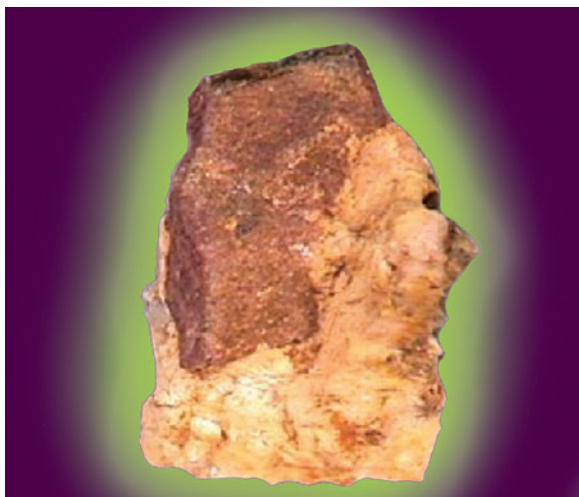


# The X-ray Spectrum of Monazite

Volker Thomsen and Debbie Schatzlein



PHOTODISC INC.

**The x-ray energy spectrum provides rapid identification of mineral samples.**

**Volker Thomsen** is senior applications scientist and **Debbie Schatzlein** is senior applications chemist at NITON, 900 Middlesex Turnpike, Billerica, MA 01821. Thomsen can be reached by e-mail at [vthomsen@niton.com](mailto:vthomsen@niton.com), and Schatzlein can be reached by e-mail at [dschatzlein@niton.com](mailto:dschatzlein@niton.com).

**T**he mineral monazite takes us to a part of the periodic table seldom explored. As a rare earth/thorium phosphate, (Ce, La, Nd, Th, Y) PO<sub>4</sub>, it is a primary ore of several of the rare earth metals.

The rare earth elements have many important industrial applications (1, 2). They may be added to specialty steels and superalloys to improve mechanical properties. Alloys of these elements, especially neodymium, produce strong permanent magnets. They are useful as catalysts in the petroleum field, ammonia synthesis, and many other catalytic applications. The rare earth elements are used to color optical glass and produce the color for televisions and CRTs — a europium–yttrium compound for red, a terbium–fluoride–zinc–sulfide for green, and a cerium–strontium–sulfide for blue. In electronic devices these elements are used to convert energy from one form to another. For example, they are added to synthetic garnet crystals to produce yttrium–aluminum–garnets (YAG) for laser applications and gadolinium–iron–garnets (GIG) with microwave applica-

tions. In medicine, cerium oxalate is used against both seasickness and morning sickness, and neodymium compounds are used to treat thrombosis.

Monazite is also an important source of thorium, and it is radioactive when this element is present. Uranium may also be present in trace amounts. Therefore, in addition to its industrial importance, this mineral is of interest in geochronology studies using U–Th–Pb dating (3). Geochronology is the dating of rocks and sediments, generally using the radioactive decay of the constituent elements present in the sample. As the half-lives and decay schemes of the radioisotopes are known, it is possible to calculate the age of the sample.

There are actually three different kinds of monazite:

- monazite (Ce) — (Ce, La, Nd, Th, Y) PO<sub>4</sub>
- monazite (La) — (La, Ce, Nd) PO<sub>4</sub>
- monazite (Nd) — (Nd, La, Ce) PO<sub>4</sub>.

The first form is the most common. These forms can easily be distinguished by x-ray spectroscopy. The technique is quick, requiring little sample preparation for qualitative analysis. In addition, it is easily distinguished from other rare earth element ores: The presence of neodymium and thorium, in particular, differentiate the sample from bastnasite (Ce, La, Y) CO<sub>3</sub>F, and the cerium, lanthanum, and neodymium differentiate it from xenotime, an yttrium phosphate.

## Experimental

Recently a sample of monazite from the Far East arrived at the NITON applications laboratory in Billerica, Massachusetts. Our laboratory was asked to determine which of the three forms of monazite this sample was, a question

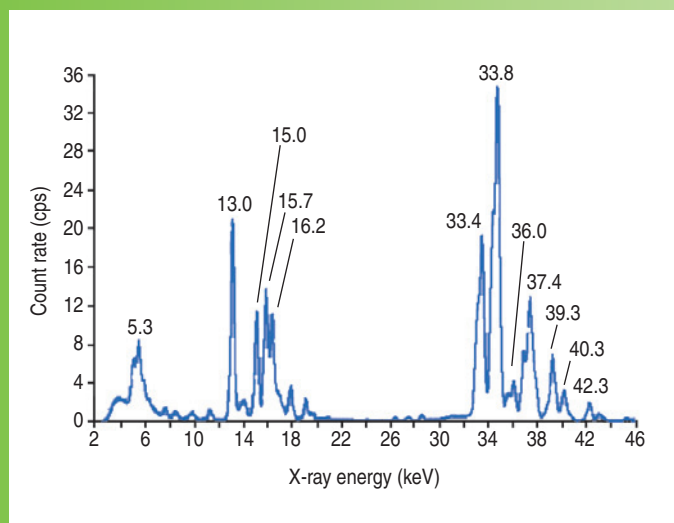


Figure 1. X-ray energy spectrum of monazite.

