KECK GEOLOGY CONSORTIUM

PROCEEDINGS OF THE TWENTY-SECOND ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

April 2009
Franklin & Marshall College, Lancaster PA.

Dr. Andrew P. de Wet, Editor
Keck Geology Consortium Director
Franklin & Marshall College

Dr. Stan Mertzman
Symposium Convenor
Franklin & Marshall College

Kelly Erb
Keck Consortium Administrative Assistant

Diane Kadyk
Academic Department Coordinator
Department of Earth & Environment
Franklin & Marshall College

Keck Geology Consortium
Franklin & Marshall College
PO Box 3003, Lancaster PA 17604-3003
717 291-4132 keckgeology.org

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2008-2009 PROJECTS

THE BLACK LAKE SHEAR ZONE: A POSSIBLE TERRANE BOUNDARY IN THE ADIRONDACK LOWLANDS (GRENVILLE PROVINCE, NEW YORK)
Faculty: *WILLIAM H. PECK*, *BRUCE W. SELLECK* and *MARTIN S. WONG*: Colgate University
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PALEOECOLOGY & PALEOENVIRONMENT OF EARLY TERTIARY ALASKAN FORESTS, MATANUSKA VALLEY, AL.
Faculty: *DAVID SUNDERLIN*: Lafayette College, *CHRISTOPHER J. WILLIAMS*: Franklin & Marshall College
Students: *GARRISON LOOPE*: Oberlin College; *DOUGLAS MERKERT*: Union College; *JOHN LINDEN NEFF*: Amherst College; *NANCY PARKER*: Lafayette College; *KYLE TROSTLE*: Franklin & Marshall College; *BEVERLY WALKER*: Colgate University

SEAFLOOR VOLCANIC AND HYDROTHERMAL PROCESSES PRESERVED IN THE ABITIBI GREENSTONE BELT OF ONTARIO AND QUEBEC, CANADA
Faculty: *LISA A. GILBERT,* Williams College and Williams-Mystic and NEIL R. BANERJEE, U. of Western Ontario
Students: *LAUREN D. ANDERSON*: Lehigh University; *STEFANIE GUGOLZ*: Beloit College; *HENRY E. KERNAN*: Williams College; *ADRIENNE LOVE*: Trinity University; *LISA SMITH:* Amherst College; *KAREN TEKVERK*: Haverford College

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GEOLOGY OF THE HÖH SERH RANGE, MONGOLIAN ALTAI
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BLOCK ISLAND, RI: A MICROCOSM FOR THE STUDY OF ANTHROPOGENIC & NATURAL ENVIRONMENTAL CHANGE
Faculty: *JOHAN C. VAREKAMP*: Wesleyan University and *ELLEN THOMAS*: Yale University & Wesleyan University
Students: *ALANA BARTOLAI*: Macalester College; *EMMA KRAVET and CONOR VEENEMAN*: Wesleyan University; *RACHEL NEURATH*: Smith College; *JESSICA SCHEICK*: Bryn Mawr College; *DAVID JAKIM*: SUNY.

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Keck Geology Consortium: Projects 2008-2009
Short Contributions – CANADA

SEAFLOOR VOLCANIC AND HYDROTHERMAL PROCESSES PRESERVED IN THE ABITIBI GREENSTONE BELT OF ONTARIO AND QUEBEC, CANADA

Project Director: ***LISA A. GILBERT*****,** Williams College and Williams-Mystic
Project Faculty: ***NEIL R. BANERJEE***, University of Western Ontario

GEOCHEMICAL INVESTIGATION OF HYDROTHERMALLY ALTERED MAFIC VOLCANIC FLOWS FROM THE 2.7 GA ABITIBI GREENSTONE BELT, ONTARIO AND QUÉBEC, CANADA

LAUREN D. ANDERSON**:** Lehigh University
Research Advisor: Gray E. Bebout

INTERPILLOW HYALOCLASTITES, PILLOW RIM ALTERATION, AND FLUID FLOW IN MAFIC VOLCANICS OF THE BLAKE RIVER GROUP, ROUYN-NORANDA, QUÉBEC

