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# OXYGEN AND HAFNIUM ISOTOPE GEOCHEMISTRY OF ZIRCON, QUARTZ, AND GARNET FROM THE CRAWFISH INLET AND KRESTOF PLUTONS, BARANOF ISLAND, ALASKA

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## GEOLOGIC BACKGROUND

The Sanak–Baranof plutonic belt (SBPB) is 2100 km magmatic belt, in which plutons intruded the Upper Cretaceous Chugach–Prince William (CPW) terrane accretionary complex along the continental margin of southwest Alaska between 61-47 Ma (Hill et al., 1981; Cowan, 2003; Madsen et al., 2006; Farris and Patterson, 2009). The Paleocene to early Eocene intrusions constituting the Sanak-Baranof plutonic belt are present across the entire arc of the Chugach-Prince William terrane, and range from tonalitic to granonodioritic in composition and vary in size from the small pluton on Sanak Island to batholiths on Kodiak (Cowan, 2003; Bradley et al., 2003). Quartz diorites to tonalites are more predominant in the eastern part of the belt (Bradley et al., 2003). Many studies suggest that the SBPB represents a forearc plutonic belt with near-trench magmatism, resulting from the subduction of a spreading ridge (Cowan 2003; Haeussler et al., 2003; Madsen et al., 2006). The SBPB has been recognized to exhibit a continuous series of eastward younging forearc intrusions with crystallization ages of ~63 Ma on Sanak Island to ~47 Ma on Baranof Island (Bradley et al., 2003) (Fig. 1). A west-to-east age progression is interpreted to be caused by the migration of a trench-ridge-trench (TRT) triple junction of the Kula, Farallon, and/or Resurrection plates (Cowan, 2003 and Haeussler et al., 2003).

Previous geochemical studies by Hill et al. (1981) focused on Kodiak, Sanak, and Shumagin Islands of southwest Alaska revealed that intrusions were preceded by a pulse of mafic to intermediate volcanism near or within the CPW accretionary prism, recorded in the Paleocene, possibly related to subduction of the Kula-Farallon ridge at ~60 Ma. Analyses of major and trace elements, and isotopic ratios of Nd, Sr, and O appear to be consistent with magmas having formed by mixing of mid-ocean ridge basalts (MORB) with melted metasedimentary components of the wedge (Hill et al., 1981).

The Eocene Crawfish Inlet pluton (CIP) was emplaced into the Upper Cretaceous to Paleocene Sitka Graywacke (Loney et al., 1975; Rick, this volume) (Fig. 1). The CIP extends across the central part of Baranof Island, and is a composite tonalite, granodiorite, and leucocratic-tonalite, suggesting a compositional range and heterogeneity in these intrusive rocks (Loney et al., 1975).

In this study, I present new oxygen and hafnium isotope analyses and U-Pb geochronology on the Crawfish Inlet Pluton (CIP) and the Krestof Pluton (KP) from the eastern part of the Sanak-Baranof Belt on Baranof Island to further evaluate the hypothesis of a crust vs. mantle origins for the SBPB. One additional sample from the Aialik pluton near Seward is also included. The goals of this project include: correlating oxygen data with available εHf (zircon) and U/Pb age (zircon) data; evaluating oxygen systematics by thermometry and by calculating inter-mineral O fractionations.

