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Alteration of submarine basaltic glass from the Ontong Java Plateau: A STXM and TEM study

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Abstract

Frequent observations of tubular to vermicular microchannels in altered basalt glass have led to increasing appreciation of a possible significant role of microbes in the low-temperature alteration of seafloor basalt. We have examined such microchannel alteration features at the nanoscale in basalt glass shards from the Ontong Java Plateau using a combination of focused ion beam milling, transmission electron microscopy and scanning transmission X-ray microscopy. Three types of materials were found in ultrathin cross-sections cut through the microchannels by FIB milling: fresh basalt glass, amorphous Si-rich rims surrounding the microchannels, and palagonite within the microchannels. X-ray absorption spectroscopy at the C K-edge and Fe $L_{2,3}$-edges showed the presence of organic carbon in association with carbonates within the microchannels and partial oxidation of iron in palagonite compared with basalt glass. Although these observations alone cannot discriminate between a biotic or abiotic origin for the microchannels, they provide new information on their mineralogical and chemical composition and thus better constrain the physical and chemical conditions prevailing during the alteration process.

Keywords: basalt; glass alteration; palagonite; TEM; bacteria

1. Introduction

The alteration of ocean basalts partly controls the composition of seawater and of the oceanic crust (*e.g.*, Edmond et al., 1979; Hart and Staudigel, 1982), which in turn influence the Earth's mantle geochemistry and dynamics (*e.g.*, Hofmann and White, 1982; Bach et al., 2003) and the O_2 content of the atmosphere (*e.g.*, Lecuyer and Ricard, 1999). Alteration of oceanic basalts may also have a significant impact on Earth's climate on geological timescale by providing a sink for atmospheric CO_2 through carbonatization of oceanic basalts (*e.g.*, Staudigel et al., 1989; Caldeira, 1995; Brady and

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Gislason, 1997; Sleep and Zahnle, 2001). Understanding the dominant mechanisms of oceanic crust alteration at low temperatures is thus critical for assessing the rate-controlling steps of chemical exchange and improving existing models of Earth's geodynamic evolution throughout geological time.

A vast literature exists about low-temperature alteration of seafloor basaltic glass (*e.g.* Staudigel and Hart, 1983; Zhou and Fyfe, 1989; Crovisier et al., 2003; Schramm et al., 2005). Over the two last decades, an increasing number of studies have proposed that microbes mediate alteration of volcanic material in the oceanic crust leading to the inference that an extensive subsurface biosphere exists within the basaltic basement of the uppermost ocean crust (*e.g.* Thorseth et al., 1992, 1995a; Staudigel et al., 1998; Furnes et al., 2001a; Banerjee and Muehlenbachs, 2003). This idea is based on textural, chemical, and microbiological observations. For example, spherules of varying sizes (0.3–10 µm) within fresh glass as well as tubes or vermicular channels (1–10 µm wide by up to 100 µm long) have been interpreted as resulting from microbes dissolving and tunnelling into the glass. The altered glass areas have elevated levels of C, N, P and K which have been attributed to the presence of microbial cells (*e.g.*, Torsvik et al., 1998; Banerjee and Muehlenbachs, 2003). The lower δ^{13}C values of carbonates disseminated in altered basalt compared to those of fresh crystalline basalt have been interpreted as resulting from oxidation of organic carbon (Furnes et al., 2001b; Banerjee and Muehlenbachs, 2003). Microbial-like forms have been observed by SEM in association with the channels (Banerjee and Muehlenbachs, 2003) and a diverse community of Bacteria and Achaea has been characterized based on 16S rRNA gene amplification of DNA in altered basalts (Thorseth et al., 2001; Lysnes et al., 2004). Positive staining by ethidium bromide, acridine orange or DAPI (4′, 6-diamidino-2-phenylindole) in the microchannels has been interpreted as evidence for the presence of nucleic acids (*e.g.*, Thorseth et al., 1995a; Banerjee and Muehlenbachs, 2003). Finally, it has been reported that these alteration features only develop in a very specific depth and temperature window that is compatible with life (Furnes et al., 2001a; Walton and Schiffman, 2003; Staudigel et al., 2006).

Despite the reports of some etch pits produced by microbes in laboratory experiments with basaltic glass (Callot et al., 1987; Staudigel et al., 1995, Thorseth et al., 1995b), the microchannel texture has not been reproduced so far either in biotic or abiotic laboratory experiments (Thorseth et al., 1995b). A consistent biochemical mechanism has, however, been suggested for localized dissolution of glass along microchannels, which are thought to result from colonizing bacteria that produce acidic substances which locally change the pH and hence dramatically enhance dissolution of the glass (*e.g.*, Staudigel et al., 2006). This texture and associated geochemical features have been used as a signature of former biological activity. One example is the use of such a texture and features to infer the existence of ~ 3.5 Ga old traces of life in weathered basalts from Archean greenstone belts (Furnes et al., 2004; Banerjee et al., 2006; Staudigel et al., 2006).

A further detailed study of such alteration textures in modern basaltic glass, in particular the speciation of carbon and characterization of associated nanophases, may provide additional constraints on the conditions of alteration. Here we present the results of a nanoscale study of microchannel features in basalt glass shards from the Ontong Java Plateau using a combination of Focused Ion Beam (FIB) milling, Transmission Electron Microscopy (TEM) and Scanning Transmission X-ray Microscopy (STXM), which is a transmission microscopy based on synchrotron radiation. These techniques provide an unprecedented insight into the compositional variations and mineralogy of the purported microbial microchannels at the nanoscale.

2. Experimental methods

2.1. Samples

The samples for this study were recovered during Leg 192 of the Ocean Drilling Project (ODP) from Hole 1184A located at depth of 1661.1 m on the eastern lobe of the Ontong Java Plateau. We studied samples from Unit 2 which are volcaniclastic rocks consisting of ash- to lapilli-sized lithic clasts and vitric shards, accretionary lapilli, armoured lapilli, and crystal fragments (plagioclase and pyroxene) in a matrix of fine grained vitric and lithic ash, clay and other alteration minerals cemented by smectite, analcime, calcite, rare celadonite, and several zeolites. Preliminary analyses of glass shards throughout the volcaniclastic unit suggest they are restricted to a narrow range of basaltic compositions and eruption of the volcaniclastic units was likely penecomtemporaneous with the main plateau magmatic event at 122 Ma (Banerjee and Muehlenbachs, 2003). We re-observed one of the thin sections prepared by Banerjee and Muehlenbachs (2003) that contained variably altered glass shards in which textures of possible microbial origin had been observed. This thin section was gold coated before Focused Ion Beam milling.

