

U- and Th- Decay Series Dating of Hydrothermal Mineral Deposits

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With support from the Ocean Ridge Initiative, we developed a project to prepare separations of hydrothermal minerals in order to conduct pilot Uranium (U)- and Thorium (Th)- decay series measurements to obtain preliminary data for a proposal to the National Science Foundation (NSF). These preliminary data were needed to demonstrate the feasibility of making high precision measurements to test assumptions that are critical for calculating the time that has passed since minerals were deposited and, thus, the age of seafloor hydrothermal vent deposits. We were successful in this goal, and this project leveraged support for our NSF project which we began on August 1, 2013.

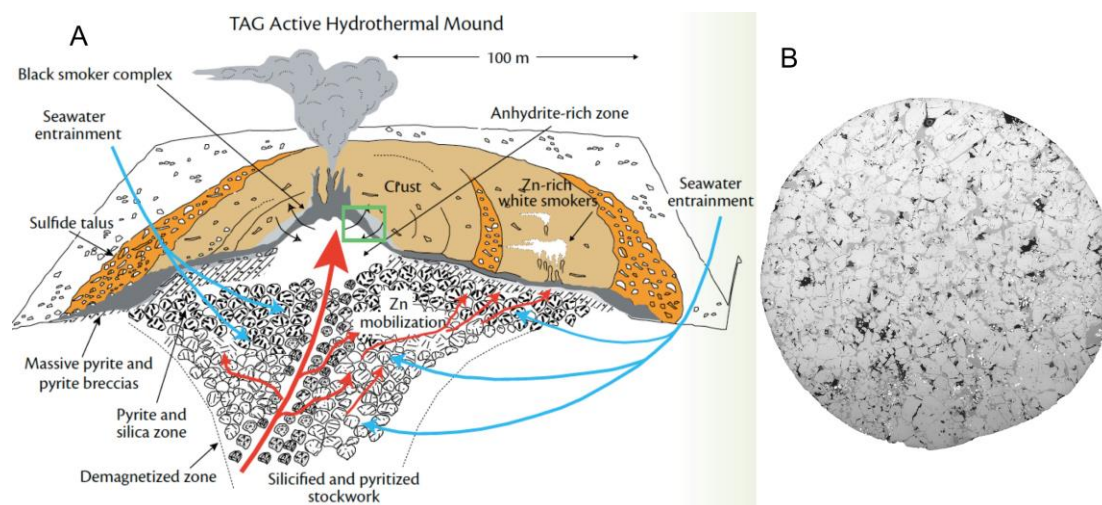


Figure 1: A. Schematic cross-section of the Trans-Atlantic Geotraverse (TAG) active mound at 26°N on the Mid-Atlantic Ridge. Hot vent fluid flows up through the mound and exits through its top, mixing with seawater and forming black smoker chimneys; seawater is also entrained into the mound forming anhydrite-rich deposits. B. Scanning electron microscope X-ray backscatter image of a 1-inch diameter thin section of massive anhydrite recovered from the TAG mound; light gray is anhydrite, darker gray (rimming anhydrite) is gypsum; black is pore space, and white is sulfide.

Seafloor hydrothermal vent deposits (Figure 1A) are probably best recognized as the dramatic black smoker chimneys that occur along mid-ocean ridge spreading centers. These smokers, which vent high temperature (up to 400°C or 750°F) fluids, form as hot metal- and sulfide-rich fluids mix with cold sulfate-rich seawater at and below the seafloor. The hot vent fluids are formed when seawater percolates down into newly formed ocean crust that is very permeable (from contraction as the rock cools and from faults that develop as the crust spreads away from the spreading center, i.e., the neo-volcanic zone). The composition and temperature of the vent fluids result from reactions between seawater and hot rock, with the resultant less dense fluid (density decreases as temperature increases) rising through channels to the seafloor. The deposits form on time-scales of minutes to thousands of years, are products of significant heat and mass transfer



from the interior of Earth to the oceans, and form in conjunction with activity that supports microbial and animal communities in the deep-sea.

