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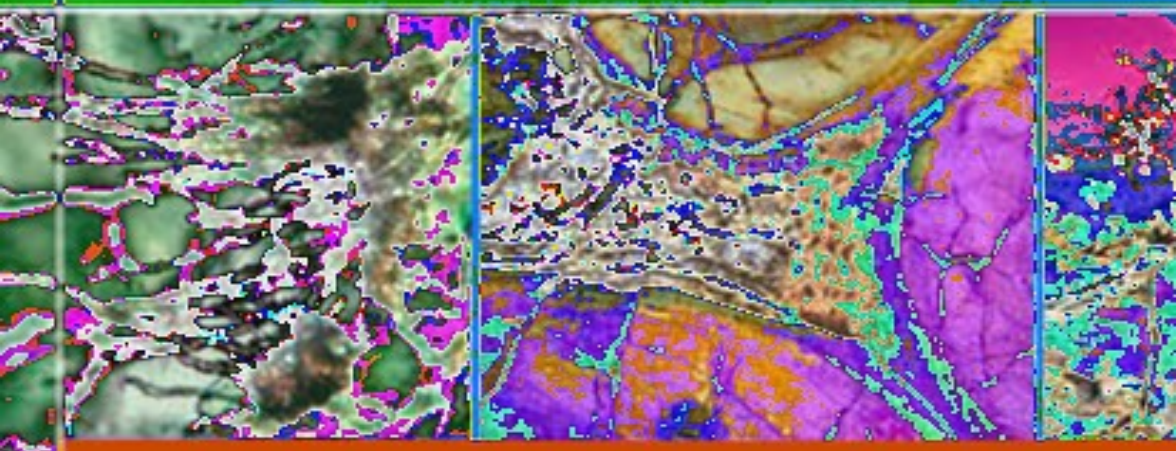

Y. Dilek H. Furnes K. Mu

Links Between Geological Processes, Microbial Activities & Evolution of Life

Modern Approaches in Solid Earth Sciences

VOLUME 4

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Y. Dilek, *Department of Geology, Miami University, Oxford, OH, U.S.A.*
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Links Between Geological Processes, Microbial Activities & Evolution of Life

Microbes and Geology

Editors

Yildirim Dilek
Department of Geology, Miami University, Oxford, OH, USA

Harald Furnes
Department of Earth Science, University of Bergen, Norway

and

Karlis Muehlenbachs
Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, Canada

Springer

Dr. Yildirim Dilek
Miami University
Dept. Geology
114 Shideler Hall
Oxford OH 45056
USA
dileky@muohio.edu

Dr. Karlis Muehlenbachs
University of Alberta
Dept. Earth & Atmospheric
Sciences, 1-26 Earth Sciences Bldg.
Edmonton AB T6G 2E3
Canada
Karlis.Muehlenbachs@ualberta.ca

Dr. Harald Furnes
University of Bergen
Dept. Earth Science
Allegaten 41
5007 Bergen
Norway
harald.furnes@geo.uib.no

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Preface

Geobiology is a rapidly growing and truly interdisciplinary field at the interface between earth and life sciences, and mainstream research in geobiology involves microbes and microbial activities at all scales in different geological environments through time in Earth's history. This research and its findings have strong implications for the evolution of life on the Earth and potentially in other planets. Microbial activities influence water-rock interaction processes and chemical transport between the major geochemical reservoirs, and the formation and transformation of minerals and rocks. On the other hand, geological processes and geochemical controls influence the microbial ecology in extreme environments. Our understanding of these links has been advancing at a fast pace in recent years. The discovery of life in extreme environments and its systematic studies have peaked during the past several decades, and new scientific programs (i.e. Deep Science Initiative) have been initiated in order to maximize international collaboration on most important scientific problems pertaining to underground research and subsurface microbial life. The deep subsurface biosphere may constitute nearly one third of the Earth's biomass, and subsurface microbial communities are major contributors to nutrient cycling through the environment.

We now know that microbes have played important roles as geological agents in mineral growth and dissolution, rock and mineral weathering and alteration, mobilization of metals in metal sulphides, metabolism of hydrocarbons and transformation of organic carbon in sediments for fossil fuel formation, cycling of elements in the global ocean, fractionation of stable isotopes facilitating rock and mineral diagenesis, porosity generation in deep-subsurface, timing of fossil appearance in Earth history, bio-remediation, and emergence of the aerobic biosphere in deep time (i.e. Archaean – Proterozoic transition). How biological activity influences geological processes and what role these processes have played in the geological evolution of the Earth through time still remain fundamental questions. How do we recognize ancient microbial activities in the rock record and what analytical methods do we use to document and to better understand the evolution of life? Can we detect the existence of microbial life in deep time by studying Archaean rocks? Microbial systems in extreme environments and in the deep biosphere may be analogous to potential life on other planetary bodies and hence may be used to investigate the possibilities of extraterrestrial life.

This book is a result of a successful Pardee Keynote Symposium held at the Geological Society of America Annual Meeting in Philadelphia (October 2006) and is intended to explore these questions and the mode and nature of links between geological processes and microbial activities for the origin and evolution of life on the Earth and possibly on other planets. It fills a particular niche in geobiology by focusing on the significance of geology and geological processes for controlling the physical conditions and characteristics of diverse habitats, in which different microorganisms thrive, the geochemical processes that these microorganisms catalyze, and the implications of microbial activities as recorded in the rocks and modern geological environments for the evolution of life. The chapters in the book are primarily concerned with the geological, biological, and geochemical processes that affect habitable environments for microbial communities in extreme conditions (i.e. oceanic crust in deep subseafloor, saline lakes, methane-rich ocean waters, deep sea sediments) and the textural, biological, and fossil evidence that microbes and microbial activities leave behind in the rock record. As such, the book is aimed at documenting some of the best examples (but not all) of links between the geological processes and microbial activities, rather than providing discussions on microbial ecology and microbial physiology, microbiological characterization, and microbial biochemistry. We do not attempt in this book to cover all aspects and examples of geobiology since that would require numerous, diverse contributions from a much larger scientific community. The book is intended for students (upper level undergraduate and graduate students) and researchers in the academia and industry who are interested in exploring the geological record of the biosphere in deep and extreme environments.

The chapters in the book are organized to provide new observations and data as well as presenting a state-of-the art overview on the topics ranging from microbial existence and related processes in the uppermost igneous layer of modern and ancient oceanic crust and deep sea sediments to cyanobacteria – produced stromatolites; microbial communities and their geological artefacts in saline lakes at high altitudes (i.e. Tibetan Plateau) and below sea-level (i.e. Dead Sea), in dry deserts (i.e. Atacama Desert in Chile, Antarctica, the Arctic and western China), and in the deep continental subsurface where high temperature, high pressure and high radiation conditions prevail; and, in ocean waters that have high rates of anaerobic oxidation of methane gas (i.e. The Black Sea). The last chapter presents a critical assessment of a widely discussed "volcanic winter to snowball Earth" hypothesis that holds extensive explosive volcanism around ~635 million years ago responsible for Neoproterozoic climate change in the Earth's history. Solid Earth geological processes, such as subduction and associated magmatism, and the interplay between surficial and atmospheric processes (i.e. glaciation) appear to have played a major role in this event during the Precambrian, and are likely to happen again to affect climate and life in the geological future. We hope that this book will serve as an exciting, contemporary guide to the geobiological literature.