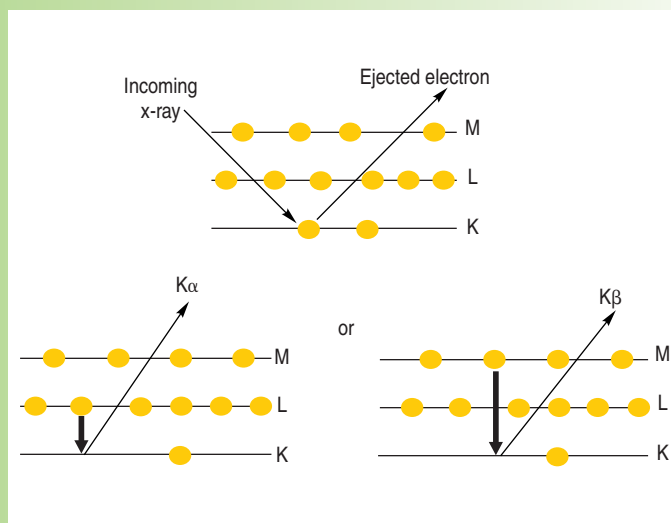


Figure 2. The x-ray fluorescence process.

prompted by financial considerations (see Table I).

Figure 1 shows an x-ray energy spectrum of the sample that was generated using the NITON model XLI 512 handheld x-ray fluorescence spectrometer, which uses Am-241 radioisotope excitation. Handheld x-ray fluorescence instruments can be powerful tools for mineral identification in the field or in the laboratory. For this application, we are using the instrument for qualitative analysis because we simply want to determine the elements present in the sample without the actual weight percentage composition. However, such spectrometers can also produce quantitative results, yielding elemental com-

position (weight percent) of ores and minerals (5–7).

In x-ray fluorescence spectrometry, a source of x-rays ejects electrons from the inner shells of the atoms of the sample. When an outer shell electron “drops down” to fill the void created in the inner shell, an x-ray characteristic of that atom is emitted. This process is called fluorescence (Figure 2).

All elements emit x-rays at their own characteristic energies. These x-rays are called “K lines” if they result from an electron filling the innermost or K shell, and “L lines” if they result from filling the next electron shell, the L shell. There are many different x-ray lines possible (Figure 3).

The energies of the x-rays identify the elements present in the sample, allowing qualitative analysis (8). Table II provides the various x-ray energies of the elements of interest in monazite.

Sometimes the K lines of one element overlap the L lines of another. An example is the  $L\alpha$  of lead ( $Pb L\alpha =$

10.55 keV) and the  $K\alpha$  of arsenic ( $As K\alpha = 10.54$  keV). So if we find a peak at 10.5 keV, how do we know which element is responsible? The answer lies in the different relative intensities of the different lines in the K and L series. The  $K\alpha$  is approximately six times more intense than the  $K\beta$ . In the L series we generally see three lines, alpha ( $\alpha$ ), beta ( $\beta$ ), and gamma ( $\gamma$ ), with relative intensities on the order of 100, 90, and 10.

An x-ray spectrometer consists of a source of x-rays to excite the atoms of the sample, a detector of the characteristic x-rays given off by the various elements of the sample, and a readout system.

### Results

Now we’re in a position to identify the elements present in the spectrum of Figure 1. Let’s start with the tallest peak at about 34.8 keV. That could well be the cerium  $K\alpha$ . Do we find the corresponding  $K\beta$  at 39.3 keV? Yes, there is a peak at this energy at approximately  $\frac{1}{6}$  the intensity.

