [*Fehn et al.*, 2000]. All of the iodine ages are older than 10 Ma, with the majority of the ages falling into a range between 20 and 35 Ma (Figure 3b). The oldest ages were found in samples from Mound 11, even disregarding the deepest which has an unusually large error attached. The two sample sets for Mound 11 gave compatible results, demonstrating the reliability of the determinations and the persistence of conditions over the sampling period.

4.3. Source of Old Iodine

[11] All ages obtained are older than the Quaternary host sediments and most of them are beyond the age of underthrust sediments (<18 Ma [*Kimura et al.*, 1997]). The shape of the depth profiles suggests mixing between several sources, which can be investigated using a plot of ^{129}I/I ratios vs. the reciprocal of iodine concentrations (Figure 4). Three different situations can be identified in this plot (Northern sites; Mound 11; Quepos Slide), although the overall behavior for them is quite similar: an old source with high iodine concentrations mixes with a young source with slightly lower concentrations. The concentration in the young source is between 100 and 200 μM, representing pore waters in recent sediments or thermally altered pore water of subducted sediments. The almost horizontal mixing lines defined by a few samples in all three cases point to the influence of seawater.

[12] The ages indicate that sources for the old iodine have to be in the upper plate. Such sources could be in the middle to upper slope where sandstone, siltstone, bioclastic limestone and turbidite layers as old as upper Cretaceous were deposited. Further landward, the forearc Sandino basin at Nicaragua contains similar layers at depths up to 10 km and has been considered to be a potential oil/gas field [*Darce et al.*, 2000]. Potential conduits for iodine to reach the outer forearc from the deep basin include the faulted unconformity between the bottom of the basin and underlying basement and the fault system in the Nicoya Complex [*Fisher et al.*, 2004; *Ranero et al.*, 2000].

[13] A different source probably is needed for the old iodine in the trench site, where fluids are likely derived from the décollement. The forearc wedge itself at CAM is assumed to be mostly composed of basement material similar to that exposed in the onshore Nicoya ophiolithic complex [*Kimura et al.*, 1997]. Sediments of Eocene to Miocene may, however, form part of the seismic basement underneath the slope sediments and provide old organic materials responsible for the iodine ages determined in the fluids, especially in the trench site. If such a source does exist, the opening of deeply reaching fluid conduits could also bring old iodine to the slope sites.

[14] The younger components mixing with these old sources could be slope sediments covering the wedge, the incoming sediments on the Cocos Plate and seawater. Several investigations from this region suggest that the underthrust sediments play a more important role than slope sediments in the fluid chemistry due to the higher temper-

Depth (cmbsf)	Cl^- (mM)	I^- (μM)	$^{129}I/I$ ($x10^{-15}$)	Depth (cmbsf)	Cl^- (mM)	I^- (μM)	$^{129}I/I$ ($x10^{-15}$)
Northern sites				**Southern sites**			
173/49 (Culebra)				***173/74 (Quepos Slide)***			
20	551	10		55	429	69	
60	540	27		80	389	84	790 ± 120
90	528	51		105	361	102	340 ± 70
140	508	83		130	334	132	572 ± 42
190	487	118		155	316	130	340 ± 70
240	465	161		180	308	144	440 ± 110
290	448	204		205	302	130	
330	428	249		230	301	136	540 ± 49
370	410	295		255	301	144	
400	404	323		285	297	146	
430	390	350	620 ± 70	310	295	138	490 ± 90
470	378	421		335	294	154	
500	366	367	580 ± 90	360	294	156	290 ± 250
530	358	381		385	294	156	730 ± 140
570	344	418	356 ± 48	410	294	152	
600	337	441		435	295	158	
630	329	466	454 ± 45	460	304	160	
660	319	480		500	293	150	
690	314	498	470 ± 80	530	297	162	
720	327	536		570	292	154	
750	304	516		***173/81 (Mound 10)***			
780	295	538		10	547	1.2	
810	292	546		30	550	4.9	
173/115 (Mound 12)				50	550	12	
30	557	2.15		70	536	29	
70	552	2.30		90	521	44	
120	553	2.35		100	519	54	
170	552	2.50		120	507	64	
210	551	2.60		140	506	78	
240	552	2.80		160	494	90	
270	555	2.95		170	493	94	
310	556	3.55		***173/127 (Mound 11)***			
360	556	6.35		0	553	0.45	
425	546	16.9		0.5	501	33	
470	544	28		2	362	128	250 ± 110
500	534	30		4	263	218	
540	529	36		6	245	224	
575	523	40		8	240	242	440 ± 60
54/14 (Trench)				10	237	244	
112.5		197	730 ± 180	12	236	240	
385		385	380 ± 110	14	235	244	350 ± 80
637.5		485	357 ± 49	16	232	240	
795		644	370 ± 70	18	229	244	
				20	228	250	
				22	227	252	
				24.5	235	242	80 ± 150
				54/138 (Mound 11)			
				3		127	590 ± 270
				10		243	220 ± 80
				20		256	
				54/80 (Quepos)			
				290		106	
				562.5		235	520 ± 140