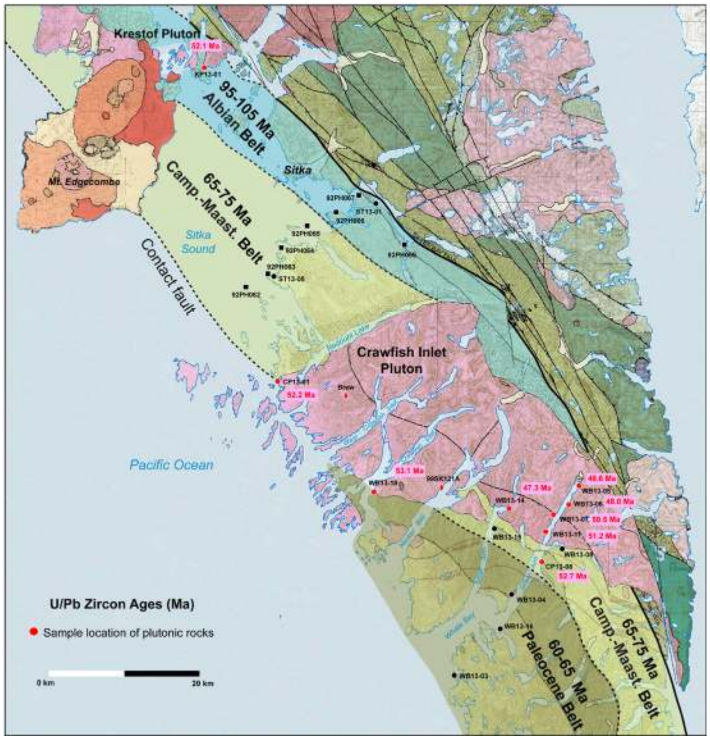


*Figure 1: Area of study on Baranof Island, Southeast Alaska and sample sites with U-Pb crystallization ages (Ma) for igneous zircons in red. A eastward-younging trend is observed in the pluton, with ages from 53.1 to 48 Ma. Sample CP13-08 just south of the Crawfish Inlet pluton is from a Grt-Ms leucogranite sill (~100 m thick) emplaced into the Sitka Greywacke. Map modified from Karl et al., in press.*

## METHODS

### Oxygen isotope analysis and sample preparation

A representative population of igneous zircons, quartz, and garnets from the CIP and KP were analyzed for $\delta^{18}O$ by laser fluorination at the University of Wisconsin-Madison using a fluorine-based agent ($BrF_5$) and a $CO_2$ laser. Analyses for $\delta^{18}O$ were made by laser fluorination from nine rock samples that contained abundant zircons of a single generation (little to no inheritance). Prior to analysis, quartz and garnet mineral samples were handpicked and treated with dilute hydrochloric acid to remove grain boundary alteration. Zircon concentrates were treated with HF and HCl to remove radiation damage domains and other phases. Oxygen isotope analyses were performed at the University of Wisconsin stable isotope laboratory. Isotope ratios were measured on a gas source Finnigan MAT 251 mass spectrometer. Analyses were standardized by five analyses of UWG-2, garnet standard. Analyses for $\delta^{18}O$ of ~2 mg were weighed for each analysis. All samples were corrected for accuracy with UWG-2 garnet ($\delta^{18}O$=5.8‰) (Valley et al., 1995).

### Hafnium isotope analysis and U/Pb geochronologic analysis sample preparation

U-Pb and Hf isotope data were collected by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) at the Arizona LaserChron Center (Gehrels et al., 2008). Prior to analysis, zircon crystals were extracted using standard techniques at Union College and Carleton College. A split of these grains (~50-100 grains) were selected and incorporated into a 1" epoxy mount together with zircon standards for U/Pb and Hf (Cecil et al., 2011). The mounts were ground to a depth of ~20 µm, polished, imaged (BSE and CL), and cleaned prior to isotopic analysis. Nine samples were analyzed for U/Pb using a 30 µm diameter spot size and 25-30 analyses (zircons) per sample. Hf isotope analyses were collected from four of the samples using a 40 µm diameter spot size located directly on top of the 30 µm pits used for the U/Pb dates. CL and BSE images were used to carefully locate the Hf pits to stay within the same zoning domain of the zircon used for the U/Pb date.

