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Students: Adam Curry, Allison Goldberg, Lauren Idleman, Allan Lerner, Max Siegrist, Clare Tochilin

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Keck Geology Consortium: Projects 2009-2010
Short Contributions – UNALASKA

LATE CENOZOIC VOLCANISM IN THE ALEUTIAN ARC: EXAMINING THE PRE-HOLOCENE RECORD ON UNALASKA ISLAND

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

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ADAM CURRY: Pomona College
Research Advisors: Jade Star Lackey and Richard Hazlett

PETROLOGIC AND VOLCANIC HISTORY OF POINT TEBENKOF IGNIMBRITE, UNALASKA, ALASKA

ALLISON R. GOLDBERG: Williams College
Research Advisor: Reinhard A. Wobus

^{40}Ar/^{39}Ar DATING OF LAVAS FROM MAKUSHIN VOLCANO, ALASKA: EVIDENCE FOR XENOCRYST CONTAMINATION

LAUREN M. IDLEMAN: Colgate University
Research Advisor: Martin S. Wong

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Research Advisor: Peter D. Crowley, Amherst College

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CLARE TOCHILIN: Whitman College

Research Advisors: Kirsten Nicolaysen and Robert Varga

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INTRODUCTION

Argon dating is an essential technique for determining the eruptive and petrogenic history of a volcano, particularly for activity as young as the Pleistocene epoch. Without age constraints, the vigor of a subduction zone or a volcano cannot be expressed in terms of volumetric magma extrusion through time (Jicha et al., 2006). The original goal of this project was to date lavas mapped as formations of Plio-Pleistocene age from Makushin Volcano, Unalaska, Alaska, using the ^{40}Ar/^{39}Ar method. New age data are important for refining our understanding of Makushin's eruptive history, and providing age constraints for geochemical modeling of the volcano's petrogenic evolution. Previous K-Ar dates of Aleutian lavas have been found to be inaccurate when compared to newer, more precise ^{40}Ar/^{39}Ar ages (Jicha and Singer, 2006). In this study, samples were collected with an emphasis on constraining the eruption ages of several lava flows, including the Lava Ramp and a sequence of lava flows on a western beach cliff, and an ignimbrite exposed in Driftwood Valley.

During the course of the study, it was found that plagioclase xenocrysts containing extraneous argon may have affected the ^{40}Ar/^{39}Ar data, as only two of the six analyzed samples gave reliable ages. Because the presence of xenocrystic plagioclase can disguise or completely overprint the eruptive age of a lava (Singer et al., 1998), both dated and undated samples were characterized petrographically and analyzed for crystal size distribution and mineral compositions in order to identify the possible presence of xenocrystic contamination.

METHODS

Six lava samples (Table 1) were prepared for ^{40}Ar/^{39}Ar geochronology at the Geochronology Lab at Lehigh University. Rocks were crushed, pulverized and washed several times to remove fine particulate matter. Groundmass and plagioclase separates were prepared using standard magnetic and heavy liquid separation techniques. Both groundmass and plagioclase separates were treated in 10% HNO_3 acid for one hour to remove carbonate and residual volcanic glass before undergoing a thorough hand-picking. The samples were sieved, washed with deionized water and acetone, and packaged in copper foil. Packets of GA1550 biotite (98.54 Ma) and Fish Canyon sanidine (28.20 Ma) were interspersed between the samples to monitor the neutron flux. The packaged samples were irradiated for one hour in the McMaster University research reactor. After irradiation the samples were step heated in an ultrahigh vacuum resistance furnace. The evolved argon was purified with Zr-Al getters and analyzed using an automated VG3600 noble gas mass spectrometer equipped with a pulse-counting electron multiplier. The data were reduced and ages calculated using ArArCalc, a Visual Basic program for ^{40}Ar/^{39}Ar data analysis (Koppers, 2002).

To investigate compositional variations in plagioclase populations in these lavas, a subset of samples was examined using a JEOL JSM-6360 LV scanning electron microscope at Colgate University in Hamilton, NY. Plagioclase compositions were determined using an energy dispersive x-ray system.

