KECK GEOLOGY CONSORTIUM

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

April 2009 Franklin & Marshall College, Lancaster PA.

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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

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

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

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HENRY E. KERNAN: Williams College Research Advisors: Reinhard A. Wobus and Lisa A. Gilbert

INTRODUCTION

Deep-sea processes, by which oceanic crust is created at mid-ocean ridges and seafloor volcanoes, are fundamental components of the plate tectonics cycle. An integral part of erupting magma onto the ocean floor is the hydrothermal circulation that occurs as the lava cools. Our knowledge of the oceanic crust can be significantly expanded with the study of ancient seafloor now accreted onto dry land. One of the most famous of these terrains is the Archean (ca. 2.7 Ga) Abitibi Greenstone Belt of the Canadian Shield.

The Abitibi Greenstone Belt is host to various volcanic centers, one of the most important of which is the Noranda Caldera located in the Blake River Group. Hydrothermal processes during the formation of this caldera created areas of massive sulfides, many of which have been mined commercially for more than a century. Indeed, the city of Rouyn-Noranda was founded as a mining town in the center of the caldera, and retains the title of "Copper Capital of Canada".

The outcrop for this study is located behind Air Liquide in Rouyn-Noranda, Quebec. It is a series of volcanic flows at the flank of the main Noranda caldera (Pearson and Daigneault, 2009). Pillow flows indicate that the basaltic lava was erupted underwater. Sulfide weathering is present throughout the outcrop, indicating syn- and, possibly, post-volcanic hydrothermal deposition of sulfide minerals. This study aims to describe the location and properties of samples with sulfide mineralization within a single large, well-exposed outcrop at the edge of Rouyn-Noranda.

FIELD SITE

Three different lithologies were identified in the study site; massive flows, pillow flows, and hyaloclastite flows (Fig. 1). In addition to the lithologies, two textures were identified. One was pillow breccia, which contains brecciated fragments of pillows without the hyaloclastite matrix. The other was Hydrothermal Zone (HTZ) areas. These HTZ areas had intense sulfide weathering visible as orange and purple coloration on the rock.

The area was first mapped on a 5-meter grid and the different lithologies and textures identified. The primary objective in the field was to collect representative samples of all the major pillow and massive units, and samples from the HTZs for comparison. The outcrop consists of alternating massive and pillow flows (Fig. 1). Three pillow flows (B, E, and H; Fig. 1) and five complete massive flows (A, D, G, I, and J; Fig. 1) were defined. The flows stretch east - west, parallel to the paleo-horizontal, which was established from the pillow horizons that dip 80° N.

The pillow flows tend to be thicker than the massive flows, and were easily identifiable by the pillows' interpillow hyaloclastite (IPH) outline. Two additional massive flows (C and F; Fig. 1) do not stretch across the entire outcrop. They are located at the center of pillow flows and probably represent smaller massive flow events, interfingered with pillows. The caldera center is to the north, but because this outcrop formed at the beginning of the volcanic activity (prior to the formation of the caldera) the direction of flow is not clear.



Figure 1. Map of the outcrop. Samples were taken from all the major flow units (identified by a letter) and Hydrothermal Zones (identified by a number). Stratigraphic up is to the North, calculated from the pillow horizons that dip 80° N.

LABORATORY METHODS

Geochemical, petrologic, and physical properties measurements were collected for this study. Twenty samples, at least one from each of the major massive, pillow, or hyaloclastite flow units, were sent to WSU GeoAnalytic lab for major and trace element XRF analysis. Fifteen polished thin sections were made from HTZ samples as well as samples from areas that were not visibly hydrothermally altered. The silicate minerals and textures of these thin sections were analyzed using transmitted light microscopy. The sulfide minerals were analyzed using reflected light microscopy. Vol% was visually estimated from an average of four or five areas at 2.5x optical magnification, and the size distribution of the grains noted in each area. Additionally, five of these thin sections were viewed with a Scanning Electric Microscope (SEM) and the chemistry of both silicates and sulfides determined using Energy Dispersive Spectroscopy (EDAX). An additional eight thin sections were made, and the vol% of opaque minerals was determined using transmitted light microscopy.

