Geol. 655 Isotope Geochemistry

lecture 6 Spring 2003

GEOCHRONOLOGY II

THE K-AR-CA SYSTEM (CONTINUED)

Other Complications Affecting ^{40}Ar-^{39}Ar Spectra

In the previous section, we saw two examples of $^{40}Ar/^{39}Ar$ release spectra: one where there was only minor loss of Ar from the rims, and another where significant fractions of the total Ar had been lost due to metamorphic heating. Figure 5.4 showed spectra that almost perfectly match theoretical patterns for diffusional loss. Such examples are relatively rare; most spectra are more complex. For example, some samples that have been reheated show false plateaus that correspond to ages intermediate between the crystallization age and the reheating age. An additional problem in interpreting such spectra is that samples that have not been subjected to reheating events but cooled slowly originally can show release spectra that mimic those of reheated samples in Figure 5.4.

Recoil of ^{39}Ar produced by the $^{39}K(n,p)^{39}Ar$ reaction during irradiation can also produce problems. The recoil results in loss of ^{29}Ar from sites near the mineral surface. For large grains, this is largely insignificant, but for small grains, this can lead to significant ^{39}Ar loss, leading in turn to erroneously old apparent ages.

In most case, the Ar present in a sample will not be pure radiogenically produced Ar. Non-radiogenic argon is often called excess Ar. $^{40}Ar/^{39}Ar$ ratios used to calculate ages in release spectra are typically corrected for the presence of atmospheric Ar by measuring the $^{40}Ar/^{36}Ar$ ratio. Atmospheric argon has a constant $^{40}Ar/^{36}Ar$ ratio of 295.5. Only ^{40}Ar present in excess of this ratio is considered radiogenic and used to calculate the $^{40}Ar/^{39}Ar$ ratio. Nevertheless, some samples can have "initial" $^{40}Ar/^{36}Ar$ ratios greater than the atmospheric ratio; this will lead to too old an age if not properly accounted for. It is this "excess" argon that is of greatest concern.

Excess Ar can have two sources. First, it can arise when minerals crystallize under a finite partial pressure of Ar. For example, mantle-derived basalts have been shown in some cases to have $^{40}Ar/^{36}Ar$ ratios in excess of 20,000. The high $^{40}Ar/^{36}Ar$ ratio reflects production of ^{40}Ar by decay of ^{40}K within the mantle. Minerals crystallizing in the presence of this gas will trap some of this ^{40}Ar, which will result an anomalously old age upon analysis. This is referred to as inherited Ar. Second, during a thermal event, ^{40}Ar diffusing out of some minerals may be taken up by other minerals. Since this ^{40}Ar is diffusing into the mineral grain, its concentration will be highest in the exterior of grains and thus will tend to be released at the lowest temperatures. An example is shown in Figure 6.1.

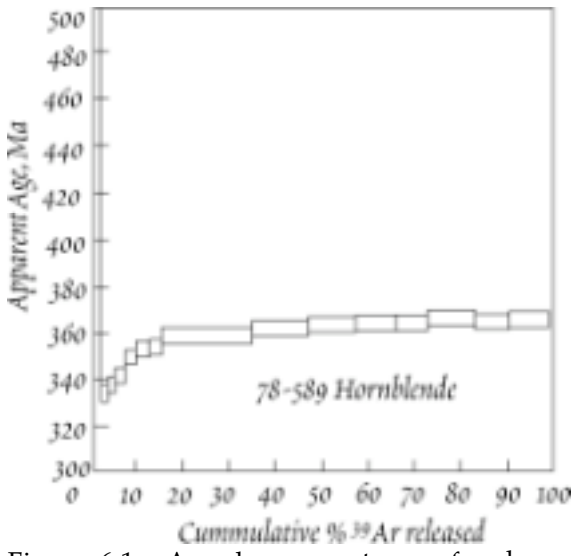


Figure 6.1. Ar release spectrum of a hornblende in a Paleozoic gabbro reheated in the Cretaceous by the intrusion of a granite. Anomalously old apparent ages in the lowest temperature release fraction results from diffusion of radiogenic Ar into the hornblende during the Cretaceous reheating. From McDougall and Harrison (1988).