*Table 1: $\delta^{18}O$ of zircon, quartz and garnet (‰ VSMOW) from Baranof Island.*

| Sample | Pluton | Mineral | $\delta^{18}O$ (meas) | $\delta^{18}O$ VSMOW | 2 SD | $\Delta^{18}O$(q-g) VSMOW | $\Delta^{18}O$(q-z) VSMOW |
|---|---|---|---|---|---|---|---|
| CP13-01 | Crawfish | qtz | 11.06 | 11.08 | 0.04 | | 3.61 |
| CP13-01 | | zircon | 7.40 | 7.47 | 0.12 | | |
| CP13-02 | Crawfish | gar | 7.27 | 7.29 | 0.04 | 4.35 | |
| CP13-02 | | qtz | 11.62 | 11.64 | 0.04 | | |
| CP13-03A | Crawfish | qtz | 10.12 | 10.14 | 0.04 | | 3.38 |
| CP13-03A | | zircon | 6.69 | 6.76 | 0.12 | | |
| CP13-04 | Crawfish | qtz | 10.37 | 10.39 | 0.04 | | 4.21 |
| CP13-04 | | zircon | 6.11 | 6.18 | 0.12 | | |
| CP13-05A | Crawfish | qtz | 9.63 | 9.65 | 0.04 | | 2.74 |
| CP13-05A | | zircon | 6.84 | 6.91 | 0.12 | | |
| CP13-07A | Crawfish | qtz | 10.45 | 10.47 | 0.04 | | 3.25 |
| CP13-07A | | zircon | 7.15 | 7.22 | 0.12 | | |
| CP13-08D | Crawfish | gar | 8.06 | 8.08 | 0.04 | 4.86 | |
| CP13-08D | | qtz | 12.92 | 12.94 | 0.04 | | |
| CP13-09A | Crawfish | qtz | 9.94 | 9.96 | 0.04 | | 3.69 |
| CP13-09A | | zircon | 6.20 | 6.27 | 0.12 | | |
| CP13-13 | Crawfish | qtz | 10.91 | 10.93 | 0.04 | | 3.45 |
| CP13-13 | | zircon | 7.41 | 7.48 | 0.12 | | |
| KP13-01 | Krestof | zircon | 6.95 | 7.02 | 0.12 | | |
| RB13-04 | Aialik | qtz | 12.43 | 12.45 | 0.04 | | 2.83 |
| RB13-04 | | zircon | 9.55 | 9.62 | 0.12 | | |

## RESULTS

### Oxygen Isotope Geochemistry

Analyses of $\delta^{18}O$ (zircon) were made by laser fluorination from seven granite samples from the Crawfish Inlet pluton, one from the Krestof pluton, and one from the Aialik pluton of the SBPB collected near Seward, Alaska (Table 1). Values of $\delta^{18}O$ (zircon) from the Crawfish and Krestof plutons on Baranof Island in Southeast Alaska range from 6.18 ± 0.12‰ (2 SD) to 7.48 ± 0.12‰, and 9.62 ± 0.12 ‰ from the Aialik pluton (uncertainty at 2σ) (Fig. 2a). All nine zircon samples lie in the "supracrustal" field, as zircon with $\delta^{18}O$ > 6‰ are not known from uncontaminated mantle-derived magmas (Valley et al., 1998; Valley, 2003; Valley et al., 2005). The elevated $\delta^{18}O$ values for magmatic zircon require a component of pre-existing crust to have been incorporated into the melt source of these magmas. Igneous zircons in high temperature equilibrium with mantle magmas have an average $\delta^{18}O$ = 5.3±0.6‰ (Valley et al., 2005). A total of ten samples from the CIP were analyzed for $\delta^{18}O$ (quartz) (Fig. 2b). $\delta^{18}O$ values ranged from 9.65 ± 0.04‰ for the CIP and KP, to 12.45 ± 0.04‰ for the Aialik pluton. Two samples from small Grt-Ms leucogranite satellite sills of the CIP yield elevated $\delta^{18}O$ (garnet) of 7.27 ± 0.04‰ and 8.06 ± 0.04‰.