We thank the contributors to this book for their time and effort, and express our gratitude to a large number of scientists who provided valuable reviews of the chapters in it. We are grateful to the Geological Society of America and its International

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December 2007 Y. Dilek, H. Furnes, and K. Muehlenbachs
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Miriam Andres, Chevron Energy Technology Center, San Ramon – CA, USA

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Neil Banerjee, University of Western Ontario, Canada

Maarten de Wit, University of Cape Town, South Africa

Yildirim Dilek, Miami University, USA

Hailiang Dong, Miami University, USA

Katerina J. Edwards, University of Southern California, USA

Kai Finster, University of Aarhus, Denmark

Martin Fisk, Oregon State University, USA

Harald Furnes, University of Bergen, Norway

Jens Herrle, University of Alberta, Canada

Nils Holm, Stockholm University, Sweden

Ingo Klaucke, IFM-Geomar, Leibniz Institute for Marine Sciences, Kiel, Germany

Paul Knauth, Arizona State University, Tempe, USA

Kurt Konhauser, University of Alberta, Canada

Ian G. Macintyre, Natural History Museum, Smithsonian Institute, USA

Nicola McLoughlin, University of Bergen, Norway

Melani R. Mormile, University of Missouri – Rolla, USA

John Mylroie, Mississippi State University, USA

Karlis Muehlanbachs, University of Alberta, Canada

Eugene A. Shinn, University of South Florida, USA

Mark Skidmore, Montana State University, Bozeman, USA

Andreas Teske, University of North Carolina – Chapel Hill, USA

Volker Thiel, Universitaet Goettingen, Germany
Tamas Torok, Lawrence Berkeley National Laboratory, USA
Marta Torres, Oregon State University, USA
Tina Treude, University of Southern California, USA
David Wacey, University of Oxford, U.K.

Contents

Contributors

Hugh Aggleton
Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK, hugh.aggletan@jesus.ox.ac.uk

D. Avigad
Institute of Earth Sciences, Hebrew University of Jerusalem, Jerusalem 95501, Israel, avigad@vms.huji.ac.il

Neil Banerjee
Department of Earth Sciences, University of Western Ontario, London, Ontario, Canada N6A 5B7, neil.banerjee@uwo.ca

M. Beyth
Geological Survey of Israel, Malkhei Yisrael St. 30, Jerusalem 95501, Israel, mbeyyth@gsi.gov.il

Jennifer F. Biddle
University of North Carolina at Chapel Hill, Department of Marine Sciences, 351 Chapman Hall, CB 3300, Chapel Hill, North Carolina 27599 USA, jfbiddle@email.unc.edu

Martin Blumenberg
Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstrasse 55, D-20146 Hamburg, Germany, martin.blumenberg@zmaw.de

Gerhard Bohrmann
Research Center Ocean Margins, University of Bremen, Klagenfurter Strasse, D-28334 Bremen, Germany, gbathrmann@uni-bremen.de

Martin Brasier
Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK, Martin.Brasier@earth.ox.ac.uk

Robin L. Brigmon
Savannah River National Laboratory, Building 999W Aiken, SC 29808, USA, Tel 803-819-8405, r03.brigmon@srnl.doe.gov

Maarten de Wit
AEON and Department of Geological Sciences, University of Cape Town, Rondebosch 7701, South Africa, maarten.De.Wit@uct.ac.za

Yildirim Dilek
Miami University, Department of Geology,114 Shideler Hall Oxford, OH 45056, USA, dileky@muohio.edu

Hailiang Dong
Department of Geology, Miami University, Oxford, OH 45056, USA, Tel: 513-529-2517, Fax: 513-529-1542, dongh@muohio.edu

Harald Furnes
Department of Earth Science & Centre for Geobiology, University of Bergen, Allegaten 41, 5007 Bergen, Norway, Tel: +47 55 583530, Fax: +47 55 583660, Harald.Furnes@geo.uib.no

Robert N. Ginsburg
University of Miami, Comparative Sedimentology Laboratory, Rosenstiel School of Marine and Atmospheric Sciences, 4600 Rickenbacker Causeway, Miami Fl, 33149, rginsburg@rsmas.miami.edu

Nils.G. Holm
Department of Geology and Geochemistry, Stockholm University, Sweden, Frescativägen 8, S-106 91 Stockholm, Sweden, nils.holm@geo.su.se

Fumio Inagaki
Geomicrobiology Group, Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Monobe B200, Nankoku, Kochi 783-8502, Japan, inagaki@jamstec.go.jp; Subground Animalcule Retrieval (SUGAR) Program, Extremobiosphere Research Center, JAMSTEC, Natsushima-cho 2-15, Yokosuka 237-0061, Japan, inagaki@jamstec.go.jp

Magnus Ivarsson
Department of Geology and Geochemistry, Stockholm University, Sweden, Frescativägen 8, S-106 91 Stockholm, Sweden, magnus.ivarsson@geo.su.se

Matt Kilburn
Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK and Centre for Microscopy and Microanalysis, University of Western Australia, 35 Stirling Highway, Crawley 6009, WA, Australia, mkilburn@cyllene.uwa.edu.au

Nicola McLoughlin
Department of Earth Science & Center for Geobiology, University of Bergan, Allegaten 41, 5007 Bergan, Norway, Nicola.NcLoughlin@geo.uib.no

Walter Michaelis
Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstrasse 55, D-20146 Hamburg, Germany, walter.michaelis@zmaw.de

N. Miller
Geosciences Department, U Texas at Dallas, Richardson TX 75083-0688 USA, Now at Department of Geological Sciences and Engineering, University of Missouri at Rolla, □ Rolla, MO 65409-0140 □, nmiller@mail.utexac.edu

Penny Morris
Department of Natural Science, University of Houston, 1 Main Street, Houston, TX 77002, penny.morris_smith1@jsc.nasa.gov

Karlis Muehlenbachs
University of Alberta, Department of Earth & Atmospheric Sciences Edmonton AB T6G 2E3 1-26 Earth Sciences Building, Canada, Karlis.Muelenbachs@ualberta.ca

Satoshi Nakagawa
Subground Animalcule Retrieval (SUGAR) Program, Extremobiosphere Research Center, JAMSTEC, Natsushima-cho 2-15, Yokosuka 237-0061, Japan, nakagawas@jamstec.go.jp

Thomas Pape
Research Center Ocean Margins, University of Bremen, Klagenfurter Strasse, D-28334 Bremen, Germany, Tel.: +49 4212183918; Fax: +49 4212188664, tpape@uni-bremen.de

Noah J. Planavsky
University of Miami, Comparative Sedimentology Laboratory, Rosenstiel School of Marine and Atmospheric Sciences, 4600 Rickenbacker Causeway, Miami Fl, 33149; University of California, Riverside, Department of Earth Sciences, 900 University Avenue, Riverside Ca, 92521, planavsky@gmail.com

Peter Schiffman
Department of Geology, University of California, Davis, One Shields Avenue, Davis, California 95616-8605, USA, PSCHIFFMAN@UCDAVIS.EDU

Richard Seifert
Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstrasse 55, D-20146 Hamburg, Germany, richard.seifert@zmaw.de

Garriet Smith
University South Carolina Aiken, 471 University Parkway, Aiken, SC 29801, smithres@aiken.sc.edu

