Integrating trace element abundances and derived temperatures for zircon and titanite to elucidate petrogenesis of a Cretaceous granodiorite, southeastern California

Frank K. Mazdab[1], Joseph L. Wooden[1] & Andrew P. Barth[2]

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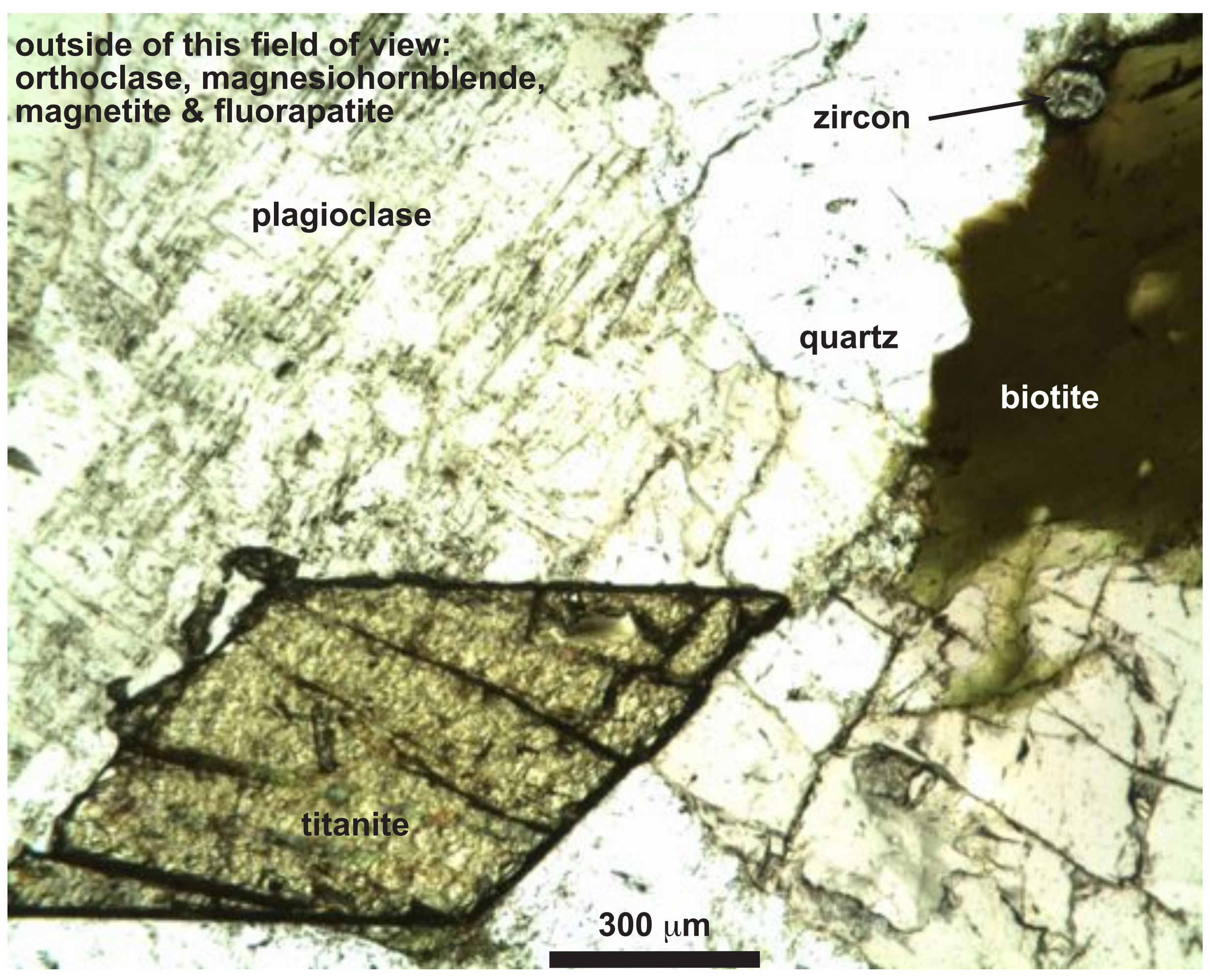
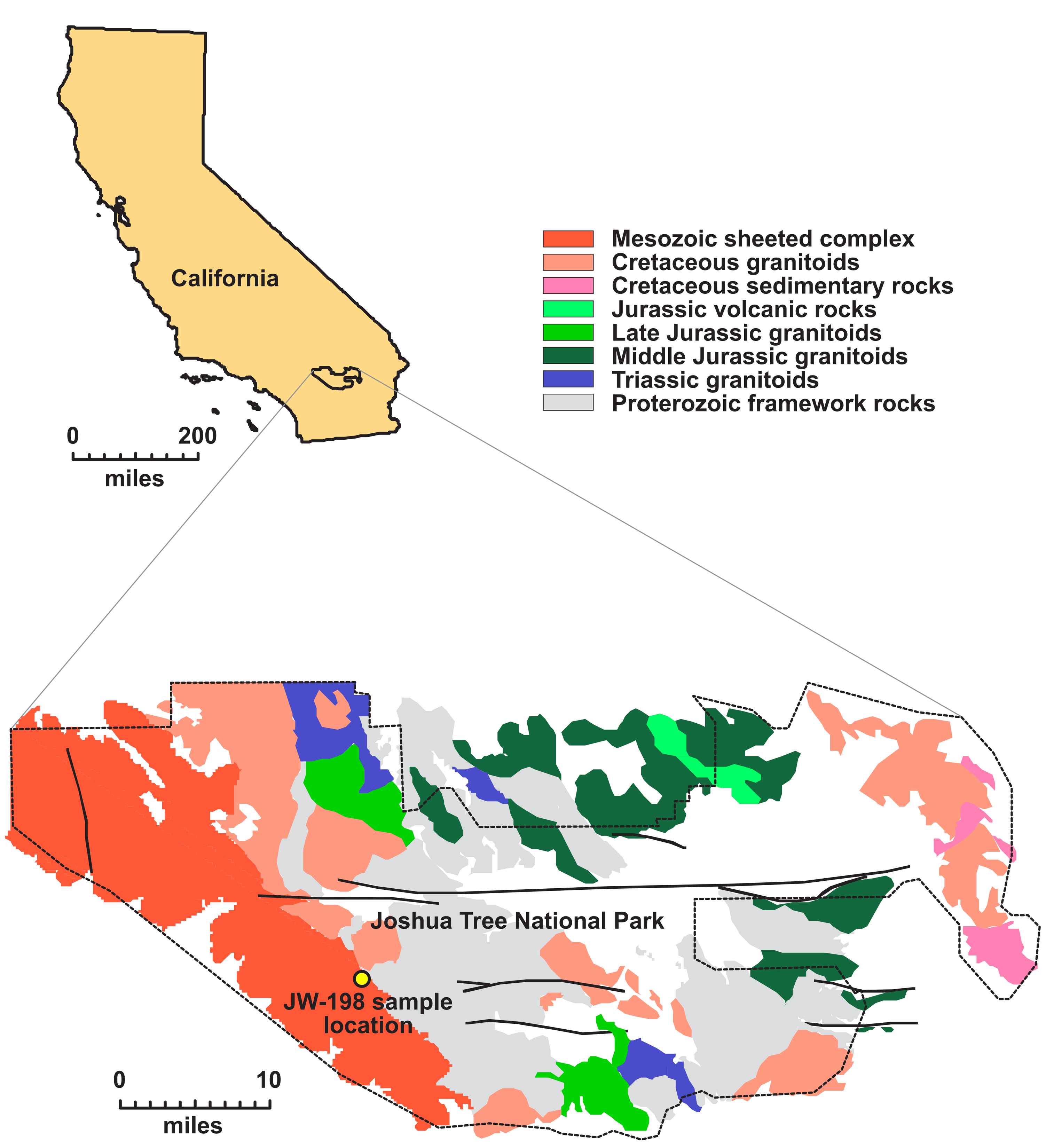
[1]U.S.G.S.-Stanford Ion Probe Laboratory, Stanford, CA 94305 USA
[2]I.U.P.U.I. Department of Geology, Indianapolis, IN 94305 USA
e-mail: fmazdab@usgs.gov; jwooden@usgs.gov; ibsz100@iupui.edu



