

Analysis of x-ray spectra excited by x rays, electrons, and protons in monazite*

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Mineral monazite from Malaysia has been investigated by energy dispersive x-ray analysis employing three different methods: x-ray, relativistic electron and proton induced excitation. An upper limit of 15 ppm has been placed on the possible concentration of the superheavy element with $Z = 126$.

[RADIOACTIVITY Monazite (Ce, La, Th)PO₄; measured x ray, electron and proton induced x-ray spectra. Deduced upper limit for concentration of element $Z = 126$.]

I. INTRODUCTION

Much interest has been stimulated by the speculated existence in nature of islands of stability in the nuclear periodic table.¹ Recently this subject has received new emphasis with direct evidence announced by Gentry *et al.*² The specific features of the work of Gentry and his collaborators are the association of giant halos surrounding monazite inclusions in biotite micas with superheavy elements on the one hand, and the use of proton induced x-ray analysis on the other. This announcement stimulated many efforts in corroboration using a plethora of analytical techniques, none of which has as yet produced confirmatory evidence.³⁻⁸

Stimulated by the work of Ref. 2, we have initiated a search for the possible existence of superheavy elements in monazite. Since to our knowledge there is no geochemical evidence as to why the supposed element $Z = 126$ should be preferentially concentrated in monazite inclusions in biotite mica, we have selected a bulk sample⁹ of monazite from Malaysia. In a collaborative effort between three laboratories we investigated the same sample by three different methods: (i) x-ray fluorescence, (ii) electron induced and (iii) proton induced x-ray emission. Methods (i) and (ii) avoid the possible occurrence of nuclear γ rays induced by protons which were found to interfere with the atomic x rays in the spectra.^{3,10} For each method an upper limit on the concentration of the supposed element $Z = 126$, calculated via the concentration of thorium in the sample, has been derived.

In Sec. II the experimental methods are described. The results, given in Sec. III, show that there are

no unaccounted for lines in the spectra. An upper limit for the occurrence of element $Z = 126$ in this sample is calculated.

II. EXPERIMENTAL METHODS

A. Target preparation, electronics, and energy calibration

The monazite sample, a (La, Ce, Th)-phosphate, consisted of grains with average dimensions between 80 to 120 μm . The targets in case of the x-ray fluorescence method were prepared by suspending the monazite powder in water and filtering it off on a Nuclepore membrane. For the electron and proton induced work a monolayer of grains was fixed onto a thin Kapton or Mylar foil, respectively, by a 0.1% starch solution. Standard energy dispersive x-ray analysis electronics were used. Energy calibrations in all cases were established using both elemental standards and major spectral peaks of zirconium, cerium, and thorium.

B. X-ray fluorescence

The x-ray induced fluorescence measurements were carried out with the KeveX-0810 system of the University of Antwerp. This system includes a high voltage generator, operated at 45 kV-20 mA, which feeds an x-ray tube with a tungsten anode. The x-ray beam was monochromated using a neodymium secondary target. The monazite target was set at 45° to the incident beam and the collimated fluorescent radiation was counted by a Si(Li) detector with a 170 eV resolution at 5.9 keV. The monazite sample was analyzed for periods up to 75 h. Some measurements were also performed

by wavelength dispersive x-ray fluorescence on a Philips PW 1450 modular x-ray spectrometer located at the University of Gent. In this case a LiF(220) crystal was used for characteristic x-ray dispersion, and detection was accomplished by means of a scintillation counter. Because of the low background in the spectra the x-ray fluorescence is the most sensitive of the three methods used in this particular case.

