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Final Technical Report for "Collaborative Research with the University of Nebraska and University of Colorado on the Age and Origin of the REE-Rich Elk Creek Carbonatite, Southeast Nebraska, USA"

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Technical Report

This project involved a petrologic and geochemical study of the Cambrian Elk Creek in south east Nebraska and was joint with Dr. Richard Kettler at the University of Nebraska. Researchers at the University of Colorado were responsible for Pb, Hf, Nd and Sr isotopic measurements of various lithologies that comprise the Elk Creek carbonatite. This report emphasizes the isotopic results, but also presents the major and trace element chemical data generated by Dr. Philip Verplanck, the USGS collaborator on the project. Data are presented in Tables 1-5 at the end of the report.

Major and Trace Element Data

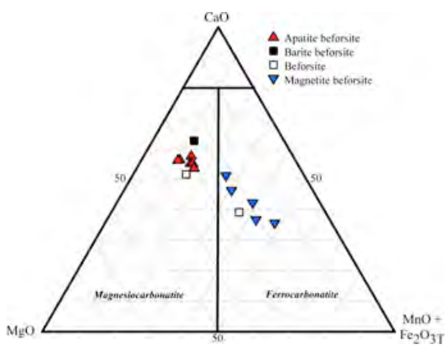

Fig. 1- Ternary compositional diagram showing classification of Elk Creek carbonatites.

All the samples used for this project were obtained from drill cores that penetrated the Elk Creek carbonatite and that are preserved and stored at the University of Nebraska, Lincoln. The mineralogy and petrology of the cores were investigated by Dr. Kettler and these results are presented in his separate technical support. The core samples can be divided on basis of mineralogy in a variety of dolomite carbonatite types, including apatite, barite and magnetite bearing varieties. Major element data (Table 1) from these lithologies demonstrate that apatite and barite bearing carbonatites are magnesiocarbonatites, while magnetite bearing rocks are ferrocarbonatites (Fig. 1). All of these lithologies have high rare earth element (REE) abundances (Table 2), and are relatively enriched in light rare earth (LREE) compared to the heavy rare earth elements (Fig. 2). The magnetite bearing rocks are also enriched in

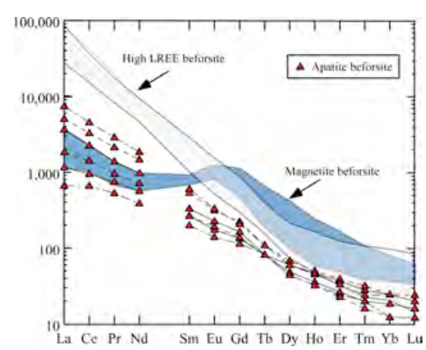

Fig. 2- Chondrite normalized whole rock REE patterns for Elk Creek carbonatite samples.

REE, but Eu, Nd and Sm abundances are low compared to REE with high and lower atomic numbers (Fig. 2).

Geochronology

Igneous zircon were recovered from carbonatite metasomatized syenites and these zircon were used for U-Pb age determinations at the Laserchron National Facility at the University of Arizona, Tucson. The U-Pb data from multiple zircon grains (Table 5) yield a range of U-Pb ages, with the "best" age estimated on basis of concordant analyses of ~ 530 Ma +/- 10 million years (Fig. 3). This zircon age is consistent within error of the Sm-Nd isochron age determined for whole rock samples (Table 3, Fig. 4). Because all of the carbonatite lithologies plot on the same Sm-Nd isochron, corresponding to an age of ~ 573 Ma +/- 23 million years, it can be concluded that all of these rock, including the magnetite carbonatites with their unusually high Sm/Nd ratios (Fig. 4), were emplaced contemporaneously and crystallized from carbonatitic melts with similar $^{143}Nd/^{144}Nd$ ratios. Whole rocks also form a Pb-Pb isochron corresponding to ~ 550 Ma (Table 3, Fig. 5), indicating that carbonatitic Pb isotope systematics have not been altered since emplacement. In contrast, whole rock Rb-Sr data so not result in a Sr isochron (Table 3, Fig. 6), suggesting either that the parental carbonatite magmas did not have uniform $^{87}Sr/^{86}Sr$ ratios, or that the Sr isotopic compositions of the carbonatites were modified by late-state carbonothermal alteration or by subsequent weathering of the carbonatites during subareal weathering in the Late Paleozoic.