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Research Advisors: Reinhard A. Wobus and Lisa A. Gilbert

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ADRIENNE LOVE**:** Trinity University
Research Advisors: Benjamin Surpless and Lara Heister

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LISA M. SMITH**:** Amherst College
Research Advisors: Peter D. Crowley: Amherst College and Lisa A. Gilbert: Maritime Studies Program of Williams College and Mystic Seaport

MINERALOGY AND METASOMATISM OF THE ROUYN-NORANDA HYALOCLASTITES IN THE ABITIBI GREENSTONE BELT

KAREN TEKVERK: Haverford College
Research Advisor: Chris Oze, Bryn Mawr College

Funding provided by: Keck Geology Consortium Member Institutions and NSF (NSF-REU: 0648782)

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INTRODUCTION

The earliest evidence of oceans and a hydrosphere on Earth comes from schists and mylonites derived from pillow lava and chert protoliths that date back to 3.7 Ga (Eriksson et al., 2005). The earliest evidence of microbial inhabitation of submarine volcanic glasses is found in 3.5 Ga pillow basalts of the Barberton Greenstone Belt (BGB) (Furnes et al., 2004; Banerjee et al., 2006). Ancient proto-glasses exhibit structures similar to biogenetic textures found in modern mafic glasses from in situ oceanic crust and are considered to have provided a habitat and energy source for the earliest life on Earth. Biotic alteration of modern mafic glasses in ocean crust hydrothermal systems releases elements that act as electron donors and create energy for chemoautolithotrophic microbes (Furnes et al., 2007). There is a great abundance of early to mid-Archean volcano-sedimentary successions that were affected by low temperature fluid alteration and these deep ocean settings are conceivably an optimal habitat for early life on a planet experiencing frequent meteoroid bombardment (Hofmann & Harris, 2008). Study of Archean mafic volcanic sequences can yield insight regarding early-Earth ocean chemistry, seafloor chemical alteration processes, and microbial activity representing the evolving Archean biosphere.

The Abitibi Greenstone Belt (AGB), located in eastern Canada, contains a sequence of mafic to felsic volcanics and related sedimentary units and is interpreted to be an uplifted ocean arc-arc collision occurring between 2730 Ma and 2640 Ma. The AGB is split into two volcanic zones of which the Southern Volcanic Zone (SVZ) represents the younger arc and is subdivided into the western Blake River Block (BRB) and eastern Malartic Block (Mueller et al., 1996). The BRB contains a tholeiitic to felsic volcanic sequence, the Blake River Group (BRG), characterized by variolitic basalts at the base (Dimroth et al., 1982). Although relatively undeformed, the units of the BRG experienced sub-greenschist to greenschist facies metamorphism by hydrothermal alteration that was penecontemporaneous with magma eruption (Hannington et al., 2002).

Seafloor hydrothermal alteration in modern crust is accompanied by biotic alteration of quenched glasses. Secondary textures of "granular" and "tubular" features, described by Furnes et al. (2007), have been identified in many in situ ocean crust volcanics (Staudigel et al., 2008). Microbes dissolve the glass to release elements, such as Fe2+ and Mn3+, to oxidize them for energy. This process thrives in shallow sub-seafloor environments with ambient temperatures below 100°C where the electrons are readily exchanged (Butterfield et al., 1997). The oldest microtubules, preserved by a titanite filling, have been identified in previously glassy shards in basalts of the 3.5 Ga Barberton Greenstone Belt (Banerjee et al., 2006) and in the 3.35 Ga pillow basalts on the Pilbara craton (Banerjee et al., 2007). Dating of magma cooling ages, secondary hydrothermal mineral formation, and direct dating of the titanite in microtubules agree that all three processes occurred coevally (Banerjee et al., 2007). Corrosion structures in the ancient volcanic glasses present morphologies with similar size, shape, and distribution to modern microbial alteration textures (Furnes

et al. 2004). Commonly, correlation between corrosion textures and elevated levels of C, N, PO_4, K, and S in the glass is observed, despite C and N abundances commonly being very low in igneous rocks. Thus, elevated signals of these two elements, especially in proximity to microtubules, are evidence of ancient biologic processes occurring in the freshly formed glass (Banerjee et al., 2006).

