

The problem of discordance in atomic ages

painted a generally gloomy picture for those seeking a chronometric tool—albeit a most revealing picture for those interested in geochemical processes. The gloom arises from the general discordance among isotopic ages based not only on uranium-235 and uranium-238 but also on thorium-232. The last radioisotope usually accompanies uranium because of its similar ionic charge and radius.

Experience shows that, with the exception of results from the mineral uraninite, the three uranium–thorium–lead ages are almost always different. Why this should be so is the subject of many scientific papers and much experimental work. Clearly, discordance is not usually due to common lead. The presence of such lead is revealed through its nonradiogenic isotope lead-204 and is corrected for by calculations involving its isotopic composition; the latter is usually obtainable from cogenetic lead minerals (e.g., galena) found in physical association with the uranium mineral being dated.

Where discordance generally seems to lie is in the failure of uranium-bearing minerals to be closed systems. This situation appears to prevail whether uranium is the dominant metal in the mineral or is merely a trace constituent. Whatever invalidates the closed-system assumption is beyond direct observation and must be inferred from analytical data on natural and laboratory-treated samples. It seems probable that lead loss is the most significant mechanism causing discordance. Of less certainty is the chronology of lead loss—specifically, whether it involved continuous diffusion beginning at the time of crystallization or was a relatively short-term process active only during a metamorphic event.

The escape of helium is also significant. Derived from alpha particles, helium accumulates within a uranium mineral in a time-dependent manner similar to lead buildup. The main difference is that for every atom of uranium or thorium decaying there are six, seven, or eight helium atoms produced, depending on whether the parent atom is thorium-232, uranium-235, or uranium-238. The escape of some helium is predictable on the basis of its small mass and incompatibility with its environment in a crystal lattice. Furthermore, there is no isotopic way to recognize common helium, for it is also alpha-particle derived. As a consequence, uranium–helium dating has received far less attention than the various lead methods. At the present time, its application to the mineral magnetite seems reliable, provided that acid leaching first removes surficial material not held within the tight magnetite lattice. Increasingly significant is the application of uranium–helium dating to the shells of marine organisms that incorporate small numbers of uranium atoms into their calcium carbonate lattices.

**Potassium-40 to argon-40.** Unlike uranium and thorium, the element potassium is of high average crustal abundance (about 2.5 percent) and occurs widely at concentrations where analysis is relatively easy. The fact that potassium is radioactive was recognized as early as 1905. Over 30 years went by, however, before potassium-40 was revealed as the radioactive isotope and another 20 years before its half-life was accurately determined. Because two decay modes are possible for potassium-40, one yielding stable argon-40 and the other stable calcium-40, potassium minerals accumulate two daughter elements. These build up in the ratio of eight calcium-40 atoms to one argon-40 atom. Clearly, once the production ratio of the two daughters has been accurately determined, both need not be measured in a radiometric-dating analysis. For example, the detection of eight trillion calcium-40 atoms in a sample implies the presence of one trillion argon-40 atoms and therefore the decay of nine trillion potassium-40 atoms over the life of the sample.

Despite the relatively greater abundance of calcium-40, it is argon-40 that is almost always measured. The reason is simply that the calcium-40 isotope in common calcium is almost always so abundant that it overwhelms radiogenic calcium-40. Only a few potassium-bearing minerals, such as lepidolite and sylvite, form under conditions where the common calcium level is low enough not to mask radiogenic calcium-40.

The two main problems that plague potassium–argon dating are like those of the uranium–lead method—common argon (sometimes called excess, or extraneous, argon) and argon leakage. Because of its inert chemical behaviour, argon tends to be almost totally excluded from most potassium-bearing minerals at the time they crystallize. Even so, minute amounts may enter the lattice and form a significant fraction of the argon-40 in samples younger than 100,000 years. Furthermore, there is no isotopic way to recognize the common argon, for it is pure argon-40 held in the crust since its formation by even earlier potassium-40 decay.

Still another source of argon contamination is an atmospheric contribution adsorbed on surfaces at the time samples come in contact with air. A significant part of this is removable by heating in a vacuum at a temperature low enough to suppress the escape of radiogenic argon-40. Through measurements of nonradiogenic argon-38 and argon-36, what is left of the atmospheric portion can be recognized and corrected for.

Far more serious than argon contamination is argon leakage. As was the case with the uranium–thorium methods, recognition is the first problem. It centres on age comparisons involving different decay schemes applied to the same rock samples. Specifically, search is made for potassium-bearing minerals associated with uraninite specimens that have shown concordant uranium–thorium–lead ages. The ubiquitous association of rubidium and potassium offers a second comparison of radiometric chronometers. As a result of such comparisons, supplemented by laboratory and field studies on leakage rates, potassium minerals have been evaluated with respect to the seriousness of argon loss. The results are much more encouraging than is true for uranium methods. Micas (biotite, muscovite, phlogopite) are especially good in retaining argon despite a priori arguments to the contrary. Hornblende is even better; potassium feldspar is poorer. Elevated temperatures—in excess of 300° C (about 600° F)—can change the rankings and ultimately cause intolerable leakage in all potassium minerals. It follows that the thermal history of a dated sample is very significant in determining how valid its potassium–argon age is.

**Rubidium-87 to strontium-87.** The geochemical similarity of rubidium to potassium is most fortunate for radiometric geochronometry. The two elements occur not only in the same rock types but also in the same minerals. Moreover, from silicate meteorites to the various common types of terrestrial igneous rocks, the atomic ratio of potassium to rubidium remains more or less constant at about 600 (about 0.25 if just the two radioisotopes are considered). Consequently, almost every potassium-bearing sample carries two geochronometers within it—one involving the decay of potassium-40, the other based on the decay of rubidium-87. The age comparisons made possible are of incomparable value.

The rubidium–strontium method is not without its problems—specifically, loss of the radiogenic daughter (strontium-87), presence of common strontium, and uncertainty about the half-life. Very little experimental work is available on which to judge strontium-87 retention by minerals. Experience in dating samples by different methods suggests the following order of decreasing retentivity, however: potassium feldspar > muscovite > biotite. Ages that are based on analyses of whole rocks show them to have the highest retention of all, an indication that those strontium atoms that do escape their parent mineral grains do not wander far.

Common strontium is the rule rather than the exception. It is recognized through its nonradiogenic isotope strontium-86 and defined isotopically by measurements of associated rubidium-free minerals such as plagioclase feldspar and apatite. Calculation then suffices to remove the nonradiogenic strontium-87 contribution from the total strontium-87 content of a sample.

The half-life of rubidium-87 has been a thorny problem that is still not fully resolved. The uncertainty centres on the difficulty of detecting every disintegration in a sample of rubidium-87. At a time when physicists were quot-

Problems in the potassium–argon method

Half-life of rubidium-87