Physical properties measurements were made for sixteen samples that had workable cores. Velocity was measured with a 200 MHz GTCS velocity meter at ambient pressure. Mass was measured with a Denver Instruments MD-220. Volume was measured with a Quantachrome Helium Pentapycnometer. Bulk density, grain density, and porosity were calculated using the methods of Blum (1997).

GEOCHEMISTRY

All the lithologies in the outcrop are metamorphosed to sub-greenshist facies and locally altered by hydrothermal circulation. In spite of this alteration and the extreme age of the outcrop, the rocks retain a clear basaltic signature. Figure 2 shows the bulk chemistry results plotted on a total alkalies vs. silica diagram (after LeBas et al., 1986). Figure 3 displays the XRF results for trace elements and major oxides. Few samples have trace element amounts similar to NMORB. Most are enriched in trace metals, with the pillow samples more enriched than the massive samples, especially in Ba and Rb. Interestingly, the pillow rim samples are less enriched than pillow center samples (Fig. 3). The hyaloclastite samples are the most depleted in trace elements,



Figure 2. Total alkalies vs. silica plot after LeBas, 1986. Despite the extreme age of the outcrop, hydrothermal alteration, and low level metamorphism the rocks retain their basaltic signature. Notice the absence of alkalines in the hyaloclastites, possibly due to increase fluid flow through this lithology.



Figure 3. Trace element and major oxide data for Air Liquide samples, plus one sample each from John Deer and Hurd outcrops for comparison. Most samples are enriched in trace elements relative to NMORB. Major oxide values for most samples match NMORB well.

falling below the NMORB standard. The major oxides have less of a range than the trace element results. Massive and pillow flows have oxides amounts slightly lower than NMORB, while the hyaloclastites have enriched oxides, except for Na₂O.

The NMORB trace metal normalization (Fig. 3) does not take into account Cu, Zn, and Ni. Figure 4 displays the sum concentration of these metals in the outcrop. The sum concentration has an average of 253 +/- 86 ppm, but ranges from 124 to 432 ppm. This variation is significant in such a small outcrop. It suggests that fluid flow intensity and composition has varied throughout the outcrop. Samples from pillow units have a higher concentration of these metals than massive units, especially in samples with IPH. The north of the outcrop is especially enriched.



Figure 4. Cu+Ni+Zn concentration across the extent of the outcrop. Each sample has its unit letter (see Fig. 1). Circled samples are IPH and pillow rim samples in Figure 3. The large range of values indicates variation in fluid composition and intensity.

PETROGRAPHY

Silicates

Original flow texture and pseudomorphs after pyroxene can be observed in some samples, while others are simply fine-grained combinations of secondary minerals. Common silicates –mostly secondary- are chlorite, epidote, quartz, amphibole, and sphene.

Hannington et al. (2003) compared the Noranda caldera, where massive sulfides are widespread with the Ben Nevis complex (to the north), which contains few sulfides. This study's outcrop is at the edge of the Noranda caldera as defined by Hannington et al. (2003). Their study reported that epidote and chlorite comprised 30 wt% and 20 wt%, respectively, of many samples. Hannington et al. (2003) described epidote in Ben Nevis samples as mainly Fe-rich (>10 wt% Fe2O3), while his Noranda samples had abundant low-Fe clinozoisite. Chlorite in the Noranda complex was described as commonly Fe-rich, while in the Ben Nevis complex it is of uniformly Mg-rich composition (Fe/Fe+Mg < 0.5).

