# 40 Ar/36 Ar ANALYSES OF HISTORIC LAVA FLOWS \*

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#### Received 16 January 1969

The ratio 40Ar/36Ar was measured for 26 subaerial historic lava flows. Approximately one-third of the samples had 40Ar/36Ar ratios either higher or lower than the atmospheric value of 295.5 at the 95% confidence level. Excess radiogenic  $^{40}$ Ar in five flows ranged from about  $1 \times 10^{-13}$  to  $1.5 \times 10^{-12}$  mol/g. Possible excess  $^{36}$ Ar in three flows was on the order of  $10^{-16}$  to  $10^{-15}$  mol/g. Upper 95% confidence limits for excess  $^{40}$ Ar in samples with normal  $^{40}$ Ar/ $^{36}$ Ar ratios are generally less than  $3 \times 10^{-13}$  mol/g. The origin of the excess  $^{36}$ Ar is unknown but it may be due either to the incorporation of primitive argon that has been stored in the mantle in very low potassium environments or to enrichment in  $^{36}$ Ar as atmospheric argon diffuses into the rocks after they cool.

#### 1. Introduction

This work was done to test the hypothesis [1] that excess radiogenic  $^{40}$ Ar could be a serious problem in potassium-argon dating studies of young volcanic rocks. Excess  $^{40}$ Ar has been found in a wide variety of minerals from intrusive and metamorphic rocks (for example [2]) and recently Damon et al. [1] have reported from 1.2 to  $10.2 \times 10^{-12}$  mol/g of excess  $^{40}$ Ar in a chilled dike border and in phenocrysts of plagioclase, olivine, and amphibole from volcanic rocks. Up to  $2.6 \times 10^{-11}$  mol/g of excess radiogenic  $^{40}$ Ar has been found in submarine basalts of Holocene age from Kilauea [3, 4], but its occurrence there is not surprising in view of the hydrostatic pressure in the ocean depths and the rapidity with which subaqueous flows are quenched.

In the present study, the ratio  $^{40}$ Ar/ $^{36}$ Ar was determined for argon that was extracted from 26 subaerial historic lava flows. The dates of eruption of all of the flows investigated are known from human observations with the exception of three flows, whose ages are established by other evidence (see appendix). The use of historic samples for these studies has two important advantages: (1) the ages of the flows are unambiguous, and (2) the material is so

\* Publication authorized by the Director, U.S.Geological Survey.

young that it is not necessary to make any correction for the  $^{40}$ Ar that is generated by the decay of  $^{40}$ K since the rock formed. Other measurements on historic flows are those of Curtis [5], who reported that the Ischia rhyolite of 1304, the Katmai rhyolite pumice of 1912, and a New Guinea trachyte erupted in 1954 contained no excess  $^{40}$ Ar within the limits of detection. However, the analytical data for these experiments have not been published.

## 2. Experimental technique

Argon extractions were done using the equipment and techniques previously described [6] for argon determinations on very young rocks. Atmospheric  $^{40}$ Ar blanks for the argon extraction lines typically range from about  $4 \times 10^{-13}$  to  $5 \times 10^{-11}$  mole and average about  $2 \times 10^{-11}$  mole per analysis. An  $^{38}$ Ar tracer was not used for these experiments. Instead, the ratio  $^{40}$ Ar/ $^{36}$ Ar was measured for each sample and the quantity of argon was determined from the mass spectrometer ion-beam intensity, which periodically was calibrated with a known amount of  $^{38}$ Ar. This method improves the ability to detect small departures of the ratio  $^{40}$ Ar/ $^{36}$ Ar from the atmospheric value by eliminating the uncertainty in the tracer composition, but it introduces some uncertainty in the quantity of argon measured. The ion-beam calibrations were done with  ${}^{38}$ Ar tracers that were loaded directly onto the mass spectrometer, and also by using the tracer  ${}^{38}$ Ar in argon samples that had been through the normal argon extraction procedure. There was no detectable systematic difference between these two methods of calibration, which indicates that the amount of argon lost in the extraction procedure probably is negligible. Five ion-beam calibrations during the period of this study have a standard deviation of 2.7%, indicating that the measured quantity of  ${}^{40}$ Ar for an experiment is within about 5 to 6% at the 95% confidence level. This uncertainty includes any loss of argon during the extraction process.