Figure 2. Iodide, chloride concentrations, and $^{129}I/I$ ratios in pore waters collected from seven mounds at CAM.

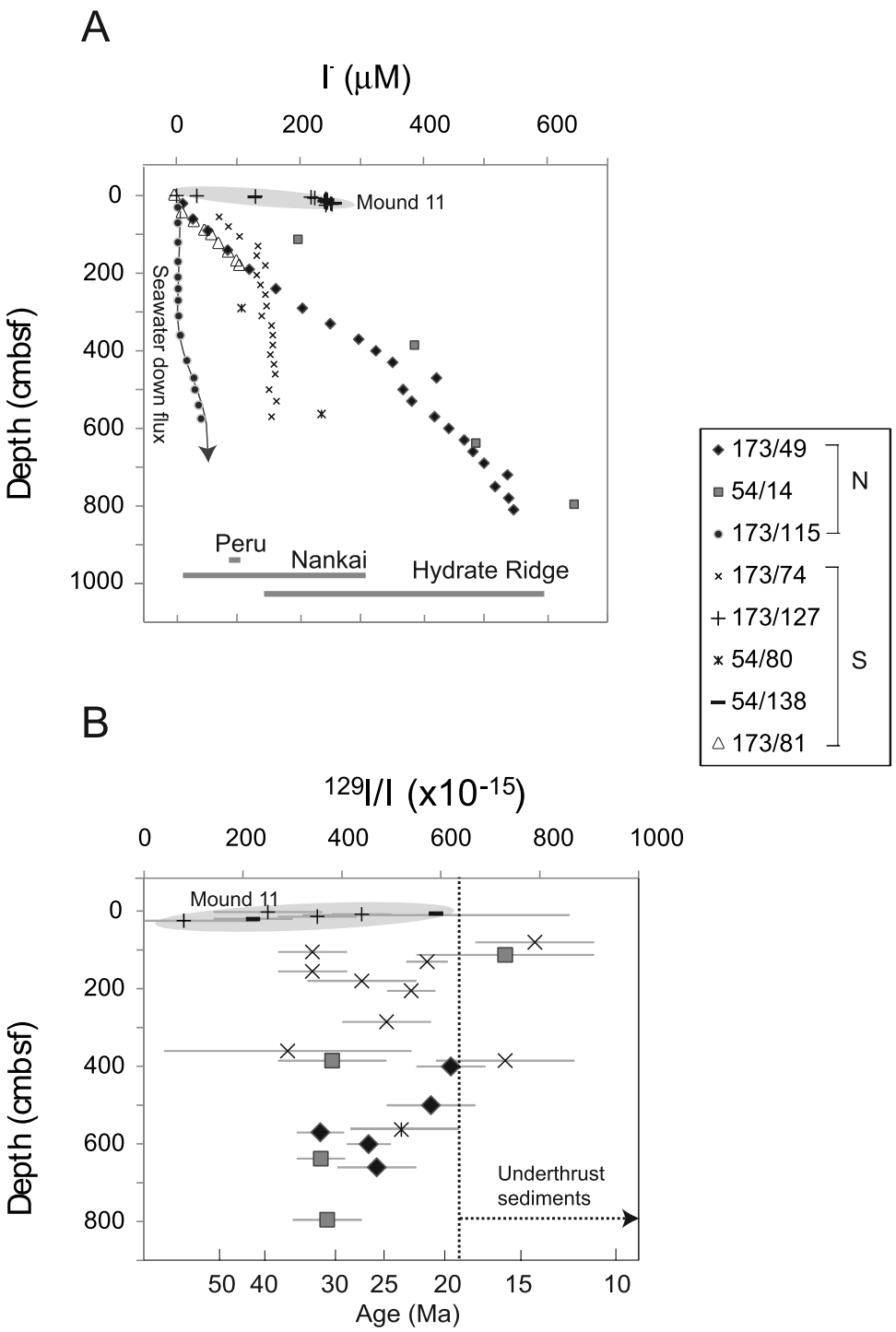

Figure 3. (a) Iodide concentrations measured at all of the dewatering sites. The gray bars indicate the ranges of iodide concentrations at around 10 m below seafloor in three gas hydrate fields. (b) ^{129}I/I ratios and iodine ages for selected samples. Ages of underthrust sediments are younger than 18 Ma [*Kimura et al.*, 1997]. Gray zone indicates results from the two sites on Mound 11.

ature in the subducting slab [*Hensen et al.*, 2004; *Schmidt et al.*, 2005].

