

Ion Microprobe Confirmation of Pb Isotope Ratios and Search for Isomer Precursors in Polonium Radiohaloes

RADIOHALOES associated with decay of several Po α emitters^{1,2} have been studied by optical microscopic techniques and more recently by mass spectrometric examination of the halo inclusion using ion microprobe techniques^{3,4}. In such cases a large excess of ²⁰⁶Pb compared with ²⁰⁷Pb was found to be incompatible with the radiogenic decay of ²³⁸U and ²³⁵U, yet was explainable on the basis of polonium decay independent of uranium³. A straightforward attempt to account for the origin of these Po haloes by assuming that Po was incorporated into the halo inclusion at the time of host mineral crystallization meets with severe geological problems: the half-lives of the polonium isotopes ($t_{1/2}=3$ min for ²¹⁸Po) are too short to permit anything but a rapid mineral crystallization, contrary to accepted theories of magmatic cooling rates.

This dilemma might be resolved (R.V.G., unpublished) if several long half-life high-spin or shape isomers of polonium (or the β -decaying precursors) were formed at nucleosynthesis and were subsequently incorporated into the halo inclusions during crystallization. This hypothesis eliminates the geological difficulties, and is open to experimental verification using several techniques such as charged particle reactions, though the long half-lives may present an obstacle. But long half-lives imply that some of the isomers may still exist, in which case a mass analysis of the polonium halo inclusions should reveal whether significant quantities are still present. We now report additional ion microprobe analyses of these Po inclusions as well as U inclusions in search of the isomers and for additional information on the Pb isotope ratios.

Mass scans were taken on areas of the biotite free from haloes. All the normal elemental constituents as well as some trace elements were seen in these scans. The mass region from 150 to 300 is conspicuously free from any mass peaks. Generally Fe_2^+ at position 112 is the only high mass peak of significance observed from the biotite itself.

In the pure uranium, thorium, or uranium-thorium inclusions, ion microprobe analysis showed that the inclusions were either zircons or monazites; in many cases the ²⁰⁴Pb ion current or signal was near background, so that it was difficult to make a common Pb correction; the ²³⁸U/²³⁵U ratio was normal in inclusions which contained uranium; and the ²³⁸U/²⁰⁶Pb signal ratio varied from 10 to 70 in the different inclusions analysed. The actual ²³⁸U/²⁰⁶Pb atom ratio is difficult to determine because of the uncertainty in the U and Pb secondary ion yield from different minerals. In general, U is detected with several times greater efficiency than Pb. The radiogenic ²⁰⁶Pb/²⁰⁷Pb ratio was difficult to evaluate in those inclusions where the ²⁰⁴Pb signal was near background. In other cases it was found to vary within normal limits.

There is a wide spectrum in the U and Th halo types—some inclusions contain just U or Th without the other element, while other inclusions contain varying amounts of U and Th and in some cases exhibit rings from both decay series; it seems that the same situation prevails with Po and U type haloes in certain micas. In the analyses thus far it seems that the larger the Po halo inclusion the greater the U content tends to be; but more work is needed to verify this. Also the larger inclusions seem to be definite mineral types (usually rare earths but not specifically identified as yet), whereas some of the point-like Po halo inclusions consist of only elemental Pb (without ²⁰⁴Pb) and Bi. Previously no detectable U was found in such cases as the latter type.