Mass analyses were made with a Reynolds-type mass spectrometer operated in the static mode. All analyses were corrected for mass spectrometer discrimination. The appropriate discrimination corrections, which ranged from -1.76% to +0.34% for four mass units, were found by analyzing atmospheric argon, which was obtained by cleaning air on an extraction line. These atmospheric argon samples were large enough (about  $3 \times 10^{-10}$  mole 40Ar) to eliminate any appreciable uncertainty due to a low signal/noise ratio of the  $^{36}$ Ar peak.

For statistical control, smaller samples of air argon also were prepared. These were approximately the same size as an average argon sample from a lava flow (about  $1 \times 10^{-10}$  mole  $^{40}$ Ar). Nine of these small air argon samples that were analyzed periodically have a standard deviation of 0.63% and an average  $^{40}$ Ar/ $^{36}$ Ar value of 296.1 when corrected for discrimination, which is not significantly different from Nier's [7] value of 295.5. In addition, eight  $^{40}$ Ar/ $^{36}$ Ar measurements on the Mt. Mihara 1951 flow and six measurements on the Sakurajima 1946 flow have standard deviations of 0.60% and 0.57%, respectively.

There was no detectable <sup>35</sup>Cl or <sup>37</sup>Cl in the mass spectrometer either before or after an analysis. <sup>36</sup>Ar background was not detectable and <sup>40</sup>Ar background was negligible. Other background peaks, such as masses 16, 28 and 44, either were absent or barely detectable. <sup>38</sup>Ar was not measured because the mass spectrometer normally is used for <sup>38</sup>Ar "spiked" analyses and the <sup>38</sup>Ar memory is too large, relative to the amount of <sup>38</sup>Ar expected in atmospheric argon, to make accurate analyses practical.

In order to minimize the effects of undetected changes in the mass spectrometer discrimination several precautions were taken. The lava flow samples were loaded onto the mass spectrometer sample line in batches, and each batch was analyzed within a few days in order to avoid uncertainties due to long-term instrumental drift. Every batch contained one or more large air argon samples for discrimination determination, and for statistical control, one or more small air argon samples and one or more argon samples from the Mt. Mihara 1951 flow. In addition, all mass analyses were made with the same accelerating voltage and emission current. Observations for a period of four years have shown that detectable changes in mass spectrometer discrimination have occurred only when the filament was turned off and on again. This also was true during the eight-month period in which the historic lava flow analyses were made. Therefore, it is likely that the discrimination correction did not vary appreciably for a given batch of samples. Mass peaks other than argon, such as 16, 28 and 44, generally were less than 20 to 30% of the total gases present during an analysis. In addition, the amount of these other gases was approximately the same for both lava flow argon samples and the air argon samples. There was no systematic variation of results with sample size, indicating that the discrimination probably did not change significantly with total pressure and that the discrimination corrections determined for air argon samples could be applied validly to the lava flow argon samples. For these reasons, the standard deviations found for the small air argons and the Mt. Mihara argon samples should include variations caused by undetected changes in the mass spectrometer discrimination.

Because of the memory effect encountered in static argon analyses, the measured isotope ratios must be plotted against time and extrapolated back to zero time, the time the gas sample was introduced into the mass spectrometer. For the present analyses, the standard error of the extrapolated value was generally 0.2% or less and in all cases is too small to account for the anomalies observed. In addition, this error should be non-systematic and therefore should be included in the statistics found for the small air argon samples and the Mt. Mihara and Mt. Sakurajima samples. Improper choice of the zero time would be systematic but could contribute an error of no more than 0.1% (estimated 95% confidence level).

The data obtained on the small air argon samples  $[x = 296.1, s = 1.87 (0.63\%), s_{\overline{x}} = 0.62 (0.21\%)]$  and the Mt. Mihara samples  $[s = 1.75 (0.60\%), s_{\overline{x}} = 0.62 (0.21\%)]$  are considered to be reasonable estimates of the precision of all analyses and indicate that at the 95% confidence level, a sample is different in composition from atmospheric argon if the ratio  $^{40}$ Ar/ $^{36}$ Ar for a single analysis of the sample is greater than 299.9 or less than 292.3. For the Mt. Mihara and Sakurajima samples, on which multiple analyses were made, statistics may be compared directly with those obtained for the small atmospheric argon samples using conventional statistical tests for comparing means [8].