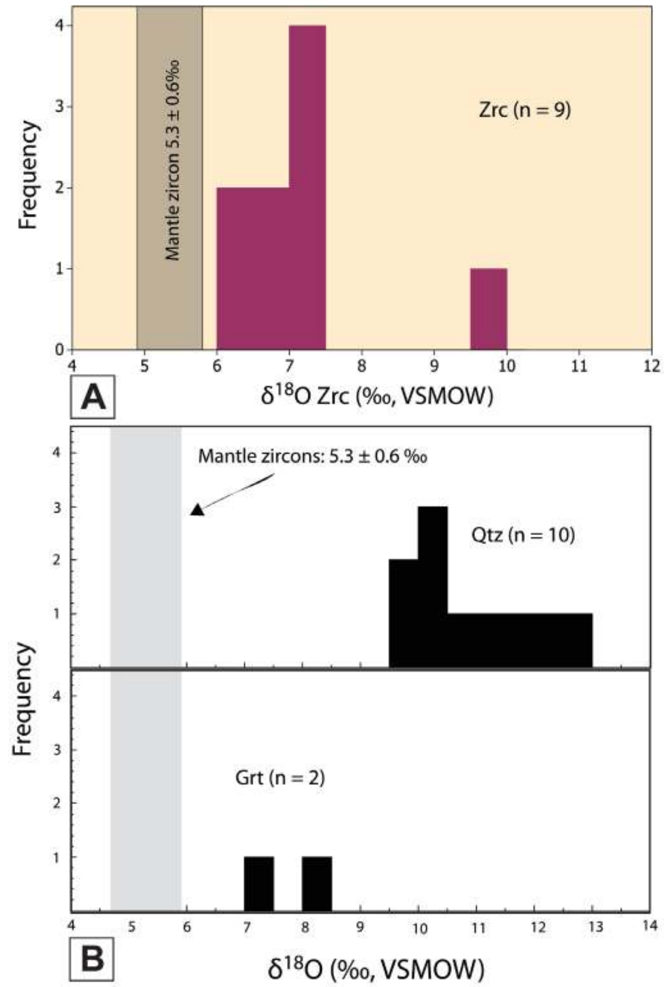


*Figure 2: (a) Histogram of $\delta^{18}O$ (zircon) from the Crawfish Inlet, Krestof, and Aialik plutons. The gray shaded vertical bar indicates range of mantle-equilibrated zircon, 5.3 ± 0.6‰ (2 SD), (Valley et al., 2005). (b) Histogram of $\delta^{18}O$ (quartz) (top) and δ18O (garnet) (bottom) from the Crawfish Inlet Pluton. The gray shaded vertical bar indicates range of mantle-equilibrated zircon, 5.3 ± 0.6‰ (2 SD), (Valley et al., 2005).*

Mineral O fractionations were calculated for quartz, zircon, and garnet pairs. Comparison of $\delta^{18}O$ (zircon) to $\delta^{18}O$ (qtz) reveals that most quartz–zircon pairs fall between isotherms of 515 and 630°C (Fig. 3a), lower temperatures than expected for magmatic temperatures (Lackey et al., 2005). Two samples fall on the 700° C isotherm, and provide the closest approximation to preserved magmatic values of quartz in those samples (Table 1). Values of quartz-garnet fractionations are also not in equilibrium (Fig. 3b), consistent with resetting of O in quartz (Lackey et al., 2005).

### U-Pb Geochronology and Hafnium Isotope Geochemistry

U/Pb ages from seven samples within the Crawfish Inlet pluton and one sample from a small satellite sill (CP13-08) range from 47.3±1.2 to 53.1±0.8 Ma. Sample KP13-01 from the Krestof pluton yields an age of 52.1±1.0 Ma (Fig. 1). These ages are