When excess Ar is held in more than one crystallographic site, for example different minerals in the analyzed sample, release spectra can reveal a saddle shape. An example is shown in Figure 6.2. This sample is a calcic plagioclase from Broken Hill in Australia. The true metamorphic age is approximately 1600 Ma. Even the minimum values in the bottom of the saddle are too old. Electron microscopy of the plagioclase revealed that it had exsolved into a Ca-rich and Na-rich plagioclase. The

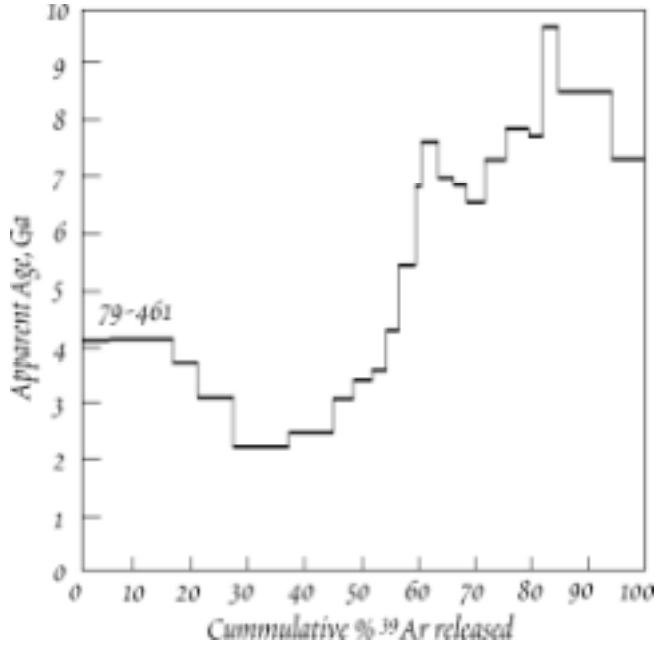


Figure 6.2. Ar release spectrum from a calcic plagioclase from Broken Hill, Australia. Low temperature and high temperature fractions both show erroneously old ages. This peculiar saddle shaped pattern, which is common in samples containing excess Ar, results from the excess Ar being held in two different lattice sites. From McDougall and Harrison (1988).

saddle shape results because Ar in one of the phases diffuses readily and is thus released at low temperature, and diffuses more slowly in the other, resulting in release at high temperature.

A new technique, developed only in the last 10 years, involves releasing Ar from small areas of a sample through laser ablation. This allows release of Ar from areas with diameters less than a millimeter, and provides the possibility of spatial resolution of Ar diffusional loss.

^{40}Ar-^{39}Ar Isochrons

The data from various temperature release steps are essentially independent observations of Ar isotopic composition. Because of this, they can be treated much the same as in conventional isochron treatment. The isochron equation, written for the K-Ar system is:

$$\frac{^{40}\mathrm{Ar}}{^{36}\mathrm{Ar}} = \left(\frac{^{40}\mathrm{Ar}}{^{36}\mathrm{Ar}}\right)_0 + \frac{^{40}\mathrm{K}}{^{36}\mathrm{Ar}}(e^{\lambda t} - 1) \quad 6.1$$

When ^{40}Ar/^{36}Ar data from a series of samples are plotted against ^{40}K/^{36}Ar, the slope of the resulting line will be proportional to age, and the intercept gives the initial ^{40}Ar/^{36}Ar ratio. Since for all release fractions of a sample the efficiency of production of ^{39}Ar from ^{39}K is the same and ^{40}K/^{39}K ratios are constant, we may substitute C^{39}Ar for ^{40}K:

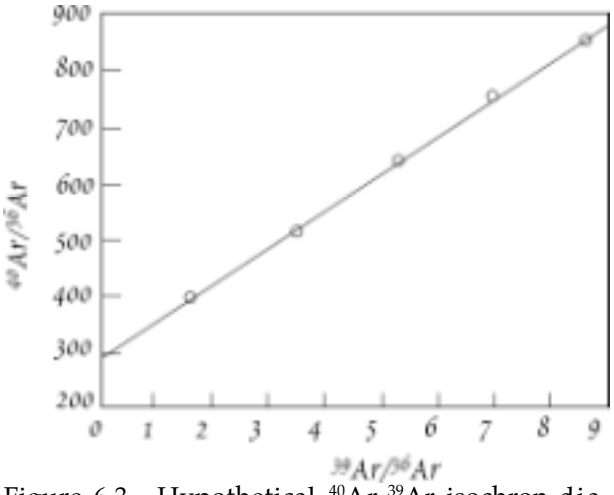


Figure 6.3. Hypothetical ^{40}Ar-^{39}Ar isochron diagram. The slope is proportional to the age and the intercept gives the initial ^{40}Ar/^{36}Ar ratio, which is commonly atmospheric, as is illustrated here.

