

Back to the roots: boron geochemistry of mud volcanoes and its implications for mobilization depth and global B cycling

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Abstract

At convergent margins, fluid flux through active mud volcanoes (MVs) has been estimated to exceed that of the frontal accretionary prism, and may have done so in earlier earth history. Often, however, it is largely unknown how deep mud volcanoes root within accretionary wedges and orogenic belts. We report results from a systematic geochemical study of fluids and clays/claystones from mud volcanoes around the world using the mobile element boron as depth indicator for progressive diagenesis. Boron shows maximum enrichment in the fluid phase, owing to desorption in the mud, when faulting roots deepest and deformation is strongest. Deep-seated, B-rich fluids liquefy clay-bearing strata to facilitate extrusion, allowing the clay to re-adsorb and incorporate large quantities of B in the process. Given the abundance and high discharge rates of mud volcanoes along subduction zones, we propose that this process has to be considered a major backflux mechanism in global B cycling from the lithosphere into the hydrosphere.

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1. Introduction

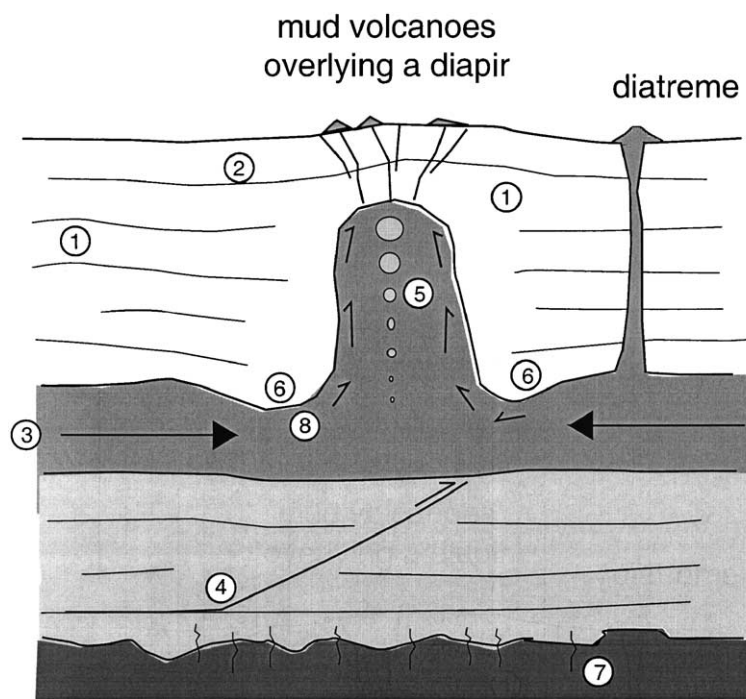
Mud volcanism has been demonstrated to be a global phenomenon (Higgins and Saunders, 1974), which is commonly associated with compressional tectonics and sediment accretion at convergent margins (e.g. Brown and Westbrook, 1988; Kopf et al., 1998). Quiescent as well as catastrophic emission of greenhouse gases (mostly methane) accompanies extrusion (Higgins and Saunders, 1974; Milkov, 2000). Mud domes and diapirs frequently occur in

marine subduction zones at the plate boundary near the toe of accretionary prisms (Henry et al., 1996), further landward in the forearc (Masle et al., 1999), but also on land where collisional processes and deformation are more accentuated (Lavrushin et al., 1996). Irrespective of the tectonic compression, the main driving force of mud extrusion is the negative buoyancy of the clay-rich material at depth (Fig. 1). Fluids may either be trapped as a result of high sedimentation rates or lateral influx into clay-bearing sediments, or may be generated in situ owing to processes like mineral dehydration reactions and hydrocarbon generation at greater depth (e.g. Hedberg, 1974) (see fluid sources in Fig. 1). Fluids and mud either extrude together (i.e. as diatremes, Fig. 1), or the fluid may be expelled more

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fluid sources for overpressuring and mud extrusion:

- (1) pore fluid expulsion from compaction
- (2) biogenic methane from degradation of organic matter
- (3) lateral fluid flux through stratigraphic horizons or fault zones
- (4) fluid migration along deep seated thrusts
- (5) thermogenic methane and higher hydrocarbons
- (6) fluids from mineral dehydration (opal, smectite)
- (7) hydrothermal fluids, alteration of crustal rock
- (8) fluid expulsion from internal deformation within the diapiric intrusion

Fig. 1. Schematic diagram of a mud diapir, MV extrusion and diatremes, including possible fluid sources (numbered 1–8); mature, B-rich fluids may be found among categories 3, 4 and 7.

rapidly than the upward-moving mud mass (i.e. mud volcanoes juxtaposing diapirs, Fig. 1) (e.g. Brown, 1990). Quantitative fluid flux estimates show expulsion at very high rates through mud volcanoes, suggesting a profound influence on geochemical cycling and fluid budgets in subduction zones (Kopf et al., 2001). During earth history, this process may have been of similar importance, although direct evidence is sparse given that mud volcanoes erode very rapidly (i.e. within a few years to 1 million years) and hence are rarely preserved.

2. Scientific rationale and method

The main objective of this mud volcano study was to evaluate how meaningful B geochemistry may be in estimating the depth of fluid and mud origin. Given that MVs consist of large quantities of smectite clay, its progressive tectonic dewatering (Fitts and Brown, 1999) as well as its temperature-driven transformation to illite (Colten-Bradley, 1987) may be reflected by a systematic trend in B geochemistry with increasing depth of origin and temperature in the various com-

pressional tectonic settings. The hypotheses to be tested included:

- (i) Is there a positive relationship between B content in pore waters and its depth of origin, e.g. due to release of B previously adsorbed to smectite? Moreover, is this release reflected by isotopic fluid signatures lighter than seawater, as proposed previously ($\delta^{11}\text{B} \sim 15\text{‰}$ for adsorbed boron, e.g. Spivack et al., 1987)?
- (ii) If a clay-rich sedimentary succession is re-hydrated by fluids, do the liquefied clay minerals re-adsorb boron in large amounts, as has been suggested by laboratory studies (e.g. Keren and Gast, 1981)?
- (iii) If a smectite-rich mud and a pore fluid re-equilibrate at depth before extruding rapidly to form a mud volcano, would B isotopes be a suitable proxy for progressive diagenesis (as has been demonstrated for $\delta^{18}\text{O}$ during illitization of smectite; Yeh and Savin, 1977)?
- (iv) Given that MVs have been proposed to discharge enormous volumes of fluid with time in some subduction zones (Kopf et al., 2001), does a systematic B study on such features support that mud volcanism is a significant player in backflux of mobile elements into the ocean?