Potassium measurements, a single analysis for each flow, were by flame photometry using a Li internal standard.

### 3. Results and discussion

The results (table 1) show that 18 of the samples have 40 Ar/36 Ar values that are not significantly different from atmospheric argon. The total amounts of 40 Ar found for the samples are, in most cases, much larger than the average extraction line blank, which indicates that most of the argon comes from the samples and not the equipment. For the 21 samples

that have 40 Ar/36 Ar ratios less than 300, it is possible to calculate 95% confidence limits for the presence of excess 40 Ar. If excess 40 Ar is present in any of these 21 samples, it should be less than the amounts shown in fig. 1. These upper limits are comparable to those calculated for seven Holocene sanidine samples from the Mono Craters [6] and more than two orders of magnitude less than excess 40 Ar from intrusive and metamorphic rocks [1, 2].

Of the eight samples with anomalous argon compositions, five have 40Ar/36Ar ratios greater than atmospheric argon and three less. The calculated amounts of excess argon and the resulting apparent potassiumargon ages are given in table 2. Duplicate analyses of both the Hualalai and Sunset Crater flows give repeatable amounts of excess <sup>40</sup>Ar despite the fact that different amounts of atmospheric argon contamination in the experiments resulted in different values for 40Ar/36Ar (table 1). The occurrence of excess 40Ar in the Hualalai flow is not surprising, because this flow is noted for its abundance and variety of ultramafic xenoliths. Naughton et al. [10] and Funkhouser [11] found ages as high as  $3.0 \times 10^9$  years for xenoliths from this flow and reported that fluid inclusions with a high <sup>40</sup>Ar content are common in minerals in the xenoliths. The consistent excess <sup>40</sup>Ar values for the Hualalai and Sunset Crater flows suggests that large single inclusions are not directly responsible for the excess argon in these flows, but instead that the



Fig. 1. Upper 95% confidence limits for excess <sup>40</sup>Ar in historic lava flows and plagioclase. Excess <sup>40</sup>Ar was *not* detected in these samples. Numbers refer to samples listed in table 1.

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Lava flow	Material	K2O (%)	Sample weight (g)	40 <sub>Ar/</sub> 36 <sub>Ar</sub>		Total 40Ar (10-12 mole)
1. Askja, 1875	Rhyolite	2.23	4.821	292.9		2117
2. Augustine, 1935	Andesite	0.847	10.360	294.6		410
3. Cinder Cone, 1851	Basalt	1.66	11.259	297.3		55
4. Glass Mtn., 130-390 B.P.	Obsidian	4 26	<b>∫ 4.701</b>	283.5		93
	Obsidian	1.20	l 4.305	290.2		52
5. Hualalai, 1800-1801	Basalt	0.906	{ 8.280 { 10.467	329.6 3 <b>5</b> 6.6		115 71
6. Kilauea, 1750 (?)	Basalt	0.480	7,150	294.0		132
7. Kilauea, 1955	Basalt	0.655	9.055	296.7		156
8. Lakagigar, 1783	Basalt	0.419	10.087	<b>294.</b> 7		90
9. Laxa Canyon, 3500 B.P.	Basalt	0.167	10.579	294.7		109
10. Mauna Loa, 1907	Basalt	0.354	11.359	295.5		164
11 Mt Etna 122 B.C	Decalt	176	7.463	306.7		48
11. ML Etha, 122 B.C.	Dasan	1./0	12.479	298.7		58
12. Mt. Etna, 252	Basalt	2.05	9.301	299.4		83
13. Mt. Etna, 1329	Basalt	1.71	8.981	297.4		64
14. Mt. Etna, 1444	Basalt	1.65	11.693	298.0		171
15. Mt. Etna, 1536	Basalt	2.08	6.634	298.0		124
16. Mt. Etna, 1669	Basalt	1.53	8.220	298.7		82
17. Mt. Etna, 1792	Basalt	1.62	6.647	303.7		84
18. Mt. Etna, 1886	Basalt	1.65	9.294	294.7		121
19. Mt. Lassen, 1915	Plagioclase	0.564	14.114	309.1		32
			(11 <b>.006</b>	293.7 )		97
			11.465	291.9		68
			14.659	296.1	$\vec{x} = 293.7$	83
20. Mt. Mihara, 1951	Basalt	0.428	11.370	295.2		73
			12.463	293.1	$s_{\overline{X}} = 0.62 \ (0.21 \ \%)$	82
			12.046	295.5		90
			8.425	292.2		68
			16.320	291.6		109
21. Mt. Vesuvius, 1944	Vesuvite	7.43	12.584	294.9		308
22. Ngauruhoe, 1954	Andesite	1.08	10.790	298.3		61
23. Paracutin, 1944	Basalt	1.19	9.239	296.1		53
			8.754	292.6		351
			7.771	290.2		271
24. Sakurajima, 1946	Andesite	1.66	9.374	292.9	$\bar{x} = 291.4$	190
			4.022	290.5 [	$s_{\vec{x}} = 0.68 \ (0.23 \ \%)$	122
			4.571	292.9		156
			6.645	289.0		
25. Sunset Crater, 1064-1065	Basalt	0.816	8.244	307.1		57
			(7.379	301.4		94
26. Surtsey, 1964	Plagioclase	0.149	<b>3.</b> 753	298.9		71

