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Too Small to Date: Statistical Limits on Analytical Spot Size

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High-precision radioisotope geochronology requires a precise and accurate decay constant. The decay constant for a given isotope is based on quantum statistics, which predicts the *decay rate* for a large number of atoms. For a single atom, however, the decay rate defines the *probability of decay*, but not when that decay will occur. Historically, radiometric dating has worked well because the sample size assured a very large number of parent isotopes; quantum predictions were accurate. Recently, however, analytical advances have reduced beam spot sizes from 60-20 μm to as low as 0.5 μm. Thus, we must consider the number of atoms in the population analyzed: Is it large enough to assure the validity of quantum statistics?

Spot analyses of Re-Os in molybdenite typically yield discordant ages, generally attributed to different diffusion rates of parent and daughter isotopes, producing heterogeneous distributions over time (decoupling; Stein et al. 2003). Another potential cause of heterogeneity is fluid-mediated coupled dissolution-reprecipitation (FMCDR). Secondary molybdenite produced by FMCDR will take in Re, while excluding incompatible Os. To investigate this, we analyzed a large Neoproterozoic molybdenite crystal for which TIMS analyses of subsamples yield highly discordant ages. These samples have extremely high Re and ^{187}Os concentrations, but effectively zero common Os. Thus, electron probe microanalyses (EPMA) using a 1.5 μm beam size, can reliably reveal spatial variability in radiogenic ^{187}Os concentrations, with no need to subtract out original ^{187}Os.

EPMA with a 1.5 μm beam size was used to quantify ^{187}Re and ^{187}Os concentrations along traverses from original pristine into secondary FMCDR-produced(?) molybdenite grains, documented with reflected light microscopy and BSE imaging. Eleven out of 12 traverses reveal a seesaw concentration pattern. Moreover, as ^{187}Re increases, ^{187}Os decreases, and vice versa. This is explained by an initially heterogeneous distribution of ^{187}Re, and a decay rate controlled by the probability for each atom to undergo decay. That is, the total population of atoms in the 1.5 μm beam spot was too small to follow quantum statistics. The volume ablated contains about 10 million atoms, providing a minimum population to assure adherence to quantum statistics.