None of the samples for this study would be considered massive sulfides like the Noranda samples from Hannington et al. (2003) (see below), and are more akin to the Ben Nevis rock descriptions. All the chlorite analyzed in the samples for this study is relatively Mg-rich, matching Hannington et al.'s Ben

	Average open porosity %	Average vol% opaques		Average P-wave Velocity (km/s)		Average bulk density (g/cm ³)	
HTZ	1.24 ± 1.09	2.93 ±	1.51	4.90	± 0.86	2.59 ±	0.13
Pillow	1.16 ± 0.17	0.44 ±	0.11	5.88	± 0.53	2.67 ±	0.04
Massive	0.41 ± 0.20	0.23 ±	0.47	5.46	± 0.44	2.80 ±	0.16
Hvaloclastite	$N/A \pm N/A$	N/A ± N	/A	5.34	± 0.66	N/A ±	N/A

Table 1. Physical properties data for samples with a workable core and a thin section. Other samples had similar physical properties. See Laboratory Methods for description of measurement techniques. Contact samples and a fracture sample were separated because they had a large vol% of opaques and represented areas of weakness.

Nevis pattern. The average Fe/Fe+/-Mg ratio is 0.64 +/- 0.05. The epidote found in the samples, however, is uniformly of clinozoisite composition, with an average of 5.2 +/- 1.2 wt% Fe. This matches the Noranda samples of Hannington et al.'s (2003) study. Hence the silicates in this case are inconclusive indicator of the amount of sulfide mineralization according to the scheme of Hannington et al. (2003).

Sulfides

Four different sulfide minerals were identified using reflected light microscopy and a SEM/EDAX unit: pyrite, pyrrhotite, chalcopyrite, and sphalerite. Oxidized Fe-sulfides were also identified using the SEM. No sample had more than 4.5 average vol% of sulfide minerals. In samples with significant (>1 vol%)sulfides, Fe-sulfides (which includes pyrrhotite, pyrite, and oxidized compositions of both) where by far the most common sulfide mineral (average of 2.0 + - 1.1 vol%), followed by sphalerite (average of 0.7 + - 0.3 vol%), and then chalcopyrite (average of 0.3 + - 0.2 vol%). Sulfide grains vary in size from $<20 \ \mu m$ to $>100 \ \mu m$. Grains $<20 \ \mu m$ are distributed evenly throughout the matrix of the samples, while larger sulfide grains occur both grouped together or evenly distributed. Most Fe-sulfides occur alone, though chalcopyrite and sphalerite are sometimes present in the same grain, most commonly in larger grains. Pyrite grains are mostly anhedral to subhedral, especially when occurring as small grains in the matrix. The larger grains, however, tend to be anhedral and elongated, squeezed between the silicates. Chalcopyrite and sphalerite are mostly anhedral.

Physical Properties

Porosity, seismic velocity, and bulk density were measured for samples that had workable cores (Table 1). Although sulfide minerals have higher densities than the primary minerals of basalt, the amount of sulfides in any sample is not enough to greatly affect density. Porosity ranges from 0 to 2%. Massive units have lower porosity than pillows, which could affect their density. Two large porosity values correspond to pillow samples, and these increased the variability in the pillow average. For further discussion of vesiculation, see Smith (this volume). P-wave velocity did not vary significantly between lithologies (average 5.7+/- 0.7 km/s). Although seismic velocities were at the higher end of the range mentioned by Jacobson (1992) for modern seafloor basalts, they were well within range of values found by seismic refraction of the upper crust in the Abitibi (Grandjean et al., 1995). Overall, HTZ samples have a higher porosity, lower P-wave velocity, and lower density than non-HTZ samples consistent with the idea that they have undergone the most hydrothermal alteration.

DISCUSSION

A natural division for the outcrop is the contact between pillow unit H and massive unit G (Fig 1). Unit H is different from the pillow flows located stratigraphicaly below it (units B and E; Fig. 1). First, it is the thickest unit in the outcrop, indicating either a prolonged lava flow at a steady rate or a larger magma supply rate. The pillows in unit H are also much smaller than those in B and E, indicating either a change in the rate of lava flow between the pillows above and below massive flow G or a change in the magma viscosity. Another indication of this change in flow pattern is the fact that the unit is capped by a pillow breccia texture that is not noticeably present in any of the other pillow units. Above pillow unit H are two thin massive flows, I and J, separated by very distinct hyaloclastite flows (Fig. 1). The predominance of brecciated fragments after the deposition of pillow unit H marks an interesting transition period in the evolution of the outcrop.