A crystal size distribution (CSD) analysis was performed on all samples. Following procedures outlined in Marsh (2007), photomicrographs of each sample were taken in plane light and digitally processed. A histogram of crystal length measurements was made, and a final CSD curve was generated by plotting the natural log of the slope of the histogram versus crystal length.

RESULTS

$^{40}Ar/^{39}Ar$ Data

Two of the analyzed lava samples provided ages that appear to be reliable based upon isotopic criteria and geological relationships: BCA, from the western beach cliff just above an ignimbrite deposit (Fig.1) yielded an age of 139 ± 8.0 ka (uncertainties in $^{40}Ar/^{39}Ar$ ages reported at 1σ confidence level), and DB9-M4 from an outcrop on the western side of the valley was found to be 2.27 ± 0.03 Ma.

Despite care in sample selection and preparation, four out of six samples yielded complex argon spectra, displaying discordant saddle-shaped spectra and positively sloping inverse isochron plots (Figs. 1, 2). Commonly, the spectra failed to define a plateau and a total fusion age was all that could be determined. Expected ages were on the order of 100-500 ka, but these samples gave ages of between 1 and 218 Ma (Figs. 1, 2). K/Ca plots suggest that in many instances, radiogenic ^{40}Ar was derived from distinct sites (or possibly distinct grains) with widely differing compositions. The presence of a population of anomalously old plagioclase xenocrysts or xenocrysts that contain extraneous argon would explain the discordant $^{40}Ar/^{39}Ar$ spectra. In order to assess whether such a population exists in these samples, their petrography was re-investigated, with particular attention paid to characterizing their plagioclase populations.

Petrography and Multiple Plagioclase Populations

The samples in this study are predominantly non-vesicular porphyritic gray to red basalts and andesites. All are dominated by plagioclase, and contain clinopyroxene, opaques, and small amounts of olivine and orthopyroxene. Preliminary petrographic observations indicate that these lavas contain multiple plagioclase populations (Fig. 3). Many of the plagioclase phenocrysts in individual samples display a diverse range of sieve textures; these phenocrysts commonly coexist with crystals lacking these textures. In addition to phenocrysts with sieve textures, several samples also contain concentrically

Table 1: Results of $^{40}Ar/^{39}Ar$ dating

Sample Name	Separate	Location	Location Description	Plateau Age †	Isochron Age	Intercept Value	MSWD	Total Fusion Age
BCA	Plag	0377650, 5982729	Lower western beach cliff	n/a	n/a	n/a	n/a	218.57±2.08 Ma
BCA	**GM**	**0377650, 5982729**	**Lower western beach cliff**	**139.3±8.0 ka**	**140.1±18.0 ka**	**295.3±6.6**	**0.73**	**123.0±12.4 ka**
BCC	Plag	0377283, 5983063	Middle western beach cliff	1.89±0.12 Ma	1.16±0.78 Ma	318±25.7	0.56	5.13±0.12 Ma
BCC	GM	0377283, 5983063	Middle western beach cliff	n/a	358.6±22.3 ka	293.2±2.3	1.79	319.2±19.1 ka
BCD	Plag	0377236, 5983089	Upper western beach cliff	n/a	n/a	n/a	n/a	1.22±0.06 Ma
BCD	GM	0377236, 5983089	Upper western beach cliff	n/a	n/a	n/a	n/a	348.2±6.6 ka
DB9-M4	**Plag**	**0378475, 5980129**	**Western beach cliff**	**2.27±0.03 Ma**	**2.24±0.04 Ma**	**298.6±3.3**	**0.52**	**2.26±0.03 Ma**
DB9-M13	Plag	0379352, 5979230	Upper lava ramp	n/a	n/a	n/a	n/a	8.85±0.10 Ma
DB9-M13	GM	0379352, 5979230	Upper lava ramp	n/a	n/a	n/a	n/a	93.7±7.4 ka
DB-09-1	Plag	0379218, 5979537	Lower lava ramp	n/a	n/a	n/a	n/a	29.55±0.30 Ma

† Reliable ages in **bold**. All $^{40}Ar/^{39}Ar$ ages reported at 1σ confidence level.

Table 1. $^{40}Ar/^{39}Ar$ data.

