Extreme oxygen isotope zoning in garnet and zircon from a metachert block in mélange reveals metasomatism at the peak of subduction metamorphism

F. Zeb Page[1], Emilia M. Cameron[1,2], Clara Margaret Flood[1], Jeffrey W. Dobbins[1], Michael J. Spicuzza[2], Kouki Kitajima[2], Ariel Strickland[2], Takayuki Ushikubo[2*], Christopher G. Mattinson[3], and John W. Valley[2]**

[1] Geology Department, Oberlin College, Oberlin, Ohio 44074, USA
[2] WiscSIMS, Department of Geoscience, University of Wisconsin -Madison, Wisconsin 53706, USA
[3]Department of Geological Sciences, Central Washington University, Ellensburg, Washington 98926
**** Present Address: Kochi Institute for Core Sample Research, JAMSTEC 200 Monobe-otsu, Nankoku, Kochi 783-8502 Japan*

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ABSTRACT

A tectonic block of garnet quartzite in the amphibolite-facies mélange of the Catalina Schist (Santa Catalina Island, California, USA) records the metasomatic pre-treatment of high-$\delta^{18}O$ sediments as they enter the subduction zone. The block is primarily quartz, but contains two generations of garnet that record extreme oxygen isotope disequilibrium and inverse fractionations between garnet cores and matrix quartz. Rare mm-scale garnet crystals record prograde cation zoning patterns, whereas more abundant ~200-μm diameter crystals have the same composition as rims on the larger garnets. Garnets of both generations have high $\delta^{18}O$ cores (20.8-26.3‰, VSMOW) that require an unusually high–$\delta^{18}O$ protolith, and lower–$\delta^{18}O$, less variable rims (10.0-11.2‰). Matrix quartz values are homogeneous (13.6‰). Zircon crystals contain detrital cores ($\delta^{18}O$ = 4.7-8.5‰, 124.6 +1.4/-2.9 Ma), with characteristic igneous trace-element composition likely sourced from arc-volcanics, surrounded by zircon with metamorphic age (115.1 ± 2.5 Ma) and trace-element compositions that suggest growth in the presence of garnet. Metamorphic zircon decreases in $\delta^{18}O$ from near-core (24.1‰) to rim (12.4‰), in equilibrium with zoned garnets.

Collectively, the data document the subduction of a mixed high-$\delta^{18}O$ siliceous ooze/volcanic ash protolith reaching temperatures of 550-625 °C prior to the nucleation of small garnets without influence from external fluids. Metasomatism is recorded in rims of both garnet and zircon populations as large volumes of broadly homogeneous subduction fluids stripped matrix quartz of its extremely high oxygen isotope signature. Zoned garnet and zircon in high-$\delta^{18}O$ subducted sediments offer a detailed window into subduction fluids.

INTRODUCTION

The nature and timing of mass transfer between the subducting plate and the sub-arc mantle is critical to our understanding of crustal formation at convergent margins and its geochemical signatures. Chemical and mechanical hybridization within subduction mélange plays an important role in these processes (e.g., Bebout and Penniston-Dorland, 2016), giving rise to models suggesting that partial melting of diapirs of hybridized mélange rocks are responsible for the classic trace element signature of arc rocks (Marschall and Schumacher, 2012) and the diversity of magma series found at convergent margins (Cruz-Uribe et al., 2018). Adding to these complications is the recent discovery that some sediments have entered the mantle and melted without mixing or hybridization, preserving extreme oxygen isotope signatures of surface weathering in their neoformed igneous zircon (Spencer et al., 2017). If subducted sediment can regularly carry its characteristically enriched oxygen isotope signature ($\delta^{18}O$ = ~7 - 42‰, VSMOW [Vienna standard mean ocean water]; Kolodny and Epstein, 1976; Eiler et al., 2001; Payne et al, 2015) into the mantle ($\delta^{18}O_{Ol}$ = 5.1‰, Eiler et al., 2000), it is surprising that oxygen isotope variability within the subarc mantle is so subtle and challenging to measure (Eiler et al., 1998). A solution to this discrepancy may be found in the fluid metasomatism of subducted sediments.