C. Electron induced x-ray emission

This method is based on the techniques for the determination of the inner-shell ionization cross sections for high relativistic electron impact,¹¹ using the Darmstadt linear accelerator (DALINAC). Considerable improvements of the beam quality from the accelerator and of the beam transport system have been achieved recently¹² which enable x-ray detection at low backgrounds. For the present experiment electron energies of 20, 40, and 60 MeV were selected. The beam impinged onto the monazite target, placed at 45° to the beam, inside a scattering chamber, and was then collected in a Faraday cup located 5.3 m downstream from the chamber. To prevent background radiation production in the vicinity of the detector, the Faraday cup was equipped with magnetic suppression, in the form of a quadrupole doublet to refocus the entire beam onto the endplate. The monazite x rays were detected using a Si(Li) detector of 180 eV resolution at 5.9 keV. The detector was placed at $\theta = 93^\circ$ outside the chamber and shielded with 10 cm of lead. The x rays passed through an Al absorber of 0.02 mm before entering the detector. In order to deflect all electrons that would be scattered from the target into the solid angle of the Si(Li) detector, a magnet was mounted between the target and the detector. For monitoring purposes a 70 MeV/c magnetic spectrometer recorded elastically scattered electrons from the target nuclei.

To reduce pileup effects in the spectra the electron beam current was kept at 1 nA corresponding to 4×10^7 electrons per linac pulse. This limited the count rate to 0.15 detected events per machine pulse. The sample was analyzed for 37 h at each energy.

A measurement of characteristic x rays against a relatively low background is in fact possible with an electron linac, since at energies above 20 MeV the very intense bremsstrahlung radiation is confined to a cone of 3° (total angle) in the forward direction. Furthermore, the *L*-shell ionization cross section for an element with $Z = 126$ at our energies is expected from scaling of known cross sections¹³ to be two orders of magnitude larger

than proton induced cross sections at few MeV bombarding energies.

D. Proton induced x-ray emission

These measurements were performed using protons from the EN Tandem van de Graaff accelerator of the University of the Witwatersrand. The target chamber incorporates carbon beam collimators, an aluminum detector collimator, and -1000 V electron suppression. The monazite grains present a thick target to MeV protons, so beam integration was performed on the target. The detection system was based on an intrinsic germanium detector with pulsed optical feedback stabilization. The detector resolution was 175 eV at 5.9 keV. A 0.12 mm Al absorber was placed in front of the detector to reduce the count rate at the low-energy end of the spectrum. By restricting the beam current to 1 nA or less, the signal count rate was maintained below 500 s^{-1} . Long runs with integrated charge of 30 μC were accumulated for $E_p = 3$ and 5 MeV. In addition, spectra were accumulated at $E_p = 2, 3, 4,$ and 5 MeV to observe any contribution from the 27 keV nuclear γ ray which is produced via the $^{140}\text{Ce}(p, n\gamma)^{140}\text{Pr}$ reaction.^{3,10} The threshold of this reaction is at 4.227 MeV. The many advantages of the proton induced x-ray analysis method have been discussed in detail in a recent review.¹⁴

III. RESULTS AND DISCUSSION

A. Spectra

Figure 1 displays x-ray spectra from each of the three methods. The spectra are closely similar in their major features; the observed lines can be grouped into three zones, namely below 20 keV, a window zone of substantially lower yield from 20 to 32 keV, and a third zone containing numerous lines, above 32 keV. The first and third zones of the spectra can be uniquely interpreted in terms of *K* and *L* lines of known elements. The prominent peaks in the window zone in the proton induced x-ray spectrum are due to Ge *K α* escape from the intrinsic germanium detector of primary lines from the upper third of the spectrum. The arrows in Fig. 1 indicate the predicted energy 27.25 keV for the $Z = 126$ *L α_1* x ray.¹⁵

For the x-ray fluorescence measurement the window zone between 24 and 28 keV is enlarged in Fig. 2. Only one significant peak is observed, the Sn *K α* line at 25.27 keV, and there is no peak at 27.25 keV. The latter result was confirmed by the wavelength-dispersive scan which was performed in this region. Note from both Figs. 1 and 2 that the background is low in the window zone,