Nitrogen is a major component of the modern Earth's atmosphere and is recognized as a key element to biologic evolution. Nitrogen concentrations in fresh MORB-like basalts fall between 0.3 and 2.8 ppm, with an average of 1.1 ppm (Busigny et al., 2005), and a $\delta^{15}N_{Air}$ around –5‰ (Marty & Humbert, 1997). Modern hydrothermally altered seafloor basalts are observed to have elevated N contents approaching 20 ppm and elevated $\delta^{15}N$ values approaching +1‰, believed to represent significant contribution of N from overlying sedimentary and organic sources (Li et al., 2007).

METHODS

FIELD WORK

Three study sites in the BRG were visited in 2008. Two sites were used for this study: the Air Liquide (AL) outcrops in Rouyn, Québec, and the Hurd property (see Fig. 1) in Harker Township, Ontario (48.48° N, 79.77° W). The AL outcrops were mapped over an area of 150 x 160 m. Three samples collected from a hyaloclastite and adjacent basalt flow in the northwestern corner of the map were chosen for this study. The Hurd outcrops were previously mapped by Bridge et al. (2008), so mapping

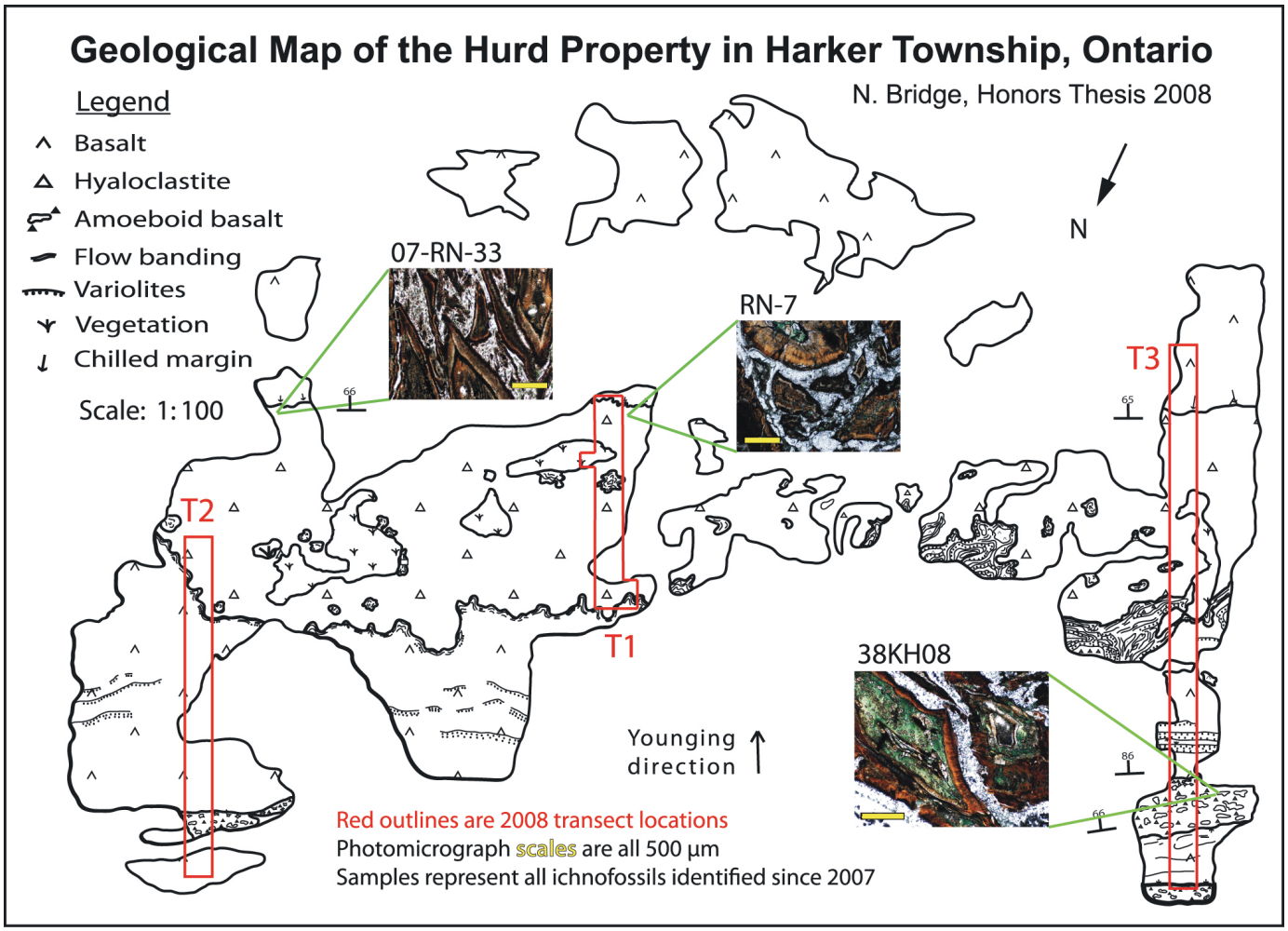

Figure 1. Geologic map of the Hurd Property modified from Bridge et al. (2008). Most samples for this study were selected from T1. See Figure 2 for more sample locations.

in 2008 focused on three transects that included all lithologies exposed in the western (T3), central (T1), and eastern (T2) portion of the outcrop (see Fig.1). Thirteen samples were selected for inclusion in this study: eight representing the length of T1 and included lithologies, four to target the highly silicified portion of the hyaloclastite unit in T1, and one sample from each of the other two transects (T2 and T3) that contain ichnofossils.

