CHAPTER 3

METHODS OF ANALYSIS

K-Ar Radiometric Dating

Radiometric ages were determined by the K-Ar method at the Oregon State University laboratory by Dr. Robert Duncan. Samples were crushed and sieved to an even size, 0.5 to 1 mm. Powdered portions were sent to University of Oregon for K analysis by atomic absorption spectrophotometry, unless already determined by XRF as discussed in the next section. Methods employed were conventional K-Ar techniques (Dalrymple and Lanphere, 1969). Measurement of the Ar-isotopic compositions were done with an AEI MS-10S mass spectrometer with on-line, high-vacuum gas extraction lines and a ^{38}Ar spike pipette system. The extraction lines were baked for 12 hours at 150°C while connected to oil diffusion pumps to remove atmospheric gases and create low pressures prior to sample fusion. Active gases released during fusion of approximately 5 g samples were removed by hot Ti-TiO_2 sponge metal getters before Ar measurement.

Ar-isotopic data were collected using a computer controlled peak-hopping algorithm with base-line correction. Peak heights were regressed to obtain initial isotope concentrations for each analysis. Reported analytical uncertainties (1 sigma) are given for each age determination. Analytical uncertaintly is a combination of uncertainties in fitted peak heights, measurement of K-content, and decay constants (Steiger and Jaeger, 1977).

All dating was done on relatively fresh rocks from the volcanic system, producing good age data. The exception to this is Ey-16, which produced an age older than what would be consistent with its stratigraphic position. This sample is from a sill and the older age is interpreted to reflect inherited argon because

it seems likely that the unit never had the opportunity to reequilibrate with atmospheric argon.

Microprobe Analysis

Microprobe analyses were performed on a Cameca SX-50 electron microprobe at Oregon State University, with the help of Dr. Roger Nielsen. Prepared samples were thin sections in the case of all minerals probed, and a plug of picked glass for the one hyaloclastite probed. Corrections for deadtime, background and matrix effects were performed using the Cameca PAP program. Olivines and pyroxenes were probed using a 15 kv beam at the smallest allowable width, with a beam current of 50 nA. Plagioclase was probed using a 15 kv beam with a dispersed width, about 5 µm, and a 30 nA current. Oxides were probed with a 15 kv beam, and a 50 nA current; glass with a 5 µm wide, 15 kv beam, and 30 nA current.

Standards were as follows:

	Olivine	Pyroxene	Plagioclase	Glass	Magnetite/Ilm.
Na2O	-	KANO	KANO	KANO	-
MgO	FO83	KAUG	KAUG	KAUG	CROM
Al2O3	LABR	KAUG	LABR	BASL	CROM
SiO2	FO83	KAUG	KANO	BASL	KAUG
P2O5	-	-	-	FLAP	-
K2O	-	-	SANI	SANI	-
CaO	KAUG	KAUG	LABR	BASL	-
TiO2	-	BASL	-	BASL	RUTI
Cr2O3	-	CROM	-	-	CROM
MnO	PYMN	PYMN	-	PYMN	PYMN
FeO	FAYL	FAYL	KAUG	BASL	MAGT

NiO	NISI	-	-	-	-
BaO	-	-	SANI	-	-
V2O5	-	-	-	-	V metal

All standards are described in detail in the laboratories at OSU. KANO = Anorthoclase; FO83 = Olivine (Forsterite 83) from the Springwater meteorite; KAUG = Augite from Kakanui, New Zealand; CROM = Chromite; LABR = Plagioclase (Labradorite) from Lake County, Oregon; BASL = Basaltic Glass from Makaopuhi Lava Lake, Hawaii; FLAP = Fluorapatite from Durango, Mexico; SANI = Sanidine; RUTI = Rutile; PYMN = Pyroxmanganite; FAYL = Fayalite from Rockport, Maine; MAGT = Magnetite from Minas Gerais, Brazil; NISI = synthetic nickel silicate, Ni_2Si; V metal = Vanadium metal (synthetic).

Oxides were calibrated to the standards at the beginning of a probe day; one standard per mineral was analyzed three times and averaged, prior to probing, after calibration, and again at the end of the day of probing. In this manner it was possible to see any variations in element abundances due to deterioration of calibration, during the day.

Samples were chosen for microprobe analysis by the amount of phenocrysts present, and the major element (XRF) compositions. Phenocrysts, microphenocrysts, and groundmass crystals were probed from samples as primitive as 15 wt% MgO, to some of the most evolved with < 2 wt% MgO. All crystals were probed across faces from rim to core.