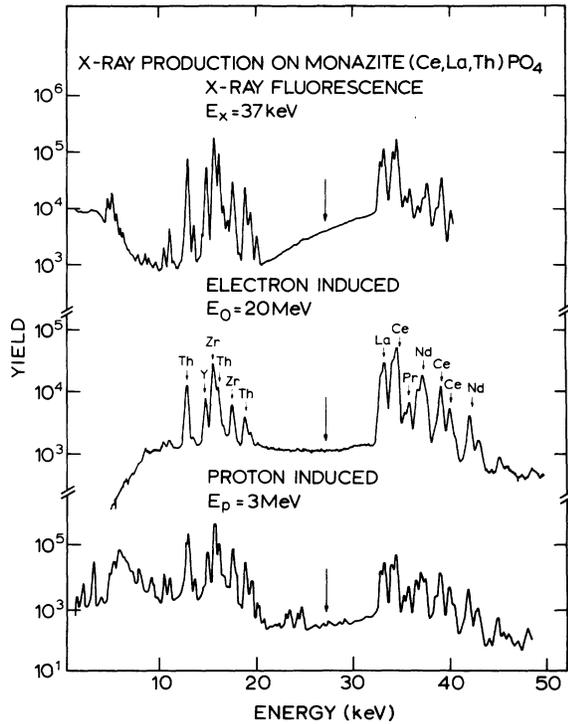


FIG. 1. Representative x-ray spectra from each of the three methods of excitation described in the text. Only the major lines are indicated. The arrow points to the location of the predicted energy for the $Z=126$ $L\alpha_1$ transition in the window zone located between 20 to 32 keV.

forming a deep valley. This is different in the corresponding electron induced x-ray spectrum (Fig. 3), where the background is high, causing the valley to be shallow. Again, the only statistically significant peak observed at all energies is the Sn $K\alpha$ line. No pileup peaks rise above the general background. In contrast to the other techniques, the window zone of the proton induced x-ray spectrum contains a number of resolved peaks which cannot be simply ascribed to specific elements [Fig. 4(a)]. The majority of these are due to Ge $K\alpha$ escape peaks as shown in Fig. 4(b). The remainder of the lines were identified as pile-up peaks by comparison at low (350 s^{-1}) and high (3500 s^{-1}) count rates. The Sn $K\alpha$ peak seen in Figs. 2 and 3 is obscured here by the escape peak from the Ce $K\alpha_1$ line. A comparison of 2, 3, 4, and 5 MeV spectra showed that the contribution of the $^{140}\text{Ce}(p, n\gamma)^{140}\text{Pr}$ γ line (27 keV) above threshold is small and can be ignored in this particular case.

B. Detection limit

In order to place a quantitative limit on the concentration of the element $Z=126$ in the monazite

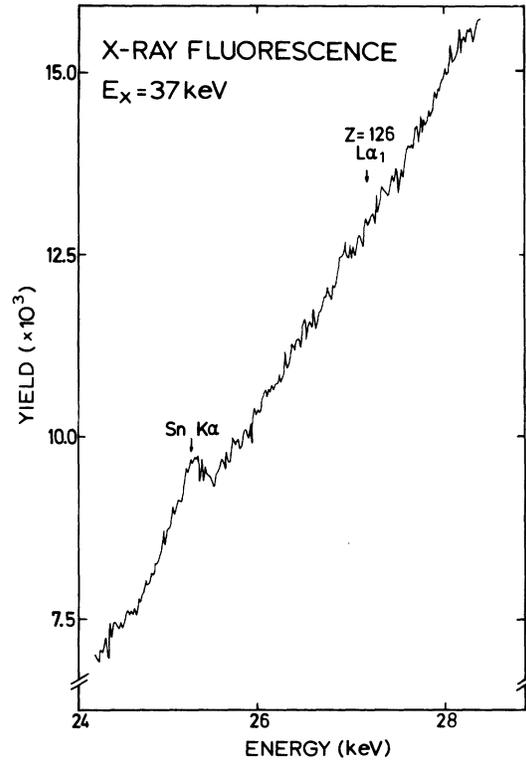


FIG. 2. Expanded section of the x-ray fluorescence spectrum from the window zone. The only significant line is due to the Sn $K\alpha$ transitions.