LAB METHODS

Detailed descriptions of the hand samples and thin sections were performed for every sample to determine mineralogy and alteration textures. Powder x-ray diffraction was performed at the University of Western Ontario to determine the qualitative mineralogy of sample powders. X-ray fluorescence spectrometry was also performed at Western Ontario to determine the major oxides contents (weight %) and trace element abundances (ppm) for 18 elements. Pilot analyses of N concentration and isotopic ratio (reported as $\delta^{15}N_{Air}$) were performed on a Finnigan MAT 252 mass spectrometer at Lehigh University after the powders were pretreated by oxidation with CuO_x to extract the N_2.

RESULTS

FIELD OBSERVATIONS

The hyaloclastite flow sampled at Air Liquide has a red weathered surface with dark grey-black basalt clasts and rinds interspersed throughout, but the fresh surface is a light grey. The adjacent massive basalt looks similar, with a dark brown-black weathered surface including some patches of orange-red and purple oxidized sulfide staining (see Kernan, 2009, this publication) but a medium to light grey fresh surface.

The majority of T1 at Hurd contains the youngest and thickest hyaloclastite flow at the outcrop (Fig. 2). The fresh and weathered surface color varies from a dark grey to a dark bluish-grey to a bluish-green to a light green color towards the southern and younger extent of the unit. Other distinguish-