2.2. Focused ion beam milling

Focused ion beam milling was performed with a FEI Model 200 TEM FIB system at the University Aix-Marseille III. The FIB lift-out method was used to prepare the sample as described in Heaney et al. (2001). The same area as that observed by optical microscopy could be located using FIB imaging capabilities. A thin layer of platinum was deposited on the specimen perpendicular to the general direction observed for the microchannels. The FIB system uses a Ga liquid metal ion source for milling. A 30 kV Ga$^+$ beam operating at $\sim$ 20 nA excavated basaltic glass from both sides of the Pt layer to a depth of 4 μm. Before removal of the thin section, the sample was further thinned to $\sim$ 80 nm with a glancing angle beam at much lower beam currents of $\sim$ 100 pA. Finally, a line pattern was drawn with the ion beam along the side and bottom edges of the thin section allowing its removal. The $\sim$ 16 μm × 4 μm × 80 nm slide was transferred at room pressure with a micromanipulator on to the membrane of a carbon-coated 200 mesh copper grid. Similar FIB cross-sections across microbe–mineral interfaces have been previously successfully prepared using the same protocol (Benzerara et al., 2005). Another study of silicate weathering using FIB and TEM, discussing potential amorphization at the surface of the FIB foil resulting from beam damages during FIB milling, is presented in Lee et al. (in press).

2.3. Transmission electron microscopy, EDXS and EELS analyses

TEM observations were carried out on a Jeol 2100F microscope operating at 200 kV, equipped with a field emission gun, a high resolution UHR pole piece and a Gatan energy filter GIF 200. Energy dispersive X-ray spectrometry (EDXS) analyses were performed using a JEOL detector with an ultrathin window allowing detection of light elements. Electron energy loss spectroscopy (EELS) spectra were acquired using a dispersion of 0.3 eV/channel in order to record spectra in the range 250 eV to 560 eV. The energy resolution was about 1.1 eV as measured by the full width at half maximum of the zero-loss peak. The dwell time was optimized to acquire sufficient signal intensity and to limit beam damage.

2.4. Scanning transmission X-ray microscopy

STXM observations were performed at the ALS branch line 11.0.2.2 following the same procedures described in Bluhm et al. (2006) and Benzerara et al. (2004a). The synchrotron storage ring operated at 1.9 GeV and 200–400 mA stored current. A 1200 l/mm grating and 40 μm exit slit were used for carbon imaging and spectroscopy, providing a theoretical energy resolution of 72 meV. A 1200 l/mm grating and 25 μm exit slit

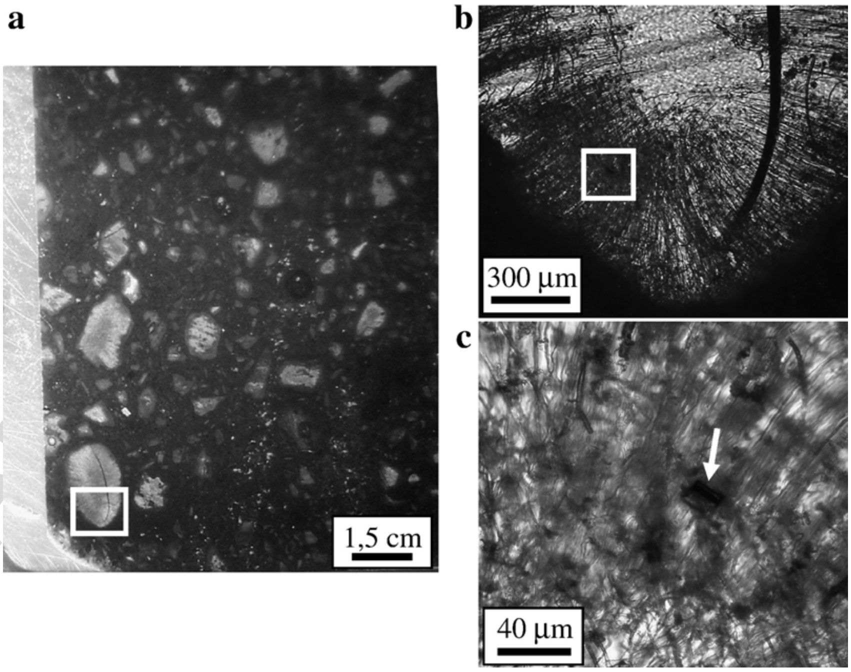


Fig. 1. Optical photomicrograph observation of the sample. (A) General view of the petrographic thin section that was sampled showing glass shards surrounded by a clay-rich matrix. (B) Close-up of the area enclosed in rectangle in (a). The photomicrograph shows abundant microchannels radiating inward from the edges of the glass shard. (C) Location of one FIB foil (arrow) oriented perpendicularly to the general direction of dense microchannels.

were used for iron imaging and spectroscopy, providing a theoretical energy resolution of 140 meV. Energy calibration was accomplished using the well-resolved 3p Rydberg peak at 294.96 eV of gaseous CO_2 for the C K-edge, and the major peak of hematite at 709.5 eV for the Fe $L_{2,3}$ edges. Rationale for STXM data acquisition and analysis can be found for example in Hitchcock (2001) and Jacobsen et al. (2000).

3. Results

The basaltic clasts in the volcanic tuffs from the Ontong Java Plateau were previously examined and characterized by optical microscopy, electron microprobe, SEM and laser scanning confocal microscopy by Banerjee and Muehlenbachs (2003). This previous study documented microchannels, 1–5 µm wide, extending up to tens of microns inward from the edge of the clasts, and they are similar to those observed by several previous studies of oceanic basaltic glass (*e.g.* Fisk et al., 1998; Alt and Mata, 2000; Furnes et al., 2001a). The same sample from the Ontong Java Plateau described by Banerjee and Muehlenbachs (sample 1184R-13R-3 142–145 cm; 2003) was studied here, and one of the glassy shards in the volcaniclastic tuff that showed a dense accumulation of microchannels was selected for FIB milling and further characterized by TEM and STXM (Fig. 1). Two FIB foils were obtained across the microchannels (Figs. 2 and 3). TEM imaging and EDXS analyses showed that the basaltic glass is very uniform texturally and compositionally (Figs. 2 and 4) and is amorphous in electron diffraction. Microchannel cross-sections have a smooth, roughly circular shape. A 30 nm wide continuous rim of amorphous silicon-rich material surrounding the microchannels was systematically observed. It differs dramatically in composition from fresh glass and from the inner filling of the channels (Fig. 4). No compositional gradient was detected between the fresh glass and the amorphous rim by EDXS. Although the sizes of single channels were sometimes difficult to measure because of coalescence of the complex structures (Fig. 2), diameters of the microchannels were estimated to range between 520 and 820 nm, based on meaurements of 14 different channels.