XRF Analysis

Major and some trace elements were analyzed with X-ray fluorescence spectroscopy (XRF) by Dr. Peter Hooper, at Washington State University. Crushed rock samples, from 2 mm to about pea-size were sent to WSU, where further preparation (fusing into glass beads) was performed. Analysis

occurred with a fully automated Rigaku 3370 X-ray spectrometer in two separate batches. Each batch included duplicate analyses for one sample in order to determine precision of analysis. This is shown in Tables 3.01 and 3.02. Only the normalized data were used for analysis, as all raw data was assumed to have varying amounts of volatiles.

INAA Analysis

Seven samples were analyzed for REE, Ta, and Hf concentrations through instrumental neutron activation analysis. These analyses were performed by Dr. Robert Walker, at the Radiation Center, Oregon State University. Sample preparation consisted of powdering approximately 1 gram of sample, which was then sealed into double vials. Standards used in analysis were 1633a (Fly ash), CRB II (Columbia River Basalt), and Allende (meteorite). These are discussed further below. Irradiation was performed at 1 MWatt for 6 hours in the outer ring rotating rack at the OSU TRIGA reactor. Gamma radiation was counted by Ge(Li) detectors, for 4,000 seconds, 7 days after irradiation, and 20,000 seconds, 30 days after irradiation.

Individual errors which are reported for the analytical results are based on one standard deviation of the sample's net counts in the photopeak of interest. Because the net counts in some photopeaks were relatively high, the standard deviation value shown for the corresponding analytical result turned out to be comparatively small (i.e., less than 1 or 2% of the analytical result). If these small standard deviation values are used as the only measure of confidence in the reported results, they will indicate an unreasonably high level of analytical accuracy. In these cases, a better estimate of the analytical accuracy can be obtained by using the percent uncertainty value listed for the element under consideration. This value is the percent or relative standard deviation (using

Table 3.01: Precision of XRF analysis.
(precision includes analytical error and sample heterogeneity)

	Ey-6 3/1/16	Ey-6R 3/1/17	error	Ey-16 3/1/16	Ey-16R 3/1/17	error	Ey-38 9/1/29	Ey-38R 9/1/30	error
UNNORMALIZED RESULTS									
SiO2	45.74	47.23	1.49	48.26	48.78	0.52	49.45	49.78	0.33
Al2O3	13.67	14.02	0.35	13.88	13.96	0.08	14.46	14.55	0.09
TiO2	3.365	3.422	0.057	3.731	3.735	0.004	3.362	3.385	0.023
FeO*	13.61	13.5	0.11	13.2	13.8	0.60	12.90	12.84	0.06
MnO	0.209	0.209	0.00	0.219	0.215	0.004	.220	0.222	0.002
CaO	9.96	10.14	0.18	9.04	9.02	0.02	8.93	8.97	0.04
MgO	5.09	5.24	0.15	4.45	4.4	0.05	4.58	4.65	0.07
K2O	0.74	0.75	0.01	0.86	0.88	0.02	0.96	0.96	0.00
Na2O	2.95	3.04	0.09	3.55	3.58	0.03	4.00	4.04	0.04
P2O5	0.392	0.395	0.003	0.507	0.511	0.004	0.614	0.618	0.004
Total	95.73	97.95	2.22	97.70	98.88	1.18	99.48	100.02	0.54
NORMALIZED RESULTS									
SiO2	47.78	48.22	0.44	49.40	49.33	0.07	49.71	49.77	0.06
Al2O3	14.28	14.31	0.03	14.21	14.12	0.09	14.54	14.55	0.01
TiO2	†3.52	†3.49	0.03	†3.82	†3.78	0.04	†3.38	†3.38	0.00
FeO*	14.22	13.78	0.44	13.51	13.96	0.45	12.97	12.84	0.13
MnO	0.218	0.213	0.005	.224	.217	.007	.221	.222	.001
CaO	10.4	10.35	0.05	9.25	9.12	0.13	8.98	8.97	0.01
MgO	5.32	5.35	0.03	4.55	4.45	0.11	4.60	4.65	0.05
K2O	0.77	0.77	0.00	0.88	0.89	0.01	0.97	0.96	0.01
Na2O	3.08	3.1	0.02	3.63	3.62	0.01	4.02	4.04	0.02
P2O5	0.41	0.403	0.007	0.52	0.52	0.00	†0.62	†0.62	0.00
Total	96.48	96.50		96.18	96.22		96.00	96.00	
Trace elements									
Ni	26	23	3	2	2	0	23	19	4
Cr	24	22	2	8	8	0	35	31	4
Sc	40	26	14	35	29	6	28	22	6
V	396	397	1	360	368	8	263	277	14
Ba	152	151	1	195	170	25	187	195	8
Rb	14	12	2	16	17	1	15	16	1
Sr	395	387	8	403	405	2	426	423	3
Zr	204	201	3	246	248	2	278	275	3
Y	32	33	1	41	42	1	43	43	0
Nb	†38	†38	0	†42	†43	1	†43	†42	1
Ga	25	24	1	25	22	3	26	25	1
Cu	109	102	7	32	24	8	44	45	1
Zn	116	113	3	†133	†132	1	†129	†131	2
Pb	0	0	0	0	0	0	0	1	1
La	16	22	6	27	31	4	15	22	7
Ce	49	56	7	72	74	2	76	84	8
Th	1	2	1	2	4	2	3	2	1