The first and perhaps most dramatic illustrations of a high degree of fluid flow within subduction mélange were studies of the oxygen isotope ratios of quartz and carbonate in veins within the Catalina Schist subduction complex (California, USA) suggesting km-scale oxygen isotope homogenization driven by large fluid fluxes (Bebout and Barton, 1989; Bebout, 1991). Over the last quarter century, the Catalina Schist has served as a laboratory for the study of subduction mélange, with numerous studies detailing fluid metasomatism and mechanical mixing processes in the subduction channel by means of stable isotopes (e.g., Bebout, 1991; Penniston-Dorland et al., 2012), major and trace elements (e.g., Sorenson and Barton, 1987; Hickmott et al., 1992; Penniston-Dorland et al., 2014) and radiogenic isotopes (King et al., 2006).

The in-situ analysis of oxygen isotopes in garnet is a powerful tool with which to decipher complex or extremely subtle fluid histories and tie them to the metamorphic record. In rocks that have experienced significant metasomatism, the extremely slow intragranular diffusion of oxygen in garnet allows it to preserve a robust geochemical record through all but the hottest and longest of metamorphic events (Vielzeuf et al., 2005). Oxygen isotope variability in garnets from eclogite has illustrated signals of infiltration by mantle (Russell et al., 2013) and supracrustal (e.g., Page et al., 2014; Martin et al., 2014; Rubatto and Angiboust, 2015) fluids that were previously undetectable using bulk methods.

Chert and siliceous schist are high–δ^{18}O lithologies (Eiler et al., 2001) that are found within the amphibolite-facies Catalina Schist mélange (Platt, 1975). In this contribution, we explore the metasomatism of a high–δ^{18}O garnet- and zircon- bearing metachert from a classic subduction mélange, in order to better understand the timing and metamorphic conditions of subduction fluid metasomatism, and to gain a more complete picture of how fluids mitigate the influence of high-δ^{18}O subduction inputs.

CATALINA GARNET QUARTZITE

Although much less numerous than the better-studied garnet-hornblende lithology, tectonic blocks of garnet quartzite are also found within the amphibolite-facies metasedimentary mélange of the Catalina Schist (Santa Catalina Island, California, USA), as well as in more coherent, faultbounded sheets (Platt, 1975; Bebout, 1991). In this study, we report on one exceptional sample of garnet quartzite collected from a meter-scale tectonic block hosted in a shale-matrix mélange from Upper Cottonwood Canyon (33°23'46.20"N, 118°24'52.80"W, Fig. 1A). The quartzite is composed primarily of quartz (93%), garnet (6%), and chlorite (<0.5%), with trace rutile, apatite, amphibole, and zircon (Fig. 1B). Garnet is present in two populations: copious fine-grained (<200µm-diameter) crystals dispersed throughout the sample and a smaller number of larger garnets (1-3mm-diameter, Fig. 1B). The larger crystals have abundant inclusions, which are primarily quartz and apatite. X-ray mapping and major element traverses show that the larger garnets display classic prograde cation-zoning profiles with decreasing Mn and increasing Mg# from core to rim, and with rim compositions similar to smaller, more homogenous (in cations) garnets in the same rock (Figs. 2A, B).

Oxygen Isotopes of Quartz and Garnet

Ion microprobe analysis of garnets (Page et al., 2010, see GSA Data Repository for full data, Tables DR-1, DR-2, and methods) shows extreme oxygen isotope zoning; values of $\delta^{18}O$ are 20.8-26.3‰ in garnet cores and 10.0-11.2‰ in garnet rims (Fig. 2A). Both large and small garnets in this sample show a similar range in $\delta^{18}O$, despite the difference in cation zoning and crystal size. Zoning in oxygen isotopes is sharp, with up to a 7‰ drop in $\delta^{18}O$ over a few micrometers, whereas cation zonation is much more gradual with slightly increased Ca and Mg in the rims of larger garnets (Fig. 2). Smaller garnets are nearly homogeneous with a slight increase in Mg# from core to rim. Matrix quartz has no systematic zoning in cathodoluminescence imaging (CL) and is homogeneous in $\delta^{18}O$ with ion microprobe analyses (13.5‰) identical (within uncertainty) to bulk (~2mg) analysis by laser fluorination (13.6‰).

