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Project Faculty: *KIRSTEN NICOLAYSEN*: Whitman College *RICHARD HAZLETT*: Pomona College

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# GEOCHEMICAL VARIATION IN PRE-CALDERA AND HOLOCENE LAVAS FROM MAKUSHIN VOLCANO, UNALASKA ISLAND, ALASKA

# MAX T. SIEGRIST

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# INTRODUCTION

Arc magmatism is a fundamental process by which new continental crust forms. Kelemen et al. (2003) document that western Aleutian arc lavas, formed in part by partial melting of subducted, eclogitic lithosphere, match the composition of continental crust. Van Avendonk et al. (2004) find that the central and eastern Aleutian arc approaches the thickness of nascent continental crust (~35 km thick) yet magma genesis in the eastern Aleutians differs significantly from that in the west for three primary reasons. First, the arcuate shape of the Aleutians causes variation in convergence style (Avé Lallement and Oldow, 2000). Second, distance from the Alaska Peninsula causes variation in the volume of sediment subducted along the arc in that sediment flux and thickness are greatest to the east (~168±4°W longitude; Kelemen et al., 2003). Third, a proposed tear in the subducted slab seems to have promoted partial melt of eclogite, yet earthquake locations suggest this tear extends no further east than about 173°E longitude. Thus in the location of Makushin Volcano (~167°W), sediment contributions to subduction zone are high but partial melts of the subducted slab are not anticipated to be important in controlling the geochemistry of Makushin and pre-Holocene lavas.

Makushin Volcano, on Unalaska Island, is located approximately 200 km west of the Alaskan Peninsula and near the transition from oceanic to continental crust. The Pleistocene lavas on Unalaska include andesite and dacite but are mainly basalt and basaltic andesite (Nye et al., 1986). Holocene lavas are more silica rich. They also have a wider compositional range when compared to Pleistocene lavas, though more mafic compositions have been seen in Late Holocene lavas (Nye et al., 1986; Miller, 1998). To determine whether the whole rock chemistry of lava erupted from Makushin or pre-existing vents changed over time, we compare twenty-eight samples collected in the field from "pre-caldera lava" flows, dikes and sills, thought to be Pleistocene in age (McConnell et al., 1997), to the Holocene deposits. In this paper I use whole rock chemistry data to: 1) characterize magmatic differentiation of the rock samples, 2) determine whether the presence of water has affected the magma genesis region, 3) constrain the degree of partial melting, and 4) constrain whether sediment contributed to parental magmas.

# METHODS

During July 14th - 27th 2009, twenty-eight rock samples were collected in the Driftwood Bay area. Samples were collected from the west side of Driftwood Valley, the "Lava Ramp", and from a stratigraphic section of seven lavas exposed in the lower cliff east of Driftwood Valley, informally named here the East Beach Cliff. This section extends the stratigraphic section obtained by Nye et al. (1986) to the oldest exposed rocks on the east side of the valley. The rock samples were gathered at these locations so that the samples would represent a variety of ages. Major and trace element compositions were attained by x-ray fluorescence (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS), all at Washington State University. Sr, Nd, and Pb isotopic compositions are being obtained at the Pacific Centre for Isotopic and Geochemical Research at the University of British Columbia.

## **GEOLOGIC SETTING**

The edifice of Makushin was formed by two unique periods of volcanism that initiated in the Pleistocene. The two periods are separated by one or more episode(s) of prominent glacial erosion. The Makushin deposits from the first period are termed "pre-caldera lavas" (PCL) and the second period of activity is defined by the Holocene age of the lavas and tephras (McConnell et al., 1997) and will be referred to as the "Holocene lavas". The oldest of the PCL lavas are 0.93 Ma in age and enlarged the northwest coast of the island by several kilometers (Nye, 1986). As suggested by the radial dips of flows, the Makushin Volcano was the main vent area for the PCL. The extensive glaciation of these flows indicates a minimum age of late Pleistocene (Begét et al., 2000).

The most significant Holocene event was the collapse of Makushin's summit during caldera-forming eruptions that produced andesitic pyroclastic flows and debris flows exposed in glacial valleys on the north, east, and west sides of the volcano (Begét, et al., 2000). Bean (1999) constrains the caldera forming eruptions to the Holocene, reporting age dates of 8,800 and 8,050 y.b.p. Numerous satellite vents erupted porphyritic lavas during the Holocene (McConnell et al., 1997; Roach, 1997), and at least seventeen explosive eruptions have been recorded since the late 1700's (Miller, 1998).