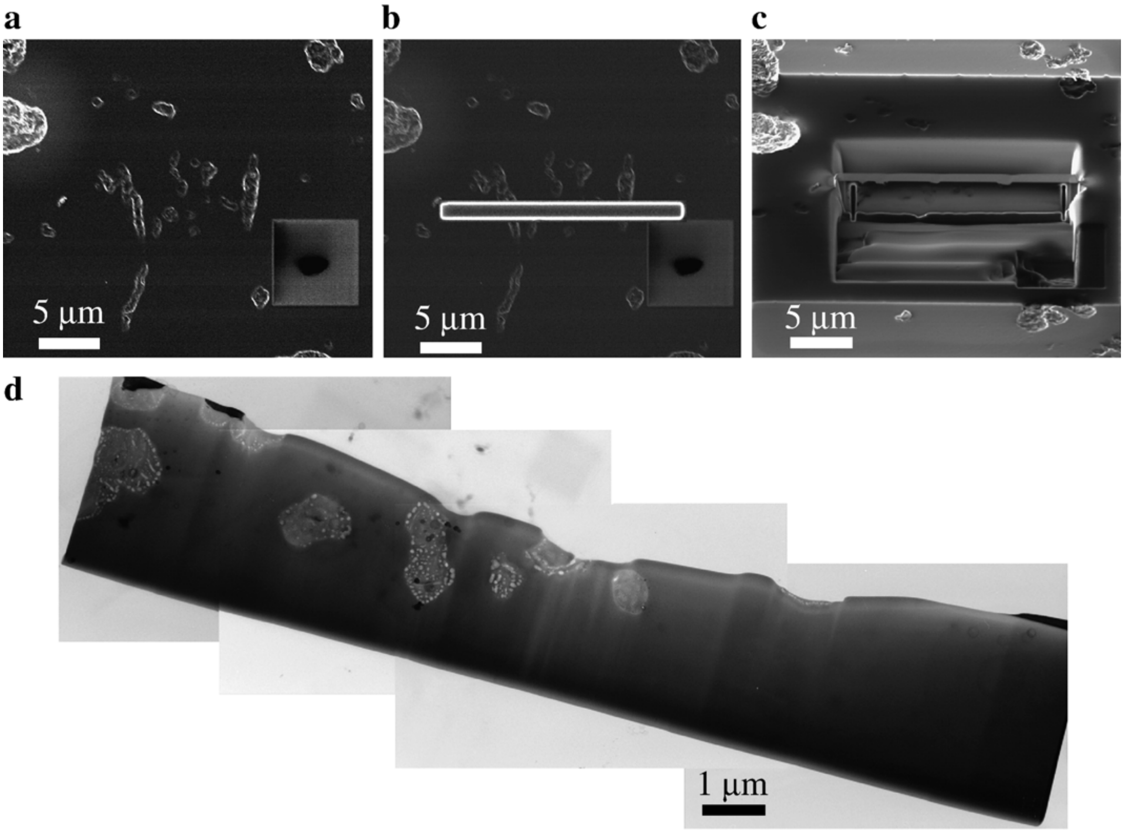


Fig. 2. Focused Ion Beam (FIB) cross-sectioning of the microchannels. (a) FIB image of the sampled area before the deposition of platinum. N–S oriented cracks correspond to the intersection of microchannels with the surface of the thin section. (b) Same area after the deposition of a platinum layer indicating the position of the FIB foil. (c) FIB image of the ultrathin foil in place before the micromanipulator-assisted extraction stage. (d) TEM image of the foil showing the basalt glass (dark grey area) and the microchannels (lighter grey ovals).

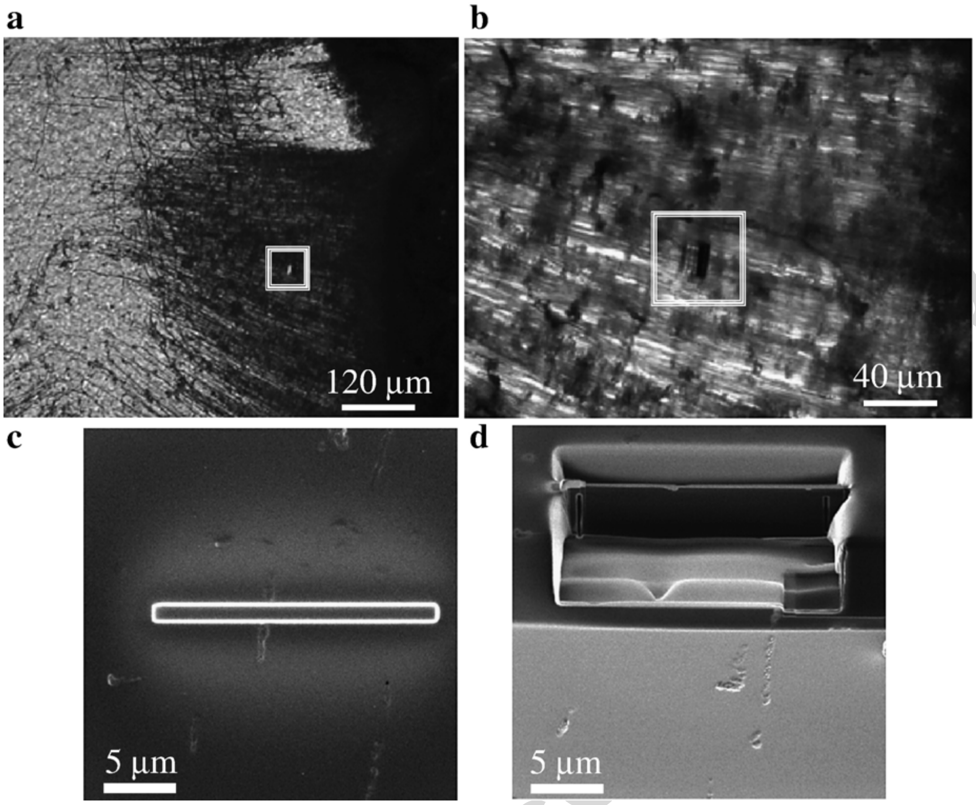


Fig. 3. Focused Ion Beam (FIB) cross-sectioning of microchannels on another area. The location of the area where this FIB cross-section was prepared is shown in (a) and (b). The platinum strap is deposited perpendicularly to the microchannels (c). The FIB image of the ultrathin foil in place before the micromanipulator-assisted extraction stage is shown in (d).