Representative mineralogy of the Cretaceous granodiorites of southeastern California. Accessory titanite and zircon are both visible in this view. *Plane-polarized light (PPL) image of sample JW93-222, from a granodiorite boulder from Joshua Tree National Park, California.*

the rock: Blue granodiorite (81 Ma); Joshua Tree National Park, CA



simplied geologic map of Joshua Tree National Park, CA, modified after Barth *et al.*, 2001

Key Points

- Co-existing titanite & zircon are abundant in many intermediate granitoids, including the 81 Ma Blue granodiorite from Joshua Tree National Park, CA.
- Titanite and zircon incorporate a variety of trace elements (U, Th, REE, etc.) during growth that are of significant geochronological and petrogenetic interest.
- The concentrations & distributions of these trace elements may be diagnostic of the local chemical and P-T conditions during mineral growth.
- The Ti-in-zircon and Zr-in-titanite thermometers permit the direct correlation of chemical features between the two minerals, as well as recording magmatic changes as a function of cooling and fractionation.
- *In-situ* micro-analytical measurements permit detailed studies of individual zones within composite grains and minimizes accidental overlap with inclusions.
- SHRIMP-RG combines the excellent spatial and depth resolution of conventional SIMS with the benefits of extreme mass resolution, while maintaining reproducible, flat-topped peaks and high transmission.

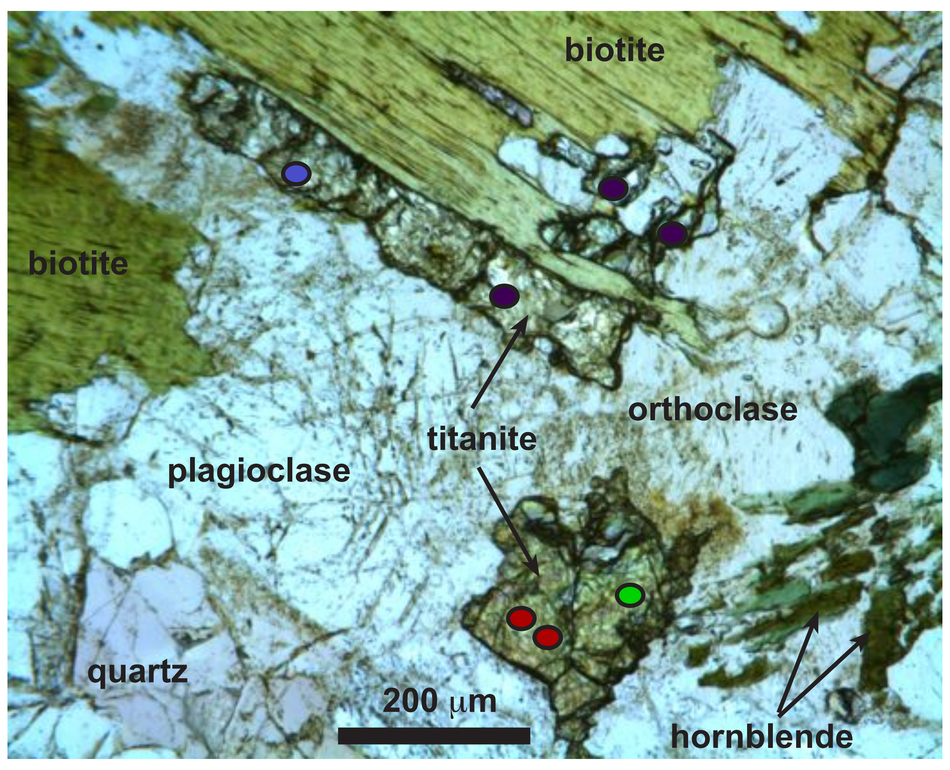
the instrumentation: SHRIMP-RG

- O_2^- primary beam; ~1.5 nA beam current; 15-20 μm spot size
- Yα slits and collector slit closed to achieve M/ΔM >~11000 at 10% peak height, + flat-topped peaks