## **SAMPLE SUITES**

Three PCL sample suites were collected; the Lava Ramp, East Beach, and West Ridge suites (Fig. 1). The Lava Ramp flows are andesites and basaltic andesites emitted from Makushin and were dated inconclusively to <13 ka and <54 ka and glacial striations on the surface corroborate the pre-glacial emplacement, though these are typically included among the Holocene eruptions of Makushin (Bean, 1999). Lava Ramp samples from this study are stratigraphically the youngest PCL. The East Beach stratigraphic section consists of seven lavas, in addition to a sill, three dikes, and a pillow basalt surrounded by thick hyaloclastite, all exposed just to the west of the stratigraphic section. Except for the andesite and dacite dikes, all of the East Beach samples are basalt or basaltic andesite. The West Ridge samples are a'a flows, which range in composition from basaltic andesite to dacite, were mapped as part of the Tertiary Unalaska Formation (McConnell et al., 1997) but a date by Idleman (this volume) suggests that these may be Middle Pleistocene as well.



Figure 1. Map of study area and sample suite locations. Suites are the Lava Ramp, East Beach, and West Ridge. Black triangle = basecamp. Contours are in feet. Tick marks represent northings and eastings for UTM NAD 27 zone 3N.

## RESULTS

These basalt to dacite (Fig. 2) samples are mostly tholeiitic, but a few plot as calc-alkaline (Fig. 3). From this study, only two dikes that cross-cut the East Beach PCL are calc-alkaline and these feed a small pre-caldera satellite vent exposed in cross-section below Mount Marshall Reese. Mg#s (molar Mg/(Mg+Fe)) for samples of this study vary from 0.27 to 0.62. The rocks show trends of decreasing Sc, Sr, Ni, (Fig. 4), Cr CaO, and FeO\* and increasing Ba, Rb, Pb, Zr, Ta, Th, Hf, U, rare earth elements (REE), SiO<sub>2</sub>, Na<sub>2</sub>O and K<sub>2</sub>O as Mg# decreases. Trace element concentrations of these rocks display patterns typical of island arc lavas, including Th and Nb anomalies, and enrichment of the large ion lithophile elements (LIL) and Pb relative to MORB (Fig.

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5). When compared to Lava Ramp and West Ridge samples, the PCL and sill from the East Beach are relatively enriched in the high field strength elements (HFSE) Zr, Nb, REE, and Ta and the LIL Ba (Fig. 5). These samples are also relatively enriched in the major elements  $TiO_2$ , FeO\*, MnO, and  $P_2O_5$  as well as transition metals Ni and Sc.

Thin sections of the East Beach samples all show the presence of olivine (ol), plagioclase (plag), clinopyroxene (cpx), and opaque minerals. Some of the samples have orthopyroxene (opx). Samples display sieve, intergranular, and glomeroporphyritic textures, and embayed plagioclase.



Figure 2. Total alkalis vs. silica diagram after LeBas et al. (1986) for Makushin volcanic rocks. Holocene rocks have filled symbols, pre-caldera are open symbols. Black symbols this study; grey field from previous studies (Roach, 1997; Nye et al., 1986). Symbols by location: Lava Ramp flows = triangles; East Beach samples: lava flows = squares, dikes = inverted triangles, sill = star, pillow lava = diamond; West Ridge flows = crosses.



Figure 3. FeO\*/MgO vs. SiO2 that includes Miyashiro's (1974) dividing line between calc-alkaline and tholeiitic rocks. Thick arrow (after Grove et al., 2003) represents fractional melting under hydrous conditions. Dashed arrow represents tholeiitic NMORB trend (Grove et al., 2003). Thin arrow represents the East Beach stratigraphic section's liquid line of descent. Symbols as in Figure 2, except grey symbols represent Makushin rocks from previous studies (Roach, 1997; Nye et al., 1986).



Figure 4. Variation diagrams of Ni, Sc, Sr, and Ce/Pb vs. Mg#. Symbols and fields as in Figure 2.

## DISCUSSION Crustal level processes

Volcanic rocks from the Makushin area show evidence of fractional crystallization of ol, cpx, and plag because Ni, Sc, and Sr begin to decrease immediately with decreasing Mg# (Fig. 4). Relative enrichment of Ni and Sc in the the East Beach PCL may be the result of either magma mixing and/or assimilation of ol and cpx cumulates (Roach, 1997; Curry, this volume; Idleman, this volume). If assimilation of cumulates are the cause of enrichment, the rate at which the magma passed through the system was quite fast.

Data from this study show Mg# decreasing and SiO<sub>2</sub> increasing upwards in the East Beach PCL, whereas Nye et al. (1986) showed much less fractionated compositions upsection, likely resulting from recharge and mixing of the magma chamber. The petrographic textures seen in samples from the East Beach PCL also suggest magma mixing or multiple stages of crystallization.



Figure 5. Whole rock elemental compositions normalized to primitive mantle (Sun and McDonough, 1989). Circles are averaged Holocene compositions; crosses are West Ridge rocks; squares are averaged compositions for the East Beach stratigraphic section; X is MORB (Sun and McDonough, 1989); blue field represents the range of the East Beach stratigraphic section.

