

# A Study of Natural and Synthetic Rubies by PIXE

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Trace element analysis of 160 natural- and synthetic rubies was carried out by using the technique of proton-induced x-ray emission (PIXE). It was found that the natural rubies contained more and higher concentrations of impurities than did their synthetic counterparts. Our results suggest that vanadium and iron are good indicators for separating synthetic rubies from the natural ones. The concentration of chromium is also helpful in many cases for source identification.

Index Headings: Proton-induced x-ray emission (PIXE); Gemstones.

## INTRODUCTION

Ruby, a red corundum, is one of the most appreciated gems that have been used as jewelry ornamentation by human kind for many centuries. It is a mineral of very limited distribution, and it commands a higher price than many other colored gemstones. The best known country

where very fine-quality rubies occur is Burma. Thailand is another major source of quality rubies and is, in fact, the world's busiest ruby trade center at present. Rubies also occur in Sri Lanka, India, Kenya, Pakistan, Afghanistan, and some other countries, but they are not usually of such good color as the Burmese and Thai stones.

As fine-quality gemstones are rare and expensive, their substitution with imitations and synthetics for ornamental purpose follows naturally. The historical record<sup>1</sup> reveals that early Egyptians made glass beads to imitate natural gemstones. However, it was not until the end of the 19th century that duplication of natural gems became a reality. The first successful commercial synthesis of ruby was achieved by Auguste Veneuil of France shortly after 1900; his technique is known as the flame fusion method.<sup>1</sup> Since the 1960s, another process, called the flux method, developed originally by C. Freymy in 1877, has also been used to grow synthetic rubies for commercial

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purpose.<sup>1</sup> Synthetic rubies such as those produced by Chatham, Kashan, Knischka, and Ramaura are all manufactured by this process.<sup>2,3</sup> Like their natural counterparts, synthetic rubies can usually be identified by their inclusions. Characteristic inclusions in flame fusion rubies are gas bubbles, as well as curved striae extending across the crystal.<sup>1</sup> Flux-grown rubies normally contain wispy veil fingerprint inclusions, platinum platelets, coarse flux residues, and other inclusions similar in appearance to those seen in the natural rubies.<sup>2</sup> While those synthetic rubies with inclusions can be identified rather easily, the nearly flawless ones are extremely difficult to identify by conventional gemological means.

As techniques of manufacturing synthetic rubies continue to improve, future synthetics will certainly create a bigger identification problem for gem dealers and gemologists alike. Even recently, one prominent scientist and research gemologist<sup>2</sup> has said, "The older generations in the gemstone and jewelry branches of our trade still look upon the new synthetics made by Chatham, Kashan, and Knischka—particularly the new synthetic rubies—with a certain amount of nostalgia for the good old days when it was comparatively easy to distinguish synthetics from their natural counterparts."

Nevertheless, many laboratory methods have been found useful for distinguishing synthetic gemstones from natural ones. These include infrared spectroscopy,<sup>4</sup> x-ray fluorescence,<sup>5</sup> electron microscopy,<sup>6</sup> electron spin resonance spectroscopy,<sup>7</sup> and neutron activation.<sup>8</sup> In our recent paper,<sup>9</sup> we reported the use of the technique of PIXE (proton-induced x-ray emission) for a study of Burmese and Thai rubies, and pointed out the advantages of this technique against the other laboratory methods. In that study, the concentrations of the trace elements in 60 Burmese and Thai rubies were measured; it was found that the former possessed the distinct characteristic of comparatively high vanadium concentration, while the latter were rich in iron content. In this article, we present the results of our further PIXE analysis of 160 natural and synthetic rubies from 14 different sources.

## EXPERIMENTAL

For the measurements, 2 MeV protons produced with the Van de Graaff accelerator at the National University of Singapore were used. A Si(Li) detector having a sensitive area of 36 mm<sup>2</sup> and a beryllium window 0.007 mm in thickness was employed to obtain the fluorescent x-ray spectra. The detector was placed in a position that was external to the target chamber, against the 0.036-mm-thick Hostaphan window of the chamber, and at an angle of 90° to the proton beam. The diameter of the proton beam at the target position was about 4 mm.

Specimens were mounted on a computer-controlled sample ladder of 220 mm total displacement length. Most of the specimens studied were wider than 2 mm. For these specimens, a mask with a 2-mm-diameter hole was used to restrict the irradiated area within the table facet. This was done to maintain a fixed geometrical condition for the measurements. The masks were made with the use of a special type of adhesive tape which had been tested and found to be free from interfering impurities. Those specimens smaller than 2 mm were supported with

TABLE I. Origins and sources for acquisition of samples.

Origin	Quantity	Source of acquisition
Natural		
Afghanistan	1	Roy Huddleston Consultancy, London
Burma	40	Wholesale markets in Thailand
India (Loc 1)	28	Gem dealer from India
India (Loc 2)	10	Gem dealer from India
Kenya	10	Bangkok gem dealer
Sri Lanka	5	Gem dealer in Sri Lanka
Thailand	39	Cutters in Chanthaburi and Bangkok gem dealers
Synthetic		
Chatham	7	GIA reference collection (2) and Chatham Created Gems, Inc. (5)
Inamori	2	GIA reference collection (1) and Kyocera Internation, Inc. (1)
Kashan	6	Hong Kong gem dealer
Knischka	1	GIA reference collection
Ramaura	5	Ramaura Division, Overland Gems Inc.
Seiko	1	Gem Testing Laboratory, London
Unknown	5	Bangkok gem dealer

the same type of adhesive tapes at the back, and no mask was used. The counting time for each sample was 150 seconds, and a proton beam current in the range of 4 to 10 nano-amperes was maintained throughout the experiment.