$$\frac{^{40}\mathrm{Ar}}{^{36}\mathrm{Ar}} = \left(\frac{^{40}\mathrm{Ar}}{^{36}\mathrm{Ar}}\right)_0 + \frac{^{39}\mathrm{Ar}}{^{36}\mathrm{Ar}}\mathrm{C}(e^{\lambda t} - 1) \quad 6.2$$

C is a constant that depends on the efficiency of ^{39}Ar production during irradiation. Thus when ^{40}Ar/^{36}Ar ratios from a series of release fractions are plotted against ^{39}Ar/^{40}Ar, the slope of the resulting line will be proportional to the age of the sample, as is illustrated in Figure 6.3.

The use of the isochron diagram can help to identify excess Ar and its nature (e.g., atmospheric, inherited, etc.). It also provides a crucial test of whether ages obtained in release spectra are meaningful or not. A drawback of this diagram is that ^{36}Ar, which is the denominator in both the ordinate and abscissa, is often present in only trace amounts and is difficult to measure precisely. Because it appears in both

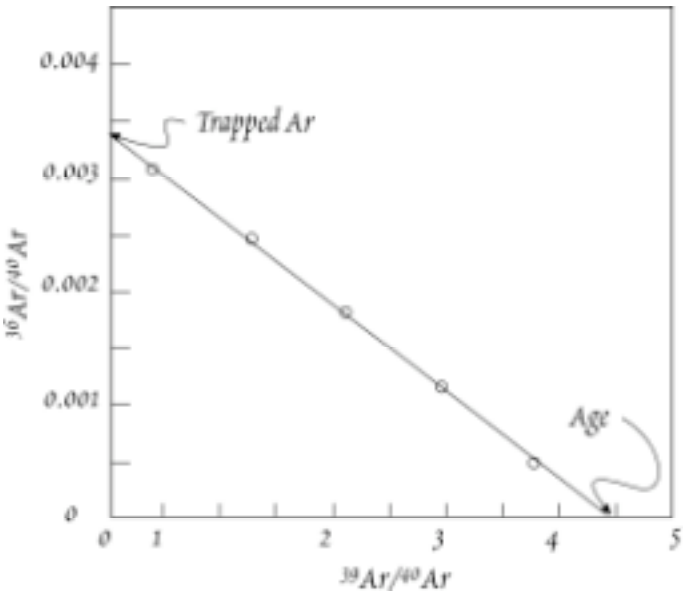


Figure 6.4. Plot of $^{36}Ar/^{40}Ar$ vs $^{39}Ar/^{40}Ar$, also called an inverse isochron diagram. Age is obtained from the value of $^{39}Ar/^{40}Ar$ corresponding to $^{36}Ar/^{40}Ar = 0$.

ordinate and abscissa, errors in its measurements can produce correlations that imitate isochrons.

An alternative is to use a plot of $^{36}Ar/^{40}Ar$ against $^{39}Ar/^{40}Ar$ (Figure 6.4), often called an inverse isochron plot. We can think of the Ar in a sample as a mixture of a trapped component and a radiogenic component. As such, the data for various release fractions should plot as a straight line on such a plot. The radiogenic component has a $^{36}Ar/^{40}Ar$ ratio of 0 (because ^{36}Ar is not produced by radioactive decay), whereas the trapped, non-radiogenic component can be found by extrapolating to a $^{39}Ar/^{40}Ar$ ratio of 0 (corresponding to a $^{39}K/^{40}Ar$ ratio of 0; since ^{39}K is proportional to ^{40}K, this also corresponds to a $^{40}K/^{40}Ar$ ratio of 0). Thus the age may be computed from the $^{39}Ar/^{40}Ar$ ratio obtained by extrapolating the correlation line to $^{36}Ar/^{40}Ar$ to 0, and the composition of the trapped component by extrapolating to $^{39}Ar/^{40}Ar$ of 0.