sample investigated and to relate the results of the three different techniques, the concentration limit (CL) in ppm by weight has been calculated. This was done by normalizing the detection limit (DL) in counts $[\text{DL} = 3 (\text{BACKGROUND})^{1/2}]$ to the thorium $L\alpha$ yield in each case, as follows:

$$\text{CL}_{126} = (\text{DL}_{126} / Y_{\text{Th}}) C_{\text{Th}} (\epsilon_{\text{Th}} / \epsilon_{126}) (\sigma_{\text{Th}} / \sigma_{126}) (\omega_{\text{Th}} / \omega_{126}).$$

Here Y denotes the integrated yield of the peak, C

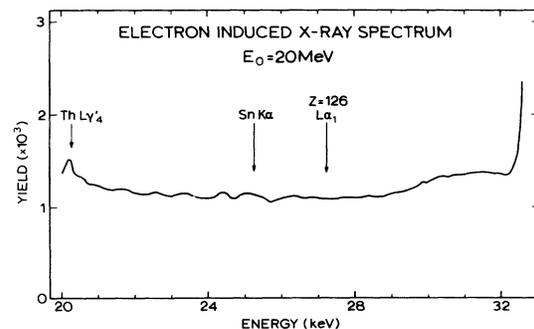


FIG. 3. Expanded section of the electron-induced x-ray spectrum in the window zone. The pileup peaks are not resolved from the background and the only significant line is due to the Sn $K\alpha$ transition.

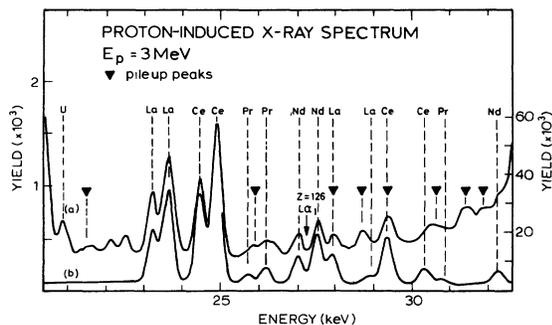


FIG. 4. (a) Expanded section of the proton-induced x-ray spectrum in the window zone. The position of the largest pileup peaks is indicated. (b) The upper third of the spectrum shown in Fig. 1 displaced by the Ge $K\alpha$ 9.885 keV escape energy. The two spectra (a) and (b) have been normalized at the largest peak in the window zone near 25 keV. All significant lines are accounted for. The left and right axis correspond to (a) and (b), respectively.

is the concentration in ppm, ϵ the detector efficiency, σ the L -shell ionization cross section, and ω the mean L -shell fluorescence yield. The subscripts stand for element $Z=126$ and Th, respectively. The cross sections for photons,¹⁶ electrons,¹³ and protons¹⁴ for $Z=126$ as well as the fluorescence yield¹⁷ were obtained by extrapolating from known data. The thorium concentration C_{Th} was determined by wavelength-dispersive x-ray fluorescence after fusing a small sample of monazite with Borax to form a glass bead. The sample contained $(59\,700 \pm 1000)$ ppm of thorium.

The results for the concentration limit of the three methods are 15, 100, and 110 ppm. The

error of these numbers amounts to $\pm 30\%$, mainly due to the uncertainty in the fluorescence yields and the cross section extrapolations. The relatively high limit obtained by the proton induced method is mainly a consequence of the interference from the Ge $K\alpha$ escape peaks. Nevertheless, this result is comparable to the result by Bosch *et al.*³ To our knowledge the electron induced x-ray technique at extreme relativistic energies has for the first time been applied for obtaining quantitative analytical data.

The absence of observable quantities of element 126 in bulk monazite leads back to the question of an alternative explanation for the giant halos in mica. Several such explanations have recently been put forward.^{3,18,19}

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¹See, e.g., *Super-Heavy Elements—Theoretical Predictions and Experimental Generation*, proceedings of the Twenty-seventh Nobel Symposium [Phys. Scr. **10A**, (1974)].

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