All the microchannels are filled in by mostly amorphous to poorly crystallized minerals that display compositional and mineralogical features similar to palagonite. Palagonite is a heterogeneous substance predominantly composed of smectite-like phases, as well as possibly other clays, zeolites, oxides, and oxyhydroxides (Honnorez, 1967; Stroncik and Schmincke, 2002; Crovisier et al., 2003). As the term palagonite has been broadly used in the past for many different materials and as Stroncik and Schmincke (2001) have suggested restricting its usage to orange to yellow replacement products of basalt glass, we prefer to use the term microchannel-filling material or smectite in the manuscript. The use of EDXS data on such material is restricted by the analytical precision and the effect of loss of alkaline elements on the cation content of the smectite formula. This latter problem may explain the variations in the intensity of the Kα peak of K that we detected. Another difficulty is that analyses are not performed on a pure phase but possibly on very fine intergrowths of clays, oxides, and/or amorphous phases. EDXS analyses and electron diffraction pattern show that this microchannel-filling material is composed basically of Si, Al, O, Fe and Mg, and some Ca and K (Fig. 4) and is mostly consistent with an assemblage of dioctaedral (nontronite) and trioctaedral (saponite or stevensite) smectite. Slight chemical variations in some EDXS analyses show small Ti and/or Ca enrichment in some areas that may be due to the presence of Ti or Ca-rich phases that were difficult to further characterize. Nearly ten electron diffraction patterns were analyzed and showed diffused diffraction rings or spots (Fig. 4) with lattice spacings of 4.59, 3.53, 2.66, and 2.18 Å; these spacings are consistent with the (020), (− 112), (023) and (132) lattice planes, respectively, of nontronite. However, other mineral phases may also be present. Neither laminations nor fibrous and concentric textures were noticeable. Abundant void spaces (~ 50 nm wide), resulting in a porous texture, were observed, however (Fig. 4). Similar pores were interpreted by Zhou et al. (2001) to result from dehydration in the vacuum of the TEM. The transition between the aluminosilicate filling and the silicon-rich amorphous rim is very sharp (Fig. 4).

Spectroscopic analyses of the same foil performed prior to TEM observations provided additional information about the presence of carbon and on the iron oxidation state. The presence of carbon inside the