Hubert Staudigel
Scripps Institution of Oceanography, University of California, La Jolla, CA 92093-0225, USA, hstaudigel@ucsd.edu

Robert J. Stern
Geosciences Dept., U Texas at Dallas, Richardson TX 75083-0688 USA, 972-883-2442 (O) 972-883-2537 (F), rjstern@utdallas.edu

Crispin Stoakes
C.A Stoakes and Associates Pty Ltd, 3185 Victoria Road, Hovea 6071, WA, Australia, stoakesca@optusnet.com.au

Andreas Teske
University of North Carolina at Chapel Hill, Department of Marine Sciences, 351 Chapman Hall, CB 3300 Chapel Hill, North Carolina 27599, USA, Phone: 919.843.2463, Fax: 919.962.1254, teske@email.unc.edu

Martin Van Kranendonk
Geological Survey of Western Australia, 100 Plain Street, East Perth, Western Australia 6004, Australia, martin.vankranendonk@doir.wa.goc.au

David Wacey
Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK, davidwa@earth.ox.ac.uk

Oceanic Pillow Lavas and Hyaloclastites as Habitats for Microbial Life Through Time – A Review

Harald Furnes, Nicola McLoughlin, Karlis Muehlenbachs, Neil Banerjee, Hubert Staudigel, Yildirim Dilek, Maarten de Wit, Martin Van Kranendonk, and Peter Schiffman

Abstract This chapter summarizes research undertaken over the past 15 years upon the microbial alteration of originally glassy basaltic rocks from submarine environments. We report textural, chemical and isotopic results from the youngest to the oldest *in-situ* oceanic crust and compare these to data obtained from ophiolite and greenstone belts dating back to c. 3.8 Ga. Petrographic descriptions of the granular and tubular microbial alteration textures found in (meta)-volcanic glasses from pillow lavas and volcanic breccias are provided and contrasted with textures produced by abiotic alteration (palagonitization). The geological setting in particular the degree of deformation and metamorphism experienced by each study site is documented in outcrop photographs, geological maps and stratigraphic columns (where possible). In addition, X-ray mapping evidence and carbon isotopic data that are consistent with a biogenic origin for these alteration textures is explained and a model for their formation is presented. Lastly, the petrographic observations and direct radiometric dating techniques that have been used to establish the antiquity and syngenicity of these microbial alteration textures are reviewed.

The combined dataset presented herein suggests that the microbial alteration of volcanic glass extends back to some of the earliest preserved seafloor crustal fragments. We use observations collected from well preserved, *in-situ* oceanic crust as a guide to interpreting comparable mineralized micro-textures from the ancient seafloor. It emerges that textural evidence is best preserved in undeformed to little-deformed, low grade, meta-volcanic rocks, and that chemical tracers, in particular the $\delta^{13}C_{carb}$ signatures, are more robust and can survive relatively strong deformation and metamorphic conditions. Drawing together all of this data we propose a tentative model for microbial life in the Archean sub-seafloor. Overall, it is argued

H. Furnes
Department of Earth Science & Centre for Geobiology, University of Bergen, Allegt. 41, 5007 Bergen, Norway
e-mail: Harald.Furnes@geo.uib.no

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that bioalteration textures in (meta)-volcanic glasses provide a valuable tracer of the deep oceanic biosphere, which constitutes one of the largest and least explored portions of the modern, and especially the ancient, biosphere.

1 Introduction

Microbial activity has until recently only been sought largely in (meta)-sedimentary rocks and environments. It is now, however, realized that microbial life can also colonise volcanic rocks within the Earth's crust to considerable depths, where carbon and energy sources are available and where physical conditions do not inhibit life (e.g., Lovley and Chapelle 1995; Pedersen 1997; Pedersen et al. 1997; Amend and Teske 2005; Schippers et al. 2005). During the last decade, it has also been demonstrated that the upper volcanic part of the *in situ* oceanic crust is a habitat for microbial life (e.g., Thorseth et al. 1992; Thorseth et al. 1995a; Furnes et al. 1996; Fisk et al. 1998; Torsvik et al. 1998; Furnes and Staudigel 1999; Furnes et al. 1999, 2001a, b; Thorseth et al. 2001, 2003; Banerjee and Muehlenbachs 2003; Fisk et al. 2003; Staudigel and Furnes 2004; Staudigel et al. 2004). The *in-situ* oceanic crust however, only extends back to approximately 170 Ma, with the oldest oceanic crust being found in the western Pacific Ocean. Evidence of microbial activity in older oceanic volcanic rocks must be sought in fragments of ancient oceanic crust preserved in ophiolites and greenstone belts. Reliable evidence for microbial life has been found in several ophiolites ranging in age from Cretaceous to Paleoproterozoic (Furnes et al. 2001c, 2002a, 2005), and putative evidence of microbial life has been described from Mesoarchean pillow lavas of the Barberton greenstone belt, South Africa (Furnes et al. 2004; Banerjee et al. 2006) and the Pilbara Craton, Western Australia (Staudigel et al. 2006; Banerjee et al. 2007).

In this chapter, we summarize the various accounts of microbial alteration that span the youngest, *in-situ* oceanic crust to the oldest greenstone belts and present new data pertaining to these findings. In particular, we provide in one manuscript a compilation of lithological logs from the *in-situ* oceanic crust where microbial alteration has been found, along with geological maps, stratigraphic sections and outcrop photographs of all of the ophiolites and greenstone belt examples studied to enable direct comparisons to be made. Previous reviews have largely treated evidence of microbial alteration from the *in situ* oceanic crust (e.g., Fisk et al. 1998; Furnes et al. 2001b) and ophiolites (e.g. Furnes and Muehlenbachs 2003) separately; or largely focussed on a single line of evidence such as textural information (e.g., Furnes et al. 2007a). This manuscript extends the study of Staudigel et al. (2006) to document in detail, the main lines of evidence that have been presented to support microbial alteration in volcanic glass from 11 drill cores from the *in-situ* oceanic crust; 5 ophiolite examples and 4 greenstone belts (Fig. 4). In addition to the review of all relevant aspects covered below, we present new textural and carbon isotope data from several of the investigated ophiolites and greenstone belts that is consistent with bioalteration.

2 Biogenicity and Antiquity – Criteria Used for Establishing Bioalteration

Alteration of basaltic glass in modern pillow lavas and hyaloclastites results from two fundamentally different processes – abiotic and biotic alteration. Abiotic alteration results in the formation of the long-recognized, but enigmatic, material termed *palagonite*. The more recently-recognized biotic alteration involves etching of the glass by rock dwelling (endolithic) microbes creating textures that can be regarded as ichnofossils. These two alteration processes may be contemporaneously active within the temperature limit of life. In a number of recent papers the abiotic and biotic alteration processes have been discussed at length. Below we will only briefly comment on abiotic alteration and focus instead upon the biotic processes of alteration. We present biogenicity and antiquity criteria developed to assess these structures, as well as a refined version of recent models proposed to explain the bioalteration of basaltic glass (Staudigel et al. 2006; Furnes et al. 2007a; McLoughlin et al. 2008). In addition, we briefly review what is currently known about the microorganisms that are thought to be responsible for the bioerosion of volcanic glass.

