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HENRY TOWBIN, Oberlin College
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INTRODUCTION

Santa Catalina Island is a cornerstone in our understanding of subduction zone metamorphic development and fluid-rock interactions. (e.g., Bebout, 2007). It provided one of the first models of subduction zone initiation (Platt, 1976) and subduction related metasomatism (Bebout and Barton, 1989). However, recent studies have challenged the previous tectonic models for the island's formation. All models that have been proposed rely on thermodynamic estimates that have not been updated despite considerable advances in the field of thermobarometry since they were originally proposed. The new tectonic models as well as updated temperature and pressure estimates could have implications for our understanding of fluid flow in subduction zones.

Santa Catalina Island lies about 20 miles off of the coast of Los Angeles, California. The island is known for its unique structure where high-grade blocks of mostly garnet hornblendite in ultra-mafic matrix, known as the amphibolite unit, overlie progressively lower grade metamorphic rocks. These lower-grade formations transition across low angle faults from epidote-blueschists to lawsonite-blueschists and finally to lawsonite-albite formations (Figure 1; Page et al., this volume). Studies have shown the source material for these metamorphic formations was forearc sediments from late Triassic-Jurassic flysch rocks, younger volcanic material from the near by Peninsular Ranges batholith, and basement rocks (Grove et al., 2008). This depositional history is consistent with an unroofing sequence likely from the nearby Peninsular Ranges batholith (Grove et al., 2008).

The current understanding of the metamorphic conditions undergone by these rocks is that the high grade amphibolites formed at ~115 Ma at ~8-11 kbar and ~640-750 ˚C then the lower grade formations accreted over the following ~20 My with the epidote-blueschist forming at ~8kbar, 450 ˚C and the lawsonite-blueschist forming at ~9kbar, 300˚C (Grove et al., 2008; Sorensen and Barton, 1987; Platt, 1975). This is unique because the rocks appear to have formed at relatively similar pressures but very different temperatures; the temperature of the amphibolites is much higher than usually observed in a subduction zone.

There are two tectonic models for Catalina Island. Amphibolite is atypical of subduction zones because cold basalts mediate the local temperature of the mantle below the heat required for their formation. It is hard to explain the presence of amphibolite in contact with blueschists without determining a mechanism for heating. The challenge for both models is to explain how high temperature amphibolites could be juxtaposed with low temperature blueschists. Both tectonic models focus much of their argument on explaining the heat available for metamorphosis of amphibolites.

To explain the inverse stacking of the units by metamorphic grade J. P. Platt proposed in 1975 that the excess heat to form the amphibolites was supplied by hanging wall peridotite that the subducting slab underthrusted. As the subduction zone pulled in cold ocean floor, the hanging wall cooled and the sediments in the accretionary wedge were exposed to lower temperatures metamorphosing to progressively lower grades. This explanation was widely accepted until 2008 when Grove et al. proposed that little evidence

exists for a new subduction zone forming at that time. Firstly, there are no ophiolites in southern California from ~122-115Ma as one would expect to find from the initiation of a subduction zone (Grove et al., 2008). Secondly the adjacent (subduction related) Peninsular Ranges batholith to the east of Catalina began forming as early as 140Ma, meaning an existing subduction zone in the region would have initiated much earlier than the Catalina amphibolites were formed (Grove et al., 2008). That subduction zone would have been colder than required to form amphibolites by the time they formed at ~115 Ma (Grove et al., 2008). Grove instead proposed that in this older subduction zone the high temperatures required to form the amphibolites was supplied when the forearc basin compressed and parts of it underthrusted the magmatic arc of the Peninsular Ranges batholith (Grove et al., 2008). It was stalled in the thrust near enough to the batholith to receive the heat necessary to form amphibolite rocks (Grove et al., 2008). The lowest grade materials, the lawsonite-blueschist and lawsonite-albite formations, formed much later in thermal conditions consistent with a subduction zone and were then accreted on to the rest of the Catalina complex with the intervening sediments removed by subduction erosion (Grove et al., 2008).