 Table 1

 Argon and potassium analytical data for historic lava flows.

	Excess		
Lava flow	40 <sub>Ar</sub> (10 <sup>-12</sup> mol/g)	36 <sub>Ar</sub> (10 <sup>-15</sup> mol/g)	Apparent age * (10 <sup>6</sup> years)
5. Hualalai, 1800-1801	1.60 ± 0.16 1.41 ± 0.08	1997	1.19 1.05
11. Mt. Etna, 122 B.C.	$0.25 \pm 0.08$		0.10
17. Mt. Etna, 1792	0.35 ± 0.14		0.15
19. Mt. Lassen, 1915	0.11 ± 0.03		0.13
25. Sunset Crater, 1064-1065	$0.27 \pm 0.09$ $0.25 \pm 0.15$		0.22 0.21
4. Glass Mountain, 130-390 B.P.		2.72 ± 1.14 0.74 ± 0.67	-0.13 -0.03
20. Mt. Mihara, 1951		<b>‡0.15 ± 0.18</b>	-0.07
24. Sakurajima, 1946		<b>‡1.65 ± 0.73</b>	-0.20

 Table 2

 Calculated "excess" argon and apparent age for samples with anomalous 40Ar/36Ar ratios.

\*  $\lambda_{e} = 0.585 \times 10^{-10} \text{ yr}^{-1}$ ,  $\lambda_{\beta} = 4.72 \times 10^{-10} \text{ yr}^{-1}$ .  $40 \text{ K/K}_{\text{total}} = 1.19 \times 10^{-4} \text{ mol/mol.}$ 

+ The ± figures are estimated deviations of precision and include the uncertainty in ion-beam intensity calibration (see text) and the effect of atmospheric contamination [9].

‡ Average of multiple measurements, see table 1.

 $^{40}$ Ar is distributed more uniformly throughout the samples. Whether the  $^{40}$ Ar resides in fluid inclusions or in mineral lattices is not known, although fluid inclusions are not apparent in the samples analyzed. The results for the Mt. Etna 122 B.C. flow are inconsistent. One sample gave an anomalously high  $^{40}$ Ar/ $^{36}$ Ar ratio whereas the other did not. In addition, the calculated amounts of excess  $^{40}$ Ar are different by a much larger amount (a factor of 5) than can be explained by experimental error. This suggests that an undetected, older xenolith may have been present in one of the basalt blocks analyzed.

Single analyses on the Mt. Etna 1792 flow and the Mt. Lassen plagioclase both indicate the presence of excess  $^{40}$ Ar, although there was insufficient material to do more than one analysis on either of these two samples. Damon et al. [1] have suggested that large phenocrysts in volcanic rocks may contain excess  $^{40}$ Ar because their size could prevent their being completely degassed before the flow cools. The results for the Mt. Lassen plagioclase and the Mt. Etna 1792 flow, which contains a high percentage of large phenocrysts, appear to support their contention. However, a single plagioclase phenocryst with a

diameter of about one cm from the 1964 eruption of Surtsey gave a  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio indistinguishable from air argon, as did 10 whole-rock samples with abundant large plagioclase phenocrysts (see Appendix). Thus, for these experiments there does not appear to be any correlation of excess  ${}^{40}$ Ar with large phenocrysts or with any other petrological or petrographic parameter.