For our case study, MV samples from various areas have been selected with the aim to provide a synthetic transect through a convergent margin setting undergoing progressive deformation (Fig. 2). Near the deep sea trench and toe of the accretionary prism, where mud domes off Barbados (Lesser Antilles) and Makran (Indian Ocean) were sampled, progressive compaction drives trapped pore fluids together with mud to the seafloor (Henry et al., 1996 and White and Loudon, 1982, respectively). However, fluid availability decreases exponentially with distance from the toe as tectonic and gravitational stresses, as well as time of burial increase towards the hinterland of the wedge (Moore and Vrolijk, 1992). Despite most of the initially captured seawater has been expelled within 10 km of the toe, mud volcanism is frequently found at the apex of accretionary prisms. In the collision zone between the African and Eurasian continental plates, several hundred MVs occur up to >150 km behind the toe of the Mediterranean Ridge ac-

cretionary prism (Kopf et al., 1998; Mascle et al., 1999). They are often related to faults in the imbricated wedge, where fluidized mud is expelled at high rates (Fig. 3A). Further landward in the uplifted forearc of a convergent margin, onshore MVs in Malaysia (Clennell, 1992) and Pakistan (Snead, 1964; Delisle et al., 2001) attest more accentuated deformation and mud extrusion on land (Fig. 2). Mud domes can be small, like the *Jeroco* MV in Sabah, Malaysia (Fig. 3B), but may reach sizes of several kilometers in diameter (Lavrushin et al., 1996; Delisle et al., 2001). With continuous subduction of ocean floor, the basin is closed and continental collision occurs. This process has proved to result in abundant mud volcanism along several collision zones, such as the Tethyan region near the Black and Caspian Seas (Jakubov et al., 1971; Lavrushin et al., 1996). MVs from Georgia (Lesser Caucasus mountain range) and the Taman Peninsula (Great Caucasus) are presently active, with gas, waters and petroleum being emitted from their edifices. As maximum collision end member, claystones and fluid precipitates of the fossil *Verrua* MV in the northwestern Italy (near Monferato), which has been preserved during the Alpine orogeny, were studied (Cavagna et al., 1998).

The synthetic profile of MV samples from near the toe of an actively subducting system (Barbados) to active (Caucasus) as well as fossil (Western Alps) mud volcanoes in orogenic wedges provides an ideal basis for the systematic investigation of variations in boron geochemistry as a function of fluid–rock interaction at variable depths, stresses and temperatures. Being commonly related to faults of the surrounding country rock (see Figs. 2 and 3A), MVs can be viewed as tectonic “windows” to understand processes at much greater depth. When tied into the results from hydrothermal geochemical experiments in the laboratory (You et al., 1996), the highly volatile element boron with its wide (almost 100‰) range of $\delta^{11}\text{B}$ isotope ratios in natural samples (Palmer and Swihart, 1996), and its abundance in clay-bearing sediments, allow us to discriminate fluid generation and exchange mechanisms during subduction–collision.

The samples studied can be subdivided into three classes. First, mud of variable consolidation state was available from all areas. While the material from the active submarine features was generally soft (Barbados, Makran, shallow samples from the Mediterranean

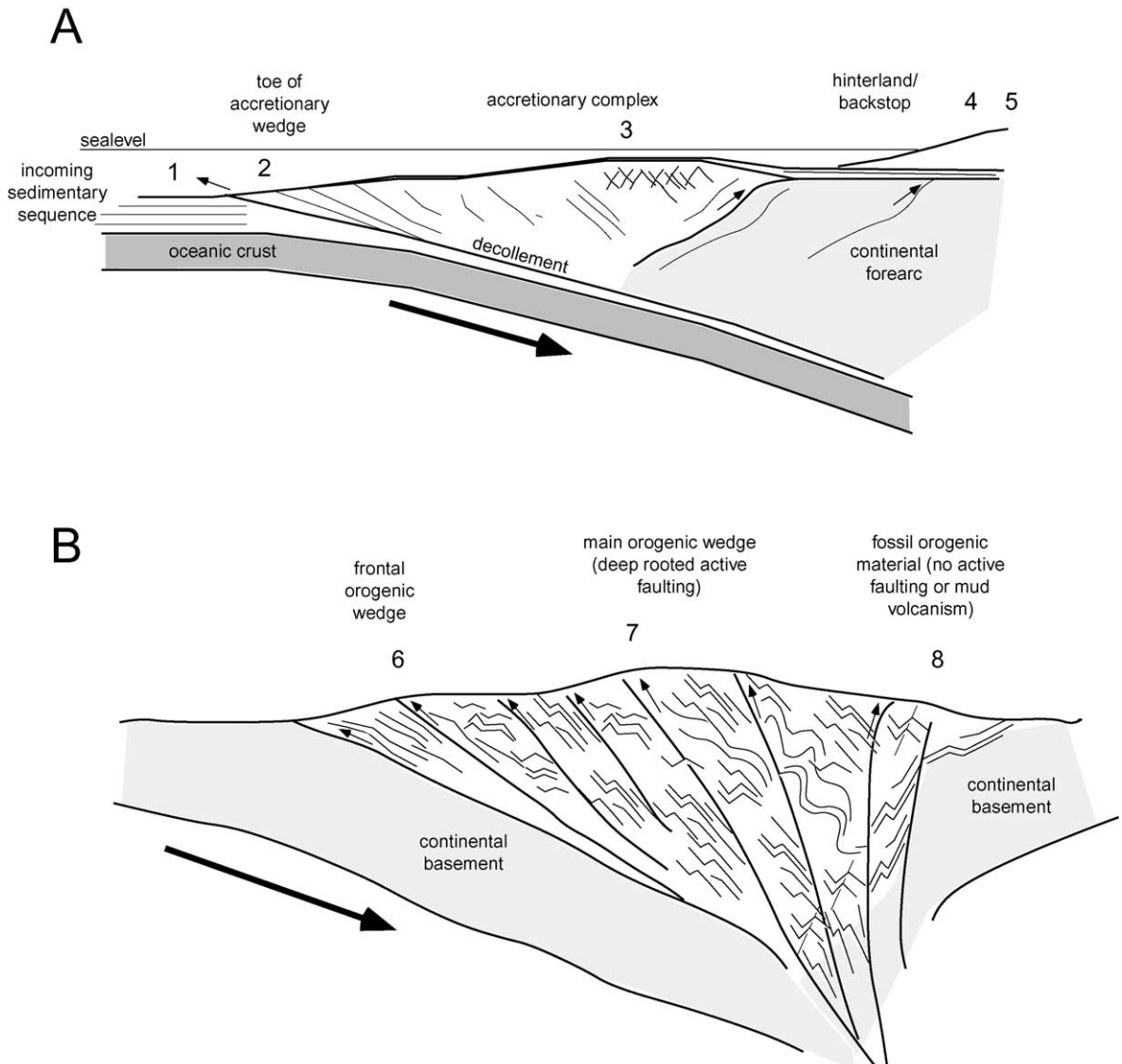


Fig. 2. Schematic cross-section across an active convergent margin illustrating the subducting stage (A) and the continent-collisional stage (B) after closure of the oceanic basin. The relative position of the MVs sampled for this study is given for reference to illustrate the progressive compressional deformation the material suffers. (1–2) Toe area of accretionary wedge: Barbados, Makran; (3) centre/apex of accretionary wedge: Mediterranean Ridge; (4–5) uplifted forearc (on land): Pakistan, Malaysia; (6–7) orogenic wedge (on land): Georgia, Taman Peninsula; (8) fossil MV preserved in the orogenic wedge: Western Alps. Deformation and depth of faulting increase from left to right.