*** Total Fe reported as FeO**

† denotes values >120% of highest standard

Table 3.02: Accuracy of XRF analysis.

Accuracy (for standards run NOT at the same time as samples)

	BCR-1 A*	BCR-1 F*	BCR-1 G*	BCR-1 average	BCR-1 WSU 1	BCR-1 WSU 2	error
NORMALIZED RESULTS							
SiO2	55.31	55.43	55.33	55.36	55.42	55.42	**0.06**
Al2O3	13.92	13.84	13.88	13.88	13.72	13.71	**0.17**
TiO2	2.29	2.238	2.26	2.26	2.245	2.244	**0.02**
FeO*	12.26	12.33	12.33	12.31	12.51	12.5	**0.20**
MnO	0.18	0.183	0.185	.183	0.188	0.186	**0.005**
CaO	7.07	7.04	7.08	7.06	7.04	7.02	**0.04**
MgO	3.53	3.52	3.51	3.52	3.46	3.48	**0.06**
K2O	1.72	1.73	1.72	1.72	1.73	1.74	**0.02**
Na2O	3.35	3.33	3.33	3.34	3.32	3.33	**0.02**
P2O5	0.365	0.366	0.377	.369	0.363	0.369	**0.006**
Total	100.00	100.01	100.00	100.00	100.00	100.00	
Trace elements							
Ni	10	15.8	13	13	4	6	**9**
Cr	15	17.6	16	16	20	17	**4**
Sc	33	33	33	33	36	33	**3**
V	420	399	404	408	388	404	**20**
Ba	680	675	678	678	644	657	**34**
Rb	47	46.6	47	47	46	48	**1**
Sr	330	330	330	330	324	326	**6**
Zr	185	190	191	189	170	174	**19**
Y	40	37.1	39	39	37	38	**2**
Nb	19	13.5	14	16	16	14	**2**
Ga	22	20	22	21	21	20	**1**
Cu	16	18.4	18	17	18	7	**10**
Zn	125	120	129	125	128	123	**3**
Pb	14	17.6	13.6	15	17	14	**2**
La	27	26	25	26	21	20	**6**
Ce	53	53.9	53.7	54	57	44	**10**
Th	6.1	6	6.04	6	7	4	**2**

*** Total Fe reported as FeO**

A* Abbey, S., 1983, Studies in "standard samples" of silicate rocks and minerals, 1969-1982. Geological Survey of Canada Paper, p. 15-83.

F* Flanagan, F.J., 1976, 1972 compilation of data on USGS standards. U.S. Geological Survey Professional Paper 840, p. 131-183.

G* Gladney, E.S., Burns, C.E., and Roelandts, I., 1983, 1982 compilation of elemental concentrations in eleven USGS rock standards. Geostandards Newsletter, 7, p. 2-226.

one standard deviation) obtained for the specific element being considered, based on repeated counts of appropriate standards for this same element.

Accuracy of the analyses can be seen by comparison of the run standards with their literature values, shown in Table 3.03.

SRM 1633a (coal fly ash) is a standard reference material prepared and certified by the National Institute of Standards and Technology. Elemental abundances given in Table 3.03 are not certified by the NIST, but represent the best value for a particular element reported in the available literature, usually Korotev, R.L. (1987).

CRB II is a rock standard prepared by the OSU Radiation Center. Samples of Columbia River basalt, collected from the type locale of BCR-1, a rock standard prepared by the U.S. Geological Survey, were cleaned, ground, homogenized, and split. Splits of CRB II have been repeatedly calibrated against BCR-1 and other standards using the OSU analytical facilities as well as other laboratories throughout the U.S. These analyses have shown that CRB II has the same elemental abundances as BCR-1. Elemental abundances for BCR-1 are taken from Tables 106 and 107 of Flanagan, F.J. (1976).

