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SHRIMP RG zircon analyses and SEM images to accompany

"Young cumulate complex beneath Veniaminof caldera, Aleutian arc, dated by

zircon in erupted plutonic blocks"

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INTRODUCTION

Recently, following Reid et al. (1997), secondary ion mass spectrometry (SIMS; ion microprobe) has been used to determine U-Th and U-Pb crystallization ages of zircon and allanite in Quaternary volcanic and plutonic rocks. The ²³⁸U–²⁰⁶Pb system requires adequate U and sufficient time to generate a measurable ²⁰⁶Pb signal, and typically is most appropriate for zircon \geq 200 ka in age. Uranium-rich minerals are amenable to SIMS U–series geochronology. In igneous rocks, in which ²³⁴U/²³⁸U activity ratios [denoted by $(^{234}U/^{238}U)$] can be assumed to be unity, the $^{238}U-^{230}$ Th chronometer is becoming widely applied to U-rich accessory minerals. If the initial ²³⁰Th/²³²Th and 238 U/ 232 Th ratios are known, model ages can be calculated for individual analyses of 230 Th/ 232 Th and 238 U/ 232 Th. Multiple analyses with a spread in 238 U/ 232 Th, and that can be assumed to have had the same initial ²³⁰Th/²³²Th, can be used to define an isochron on a $(^{230}\text{Th}/^{232}\text{Th}) - (^{238}\text{U}/^{232}\text{Th})$ diagram without independent knowledge of initial ratios. Precision in measuring ²³⁰Th limits the SIMS method to 3–4 half-lives, or ~250 ka $(t_{1/2}^{230}\text{Th} = 75,690 \pm 230 \text{ yr}; \text{ Cheng et al., 2000}).$ Obtaining sufficient counts on ²³⁰Th (measured as ²³⁰Th¹⁶O) with large-format ion microprobes typically necessitates a spot size of $\sim 20 \times 30 \,\mu\text{m}$. In many igneous rocks, zircon and other U-rich accessory minerals (e.g., allanite; Vazquez and Reid, 2004) are sufficiently large for ²³⁸U–²³⁰Th by SIMS.

ANALYTICAL PROCEDURES

Sampling and preparation

Samples were collected from the ground surface during geologic mapping of the Mount Veniaminof edifice. Zircon was separated from the whole rocks, mounted in epoxy along with zircon standards AS57 and R33 (Charlier et al., 2005), polished, cleaned in EDTA solution, and coated with 100 nm of Au prior to SEM cathodoluminescence (CL) imaging and SIMS.

Zircon geochronology

Zircons were analyzed for U-Th and U-Pb geochronology with the USGS-Stanford SHRIMP RG (http://shrimprg.stanford.edu) in December 2002 (sample 02TSV060) and in a 3-day session in October 2005 (all other samples). Data are presented in Table DR1. Analysis conditions and protocol were similar to those reported by Bacon and Lowenstern (2005) except that a 16–22 nA ¹⁶O⁻ primary beam was used and each analysis consisted of 10 scans through the mass range. The empirical U-Th fractionation factor necessary to bring the $(^{230}\text{Th}/^{238}\text{U})$ activity ratio to unity for analyzed standards and other pre-Quaternary zircons during the October 2005 session was 1.094. Following Charlier et al. (2005), we assigned this factor a conservative 1σ uncertainty of 0.03 in error calculations. Zircon U concentrations were obtained by comparison of 238 U/ 90 Zr₂ 16 O ratios with that of zircon standard CZ3 (Ireland and Williams, 2003), recognizing that this leads to slight overestimation of U and Th concentrations in U- and Th-rich zircons. Most zircons had minimum exposed diameters of $\sim 40-60 \,\mu m$, necessitating placement of the ion beam near the center of the crystal. A few zircons were sufficiently large for multiple analysis points. Some grains were analyzed a second time after re-polishing and Au coating the mount. Each analysis was treated independently in the figures.

The small zircons commonly are difficult to analyze because overlap of the primary ion beam on the epoxy mounting medium or any epoxy in a cracked zircon produces excess apparent ²³⁰Th¹⁶O from a molecular interference involving epoxy constituents. Schmitt (2006; GSA Data Repository item 2006112) has identified the isobaric interference as due to ²³²Th₂¹²C¹⁶O²⁺ (see also Schmidt et al., 2006, Appendix A). Analyses affected by epoxy contamination are presented in Table DR1 with values for (²³⁰Th/²³²Th) indicated by strikethrough type and are retained because U and Th concentrations and (²³⁸U/²³²Th) are not affected.