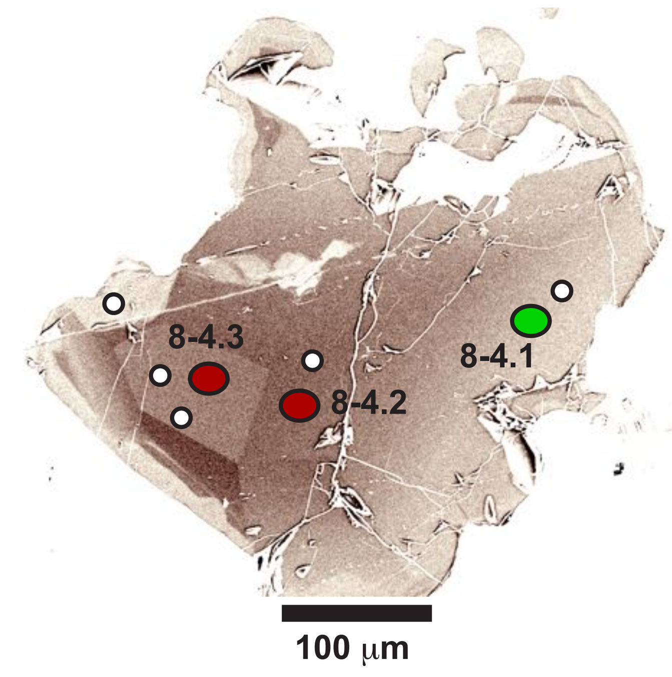
The SHRIMP-RG at the U.S.G.S.-Stanford Ion Probe Laboratory in Stanford, California.
http://shrimprg.stanford.edu

titanite chemistry

Major and trace element chemistry by electron microprobe and SHRIMP-RG (*in-situ*)



Plane-polarized transmitted light image of JW-198, frame 8. Colored ovals are locations of SHRIMP trace element analyses (EPMA analyses at right are from closely adjacent spots); colors are matched to the colored groups of observed REE patterns and other trace element data (below).



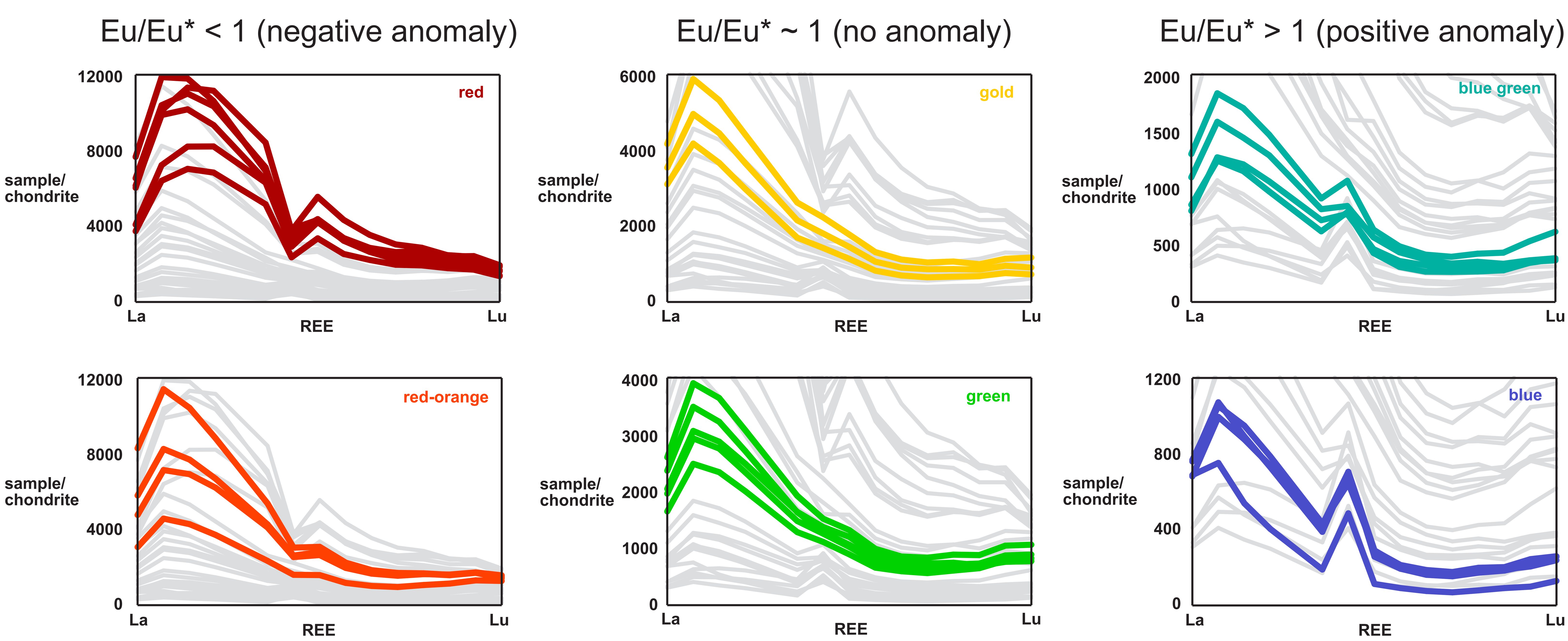
False-color, inverted back-scattered electron (BSE) view of compositional zoning in grain 8-4 (at left) with locations of SHRIMP trace element analysis spots (colored ovals) and locations of complementary electron microprobe analyses (small circles).

Combined electron microprobe and SHRIMP-RG analyses of titanite from JW-198, frame 8.