The origin of the excess  $^{40}$ Ar is not entirely clear, but the discovery of excess  $^{40}$ Ar in Holocene quenched basalt glass [3] indicates that radiogenic argon, released when older rocks are heated or melted, is dissolved in the melt and may be occluded by minerals as they crystallize.

The occurrence in three samples of mass 40/36 ratios significantly lower than the  ${}^{40}\text{Ar}/{}^{32}\text{Ar}$  ratio of air argon was not anticipated. These ratios probably are not due to  $({}^{1}\text{H}{}^{35}\text{Cl})^+$  contamination because, as mentioned above, chlorine was not present in detectable amounts. It also seems unlikely that they can be due to  $({}^{1}\text{H}{}_{2}{}^{16}\text{O})^{\frac{1}{2}}$  because water was present in about subequal amounts in all of the gas samples analysed. Therefore, the hypothesis that these anomalously low 40/36 ratios represent argon ratios and are due to an "excess" of  ${}^{36}$ Ar or a "deficiency" of  ${}^{40}$ Ar will be adopted for the present. However, the hypothesis that they are due to some unidentified hydrocarbon or other substance of mass 36 cannot be entirely precluded.

The Glass Mountain obsidian gave the lowest values and the calculated amounts of "excess"  ${}^{36}$ Ar for the two experiments are within the experimental error at the 95% confidence level. The  ${}^{36}$ Ar anomalies for the Mt. Mihara and Sakurajima flows are less than for the Glass Mountain obsidian but are still significantly different from air argon at the 95% confidence level. This is true if an atmospheric value of either 296.1 or 295.5 is used for the statistical test. The amounts of "excess"  ${}^{36}$ Ar found in the Glass Mountain and Sakurajima samples are within the capabilities of the mass spectrometer. However, the amount in the Mt. Mihara samples is near the limit of detectability and the apparent anomaly may not be real.

The origin of these anomalously low 40Ar/36Ar ratios is uncertain but they might be produced in several ways: (1) incorporation of primitive argon from a low potassium environment, (2) production of 36Ar by the radioactive decay of 36Cl, or (3) fractionation of atmospheric argon by diffusion.

Cherdyntsev and Shitov [12] reported from 1% to 6% excess  ${}^{36}$ Ar in gases from several Kamtchatka volcanoes. They proposed that argon from the ancient earth's atmosphere has been stored in the upper mantle in rocks of very low potassium content and that the gas is released when these rocks are melted. If this actually happens, some of this argon could be incorporated into volcanic rocks. Although this explanation cannot be precluded, it seems unlikely in view of the high K<sub>2</sub>O contents in these three samples. It is difficult to see how this ancient argon could remain relatively undiluted by radiogenic  ${}^{40}$ Ar that would be released during the formation of rocks of such high potassium contents.

Mechanism (2) is the least likely because the chlorine content of basaltic rocks [13] and the production rate of  $^{36}$ Cl by cosmic-ray neutrons [14] both are too low to account for any significant amount of  $^{36}$ Ar.

A stepwise heating experiment was done on a sample of the Sakurajima flow. The sample was baked overnight at  $300^{\circ}$ C, then held for one hour at temperatures of  $400^{\circ}$ ,  $600^{\circ}$ ,  $800^{\circ}$ , and  $970^{\circ}$ C,

after which it was fused. Within experimental error, the <sup>40</sup>Ar/<sup>36</sup>Ar ratios of the argon released during each temperature step were the same. It has been shown [15, 16] that a large percentage of the atmospheric argon contamination in basalt is held tightly within the rock. Unlike radiogenic <sup>40</sup>Ar, which is released mostly at high temperatures, atmospheric argon is released over a broad temperature range. Apparently, atmospheric argon that diffuses into a rock occupies sites with a broad range of stabilities. Some of the argon probably enters crystal lattices and is not simply adsorbed onto crystal surfaces. [17]. The lack of enrichment of <sup>36</sup>Ar in any of the heating steps suggests that the excess <sup>36</sup>Ar is distributed in sites occupied in equal proportions by normal atmospheric argon. This implies that the excess <sup>36</sup>Ar actually may be atmospheric argon and that it may be produced by isotopic fractionation as argon diffuses into the rock from the atmosphere. A weakness in this argument is that it is difficult to explain why three samples were enriched in <sup>36</sup>Ar whereas the majority of the samples were not.