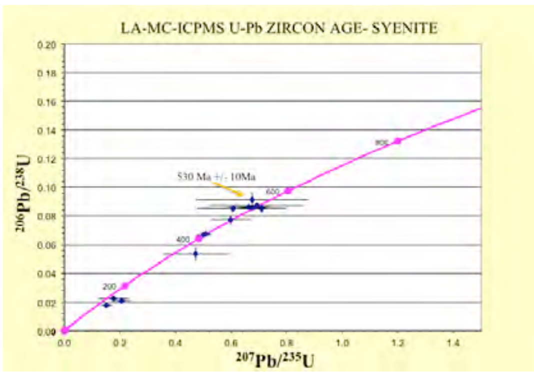

Fig. 3- Laser ablation ICPMS U-Pb ages for zircon obtained from an altered syenite from core EC4-2170. Data obtained at University of Arizona Laserchron center.

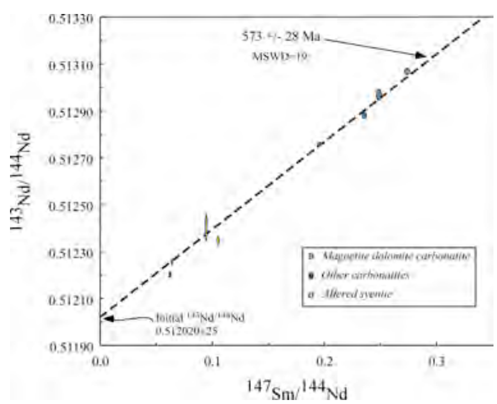

Fig. 4 Whole rock Sm-Nd isochron plot.

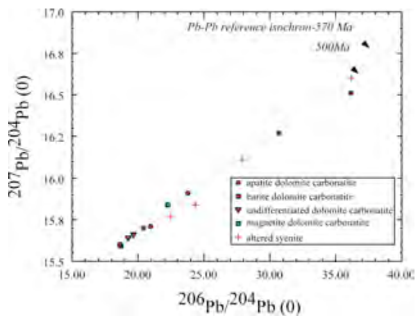

Fig. 5 Whole rock Pb-Pb isochron.

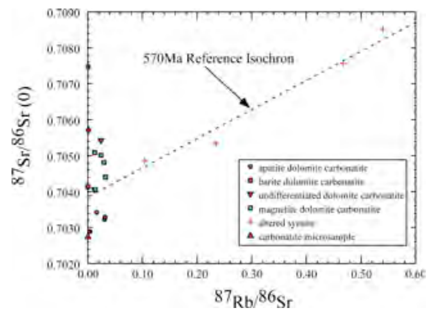

Fig. 6 Whole rock Rb-Sr isochron.

Radiogenic Isotope Tracing of Sources of Parental Melts

The Hf isotopic compositions of zircon from one altered syenite sample (EC4-2170) were determined by laser ablation ICPMS at the University of Arizona Laserchron Center. These analyses form a unimodal population with measured ε_{Hf} (0) of ~-10 (Table 4, Fig. 7). The ε_{Hf} (T) of the zircon at 550 Ma the zircon isotopic compositions are still low compared to depleted mantle (DMM) at 550 Ma, the approximate crystallization of Elk Creek carbonatite (Fig. 7). The conclusion is that Hf incorporated in zircon had a residence time in reservoir other than DMM prior to the formation time of carbonatite.

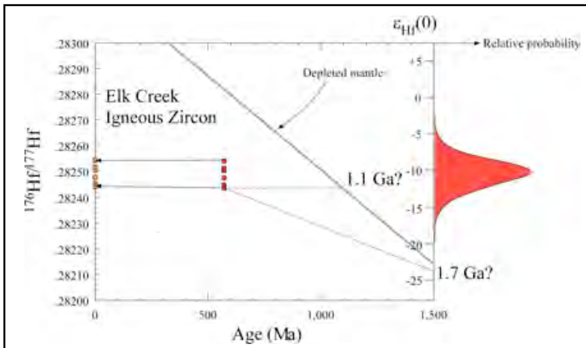

Fig. 7- Zircon Hf isotopic evolution plot from sample EC4-2170; altered syenite). Right hand side of diagram shows relative probability function for measured zircon Hf isotopic compositions in ε_{Hf} units.