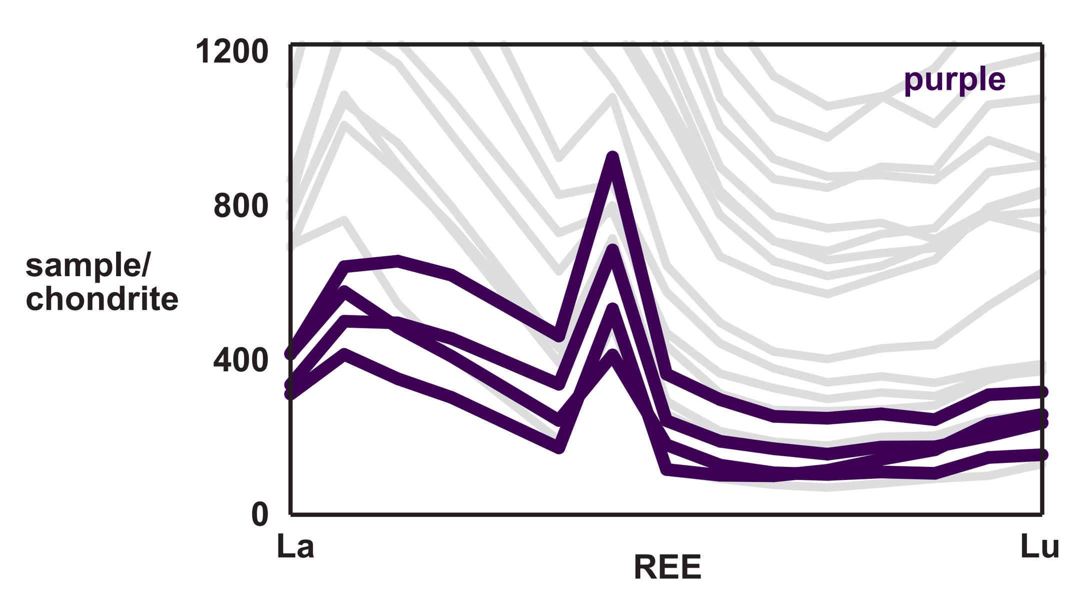
	8-1.1	8-2.1	8-3.1	8-3.2	8-4.1	8-4.2	8-4.3
(wt. %)							
SiO_2	30.89	30.85	30.75	30.69	30.48	29.78	29.68
TiO_2	36.65	36.82	36.99	35.96	35.77	34.82	35.19
Al_2O_3	1.25	1.18	1.09	1.53	1.55	1.59	1.38
Fe_2O_3	1.08	0.96	1.03	1.35	1.53	2.04	1.87
MnO	0.15	0.16	0.20	0.16	0.24	0.21	0.24
CaO	29.08	28.95	28.90	28.97	28.40	27.39	27.62
F	0.54	0.53	0.43	0.54	0.48	0.47	0.43
-O=F	-0.23	-0.22	-0.18	-0.23	-0.20	-0.20	-0.18
H_2O	(0.59)	(0.61)	(0.52)	(0.54)	(0.50)	(0.35)	(0.22)
TOTAL*	**100.00**	**99.84**	**99.73**	**99.51**	**98.75**	**96.45**	**96.45**
(ppm)							
Li	0.2	0.1	0.0	0.1	0.1	0.0	0.2
B	1.8	0.3	0.1	1.4	0.3	0.0	0.1
Na	35	39	44	48	46	67	85
Mg	34	14	30	20	66	112	112
P	90	88	95	105	153	190	218
Cl	7	11	9	12	12	8	16
K	4	1	2	7	2	3	2
Sc	5.6	5.1	15.0	8.0	13.1	13.7	13.3
V	631	658	630	660	585	548	544
Cr	24	23	26	20	17	18	17
Co	0.0	0.1	0.1	0.1	0.1	0.1	0.1
Ni	0.6	0.6	0.7	0.7	0.7	0.7	0.5
Zn	48	53	51	62	48	59	62
Ga	1.3	1.4	2.1	1.4	2.2	2.5	2.5
Ge	6.0	5.1	9.4	6.6	5.4	4.3	3.3
Sr	18	20	22	21	29	36	33
Y	387	545	242	395	1832	5094	4139
Zr	134	140	197	164	366	492	495
Nb	386	390	400	546	1014	1374	1608
La	106	131	131	217	829	1302	1193
Ce	405	519	467	815	3200	5922	5245
Pr	59	78	58	106	441	993	851
Nd	276	376	249	453	1892	5049	4204
Sm	67	91	48	85	385	1261	1032
Eu	51	69	31	54	116	222	180
Gd	64	96	48	78	352	1126	897
Tb	9	14	6	10	49	161	125
Dy	56	83	35	61	283	902	732
Ho	12	19	8	13	63	185	149
Er	37	56	24	40	192	521	417
Tm	6	8	3	6	29	71	59
Yb	44	68	32	45	231	477	377
Lu	8	10	5	8	35	55	45
Hf	7	9	19	11	27	33	35
Ta	8	9	9	6	65	257	299
Th	16	19	53	97	686	765	553
U	103	101	354	404	113	88	89

Spot locations are color-coded to the diagrams at left and below. Totals only include the wt% listed major elements.

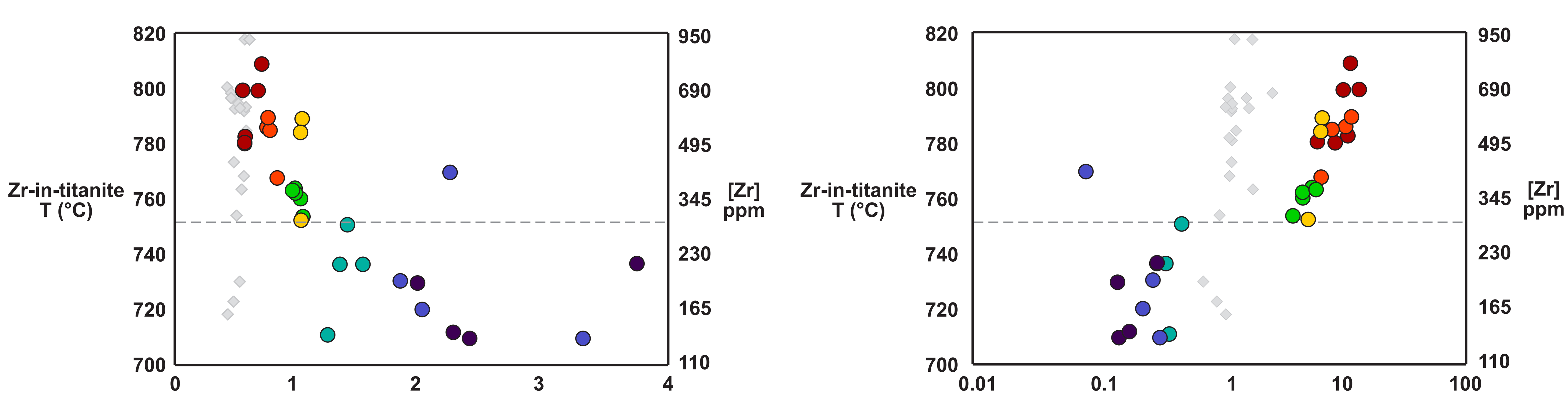
Rare earth element (REE) characteristics



Seven groups of REE patterns can be differentiated from among the different grains and BSE-visible compositional zones in titanite from JW-198. Note the change of scale. The patterns are characteristically sub-parallel and show the Eu anomaly transitioning from negative (Eu/Eu* < 1) to positive (Eu/Eu* > 1) with decreasing temperature (see below).