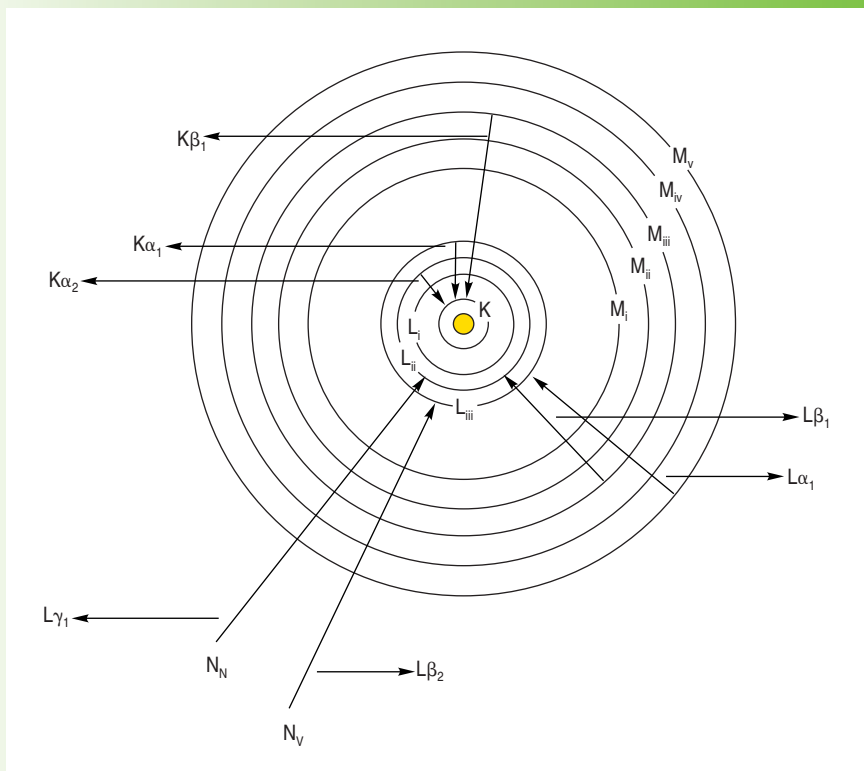
The next tallest peak is at 13.0 keV. This corresponds to the thorium  $L\alpha$ . Furthermore, we find peaks at 16.2, 15.7, and 19.1 keV corresponding to the thorium  $L\beta1$ ,  $L\beta2$ , and  $L\gamma$  respectively. Here the  $L\beta$  line has been resolved into two peaks,  $L\beta1$  and  $L\beta2$ , whose sum would be about 110% of the  $L\alpha$ . The  $L\gamma$  is about 10% of the  $L\alpha$ , so we have the characteristic relative intensities of the L series.

Table I. 1998 year-end price per kilogram (4).

|           |       |
|-----------|-------|
| Yttrium   | \$450 |
| Lanthanum | \$350 |
| Cerium    | \$350 |
| Neodymium | \$450 |

Table II. X-ray energies of elements in monazite (keV).

| Element | Atomic number | $K\alpha$ | $K\beta$ | $L\alpha$ | $L\beta1$ | $L\beta2$ | $L\gamma$ |
|---------|---------------|-----------|----------|-----------|-----------|-----------|-----------|
| Y       | 39            | 14.96     | 16.74    |           |           |           |           |
| La      | 57            | 33.44     | 37.80    | 4.65      | 5.04      |           |           |
| Ce      | 58            | 34.72     | 39.26    | 4.84      | 5.26      |           |           |
| Nd      | 60            | 37.36     | 42.27    | 5.23      | 5.72      |           |           |
| Th      | 90            | —         | —        | 12.97     | 16.20     | 15.62     | 18.98     |



**Figure 3.** Many possible electron transitions lead to many different spectral lines.

Next we have a peak at 33.4 keV, which would be the lanthanum Kα. The Kβ peak at 37.8 keV is barely discernable on the right flank of the peak at 37.4 keV. This peak is the neodymium Kα. The neodymium Kβ is visible at 42.3 keV.

Lastly we note the peak at 15.0 keV. This would be the yttrium Kα. The Kβ appears as a slight hump on the right flank of the thorium Kβ1.

## Conclusion

We have clearly identified our sample as monazite (Ce) due to the presence of thorium and yttrium. This was the hoped-for outcome, as it is the more valuable of the three forms of monazite.

Whether qualitative, as in this example, or quantitative, field-portable x-ray fluorescence instrumentation allows rapid analysis of mineral samples on-site or in the laboratory.

## References

1. P.W. Harben, *The Industrial Minerals HandyBook* (Industrial Minerals Information, Surrey, UK, 1999) 172–176.
2. G.B. Haxel, J.B. Hedrick, and G.J. Orris, *Rare-Earth Elements – Critical Resources for High Technology*, U.S. Geological Survey Fact Sheet 087-02 (2002); <http://geopubs.wr.usgs.gov/fact-sheet/fs087-02/>.
3. U.S. Geological Survey website: <http://geology.cr.usgs.gov/capabilities/gronemtrac/geochron/geochron.html>.
4. J.B. Hedrick, *Rare-Earth Metals*, [http://minerals.usgs.gov/minerals/pubs/commodity/rare\\_earths/740798.pdf](http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/740798.pdf).
5. R. Jenkins, *X-Ray Fluorescence Spectrometry* (Wiley & Sons, New York, NY, 1999).
6. E.P. Bertin, *Introduction to X-Ray Spectrometric Analysis* (Plenum Press, New York, NY, 1978).
7. R. Tertian and F. Claisse, *Principles of Quantitative X-Ray Fluorescence Analysis* (Heyden, London, 1982).
8. G. Rech, J. Lee, E.B. Norman, R. Larimer, and L. Guthrie, *Viewing the Periodic Table of the Elements with X-rays*, <http://ie.lbl.gov/xray/xrf.htm>. ■