Ridge), soft mud (Pakistan, Malaysia, Lesser and Greater Caucasus) as well as consolidated mud to cemented mudstone (deep samples from the Mediterranean Ridge, Malaysia, Western Alps) was collected. Some of the marine MVs also had cemented mudstone clasts in a softer matrix (MedRidge; see Kopf et

al., 1998). Both muds and mudstones are dominated by various clay minerals (see below). Second, pore fluids from the muds and mudstones were sampled directly (in case of the soft mud: Barbados, Makran, shallow samples from the Mediterranean Ridge, Pakistan, Lesser and Greater Caucasus) when possible,

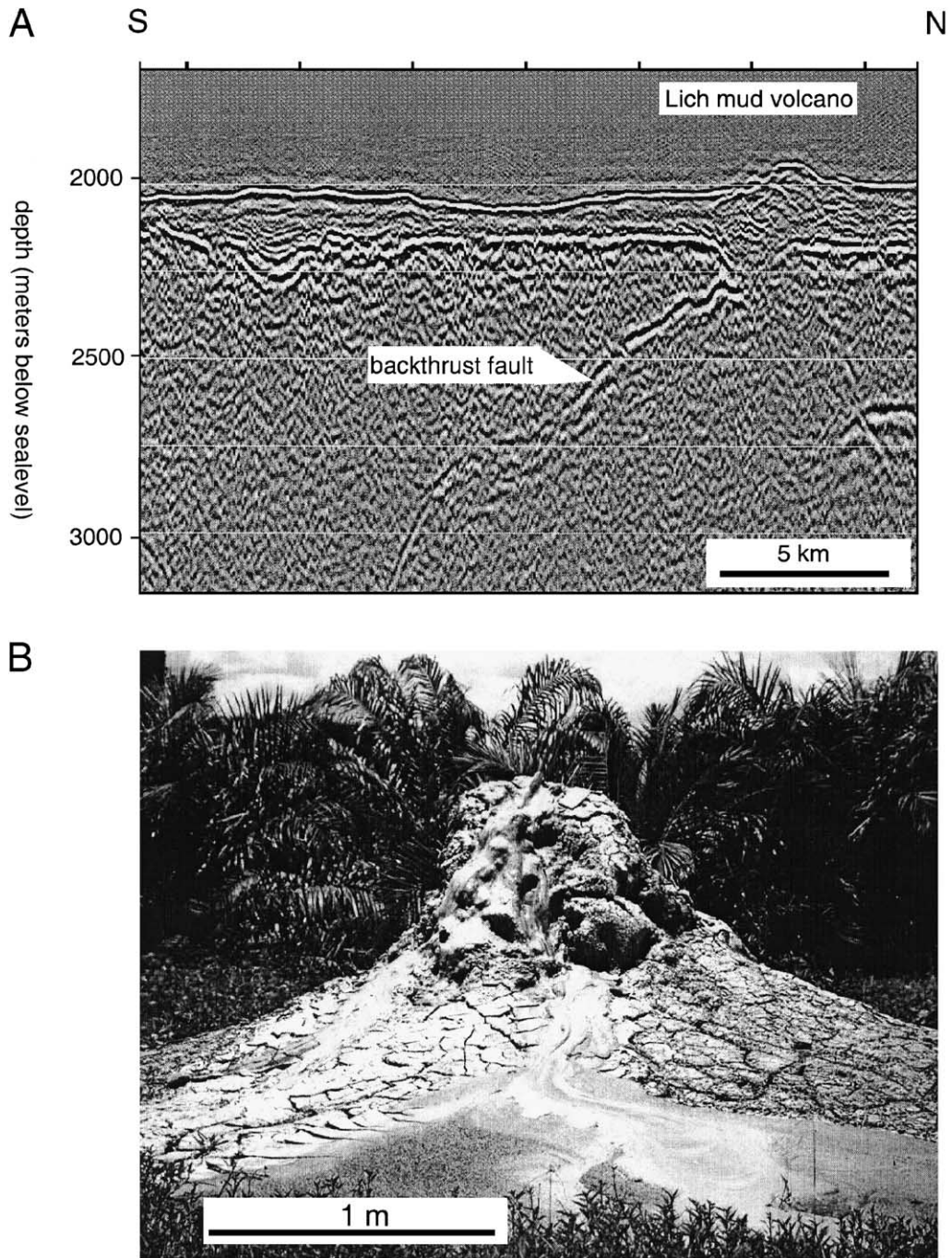


Fig. 3. Examples of typical mud volcanic edifices. (A) Seismic reflection profile showing the seafloor mud volcano *Lich* juxtaposing a backthrust fault on the Mediterranean Ridge accretionary complex (Masche et al., 1999); (B) Small onshore mud volcano *Jeroco* at Sabah, Malaysia (Clennell, 1992).

Table 1
Results from XRD and geochemical study of B and $\delta^{11}\text{B}$ isotopes