Figure 6.5 provides an example of how the inverse isochron plot may be used to identify trapped components. The original release data showed a disturbed pattern and lacked a plateau (not shown). The inverse isochron plot (Figure 6.5a) revealed two correlations suggesting the presence of two distinct trapped components. The lower intercept yielded an age of 149.1 Ma. When the data were corrected for the trapped component and replotted on a release spectrum, they produced a plateau corresponding to the same age as the isochron age.

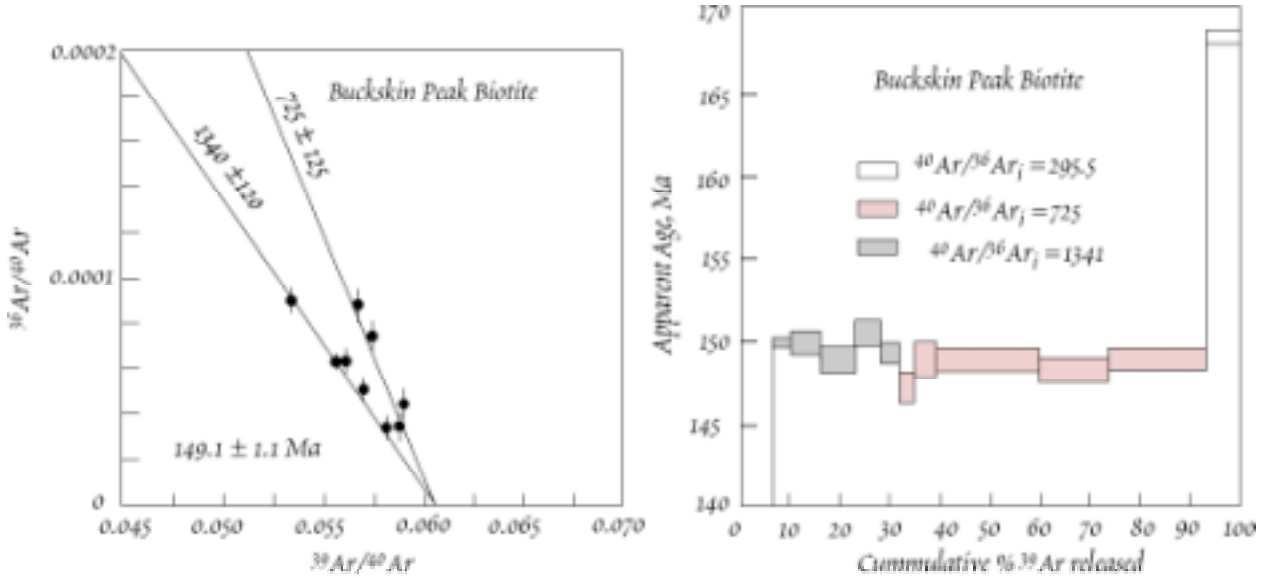


Figure 6.5. (a) Inverse isochron diagram revealing the presence of two excess Ar components. (b) Ar release spectrum for the same sample after correction for non-atmospheric excess Ar.

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THE RB-SR SYSTEM

Unlike the K-Ar system, in the Rb-Sr and Sm-Nd systems, both the initial ratio and the age are virtually always unknown, meaning we must solve for both simultaneously through the isochron method. It is worthwhile to briefly review and summarize the conditions that must be met to obtain a meaningful isochron.