A selection of grains yielding equilibrium U–Th activity ratios (plotting on the equiline) were reanalyzed by the U–Pb method (Miller and Wooden, 2004) to check if these were old (> 200 kyr) zircons. None gave measurable U–Pb ages, suggesting that the ~equilibrium activity ratios are coincidental.

Trace element concentrations in zircon

Trace element measurements in zircon were also made with the USGS–Stanford SHRIMP RG (Mazdab and Wooden, 2006). Results for the Veniaminof zircons are presented in Table DR2. Resolution of interfering isobars on certain trace elements is achieved by operating at a mass resolution (M/ Δ M) of ~11,000 at 10% peak height. This is sufficient to effectively resolve ⁴⁵Sc⁺ from ⁹⁰Zr²⁺ (M/ Δ M = 12660), ⁴⁸Ti⁺ from ⁹⁶Zr⁺

 $(M/\Delta M = 7660)$, and the HREE from the MREE oxides $(M/\Delta M = ~8000-9100)$, while maintaining flat-topped peaks and high transmission. The high transmission allows for the use of a small spot size; a 5 nA primary beam current and 20 µm spot were used for this work.

Of the elements currently calibrated against synthetic zircon standards (Mazdab and Wooden, 2006), ionization efficiency ranges from a high of 200 cps/nA/ppm for Sc down to 2 cps/nA/ppm for P. For phosphorus, although greater sensitivity could be realized if it were measured as ³¹P⁻ with a Cs⁺ primary beam, we can nonetheless achieve a practical detection limit of about 50 ppb, a level well below that observed in natural zircon thus far. Sensitivity for yttrium and the REE are nearly that of scandium, and practical detection limits are in the 1-5 ppb range.

Each measurement consisted of one block of three cycles. Each cycle peak-stepped sequentially through masses 30–254 for the elements listed in Table DR2. From the middle REE through hafnium, thorium and uranium, the oxide peaks are measured rather than the elements due to their greater ion production. The total run time is approximately 20 minutes per analysis. Final crater depth in zircon is typically <2 μ m. Analyses of unknowns are interspersed with periodic analyses of two concentration standards. The standards are currently a megacryst from Sri Lanka (CZ3, Ireland and Williams, 2003), and a gem quality crystal from Samé, Tanzania. Both standards have been repeatedly analyzed against synthetic trace element-doped zircons to verify their concentrations and homogeneity. Over the course of a typical analytical session, 5-10 analyses of the primary standard (CZ3) and an additional 4-6 analyses of the secondary standard (Samé) are obtained.

The data are processed in MS Excel. $M^{+/30}Si^{+}$ ratios are derived from the timeaveraged counts for each mass of interest for both the standards and unknowns. Values for the unknowns are then compared to those of the primary standard to determine concentrations; the secondary standard provides an independent check of the quality of the data. For P, Sc, Ti, and Y, 1 σ precision is less than 3%; for the measured REE (excluding La), Hf, Th and U, the 1 σ precision ranges from 4% to 9%; for La, the precision is ~15%.

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TABLES

Table DR1. SHRIMP RG U-series data for zircons from plutonic blocks ejected by Mount Veniaminof volcano, Alaska.

Table DR2. SHRIMP RG trace element analyses of zircons from plutonic blocks ejected by Mount Veniaminof volcano, Alaska.

FIGURES

Figure DR1. Cathodoluminescence images of polished surfaces of zircons from plutonic blocks ejected by Mount Veniaminof volcano, Alaska.

Figure DR2. Secondary electron and backscattered-electron images of polished surfaces of zircons from plutonic blocks ejected by Mount Veniaminof volcano, Alaska.

Figure DR3. Secondary electron and backscattered-electron images of cavities in diorite and granodiorite blocks ejected by Mount Veniaminof volcano, Alaska.