Sampling location	Relative mineralogical abundance from XRD (in decreasing order)	Illite/total clay from semi-quantitative XRD	Solid fraction	Fluid fraction	B (ppm)	$\delta^{11}\text{B}$ (‰)	$\delta^{11}\text{B}$ parent solution at pH 8 (‰)
<i>Barbados</i>							
Atalante MV	sm, kaol, chl, qtz, cc, py	0.02	mud		106	1.8	
Atalante MV					106	3.3	
Atalante MV				pore fluid	5	17.3	
Atalante MV				authigenic crust	29	-4.7	11.8
<i>Makran</i>							
217 KL	sm, kaol, il, qtz, cc, musc	0.08	mud		135	6.3	
217 KL			mud		135	2.6	
217 KL				pore fluid	7	28.1	
325 KL	sm, il, chl, qtz, cc, kaol	0.09	mud		91	3.0	
325 KL			mud		91	3.1	
325 KL				pore fluid	5	31.1	
<i>Eastern Mediterranean</i>							
Milano MV			mud		179	1.4	
Milano MV			mud		200	2.2	
Milano MV	kaol, sm, hall, qtz, cc, il	0.05	mud		143	7.2	
Milano MV			mud		106	6.8	
Milano MV			mudstone		73	2.1	
Milano MV	il, sm, pal, qtz, kaol, cc, chl	0.34	mudstone		11	-1.2	
Milano MV				authigenic cement	53	10	26.5
Milano MV				authigenic cement	121	21.3	37.8
Milano MV				authigenic cement	62	13.5	30
Milano MV				authigenic cement	23	8.4	24.9
Milano MV				authigenic cement	27	6.9	23.4
Napoli MV			mud		86	6.3	
Napoli MV			mud		134	-1.4	
Napoli MV	kaol, sm, chl, hall, qtz, cc, il	0.04	mud		98	4.8	
Napoli MV			mud		194	-3.1	
Napoli MV	sm, hall, il, qtz, pal, cc, ep	0.12	mudstone		44	6	
Napoli MV				authigenic cement	84	14.9	31.4
Napoli MV				authigenic cement	95	24.4	40.9
Napoli MV				authigenic crust	14	9.6	26.1
Napoli MV				authigenic crust	19	12.1	28.6
Napoli MV				authigenic crust	106	21.6	38.1
Napoli MV				pore fluid	22	25.5	
Napoli MV				pore fluid	39	33.6	
Napoli MV				pore fluid	52	28.8	
Moscow MV			mud		72	4.3	
Moscow MV				authigenic crust	42	20.3	36.8
Amsterdam MV	il, pal, qtz, cc, sm, chl	0.28	mud		108	-2.5	
Amsterdam MV				authigenic crust	40	16.7	33.2
Kula MV			mud		155	1.7	
Kula MV				authigenic crust	34	18.9	35.4
Kazan MV			mud		173	-0.9	
Kazan MV				authigenic crust	69	19.5	36

Table 1 (continued)

Sampling location	Relative mineralogical abundance from XRD (in decreasing order)	Illite/total clay from semi-quantitative XRD	Solid fraction	Fluid fraction	B (ppm)	$\delta^{11}\text{B}$ (‰)	$\delta^{11}\text{B}$ parent solution at pH 8 (‰)
<i>Pakistan</i>							
ChandraGup I	sm, sep, il, pal, qtz, cc	0.17	mud		79	14.9	
ChandraGup I				pore fluid	5	35.1	
ChandraGup II	sm, chl, qtz, sep, il, pal, cc	0.16	mud		181	14.9	
ChandraGup II				pore fluid	5	35.5	
<i>Malaysia</i>							
MV near Telupid, Sabah	il, kaol, qtz, gyp, cc, ba	0.44	mud		66	− 5.4	
MV				pore fluid	2	15.7	
<i>Lesser Caucasus, Georgia</i>							
Pchoveli MV	chl, il, qtz, cc, fsp, py, glau	0.32	mud		248	5.1	
Pchoveli MV				pore fluid	39	36.5	
Kila-Kupra MV	chl, il, qtz, sm, kaol, cc, pyrr	0.35	mud		144	− 0.1	
Kila-Kupra MV				pore fluid	20	39.5	
Bayda MV	il, sm, chl, kaol, qtz	0.45	mud		256	7.4	
Bayda MV				pore fluid	62	38.3	
Ahtala MV (Gurdjaani)	qtz, chl, il, sm, cc, fsp, musc	0.26	mud		323	− 1.2	
Ahtala MV (Gurdjaani)				pore fluid	115	22.5	
<i>Greater Caucasus (Taman Peninsula)</i>							
Kuchugurski MV	qtz, chl, il, kaol, cc, fsp, ep	0.28	mud		339	3.75	
Polivadina MV	chl, il, qtz, kaol, sm, musc, pyrr	0.4	mud		317	1.38	
Semigorski MV	chl, il, qtz, cc, fsp, py, glau	0.42	mud		539	− 4.44	
Gladkovski MV	il, chl, qtz, kaol, sm, cc, pyrr	0.52	mud		280	− 6.04	
Shugo MV	qtz, chl, il, sm, cc, fsp	0.41	mud		422	− 7.67	
Ahtanizovski MV	chl, qtz, il, sm, kaol, cc, fsp, bio	0.38	mud		868	− 0.57	
Shapurski MV	chl, il, qtz, kaol, cc, fsp, amph	0.39	mud		367	7	
m.v. Golubicriy	qtz, chl, il, sm, cc, fsp	0.33	mud		322	− 1.45	
m.v. Karabetovski	il, qtz, chl, kaol, sm, fsp	0.46	mud		143	2.36	
<i>Western Alps, Italy</i>							
Verrua MV near Monferrato	il, chl, qtz, fsp, bio, ep	0.51	mudstone		138	− 5.3	
Verrua MV near Monferrato	il, chl, qtz, bio, fsp, ep	0.39	mudstone		119	− 2.7	

(continued on next page)

Table 1 (continued)

Sampling location	Relative mineralogical abundance from XRD (in decreasing order)	Illite/total clay from semi-quantitative XRD	Solid fraction	Fluid fraction	B (ppm)	$\delta^{11}\text{B}$ (‰)	$\delta^{11}\text{B}$ parent solution at pH 8 (‰)
<i>Western Alps, Italy</i>							
Verrua MV near Monferrato				authigenic chimney	4	14.4	30.9
Verrua MV near Monferrato				authigenic chimney	4	12.5	29
<i>Background sediment</i>							
Mediterranean Sea	cc, kaol, qtz, hall, sm	<0.01	nannofossil ooze		110	21.4	37.9

Column 2 gives relative abundance of mineral phases decreasing from left to right; column 3 gives normalized ratio of illite relative to total clay. The right column accommodates for the pH-dependent fractionation of B, which results in a shift of 16.5‰ between carbonate precipitate and corresponding parent solution at pH 8 (Hemming et al., 1995).

Mineralogical abbreviations: amph = amphibole, ba = barite, bio = biotite, cc = calcite, chl = chlorite, ep = epidote, fsp = feldspar, glau = glauconite, gy = gypsum, hall = hallyosite, il = illite, kaol = kaolinite, musc = muscovite, pal = palygorskyte, py = pyrite, pyr = pyrrhotite, qtz = quartz, sep = sepiolite.

and were then filtered (0.2- μm mesh). More indurated samples were carefully squeezed (deep samples from the Mediterranean Ridge, Malaysia). Third, authigenic precipitates of ancient pore waters were collected from some of the study areas (Barbados, MedRidge, Western Alps). Such carbonates either occur as crusts in the crestral area of the MVs, or precipitated as concentric cements in conduits (often referred to as chimneys) that expel fluid through the MV. Authigenic carbonates also served as a control whether squeezing may have artificially affected B fractionation (see below). A full list of samples is provided in Table 1.