2.1 Abiotic Alteration

The aqueous alteration of basaltic glass produces a pale yellow to dark brown material referred to as palagonite. Palagonitization has traditionally been regarded as a purely physico-chemical phenomenon and is a complex and continuous aging process involving incongruent and congruent dissolution accompanied by precipitation, hydration and pronounced chemical exchange that occurs at low to high-temperatures (e.g., Thorseth et al. 1991; Stroncik and Schmincke 2001; Walton and Schiffman 2003; Walton et al. 2005). The resulting palagonite occurs around the rims of glass shards and as banded material on either side of fractures with a relatively smooth interface between the fresh and altered glass. Palagonite can be divided into two types: (1) early stage amorphous gel-palagonite that matures to form, (2) fibro-palagonite which consists of clays, zeolites and iron-oxy-hydroxides (Peacock 1926).

2.2 Biotic Alteration

Over recent years mounting evidence has been collected to support the biological mediation of processes involved in the alteration of volcanic glass. One of the earliest reports of the biological etching of glass is the description of surface pitting on church window-pane glass in the vicinity of growing lichens (Mellor 1922; see also Krumbein et al. 1991 for review). Bioerosion of natural glasses was reported somewhat later with the finding of surface grooves on glass shards from Miocene

tephra that were likened to those produced by fungi which bore into carbonate grains (Ross and Fisher 1986). This scenario was confirmed with the observation of bacteria within surface pitting textures on sub-glacial volcanic breccias from Iceland, which lead Thorseth et al. (1992) to propose that the microbes locally modify the pH and thereby accelerate glass dissolution. A range of biochemical mechanisms are employed by microorganisms to dissolve volcanic glass and are thought to include secretion of organic acids, production of siderophores and complexing agents that help to complex metal ions, particularly Al whilst modifying the pH to promote silica glass dissolution (Paul and Zaman 1978). The initial stages of glass pitting have been experimentally investigated by Thorseth et al. (1995b), and Staudigel et al. (1995,1998), who confirmed that volcanic and synthetic glasses inoculated with microbes develop etch pits and surface alteration rinds under laboratory conditions.

Numerous studies have followed to document the widespread occurrence of microbial bioerosion textures in volcanic glass from Ocean Drilling Program (ODP) and Deep Sea Drilling Project (DSDP) drill cores from *in-situ* oceanic crust (e.g., Thorseth et al. 1995a; Furnes et al. 1996; Fisk et al. 1998; Furnes et al. 2001a, b; Thorseth et al. 2001, 2003; Banerjee and Muehlenbachs 2003). Distinct textural, elemental and isotopic signatures are produced by these microbial alteration processes and are reviewed below. As a preface to the individual studies it is first informative to draw together and explain the various lines of evidence and the key observations used to distinguish such bioalteration textures from the products of abiotic palagonitization (see also McLoughlin et al. 2007).

2.2.1 Textures

The bioalteration of volcanic glass produces two principal types of textures that have been termed *granular* and *tubular* textures (Furnes and Staudigel 1999). These are markedly different from the regularly banded alteration rinds that result from abiotic palagonitization (Fig. 1A), and we regard these textures as our prime evidence for the bioalteration of basaltic glass. A model for the textural development of such bioerosion traces is given in Fig. 1. The top line shows abiogenic alteration which results in the production of banded palagonite around glass fragments and along the margins of fractures, with a relatively smooth interface between the fresh and altered glass. This should be contrasted with the granular and tubular ichnofossils shown in the lower lines of the figure which are formed by microorganisms carried by circulating fluids into fractures in the rock. These microbial consortia progressively etch the fresh glass, generating more abundant tubes and granular aggregates around fractures and creating an increasingly ramified alteration front between the fresh and altered glass. In Fig. 1, this is schematically shown from left to right across the diagram and illustrated by the back-scatter electron (BSE) images of real examples. The granular alteration textures consist of micron-sized spherical cavities filled with amorphous to very fine-grained phyllosilicate phases. At the initial stage of bioalteration the granular textures appear as isolated spherical bodies along fractures in the glass (Fig. 1B, stage t_1). With progression of bioalteration these become more

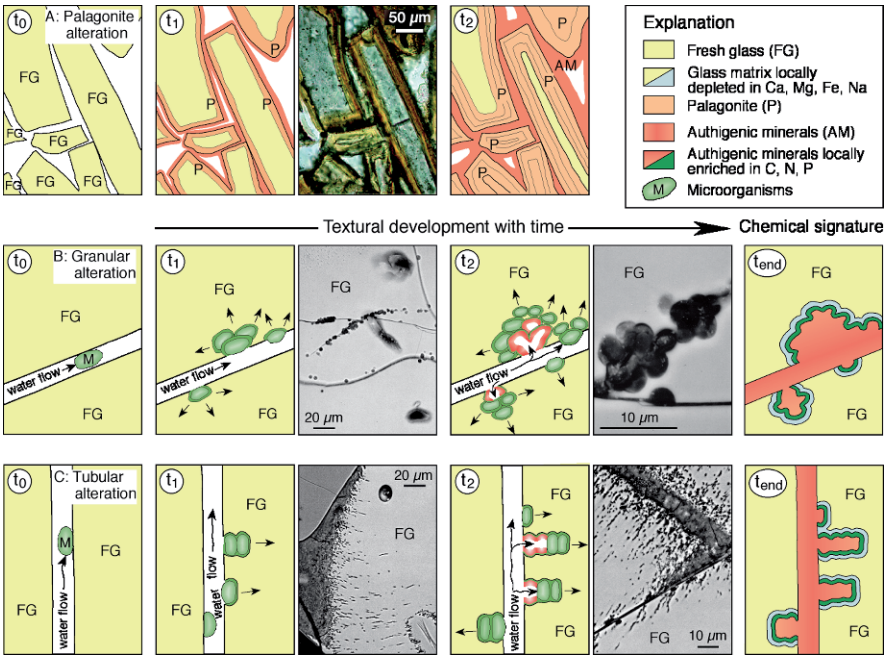

Fig. 1 Schematic diagram showing the generation of alteration textures in fresh volcanic glass (FG) from initial time (t_0) to the final time (t_{end}), accompanied by back scattered electron and thin section images of real examples. The *top line* (**A**) shows abiotic palagonite alteration which produces banded palagonite rims and authigenic minerals around glass fragments. The *middle line* (**B**) shows the growth of granular type textures from isolated spheres in the early stages (t_1) to dense granular aggregates (t_2). The *lower line* (**C**) shows the growth of tubular type from incipient short tubes at stage (t_1) to longer tubes at (t_2). The *right* hand column in (**B**) and (**C**) shows the resulting compositional signatures that are found when these bioalteration textures are infilled by authigenic mineral phases

numerous and coalesce into aggregates that form irregular bands which protrude into the fresh glass along fractures (Fig. 1B, stage t_2). The tubular alteration textures (Fig. 1C) are also concentrated along surfaces in volcanic glass where water once permeated, and become longer and form denser aggregates with progressive alteration.