Much of the thermobarometric history of these rocks used by Grove and other authors to justify their tectonic hypotheses relies on Platt's 1975 paper and Sorensen and Barton (1987). Both papers focus most of their analysis on the amphibolite unit and give similar estimates for its peak temperature and pressure. Platt places the units in a pressure range of 8.5 to 12.5 kbar and a temperature range of 580 to 620 ˚C, Sorensen and Barton gives a higher temperature range with their estimate of 8.5 -11 kbar and 640 to 750˚ C. These estimates both predate computational database approaches to thermobarometry that are standards in the field. This study reevaluates the temperature and pressure estimates by Platt 1975 and Sorensen and Barton 1987 using equilibrium assemblage diagram (EAD) analysis on one large clinopyroxene bearing garnet hornblendite block.

METHODS

Petrography was performed using optical microscopy and by Scanning Electron Microscope/Energy Dispersive X-Ray Spectrometer (SEM/ EDS) at Oberlin College. Garnet, hornblende and clinopyroxene were analyzed quantitatively using the Cameca SX100 Electron Microprobe at the University of Michigan, Minerals were analyzed with a 15 kV, 10 nA point beam, and natural and synthetic silicate standards were used. Ferric iron estimates for amphiboles were made in accordance with the methods described in Hawethorn et al. (2012). Approximately 2 mg samples of pure garnet, hornblende, and clinopyroxene were analyzed for their oxygen isotope ratios by laser fluorination at the University of Wisconsin-Madison. Major and trace element analyses of whole rock samples were analyzed at the Franklin and Marshall College using X-ray Fluorescence Spectrometry.

Equilibrium assemblage diagrams (EAD), also known as pseudosections, were created using Theriak Domino (de Capitani and Petrakakis, 2010) and Holland and Powell's Thermocalc database updated 2003 (version 5.5). Models were run in the system NCFMASHTO. Because of the substantial phosphorus content (present mostly as apatite) in some samples sufficient CaO to form apatite was sequestered from the modeled bulk composition. The solution models used were garnet (White et al., 2007), clinopyroxene (Green et al., 2007), clinoamphibole (Diener et al., 2007), epidote (Holland & Powell, 1998), chlorite (Holland et al., 1998), plagioclase (Holland & Powell, 2003), magnetite (White et al., 2002), ilmentite and hematite (White et al., 2000), olivine (ideal), and liquid melt (White et al., 2007). Estimates of ferric iron in bulk composition are a complicating factor in the development of pseudosections and of all thermobarometry in metamafic rocks. EADs were calculated in the range of 1 to 12% ferric iron of total iron to determine their effects on the system.

Because of widespread evidence of high-flux fluid flow throughout the Catalina Schist (e.g., Bebout and Barton, 1989) excess H_2O included in the models.

PETROGRAPHY AND MINERAL COMPOSITION

Sample H121A is from a large mafic block located near the airport (33.408441 ˚N, 118.419343 ˚W) previously studied by Sorensen et al. (1987,1988). It consists of fine-grained garnet, hornblende, and clinopyroxene crystals with accessory minerals of sphene, apatite,

ilmenite, rutile, and zircon. Plagioclase coronas exist around some garnets. Two distinct layers of mineral assemblages exist. One is comprised of small hedral garnets (~0.3mm) grown with clinopyroxene and accessory minerals (Fig. 1a). Garnets make up approximately 80% of the mode of these regions. The other type of layer is of coarser crystals of garnets (~1mm), clinopyroxene and hornblende (Fig. 1b). Between many of the contacts of garnet and hornblende in these layers there are plagioclase coronas with a composition of 75 to 80 mole% albite. Many of the rutile and ilmenite crystals are intergrown and have sphene rims (Fig. 1c). Occasionally thin bands of hornblende are found surrounding garnets between clinopyroxene crystals in Figure 1d.