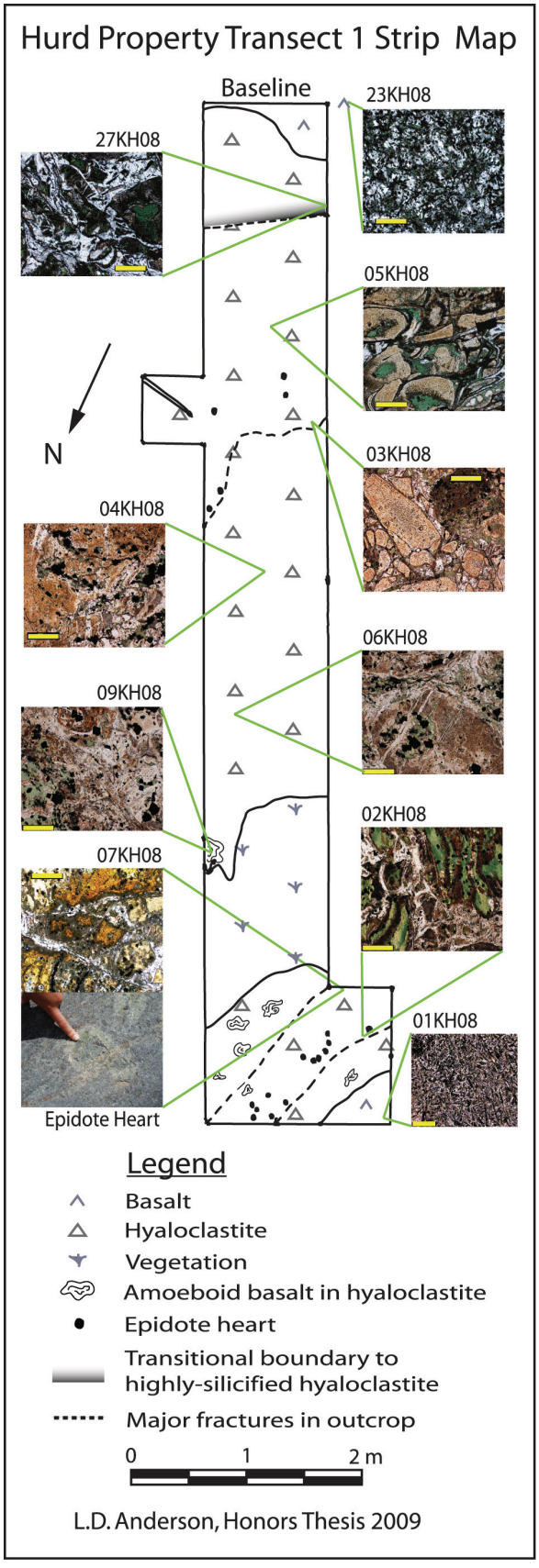

Figure 2. Strip map created of T1 at the Hurd Property with locations of samples included in this study.

ing characteristics that are perhaps indicative of different flow deposits are: the presence of large (10's of cm in diameter) amoeboid basalt clasts; epidote hearts, which are plagioclase-replaced epidote haloes around basalt clasts; and large fractures, which separate outcrop surface color and heights. The hyaloclastites are described in more detail by Love (2009, this publication). The massive basalt units that appear at the far corners of T1 are dark grey, aphanitic, and exhibit some flow banding.

PETROGRAPHY

Inspection of the fractured textures and bleached colors of the AL thin sections confirm that the AL outcrop was more highly altered at higher temperatures than the Hurd outcrop. Mineralogy in these fine-grained rocks is difficult to determine petrographically, but there is an abundance of quartz and variolitic textures within the hyaloclastite samples. The Hurd samples present a range of alteration textures within the hyaloclastite unit. Samples from the northern extent of the youngest hyaloclastite are more thoroughly palagonitized with highly fractured previously-glass clasts, where as the southern samples have more cuspate shards with distinct palagonite-rims. Chlorite, quartz and some opaque minerals, most likely sulfides, dominate the mineralogy in these samples. The powder XRD data are yet to be fully interpreted but show peaks at 2-theta angles representing quartz and chlorite. Microtubules of likely biological origin were identified in one of the samples collected in 2008, 38KH08 (Fig. 3), as well as in two of the samples collected by Bridge et al. (2008) and incorporated into this study (see photomicrographs in Fig. 1).