The bulk mineralogy of the mud volcano clays was determined using an automated X-ray diffractometer (Philips PW1800) at the University of Bristol, UK. X-ray diffraction patterns of smear slides were scanned from 3° to $68^\circ 2\theta$ at $0.02^\circ/\text{s}$ using 45-kV accelerating voltage and 30-mA current with a copper k_α source (1.5405- \AA wavelength). In addition, analyses were run on the separated clay fraction ($<2 \mu\text{m}$) at scanning angles from 3° to 37° to achieve a better recognition of the clay mineral phases. Abundance of total expandable clays (discrete and mixed-layered) were then verified by reruns of air-dried, glycolated and heated specimens. Peak heights of diffractograms were then used for a semi-quantitative estimate of the relative abundance of each clay mineral phase (i.e. smectite relative to illite as a measure of degree of transformation/diagenetic alteration).

B concentrations were determined by ICP-AES (JY 170 Ultratrace), and $\delta^{11}\text{B}$ isotope analyses were carried out by positive (clays, claystones) and negative (fluids, authigenic carbonates) thermal ionization mass spectrometry (TIMS; Finnigan MAT 262 at GEOMAR Research Centre, Kiel, Germany) with a reproducibility of $\pm 0.5 \text{‰}$ and $\pm 0.11 \text{‰}$ ($2\sigma_{\text{mean}}$), respectively (for details, see Deyhle, 2001 and Deyhle et al., 2001, respectively). Authigenic carbonates, which represent precipitated fluids at the crest of the mud domes, are shown as recalculated parent fluid ratios assuming pH 8 (Hemming et al., 1995; Deyhle et al., 2001) (see Table 1). All $\delta^{11}\text{B}$ compositions are reported as ‰ deviation from standard NBS SRM 951 (Cantanzaro et al., 1970).

3. Boron at convergent margins

Because of its highly volatile character and its wide range of isotope ratios in geomaterials, boron is a unique geochemical tracer. Early work on shales established that reversible adsorption of B at low temperatures occurs (e.g. Harder, 1961; Couch and Grim, 1968; Keren and Mezuman, 1981; Palmer et al., 1987). With increasing temperature and stress (e.g. during burial or tectonic processes), adsorbed boron becomes enriched in the fluid phase and subsequently depleted in the clay (e.g. You et al., 1996). The adsorbed species is predominantly the light isotope

^{10}B , so that fluids originating from clay-rich pore fluids obtain lighter $\delta^{11}\text{B}$ values than seawater (e.g. Spivack et al., 1987). In general, B gets enriched in fluids by processes such as desorption from clay particles, mineral dehydration reactions, increasing temperature and alteration of volcanic or igneous rocks (see Palmer and Swihart, 1996 and references therein). Among others, You et al. (1993, 1996) and Deyhle et al. (2001) found that fluids which were tectonically released in a subduction zone generally have elevated B contents, and often show a bimodal $\delta^{11}\text{B}$ variation with depth. Isotopes increase to compositions heavier than seawater (up to $>50\text{‰}$) at moderate depth (seawater = 39.5‰ ; Spivack et al., 1987), before decreasing again to lower $\delta^{11}\text{B}$ values ($25\text{--}30\text{‰}$) at greater depth. The absolute depth is a function of the geothermal gradient of the area regarded, so that increasing and decreasing $\delta^{11}\text{B}$ values may occur at different depth levels at the different convergent margins. Alteration of igneous rocks usually leads to $\delta^{11}\text{B}$ lighter than seawater, with a less profound enrichment in B content of the fluid (Palmer, 1991).

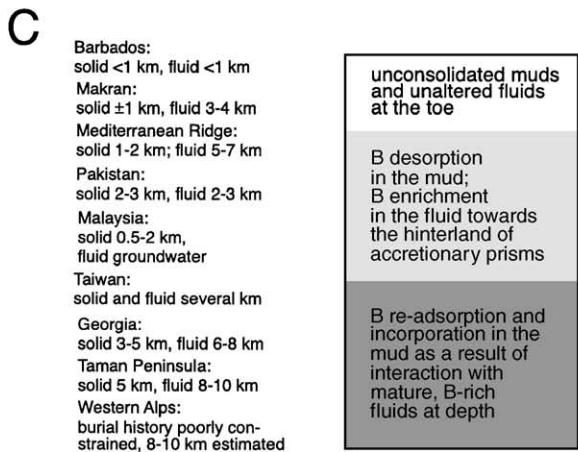
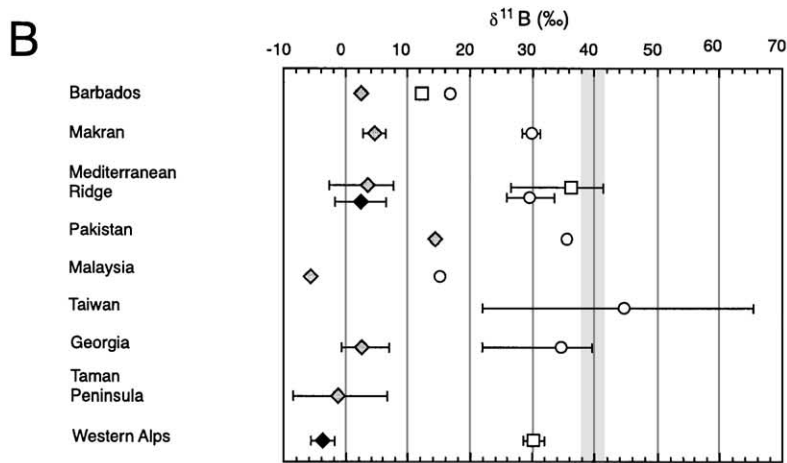
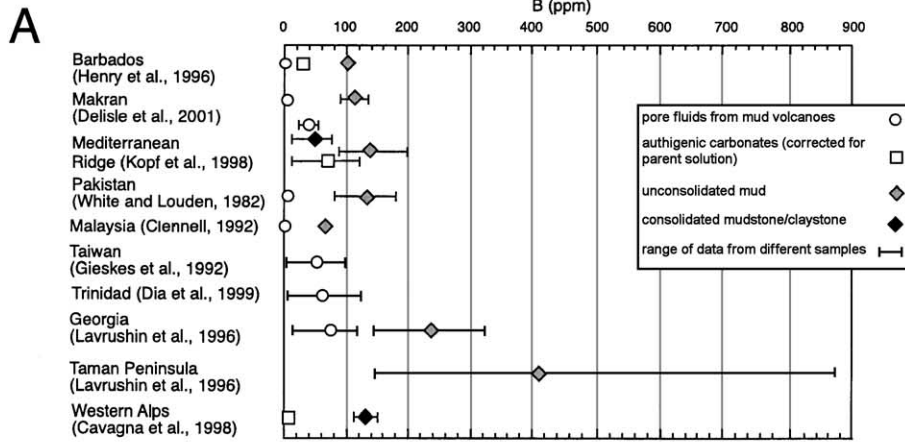
One aspect which complicates the behaviour of B in clays is the transformation of smectite to illite when temperature and stress increase (e.g. Colten-Bradley, 1987). Hydrothermal experiments have demonstrated that some of the B in the pore fluid can be incorporated into the illite mineral lattice (substituting Si; e.g. Williams et al., 2001), but may also be re-adsorbed if confining pressures are sufficiently low (or porosity sufficiently high) to allow for fluid saturation of the clay (see discussion in Fitts and Brown, 1999). These laboratory results suggest that in a natural MV scenario, both muds and fluids may have high B concentrations. With progressive illitization (i.e. greater mobilization depth of the mud), the B content in the mud is expected to increase (e.g. Perry, 1972), while $\delta^{11}\text{B}$ of the mud decreases (Williams et al., 2001).