#### Source components represented in the magma

Yogodzinski and Kelemen (1998) and Kelemen et al. (2003) used high Sr/Y and high La/Yb as an indication of partial melting eclogitic subducted lithosphere with abundant residual garnet. Contribution of this melt to parental magmas also creates steeply inclined rare earth element patterns. Unalaska samples show low values of Sr/Y and La/Tb and have a flat slope on a chondrite-normalized REE diagram (see Nd through Lu portion of Fig. 5) indicating that melting of eclogite facies subducted oceanic lithosphere did not contribute to their magma generation.

Fractional crystallization of Makushin rocks documented, in samples from previous studies (grey symbols) as well as Lava Ramp, Unalaska Formation, and Mt. Marshall Reese dike samples from this study, by trends toward high FeO\*/MgO and SiO, (Fig. 3). The fractionation trend of the East Beach PCL is parallel to the other samples' fractionation trends, but has higher FeO\*/MgO at a given SiO<sub>2</sub>. The shift to a parallel fractionation trend toward lower FeO\*/MgO at a given SiO2 on the Miyashiro plot (the thick arrow in Fig. 3) has been interpreted as an indication of an increase in the degree of partial melting of the sub-arc asthenosphere (Grove et al. 2003). Grove et al. (2003) calculated mass balance models of mantle melting reactions from Gaetani and Grove's (1998) experiments at 1.2 GPa. They suggest this trend represents the incongruent melting of opx to form olivine and liquid in a mantle source no longer containing cpx or spinel. In addition to changing the FeO\*/MgO relative to silica content, incongruent melting of opx will increase the MgO relative to FeO\* in the melt. From the reasoning above, compared to Holocene lavas, younger Mt. Marshall Reese dikes, West Ridge lavas, and the East Beach PCL are possibly the result of a lower degree of partial melting.

The observed difference in trace element enrichment between the East Beach PCL and other lavas on Unalaska may be partially explained by different degrees of partial melting of the mantle below the arc. Melting of asthenospheric mantle contributes significantly to arc parental magmas (e.g., Gaetani and Grove, 1998) due to upwelling in the corner region to replace asthenosphere dragged downward by the descending slab (e.g., Kneller and van Keken, 2007). The REE patterns of the East Beach PCL are roughly parallel to those of the Holocene lavas with similar Mg#, suggesting a similar source, but the East Beach PCL are more enriched (Fig. 5). The difference in enrichment can be explained by smaller degrees of melting for the East Beach PCL, though the lack of more primitive, low Mg# samples from the East Beach complicates this interpretation as fractionation of ol + cpx + plag can enrich trace element concentrations while preserving spider diagram pattern shape.

If hydrated mantle peridotite is a component contributing to Unalaska magma generation with in the subduction zone, it is not the only contributor. Though the convergent margin community is still in debate whether elements abundant in sediment are added through a hydrous fluid or a partial melt, there is agreement that there is a sediment component (Elliott, 2003). Plank and Langmuir (1998) observed negative Ce anomalies, Ce/Ce\*, in pelagic sediment subducted in the Mariana trench. In the Aleutian Arc the most negative Ce anomalies occur where convergence and sediment flux are greatest (George et al., 2003). Because Ce/Ce\* for the East Beach PCL range from 0.95 - 0.99 and Holocene lavas from 0.88 - 0.99, sediment is implicated in the genesis of magma beneath Unalaska. More negative Ce/Ce\* values for the Holocene lavas suggest more sediment input relative to the East Beach PCL, and the East Beach PCL have lower values of other indicators of sediment input such as Th/Nb or Th/Nd as well.

Low Ce/Pb relative to oceanic basalts are found in lavas from Umnak Island, to the west of Unalaska, indicating a contribution to the mantle wedge by a fluid component (Class et al., 2000). Pb is very mobile in aqueous fluids and Ce is immobile, so the ratio can distinguish between Pb transported by an aqueous fluid (Ce/Pb < 10) or Pb transported by melts of subducted oceanic lithosphere and/or Aleutian mantle (Ce/Pb >10) (Miller et al., 1994). Figure 4c shows Ce/Pb for Unalaska lavas are all lower than 10. The Holocene lavas' Ce/Pb range from  $2 \sim 5$  and the East Beach PCL values range from 5 - 7 with the exception of one sample plotting around 2.5.

## CONCLUSIONS

The geochemical data from Unalaska Island reveal differences between the East Beach PCL and West Ridge PCL, Mt. Marshall Reese dikes, as well as Holocene lavas. Vertical trends in Ni and Sc vs Mg# for East Beach samples may document accumulation of olivine and pyroxene and possibly magnetite. The high FeO\*/MgO at a given SiO, and high REE concentrations in East Beach lavas both suggest these rocks record smaller degrees of mantle melting, however REE enrichment in these non-primitive samples is at least in part due to fractional crystallization of olivine, pyroxene and plagioclase. Unalaska samples show variable additions of subducted components that include either a hydrous component from sediment or altered oceanic crust and possibly a sediment melt component, but not melt of eclogite.

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