GEOCHEMISTRY

The AL samples can be further distinguished by their major oxides contents. At least one out of the three samples has a maximum or minimum concentration for every major oxide, relative to the full sample suite, and they have both the maximum (L+L#5) and minimum (L+L#3) volatile content, based on loss on ignition (LOI). Hurd samples generally have higher SiO_2 concentrations (47–63 wt. %)

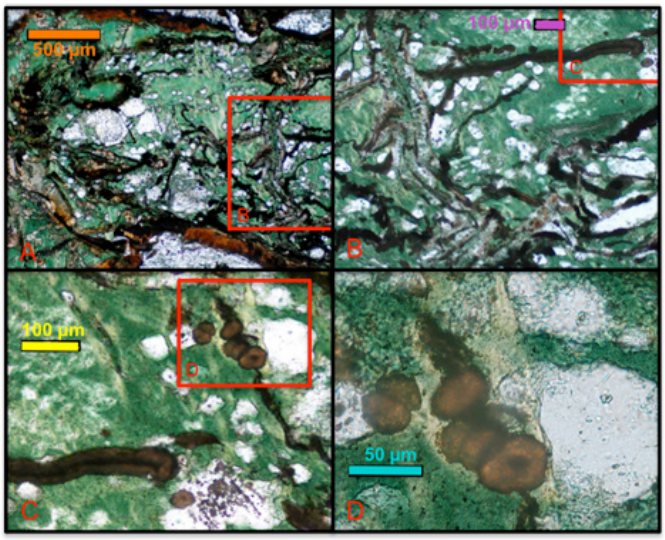

Figure 3. A-D) Photomicrographs of the microtubule ichnofossils most recently discovered at the Hurd Property in hyaloclastite sample 38KH08. The green material is chlorite, brown is titanite, and colorless is quartz and calcite.

despite the bleached appearances of the AL samples (contents ranging 40–49 wt. %), but Air Liquide samples have higher Al_2O_3 concentrations (15–19 wt. % versus 10–14 wt. %). Diagrams showing the major element oxides of the individual samples, normalized to NMORB, are shown in Figure 4. In Figure 5, variations in concentrations of some selected oxides are plotted against horizontal distance along T1 to represent chemical variations related to hydrothermal water-rock reactions.

Initial inspection of the trace element data shows that, for many samples, elements such as U and Th occur in abundances lower than the detection limits of the XRF spectrometer. A plot of Rb (ppm) versus K_2O (wt. %) shows a direct linear relationship indicating co-enrichment of the two elements. This is consistent with the preservation of chemical effects of seafloor hydrothermal alteration, as these elements are commonly co-enriched in modern altered oceanic crust (AOC; Alt, 2003). Successful pilot analyses of N have thus far provided N contents and $\delta^{15}N$ values of 3.5 ppm, +1.3‰ (04KH08), 2.4 ppm, -8.4‰ (05KH08), and 1.7 ppm, +3.0‰ (09KH08). These concentrations and $\delta^{15}N$ values in general fall within the ranges for modern seafloor volcanic glasses and whole-rocks (see Li et al., 2007; unpublished data, G. Bebout et al.).

DISCUSSION

Low temperature hydrothermal fluids commonly enrich basalts in Na and K, and leach Mg and Ca. Higher temperature fluids will enrich basalts in Mg but leach Ca and some alkali metals (Alt, 2003). The Hurd samples are generally depleted in Mg and Ca, and enriched in Na and K, whereas the AL samples are slightly enriched in Mg and Ca, and mostly depleted in Na and K. This confirms the assumption that the AL samples represent a higher temperature hydrothermal system (most likely over 200°C) than the Hurd samples. It is also apparent that, for the AL and Hurd samples, the TiO_2 and Al_2O_3 (considered moderately immobile elements) are inversely correlated.