One option is that carbonatites were derived from a deep mantle source with Lu/Hf lower than that of upper mantle DDM reservoir at or near the time of carbonatite emplacement. Another option is that the carbonatites represent remobilization of carbonated portions of the continental lithospheric mantle beneath southern Nebraska. We prefer this possibility based on neodymium isotopic data from the State Line kimberlites found to east in Colorado. Kimberlites emplaced into Paleproteroic crust in this region show a trend in initial Nd isotopic compositions through time, with Neoproterozoic kimberlites having higher initial ε_{Nd} (T) values than their Devonian counterparts as expected if these rocks were derived from periodic tapping of the same LREE enriched mantle source. The neodymium model ages for these rocks are ~1.1 Ga, the timing of the Grenville Orogeny and formation of the

Mid-Continent Rift (Fig. 8). The initial Nd isotopic compositions of the Elk Creek carbonatite falls on this same Nd evolution line (Fig. 8). It is plausible, then, that both the Hf and Nd isotopic compositions of the Elk Creek carbonatite reflect those of metasomes that developed in the continental mantle lithosphere during formation of Mid Continent Rift and the final assembly of the Rodinian supercontinent and were remobilized during extensional tectonism associated supercontinent break up and the formation of the southern margin of Laurentia at ~550 Ma.

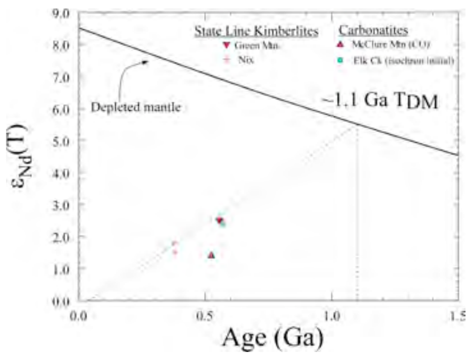

Fig. 7 Nd isotopic evolution plot for Elk Creek carbonatite and for State Line kimberlites (literature data from Yang et al, Chem. Geology, v. 385, 2014; Lester et al., Rocky Mtn Geology, v. 36, 2001).

TABLES

Table 1. WHOLE ROCK MAJOR and MINOR ELEMENT OXIDE ABUNDANCES OF ELK CREEK CARBONATITE*

Sample	SiO_2	Al_2O_3	Fe_2O_3(T)†	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	BaO	LOI	Total
Apatite dolomite carbonatite													
EC10-1490	7.13	0.37	4.59	0.47	15.3	26.6	0.23	0.13	0.31	2.17	3.82	36.8	97.9
EC10-1530	3.87	0.23	6.07	0.75	14.6	29.3	0.05	<0.01	0.16	3.65	1.09	38.2	96.9
EC39-2030	2.13	0.59	4.74	0.55	17.0	28.9	0.08	0.11	0.07	2.92	0.06	38.8	96.0
EC43-1060	13.8	3.78	5.44	0.72	13.0	23.7	0.25	3.16	0.23	2.68	0.29	29.6	96.7
EC43-1070	12.4	3.17	6.06	0.68	13.2	24.7	0.25	2.35	0.31	3.58	0.27	28.4	95.4
EC43-1140	7.48	1.40	6.15	1.3	13.7	24.6	0.14	1.27	0.15	1.34	2.29	34.8	94.7
Barite dolomite carbonatite													
EC43-1010	2.02	0.03	3.83	1.65	11.9	29.1	0.11	<0.01	<0.01	0.54	6.73	31	78.2
Dolomite carbonatite													
EC17-1870	3.59	0.81	5.91	1.25	15.9	24.6	0.18	0.67	0.59	1.46	3.52	35.9	94.4
EC93-510	7.41	1.96	13.8	0.84	9.88	15.8	0.22	0.44	0.55	2.34	8.51	23.6	85.4
Magnetite dolomite carbonatite													
EC29-1480	6.83	1.57	21.7	0.64	11.1	19.3	0.27	1.07	3.91	0.93	4.62	26.7	98.6
EC11-2425	10.9	1.96	19.4	0.61	6.73	14.7	0.25	1.58	5.37	0.44	9.31	20.6	91.9
EC16-1380	10.3	2.01	12.7	0.66	10.1	20.2	0.16	1.65	3.07	0.63	4.99	29.3	95.8
EC28-1800	9.44	2.21	16.7	0.65	8.6	18.9	0.29	1.73	3.94	0.31	4.71	27.5	95.0
EC29-1120	8.64	1.13	11.3	0.6	9.92	22.8	0.11	0.87	3.02	2.28	4.58	30.6	95.9
Altered syenite													
EC4-2400	27.9	8.65	5.98	0.61	5.69	13.4	0.29	6.62	0.51	1.23	5.09	18.6	94.6
EC4-2405	34.1	12.5	7.71	0.41	5.38	10.4	0.46	7.28	1.37	1.1	1.76	15.2	97.7
EC4-2170	31.8	11.5	10.8	0.32	7.31	11.5	0.66	6.38	0.98	1.34	0.45	16	99.0
EC4-2155	36.3	13.6	11	0.27	5.08	8.99	0.49	7.55	0.9	1.29	0.83	12.7	99.0