Allende is a meteorite standard prepared by the OSU Radiation Center. Elemental abundances are "best" literature values as determined by Professor Roman A. Schmitt, OSU Department of Chemistry and the Radiation Center.

Helium Isotopic Analyses

Four samples were analyzed for Helium isotope composition, Ey-32, Ey-39, Ey-49, Ey-50. I hand-picked olivine phenocrysts from these samples under a microscope and then sent them to Dr. David Graham at the University of California, Santa Barbara. The helium trapped in inclusions was extracted by in vacuo crushing, and isotopes were measured on a mass spectrometer.

Table 3.03: Standard analyses and associated error for INAA accuracy.

	Allende literature	Allende analysis	Allende error	CRB literature	CRB analysis	CRB error
La (ppm)	0.48	0.8 ±0.1	0.3	25.00	25.6 ±0.3	0.6
Ce (ppm)		1.3 ±0.1		53.7	52.4 ±1.5	1.3
Nd (ppm)		<63		28.7	27.4 ±5.4	1.3
Sm (ppm)	0.28	0.40 ±0.02	0.12	6.58	6.65 ±0.04	0.07
Eu (ppm)	0.116	0.14 ±0.02	0.024	1.96	2.03 ±0.04	0.07
Tb (ppm)		<0.57		1.05	1.05 ±0.08	0
Yb (ppm)		0.52 ±0.12		3.39	3.02 ±0.26	0.27
Lu (ppm)		<0.36		0.512	0.61 ±0.08	0.102
Ta (ppm)		<0.78		0.79	0.8±0.1	0
Hf (ppm)		<1.8		4.9	5.5±0.2	0.6

	1633A literature	1633A analysis	1633A error	Reported INAA uncertainty
La (ppm)	79.1	78.8±0.6	0.3	3%
Ce (ppm)	168.3	169.6±1.5	1.3	7%
Nd (ppm)	75.7	75.7±12.0	0	12%
Sm (ppm)	16.83	16.88±0.08	0.05	5%
Eu (ppm)	3.58	3.52±0.04	0.06	5%
Tb (ppm)	2.53	2.53±0.09	0	5%
Yb (ppm)	7.5	7.79±0.29	0.3	5%
Lu (ppm)	1.075	1.06±0.09	0.02	5%
Ta (ppm)	1.93	1.9±0.1	0	5%
Hf (ppm)	7.29	6.8±0.2	0.5	5%

"The instrument is a 90° curvature, 21-cm radius, statically operated, double-collector mass spectrometer. The sensitivity for He is $>10^{-4}$ $Atorr^{-1}$, and the absolute detection limit is $<10^4$ atoms of ^3He. The inlet system uses a low-temperature (40K) charcoal trap for separation of He from other rare gases. The precision for He isotopic ratio determinations is very close to the limit based on ion counting statistics for the weak ^3He beam. The total system blank is $\approx 1x10^{-10}$ cm^3 STP ^4He. Blanks were always run before samples. A secondary standard of Yellowstone Park gas was always run after samples, with standard size similar to the size of the samle just analysed. This gas has been routinely calibrated against marine air at UCSB and has a $^3He/^4He$ ratio of 16.49±0.04 (2 sigma) R_A (R_A is the atmospheric ratio of 1.39×10^{-6}). This procedure allows very small samples to be analysed and a precise check of sample isotopic ratios in the size range of the analysis." (from Graham et al., 1990)

Modeling Programs

In order to simulate perfect fractional crystallization at the NNO and QFM oxygen fugacity buffers, the modeling program, MIXNFRAC, was used. This program was written by Dr. Roger Nielsen, Oregon State University. Given a starting parent composition (major and some trace elements), assimilant composition, oxygen fugacity of the system, and assimilation, fractionation, eruption, recharge ratios, MIXNFRAC will calculate the evolution of the composition and temperature of the liquids and equilibrium minerals as fractionation occurs.

MIXNFRAC is used in this thesis to model two different processes, all with parent composition, Ey-49. An ideal parent composition is one that

represents the end of olivine fractionation, just prior to the addition of plagioclase to the liquidus (for 1 atm models). A hypothetical parent was created from the trends observed in the oxide variation diagrams to coincide with this change in crystallizing phases. Addition of olivine to this hypothetical parent creates compositions similar to Ey-49 (which is a cumulate, though dominantly olivine), and therefore it is believed that Ey-49 can represent a possible parent composition.

The first scenario calculated with MIXNFRAC was perfect fractional crystallization, with an oxygen fugacity at QFM. The second scenario was perfect fractional crystallization with oxygen fugacity at NNO.