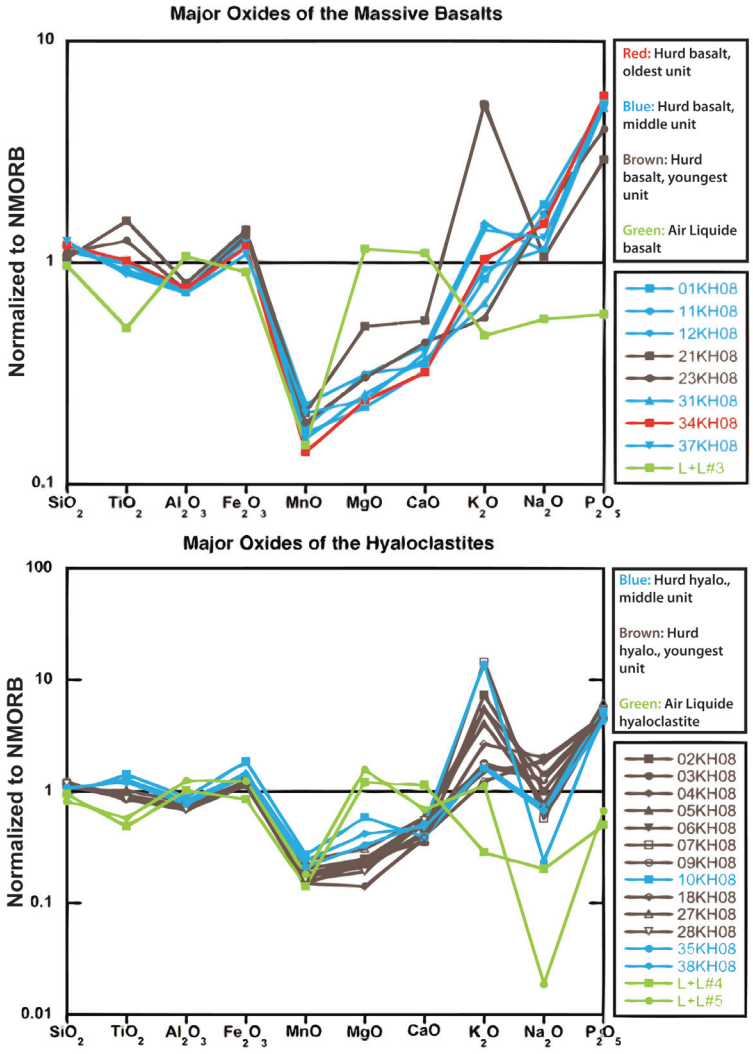

Figure 4. Major element oxides normalized to NMORB as defined by Hofmann (1989).

For some major oxides (e.g., MnO, Fe_2O_3), concentrations appear to be similar for all samples. This suggests that most hydrothermal water-rock interactions, regardless of temperature, remove Mn and do not greatly affect Fe concentrations. The fact that Fe is not significantly altered by water-rock interactions makes it possible to infer other causes of the variations in Fe concentrations. As seen in Figure 5, Fe_2O_3 content decreases significantly near the baseline of T1, correlating with the location of the highly silicified hyaloclastite in which microtubules were identified. This may reflect microbial activity dissolving the glass and oxidizing the Fe^{2+} to Fe^{3+}, the water phase. Potassium, known to be commonly enriched by low-temperature fluid-rock interactions, also decreases near the highly silicified hyaloclastite, possibly reflecting a process in which biotic element depletions are superimposed on chemical change due to abiotic hydrothermal alteration.

Highly silicified hydrothermally altered zones were discovered in BRG volcanics, under a sedimentary chert horizon, and were proposed to have focused flow of rising fluid after the capping of the volcanic rocks by relatively impermeable sediments (Hofmann & Harris, 2008). The massive basalt unit directly above the youngest hyaloclastite could have provided an impermeable cap preventing hydrothermal fluid discharge, although the extensive element depletion in the highly silicified rocks seems to indicate that there was an exit route for the water carrying these dissolved elements. Such an environment, a glass-rich flow sufficiently porous to allow infiltration by rising and cooling hydrothermal fluids and the discharge of these fluids, would be an ideal setting for chemoautolithotrophs.