During the formation of both morphologies of microbially-driven glass dissolution, the total surface area of fresh glass available progressively increases. Staudigel et al. (2004) calculated that the surface area of fresh glass would increase by factors of 2.4 and 200 during the formation of tubular and granular morphotypes, respectively. In contrast, abiotic alteration causes the surface area of fresh glass to progressively decrease, acting as a negative feedback that inhibits further alteration. As long as seawater is accessible to the fresh glass, alteration, whether biotic or abiotic, will continue until all of the fresh glass is altered. With time, the bioalteration textures are filled with authigenic phases and alteration will proceed at a much slower rate until, seawater no longer has access to the fresh glass and alteration will

stop. The final column in Fig. 1 shows the chemical signatures that are preserved, including enrichment in C, N and P along the margins of the bioerosion traces, and depletion in Mg, Fe, Ca, and Na in the surrounding modified glass (discussed further in Section 5, below). We stress that this is a schematic diagram and that the distribution of bioalteration textures will differ in fractures of varying geometries under different fluid flow regimes in and around vesicles and as authigenic minerals precipitate and thereby modify the diffusion processes. Further real examples of bioalteration textures from *in-situ* oceanic crust are described in Section 4.1 and Figs. 23 and 24; from ophiolites in Section 4.2 and Fig. 25; and from greenstone belts in Section 4.3 and Fig. 26.

2.2.2 Syngenicity and Antiquity

To establish the syngenicity of bioalteration textures and exclude an origin from modern endolithic organisms relies in the first instance upon relative age relationships observed by optical microscopy. In volcanic glasses and hyaloclastites (i.e., brecciated volcanic glass), it is therefore necessary to check the distribution of bioalteration textures in pillow margins or glass fragments with respect to fractures that may have acted as conduits for younger fluids and, possibly, also for microbes. In ancient metamorphic samples, the originally hollow bioalteration textures are now filled by secondary minerals (e.g., quartz, chlorite, titanite) and have been overgrown by metamorphic minerals (e.g., Figs. 26 and 27). In such cases, the metamorphic age of the overgrowing mineral gives a minimum age constraint for the bioalteration of the rock, as for example in the case of the $\sim$3.5 Ga bio-etching of the pillow lavas of the Barberton greenstone belt, South Africa (Furnes et al. 2004; Banerjee et al. 2006). This may not always be a trivial task and in some cases it is not possible to confidently establish the timing of bioalteration. However, direct radiometric U-Pb dating of titanite that is commonly found to fill the bioalteration textures, is sometimes possible and has been done for tubular alteration textures in hyaloclastites of the 3350 Ma Euro Basalt of the Kelly Group (Pilbara Craton, Western Australia), yielding a minimum age estimate for bioalteration of $2921 +/- 110$ Ma (Banerjee et al. 2007); this study is discussed in more detail in Section 7.4, below.

2.2.3 Geochemistry

The localised concentration of biologically significant elements in and around volcanic bioalteration textures offers support for the biogenicity of these textures. X-ray element mapping in the vicinity of bioalteration textures (e.g., Furnes et al. 2001b; Banerjee and Muehlenbachs 2003; also Section 5 below and Figs. 28–30), has shown that the tubular and granular textures are commonly lined with carbon. Importantly, these elevated levels of carbon are not associated with enrichments of elements such as calcium, iron, or magnesium that commonly form carbonates. Instead, the source of the carbon is likely residual organic matter (Torsvik et al. 1998). Element maps of bioalteration textures also commonly show enrichments and/or uneven distributions of K, Fe, P, N, and S. For example, Alt and Mata (2000) used

TEM to study nano- to micro- sized alteration textures in 6 Ma-old basaltic glasses and proposed an incongruent dissolution process with significant losses of Mg, Fe, Ca and Na, accompanied by slight loss of Al and Mn and a substantial increase in K due to the circulation of >100 fracture volumes of seawater. Intriguingly, their data lead them to highlight the possible contribution of nano-sized organisms in the bioalteration processes. In another study, Storrie-Lombardi and Fisk (2004) investigated the local chemical composition of biotically and abiotically altered 0.5–170 Ma-old volcanic glasses by electron microprobe and showed through principal component analysis that the alteration products of biotic and abiotic alteration are distinct. In brief, the clays produced by biotic alteration had higher Fe and K contents, whereas abiotic alteration produced clays with higher Mg values. Further geochemical work, applying methods like those just described may help to distinguish between biotic and abiotic alteration structures.

Fresh volcanic glass is scarce throughout the rock record (e.g., Shervais and Hanan 1989), and the oldest reported occurrence is of Mesoproterozoic (ca. 1.1 Ga) age (Palmer et al. 1988). Textural evidence for bioalteration in ophiolites and greenstone belts is therefore more unlikely and of diminishing quality with increasing geological age and thus geochemical fingerprints in the form of elevated levels of biologically important elements provide useful substantiating evidence. These geochemical signatures from *in-situ* oceanic crust, ophiolites and greenstone belts are described and discussed in further detail in Section 5 below.

2.2.4 Stable Carbon Isotope Signatures

Systematic shifts in the carbon isotope values measured from disseminated carbonate in the glassy rims and crystalline cores of pillow basalts have been taken to support the operation of bioalteration processes (e.g., Furnes et al. 2001a). These carbon isotope patterns can also give clues as to the putative microbial metabolisms that may be involved. Typical pillow basalts contain less than 1 wt.% of disseminated carbonate and the $\delta^{13}C_{carb}$ values obtained from fresh unaltered basalts yield values similar to mantle CO_2 between $-5‰$ to $-7‰$ (Alt et al. 1996; Hoefs 1997). These contrast with $\delta^{13}C_{carb}$ values of marine carbonate of $0‰$ and provide the reference frame for the interpretation of $\delta^{13}C_{carb}$ values obtained from volcanic glass (see Fig. 2). The microbial oxidation of organic matter produces ^{12}C-enriched CO_2, which may subsequently be precipitated in carbonate depleted in $^{13}C(-\delta^{13}C)$, as shown by the left hand arrow on Fig. 2. Positive $\delta^{13}C_{carbonate}$ values on the other hand, can result from the lithotrophic utilization of CO_2 by methanogenic Archaea. These microorganisms produce methane from H_2 and CO_2 preferentially producing ^{12}C-enriched methane and leaving the remaining CO_2 enriched in ^{13}C, which will be recorded in any precipitated carbonate as shown by the right hand arrow on Fig. 2. The existence of the latter archaeal processes is supported by the discovery of diagenetic dolomite with $\delta^{13}C$ as high as $+14‰$ in sediments from DSDP Hole 479 (Gulf of California), suggesting a biogenic CO_2 reservoir related to active methanogenesis (Kelts and McKenzie 1982). Compiled $\delta^{13}C_{carbonate}$ data from the *in-situ* ocean crust, ophiolites and greenstone belts of different metamorphic grades is presented