4. Results and discussion

The mineralogical composition of the muds and mudstones shows some general similarities, with clay minerals being the dominant phase in all samples (see relative abundance in decreasing order; Table 1). Variations between samples from the same MV area,

or even the same mud volcano, can best be explained by the chaotic nature of mud breccias. As has been shown earlier (e.g. Kopf et al., 1998), the mud matrix is often peppered with polymeric clasts. These clasts are believed to be collected during ascent of the mud mass, and hence represent the overburden rock in the area. During the sometimes vigorous upward migration and extrusion, some of the material from the overlying rock may be abraded and incorporated into the mud matrix. We consider this process to be of marginal importance as long as the number of measured specimens is sufficient to discriminate possible contamination. Note here that for the MVs with highest abundance of peculiar clast lithologies (e.g. Mediterranean Ridge; see Kopf et al., 1998), we have studied a larger number of specimens than for homogeneous, often clast-free mud domes (e.g. Barbados, Makran). The main minerals detected in samples from the Caucasus, Pakistan and the Western Alps are smectite/illite, quartz, kaolinite and chlorite. Illite is almost absent in the marine features. Albite, plagioclase or other feldspar minerals are rarely observed in the muds/mudstones. Minerals of the palygorskite group, pyrite, sepiolite and muscovite/biotite also occur in minor, but significant quantities (Table 1). The clay fraction ($<2\ \mu\text{m}$) shows a more or less systematic increase in illite over smectite content when approaching the deep-seated mud domes in continental collision zones. It can be seen that the relative abundance of illite over smectite is higher in the continental MVs (Caucasus, Pakistan, Western Alps; see Table 1, column 3), whereas MVs on the Mediterranean Ridge and Barbados show little illite. A recent study on the Mediterranean MVs confirms that the muds contain largely kaolinite, halloysite, to a lesser extent smectite (sometimes chloritized), but only traces of illite (Zitter et al., 2001). All data presented are normalized ratios of illite compared to total clay fraction (Table 1, third column from left).

Boron concentrations in the mud matrix and mudstone clasts range around 100 ppm in the modern MVs of the accretionary prisms of Barbados and Makran, and increase to up to ~ 200 ppm in the mature, hinterlandward MVs of the Mediterranean Ridge, Pakistan and Malaysia (Table 1 and Fig. 4A). In the Caucasus, where illite dominates over smectite, B reaches maximum concentrations of 323 ppm (Geor-



gia) and 868 ppm (Taman Peninsula; Fig. 4A) in the unconsolidated mud. The fossil, well-lithified MV in the Italian Alps, has 118–138 ppm B (Table 1), which is remarkably high given that this feature has experienced the entire Alpine orogeny including B-removal by diagenetic alteration, B desorption and lithification. As for the corresponding fluids to the muds/mudstones, a similarly systematic trend is seen across the synthetic transect studied (Fig. 4A). While the frontal accretionary wedges of Barbados and Makran have <10 ppm B in their MV pore fluids, both modern fluids and their authigenic precipitates in the Mediterranean MVs reach up to 95 and 52 ppm, respectively. In the uplifted forearcs on land, both Pakistan and Malaysia MV fluids have low B contents; however, these data probably reflect an influx of meteoric water (Haile and Wong, 1965) rather than release of clay mineral water due to increasing compressional stress. The Caucasian mud volcano pore waters show B enrichment with up to 115 ppm, indicating that a deep-seated, mature fluid migrated 6–10 km up-dip along the abundant faults in the orogenic wedge (Lavrushin et al., 1996). This upper range in Caucasian pore fluids is equivalent to an approximately 25-fold B enrichment compared to modern seawater. By contrast, fluid composition of the *Verrua* MV in the northern Italy has been related back from cemented chimneys, which are believed to represent ancient fluid conduits. B concentration is found to be only 4 ppm, which either reflects freshening owing to mineral dehydration reactions, or diagenetic alteration of the carbonate during and after Alpine orogeny. When excluding this value as well as the one of proposed meteoric overprint (i.e. Malaysia), a profound increase in B correlates with the inferred regional mobilization depth of the fluid (see next paragraph, Fig. 4A and C and references therein). The considerable scatter in the data is mostly caused by variable composition of the extruding, inhomogeneous mud mass. As mentioned before, admixture of abraded wall rock or clast material may locally affect the mud matrix composition. For this reason, average values are presented in Fig. 4; how-

ever, the full range of data is expressed by the horizontal bars and is also given in Table 1.

$\delta^{11}\text{B}$ isotopes of the clays and claystones do not exceed 15‰, which agrees in broad terms with earlier studies on marine sediments (Ishikawa and Nakamura, 1993). The scatter in the data reflects regional variation of the source bed the mud volcanoes originate from, so that their use for depth estimates is limited. However, the isotopes are an important tool, as illustrated by the fact that older, well-lithified mudstones show lower $\delta^{11}\text{B}$ than unconsolidated muds in the same setting (cf. Mediterranean Ridge, av. 3.7‰ for mud, av. 2.4‰ for mudstone, Table 1). This can be attributed to preferential loss of the heavy ^{11}B isotope during diagenesis and smectite–illite transition (You et al., 1993, 1996). Also, less pronounced deformation in the Lesser Caucasus (av. 2.8‰) compared to the main collision zone (Greater Caucasus, av. –0.6‰; Table 1) is reflected by the lower $\delta^{11}\text{B}$ ratio of the muds. The fluid isotope ratios scatter across the synthetic transect of MV domains for a variety of reasons, e.g. influx of warm fluids in the case of Barbados (e.g. Henry et al., 1996), and meteoric water as well as near-surface ground waters in Malaysia (Haile and Wong, 1965; Clennell, 1992). All other sampling locations are characterized by pore fluids scattering around 30‰, some more closely (e.g. Makran: 28.1–31.1‰) than others (e.g. Georgia: 22.4–40‰). $\delta^{11}\text{B}$ values from pore fluids also agree with those from authigenic crusts and cements of the same mud dome province. On the Mediterranean Ridge, $\delta^{11}\text{B}$ ratios obtained from HCl-soluble crusts range between 23.4‰ and 38.1‰ (calculated parent solution), while the pore fluid yielded 25.5–33.6‰ (direct measurement; see Table 1). In general, the wealth of fluid $\delta^{11}\text{B}$ ratios is similar to those reported from other large accretionary complexes where deep-seated fluid was recovered at the décollement fault zones (e.g. Nankai and Barbados; You et al., 1993). The high B concentrations and low (relative to seawater) $\delta^{11}\text{B}$ data of the décollement fluids have been explained by B desorption at greater depth.

