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EOCENE MAGMATISM AT TWO BUTTES, COLORADO
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CHEMICAL COMPOSITIONS OF SELECTED ROCKS AT TWO BUTTES, COLORADO

Table A1 contains averages of replicate analyses of rocks (2 to 11) from Two Buttes, Colorado. Complete analytical details and replicate analyses are in Appendices A, B, and E of Davis (1993), but here we briefly describe the analytical methods used for the various elements and samples. SiO_2, TiO_2, Al_2O_3, Fe_2O_3(total), MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5 were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). FeO was determined by titration. In addition, P_2O_5, TiO_2, and Fe_2O_3(total) abundances were cross checked by colorimetry or atomic absorption spectroscopy (AA). Total H_2O was determined by the Penfield method and absorbed H_2O was determined by difference. CO_2 was determined by difference using an adsorption technique developed by G. K. Hoops [date].

Sr, Ba, and Ni were determined by X-ray florenscence spectrometry (XRF) and ICP-AES, Rb and Zr were obtained by XRF, and Cr by ICP-AES at the University of Texas (UT) Geology Department. Samples 28, 45, 81, and 88a were analyzed for Ni, Cr, Ba, Rb, Sr, Zr, Y, and Nb by XRF at Washington State University (WSU). Y for sample 88a was also determined by ICP-AES at UT. Th, Ta, La, Ce, Nd, Sm, Hf, Tb, Yb, Eu, and Lu were determined by thermal instrumental neutron activation analysis (INAA). Samples were irradiated at Texas A&M University and gamma rays were counted at the UT Nuclear Engineering Teaching Laboratory. Ta reported for samples 88a and 45 was determined by epithermal INAA: 45 and 88a were irradiated at the Oregon State University Radiation Center and gamma ray spectral data were obtained in the

Idaho State University Geology NAA laboratory. Ce/Yb is normalized to average C1 chondrite values of Anders and Grevesse (1989).

Estimates of accuracy and precision are shown in Table A2. As an indication of accuracy, averaged values for international standard BHVO-1 are presented. Precision is estimated using the standard deviation (1σ) of replicate analyses of BHVO-1 for SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5. Precision estimates for Y and Nb were provided by WSU, and were determined by replicate analyses of BCR-P. For elements determined by INAA, the values for BHVO-1 do not adequately represent "true" accuracy. Two samples of BHVO-1 were submitted with the Two Buttes rock samples; one to be used as a primary standard and the other as an unknown. La and Sm for the BHVO-1 sample submitted as an unknown are apparently high and Yb is low (Table A2). We have confidence, however, in the ranges in Yb, La, and Sm that we obtained for the Two Buttes rocks; they are almost the same as those obtained by Gibson et al. (1993) (Yb, 1.95 to 3.85 ppm; La, 50 to 130 ppm; Sm, 9.80 to 18.95). Precision estimates for elements determined by INAA are based on counting statistics with one exception; for Ta determined by epithermal neutron activation (samples 45 and 88a), an error estimate is ± 0.011 ppm, based on accuracy and counting statistics.

Precision and accuracy estimations for trace elements we determined by XRF and ICP-AES are not straightforward. Cr, Ni, Sr, and Ba values presented here are a combination of replicate analyses by XRF and ICP-AES. Rb and Zr values for several samples are a combination of replicate analyses by XRF from UT and WSU. BHVO-1 was not used as a secondary standard for the XRF determinations, although it was for the ICP-AES determinations. WSU used BCR-P as a secondary standard to check precision. Rather than combine the precision estimates from the different laboratories or methods, we discuss precision for each. The agreement between methods and laboratories is very good, which is why the values for these elements were averaged (Table A3). For those samples where XRF and ICP-AES values were averaged, the number of replicate analyses by ICP-AES outweighs those by XRF, except for sample 45, for which the opposite is true. For Sr, Rb, Zr, Ba, and Ni determined by XRF at UT, precision based on the standard

deviation (1σ) of replicate analyses of sample 45 (4 to 11 analyses) is 12, 3, 8, 37, and 8 ppm, respectively. For Cr, Ni, Sr, and Ba determined by ICP-AES at UT, precision based on the standard deviation (1σ) of replicate analysis of BHVO-1 (6 analyses) is 22, 9.5, 9, and 35 ppm, respectively. Analyses for rocks 28, 45, and 88a have single XRF values from WSU averaged in for Ni, Cr, Ba, Rb, Sr, Zr, Y, and Nb (values for Nb are solely XRF). Values for Y were determined by XRF (rocks 28, 45, 81, and 88a at WSU) and ICP-AES (88a). We have no precision estimate for Y determined by ICP-AES. WSU provided the following precision estimates in ppm based upon standard deviation (1σ) of replicate analyses of BCR-P: Ni, 0.32; Cr, 1.83; Ba, 12.64; Rb, 0.84; Sr, 2.32; Zr, 0.70; Y, 0.52; and Nb, 0.521.