With the exception of the Hualalai flow, the amounts of excess  ${}^{40}$ Ar and  ${}^{36}$ Ar found in the flows with anomalous  ${}^{40}$ Ar/ ${}^{36}$ Ar ratios were too small to cause serious errors in potassium-argon dating of rocks a few million years old or older. However, these anomalous  ${}^{40}$ Ar/ ${}^{36}$ Ar ratios could be a problem in dating very young rocks. If the present data are representative, argon of slightly anomalous composition can be expected in approximately one out of three volcanic rocks.

#### 4. Appendix

Following are brief descriptions of the material studied, notes on the evidence for age where appropriate, and references where additional information, descriptions, analyses and literature may be found. Only major silicates, in order of abundance, are listed.

1. Askja, 1875. Iceland. Eruption from crater Viti. Rhyolite obsidian with sparse phenocrysts of plagioclase, hornblende, and quartz. Ref. [18]. Collected by R.L.Smith.

2. Augustine, 1935. Augustine Island, Alaska. Hypersthene-augite andesite containing 20–30% phenocrysts of plagioclase (to 2 mm), hypersthene, and augite in a fine-grained groundmass of plagioclase and pyroxene. Ref. [19]. Collected by R.L.Detterman.

3. Cinder Cone, 1851. Lassen Volcanic National Park, California. "Quartz" basalt containing 10% phenocrysts of plagioclase, pyroxene and quartz in glassy groundmass. The quartz is thought to be xenocrystic. Ref. [20]. Collected by K.J.Murata.

4. Glass Mountain, 130-390 B.P. Medicine Lake, California. Rhyolite obsidian with rare feldspar microlites. Trees burned by the rhyolite flow give  $^{14}$ C ages of 390, 380, 190 and 130 years, all ± 200 years [21]. Ref. [22]. Collected by Irving Friedman.

5. Hualalai, 1800-1801. Kaupulehu flow from Hualalai, Hawaii. Vesicular olivine basalt with phenocrysts of olivine in a fine-grained groundmass of plagioclase, olivine, and pyroxene. Ref. [23]. Collected by R.R. Doell,

6. Kilauea, 1750 (?). East rift zone of Kilauea Volcano, Hawaii. Vesicular olivine basalt. Sparse phenocrysts of olivine, plagioclase, and pyroxene in a finegrained groundmass of plagioclase, pyroxene, and olivine. Ref. [23]. Collected by R.R.Doell.

7. Kilauea, 1955. East rift zone of Kilauea Volcano, Hawaii. Vesicular olivine basalt similar to sample 6. Ref. [23]. Collected by R.R.Doell.

8. Lakagigar, 1783. Laki lava flow from Lakagigar, Iceland. Vesicular basalt with sparse phenocrysts of plagioclase and pyroxene in a groundmass of plagioclase, pyroxene, and olivine. Ref. [24]. Collected by R.R.Doell.

9. Laxa Canyon, 3500 B.P. "Older Laxa lava flow" from summit crater of Ketildyngja volcano, Iceland. Basalt containing 5% plagioclase (to 2 mm) in groundmass of plagioclase and pyroxene. Underlain by tephra with <sup>14</sup>C age of  $3830 \pm 120$  years and overlain by tephra with <sup>14</sup>C age of  $2712 \pm 130$ years. Soil profiles suggest age of about 3500 years [25]. Ref. [26]. Collected by R.R.Doell.

10. Mauna Loa, 1907. S.W. rift zone of Mauna Loa, Hawaii. Vesicular basalt similar to sample 6. Ref. [23]. Collected by R.R.Doell.

11. Mt. Etna, 122 B.C. Sicily. Basalt containing 30-40% phenocrysts of plagioclase (to 2 mm), pyroxene, and olivine in a groundmass of plagioclase, pyroxene, and olivine. Ref. [27]. Collected by J.Cl.Tanguy.