Garnet-core and quartz pairs yield reversed fractionations ($\delta^{18}O_{grt} > \delta^{18}O_{qz}$), indicating profound disequilibrium. Eleven analyses of quartz inclusions in large garnet cores yield $\delta^{18}O$ = 13.8-16.2‰, higher than matrix quartz, but not in equilibrium with host garnet. Inclusions were generally >50µm, and commonly along cracks and so are unlikely to preserve their original values.

Oxygen Isotopes in Zircon

Zircons were separated from the sample and mounted in epoxy for analysis (see GSA Data Repository). CL imaging (Fig. 3A) reveal oscillatory-zoned cores, often as fragments of crystals, containing inclusions of quartz, K-feldspar, and biotite. These detrital cores are surrounded by annuli of variable intensity, somewhat mottled zircon, containing inclusions of quartz, biotite, sphene, and rutile. Outside of this mottled zone, zircons typically have darker-intensity-CL oscillatory-zoned rims, with rare crystals containing a brighter outer rim with faint oscillatory zoning.

Zircons were analyzed for their oxygen isotope ratios by ion microprobe using both a ~15- and a sub-1-µm diameter beam (Tables DR-4, -5). Highly precise and accurate oxygen isotope ratios from the larger analysis pits are correlated with CL zonation and inclusion population. Zircon cores (n=7) have $\delta^{18}O$ from 4.7 to 8.4‰ (Figs. 3A, 3B). Zircon with mottled CL immediately outside of detrital cores (n=17) has an extremely high $\delta^{18}O$ (Fig. 3A, 3B) of 22.6 ±3.3‰ (2 SD, sample) if one anomalously low analysis is discounted. Intermediate-intensity oscillatory-zoned rims (n=20) have lower $\delta^{18}O$ values (17.3 ±3.9‰), and rare bright outer rims have lower-still $\delta^{18}O$ values (12.9 ±3.3‰). To further determine if there is a systematic zoning pattern in zircon like that found in garnet, 29 sub-1-µm analyses (following the method of Page et al., 2007) were made in traverses across a single zircon (Fig. 3A). These high-spatial resolution (but less precise, ±0.9-1.7‰, 2S.D.) analyses confirm the presence of a low $\delta^{18}O$ core (6.3 ±1.1‰, 2S.D., n=6), surrounded by an extremely high-$\delta^{18}O$ mottled CL region (22.6 ±2.4‰, n=15), indistinguishable within the uncertainty of the sub-1-µm data from the 15-µm-diameter analyses of the same zones. An outer, darker oscillatory-zoned rim has $\delta^{18}O$ of 17.0 ±2.5‰, n=8). The zircon chosen for this analysis does not have an outermost, lighter rim.

PRESSURE, TEMPERATURE, AND TIME HISTORY

The limited mineralogy of this sample coupled with its metasomatic history and zoned minerals, makes thermobarometry challenging. However, an equilibrium assemblage diagram calculated using an estimate of the bulk composition and the computer package Perple_X (Connolly, 2009; Fig. DR-1) yields reasonable results. The observed assemblage (qz+grt+ru±chl) is predicted to form at pressures greater than 8kbar and temperatures greater than 550˚C. The core to rim increase of Mg# observed in the large garnets is consistent with growth during increasing temperatures in the presence of chlorite, and is predicted by the model to have taken place at ~550-650˚C, at pressures of greater than 11kbar, consistent with existing pressure and temperature estimates of amphibolite blocks in the same mélange and [Zr]-in-rutile thermometry from this same sample (Sorenson and Barton, 1987; Hartley et al., 2016; Penniston-Dorland et al., 2018). The closeness between the conditions predicted by the model and existing thermobarometry from Catalina suggests that the metasomatism of this block did not involve substantial change in cation composition. Regardless of the precise conditions of metamorphism, the concomitant decrease in $\delta^{18}O$ with increasing Mg# in garnet requires metasomatism as the sample increased in temperature within the subduction environment.