The initial results of the N isotope analyses demonstrate that the few samples analyzed have $\delta^{15}N$ within the range of those for modern in situ altered ocean crust. This similarity is an early, encouraging indication that

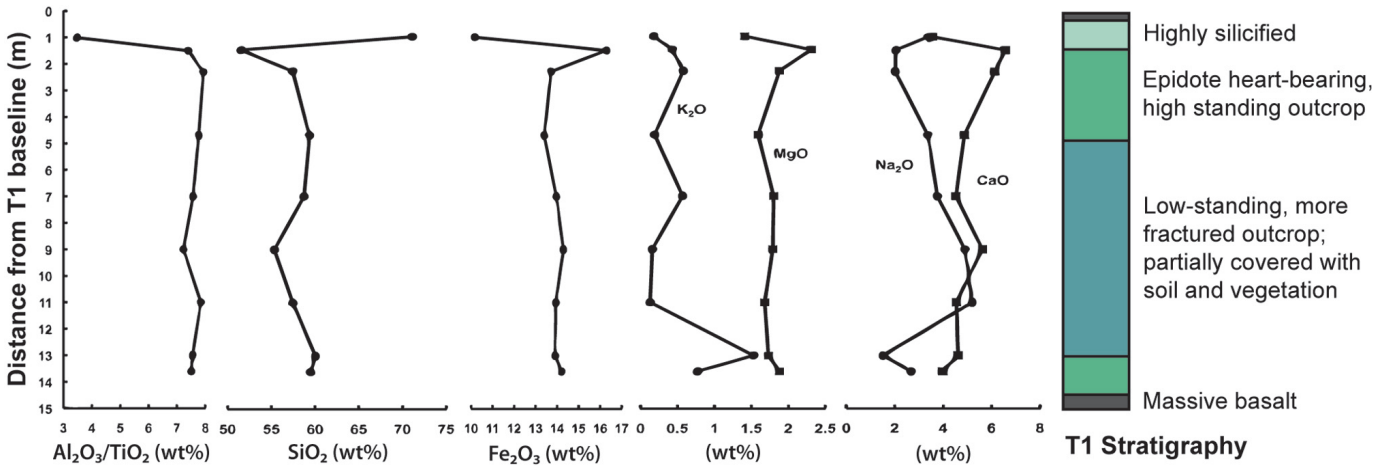

Figure 5. Along-transect variations in select major oxides for the Hurd Property T1. The highly silicified unit at the top is capped by a less permeable basalt flow and contains ichnofossils in the proto-glass chards.

N concentrations and isotopic compositions could serve as tracers of ancient fluid-related chemical alteration (in this case, partly biotic).

CONCLUSION AND SIGNIFICANCE

If the present is the key to the past, the recent work on modern seafloor volcanic glasses, revealing microbial chemical alteration, indicates that ancient greenstone belts and ophiolites are optimal locations to look for Earth's earliest life. Variations in geochemistry between outcrops affected by varying hydrothermal fluid temperatures, and between volcanic flow facies with varying porosity, are suggestive that particularly the hyaloclastites were optimal environments for colonization by microbes. Based on this study, similar lithologies in other Archean metavolanic suites (e.g., Barberton, Hofmann and Harris, 2008) could be targeted as possibly harboring evidence of ancient life. This work could also provide a foundation for investigation of past (and modern) life in hydrothermally altered basaltic rocks on Mars (see Banerjee et al., 2009).

FUTURE WORK

Continuation of this study will include analysis of samples from the other two Hurd transects. Also planned are a more thorough analysis of N concentrations and $\delta^{15}N$ in this suite, in addition to O and C isotope analyses. The XRD and trace element dataset will be further interpreted, and we will consider obtaining data for a more complete suite of elements (e.g., Cs, As, Sb, B, Li, and all of the REE) from a commercial laboratory.

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