

Crystallographic Controls on Porosity in Exhumed Metamorphic Rocks

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In metamorphic rocks, grain boundaries, or the interfaces between mineral grains, are pathways for the migration of elemental complexes and fluids, serve as nucleation sites for new minerals, and may control the strength of rocks in the upper crust. However, grain boundaries are: i) poorly characterized on the nanoscale and ii) it is unclear as to which stage of a metamorphic pressure-temperature (*P-T*) path grain boundary structure is representative of in an exhumed rock.

In order to resolve these questions, we characterized garnet-quartz and quartz-quartz grain boundaries from two contact metamorphic aureoles: the Nelson Aureole in British Columbia, Canada and the Harkless Quartzite in California, United States. We employed multiple analytical techniques including: nanoscale Transmission Electron Microscopy (TEM) analysis of the structure and chemistry of grain boundaries, Scanning Electron Microscopy (SEM) imaging of the grain boundaries, Electron Dispersive Spectroscopy (EDS) imaging of the composition of the minerals, and Electron Back Scattered Diffraction (EBSD) analysis on the orientation of mineral grains in the samples.

Our results reveal that, on the nanoscale, garnet-quartz grain boundaries are heterogeneous. In one sample that reached peaked metamorphic conditions of 530°C and 3.5 kbar [1], the garnet-quartz grain boundary is a planar and linear feature, with no void space. Garnet is free of dislocations, while the quartz contains a network of dislocations. The density of dislocations in the quartz crystal decreases approaching the garnet-quartz grain boundary and there are no visible dislocations within ~100 nm of the boundary. In another sample that reached 650° and 3.5 kbar [1], at the boundary between the garnet and the quartz there is void space that measures 420 nm. Part of that void space is partially taken up by an amorphous material. In the garnet and quartz on either side of the grain boundary, the minerals do not contain any visible dislocations. At distances greater than 500 nm from the grain boundary, the quartz contains multiple tilt walls with closely arranged rows of dislocations. Dislocation density varies greatly in the quartz on either side of the tilt walls. Analysis of the width of void spaces at grain boundaries reveals that there are wider void spaces (~600 nm) at orientations such that the *a*-axis of quartz is normal to the grain boundary. This is compared to < 200 nm wide voids at other orientations of adjacent quartz grains.

In the quartzite samples, SEM imaging reveals a non-random distribution of void space at quartz-quartz grain boundaries. Comparison of void spaces with the crystallographic orientation of the quartz grains shows that there is a correlation between the distribution of void spaces and the orientation of at least one of the surrounding quartz crystals. There are more void spaces at orientations such that the *a*-axis of neighboring quartz grains is orthogonal to the grain boundary [2].

The distribution and width of void spaces at quartz-quartz and garnet-quartz grain boundaries in exhumed metamorphic rocks is likely the result of the anisotropic volume decrease in quartz during exhumation [2,3,4]. Over these *P-T* conditions, the length of the *a*-axis of quartz decreases by more than the *c*-axis of quartz during exhumation (decreasing pressure and temperature), which results in either: i)

more or ii) larger void spaces at grain boundaries that are normal to the a-axis of neighboring quartz grains.

This work shows how grain boundary structure in metamorphic rocks may not always be 'locked in' at peak *P-T* conditions, but instead, in some cases, may record processes that occurred post peak metamorphism. More broadly, this work highlights how analytical mapping techniques (SEM, EBSD) can be combined with nanoscale analysis (TEM) to decipher the textures of metamorphic rocks.

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