12. Mt. Etna, 252. Sicily. Basalt containing 40-50% phenocrysts (to 3 mm), pyroxene, and olivine in a

groundmass of plagioclase, pyroxene and olivine. Ref. [27]. Collected by J.Cl.Tanguy.

13. Mt. Etna, 1329. Sicily. Basalt containing 20-30% phenocrysts of plagioclase (to 4 mm), olivine, and pyroxene in a groundmass of plagioclase, pyroxene, and olivine. Ref. [27]. Collected by J.Cl.Tanguy.

14. Mt. Etna, 1444. Sicily. Basalt similar to sample 11. Ref. [27]. Collected by J.Cl.Tanguy.

15. Mt. Etna, 1536. Sicily. Basalt containing 20– 30% phenocrysts of plagioclase (to 4 mm) and olivine in a groundmass of plagioclase, pyroxene, and olivine. Ref. [27]. Collected by J.Cl.Tanguy.

16. Mt. Etna, 1669, Sicily. Basalt containing 30– 40% phenocrysts of plagioclase (to 5 mm), pyroxene, and olivine in a groundmass of plagioclase, pyroxene, and olivine. Ref. [27]. Collected by J.Cl.Tanguy.

17. Mt. Etna, 1792. Sicily. Basalt containing 20– 30% phenocrysts of plagioclase (to 2 mm), pyroxene, and olivine in a groundmass of plagioclase, pyroxene, and olivine. Ref. [27]. Collected by J.Cl.Tanguy.

18. Mt. Etna, 1886. Sicily. Basalt containing 20– 30% phenocrysts of plagioclase (to 2 mm), pyroxene and olivine in a groundmass of plagioclase, pyroxene, and olivine. Ref. [27]. Collected by R.L.Smith.

19. Mt. Lassen, 1915. Lassen Volcanic National Park, California. Plagioclase phenocrysts about 0.5 cm long separated from glassy dacite. Ref. [28]. Collected by Allan Cox and G.B.Dalrymple.

20. Mt. Mihara, 1951.  $\overline{O}$ -Sima Island, Japan. Vesicular hypersthene basalt containing 5–10% phenocrysts of plagioclase (to 1.5 mm), hypersthene, and augite in a groundmass of plagioclase, pyroxene, and glass (5–10%). Ref. [29]. Collected by M.Ozima.

21. Mt. Vesuvius, 1944. Italy. Vesuvite containing 40-50% phenocrysts of leucite (to 1 cm), pyroxene, and plagioclase (to 1 mm) in a groundmass of plagioclase, leucite, and pyroxene. Ref. [27]. Collected by R.L.Smith.

22. Ngauruhoe. 1954. New Zealand. Andesite containing 20-30% phenocrysts of plagioclase (to 0.5 mm), hypersthene, and augite in a fine-grained groundmass of plagioclase, pyroxene, and glass (5-10%). Ref. [30]. Collected by R.A.Bailey.

23. Paracutin, 1944. Mexico. Basalt containing 20– 30% phenocrysts of plagioclase (to 0.2 mm) and olivine in a groundmass of plagioclase, pyroxene, olivine, and glass (30–40%). Ref. [31]. Collected by K.J. Murata. 24. Sakurajima, 1946. Japan. Vesicular andesite containing 10-20% phenocrysts of plagioclase (to 2 mm), augite, and hypersthene in a trachytic ground-mass of plagioclase, pyroxene, and glass (10-20%). Ref. [29]. Collected by R.A.Bailey.

25. Sunset Crater, 1064-1065. Kana-a flow from Sunset Crater, Arizona. Basalt with sparse phenocrysts of olivine in a groundmass of plagioclase, pyroxene, and olivine. Tree-ring dating gives date of 1064 or 1065 A.D. for eruption [32]. Ref. [33]. Collected by R.A.Loney.

26. Surtsey, 1964. Island of Surtsey, Iceland. Single plagioclase crystal about  $1 \text{ cm} \times 1.5 \text{ cm}$  from glassy basalt. Ref. [34]. Collected by R.R.Doell.

# 5. Acknowledgements

I would like to thank Wilfrid Davis and Barbara Myers for their assistance with the argon analyses, Lois Schlocker, who did the potassium determinations, and my colleagues (see Appendix) who kindly contributed samples.

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