Zr-in-titanite thermometry and elemental variations



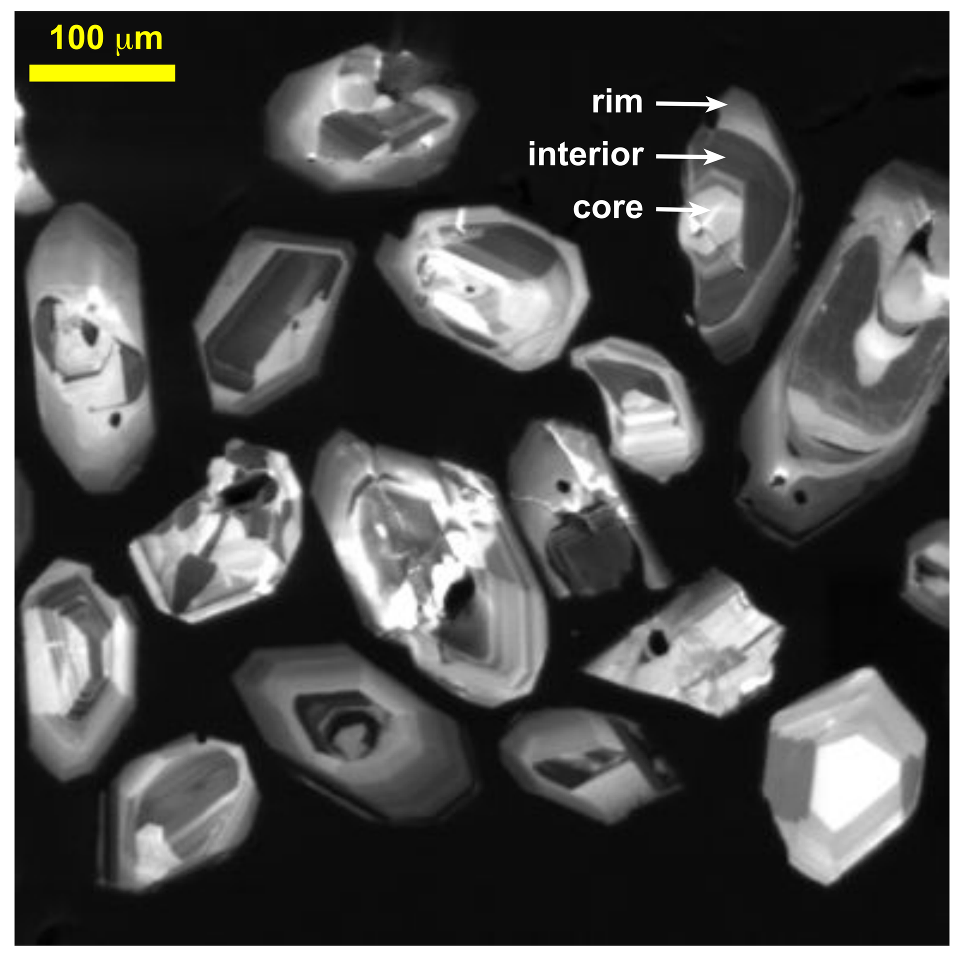
Plots of Zr-in-titanite temperatures vs. Eu/Eu* and Th/U for titanite from JW-198. Calibration for Zr-in-titanite thermometer comes from Hayden *et al.* (abstract: Goldschmidt conference, 2006). Pressure estimate is 0.5 GPa. Symbol coloration corresponds to the REE pattern colors (above). The gray diamonds represent equivalent data for zircon from JW-198. Temperatures for zircon are derived from the Watson & Harrison (2005) and Ferry & Watson (2007) calibrations of the Ti-in-zircon thermometer, assuming a_{SiO_2}=0.95 and a_{TiO_2}=0.7.

A marked transition in titanite Th/U occurs ~750 °C and Eu/Eu* ~ 1. These transitions indicates a large-scale physio-chemical change in the magma or a new, different titanite-forming event.

zircon chemistry

Trace element chemistry by SHRIMP-RG (grain mount)

Zircon separate from the Blue granodiorite, sample JW-198.