In contrast to the Pb ratios in the U and Th halo inclusions, we again report exceptionally high ²⁰⁶Pb/²⁰⁷Pb ratios which are characteristic of the ²¹⁸Po decay sequence type Po halo. The results may be summarized as follows: ²⁰⁶Pb/²⁰⁷Pb ratios of 10, 12, 18, 22, 25, 40, and 100 were observed. In four of these cases no ²⁰⁴Pb was detected. In the other two cases ²⁰⁴Pb was almost background, so that no common Pb correction was made on any of the ratios (any such correction would have produced a larger ²⁰⁶Pb/²⁰⁷Pb ratio). In three of the cases (10, 12, and 22) the small uranium signal seen was 10 to 100 times less than that required to support the Pb observed. These results confirm the earlier ion microprobe analyses of Po halo inclusions in which Pb ratios were found that were impossible to explain on the basis of U decay. They give confidence that we are indeed dealing with a class of haloes that is distinct from the ordinary U and Th types as the optical microscopic measurements invariably suggest. Otherwise, the most important aspect of the results is that the decay product of the polonium (Pb) still exists in these inclusions in measurable quantities (10^8 - 10^{10} atoms) and has not diffused away. On such a basis we then expect that any isomer precursor of Po, if the half-lives were sufficiently long, would also still exist and be detectable by ion microprobe techniques.

The only source of geochemical data about the postulated isomer is derived by inference from the type of halo inclusion. Some Po halo inclusions are of the rare earth variety while others contain only elemental Pb and Bi. The latter case might suggest the existence of an isomer geochemically similar to those elements, whereas the former case is rather non-specific. Fortunately ion probe mass analysis techniques do not depend on knowing the chemical identity of the postulated isomer.

To obtain these Pb ratios, we first cleaved the mica until the halo inclusion appeared on the surface. In some cases the sample was coated with a thin conducting layer of carbon, but it was better to overlay the sample with

electron microscope-type Cu grids. In the latter case there was no extraneous material introduced anywhere near the region of interest. Before taking mass scans on the Po haloes the ion microprobe was optimized to obtain the best Pb signal from large U type halo inclusions that were mounted on the same sample but in a different area. In many cases the ion probe was peaked on mass 206 position and then moved to the area in the vicinity of the Po halo inclusion. The signal at this mass position remained at background (1 Hz) until the beam was shifted to the Po inclusion itself. In some cases several minutes elapsed before the signal reached maximum intensity. Generally mass positions 204, 207, 208, 218 and 238 were monitored, as well as the regions considerably below Pb, for possible interference from molecular ions. In other cases mass scans of the entire region from mass 1 to 250 were taken. It can be definitely stated that the exceptionally high 206 signal, compared with 207, occurs only in the Po halo inclusions and is not an artifact due to a molecular ion originating with the mica itself, the inclusion, or a combination of the mica and the elemental constituents of the inclusion. This is not to say the ion microprobe does not generate molecular ions, for in certain cases it does so very efficiently. But in the case of the Po haloes, we took care to monitor the various possibilities, which could have interfered with the results.

The search for the isomer consisted of carefully scanning the region around mass 218, for the Po haloes used in these experiments originated with ^{218}Po α decay. To be certain of the mass position, a small amount of Hg was placed on the sample holder to use as a mass marker at the 218 position ($^{202}\text{Hg}^{16}\text{O}$). In all Po inclusions except one no signal was observed at the 218 position. That one exception was due to interfering HgO ions from the presence of Hg in the inclusion itself.

A very rough estimate of what these results mean in terms of the present existence of the isomer in the inclusion may be obtained because the ^{206}Pb sputtered ion count rate was greater than 1,000 Hz in some Po inclusions. If it is assumed the isomer resembles Pb in sputtered ion efficiency (Pb has a relatively poor sputtered ion yield), then the present abundance of the isomer in the inclusion is $\leq 10^{-3}$ that of the ^{206}Pb . One interpretation of these results is the isomer has simply decayed to the point where it was not detected in these experiments. (These samples were from an early Precambrian pegmatite in Scandinavia.) It is yet to be determined whether this information is consistent with the half-lives of the proposed isomers that can be ascertained by determining the latest geological epoch in which such haloes occur.

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¹ Henderson, G. H., *Proc. R. Soc.*, **A**, **173**, 250 (1939).

² Gentry, R. V., *Science, N. Y.*, 160, 1228 (1968).

³ Gentry, R. V., *Science, N. Y.*, 173, 727 (1971).

⁴ Andersen, C. A., and Hinthorne, J. R., *Science, N. Y.*, **175**, 853 (1972).