Zircons were additionally analyzed by SHRIMP-RG for U-Pb isotopes and select trace elements (GSA Data Repository). Detrital zircon cores have more elevated Th/U ratios (0.36-0.89), and are older than rims; 8 of 9 analyses yield a coherent ^{204}Pb-corrected ^{206}Pb*/^{238}U age of 124.6 +1.4/-2.9 Ma (Fig. 3C). Th/U ratios of rims are lower (0.02-0.13) and yield an age of 115.1±2.4 Ma consistent with an igneous origin for zircon cores, and a metamorphic one for the rims (Fig. 3C). Zircon rims also have smaller Eu-anomalies (Eu/Eu* close to 1) and flatter HREE patterns, consistent with a metamorphic origin in a garnet-present, plagioclase-absent high-pressure environment (Fig. 3D).

DISCUSSION

Taken together, the P-T-t-fluid data preserved in garnet and zircon from this sample provide a detailed record of metasomatic events within the subduction channel. A mixed-lithology protolith containing both extremely high-δ^{18}O siliceous material intermixed with intermediate/mafic igneous material including detrital igneous zircon grains was subducted in the Catalina trench. The most plausible interpretation is that the protolith was a mixture of chert or siliceous ooze mixed with ~124 Ma arc volcanoclastic material. The relative purity of the quartzite and the narrow range of zircon core ages seems to preclude weathering of plutonic source material as an origin for the inherited cores. This mixed sediment was subducted and metamorphosed initially as a closed system, with larger, prograde garnet cores having high and unchanging δ^{18}O values. The extreme oxygen isotope ratio of this sample (quartz in equilibrium with garnet cores at 550˚C would have been greater than 30‰, Valley et al., 2003) makes it highly sensitive to infiltration from external fluids with lower δ^{18}O. A second generation of garnets nucleated near the peak of metamorphism, but their growth was not initiated by an external fluid, as core $\delta^{18}O$ compositions are identical to larger garnets. As metamorphic temperatures reached their peak, an external fluid permeated the sample, perhaps due to introduction of the block into the subduction mélange, shifting matrix quartz $\delta^{18}O$ from ~30‰ to 13.6‰. Slow rates of intragranular diffusion preserve a record of the original high-$\delta^{18}O$ composition of garnet and zircon, and their continued growth documents decreasing $\delta^{18}O$ from ~24‰ to ~17‰ to ~11‰ VSMOW, possibly in two discreet pulses. Fractionation between matrix quartz and garnet rim compositions yield temperatures of ~600-750˚C (Valley et al., 2003), consistent with estimates of peak metamorphic temperatures for the block and the region. Likewise, garnet cation composition records increasing temperature (pressure is not well constrained) during metasomatism. Perhaps upwelling within the subduction channel stopped quartz recrystallization and garnet growth simultaneously, effectively ending the record preserved in this sample.

The limited range of $\delta^{18}O$ in quartz and calcite veins within the Catalina Schist first reported by Bebout and Barton (1989) suggests that the entire package of subduction rocks on Catalina Island interacted with a remarkably homogeneous supracrustal fluid reservoir derived from metamorphic dehydration of minerals deeper along the subducting slab with an oxygen isotope composition of 13±1.0‰ VSMOW. The quartz $\delta^{18}O$ value for the block in mélange in this study (13.6‰ VSMOW) yields a calculated water $\delta^{18}O$ value of 12.3‰ VSMOW (650˚C, Friedman and O'Neil, 1977) in close agreement with the range reported by Bebout and Barton.