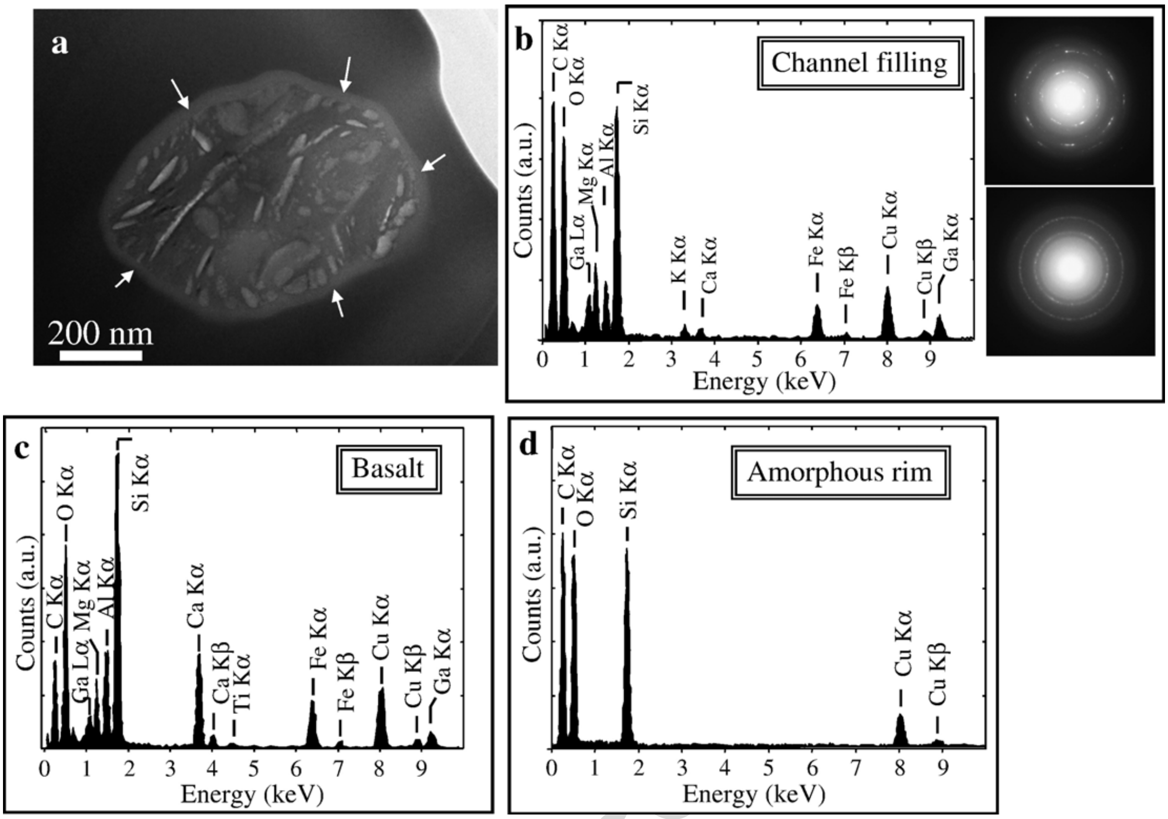


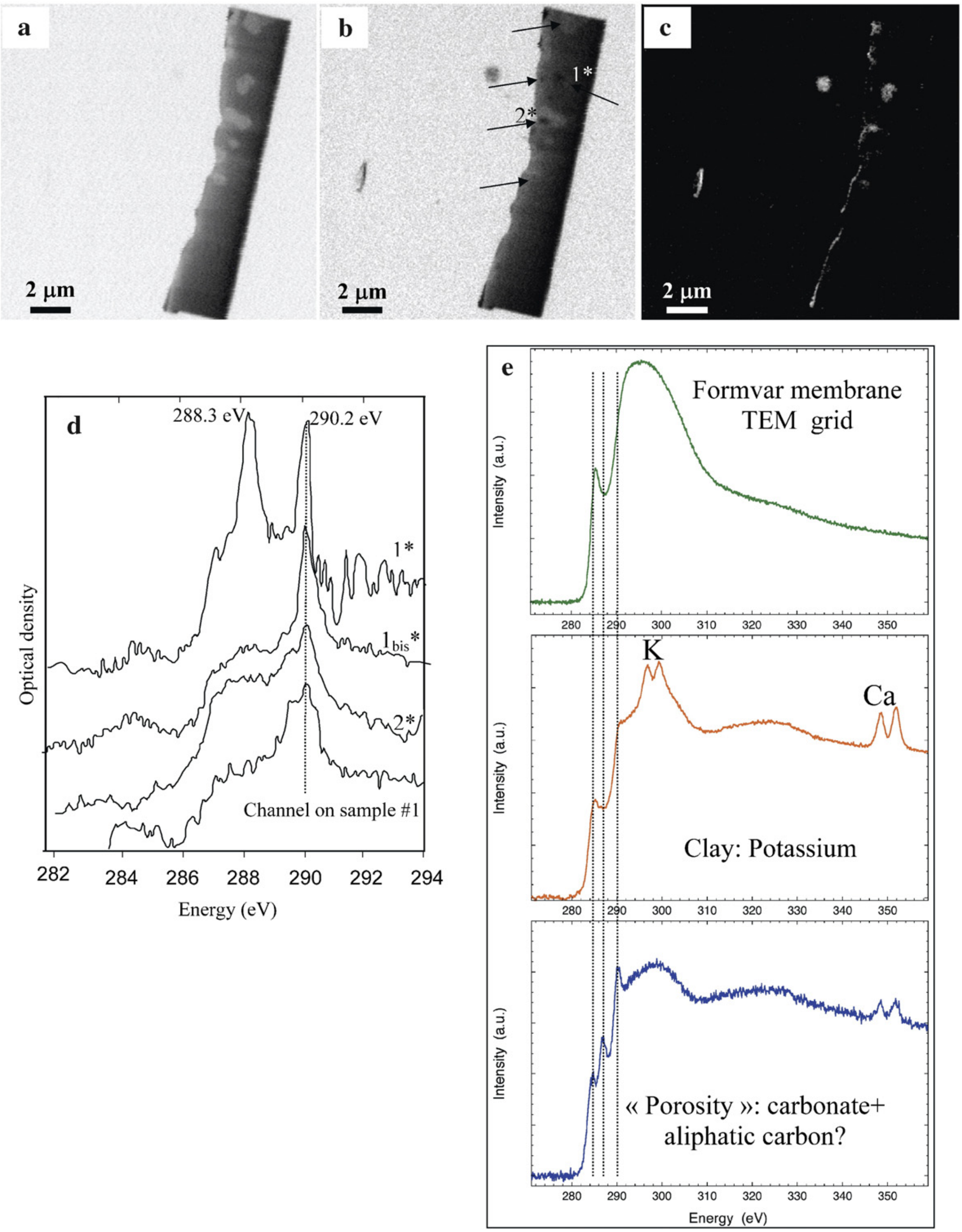
Fig. 4. TEM analysis of a microchannel. (a) TEM image of a microchannel showing the basalt glass (dark grey) surrounding an amorphous Si-rich rim (arrows) that surrounds the aluminosilicate filling within the microchannel. (b) EDX analysis of material filling the microchannel and electron diffraction patterns obtained on this material. (c) EDX analysis of the basalt glass. (d) EDX analysis of the Si-rich amorphous rim layer.

channels was shown by both STXM and electron energy loss spectroscopy (EELS) (Fig. 5). These spectroscopies provide additional constraints on the speciation of carbon because the edge energy and near-edge fine structure are sensitive to carbon oxidation state and the average local structural environment around carbon, respectively. Some of the carbon is unambiguously accounted for by carbonate groups as indicated by a peak at 290.3 eV in the spectra (Fig. 5) (*e.g.* Benzerara et al., 2006). The other peak noticeable in the spectra at 288.4 eV is tentatively interpreted as organic carbon, possibly carbonyl groups (Brandes et al., 2004). The quality of the spectra that could be obtained by STXM at the C K-edge was relatively poor due to a high absorption of the matrix and the relatively low carbon content. The STXM results were however supported by EELS results. Despite the theoretically high spatial resolution of EELS, it was difficult to locate these different compounds at the nm-scale. However, potassium (peaks at 297 and 299.5 eV, assigned to the K $L_{2,3}$-edge absorption) and carbon were both detected by EELS spectroscopy. Some EELS spectra showed the presence of organic carbon and carbonate but no potassium. Assuming that potassium is indicative of clays in these samples, this observation suggests that carbon is not intrinsically associated with the clays. Direct comparison with reference spectra (Fig. 5) showed that the organic carbon detected by EELS is not that the formvar membrane on which the FIB foil was deposited.

XANES spectra at the iron $L_{2,3}$ ($2p_{1/2,3/2} \rightarrow 3d$) edges were measured on the fresh glass and in the microchannels to obtain qualitative information on $Fe^{3+}/\Sigma Fe$ (see, *e.g.*,

Fig. 5. STXM and EELS analyses of the microchannels at the C K-edge. (a) STXM image below the C K-edge (280 eV). Channels appear in bright whereas the basalt glass appears in dark grey. (b) STXM image above the C K-edge at 288.2 eV; dark spots that were invisible on the image below the C K-edge can be observed inside microchannels indicating the presence of carbon (see arrows). (c) Map of carbon-containing areas absorbing at 288.2 eV (bright spots). The map was obtained by subtracting image (a) from image (b) after conversion in optical density units. The spots observed outside the FIB foil (on the left) are likely related to the cross-section itself and were detached from it during deposition of the section on the TEM grid by micromanipulation. (d) XANES spectrum at the C K-edge on a microchannel showing peaks at 288.3 eV and 290.2 eV. (e) EELS spectra measured on: (top) the formvar membrane of the TEM grid, (middle) a Potassium-containing (likely clay) spot, (bottom) a microchannel. Dashed lines indicate energy positions at around 285.5, 288 and 290 eV.