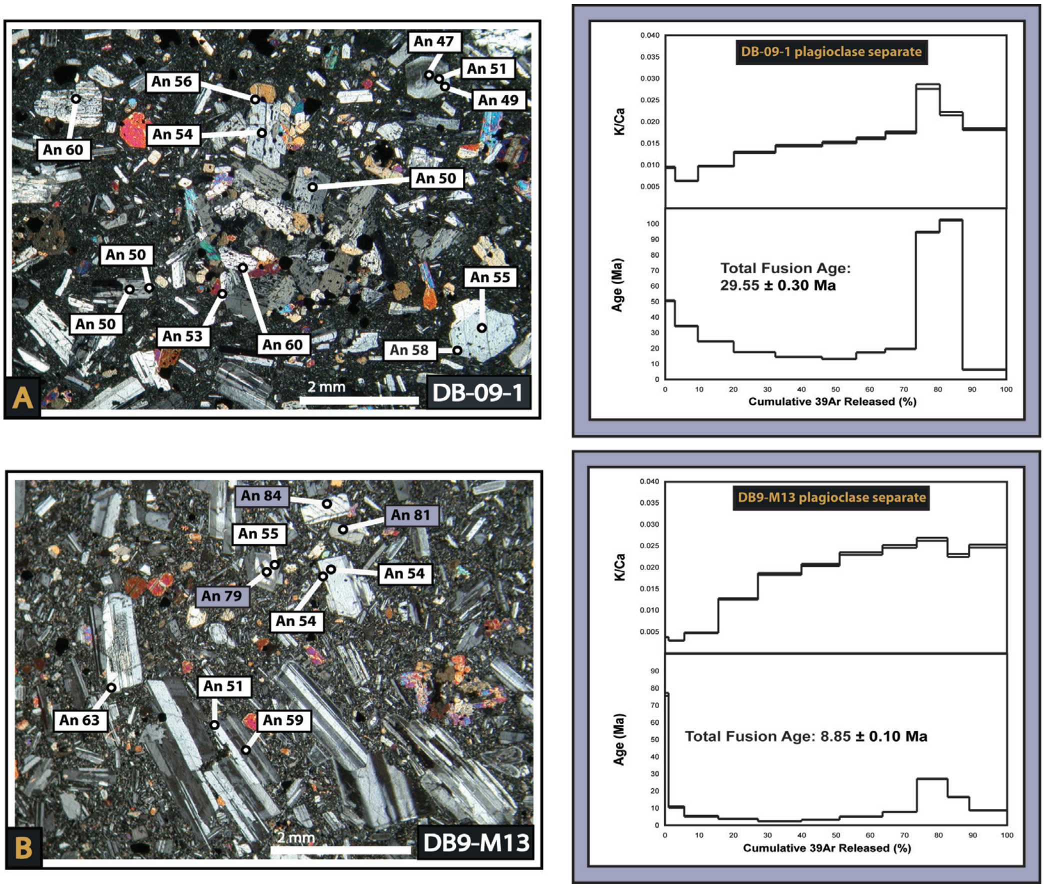

Figure 1. A) The only reliable plagioclase age from this study. B) An age which appears reliable, but contradicts observed stratigraphy. This sample contained many crystal clots, which may have contaminated the groundmass. C) The groundmass separate for BCA gave a reliable young age of 139 ± 0.8 ka. D) The plagioclase separate for the same sample shows a discordant $^{40}Ar/^{39}Ar$ spectrum and an indecipherable inverse isochron.

zoned plagioclase phenocrysts.

All samples contain distinctive crystal clots that exhibit a range of mineral assemblages, most commonly Pl+Ol+Cpx (Fig. 3). The clots are between 1 and 7 mm in size, and many display cumulate textures. Plagioclase crystals within the clots commonly vary in size and morphology, ranging from small, sub- to anhedral grains in the center of the clots to large euhedral crystals at their edges. These euhedral plagioclase crystals are often larger than the majority of plagioclase phenocrysts found in the samples.