* Major element measurements reported as oxides (unnormalized) obtained by wavelength dispersive XRF, with the exception of BaO which was obtained by ICP atomic emission spectroscopy. LOI=Loss on ignition.
†Total iron reported as Fe_2O_3.

Table 2. WHOLE-ROCK TRACE-ELEMENT ANALYSES (PPM) OF EIK CREEK CARBONATITE

Sample	Sc	V	Co	Zn	Ga	Rb	Sr	Y	Zr	Nb	Sn	Cs	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U	F
Apatite dolomite carbonatite																																
EC10-1490	<5	63	23	38	3	0.7	3190	63	121	139	<1	<0.1	880	1400	130	450	50	13	33	3.0	15	2.6	6	0.7	4.0	0.5	2	12	12	40	28	2020
EC10-1530	<5	54	21	49	3	0.6	1330	67	64	120	<1	<0.1	1220	2040	200	680	80	18	45	4.0	17	2.8	6.3	0.8	4.0	0.6	<1	11	9	45	36	3140
EC39-2030	8	30	24	723	6	4.2	3020	41	106	11400	11	0.2	160	410	50	180	30	8	23	3.0	11	1.8	4	0.5	2.0	0.3	3	229	426	272	208	2240
EC43-1060	17	64	12	114	10	47	4400	45	89	6870	6	0.5	280	590	70	260	40	10	27	3.0	12	2	4.3	0.5	3.0	0.4	2	8.1	46	31	8	7850
EC43-1070	16	54	17	111	10	47	4310	38	43	12400	9	0.7	440	880	90	330	40	11	28	3.0	11	1.8	3.7	0.4	2.0	0.3	1	8.2	24	24	8	9910
EC43-1140	12	106	11	666	5	23	4090	58	47	456	2	0.3	1780	2820	270	860	90	19	42	4.0	15	2.5	5.4	0.6	4.0	0.5	<1	1	146	37	6	4920
Barite dolomite carbonatite																																
EC43-1010	31	80	3.7	318	6	0.3	4130	144	63	15	<1	<0.1	6840	11600	1110	3610	380	78	161	13	43	6.5	14	1.7	10.0	1.3	1	<0.5	25	102	1	39100
Dolomite carbonatite																																
EC17-1870	9	46	14	109	6	17	3980	53	67	257	1	0.4	6090	8480	700	1940	140	27	53	5.0	17	2.4	4.7	0.5	3.0	0.3	2	1.3	34	36	2	4470
EC93-510	13	281	8.1	259	10	26	3120	192	144	400	1	3.9	18700	20700	1520	3830	270	54	117	13	48	8.2	18	2.3	14	1.9	3	1.9	60	74	13	2910
Magnetite dolomite carbonatite																																
EC29-1480	65	176	16	1090	13	12	1410	273	49	10400	25	<0.1	410	790	90	340	140	71	227	24	87	12	22	2.3	12	1.4	2	26	130	512	88	1250
EC11-2425	56	231	27	249		24	2360	88	95	8400	77	1.8	407	848	79.7	300	136	49	95	6.7	24	3.2	8	1.0	6.0	0.8		6.5	42	191	47	1930
EC16-1380	78	277	27	696		25	2250	163	100	5970	15	0.6	879	1460	128	448	100	46	138	15	55	6.7	14	1.7	10	1.4		12	158	140	46	1860
EC28-1800	72	265	27	1200		15	3240	125	68	6800	27	0.2	588	1060	99.4	365	118	58	149	13	41	4.8	10	1.2	7.2	1.1		12	152	430	81	1190
EC29-1120	64	176	21	375		12	2800	331	116	6450	20	0.5	273	634	64.3	264	103	54	180	24	104	13	26	2.7	13	1.5		35	94	249	122	2410
Altered syenite																																
EC4-2400	6	82	5.4	51	14	89	2460	60	486	258	2	0.6	3340	4740	400	1170	120	24	52	5.0	18	2.9	6.1	0.7	4.0	0.5	7	6.6	16	85	19	1960
EC4-2405	9	192	21	67	24	120	1480	48	845	386	7	3.3	1460	2120	190	570	60	14	33	3.0	12	2.1	4.7	0.6	3.0	0.4	15	9	24	56	14	3420
EC4-2170	15	188	14	89	23	122	653	33	1080	397	8	3.6	300	550	60	230	40	9	21	2.0	9	1.5	3.5	0.4	3.0	0.4	18	12	11	50	37	4120
EC4-2155	14	192	27	78	25	135	835	46	1230	405	8	3.9	380	750	80	320	50	13	32	3.0	12	1.9	4.1	0.5	3.0	0.4	20	12	21	63	23	3230
Reproducibility Percent†	6	-	7	23	-	10	15	19	10	4	-	-	7	3	3	3	2	4	7	1	3	3	5	2	3	3	7	9	17	1	2	-