Understanding the time-scales over which vent deposits form – whether continuously or episodically – and identifying relationships of age with geologic features (e.g., faults, fissures, lava flows, distance from neo-volcanic axis) can provide important information both about energy and mass transfer and the resulting feedback within the ocean crust and lithosphere, and about environments, energy, and nutrient sources for hydrothermal biological communities. Several methods have been used in the past to date seafloor hydrothermal deposits, mostly using ^{238}U - and ^{232}Th - decay series data because of the range of ages that can be dated (Figure 2). These methods rely on the behavior of radioisotopes. An isotope is an atom of an element that has the same number of protons but different numbers of neutrons. A radioisotope is an isotope that has an unstable nucleus that decays, emitting alpha, beta, or gamma rays, until stability is reached. The different parent-daughter nuclides in the ^{238}U decay chain (see decay chain in Figure 2 that ends with stable ^{206}Pb) include ^{234}U - ^{230}Th with a half-life (the amount of time for half of the atoms in the sample to decay) of 75,000 years, ^{230}Th - ^{226}Ra with a half-life of 1,600 years, and ^{226}Ra - ^{210}Pb with a half-life of 22 years. In the ^{232}Th decay chain (see decay chain in Figure 2 that ends with stable ^{208}Pb), relevant parent-daughter nuclides are ^{232}Th - ^{228}Ra with a half-life of 5.77 years, and ^{228}Ra - ^{228}Th with a half-life of 1.91 years.

If the system stays closed over time, i.e., the decaying parent and ingrowing daughter nuclides stay within the mineral over time, then the ratios of parent and daughter

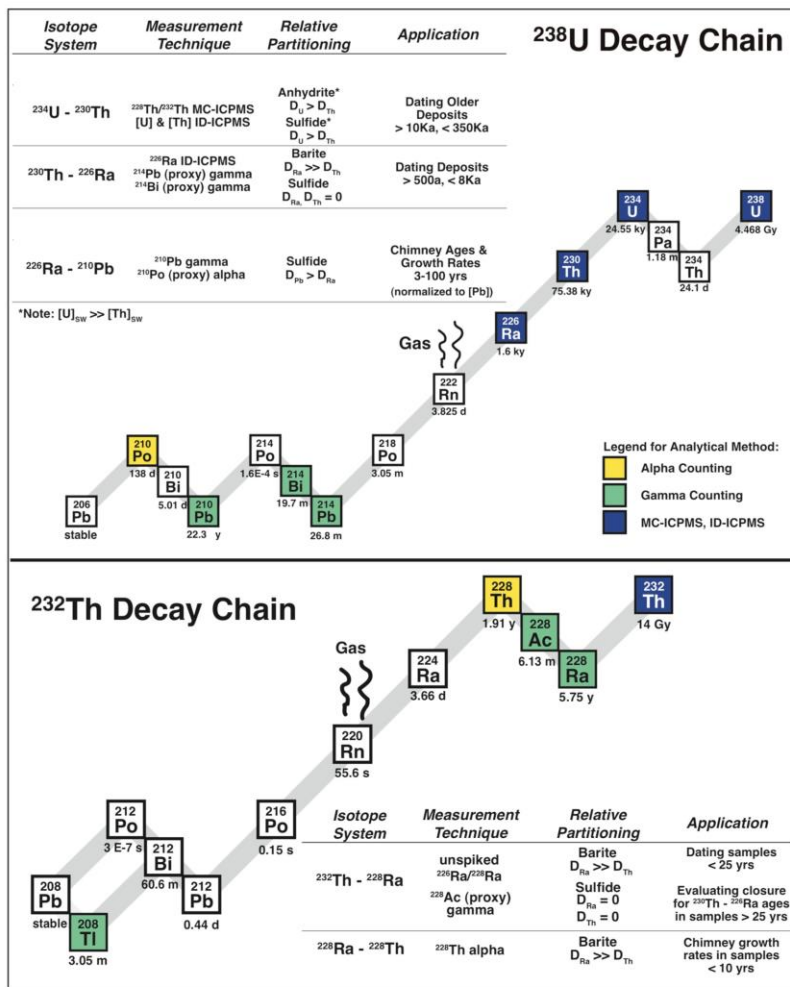


Figure 2: Decay chains of both ^{238}U and ^{232}Th .
Key: Ac=Actinium, Bi=Bismuth, Pa=Protactinium, Pb=Lead, Po=Polonium, Ra=Radium, Rn=Radon, Th=Thorium, Tl=Thallium, and U=Uranium



nuclides can be used to date the time at which the mineral(s) first formed. These techniques have been used to date relatively young deposits on the East Pacific Rise and the Juan de Fuca Ridge (<100 years old), and much older deposits on the Mid-Atlantic Ridge (~10,000 to 50,000 years old). However these techniques have not been systematically tested, and questions of open-system behavior persist (both during chimney growth and post-depositional alteration).