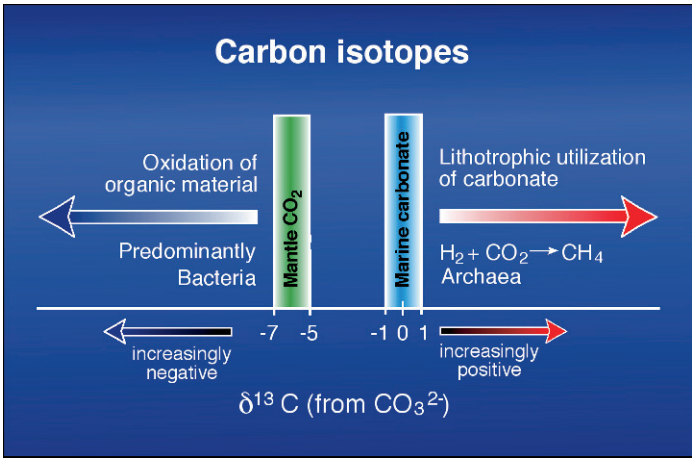

Fig. 2 Diagram summarizing the interpretation of $\delta^{13}C$ values measured on disseminated carbonates from pillow lavas. For reference the $\delta^{13}C$ values of mantle CO_2 and marine carbonates are plotted. The oxidation of organic matter in pillow rims by bacteria is argued to shift the $\delta^{13}C_{carb}$ to progressively more negative values, as low as −25‰ (see for example Fig. 31B). Whereas the lithotrophic utilization of carbonate in pillow rims by archaea shifts the $\delta^{13}C_{carb}$ to more positive values as high as +3.9‰ (see for example Figs. 30 and 31). In contrast, carbonate measured from pillow cores yields a mantle value and carbonate from amygdales gives a marine value. Actual $\delta^{13}C_{carbonate}$ data from pillow lavas are plotted in Figs. 31, 32 and 33

and discussed in detail below (see Section 6 and Figs. 30–32). In summary, it is found that values obtained from pillow interiors are bracketed between primary mantle CO_2 values and those expected from marine carbonates whereas those measured from pillow rims and hyaloclastites display a significantly greater range in $\delta^{13}C_{carbonate}$ values that is consistent with microbial activity. In addition, it has been suggested that variations in the structure and lithology of the oceanic crust may influence the colonizing microbes and resultant carbon isotope signatures (Furnes et al. 2006 and Section 7.3, below).

2.2.5 DNA-Analyses and Microfossil Remains

Nucleic acids derived from bacterial and archaeal DNA are commonly localized within recent bioalteration textures in pillow lavas of young, *in-situ* oceanic crust (Thorseth et al. 1995a, 2001; Giovannoni et al. 1996; Torsvik et al. 1998). The application of DAPI (4, 6 diamino-phenyl-indole) dye which binds to nucleic-acids, along with fluorescent oligonucleotide probes that target bacterial and archaeal RNA has revealed that biological material is concentrated at the ramified interface between fresh and altered glass (e.g., Giovannoni et al. 1996; Torsvik et al. 1998, Fig. 2; Banerjee and Muehlenbachs 2003, Fig. 14; Walton and Schiffman 2003, Fig. 8). For example, staining of volcanic glass samples from the Costa Rica Rift (Fig. 3) show that the most concentrated biological material occurs at the interface of fresh and altered glass, especially in the tips of tubular structures and that the

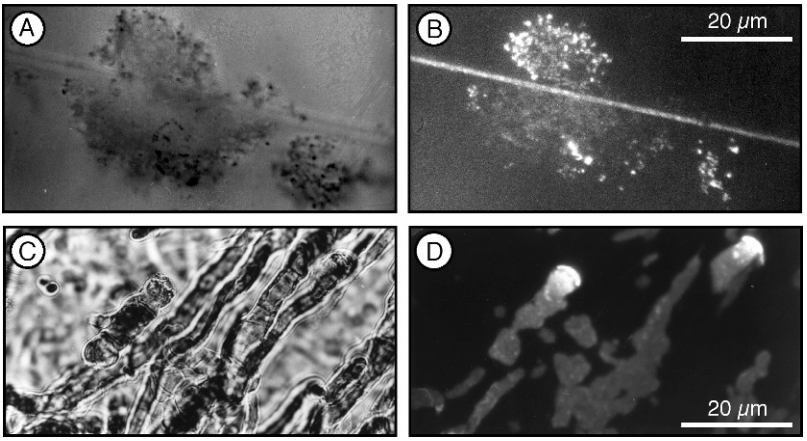

Fig. 3 (**A**) Transmitted light image of the granular bioalteration type; (**B**) epiflourescence image of the same sample showing that the biological material is concentrated along the edges of the granular alteration and within the fracture; (**C**) transmitted light image of the tubular bioalteration type; (**D**) epiflourescence image of the same sample showing that the biological material is concentrated at the ends of the tubes. Both samples (**A** and **C**) are from hole 148-896A-11R-1, 73-73 cm from the Costa Rica Rift (Furnes et al. 1996). The epiflourescent images were obtained using a Nikon Microphot microscope with excitation at 365 nm and emission at 420 nm on samples stained with 10 g/mL DAPI

biogenic material decreases in concentration towards the centre of fractures (Furnes et al. 1996; Giovannoni et al. 1996). We find it appropriate to mention that the application of DAPI may result in ambiguities since some clay minerals may autofluoresce. To ascertain the extent of autofluoresence, Giovannoni et al. (1996) used three different DNA-binding dyes (Hoechst 33342, PO-PRO-3, and Syto 11), which all supported the conclusions of Thorseth et al. (1995a) and Furnes et al. (1996) that microorganisms were present at the glass-alteration interface. Genetic material is not stable over geological lengths of time and so this type of data is not found in ophiolites and greenstone belts. The finding of DNA from *in-situ* oceanic crust that is 122 million-years-old has lead to the suggestion that viable microorganisms may still be active within these bioalteration textures long after eruption of the lavas (Banerjee and Muehlenbachs 2003).

Partially fossilized, mineral encrusted microbial cells have also been observed by scanning electron microscopy (SEM) on the surface of altered glasses from *in-situ* oceanic crust, with morphologies that included filamentous, coccoid, oval, rod and stalked forms (e.g., Thorseth et al. 2001). Moreover, these forms commonly occur in, or near, etch marks in the glass that exhibit forms and sizes resembling the attached microbes, suggesting that it was the microbes that were responsible for the formation of the etch marks (e.g., Thorseth et al. 2003). Within microtubules in volcanic glass fragments from the Ontong Java Plateau, delicate hollow and filled filaments attached to the tube walls have been observed (e.g., Banerjee and Muehlenbachs 2003, Figs. 5–9), along with spherical bodies and thin films

interpreted to represent desiccated biofilms (e.g., Banerjee and Muehlenbachs 2003, Figs. 5–9).

2.2.6 Microbiological Constraints

A consortium of microorganisms that includes heterotrophs and chemolithoautotrophs is thought to be involved in the bioalteration of volcanic glass. Heterotrophs use organic carbon delivered by circulating seawater as a carbon source and chemolithoautotrophs use oxidized compounds principally O_2 and NO_3^- derived from circulating seawater as electron acceptors within the modern sub-seafloor along with Fe(II) and Mn(II) in volcanic glass as electron donors (Edwards et al. 2005). The energetically viable reactions that are possible in these environments and their energy yields are given in Table 1 of Edwards et al. (2005). Under anaerobic conditions hydrogen consuming reactions can support appreciable biomass production and this H_2 may have been supplied by abiotic sources especially on the early earth. In addition, the microbial consortia may derive key nutrients especially phosphorus from the glass, which is found only in low concentration in typically nutrient poor, sub-seafloor conditions.

The suggestion that Mn oxidation is a potentially important chemolithoautotrophic metabolism involved in the bioerosion process is supported by the isolation of diverse manganese oxidizing bacteria from basaltic seamounts where they enhance the rate of Mn oxidation (e.g., Templeton et al. 2005). The possibility that these microbial consortia may also employ iron oxidation is consistent with the resemblance of bacterial moulds found on volcanic glass fragments to the branched and twisted filaments of the Fe-oxidizing bacteria *Gallionella* (e.g., Thorseth et al. 2001, 2003). Moreover it has recently been discovered that a group of bacteria distantly related to the heterotrophic organisms *Marinobacter sp*. and *Hyphomonas sp*. are also capable of chemolithoautrophic growth and employ Fe-oxidation at around pH 7 on substrates including basaltic glass (Edwards et al. 2003). Isolation of a new anaerobic, thermophilic facultative chemolithoautotrophic bacterium from a terrestrial hot spring that is capable of Fe (III) reduction using molecular H as the only energy source and CO_2 as a carbon source (Zavarzina et al. 2007), is also relevant to mention in this connection (see Section 7.3).