Table DR1. Alaska	SHRIMP RG U-series data for zircons from plutonic blocks ejected by Mount Veniaminof volcano,								
Sample	Grain.Point	U ppm (±10%)	Th ppm (±10%)	(²³⁸ U/ ²³² Th)	error	(²³⁰ Th/ ²³² Th)*	error*		
01CBV047	1.1	10500	24700	1.33	0.04	1.32	0.01		
01CBV047	2-1.1	7400	13200	1.76	0.05	1.45	0.02		
01CBV047	2.1	2100	3800	1.77	0.05	1.35	0.04		
01CBV047	2-2.1	3600	5900	1.92	0.06	1.39	0.03		
01CBV047	3.1	3700	9400	1.24	0.04	1.49	0.02		
01CBV047	4.1	4700	8700	1.69	0.05	1.49	0.02		
01CBV047	2-4.1	7000	12600	1.74	0.05	1.35	0.02		
01CBV047	5.1	5300	15100	1.11	0.03	1.30	0.02		
01CBV047	2-5.1	5400	12500	1.35	0.04	1.35	0.02		
01CBV047	2-5.2	2200	5300	1.28	0.04	2.39	0.04		
01CBV047	6.1	10800	14400	2.35	0.07	1.46	0.02		
01CBV047	7.1	7300	13800	1.66	0.05	1.36	0.02		
01CBV047	8.1	4400	20100	0.69	0.02	1.34	0.02		
01CBV047	2-8.2	1300	4700	0.85	0.03	1.32	0.03		
01CBV047	9.1	1800	3400	1.66	0.05	1.53	0.04		
01CBV047	2-9.2	3400	5200	2.09	0.06	1.33	0.02		
01CBV047	11.1	6500	12000	1.69	0.05	1.40	0.02		
01CBV047	2-11.2	5900	10000	1.85	0.06	2.69	0.02		
02TSV060	1.1	9000	12700	2.23	0.01	1.50	0.03		
02TSV060	2.1	14200	26300	1.70	0.01	1.36	0.02		
02TSV060	2.2	5400	6100	2.74	0.001	1.42	0.05		
02TSV060	2.3	11800	31900	1.16	0.03	1.36	0.02		
02TSV060	2.4	14400	42700	1.06	0.03	1.39	0.02		
02TSV060	3.1	13000	33700	1.21	0.003	1.37	0.02		
02TSV060	3.2	5400	6100	2.74	0.001	1.41	0.05		
02TSV060	3.3	8300	14700	1.78	0.05	1.35	0.03		
03TSV148	1.1	9600	20100	1.51	0.05	1.35	0.01		
03TSV148	2.1	3200	5300	1.90	0.06	1.82	0.05		
03TSV148	3.1	3000	19600	0.47	0.01	1.21	0.02		
03TSV148	4.1	10700	34000	0.99	0.03	1.28	0.02		
03TSV148	5.1	4800	15700	0.96	0.03	1.29	0.02		
03TSV148	6.1	9700	13900	2.21	0.07	1.39	0.03		
03TSV148	6.2	3200	3700	2.69	0.08	4.21	0.07		
03TSV148	6.3	5500	12600	1.37	0.04	2.41	0.03		
03TSV148	7.1	2100	3800	1.75	0.05	1.46	0.05		
03TSV148	8.1	4300	8700	1.54	0.05	1.59	0.03		
03TSV148	9.1	5800	11500	1.58	0.05	1.49	0.03		
03TSV148	10.1	5500	13700	1.26	0.04	1.24	0.02		
03TSV148	11.1	3100	6000	1.61	0.05	1.60	0.04		
03TSV148	13.1	3000	4900	1.97	0.06	1.43	0.04		
03TSV148	14.1	5700	7800	2.30	0.07	1.68	0.03		
03TSV148	15.1	5900	10300	1.79	0.05	1.42	0.03		