PROCEDURES FOR SAMPLE PREPARATION FOR ISOTOPIC ANALYSIS

Comprehensive details of analytical procedures for Rb, Sr, and Nd were given by Davis (1993), and for Pb by Borg (1995); important analytical details are footnoted here in Table 2. Rb, Sr, Sm, Nd, and Pb were separated using standard cation/anion exchange techniques. Rb concentrations were determined using an automated NBS-type single-collector mass spectrometer, whereas Sr, Sm, Nd, and Pb isotopic ratios and Sr, Sm, and Nd concentrations were determined statically on a Finnigan MAT 261 multicollector mass spectrometer (Table 2). Pyroxenes were first sonically cleaned in cold distilled H_2O and dried, leached in 2N HNO_3 for 15 min on a hot plate, and finally rinsed in double-distilled H_2O prior to digestion and analysis. Nd error is within 0.3 ε_{Nd}, and Sr isotopic ratios are probably accurate to within 2 x 10^{-5}. A typical Pb blank of 62 pg per analysis was obtained for analyses reported herein.

To concentrate phlogopite for K-Ar analysis, cleaned 60–80 mesh fractions of crushed rock were run across a small vibrating mica table and a hand magnet was drawn across and through the samples to remove large or strongly magnetic grains. Samples were resieved through 115 mesh to rid the sample of fines. The remaining fraction was then run through Frantz isodynamic separators. The least and most magnetic fractions at low amperage (0.1–0.16 amps) were

removed. A very small split was taken and checked by X-ray diffraction for alteration to chlorite or broadening of peaks. The patterns for splits from samples reported here showed no broadening of phlogopite peaks or alteration to another phyllosilicate.

Table A1. Major, minor (wt%) and trace (ppm) element compositions of Two Buttes rocks.

sample	88a	45	81	70	59	28	31	105
SiO_2	47.6	48.3	50.2	49.1	52.4	55.1	53.9	57.1
TiO_2	1.01	0.98	1.09	0.97	1.16	0.94	1.01	0.86
Al_2O_3	9.50	9.80	11.3	10.9	13.8	14.0	15.7	16.6
Fe_2O_3	2.66	2.39	2.74	1.78	6.23	7.59	4.55	5.62
FeO	5.84	5.22	4.66	5.37	2.80	n.d.	2.33	1.07
MnO	0.14	0.13	0.13	0.14	0.10	0.13	0.23	0.16
MgO	16.4	17.9	13.2	15.5	5.91	5.96	2.72	1.83
CaO	8.52	7.44	8.57	7.02	5.32	5.69	5.23	3.45
Na_2O	1.82	1.98	2.30	2.29	2.50	3.34	2.05	4.27
K_2O	3.81	3.84	4.19	4.50	6.29	5.94	7.64	6.24
P_2O_5	0.38	0.27	0.33	0.30	0.49	0.40	0.43	0.29
CO_2	0.18	0.00	0.08	0.23	0.58	0.42	1.37	0.51
H_2O^+	1.22	1.08	0.72	1.28	1.85	1.19	1.51	1.14
H_2O^-	0.20	0.20	0.13	0.22	0.67	0.25	0.35	0.42
Total	99.36	99.48	99.67	99.66	100.08	100.99	99.05	99.6
recalculated analyses (Fe_2O_3 = 0.15 * FeO total) and mg = $Mg^{2+}/(Mg^{2+} + Fe^{2+})$								
FeO	6.99	6.26	6.06	5.92	7.15	5.81	5.46	5.21
Fe_2O_3	1.24	1.11	1.07	1.05	1.26	1.02	0.96	0.92
mg	80.7	83.6	79.5	82.3	59.6	64.7	47.0	38.5
Cr	936	875	580	728	251	232	68	42
Ni	543	498	276	405	83	113	29	24
Rb	100	119	137	132	151	146	201	142
Sr	666	664	758	832	418	413	1353	2014
Y	22.5	21.0	26	-	-	36.0	-	-
Zr	150	148	186	160	294	297	675	501
Nb	11.7	10.6	13.7	-	-	22.7	-	-
Ba	990	1104	1097	1164	1689	1181	2681	3717
La	36.1	22.2	41.3	40.6	67.3	71.2	198.7	94.4
Ce	79.4	65.4	86.0	78.3	142	141	262	271
Nd	39.0	32.0	54.9	70.1	36.3	63.1	85.2	88.2
Sm	9.16	4.83	8.54	7.77	12.0	12.0	27.7	12.7
Eu	2.40	1.57	2.35	2.00	3.10	2.93	5.21	4.00
Tb	1.10	0.79	1.09	0.74	1.34	1.22	1.76	1.70
Yb	1.92	1.10	1.63	2.39	1.76	2.15	3.52	2.44
Lu	0.28	0.19	0.28	0.31	0.33	0.46	0.28	0.46
Hf	4.07	3.30	5.64	4.86	7.65	8.20	13.3	10.5
Ta	0.73	0.63	2.31	0.69	1.70	1.40	2.52	2.14
Th	5.50	4.85	7.50	6.67	14.4	14.5	28.2	28.8
$(Ce/Yb)_n$	11.2	16.1	14.3	8.9	21.8	17.7	20.1	30.0