Culture independent molecular profiling studies have found that basaltic glass is colonized by microorganisms that are distinct from those found in both deep seawater and seafloor sediments. For example, indigenous microbial sequences obtained from basaltic glass samples dredged from the Arctic seafloor ranging in age from 1 Ma to 20 Ma were found to be affiliated with eight main phylogenetic groups of bacteria and a single marine Crenarchaeota group (Lysnes et al. 2004). Although it is not possible to confidently infer the metabolisms of uncultured microorganisms from molecular phylogenetic relationships, this study did find sequences that were related to known Fe and S metabolizing bacteria and methanogenic archea. Furthermore, it is reported that autotrophic microbes tend to dominate the early colonizing communities and that heterotrophic microbes are more abundant in older,

more altered samples (Thorseth et al. 2001; Santelli et al. 2006). In other words, it appears that prokaryotic microbial consortia, which include microorganisms that employ Fe and Mn oxidation, are plausible candidates for the bioerosion of basaltic glass and that these are associated with a heterotrophic community. There are even reports of eukaryotes from within the oceanic crust, with the finding of microbial remains argued to be marine, cryptoendolithic fungi in carbonate filled amygdales from Eocene Pacific seafloor basalts (Schumann et al. 2004).

Efforts to generate bioalteration textures in laboratory experiments using natural inoculums and various glass substrates have generated useful insights, although each with their own limitations. This work was motivated in part by etch pits found in Icelandic hyaloclastites that show "growth rings", which were taken to suggest that they might develop into tubular shaped alteration structures (Thorseth et al. 1992), although no such extended tubular morphologies have yet to be produced in the laboratory. These early studies involved basaltic glass inoculated with microbes taken from the submarine Surtsey volcano that were cultivated in 1% glucose solution at room temperatures for one year and produced etch pits and alteration rinds (Thorseth et al. 1995b). Monitoring of these experiments over time suggested that the microbes corrode the volcanic glass first via congruent dissolution, followed by incongruent dissolution and it was hypothesized that these involved the secretion of organic acids and metal complexing agents by the microbes (Thorseth et al. 1995b). The limitation of this work was the use of a nutrient rich media that is not comparable to sub-seafloor conditions. Another experimental approach was utilized by Staudigel et al. (1998) who constructed flow through experiments with basaltic glass that was continuously flushed with a natural seawater microbial population and monitored both chemically and isotopically for periods of up to 583 days. These biologically mediated experiments produced twice the mass of authigenic phases compared to the abiotic controls and caused particularly marked Sr exchange. Again, however, these experiments are not directly analogous to sub-seafloor conditions because surface seawater inoculums were used.

Thus, in summary it appears that heterotrophic bacteria, along with chemolithoautotrophs which utilize Fe and Mn oxidation, are responsible for the bioalteration of volcanic glass. However, the full diversity of microorganisms involved is yet to be fully documented, and the conditions under which tubular alteration structures are formed are yet to be replicated in the laboratory.

3 Material Investigated

We have investigated pillow lava and hyaloclastite samples from a large number of DSDP/ODP sites from the *in-situ* (modern) oceanic crust spanning the youngest to the oldest oceanic basins (0–170 Ma). The search for bioalteration has been extended into fragments of ancient oceanic crust preserved in ophiolites of different ages (Section 3.2) and Proterozoic to Archean greenstone belts (Section 3.3). All of

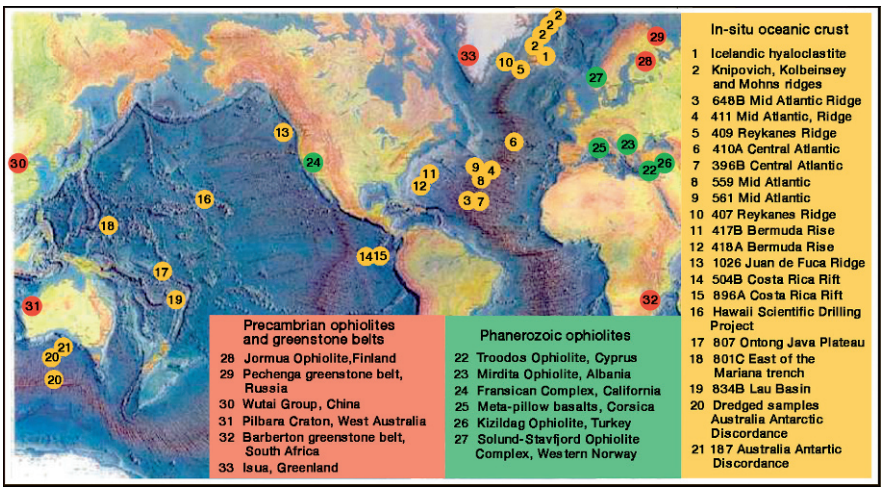

Fig. 4 Map showing the distribution of bioalteration textures documented to date in volcanic glass: examples from *in situ* oceanic basins are shown by *yellow circles*; from fragments of oceanic crust preserved in Phanerozoic ophiolites by *green circles*; and from Precambrian ophiolites and greenstone belts by *red circles*. References for each locality: (1) Thorseth et al. 1991; (2) Thorseth et al. 2001; (3) and (4) Furnes et al. 2001b, Lysnes et al. 2004; (5) Furnes et al. 2001b and Staudigel et al. 2004; (6) H. Furnes et al. 2001b; (7) Furnes et al. 2001b; (8) and (9) Fisk et al. 1998; (10) Staudigel and Furnes 2004; (11) Furnes et al. 2001b; (12) Staudigel and Furnes 2004; (13) Fisk et al. 2000; (14) Furnes et al. 1999; (15) Torsvik et al. 1998; (16) Walton and Schiffman 2003; (17) Banerjee and Muehlenbachs 2003; (18) Fisk et al. 1999; (19) Furnes et al. 2001a,b; (20) and (21) Thorseth et al. 2003; (22) Furnes et al. 2001b; (23) Furnes and Muehlenbachs 2003; (24) herein and K Muehlenbachs, unpub; (25) and (26) herein; (27) Furnes et al. 2002a; (28) Furnes et al. 2005; (29) herein; (30) herein; (31) Banerjee et al. 2007; (32) Furnes et al. 2004; Banerjee et al. 2006; (33) herein

the material discussed in this review are located on the world map shown in (Fig. 4) and plotted on the geological timescale shown in Fig. 36.