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Table DR1. Alaska	SHRIMP RG U-series data for zircons from plutonic blocks ejected by Mount Veniaminof volcano,								
Sample	Grain.Point	U ppm (±10%)	Th ppm (±10%)	(²³⁸ U/ ²³² Th)	error	(²³⁰ Th/ ²³² Th)*	error*		
03TSV148	16.1	3100	9200	1.06	0.03	1.40	0.03		
03TSV148	17.1	4500	12400	1.15	0.03	1.32	0.02		
03TSV148	18.1	8000	15900	1.59	0.05	1.37	0.02		
03TSV148	19.1	3900	6100	2.00	0.06	1.45	0.04		
03TSV148	20.1	3200	6300	1.61	0.05	1.43	0.03		
03TSV148	21.1	3700	5200	2.23	0.07	1.48	0.04		
03TSV148	22.1	4100	6000	2.14	0.06	1.46	0.03		
03TSV148	23.1	7400	20300	1.14	0.03	1.68	0.02		
03TSV148	24.1	6800	23200	0.92	0.03	1.30	0.02		
03TSV148	25.1	6400	25900	0.78	0.02	1.26	0.02		
03TSV148	26.1	950	160	18.65	0.56	3.78	0.29		
03TSV148	26.2	880	200	13.59	0.41	3.57	0.22		
03TSV148	27.1	2400	9700	0.77	0.02	1.30	0.02		
03TSV148	28.1	3800	5400	2.20	0.07	1.86	0.03		
03TSV148	28.2	6700	18400	1.13	0.03	1.29	0.01		
03TSV148	29.1	1600	3500	1.41	0.04	1.45	0.04		
03TSV148	30.1	1500	3500	1.34	0.04	2.10	0.04		
03TSV148	31.1	5900	8400	2.20	0.07	1.45	0.02		
03TSV148	31.2	7200	13500	1.67	0.05	1.36	0.02		
03TSV148	32.1	2800	3500	2.54	0.08	1.50	0.03		
03TSV148	32.2	2900	4700	1.91	0.06	1.48	0.03		
03TSV148	33.1	7000	11600	1.89	0.06	1.49	0.02		
03TSV148	34.1	1700	2700	2.06	0.06	1.48	0.04		
03TSV148	35.1	3900	10100	1.22	0.04	1.34	0.02		
03TSV148	36.1	12400	44800	0.87	0.03	1.39	0.01		
03TSV148	37.1	3100	6600	1.49	0.04	1.32	0.02		
03TSV148	37.2	6700	22500	0.93	0.03	1.26	0.01		
03TSV/150	11	1170	1000	3.67	0.11	1.04	0.09		
03TSV150	1.1	1090	930	3.70	0.11	1.94	0.03		
03TSV150	1.2	1030	870	3.70	0.11	2 15	0.09		
00101100	1.0	1000	070	0.14	0.11	2.10	0.00		
04CBV334	1.1	1110	1120	3.11	0.09	1.72	0.10		
04CBV334	1.2	960	870	3.47	0.10	1.79	0.11		
04CBV334	2-1.2	850	710	3.73	0.11	1.78	0.11		
04CBV334	2.1	810	780	3.26	0.10	1.76	0.12		
04CBV334	2-2.1	760	710	3.39	0.10	1.80	0.10		
*Lined-out values not included in isochron calculation because of epoxy contamination affecting ¹⁶ O ²³⁰ Th ⁺ measurement.									
All analyses analyzed by	by C.R. Bacon J.B. Lowenster	, T.W. Sisson, ar m in December 2	nd F.K. Mazdab in 0 002.	October 2005 ex	cept those fo	or 02TSV060 whic	h were		

Table DR207SHRIMP RG trace element analyses of zircons from plutonic blocks ejected by Mount								
Trace element	2-148HDR-	2-148HDR	2-TSV/148-	2-148HDR-	2-TSV/148-	2-TSV/148-	2-148HDR-	
analysis no.	23a	211011D1	1b	21a	4	5	22a	
Zircon from U–Th goechronology	TSV148-6	TSV148-4	2-TSV148- 33	TSV148- 9?				
Analysis spot location	near 6.3	center	end	near end	dark CL sector	dark CL sector near end	center narrow gr	
Cavities or fluid inclusions	many	many	many	few	few	many	some	
ppm								
P	4132	4397	4661	2866	3399	3240	3007	
Sc	371	132	156	42	30	87	42	
Ti	191	143	61	34	27	26	16	
Y	13120	22050	43260	21780	26730	22730	28960	
la la	76.99	233.8	2 21	0.73	0.64	5 14	2 16	
Ce	432	1230	1483	745	887	650	726	
Pr	15.33	49.57	7.75	1.93	2.18	3.66	3.19	
Nd	56.5	188.3	119.6	25.9	33.3	25.5	31.9	
Sm	39	135	268	59	68	54	72	
Eu	3.29	6.11	0.82	1.68	2.59	1.68	2.26	
Gd	233	751	2019	504	645	505	676	
Tb	88	236	633	165	216	169	239	
Dv	1081	2342	5783	1769	2350	1837	2611	
Ho	507	907	1688	689	918	710	992	
Er	2266	3226	5651	2904	3820	3007	4033	
Tm	507	624	929	574	730	599	770	
Yb	4390	4792	6049	4215	5252	4506	5582	
Lu	786	765	790	641	754	703	800	
Hf	11130	11130	9291	7952	7881	8285	7517	
206Pb	0.6	4.7	0.12	0.1	0.13	0.31	0.2	
Th	5370	17400	12640	21620	23870	6657	8190	
U	4954	7220	7657	4052	6919	3511	3922	
Zircon/Chondrite								
La	241	733	7	2	2	16	7	
Ce	527	1499	1809	908	1081	793	886	
Pr	127	410	64	16	18	30	26	
Nd	92	306	195	42	54	41	52	
Sm	194	673	1340	297	338	270	361	
Eu	43	80	11	22	34	22	30	
Gd	871	2814	7562	1887	2414	1890	2531	
Tb	1788	4795	12839	3350	4385	3418	4839	
Dy	3275	7097	17520	5360	7120	5567	7913	
Но	6716	12020	22360	9131	12160	9404	13130	
Er	10490	14940	26160	13450	17680	13920	18670	
Tm	15410	18970	28250	17440	22180	18200	23400	
Yb	19870	21680	27370	19070	23760	20390	25260	
Lu	23820	23190	23950	19410	22840	21310	24250	
Ce/Ce*	3.0	2.7	85.8	150.1	179.7	35.9	66.3	
Eu/Eu*	0.105	0.058	0.003	0.029	0.038	0.031	0.031	
Analyses by F.K. Mazdab, February 2006								