SEM-EDS Data

Semi-quantitative EDS analysis revealed that some samples contain at least two distinct plagioclase compositions, characterized by An values of An_{51}-An_{63} and An_{79}-An_{84} (Fig. 3). Plagioclase phenocrysts and clots in other samples were surprisingly homogeneous, ranging from An_{47}-An_{60}. In addition to distinct plagioclase populations, EDS analysis also found evidence of entrained cumulates in the form of an unusually large (4.5 mm) olivine phenocryst in one sample. Opaques within the olivine are chrome spinel, while those in the surrounding groundmass are iron-titanium oxides. The distinct chemical differences between opaques within the large olivine and groundmass opaques supports the idea that this crystal may represent an entrained cumulate grain which crystallized from a more primitive melt.

Crystal Size Distribution Analysis

CSDs for all samples are remarkably similar, and suggest the presence of at least three distinct crystal populations in addition to groundmass microlites.

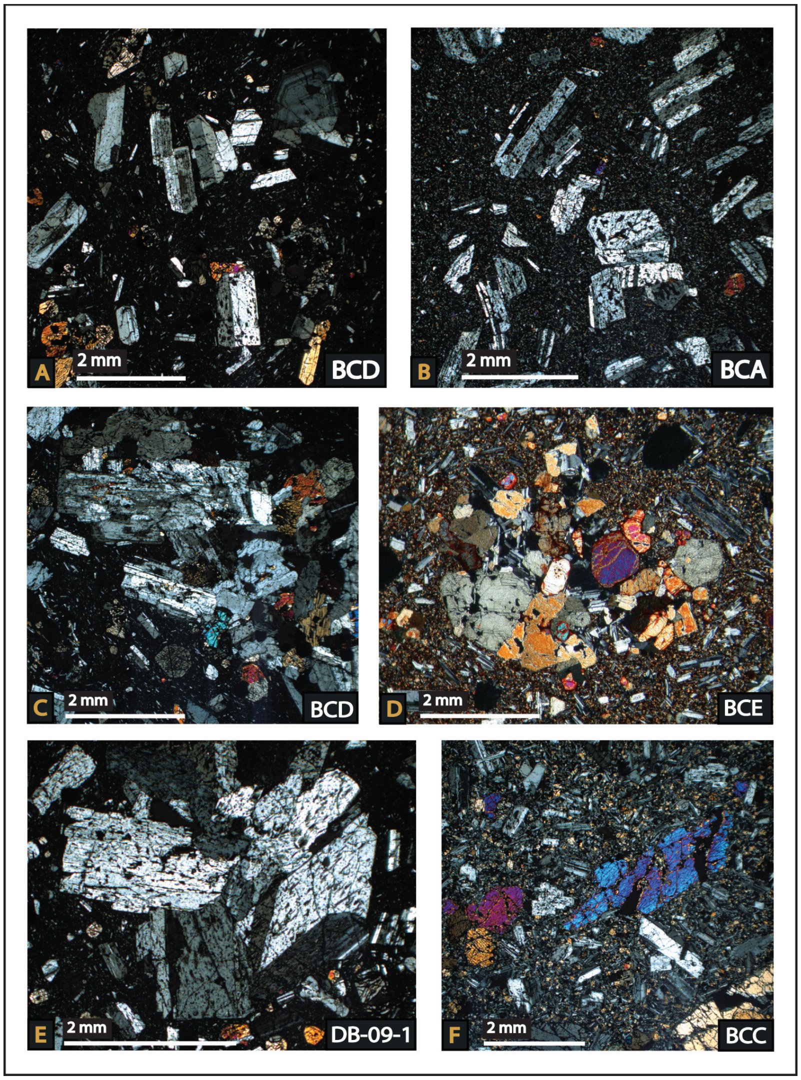

Figure 3. Petrographic evidence for multiple plagioclase populations. A) Twinned and untwinned plagioclase phenocrysts, phenocrysts showing concentric zoning, sieve textures, and lack of sieve textures in a single sample. B) The only sample lacking petrographic evidence for multiple plagioclase populations, but which may represent an aphanitic lava which entrained a single population of plagioclase xenocrysts. C) Large Pl-Cpx-Ol clot. D) Pl-Cpx-Ol (altered to iddingsite) clot in a vesicular red basalt. E) Monomineralic plagioclase clot. F) Olivine phenocryst that may be an entrained cumulate.

In most samples, a break in slope occurs at crystal lengths between 0.10 and 0.15 cm (Fig. 4). The steeply sloping portion of each curve represents a large population of relatively small crystals (<0.1-0.3 cm), while the flatter portion of each curve is indicative of a smaller population of larger crystals.