* Trace element determinations by ICPMS, with the exception of Sn and Sr which are ICP-AES determinations
† Estimated external reproducibilities (as % of mean standard concentrations measured during study period)

Table 3. WHOLE ROCK Nd, Sr AND Pb ISOTOPIC COMPOSITIONS OF ELK CREEK CARBONATITE[1]

Sample	$^{87}Rb/^{86}Sr$[2]	$^{87}Sr/^{86}Sr(m)$[3]	2σ	$^{87}Sr/^{86}Sr$ (T)[3]	$^{147}Sm/^{144}Nd$[2]	$^{143}Nd/^{144}Nd(m)$[3]	2σ	ε_{Nd} (0)[4]	T_{DM} (Ga)	μ[2]	κ[2]	$^{208}Pb/^{204}Pb$ (m)[5]	$^{207}Pb/^{204}Pb(m)$	$^{206}Pb/^{204}Pb(m)$	$^{208}Pb/^{204}Pb$ (T)[6]	$^{207}Pb/^{204}Pb(T)$	$^{206}Pb/^{204}Pb$ (T)
Apatite dolomite carbonatite																	
EC10-1490	0.0006	0.707475 ±	11	0.707470	0.0672	0.512271 ±	8	2.3	0.8	194	1.5	48.25	16.27	30.68	40.06	16.14	12.76
EC10-1530	0.0013	0.705703 ±	10	0.705692	0.0712	0.512268 ±	11	1.9	0.8	362	1.3	51.04	16.51	36.15	37.67	16.27	2.71
EC39-2030	0.0040	0.702890 ±	11	0.702857	0.1008	0.512399 ±	35	2.3	0.9	35	1.4	43.30	15.91	23.78	41.93	15.88	20.51
EC43-1060	0.0307	0.703232 ±	9	0.702983	0.0931	0.512372 ±	10	2.4	0.9	12	4.0	40.79	15.70	20.42	39.45	15.69	19.34
EC43-1070	0.0317	0.703289 ±	10	0.703031	0.0733	0.512299 ±	18	2.4	0.8	23	3.1	41.55	15.71	20.96	39.52	15.70	18.85
EC43-1140	0.0163	0.703424 ±	7	0.703292	0.0633	0.512262 ±	14	2.4	0.8	2.6	6.4	38.86	15.59	18.73	38.38	15.59	18.48
EC43-1010	0.0002	0.704136 ±	14	0.704134	0.0637	0.512294 ±	9	3.0	0.8	2.7	105	42.56	15.60	18.63	34.45	15.60	18.38
Dolomite carbonatite																	
EC17-1870	0.0123	0.704048 ±	7	0.703948	0.0437	0.512220 ±	15	3.0	0.7	3.9	19	40.71	15.64	19.26	38.64	15.64	18.90
EC93-510	0.0243	0.705418 ±	11	0.705221	0.0427	0.512177 ±	18	2.2	0.8	14	5.9	40.70	15.66	19.66	38.27	15.65	18.32
Magnetite dolomite carbonatite																	
EC29-1480	0.0240	0.705009 ±	9	0.704814	0.2491	0.512968 ±	19	2.6	UD	49	6.0	44.74	15.84	22.26	36.30	15.80	17.72
EC11-2425	0.0293	0.704813 ±	8	0.704575	0.2743	0.513065 ±	11	2.7	UD								