1. *The ratio of parent to daughter should be large*. When this is the case, variations in the isotopic composition of the daughter will be large relative to our ability to measure them. Under the best of circumstances, isotope ratios can be measured with a precision of 10 ppm or so. If the total amount of radioactively produced daughter is small relative to the amount present initially, for example if the proportion of radiogenically produced daughter is only a few 10's of ppm or less of the total amount of daughter, there is little hope of using the system to produce accurate 'ages'.
2. *The parent/daughter should have a large range*. A large range in parent/daughter ratio leads to a large range in isotope ratios in the daughter. The error on the regression slope is a function of the range of values used in the computation. So given similar analytical precisions, we will obtain a more precise date with a decay system where the variations in parent-daughter ratio are large than with one where these variations are small.
3. *Deviations from closed system behavior must be minimal* subsequent to the event we are attempting to date. This should be considered when choosing both the decay system and the samples we plan to analyze. As we shall see, some elements tend to be more mobile than others, and some minerals are less reactive than others. Size also plays some role. A large sample is more likely to meet the closed system requirement than a small one (the elements have further to diffuse). Often, metamorphism will disturb a system on the scale of mineral grains, but not a scale of 'whole rock' samples taken hundreds of meters apart (however, whole rocks will generally show less variation in parent/daughter ratios than minerals). One must also bear in mind that an atom created by radioactive decay will generally be a misfit in the lattice site it occupies (since the site was originally occupied by the parent). Furthermore, the site may be damaged by the decay process. Such damage is more likely in the case of alpha decay than beta decay or electron capture because of the high energy of the alpha (typically 4 MeV), and the kinetic recoil energy of the daughter nucleus.
4. *The isotopic composition of the daughter must have been homogeneous* at the time of the event we wish to date. On a small scale, homogenization takes place through diffusion, which, as we have seen, is highly temperature dependent. The higher the temperatures obtained during the 'event', the more homogenized the system will be. On scales larger than 10 meters or so, homogenization can only be achieved through convective-driven advective transport. This effectively means homogenization requires the presence of a liquid. This might be a magma or a hydrous fluid circulating through rocks undergoing metamorphism. In any case, both convection and diffusion will be more efficient at higher temperatures, so homogenization is more likely to be achieved at high temperatures than at low ones. Finally, the larger the range in parent/daughter ratios, and hence isotopic composition at the time we measure them, the less important will be any initial variations in isotopic composition.

We will now continue with our consideration of the various decay systems. Rb-Sr geochronology does not differ in principle from Sm-Nd geochronology or Re-Os geochronology, however. Thus our discussion will focus mainly on the geochemistry of these elements and the behavior of these systems with reference to the four points above.

Chemistry of Rb and Sr

Both Rb and Sr are trace elements in the Earth: their concentrations are generally measured in ppm. Rb is an alkali element (Group 1) with a valence of +1. Like other alkalis, it is generally quite soluble in water and hydrous fluids. As a result, it is among the more mobile elements. Rb has an ionic radius of 1.48 Å. This large ionic radius means it is excluded from many minerals: it is simply too large

to fit in the sites available. Hence it is among the most *incompatible* elements. However, its radius is sufficiently similar to that of potassium (1.33 Å) that it substitutes readily for K in K-bearing minerals such as mica and K-feldspar. As a result, no Rb minerals occur in nature: that is, it is not a stoichiometric component of any mineral. Because of its incompatible nature, it is strongly concentrated in the crust and depleted in the mantle.

Sr is an alkaline earth element (Group IIA) with a valence of +2. The alkaline earths are also reasonably soluble in water and hydrous fluids, but not as soluble as the alkalis. Sr is therefore a moderately mobile element. Its ionic radius is 1.13Å, which is still sufficiently large for it to be excluded from many minerals, and it is also an incompatible element, but not a highly incompatible one. It substitutes for Ca (ionic radius 0.99Å) to varying degrees. It is quite comfortable in the Ca site in plagioclase, the solid/liquid partition[1] coefficient being about 2. It seems to be considerably less comfortable in the Ca site in clinopyroxene; the Sr partition coefficient being only about 0.1. In igneous and high-grade metamorphic rocks, most Sr will be in plagioclase (which typically constitutes about 50% of mafic igneous rocks). Sr can also substitute for Ca in other minerals such as calcite, apatite, gypsum, sphene, etc. Sr is also concentrated in the crust relative to the mantle, but not to the degree that Rb is.

The Rb/Sr in the Earth as a whole is about 0.029, though we do not know this ratio exactly[2]. The ratio is much lower in the mantle, and much higher in the crust. Mantle-derived rocks such as basalts also have low Rb/Sr ratios. Low ratios such as these violate condition 1 above; as a result, it is very difficult to obtain good Rb/Sr ages on mafic[3] and ultramafic rocks. However, igneous differentiation tends to increase the Rb/Sr ratio because Sr is removed by fractional crystallization of plagioclase, while Rb remains in the melt. In acid (i.e., silica-rich) igneous rocks, the Rb/Sr ratio often exceeds 1 (a Rb/Sr ratio of 1 corresponds to a $^{87}Rb/^{86}Sr$ ratio of 2.9, depending somewhat on the $^{87}Sr/^{86}Sr$ ratio). As a result, Rb/Sr dating can often be applied successfully to acid igneous rocks. A large range in Rb/Sr ratio is also reasonably common. It may occur in whole rock samples when the whole rocks represent various members of a comagmatic differentiation suite, or in mineral samples when both K- and Ca-bearing minerals are present. Rb-Sr geochronology can also be applied to metamorphic rocks, provided K-bearing, Rb-rich minerals