The CSD curves also show the presence of large crystal clots, which make up a third population of plagioclase crystals. In most cases, there are too few clots per analyzed photomicrograph to clearly define a third trend on the CSD curve. Nonetheless, the clots typically comprise a distinct group of points which fall significantly to the right of other points on the plots (Fig. 4). Although there is a clear correlation between the CSDs and the petrographic observations, the CSD method does not distinguish chemically distinct yet similarly-sized populations of crystals.

DISCUSSION

Only two samples analyzed in this study yielded geologically reasonable ages. Sample BCA had simple $^{40}Ar/^{39}Ar$ systematics and yielded a geologically reasonable age of 139 ± 8.0 ka. This sample was the

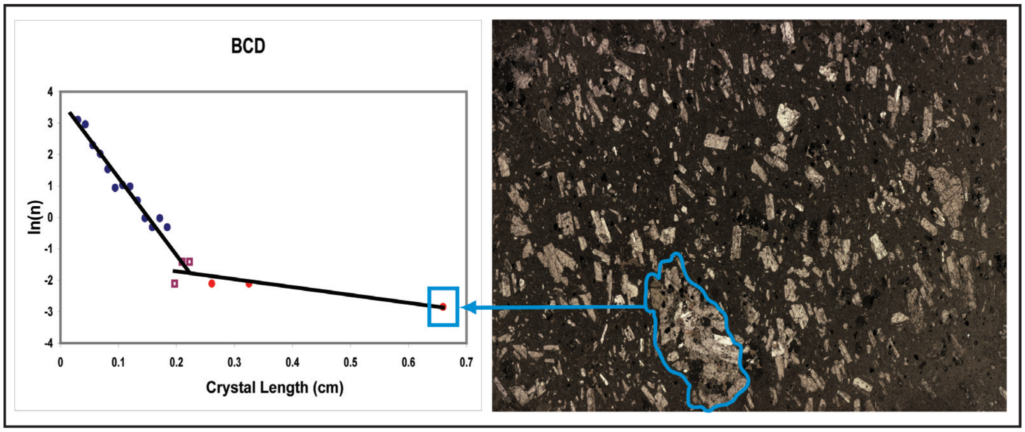

Figure 4. Effects of crystal clots on CSD curves: This sample contains a clot twice the size of the next-largest measured particle, represented by a single outlying point on the CSD curve. Red and blue points belong to distinct crystal populations; purple squares may belong to either population.

stratigraphically oldest sample from a series of lava flows on the western wall of Driftwood Valley. This age is of particular importance because it provides a minimum age of the Point Tebenkof ignimbrite (see Goldberg and Curry contributions, this volume). This ignimbrite evidently marks a significant explosive eruption sometime prior to 139 ka.

DB9-M4, the other well-behaved sample, is from the stratigraphically lowest portion of the western wall of Driftwood Valley, but at a location ~2.5 km south of the stratigraphic section of BCA-BCD. The flow from which DB9-M4 was collected was mapped as a member of the Tertiary Unalaska Formation by McConnell et al. (1997), a reclassification from its previous interpretation as part of the Quaternary older Makushin lava sequence (Nye et al., 1986). The $^{40}Ar/^{39}Ar$ age of this sample was found to be 2.27 ± 0.03 Ma, suggesting that McConnell et al.'s reclassification is correct.

The other lava samples dated in this study yielded highly discordant $^{40}Ar/^{39}Ar$ spectra and gave anomalously old ages. Interestingly, there were large differences in $^{40}Ar/^{39}Ar$ behavior between groundmass and plagioclase separates from the same sample. Groundmass separates commonly yielded $^{40}Ar/^{39}Ar$ ages that are younger and geologically more reasonable than their plagioclase counterparts, although many groundmass ages are still somewhat problematic (Fig. 1), and in one case do not agree with observed stratigraphy. These trends in the 40Ar/39Ar behavior indicate that there is a source of extraneous argon in many samples, especially in plagioclase separates. Since particular care was taken in the field and through petrographic examination to select samples with minimal evidence of alteration, it is unlikely that fluid alteration is the cause of the discordant $^{40}Ar/^{39}Ar$ spectra.