3.1 Modern Oceanic Crust (Atlantic, Costa Rica, Lau Basin)

The material from the modern oceanic crust has been collected from DSDP/ODP cores from the Atlantic Ocean, Lau Basin, Costa Rica Rift and the Ontong Java Plateau. The basaltic glass from the Atlantic (Fig. 5) forms the bulk of the investigated samples and was collected from eight drill sites (Holes 407, 409, 410A, 411, 417D, 418A, 396B and 634B). Holes 417D and 418A were drilled during DSDP Legs 51, 52 and 53, and have been described by Robinson et al. (1979). Holes 407, 409, 410A and 411, are situated in the north-central Atlantic Ocean and at the Reykjanes Ridge (Fig. 4), and were drilled during DSDP Leg 49 described by Luydendyk et al. (1978). Holes 396B and 648B are located in the central Atlantic Ocean and were drilled during DSDP Leg 46 and ODP Legs 106/109, described

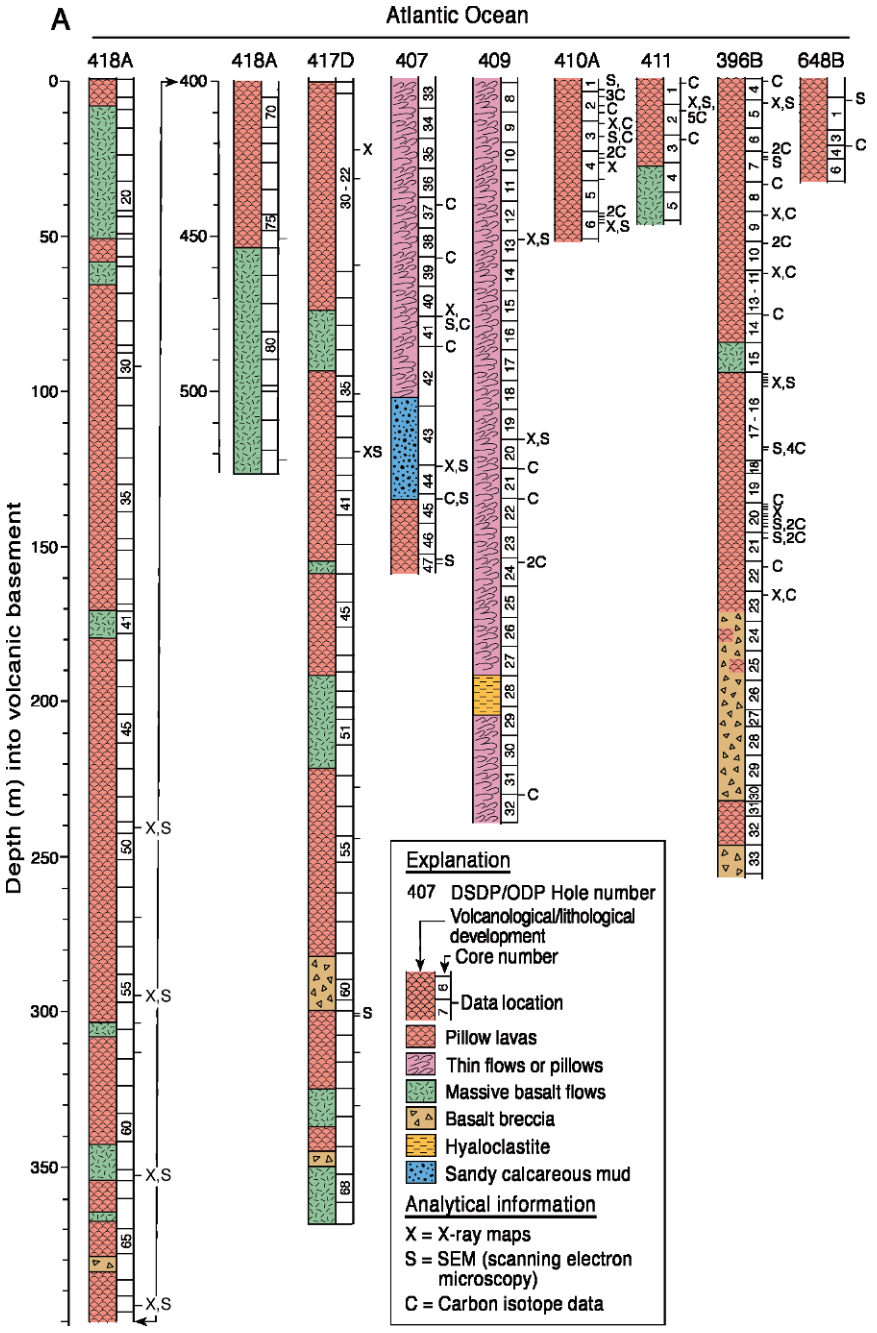

Fig. 5 *Continued*

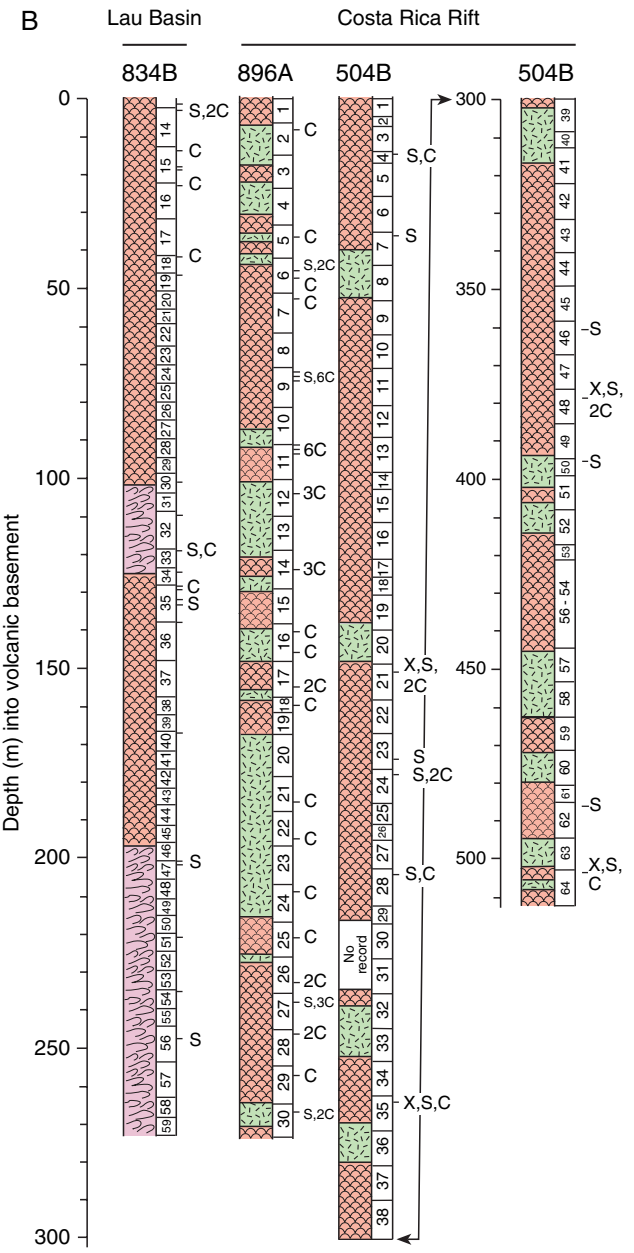

Fig. 5 Compilation of DSDP and ODP holes from the Atlantic Ocean (holes 418A, 417D, 407, 409, 410A, 411, 396B and 648B), the Lau Basin (hole 834A) and Costa Rica Rift (holes 896A and 504B) showing the lithological variations with depth into the volcanic basement. Heights at which bioalteration textures have been studied using scanning electron microscopy (SEM), X-ray mapping (X) and carbon isotopes (C) are shown along with the numbers of samples collected