Fig. 4. (A) Boron content versus proposed depth of mud and fluid mobilization based on regional geology and B data from the literature; (B) $\delta^{11}\text{B}$ versus proposed depth of mud and fluid mobilization based on regional geology and B data from the literature. The symbols in the plots represent mean average, while bars show the range of results. (C) Corresponding processes in the mud volcano provinces with respect to mud mobilization mechanism and B geochemistry. The depths of mobilization for solid and fluid components of the mud breccias are also shown (see references in A for source of data); note that we extrapolated the thickness of the overburden for the fossil example from the Alps.

To assess the effect of increasing burial temperatures in the mud reservoir at depth on the B geochemistry, regional thermal gradients, heat flow data and geological depth estimates of the parent bed are required. Once in situ heat flow measurements are used to define the thermal gradient, this value can be multiplied with the depth of the parent bed, and the inferred in situ temperature at the depth of the mud reservoir results. We have compiled such data from the literature for each of the mud volcano provinces studied. In many areas, both the thermal gradient and the parent layers have been characterized by scientific (e.g. Mediterranean Ridge, Robertson et al., 1996) or industry drilling (Caucasus, Lavrushin et al., 1996). In other areas, local outcrops (Malaysia, Pakistan) or the maturity of organic compounds in the mud (Mediterranean Ridge) provide clues to the depth of origin. The depth estimates for both fluid and mud mobilization are given on the y -axis of Fig. 4C (refer to the y -axis of Fig. 4A for the references where information was compiled from). In addition, some regional information was taken from the global MV compilation by Kopf (in press).

Plotting the difference between $\delta^{11}\text{B}_{\text{mud/mudstone}}$ and $\delta^{11}\text{B}_{\text{fluid}}$ versus temperature has previously been used to illustrate B fractionation between fluids and silicates in closed laboratory experiments (Williams et al., 2001). If the same is done with the $\delta^{11}\text{B}$ results from the MV specimens, we observe a good correlation of the different areas with prograde illitization due to inferred burial depth (Fig. 5). With the exception of the Malaysia feature, our MV data resemble a trend established earlier from $\delta^{18}\text{O}$ isotopes of smectite–illite clays (Yeh and Savin, 1977). This suggests to us that, despite active flux may occur at some of the mud domes sampled (e.g. Napoli MV on the Mediterranean Ridge; see Corselli and Basso, 1996), re-equilibration between mud and fluid at depth has occurred in the majority of the MV areas. As already mentioned in the discussion of the B fluid concentration (see above), the excursion of the Malaysian mud dome very likely results from the anomalous $\delta^{11}\text{B}$ from meteoric water influx. However, the overall agreement of the data supports our hypothesis that B geochemistry can be used to trace the depth of mud volcano roots (i.e. faults) in an accretionary or oro-

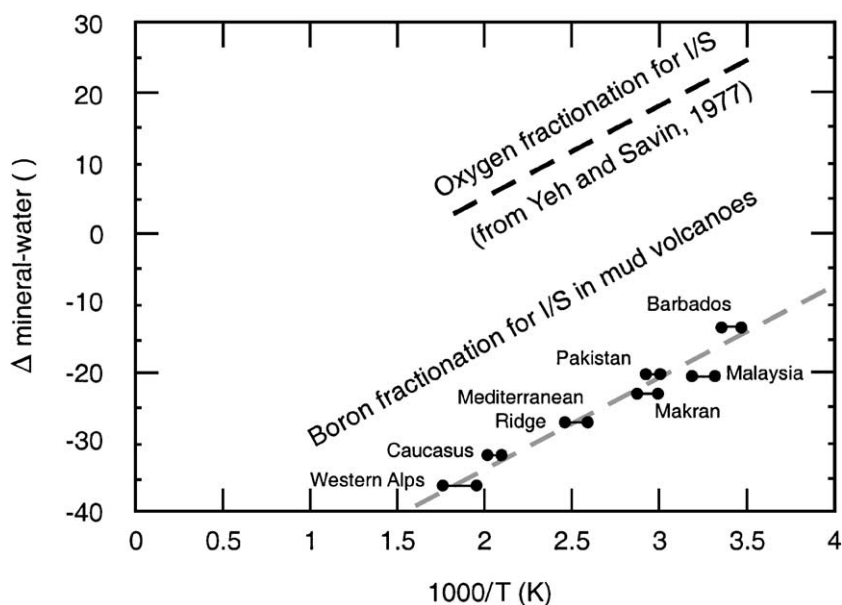


Fig. 5. Boron isotope ratios of different mud volcano provinces (as $\Delta\delta^{11}\text{B}$ mud and $\delta^{11}\text{B}$ fluid) versus temperature (as $1000/T$ K), where the temperatures are estimated from the average depth of the mud and fluid in each area using the regional geothermal gradient (see Fig. 4) and average $\delta^{11}\text{B}$ data are taken from Table 1. For reference, we show $\delta^{18}\text{O}$ isotope data of smectite–illite clays from Yeh and Savin (1977). Note that the dashed line through the mud volcano data is not a calculated best fit, but the projected relationship from the oxygen isotopes during illitization.

genic wedge (Fig. 2). At first glance, however, it may be intriguing that B fractionation appears to increase with increasing temperature, while it has been generally agreed upon that fractionation decreases. One explanation for the observed increase may be the uptake and incorporation of light structural B ($\delta^{11}\text{B} \sim -5\text{‰}$; Spivack et al., 1987) into the illite lattice, which clearly coincides with the fluid isotope ratio getting heavier, so that $\Delta\delta^{11}\text{B}$ becomes more negative (Fig. 5). Consequently, the trend of $\Delta\delta^{11}\text{B}$ versus temperature based on the mud volcano results is opposite to that from laboratory experiments on highly variable silicate rocks (Williams et al., 2001), but similar to the oxygen isotopic evidence (see Fig. 5 and Yeh and Savin, 1977). Most likely, Williams et al. (2001) failed to notice the relative enrichment of the fluid phase in ^{11}B because the fluid isotopic ratio was estimated, not measured.