When the $^{40}Ar/^{39}Ar$ data are examined, there is evidence in many samples for xenocryst contamination. Singer et al. (1998) proposed that young lavas characterized by saddle-shaped spectra and ages older than those expected based on geologic evidence may contain undegassed xenocrysts, which may be older than the host lava and/or contain extraneous argon. They showed that Paleozoic plagioclase phenocrysts degassed in a magma at 1000 °C would lose more than 80% of their radiogenic ^{40}Ar after only twenty days, which suggests that xenocrysts in the Makushin lavas spent only days in the host magma, perhaps entrained as the magma rose rapidly and plucked crystals from wall rock prior to eruption. This conclusion contrasts with the interpretations of George et al. (2004), who suggested crustal residence times on the order of several thousand years for neighboring Akutan Volcano. The petrographic, chemical, and CSD data collected from Makushin lavas indicate that most samples contain multiple plagioclase populations and may therefore have a high probability of containing entrained undegassed xenocrysts.

However, relying on the evidence of multiple plagioclase populations as an indicator of xenocryst contamination is not foolproof, and other petrographic observations and $^{40}Ar/^{39}Ar$ results must also be considered. Sample BCA (Fig. 1), one of only two samples to give apparently reliable ages, contains a single plagioclase population comprised of small plagioclase phenocrysts with numerous inclusions. The sample does contain some clots, but they are also very small (less than 1 mm), and few in number. Interestingly, this sample gave the youngest groundmass age found in this study (139 ± 8.0 ka), but also gave the oldest plagioclase age (218.5 ± 2.08 Ma). Given the age of the plagioclase separate and petrographic observations, this sample probably contains a single population of plagioclase xenocrysts containing extraneous argon. These crystals may have been incorporated during magma mixing, but some appear to be broken, suggesting incorporation into a rapidly moving magma. This idea is supported by the fact that these crystals have clearly not degassed in the host magma, as indicated by the anomalously old age and discordant $^{40}Ar/^{39}Ar$ spectrum. The groundmass separate for this sample was particularly clean and gave a well-defined plateau and inverse isochron, suggesting that the groundmass age is reliable and the separate does not suffer from xenocrystic plagioclase contamination.

In an individual sample, it may be impossible to pinpoint which population of plagioclase crystals is affecting the $^{40}Ar/^{39}Ar$ data. However, the presence of multiple plagioclase populations suggests that Makushin has a complex magmatic system characterized by extensive assimilation of wall rocks and/or magma mixing. In particular, crystal clots seem to be quite common in Makushin lavas. Roach (1997) noted that they sometimes comprise up to 28% of lavas erupted from Makushin's central vent, and interpreted the clots as entrained cumulate material. These clots may have been derived from older arc plutons or from the oceanic Kula plate stranded in the mid crust; then they may simply represent material significantly older than the host lava. The presence of xenocrysts derived from old plutons or Aleutian oceanic crust in Makushin lavas would necessitate extremely rapid magma ascent rates in order to bring old xenocrysts to the surface with minimal degassing, and would imply that Makushin's magmatic system is much deeper and vigorous than previously proposed (Nye et al., 1986). If, on the other hand, they represent cumulates crystallized at depth from a recent melt, then extraneous argon (i.e., a high concentration of ^{40}Ar dissolved in the magma itself) is likely responsible for the discordant $^{40}Ar/^{39}Ar$ spectra. A final possibility is that a population of single phenocrysts could be responsible for the discordant $^{40}Ar/^{39}Ar$ spectra, perhaps incorporated in the host lava due to mixing with a magma containing a high concentration of ^{40}Ar.

Identification of the source of these clots and/or other xenocrysts in these lavas is beyond the scope of this project. However, the prevalence of undegassed xenocrysts in the samples collected in this study, as well as the prevalence of crystal clots, suggests that Makushin's magmatic system is well-established and capable of bringing magma to the surface quite rapidly. $^{40}Ar/^{39}Ar$ dates from other Aleutian volcanic centers, such as Seguam Island in the west-central Aleutians, are not affected by extraneous argon (Jicha and Singer, 2006), indicating that Makushin's volcanic system may be particularly robust.

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