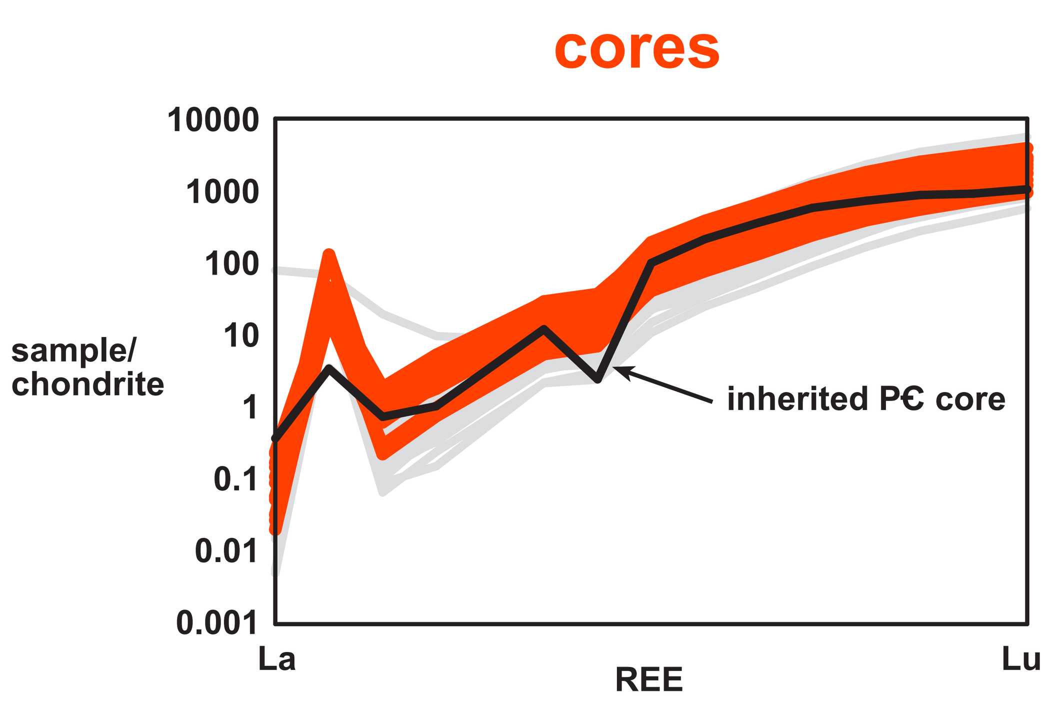


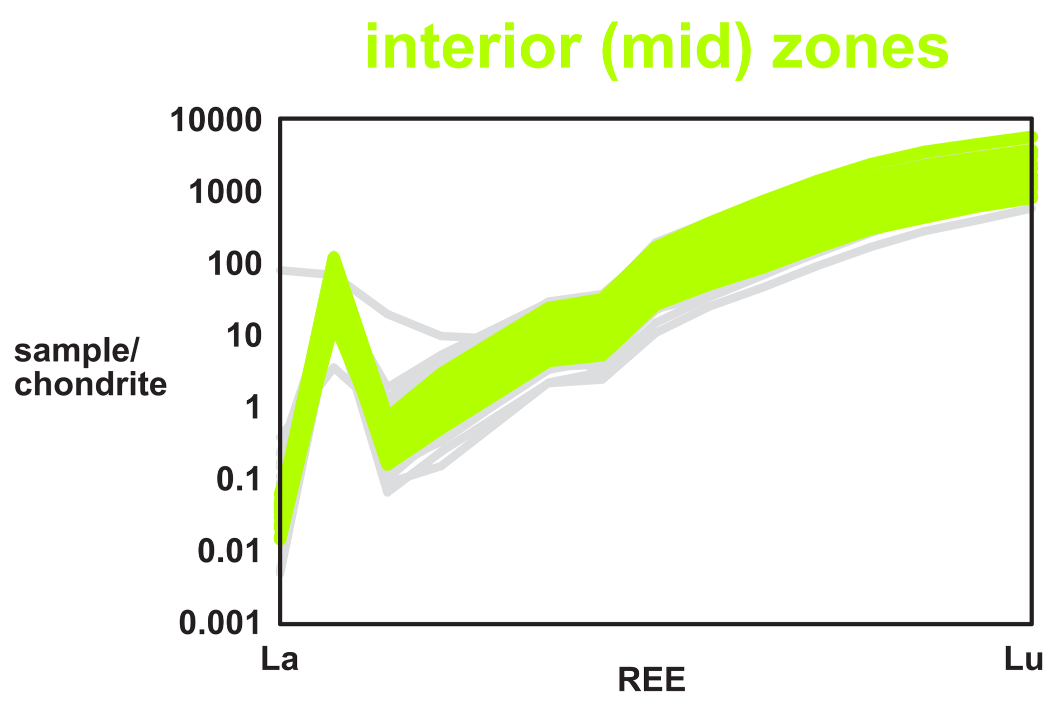
Cathodoluminescence (CL) image of zircon from JW-198. CL zones identified as "rim", "interior" and "core" are shown for an example grain. Comparable zones are widespread among the grains.

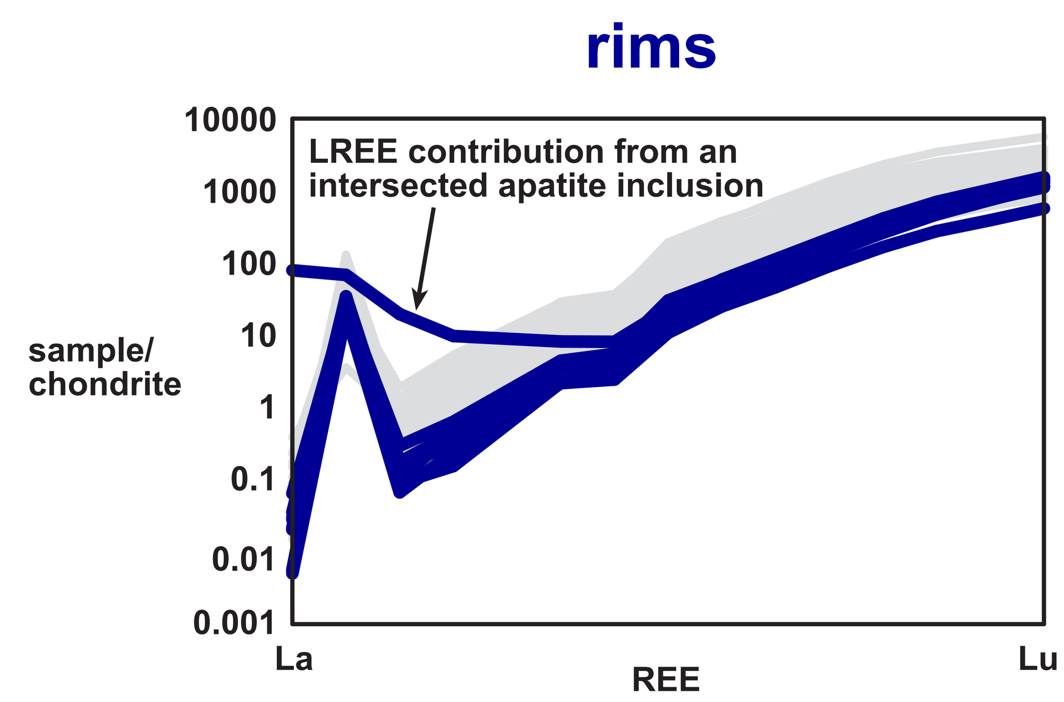
Representative SHRIMP-RG analyses of zircon from sample JW-198, Blue granodiorite

	17IB	6Tit	20M	8M3	16T	22T
zone	core	core	interior	interior	rim	rim
(ppm)						
Li	0.02	0.04	0.02	0.02	0.07	0.04
B	0.07	0.07	0.06	0.20	0.19	0.17
F	13	15	11	12	18	11
Na	3	5	4	6	5	4
Mg	1	4	1	1	2	1
Al	7	15	20	34	15	20
P	263	303	220	352	132	128
S	0.5	1.1	--	0.5	0.3	0.3
K	1	1	1	2	1	1
Ca	1	1	1	2	1	1
Sc	72	63	46	88	25	21
Ti	21	12	13	20	4	8
V	0.61	0.13	0.19	0.16	0.19	0.10
Cr	0.03	0.04	0.04	0.07	0.05	0.05
Mn	--	--	0.1	0.1	0.1	0.1
Fe	0.3	0.6	0.5	0.4	0.9	0.8
Ge	0.3	0.3	0.2	0.3	0.2	0.2
Y	1121	539	394	596	457	196
Nb	1.2	2.8	1.9	1.6	3.1	1.5
La	0.029	0.006	0.011	0.010	0.007	0.002
Ce	25	26	22	13	28	17
Pr	0.155	0.027	0.030	0.040	0.017	0.008
Nd	2.98	0.46	0.40	0.67	0.22	0.15
Sm	5.58	1.10	1.11	1.32	0.86	0.43
Eu	2.23	0.54	0.42	0.86	0.40	0.19
Gd	37	12	8	10	7	3
Tb	11.5	4.2	3.0	3.8	2.9	1.2
Dy	120	50	35	44	37	15
Ho	45	21	14	21	15	7
Er	195	98	70	106	85	36
Tm	40	23	17	25	22	9
Yb	318	199	148	236	224	87
Lu	58	39	29	51	48	19
Hf	9883	10115	10826	8286	14372	12024
^{206}Pb	1	1	1	2	1	1
Th	110	128	70	54	159	46
U	53	78	58	52	167	47