4.4. Iodine in Mud Volcanoes and Gas Hydrate Fields

[15] In addition to CAM, high iodine concentration and ancient fluids have been reported in fluids associated with mud volcanoes in the Black Sea, Mediterranean Ridge and Norwegian Sea [*Aloisi et al.*, 2004; *Deyhle and Kopf*, 2001; *Pavlova*, 2005], and in all gas hydrate fields where iodine has been measured [*Egeberg and Dickens*, 1999; *Fehn et al.*, 2000, 2003, 2006; *Tomaru et al.*, 2007a]. The ranges of iodine concentrations in three gas hydrate fields (Peru Margin [*Fehn et al.*, 2007b]; Nankai [*Tomaru et al.*, 2007b]; Hydrate Ridge [*Fehn et al.*, 2006]) and ^{129}I/I ratios

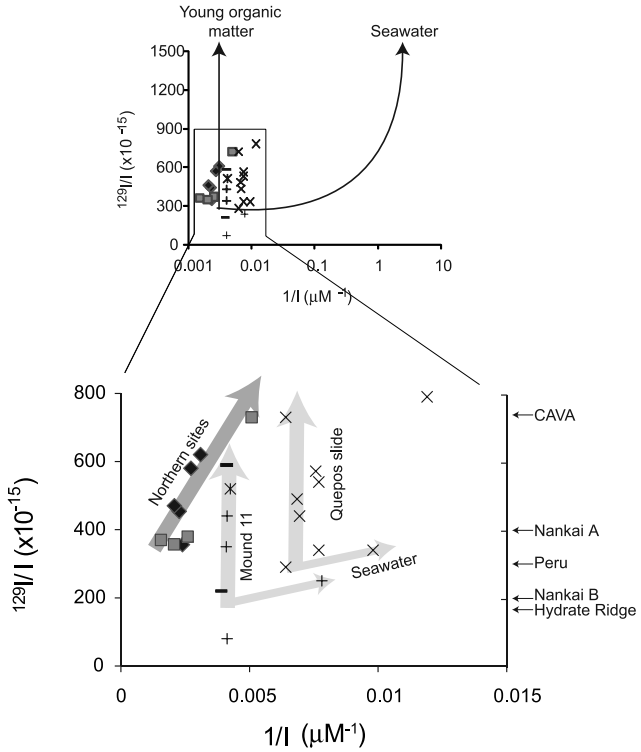

Figure 4. Mixing plot showing end-members with high ^{129}I/I ratios (seawater and young organic matter) and end-members with low ^{129}I/I ratios (old ages), compared with source ages in gas hydrate fields and main arc volcanic fluids from CAM. Symbols as in Figure 3.

are compared to the results from CAM (see Figures 3 and 4). Both, the concentration range and source ages at CAM, are comparable with those of hydrate fields. In contrast, volcanic fluids of the main arc at CAM (CAVA) [*Snyder and Fehn*, 2002], have ^{129}I/I ratios above 700×10^{-15}, which are compatible with derivation from subducting marine sediments, indicating distinctly different pathways for fluids in the main arc and the fore arc in this area. The results for fore arc systems suggest that fluids flowing back into the ocean reservoir are enriched in old iodine and, as an ubiquitous phenomenon along the subduction zones at both accretionary and erosional margins, might be an important mechanism for maintaining mass balance of the global iodine cycle and associated organic material.

5. Conclusions

[16] Pore water samples collected at CAM mud volcanoes were found to be highly enriched in iodine compared to seawater, consistent with results from mud volcanoes at other convergent margins. A large proportion of iodine ages calculated from ^{129}I/I ratios are older than 25 Ma, indicating derivation from old sources in the upper plate. Possible sources include sediment layers deposited on the upper slope and the lower parts of the poorly constrained seismic basement. The similarity of our results to those from marine gas hydrate systems suggests that deep-sourced fluids enriched in old iodine are common at active margins, serving as an important cycling mechanism for iodine and associated organic carbon.

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