If put into a global context, our results bear some significant ramifications for boron budgets in the hydrosphere. Despite the regional variations of the MV settings and the scatter resulting from the potpourri of materials involved in these ejected mélanges and breccias (e.g. Barber et al., 1986; Kopf et al., 1998), boron seems to follow systematic enrichment-depletion patterns with more pronounced collision (Fig. 4C). In order to fully acknowledge B cycling, we briefly discuss the mechanism of mud extrusion. The lithologic sedimentary unit the ascending and extruding mud originates from (i.e. parent bed) is often deeply buried for several million years (Higgins and Saunders, 1974; Kopf, in press). Consequently, even thick, low-permeability sediments compact, and remobilization and liquefaction (Terzaghi, 1947; Brown, 1990) is required prior to mud extrusion. Fluid entrainment, originating from greater depth or a lateral source (Fig. 1), can generate secondary overpressure in low porosity rocks (Moore and Vrolijk, 1992), and this may disaggregate the mudstone fabric. Although physical compaction of fine-grained sediments is largely irrecoverable, swelling clays such as smectites may re-adsorb considerable amounts of water, thereby decreasing bulk density. Being less dense than the overburden, the swelled muds start to ascend diapirically, form piercements or exploit zones of structural weakness such as faults or fractures (Figs. 1 and 3A). In the end, B from several kilometers subbottom depth may

end up on the earth's surface, and hence often in the ocean.

When related to our boron results, the mud volcanic dynamics are mirrored by a trimodal distribution (Fig. 4C). The B geochemistry of the frontal end members ([1–3] in Fig. 2) reflects extrusion of marine mud containing its initial, unaltered pore fluid. Towards the hinterland, muds consolidate under increasing PT conditions, donating adsorbed B to the pore fluid. This continuous desorption (Fig. 4C, light gray shading) results in geochemically mature, B-rich fluids with isotope ratios around 30‰ (Fig. 4A and B). Fluid signatures do not change significantly in MVs of orogenic wedges (cf. Georgia and Taman Peninsula, where the fluid originates at 6–10 km depth; Lavrushin et al., 1996), which coincides with fluid compositions from prominent MV provinces in Taiwan (Gieskes et al., 1992) and Trinidad (Dia et al., 1999) (Fig. 4B). However, the muds from these evolved collisional belts show strong enrichment in B, its maximum values of 868 ppm (Taman Peninsula) exceeding those of marine clays (Ishikawa and Nakamura, 1993) by a factor of 8. Such elevated concentrations may originate from secondary processes related to the liquefaction of the mud source layer. Our results suggest that interaction of deep-seated, B-rich fluids allow liquefying clays to re-adsorb and incorporate large quantities of dissolved B (Fig. 4C, dark gray shading; see also Keren and Gast, 1981). During swelling of the clays, two distinct mechanisms may cause enrichment in boron. In a first, relatively rapid process, adsorption of dissolved $\text{B}(\text{OH})_4^-$ anion occurs at the “frayed-edge” of the clay mineral surface (Couch and Grim, 1968). Owing to concentrations above the limit of maximum adsorption for clay minerals (Keren and Mezuman, 1981), this process is followed by the much slower diffusion of dissolved B into the clay mineral structure, and namely the sheets of linked (Si, Al) O_4 tetrahedra (Couch and Grim, 1968). Keren and Gast (1981) have demonstrated that repeated hydration (termed “re-wetting” by these authors) of clays enhances their capacity of B uptake. A priori, a liquefied parent bed claystone is expected to have higher B concentrations than a fresh clay of the same composition. In addition, early workers have shown that during the temperature-driven transformation from smectite to illite, B contents increase as well (e.g. Perry, 1972). In fact,

illite can incorporate about twice as much B into its mineral lattice than smectite. The transformation reaction at the depth of the parent bed layer, where temperatures can be quite high (see Figs. 4 and 5), may hence significantly increase the B content of the mud. Our data (Fig. 4A) show exactly this behaviour of increasing B content with progressive illitization due to deeper re-equilibration at parent bed level.

5. Conclusions

As a consequence of the locally high fluid discharge of MVs (Kopf et al., 2001) and the generally high B concentrations involved (Table 1 and Fig. 4), we propose that mud volcanism may have a significant influence on the global geochemical cycle of boron, which has previously not been accounted for. Whereas sinks of dissolved seawater B have been identified (including alteration of oceanic crust, adsorption to sediments and incorporation into biogenic and inorganic carbonates; e.g. Spivack et al., 1987; Vengosh et al., 1991; You et al., 1993), the knowledge about B sources to the ocean is rather limited. Hydrothermal vents at mid-ocean ridges contribute only marginally (Spivack et al., 1987), so that venting along faults rooting deep in subduction zones has been put forward as main B donor (You et al., 1993). This B backflux from subduction zones likely exceeds the amount of B being recycled in volcanic arc magmas, or the earth's mantle. We suggest that, next to fluid flow along faults, mud volcanism is a main contributor to boron backflux into the ocean (see hypotheses (i) and (iv) above). As a result of the complex trend of desorption and re-adsorption and diffusion of boron to clay minerals, large quantities of B can be fixated temporarily and transported upwards over several kilometers in extruding liquefied muds (see hypothesis (ii) above). Mud B contents are up to $8 \times$ higher than other modern marine sediments, while MV fluids are up to $25 \times$ more enriched in B than modern seawater. Also, mud volcano fluids are generally characterised by $\delta^{11}\text{B}$ ratios lower than seawater (see hypothesis (i) above), resulting from adsorbed B values around 15‰ (Spivack et al., 1987; Williams et al., 2001). The re-equilibration between mud and fluid in MVs is suggested from the linear relationship between $\Delta\delta^{11}\text{B}_{\text{rock/mineral}} - \delta^{11}\text{B}_{\text{fluid}}$ of the

features studied (Fig. 5). Hence, B isotopes may be used as a proxy to estimate burial history as a function of progressive illitization of smectite in mud volcano clays (see hypothesis (iii) above). Given that the B contents of both muds and fluids are much higher than those of average marine sediments and pore fluids (e.g. Ishikawa and Nakamura, 1993), and given further the large number of MVs on earth (Kopf, in press) and the extremely high discharge rates in some mud dome areas (Kopf et al., 2001), we propose that active mud volcanism is an important mechanism of global B backflux into the hydrosphere. Having said this, we also acknowledge that MV fluid discharge may vary considerably in both space and time, which severely hinders reliable estimates for all convergence zones on earth. However, the quantification of B flux through MVs on a global basis, especially in comparison with riverine input and other players in the global B budget (see Lemarchand et al., 2000), will be a challenging endeavour in the future.

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