Garnets from all samples range from 54-60% almandine, 23-30% grossular, 10-15% pyrope, and 1-7% spessartine. The cores contain dense clouds of fine inclusions (~10μm), dominantly sphene.

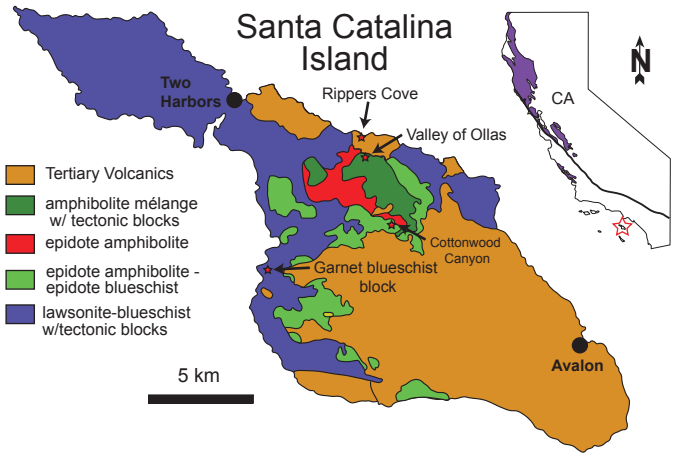

Figure 1. Photomicrographs of sample H121A. (a) Layer of fine densely packed garnets and clinopyroxene. (b) Contact between coarser grained hornblende rich layer (right) and fine garnet clinopyroxene layer (left). Plagioclase coronas grow between large garnets and hornblende in the coarser layers. (c) Intergrown ilmenite and rutile crystals surrounded by sphene rim. (d) Thin band of hornblende surrounding garnet and plagioclase between clinopyroxene.

Garnets in sample H121A are slightly zoned in manganese, calcium, magnesium and iron. The cores are enriched in manganese and calcium, and the rims are richer in iron and magnesium. Sphene and rutile are present as larger inclusions; less common are inclusions of quartz and plagioclase.

Clinopyroxenes are dominantly diopside-hedenbergite with less than 9 mole% jadeite and 8 mole% acmite. There is slight compositional zoning in sodium, ferrous and ferric iron. The cores exhibit more Na and Fe^{3+} but less Fe^{2+} than the rims.

Amphibole in H121A is classified as magnesio-hornblende in the classification scheme of Hawethorn et al. (2012); the rims are richer in aluminum and sodium with respect to the cores. Hornblende has inclusions of intergrown rutile and ilmenite.

Sample 12C-3 is from a garnet pyroxenite block in Cottonwood Canyon (33.395698 ˚N, 118.414577 ˚W). Fine to medium grained equigranular garnets, and clinopyroxenes are found with millimeter to centimeter scale bands containing more magnesio-hornblende (Hawethorn et al. 2012). Sphene is abundant, and there are small amounts of ilmenite, but rutile is rare. Garnets range in size from 0.2 to 2 mm and contain inclusions of pargasite, quartz, and plagioclase that is ~70 mole % albite (Hawethorn et al. 2012). In garnets there is slight iron zoning with the rims being richer in iron. Clinopyroxenes are diopside-hedenbergite with less and 8 mole% acmite and no jadeite component. Magnesio-hornblende is zoned with the rims enriched in aluminum and sodium. Inclusions of amphibole in garnet are enriched in aluminum and sodium compared to other amphiboles. They lie on boundary between pargasite and sadanagaite (Hawethorn et al. 2012).

Stable oxygen isotope analysis for garnet, hornblende and clinopyroxene is consistent with equilibrium for both samples. $\delta^{18}O$ values for samples range from 7.65 to 8.53 ‰. Individual pairs of minerals analyzed together are with in 0.20 ‰.