With funding from the Ocean Ridge Initiative, we began a careful examination of the assumptions behind the use of ^{238}U - and ^{232}Th - decay series to date the age of formation of seafloor hydrothermal deposits. We carefully selected samples of young deposits of known age, and also samples of much older, unknown age ("relict" deposits). Our next step was to conduct a detailed characterization of the samples (mineralogically, chemically and texturally) and, when possible, pick pure mineral separates (e.g., pyrite - FeS_2 , chalcopyrite - CuFeS_2 , anhydrite - CaSO_4 , and barite - BaSO_4) to allow estimates to be made of likely amounts of incorporated U, Ra, Pb, and/or Th via gamma counting. This counting information is used to determine the minimum amount of pure mineral separate needed to be analyzed using state-of-the-art analytical techniques. The mineral separates that we prepared included samples with hydrothermal sulfide and sulfate minerals to address the following goals:

Goal 1 - to test the potential of measuring isotopic ratios in *barite* over a wide range of ages of both actively forming and older deposits;

Goal 2 - to test assumptions in using ^{210}Pb in *chalcopyrite* for study of very young (zero or near-zero age actively forming black smoker chimneys);

Goal 3 - to test the potential of using *anhydrite* and *pyrite* for dating older deposits.

Samples of anhydrite, pyrite, and chalcopyrite were chosen and carefully examined under a stereomicroscope. Pure two to three gram separates of pyrite and chalcopyrite were sent to our collaborator Ken Sims at the University of Wyoming for analysis. Separates of anhydrite (10 to 15 grams) were also chosen, but these contained very fine inclusions of sulfide minerals that could not be separated mechanically, and chemical separation methods could not be used because of uncertainties in the behavior of the elements of interest (U, Th, Pb, Ra) during chemical reactions; thus the samples will need to be completely digested (dissolved with no remnant) before analysis. We also examined textures of the samples and, using a scanning electron microscope, created X-ray images of the massive anhydrite samples that showed evidence for alteration of anhydrite (CaSO_4) to gypsum ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$), thus documenting open-system behavior in the exteriors of anhydrite mineral grains in these samples (Figure 1B). Because of this result, we will use at least two different parent-daughter pairs to obtain dates for these samples, and will look for self-consistency between results for each pair to examine consequences of open system behavior.



Additionally, we will examine whether age dates for pure separates of co-precipitated pyrite give similar results as the anhydrite. Similarly, we found that for both young and old samples, barite minerals are so intimately inter-grown with sulfide minerals (particularly sphalerite – (Zn,Fe)S) that they cannot be mechanically separated, again requiring complete digestion and analysis of more than one parent- daughter pair to look for consistent results. We were able to begin this work using funds from the Ocean Ridge Initiative, which have leveraged support from NSF to continue the study.

Our results to date include ^{210}Pb activities in samples from the western Pacific (that were actively venting when sampled in 2009) that indicate ages <100 years, and data from barite within some of the same samples that indicate ages >10 years old (self-consistent with the ^{210}Pb data). However, the barite is within samples that were actively venting in 2009 so at least some minerals should be only 5 years old. This discrepancy provides a target that we will use to test the assumptions associated with the U- and Th-series dating method, as well as the analytical resolution of differing spectrometric techniques (i.e., gamma vs. alpha vs. MC-ICP-MS). Other results include ^{210}Pb activities in a massive anhydrite sample from the TAG active mound that suggest an age of <100 years old, and ^{210}Pb activities in two massive anhydrite samples from the western Pacific that suggest the samples are both <100 years old. One of the two Pacific samples also contains barite, and data from barite for that sample suggest it is >10 years old, self-consistent with the ^{210}Pb data.