Rare earth element (REE) characteristics

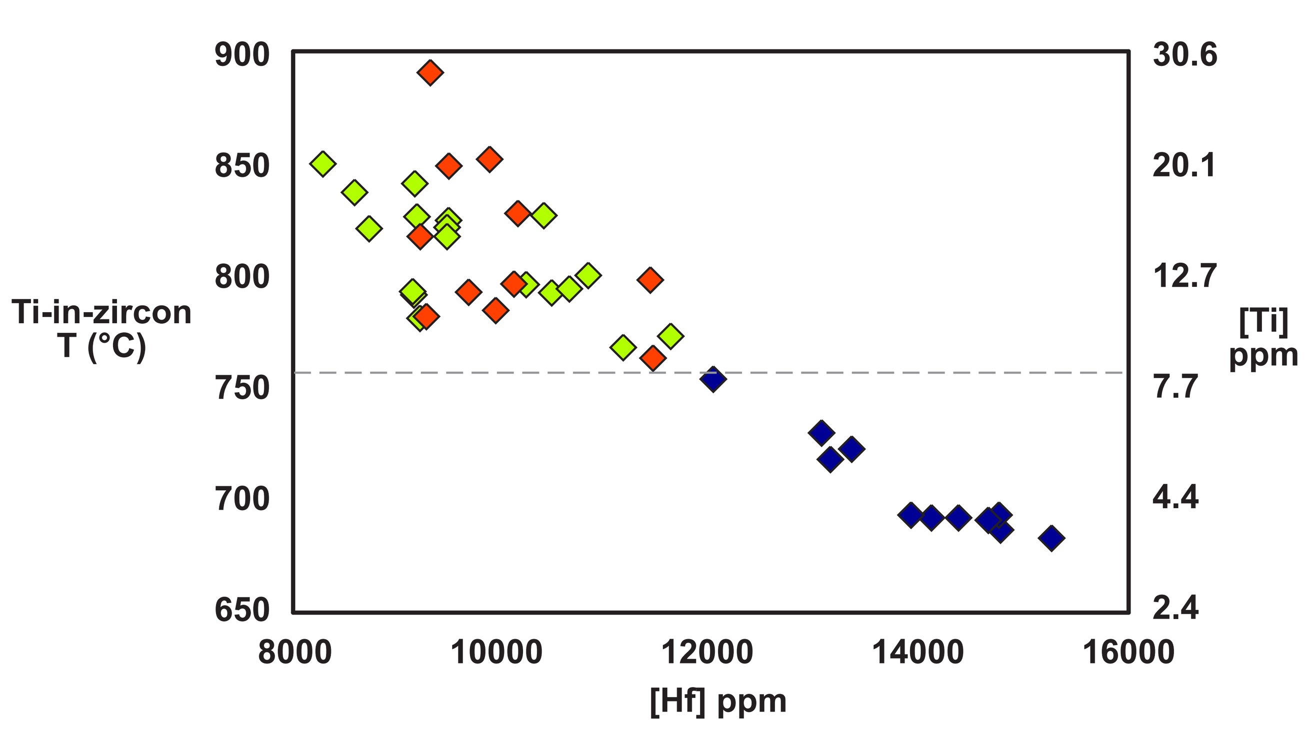


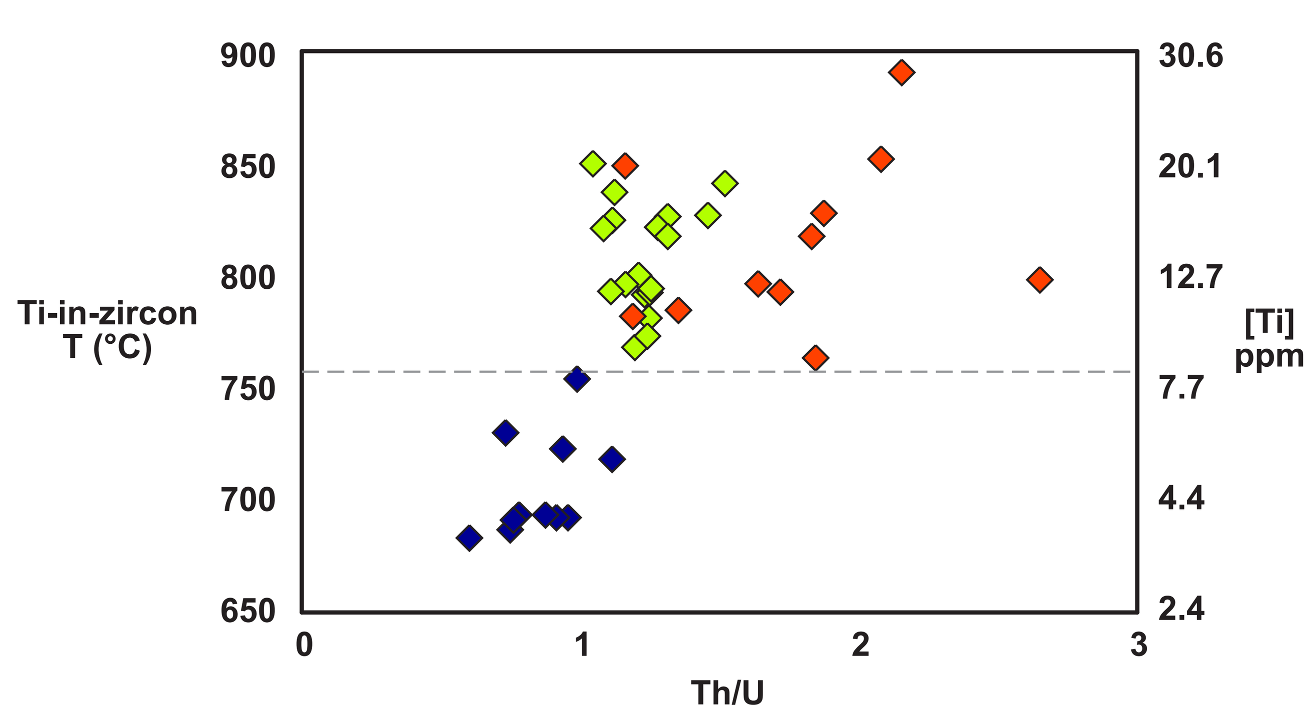


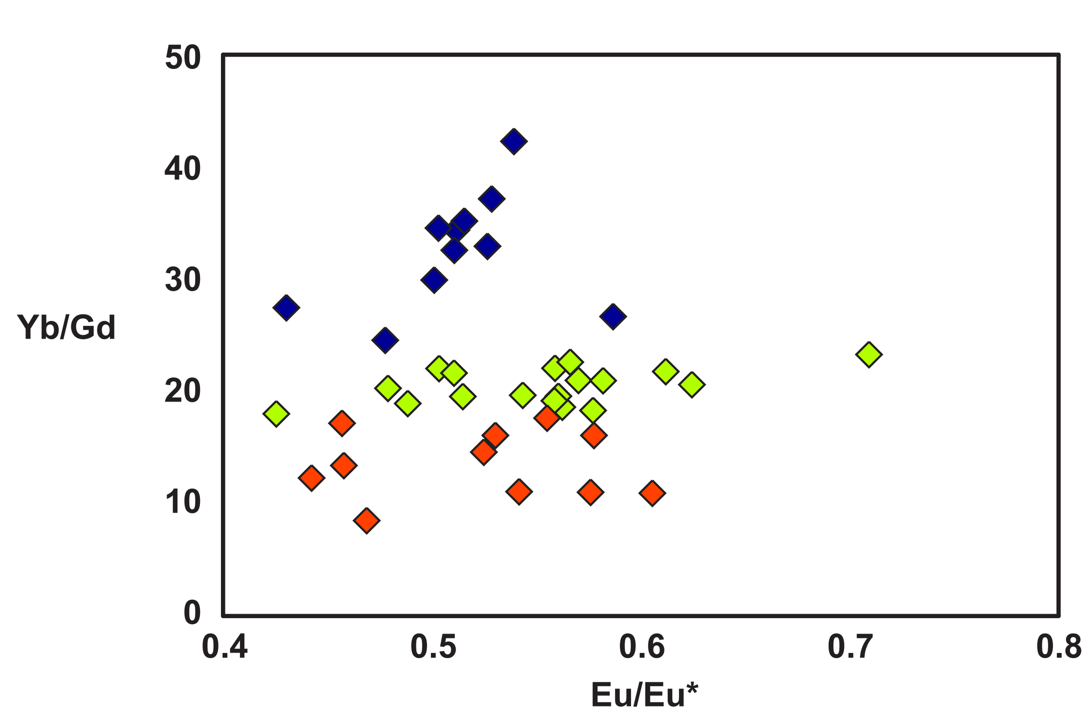


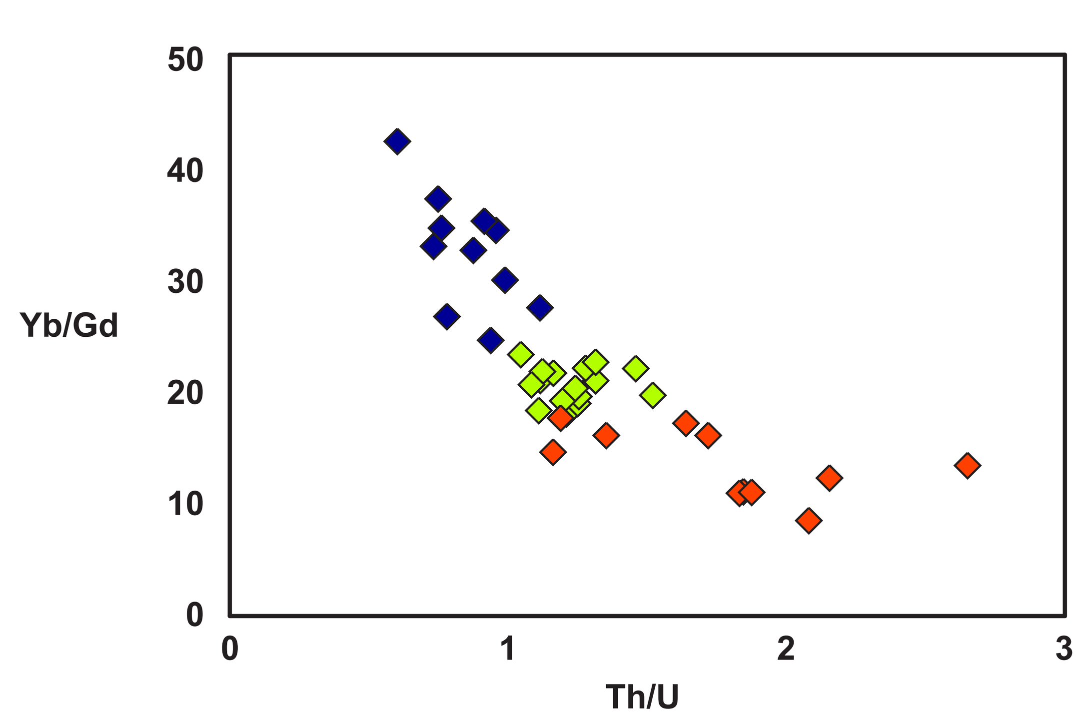
Unlike the diverse REE patterns observed in titanite, the REE patterns from the core, interior and rim zones of JW-198 zircon are all strongly sub-parallel, with comparable values for Eu/Eu* and Ce/Ce*. Patterns for the core and interior zones overlap significantly, whereas those of the rims are notable lower in total REE. The consistency of the patterns is accentuated by the marked deviations observed for an inherited PЄ core and overlap with an apatite inclusion.

Ti-in-zircon thermometry and elemental variations









Plots of Ti-in-zircon temperatures vs. Hf concentration and Th/U, and Yb/Gd vs. Th/U and Eu/Eu*, for zircon from the Blue granodiorite (sample JW-198). Calibration for Ti-in-zircon thermometer comes from Watson & Harrison (2005) and Ferry & Watson (2007) assuming a_{SiO_2}=0.95 and a_{TiO_2}=0.7. Symbol coloration corresponds to the REE pattern colors (above). The temperature vs. Hf plot shows a typical fractionation trend for granitoid plutonic magmas. Yb/Gd emphasizes slope differences in zircon REE patterns and shows that despite a general overlap in the REE patterns of the core and interior zones (see above), the patterns do steepen from core to mid interior, which is also characteristic of fractionation. Although Th/U typically decreases with fractionation, U and Th concentrations are more variable and may indeed increase (e.g. analysis 16T, above). Eu/Eu*appears to slightly increase (hence, anomaly magnitude diminishing) with fractionation within the interior zone, and more notably within the rims.

Although more subtle than the Th/U transition in titanite, comparable transitions in Th/U, Yb/Gd and Hf concentration occur in zircon, also at ~750 °C. These transitions record a different manifestation of the same large-scale physio-chemical change in the magma that is observed in titanite.