THERMOBAROMETRY

In order to better constrain the conditions of metamorphism, an equilibrium assemblage diagram

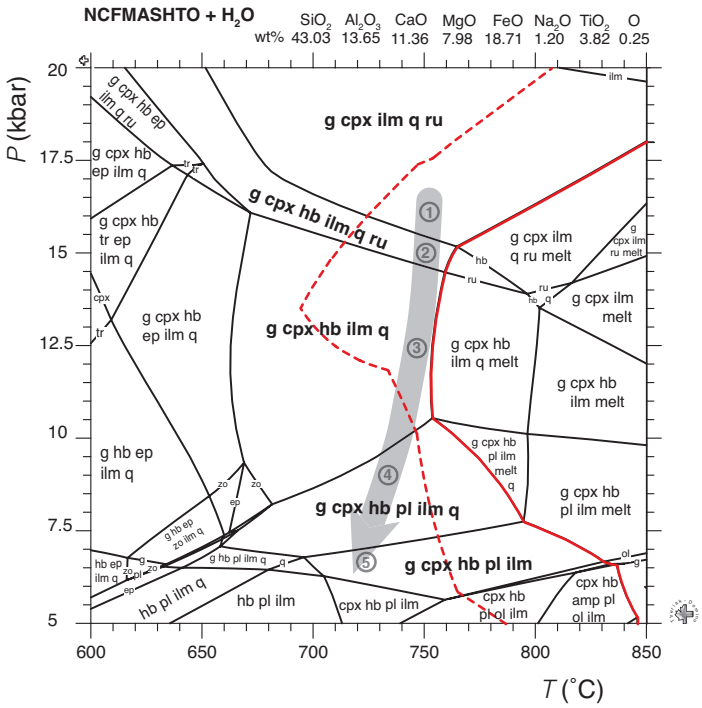

Figure 2. Equilibrium assemblage diagram (EAD) for sample H121A calculated in the system NCFMASHTO water is in excess and ferric iron is 12% of total iron. Red lines are solid. The dashed line is for MORB compositions (sample 104 -16 of Sun and McDonough, 1989), and the solid line is the solids for this EAD. Proposed decompression path of sample shown by the arrow. (1) Iron-rich tholeiite is emplaced to ~750 ˚C and 15 kbar where partial melting occurs and an assemblage of garnet, clinopyroxene, ilmenite, quartz and rutile forms. (2) As decompression occurs hornblende is stabilized. (3) Rutile is no longer stable in the assemblage. (4) Plagioclase stabilizes. (5) Quartz disappears from the assemblage.

(EAD) was calculated for sample H121A (Fig. 2). Whole rock compositional analysis shows the samples are broadly basaltic but are low in silica, sodium and potassium. They are greatly enriched in iron and titanium. Sorenesen and Barton (1987) and Sorenesen (1988) argued that the protolith for these samples was a tholeiitic basalt with a large albite component removed due to partial melting.

The EAD predicts peak conditions of metamorphism for the observed equilibrium mineral assemblage of ~ 750 ˚C and above 15 kbar and below 20 kbar (where ilmenite is destabilized) followed by a near isothermal decompression path (Fig. 2). In region 1 of Figure 2 the assemblage of garnet, clinopyroxene, quartz and rutile matches the layers of sample H121A with small garnets and clinopyroxene (Fig. 1a). The quartz in the assemblage is recorded as inclusions throughout garnet. As pressure decreased, hornblende becomes stable, which explains the separate hornblende rich layers (Fig. 1b). When pressure dropped below 14 kbar rutile was destabilized, which possibly explains the intergrown rutile and ilmenite crystals observed in Figure 1a. Below 10 kbar plagioclase is stable explaining plagioclase coronas around the garnets (Fig. 2b). Finally the rock decompressed to below 8 kbar where quartz was destabilized and was consumed to form more plagioclase. Sphene rims on rutile and ilmenite are likely a later retrograde overprint.

