1. Publishable Summary

The objectives of the research portion of this project were to develop methods for radioisotopic dating and geochemical characterization of secondary iron- and manganese-oxide minerals in rocks, and to use these approaches to understand the timing and nature of fluid flow in the shallow crust of the Earth (and potentially other planets). More specifically, we seek to use the (U-Th)/He radioisotopic system to measure formation ages and time-temperature histories of these minerals and the oxygen-isotope compositions of the fluids that created them. These minerals are common in rocks near the Earth's surface, but little is known about when they formed and what their formation tells us about tectonic, climatic, or hydrologic conditions through time.

Our work focused primarily on mineralogic and textural characterization by scanning-electron microscopy (SEM), developing dating methods by several techniques, and measurement of oxygen-isotope compositions by secondary-ion mass spectrometry (ion probe). This was done on a variety of secondary oxide samples from bedrock in Arizona and Colorado. A larger number of samples from a wider variety of locations were dated by (U-Th)/He methods.

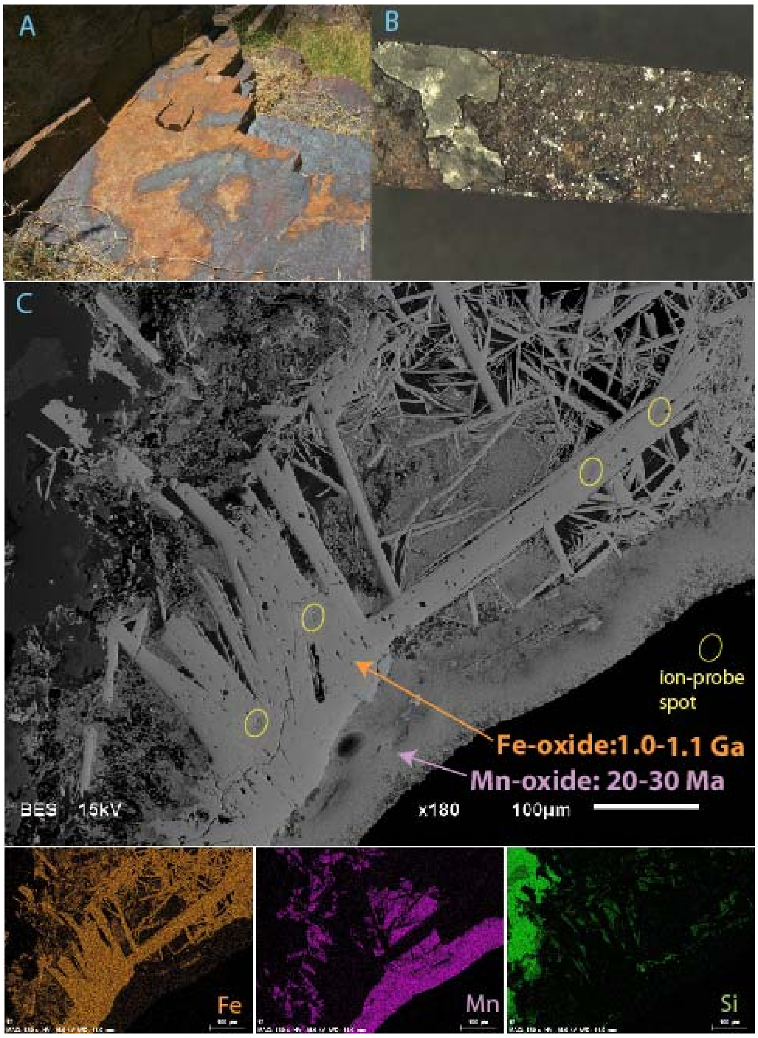

Figure 1. Example of secondary Fe- and Mn-oxide coating in bedrock. A. Outcrop photo of oxide-layer; B. Close-up of dual-layer (width of field 2 mm). C. SEM photo (BSE/SE) of hematite underlying Mn-oxide; lower row: X-ray element maps showing Fe-, Mn-, and Si-rich regions. (U-Th)/He dates of hematite are 1.0-1.1 Ga whereas Mn-oxide dates are 20-30 Ma.

Figure 1 shows an example of a typical secondary Fe-oxide (and Mn-oxide) layer coating a fracture surface of a 1.6-Ga rhyolite in Arizona. The SEM and ion-probe analyses were performed at CRPG. This representative sample shows the polycrystalline and polymineralic textures common in these types of specimens, and examples of the ion-probe spots we use to measure O-isotope compositions. This particular specimen yielded (U-Th)/He dates of 1.0-1.1 Ga on the Fe-oxide (hematite) and 20-30 Ma on the Mn-oxide. The hematite showed a wider range of oxygen isotope compositions compared with the Mn-oxide ($\delta^{18}O$ of about -4 to -2 and -1, respectively).

Our study included attempts to develop a new and relatively rapid analytical approach to dating secondary oxides that involves in-situ excimer laser ablation for He extraction and measurement. Unfortunately, this method proved inefficient because of poor laser-oxide coupling. After two weeks of mass spectrometer time, this approach was abandoned. However, routine conventional (U-Th)/He dating at UA provided a suitable approach by which we successfully dated a large number of specimens.

In all, we successfully dated dozens of aliquots from about six secondary oxide samples from veins, fractures, and faults by the (U-Th)/He method and combined these with oxygen-isotope analyses determined by ion-probe. We determined that most secondary hematite has $\delta^{18}O$ of about -5 to 0‰. In some cases, (U-Th)/He dates are quite reproducible and match expectations based regional geologic constraints. For example, hematite in 14-16-Ma Basin and Range normal faults yield (U-Th)/He ages matching those of faulting and dates from other isotopic systems, and hematite from faults in crystalline bedrock in several other regions yields dates of 1.0-1.1 Ga, corresponding to major tectonic and magmatic episodes in the Arizona. In some cases, however, secondary oxide dates are variable show poor reproducibility. Our analyses suggest that this reflects a wide range crystal sizes, chemistry, and thermal histories involving slow cooling.

The next phase of this research will involve better characterizing He diffusion properties in hematite so that we can better understand the variable (U-Th)/He dates seen in some samples. We will also combine the ion-probe oxygen isotope measurements with those of conventional analyses and interpret them in terms of the sources and temperatures of fluids that created the minerals. These results will allow us to understand the timing of fluid flow and sources of fluids that move through the shallow crust. This will have implications for fault behavior, groundwater flow, and supergene formation of economic ores.