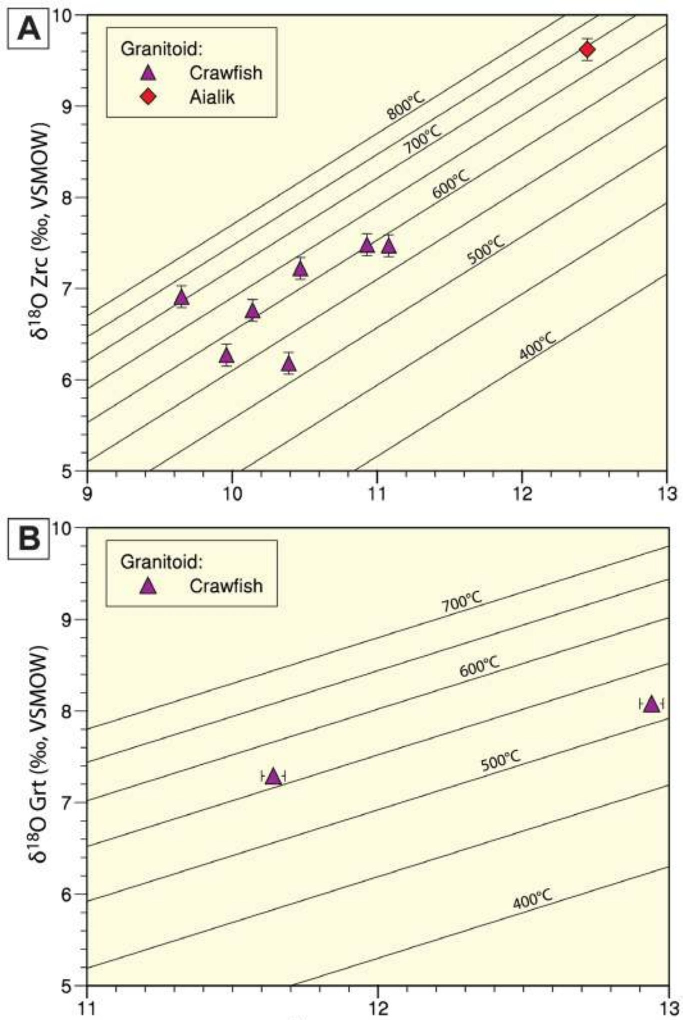


*Figure 3: (a) δ-δ plot for coexisting quartz and zircon from the Crawfish Inlet and Aialik granitoids of the Sanak-Baranof Plutonic Belt (SBPB). Analyses are represented by triangles with uncertainty shown at 2 sd (standard deviation). Most quartz–zircon fractionations yield apparent temperatures that are lower than magmatic temperatures and suggest $\delta^{18}O$ (quartz) is reset. Fractionation factors are from Valley et al. (2003). (b) Quartz–garnet fractionations for coexisting quartz- garnet from the Crawfish Inlet Pluton granitoids. Analyses are represented by triangles with uncertainty shown at 2 sd. Note that none of the samples yield magmatic temperatures. Fractionation factors are from (Valley et al., 2003).*