DISCUSSION

Determining the equilibrium assemblage of a sample is essential for thermometry. Textural observations of minerals are key to determining which minerals were present at various stages of metamorphism, but these are only qualitative. Oxygen isotope analysis can be an important quantitative discriminant for equilibrium. While it cannot prove that current mineral composition is in equilibrium it can definitively establish disequilibrium. In plagioclase-free mafic rocks, garnet-pyroxene and hornblende are predicted to fractionate oxygen isotopes by less than 0.5‰ (Kohn and Valley, 1998a,b,c) By the standards of textural and oxygen isotope analysis, garnet hornblende and pyroxene in these samples appear to be equilibrated. Since these rocks have likely experienced significant metasomatism and have been hypothesized to be the residues of partial melting, the whole rock geochemistry used in creating this model is only representative of post-metasomatic histories of these rocks.

The explanation seen in the EAD of a peak temperature between 650 and 750 ˚C and a decompression path starting around 15 kbar fits well with the temperature estimates of Sorensen (1987), but suggests slightly higher pressures (Fig. 2). Sorensen and Barton 1988 argued that the composition of the clinopyroxene bearing blocks resulted from partial melting of an albite component out of tholeiitic basalts. To test this theory an EAD of a MORB composition (sample 104 -16 of Sun and McDonough, 1989) was calculated. The P-T locus of melt-in reactions for this possible protolith is overlain on the EAD of sample H121A (Fig. 2). The melt curve of sample H121A is at higher

temperatures in regard to the MORB composition, suggesting that partial melting may have pushed the temperatures of melt formation higher as components were removed. The model proposed in this paper supports Sorenesen and Barton (1987) and Sorenesen (1988) theory for the protolith of the clinopyroxene bearing blocks and provides P-T constraints consistent with the melting curve of MORB.

Sorensen and Barton (1987) proposed that textures observed in Figure 1d, where garnet crystals are surrounded by plagioclase and hornblende coronas between larger clinopyroxenes, could be explained by a reaction of garnet + clinopyroxene + H2O = hornblende + plagioclase. The EAD shows these coronas did not form in a single reaction but at separate point along the decompression path (Fig. 2). As pressures fell below 15 kbar, hornblende could have formed as a reaction between clinopyroxene, garnet and water (Fig. 1d). Then after decompression to below 10 kbar hornblende and garnet reacted to form plagioclase (Fig. 1d).

The narrative proposed above does not explain the compositions observed in the minerals well enough to be taken at face value. The first indicator of this is that, according to the EAD, if the rocks equilibrated at pressures above 15 kbar the sum of the sodic-endmember (jadeite and acmite) component of the clinopyroxene should be higher (>16 mole %). The observed sum is generally around 12 mole%. Calculations done with only 5% ferric iron of total iron and at 700 ˚C and 10 kbar show mineral compositions within the observed range of garnet clinopyroxene and hornblende compositions. This temperature and pressure is in line with Platt 1975 and Sorensen 1987's original estimates but it fails to describe the observed mineral assemblage. The assemblage under these conditions is garnet, clinopyroxene, hornblende, ilmenite and quartz, which lacks the rutile observed in the sample. Rutile does not stabilize at pressures below 13 kbar within 50 ˚C above or below 700 ˚C in either the MORB or H121A EAD. The rock would not exhibit melt at pressures below 12 kbar as shown by the MORB melt curve (Fig. 2). Higher pressures than 10 kbar are needed to explain the assemblage.

One possible explanation for the compositional discrepancies between the EAD and the samples is the complicated nature of amphibole solution models (Diener 2007).

CONCLUSION

Santa Catalina island has a complicated tectonic and metamorphic history that has been important in the development of our understanding of subduction related metamorphism and metasomatism (e.g. Platt, 1975. Bebout & Barton, 1989). While unable to provide definitive pressure and temperature estimates this paper has shown that previous studies likely underestimated peak pressures of metamorphism for the amphibolite unit. This has implications in how the tectonic and metasomatic models of the island are interpreted. These models should be reevaluated to include higher-pressure scenarios (e.g. Grove et al. 2008). EAD are powerful tools but at they are models and as with any model one must evaluate how well they reflect the real world. This study's analysis does not tell a simple story for these rocks. Further studies are needed to identify how the models can more accurately represent these samples but one can draw powerful conclusions from the results presented here.

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