Crocombette et al., 1995). Iron spectra taken on the fresh glass show a major peak at 707.8 eV indicative of predominantly Fe^{2+} (Fig. 6). Microchannels displayed peaks at 707.8 eV and 709.5 eV indicating partial oxidation of iron (Fig. 6). As the $L_{2,3}$ X-ray absorption spectra are sensitive to iron coordination and crystal field strength, a



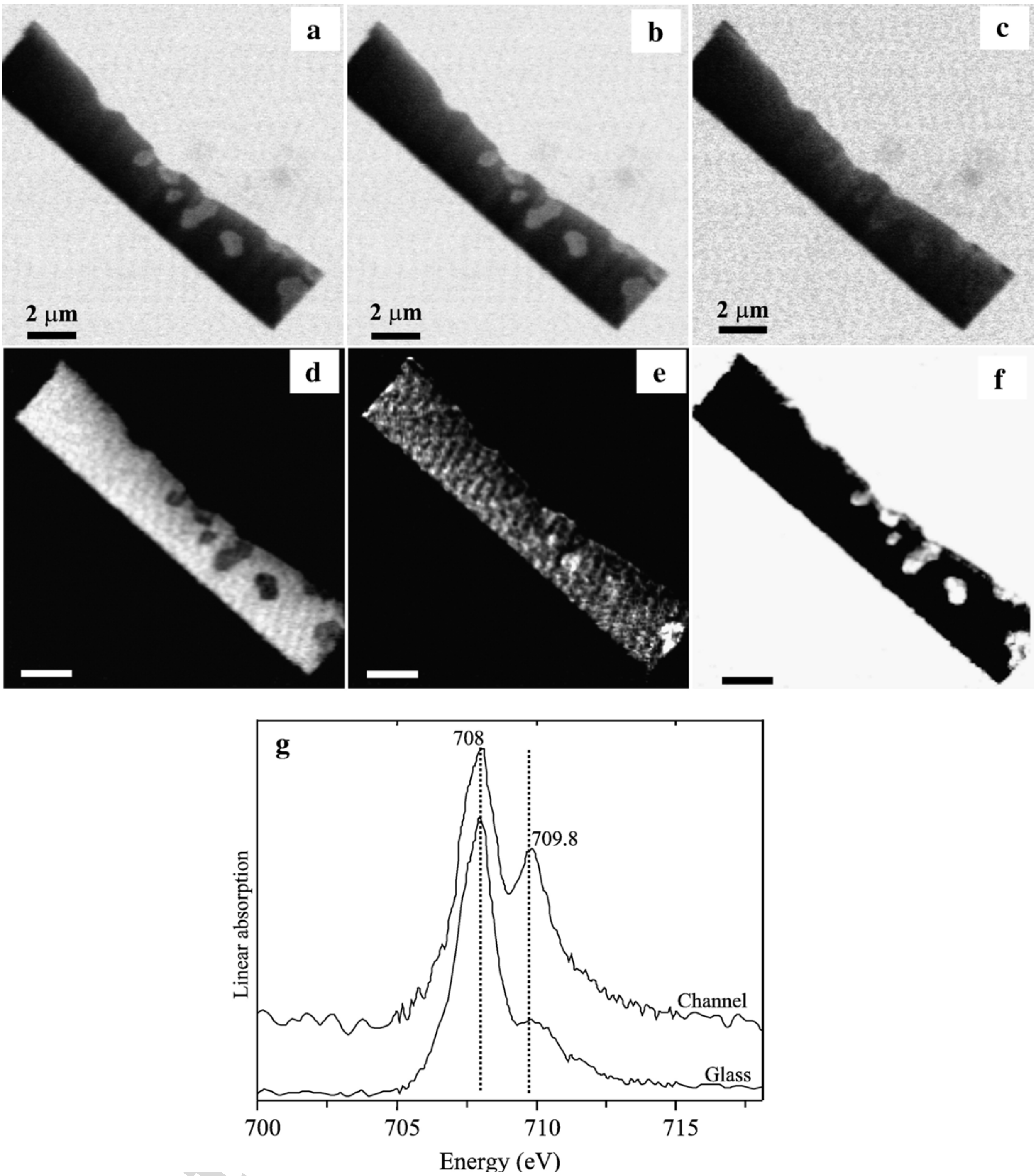


Fig. 6. STXM observations of the FIB cross-section at the Fe L_3 edge. (a) STXM image below the Fe L_3 edges (700 eV). (b) STXM image at 708 eV (corresponding to the energy where mostly Fe^{2+} is absorbing) (c) STXM image at 709.8 eV (mostly Fe^{3+} absorbing). (d) Map of areas absorbing at 708 eV obtained by subtracting image (a) from image (b) and indicating mostly Fe^{2+}-rich areas. (e) Map of areas absorbing at 709.8 eV *i.e.* both Fe^{2+}- and Fe^{3+}-containing areas. (f) Subtraction of (f) minus (e) indicating areas containing mostly Fe^{3+}. (g) XANES spectra in the basalt glass and in the microchannels at the Fe L_3 edge. Dashed lines represent the positions of Fe L_3 maxima for Fe^{2+} and Fe^{3+} at 708 and 709.8 eV, respectively.

quantitative analysis could not be achieved as it would require a more precise structural characterization of the microchannel-filling material than was possible here. Quick and longer spectra were acquired consecutively on the same area. No evolution of the spectra was detected upon time under the beam showing the absence of oxidation during data acquisition. FIB milling could potentially have produced indirectly redox artefacts by forming a thin amorphous layer at the surface of the FIB foil that could be more sensitive to iron oxidation. As this layer would form both on the basalt glass and on the microchannels, we would expect oxidation to occur everywhere. While this hypothesis needs to be further tested, artefactual oxidation seems to be invisible in the signal measured in transmission on the total thickness of the foil as almost only Fe(II) is measured on the basalt glass.