Table DR207SHRIMP RG trace element analyses of zircons from plutonic blocks ejected by Mount Veniaminof volcano. Alaska								
Trace element	2-TSV148-	2-047H-1	2-047H-6a	2-047H-2	2-047H-5a	2-047H-4a	2-334HB-	
Zircon from U–Th goechronology			CBV047-7	CBV047- 11	CBV047-8	CBV047-9	CBV334	
Analysis spot location	dark CL sector near end	end	center	corner near 11.1	corner	end	end near 1.1	
Cavities or fluid inclusions	some	some	many	few/none	some	none	none	
maa								
P	2024	1465	1021	1022	1276	798	356	
Sc	51	144	91	78	68	47	71	
Ti	15	26	24	20	20	14	40	
Y	19860	11600	11590	9469	8288	6971	1450	
La	5.22	1.27	7.41	0.17	0.47	0.79	0.09	
Ce	469	445	290	305	317	170	7	
Pr	3.43	1.75	3.32	0.75	0.90	0.88	0.32	
Nd	22.9	16.9	18.3	12.8	10.3	7.6	4.8	
Sm	47	34.0	25	28.8	22	16	10	
Eu	1.28	0.73	0.45	0.76	0.31	0.28	1.19	
Gd	405	281	199	243	187	143	67	
Tb	149	95	72	85	63	52	22	
Dy	1731	1054	834	945	705	597	219	
Ho	698	396	363	354	276	241	67	
Er	3083	1843	1657	1612	1281	1115	253	
Tm	627	397	372	322	284	242	47	
Yb	4774	3320	3154	2497	2388	1954	343	
Lu	722	574	569	388	420	345	50	
Hf	8107	12580	16580	10140	9931	13130	8669	
206Pb	0.25	0.7	2.4	0.1	0.1	0.2	0.1	
Th	8233	20480	14010	20670	12990	3770	713	
U	3664	8638	5913	12340	4782	2294	810	
Zircon/Chondrite								
La	16	4	23	1	1	2	0	
Ce	572	542	353	372	387	207	9	
Pr	28	14	27	6	7	7	3	
Nd	37	27	30	21	17	12	8	
Sm	234	170	123	144	110	80	49	
Eu	17	10	6	10	4	4	16	
Gd	1516	1051	746	911	701	536	251	
Tb	3024	1918	1451	1722	1277	1051	445	
Dy	5245	3193	2526	2863	2137	1809	665	
Ho	9247	5245	4805	4692	3660	3187	891	
Er	14270	8534	7670	7463	5933	5161	1171	
Tm	19040	12070	11300	9793	8636	7351	1439	
Yb	21600	15020	14270	11300	10810	8843	1553	
Lu	21880	17390	17240	11740	12740	10460	1516	
Ce/Ce*	26.6	71.6	14.0	202.8	117.2	48.7	10.3	
Eu/Eu*	0.028	0.023	0.020	0.028	0.014	0.017	0.142	
Analyses by F.K. Mazdab, February 2006								

























x1000 20Pm; #66 T5V148 ZC 19 1.580 1