Figure 5. Sample from HTZ 5 (Fig. 1) at a pillow edge. A. Outcrop picture of the sample location. The pillows are outlined by orange and purple sulfide weathering in the interpillow hyaloclastic. B. Thin section of sample HTZ 5. The dashed line represents the pillow edge. C. SEM image of a Fe-sulfide grain along the pillow edge with significant oxidation. Notice the incomplete ringed zones. Darker areas have less Fe content. D. SEM image of a pure pyrrhotite (prh) grain inside the pillow, 1.5 cm from the pillow edge.

The contact between H and G is mostly eroded, but where it still exists, sulfide weathering is prevalent. HTZ 4 is a sample taken directly from the contact, and it has a high amount of opaques (>2.5 vol%). HTZ 6 is just 3 meters away from the contact in the pillow unit and also has a high amount of opaques. A sample taken from massive unit G, less than 10 meters south of HTZ 6, yielded very few opaques (<1 vol%). The difference of vol% of opaques within such close proximity suggests that the contact zone was a significant conduit for post-depositional hydrothermal fluid. Pillow unit H has a large number of HTZ textures (numbers 5, 6, and 7), indicating it experienced a significant volume of hydrothermal activity. The absence of intense hydrothermal alteration at other contacts could be due to a lack of hydrothermal activity below pillow unit H, or the effects of erosion.

One sample of particular interest is HTZ 5 (Fig. 1), which came from a core drilled at the intersection of two pillows in the center of pillow unit H (Fig. 5). The sulfides at the pillow edge are all elongated oxidized Fe-sulfides. The amount of oxides in the samples range from 7.5 wt% to 26.8 wt%, and contrasting areas are arranged in a ringed pattern (Fig. 5). Pyrite is present in a few of these mostly oxidized Fe-sulfide grains. Further inside the pillow, Fe-sulfides are pure pyrrhotite (Fe_{1-x}S), with x analyzed to be 0.14 (Fig. 5). The grains of this mineral are more subhedral in shape and there are no oxidized areas. Pyrite was also observed in this area of the pillow. Pyrrhotite grains occurred up to the edge of the thin section, about 2 cm from the oxidized Fe-sulfides at the pillow edge.

Previous researchers have noted the potential hydrothermal conductivity of IPH material (Polat, 2007).

This characteristic of IPH may explain the presence of oxidized Fe-sulfides along the pillow edge of HTZ 5. A primary hydrothermal flow would have deposited Fe-sulfides on the pillow edge and at least 2 cm into the pillow. Subsequent fluid flow would have altered these sulfides, in some cases dissolving parts of the grain. The fact that oxidation and shape alteration are present only in the IPH of HTZ 5 (as compared to further inside the pillow of that sample) suggests more of this subsequent fluid passed through the IPH. A similar pattern is present in the major and trace element data. In Figure 3 the IPH and pillow rim samples are more depleted in trace metals than samples from pillow centers. The elements could have been remobilized by large amounts of fluid flow. Interestingly, the hyaloclastite flows are most depleted in trace metals, and the hyaloclastite flow samples in Figure 2 have no alkalis left. This strengthens the conclusion that hyaloclastite material allows fluid to flow more freely. However, because of the age of this outcrop (2.7 Ga) the timing of any postdepositional fluid flow cannot, with these methods, be significantly constrained.

CONCLUSIONS

This study aimed to characterize the hydrothermal sulfide mineralization and geochemistry of the outcrop studied behind Air Liquide. Massive sulfide mineralization is not present in this outcrop. Certain areas, however, have had more hydrothermal activity than others, based upon the minerals and elements present. Hyaloclastite material, whether as a matrix or in between pillows, seems to act as a conduit. Changes in lithology also form natural zones of weakness through which fluid can pass. In part due to these factors, hydrothermal fluid flow has varied intensity and composition throughout the outcrop.

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