4. Discussion

4.1. Geochemical significance of microchannel formation

The microchannels that we have studied here at high spatial resolution seem from the literature to be pervasive in environments where basaltic glasses were altered at low temperature (*e.g.* Staudigel and Hart, 1983; Torsvik et al., 1998; Furnes et al., 2001a; Thorseth et al., 2001; Stroncik and Schmincke, 2002, Walton and Schiffman, 2003). It is therefore important to discuss their potential global geochemical significance.

Alt and Mata (2000) did not find evidence for Fe(III)-bearing oxides in microchannels and concluded that a reducing environment is present in microchannels with iron incorporated into secondary phases as ferrous ion. Minor amounts of Fe(III) exist in the magma and Fe(II)/Fe(III) was estimated to be 0.07 ± 0.03 in unaltered basaltic glasses by Christie et al. (1986). In the present study, we show that a significant part of the iron present in the microchannels is oxidized. This oxidation is very difficult to detect by conventional methods due to the small size of the structures and to the few nanometre size of the Fe(III)-bearing phases. Hence, the oxidation of iron in secondary phases reported in the present study could only be detected by STXM. It is very likely that Fe (II) from the basalt glass was partly oxidized leading to an Fe(III) bearing microchannel-filling material. The amount of iron that has been oxidized, however, cannot be assessed because of the difficulty of quantifying how much iron escaped during glass dissolution. Estimation of iron loss is further hindered by the need for ferrous and ferric iron standards with the same structure and matrix effects as the minerals comprising the microchannel-filling material in the sample to derive an accurate ferrous/ferric iron ratio from the Fe $L_{2,3}$ edges NEXAFS spectra shown here. The significance of this first microchannel-shaped alteration stage of oceanic basalt glass in establishing oxidation rate and the final global Fe(III)/Fe(II) ratio of the ocean crust is a question of interest that will require coupling such observations at the nanoscale with isotopic data potentially allowing mass balance estimates (*e.g.* Rouxel et al., 2003). Which oxidant and oxidation mechanism are involved is another issue to question. As an alternative to purely abiotic scenarios, microorganisms living on oceanic basalts using the oxidation of ferrous to ferric iron as an energy source (Edwards et al., 2004) are possible candidates for causing basalt Fe(II) oxidation, a process which has been substantiated by the finding of abundant iron oxidizers in oceanic environments (*e.g.* Emerson, 2002; Bach and Edwards, 2003). The possible relationships between microorganisms and microchannels will be discussed below.

The detection of pervasive carbonates inside the microchannels is another feature that has important geochemical implications. As mentioned above, the poor crystallinity (possibly partly resulting from FIB milling damages) and/or small size of the crystallites make the detection of carbonate minerals or carbonate groups impossible by most existing mineralogical characterization techniques. Using NEXAFS and EELS spectroscopy in this study, carbonate groups were detected systematically in all the microchannels investigated. They could not, however, be further characterized by electron diffraction due to their small size and the complex assemblage of mineral phases at the submicrometer scale, each phase being possibly much smaller than the thickness of the FIB section. This leaves open the question of the carrier phases of those carbonate groups. They might be associated with a phase such as hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}.4H_2O$), which was found in experimental studies of basalt glass alteration by Thomassin and Touray (1982), or with small-grained Fe and/or Mg and/or Ca carbonates. EELS spectroscopy revealed intriguing spatial correlations of carbonates groups with organic carbon, whereas some phyllosilicates were found to be clearly spatially distinct from carbonates. The questions of what temperature and pH conditions existed during carbonate formation and whether the source of carbonates is biologic or not will have to be addressed in future studies requiring sophisticated high spatial resolution analytical techniques to measure trace element concentrations and/or isotopic compositions *in situ*. The amounts of such carbonates not detected by standard techniques will also have to be quantified as well as the proportion containing cations released by basaltic glass dissolution. This information is indeed important for mass balance estimates of basalt carbonatization which may be an important process in the global carbon cycle (*e.g.* Brady and Gislason, 1997; Alt and Teagle, 1999; Sleep and Zahnle, 2001).

Finally, detailed studies of the mineralogy of the basaltic glass alteration phases may also provide constraints on the physical and chemical conditions that prevailed during the formation of the microchannels. In particular, further characterization of the phases comprising the tube-filling material may help in deciding whether they were formed under biocompatible conditions or not. The amorphous Si-rich layer that we observed in the microchannels (see also Alt and Mata, 2000; Drief and Schiffman, 2004) indicates that the dissolution of glass was incongruent which has been reported from basalt alteration experiments under neutral to acid pH conditions (Crovisier et al., 1983a,b; Berger et al., 1987). The amorphous Si-rich layer could result from the secondary precipitation of a Si-rich phase after the dissolution of the basalt glass. In that case, two steps of precipitation would be needed for generating the structure of the microchannels with first involving the deposition of a Si-rich rim, and the second involving the deposition of smectite. Another possibility is to consider the Si-rich amorphous layer as a leached layer (*e.g.* Gislason and Oelkers, 2003). Although such a layer has rarely been observed, it has been reported in most TEM studies of altered basaltic glasses and has indeed been classically interpreted as a leached layer (*e.g.* Crovisier et al., 1983a; Berger et al., 1987; Thorseth et al., 1991; Alt and Mata, 2000). Previous studies (*e.g.* Alt and Mata, 2000) have reported a progressive transition between the leached layer and palagonite suggesting that the latter results from recrystallization of the former. Here, we observe a very sharp textural and compositional transition that is inconsistent with such a scenario and thus favor a two-stage process with glass dissolution and formation of an empty microchannel occurring first followed by palagonite precipitation. The extent of decoupling between these two stages in time cannot be accurately assessed. However, since the compositions of the microchannel-filling material and the basalt glass are strongly related to each other (Fig. 4), dissolution and precipitation are likely penecontemporaneous.