EC16-1380	0.0324	0.704403 ±	9	0.704140	0.1350	0.512524 ±	8	2.3	1.0								
EC28-1800	0.0136	0.704059 ±	9	0.703949	0.1956	0.512758 ±	7	2.4	2.4								
EC29-1120	0.0127	0.705087 ±	8	0.704984	0.2360	0.512880 ±	10	1.9	UD								
Altered syenite																	
EC4-2400	0.1041	0.704857 ±	9	0.704011	0.0621	0.512207 ±	9	1.4	0.8	90	4.6	46.38	15.84	24.36	34.50	15.78	16.05
EC4-2405	0.2343	0.705342 ±	10	0.703438	0.0637	0.512258 ±	8	2.3	0.8	41	4.1	42.77	15.77	22.47	37.89	15.74	18.65
EC4-2170	0.5399	0.708521 ±	8	0.704133	0.1052	0.512351 ±	14	1.1	1.0	295	1.4	47.67	16.60	36.19	35.90	16.41	8.95
EC4-2155	0.4672	0.707570 ±	6	0.703773	0.0945	0.512407 ±	46	2.9	0.8	87	2.8	46.93	16.11	27.88	39.89	16.05	19.84

[1]Total procedural blanks averaged ~1ng for Pb and Sr, and 100pg for Nd, during study period.

[2] ratios calculated using ICPMS determined elemental abundances (Table 2).

[3] Measured $^{87}Sr/^{86}Sr$ ratios were analyzed using four-collector static mode measurements. Thirty measurements of SRM-987 during study period yielded mean $^{87}Sr/^{86}Sr$=0.71032+/- 2. Initial ratios calculated at 570 Ma.

Measured $^{143}Nd/^{144}Nd$ normalized to $^{146}Nd/^{144}Nd$=0.7219. Analyses were dynamic mode, three-collector measurements. Thirty-three measurements of the La Jolla Nd standard during the study period yielded a mean $^{143}Nd/^{144}Nd$=0.511838+/-8 (2-σ mean).

[4] ε_{Nd} values calculated using a present-day $^{143}Nd/^{144}Nd$ (CHUR)=0.512638. Initial ratios calculated at 570 Ma.

[5] Pb isotopic analyses were four-collector static mode measurements. Sixteen measurements of SRM-981 during the study period yielded $^{208}Pb/^{204}Pb$=36.56 +/- 0.03, $^{207}Pb/^{204}Pb$=15.449+/-0.008, $^{206}Pb/^{204}Pb$=16.905+/-0.007 (2-σ mean). Measured Pb isotope ratios were corrected to SRM-981 values ($^{208}Pb/^{204}Pb$=36.721, $^{207}Pb/^{204}Pb$=15.491, $^{206}Pb/^{204}Pb$=16.937).