Although high−$\delta^{18}O$ sediments make up a volumetrically small portion of subducted material, the extreme contrast between their isotope ratios and those of the mantle make them likely candidates for introducing fine-scale isotope anomalies in the sub-arc mantle. Indeed, the recent discovery of high−$\delta^{18}O$ S-type granite within supra-subduction-zone mantle as well as this contribution show that this can happen (Spencer et al., 2017). The sample documented in this study is an example of the most extreme contrast in $\delta^{18}O$ that one might expect to be subducted, with an estimated protolith $\delta^{18}O$ of 30‰. However, the metasomatic processes documented by garnet and zircon zonation in this metachert from Catalina show that subduction fluids can all but wipe out extremely high–$\delta^{18}O$ inputs to subduction zones. Given the modest modal proportion of garnet (7%) with respect to quartz (93%) in this sample, and assuming $\delta^{18}O$ values of 24‰ for garnet and 14‰ for quartz, the whole rock $\delta^{18}O$ of this rock must be less than 15‰, a value that can also be found in the much more abundant subducted metabasalts with protoliths enriched in ^{18}O by low-temperature interaction with sea water (Eiler, 2001). Subduction fluids play a vital role in the generation of arc magmatism and continental growth, but is also seems that they play an important role in buffering the $\delta^{18}O$ of rocks that are recycled into the mantle by subduction, with only strongly refractory (and volumetrically minor) phases such as zircon and garnet able to carry extreme oxygen isotope ratios into the mantle.

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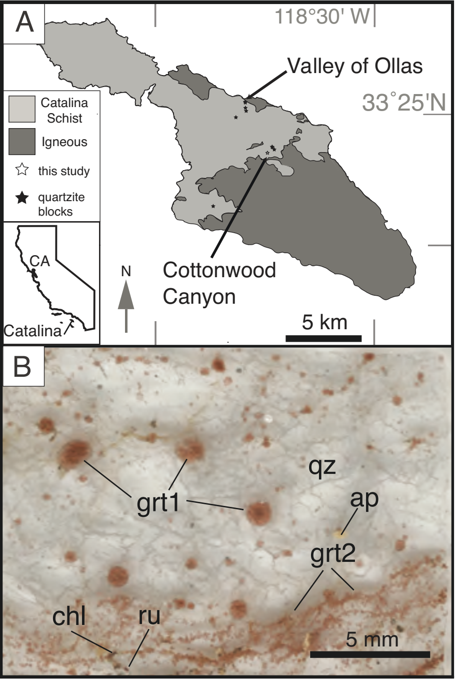
FIGURE CAPTIONS

Figure 1. A) Geologic sketch map of Santa Catalina Island, California (after Platt, 1975) showing sample locations. B) Polished thick section of a garnet quartzite showing two garnet sizes. (grt1 – larger, cation-zoned garnet, grt2 – smaller, garnet crystals, homogeneous in cations, qz-quartz, ru – rutile, ap – apatite, chl – chlorite)

Figure 2. A) $\delta^{18}O$ and cation traverse, rim to rim, of a single ~2.5mm dia. garnet. The core region is generally homogeneous at ~25‰ (aquamarine points), transitions to intermediate values (orange) and low, ~10‰ rims (purple) over short intervals, although zoning is asymmetric. Mg/(Mg+Fe) (Mg#, solid line) increases continuously core to rim. B) Ternary diagram of garnet cation compositions, mm-scale garnets are shown as solid circles, ~100µm-scale garnets shown as open circles. Analysis location (core, intermediate, rim) is also correlated with $\delta^{18}O$, and indicated by color, as in A. Larger garnets have greater cation zoning than smaller garnets (dashed arrow), and all oxygen isotope zonation takes place at the most pyrope-rich compositions for both sizes (alm - almandine, pyp – pyrope, grs -- grossular, sps – spessartine).