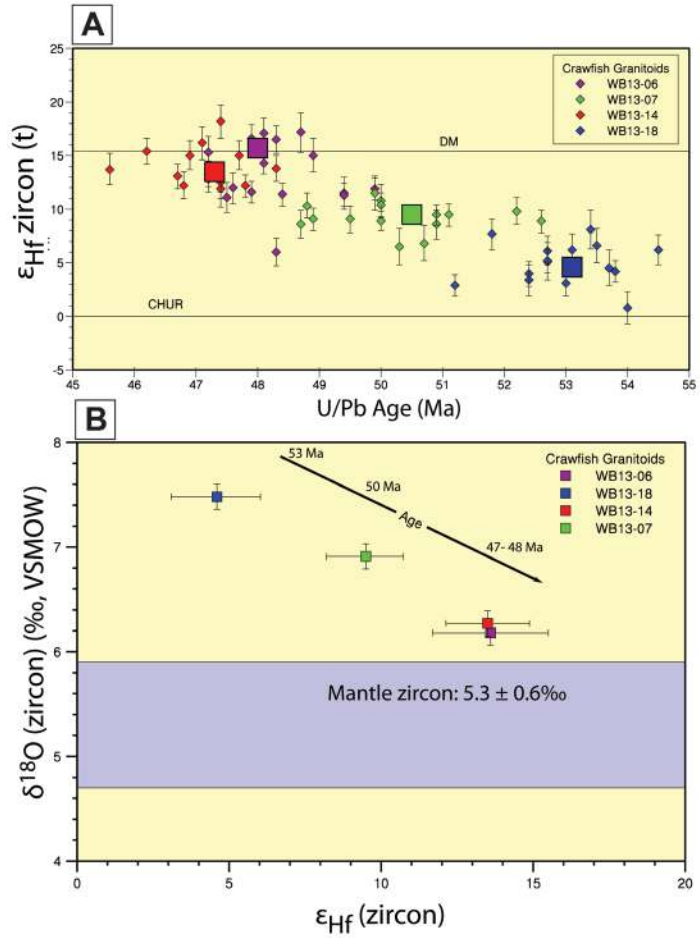


*Figure 4: (a) εHf vs. U/Pb age evolution for four granitoid samples from the Crawfish Inlet Pluton. Zircons are represented by diamonds with ± 2 se (standard error) uncertainties. Age progression shows a distinctive magmatic evolution as measured by Hf isotopes. (b) $\delta^{18}O$ (zircon) vs. ε Hf (zircon) from Crawfish pluton granitoids. The data set, although small, shows a strong correlation indicating that the more primitive (juvenile) granitoid zircons with higher ε Hf values record the least evolved oxygen isotope ratios. This trend is also temporal; the black arrow indicates the U-Pb age of the four samples, which shows the decreasing importance of crustal recycling with time during the genesis of these granitoids, as the magmas became more dominated by mantle-derived melts.*

interpreted to represent the crystallization ages of these rocks. Hf isotopes collected from four samples within the Crawfish Inlet pluton yield εHf values ranging from +18.2 ± 1.5 (1σ) at 47.4 Ma to +0.8 ± 1.5 (1σ) at 54.0 Ma, indicating a distinct trend within the CIP (Fig. 4a).

## DISCUSSION AND CONCLUSIONS

Age progression shows a distinctive magmatic evolution as measured by Hf isotopes (Fig. 4a). A near linear trend shows the evolution from initially evolved magmas with a crustal component (lowest εHf values), to magmas with a more pronounced mantle contribution through time (highest εHf).

Oxygen isotope ratio versus epsilon Hf for zircon from Crawfish pluton granitoids shows a strong correlation indicating that the more primitive (juvenile) granitoid zircons with higher epsilon Hf values record the least evolved oxygen isotope ratios. As shown in Figure 4b, this trend is also temporal;

the U-Pb age of the four samples shows decreasing importance of crustal recycling with time during the genesis of these granitoids. The magmas became more dominated by mantle-derived melts as shown by higher εHf values, with continued magmatism. All the zircons show evidence for the incorporation of recycled crust, as they uniformly plot above the range for mantle equilibrated zircon (Valley et al., 2005).

Spatial heterogeneity in composition, age, and isotopic chemistry in the Crawfish Inlet, and Krestof plutons raises the question on the possible source and petrogenesis of these granitoids. U/Pb crystalization ages show that this is likely a composite pluton made up of multiple pulses of magmatism spanning from 53-47 Ma (Fig. 1). The increase in the range of $\delta^{18}O$, εHf, and U-Pb ages in the CIP, appears to indicate lesser supracrustal input with time (Fig. 4b).

Oxygen isotope ratio (zircon) versus εHf (zircon) in Figure 4b shows a strong correlation indicating that the more primitive (juvenile) granitoid zircons with higher εHf records the least evolved oxygen isotope ratio. All zircons show elevated $\delta^{18}O$ values, evidence for the incorporation of recycled crust from the accretionary wedge or from altered basalt derived from a subducted slab into the melt source of the magmas. $\delta^{18}O$ (Qtz–Zrc) and (Qtz- Grt) mineral fractionations yield temperatures that are lower than those considered magmatic temperatures, thus indicating resetting of $\delta^{18}O$ (quartz) by oxygen diffusion in quartz (Lackey et al., 2005). Age progression of the Crawfish Inlet Pluton, as measured by Hf isotopes, shows a near linear trend of magmatic evolution from initially evolved magmas with a crustal component, to more juvenile-mantle derived magmas. An interpreted scenario that can potentially be consistent with my findings would imply the subduction of young-oceanic crust (MORB), mixing and hybridization of mafic magmas with crustal partial melts or supracrustal rocks, and subsequent modification by crustal contamination (assimilation).

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