Table A2. Precision and accuracy estimation.

sample	Our Averaged BHVO-1	Recommended BHVO-1	standard deviation (# of analyses)
SiO_2	50.3	49.9	0.66 (12)
TiO_2	2.72	2.71	0.17 (6)
Al_2O_3	13.9	13.8	0.07 (12)
Fe_2O_3	2.24	2.82	0.27 (12)
FeO	8.78	8.58	(1)
MnO	0.17	0.17	0.01 (6)
MgO	7.14	7.23	0.77 (12)
CaO	11.38	11.4	1.01 (12)
Na_2O	2.27	2.26	0.12 (6)
K_2O	0.54	0.52	0.10 (6)
P_2O_5	0.27	0.27	0.03 (6)
Cr	293	289	
Ni	122	121	
Rb	†		
Sr	381	403	
Y	††		0.52
Zr	†		
Nb	††		0.52
Ba	154	139	
La	19.9	15.8	0.8 (1)
Ce	37.7	39	8 (1)
Nd	26.2	25.2	18 (1)
Sm	7.05	6.2	0.10 (1)
Eu	1.92	2.06	0.08 (1)
Tb	0.90	0.96	0.04 (1)
Yb	1.62	2.02	0.50 (1)
Lu	0.26	0.291	0.07 (1)
Hf	4.05	4.38	0.70 (1)
Ta	1.22	1.23	0.06 (1)
Th	1.02	1.08	0.15 (1)

Note: BHVO-1 values for major oxides are averages of repeated analyses of international standard BHVO-1 digested and analyzed at the same time as Two Buttes samples. The standard deviation of these analyses is given as an estimate of precision. Secondary standards other than BHVO-1 were used to examine accuracy and precision for FeO, CO_2, H_2O^-, H_2O^+, Rb, Y, Zr, and Nb. †Secondary standard, BPR-5 (Roden, 1981), was used: Roden obtained 127 ppm Rb and 359 ppm Zr. We obtained averages of 122 ppm Rb and 350 ppm Zr. †† Precision is based upon replicate analysis of BCR-P at Washington State University. Recommended values for BHVO-1 are from Govindaraju (1989).

Table A3. Comparison of trace element analyses (ppm) obtained by XRF and ICP-AES by different laboratories.

Sample	45	45	45	88a	88a	88a	28	28	28
Lab.	WSU XRF	UT XRF	UT ICP	WSU XRF	UT XRF	UT ICP	WSU XRF	UT XRF	UT ICP
Rb	116	119		99	100		150	146	
Sr	655	656	671	661	665	667	416	420	406
Zr	154	142		155	145		289	305	
Ba	964	1115	1094	840	1074	906	1183	1192	1170
Ni	487	483	513	515	529	557	109	102	123

Note: WSU is Washington State University, UT is The University of Texas.

Table A4: Selected Cr-rich and "salitic" pyroxene analyses.

Sample	31s	31s	45	45
SiO_2	50.4	49.0	48.3	52.1
TiO_2	0.38	1.13	1.44	0.54
Al_2O_3	2.54	3.35	4.92	2.08
FeO*	12.2	9.14	7.07	0.96
Cr_2O_3	0.00	0.00	0.04	3.49
MnO	0.48	0.32	0.11	0.10
MgO	10.5	12.3	14.3	16.5
CaO	21.0	22.5	22.8	23.6
Na_2O	1.66	0.84	0.30	0.21
Total	99.2	98.6	99.3	99.6
cations normalized to 4				
Si	1.907	1.854	1.797	1.911
Al^{IV}	0.011	0.032	0.040	0.089
Al^{VI}	0.093	0.146	0.203	0.001
Ti	0.020	0.003	0.013	0.015
Cr	0.000	0.000	0.001	0.028
Fe^{3+}	0.173	0.140	0.130	0.045
Fe^{2+}	0.215	0.149	0.090	0.062
Mn	0.015	0.010	0.003	0.003
Mg^{VI}	0.566	0.665	0.722	0.846
Mg^{VIII}	0.024	0.028	0.069	0.058
Ca	0.854	0.910	0.910	0.927
Na	0.122	0.062	0.021	0.015

Note: Pyroxenes analyzed using a JEOL 733 superprobe operated at 15 kv, with sample currents between 30 and 45 nA on brass, count times of 40 to 70 seconds for minor and trace elements and minimum beam diameters. Estimates of precision and accuracy are in Davis (1993) along with descriptions of standards used. Analyses for sample 31 are from one grain with "simple" zoning. Analyses for sample 45 are from different zones in one oscillatory zoned pyroxene.

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