Figure 3. Catalina quartzite zircon chemistry and age A) CL images (25µm scale bars) of three zircons showing different CL domains (see text for details). Analysis of $\delta^{18}O$ are shown with two spot sizes and labeled with values in VSMOW (~15µm, ±0.2-0.4‰ 2S.D., Table DR-5; <1µm, ± 2.5‰ 2S.D., Table DR-6). B) Histogram of analyses of zircon and garnet with a 15µm diameter spot from sample 05C-09 grouped by CL domain and/or location across a traverse, colors as in Figure 2.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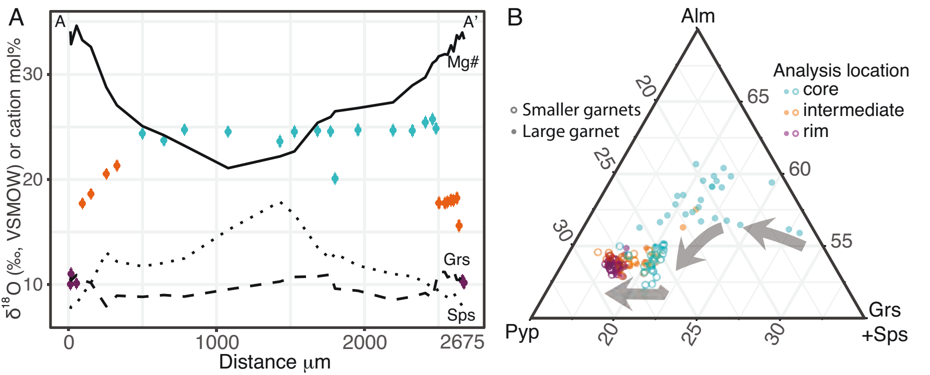

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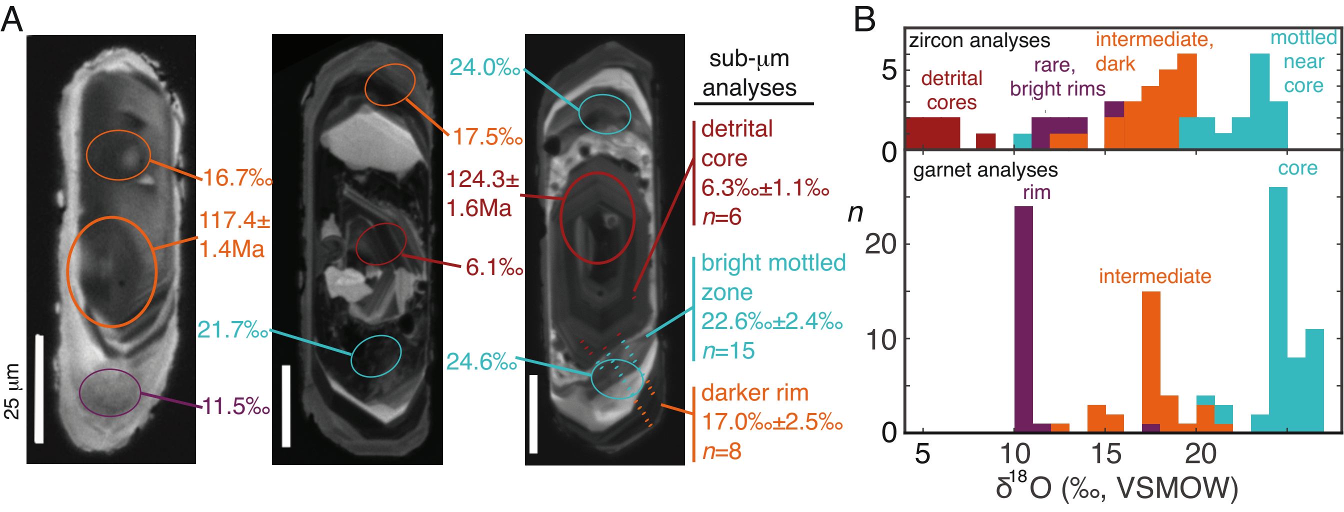

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detrital
core
6.3‰±1.1‰
n=6
bright mottled
zone
22.6‰±2.4‰
n=15
darker rim
17.0‰±2.5‰
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