[6] Initial ratios calculated at 570 Ma

Table 4. Zircon LA-ICPMS Hf isotopic compositions

Sample	($^{176}Yb + ^{176}Lu)/^{176}Hf$ (%)	Volts Hf	$^{176}Hf/^{177}Hf$	±1σ	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$ (T)	$\varepsilon_{Hf}(0)$	±1σ	$\varepsilon_{Hf}(T)$[1]
EC4_2170_2175-	5.1	2.5	0.282505	0.000037	0.000248	0.282503	-9.9	1.3	2.7
EC4_2170_2175-11	4.3	2.2	0.282477	0.000038	0.000264	0.282474	-10.9	1.3	1.7
EC4_2170_2175-10	4.8	2.5	0.282543	0.000053	0.000297	0.282540	-8.6	1.9	4.1
EC4_2170_2175-8	7.3	2.0	0.282452	0.000050	0.000395	0.282447	-11.8	1.8	0.8
EC4_2170_2175-7	6.2	3.1	0.282516	0.000035	0.000313	0.282512	-9.5	1.3	3.1
EC4_2170_2175-13	10.2	1.6	0.282443	0.000064	0.000534	0.282437	-12.1	2.3	0.4

Table 5. Zircon LA-ICPMS U-Pb analyses

Analysis	U (ppm)	206Pb 204Pb	U/Th	206Pb* 207Pb*	± (%)	207Pb* 235U*	± (%)	206Pb* 238U	± (%)	error corr.	206Pb* 238U*	± (Ma)	207Pb* 235U	± (Ma)	206Pb* 207Pb*	± (Ma)	Best age (Ma)	± (Ma)	Conc (%)
EC4 2170-2175-16	131	1891	0.16	15.9131	12.1	0.1510	13.3	0.0174	5.5	0.41	111.4	6.0	142.8	17.7	702.9	258.1	111.4	6.0	NA
EC4 2170-2175-03	115	4833	0.07	14.2281	14.7	0.2048	17.0	0.0211	8.6	0.50	134.8	11.5	189.2	29.4	936.7	303.2	134.8	11.5	NA
EC4 2170-2175-09	39	5875	0.10	17.4179	29.9	0.1779	30.7	0.0225	7.0	0.23	143.2	9.9	166.2	47.1	507.4	671.7	143.2	9.9	NA
EC4 2170-2175-15	41	2818	0.02	15.6621	23.7	0.4728	25.4	0.0537	9.2	0.36	337.2	30.1	393.1	83.0	736.6	507.9	337.2	30.1	NA
EC4 2170-2175-12	46	9094	0.01	17.8235	11.4	0.5985	12.2	0.0774	4.4	0.36	480.4	20.5	476.3	46.5	456.5	253.4	480.4	20.5	105.2
EC4 2170-2175-01	23	8648	0.01	19.3605	21.0	0.6058	21.2	0.0851	3.3	0.15	526.3	16.6	480.9	81.5	270.0	485.4	526.3	16.6	194.9
EC4 2170-2175-11	23	8233	0.08	16.5608	11.8	0.7111	12.4	0.0854	3.8	0.30	528.3	19.0	545.4	52.4	617.3	256.4	528.3	19.0	85.6
EC4 2170-2175-13	68	7962	0.05	17.4895	6.7	0.6787	6.8	0.0861	1.3	0.19	532.4	6.6	526.0	27.9	498.3	147.2	532.4	6.6	106.8
EC4 2170-2175-07	23	13236	0.01	17.9195	11.0	0.6650	11.2	0.0864	1.9	0.17	534.4	9.6	517.7	45.3	444.6	245.1	534.4	9.6	120.2
EC4 2170-2175-10	12	7562	0.01	17.3930	24.5	0.6920	24.6	0.0873	2.7	0.11	539.5	14.2	534.0	102.7	510.5	545.9	539.5	14.2	105.7
EC4 2170-2175-08	13	1644	0.01	18.6351	29.5	0.6764	30.2	0.0914	6.2	0.21	563.9	33.4	524.6	124.2	356.9	679.7	563.9	33.4	158.0