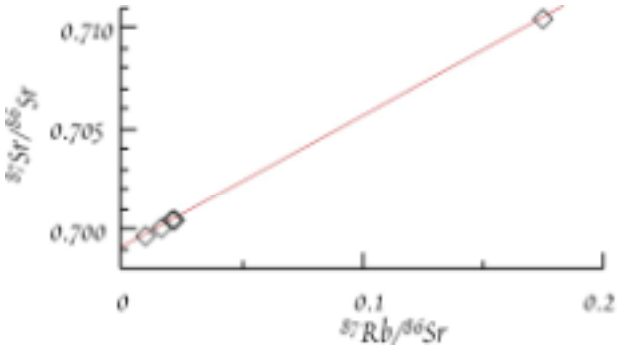


Figure 6.6. A Rb-Sr isochron. Five analyses from a clast in the Bholghati meteorite fall on an isochron, whose slope is related to the age of the system. The age in this case is 4.54 Ga. Data from Nyquist et al. (1990).

[1]The solid-liquid partition (or distribution) coefficient is quite a useful parameter is igneous trace element geochemistry. It is defined simply as the *equilibrium* ratio of the concentration of the element in the solid phase (e.g., a mineral such as plagioclase) to the concentration in the magma.

[2]A reasonable compositional model for the Earth is that of carbonaceous chondritic meteorites, which we consider representative of the concentrations of non-gaseous elements in the solar system. However, the Earth is demonstrably depleted in the more volatile of the non-gaseous elements; in other words, the chondritic model of the Earth is valid only for the more refractory elements. The alkalis are among this group of volatile elements, so we do not have a good estimate of the Rb concentration of the Earth.

[3] Mafic rocks are those rich in magnesium and iron (the term "mafic comes from "MAgenesium and Ferric or Ferrous (fer being the latin root meaning iron). Ultamafic rocks are simply very rich in magnesium and iron. Basalt, the composition typical of many lavas, is mafic. The Earth's mantle is composed of peridotite, an ultramafic rock.

are present, as they typically are. Figure 6.6 shows an example isochron of a meteorite.

A serious disadvantage of the Rb-Sr system is the mobility of these elements, particularly Rb. Because of their solubilities, they are readily transported by fluids, and may be moved into or out of the system. Furthermore, some K-bearing minerals such as micas are comparatively reactive, in the sense that some or much of the Rb may be present in exchangeable sites. These minerals are also subject to metamorphic resetting or partial resetting at relatively low temperatures. Thus, *Rb-Sr is a good system for dating acid igneous rocks where no intervening metamorphism or alteration has occurred, and for metamorphic rocks*.

Rb-Sr dating can in special instances be applied to sedimentary rocks. Sedimentary rocks are generally difficult to date by any method because of the lack of the high-temperatures necessary for homogenization of initial Sr isotope ratios. But minerals crystallizing from a homogeneous solution, such as seawater, will all have identical initial ratios. Thus dates have been obtained using minerals such as authigenic celadonite (a Rb-rich mineral) and calcite (a Rb-poor, Sr-rich mineral). An additional advantage is that the evolution of $^{87}Sr/^{86}Sr$ in seawater is known. Thus a reasonable assumption about the initial $^{87}Sr/^{86}Sr$ ratio may be made if the approximate age is known. However, successful dates of sediments are certainly rare.

A rapidly developing field is what one might call Sr isotope chronostratigraphy. Since the history of $^{87}Sr/^{86}Sr$ in seawater is known, an estimate of the age of an authigenic mineral such as calcite can be obtained simply by determining its initial $^{87}Sr/^{86}Sr$ and comparing that with the seawater evolution curve. We will discuss this in detail in a subsequent lecture.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

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