4.2. Biogenicity of the microchannels

An important question concerns the possible relationships between the microchannnels and the microbial activity in the basalt. The presence of microbes in basaltic glass altered at low temperatures is substantiated by microbiological studies (Thorseth et al., 2001; Edwards et al., 2004; Lysnes et al., 2004; Templeton et al., 2005; Huber et al., 2006) and by SEM observation (*e.g.* Banerjee and Muehlenbachs, 2003). Although in some cases microbes can decrease dissolution rates (*e.g.* Benzerara et al., 2004b), it has been demonstrated both in model system experiements and in natural samples that some microbes can enhance mineral dissolution (*e.g.* Ullman et al., 1996; Welch and Ullman, 1999; Kalinowski et al., 2000; Brantley et al., 2001) and might thus form such microchannel dissolution features. Moreover, many studies have proposed that some microorganisms may benefit from basalt glass dissolution by obtaining essential elements like Mn, P, Mg, and trace metals (*e.g.*, Aouad et al., 2006a,b). Although microchannels have been interpreted by some authors as a direct product of the activity of some microbes (*e.g.* Thorseth et al., 1995a; Torsvik et al., 1998; Furnes et al., 2001a,b; Thorseth et al., 2001; Banerjee and Muehlenbachs, 2003; Staudigel et al., 2006), they have been interpreted by Crovisier et al. (1987), as microcracks, *i.e.* a regular abiotic physical step in the dissolution of basaltic glass. One question then is whether the microchannels are formed purely abiotically, possibly colonized secondarily by microbes, or directly by microbes?

Some experimental studies have attempted to detect compositional differences between microbially mediated dissolution of glass in seawater and abiotic alteration (*e.g.* Staudigel et al., 1998; Daughney et al., 2004). It has been proposed for example that abiotic alteration of glass dissolves basaltic Si and Ca and scavenges seawater Mg, while biotic alteration removes Ca from seawater as a result of aragonite precipitation (Staudigel et al., 1998). Furthermore, several chemical elements detected by electron microprobe or SEM coupled with EDX were proposed as indicators of biogenicity: carbon, nitrogen, phosphorus, potassium and calcium (*e.g.* Torsvik et al., 1998). In the present study, we detected carbon, potassium and calcium in the microchannels in the FIB-generated foil. Similar to Alt and Mata (2000), we propose that high K_2O content is associated with phyllosilicates and does not require live cells. Calcium may be associated with the phyllosilicates and/or the carbonates detected by STXM. The nitrogen and phosphorus documented by Banerjee and Muehlenbachs (2003) in the same petrographic thin sections could not be detected in the channels intersected by the FIB-generated foils prepared for this study, preventing us from determining their speciation. This difference may reflect compositional heterogeneities along microchannels that could not be documented in such a highly spatially focused study.

Whether palagonite is formed by biotic or abiotic process is another issue that has been partly addressed in the literature. Reviews by Honnorez (1981), and Stroncik and Schmincke (2001) summarize the considerable literature in usage of the term palagonite and the chemical changes during the formation of palagonite. For the most part, the palagonitization process is considered to be a low-temperature process (possibly much lower than 100 °C, *e.g.* (Alt and Mara, 2000; Walton and Schiffman, 2003; Daughney et al., 2004), although these last authors examined palagonite with a different morphology and texture than the tube-filling material described here), and hence compatible with possible biological activity. This observation, in addition to the numerous studies that have shown how microorganisms can form authigenic phyllosilicates, question the potential role that microbes might have played in the formation of the microchannel-filling smectite in Ontong Java Plateau samples. Several studies have noticed that microbes in natural and laboratory systems can accumulate elements such as Fe, Si and Al and initiate phyllosilicate formation (*e.g.* Fortin et al., 1998; Konhauser and Urrutia, 1999; Tazaki, 2005). Microbes are then fossilized, and complex textures can be preserved and observed (Fortin et al., 1998). Pervasive organic carbon was detected in this study in the Ontong Java Plateau microchannels. It may result from degradation of microbes that once might have inhabited the microchannels. Banerjee and Muehlenbachs (2003) reported positive ethidium bromide staining within the microchannels using stacked laser scanning confocal microscopy imaging and proposed the presence of nucleic acids. Previous STXM and TEM studies of fossil microbes (*e.g.* Benzerara et al., 2006), have detected nitrogen and possibly phosphorus in association with organic carbon, but we were not able to detect these elements in the Ontong Java samples. This could be due to their dilution or because FIB foils were not prepared at the appropriate location. Meanwhile, a purely abiotic origin of the organic carbon detected by STXM and TEM resulting from Fischer–Tropsch reactions cannot be discounted although higher temperatures are usually proposed for this process (*e.g.* Holm and Andersson, 2005). The absence of morphologically recognizable fossils similar to those observed by Fortin et al. (1998) suggests that although some microbes may be involved in biomineralization, they are probably not the major catalysts of precipitation of the microchannel-filling material. Moreover, finding direct evidences for traces of life in ancient microchannels is difficult and will require indirect clues such as the morphologies and arrangements of channels or carbon isotopic compositions (Furnes et al., 2005).

It has been shown that microbes can produce etch marks, corresponding in size, shape and depth to the dimensions of the cells (*e.g.*, Krumbein et al., 1991). Hence, the size distribution of the microchannels is an interesting though indirect indication of potential biogenicity of these structures. Alt and Mata (2000) reported that in altered basaltic glass from the eastern Pacific oceanic crust much of the microchannel interiors consist of an amorphous rim and that they could not have been occupied by bacteria before clay precipitation, unless living forms significantly smaller than any known bacteria are inferred. In our study, all the microchannel sections observed are compatible with microbe diameters even when the amorphous rim is considered. Moreover, the size variations of the channels are relatively small, considering that some variations may result from slight differences in the orientations of the microchannels. The size distribution of microchannels in the Ontong Java Plateau samples is thus compatible with a biogenic origin.

5. Summary and conclusions

In summary, this study presents a methodology that could provide valuable information if used systematically on samples of modern basalts altered at low temperatures. Our results revealed the nanoscale mineralogy of alteration microchannels in basaltic glass with unprecedented spatial resolution. We also found that partially oxidized Fe(II) and pervasive carbonate groups are intimately associated with organic carbon in the channel-filling smectite, which is separated from the fresh basalt glass by very regular 30 nm-wide silica-rich rims. In spite of the presence of pervasive organic carbon, our observations do not confirm or refute a biogenic scenario for microchannel formation in the Ontong Java Plateau basalt glasses. However, such a study at the nanoscale is a necessary step for determining the chemical and physical conditions prevailing during basalt alteration by identification of existing mineral phases. Using such an approach on very old Precambrian basalts (*e.g.*, Furnes et al., 2004; Banerjee et al., 2006) may provide valuable information both on the potential existence of life and on the similarity of alteration processes that may have been operating during those periods.

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