## THE SAMPLES

Of the 160 samples studied, 133 were natural rubies and the remaining 27 were synthetics. These included those Burmese and Thai rubies used in the previous study.<sup>9</sup> The origins and the sources for the acquisition of these samples are tabulated in Table I.

The majority of the Burmese and Thai rubies could be identified by their color and inclusions. Typically, Burmese rubies display a light-to-medium pinkish-red color and contain rutile needles, spinel crystals,<sup>10</sup> or heat-wave-effect<sup>11</sup> inclusions. Thai rubies show a light-to-dark purple-brownish-red color<sup>12</sup> and have characteristic inclusions such as subhexagonal to rounded opaque metallic grains of pyrrhotite, yellowish hexagonal platelets of apatite, reddish brown almandite garnets,<sup>13,14</sup> circular feathers, and polysynthetic twinning planes.<sup>15</sup>

The Sri Lankan samples were acquired in Sri Lanka. Sri Lankan rubies have rich rose-red color and their characteristic inclusions are long rutile needles, small zircon crystals, irregular gas- to liquid-filled cavities, and well-defined fingerprints.<sup>16</sup>

The origins of the rest of the natural rubies were furnished by the suppliers. These samples were all translucent, in contrast to the transparent specimens mentioned above, and hence verification of their origins was not possible by examination of inclusions. However, the Indian rubies could usually be distinguished by their dull, dark, purplish-red color, and the Kenyan and Afghanistan rubies by their medium pinkish-red color.

Six of the synthetic samples were from the GIA (Gemological Institute of America) reference collection, and most of the rest were acquired from their respective manufacturers or dealers. The five of unknown origin were bought at the same time from a gem dealer in Bangkok and were identified to be of the flame fusion type. These

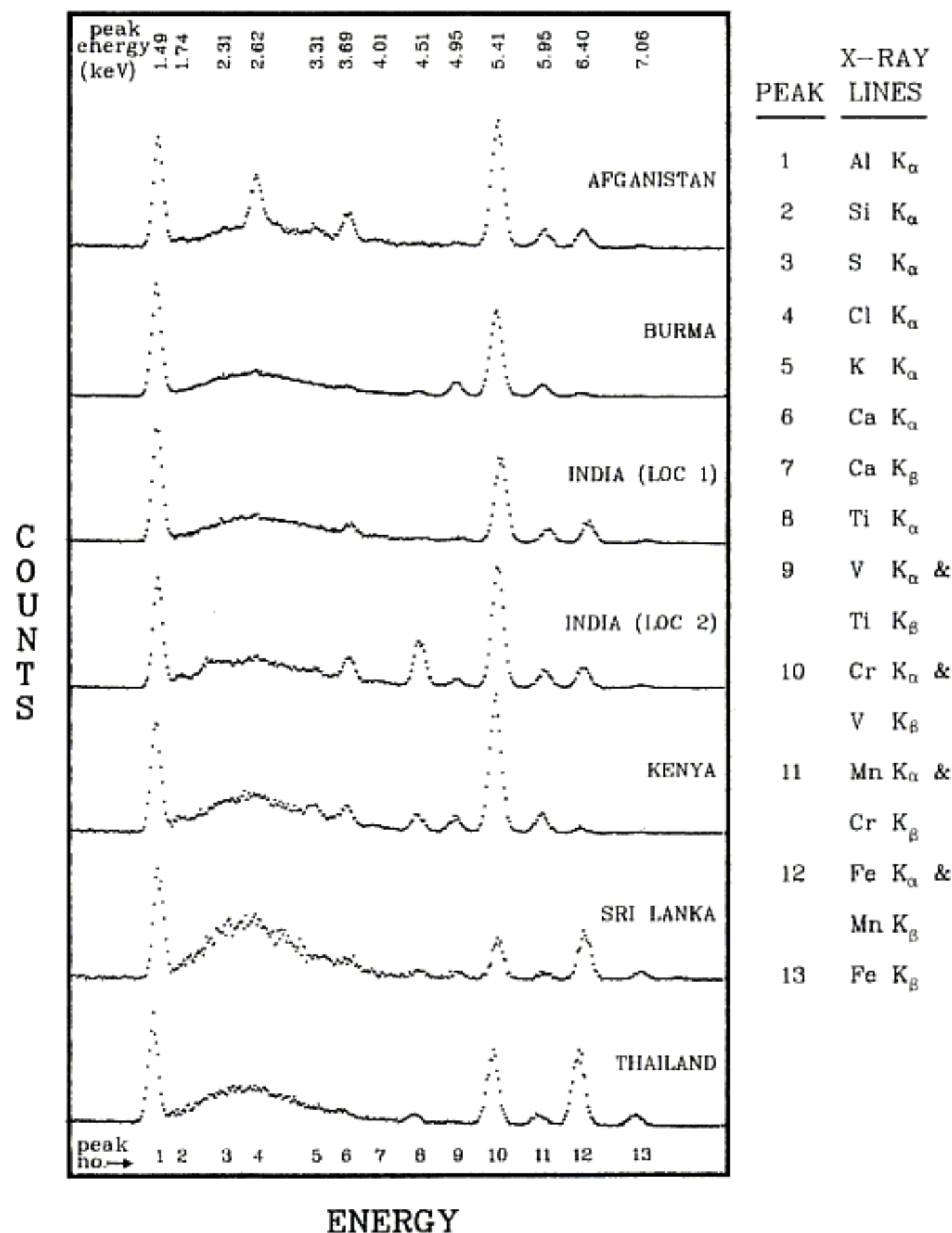


FIG. 1. X-ray spectra of seven natural rubies of different origins.

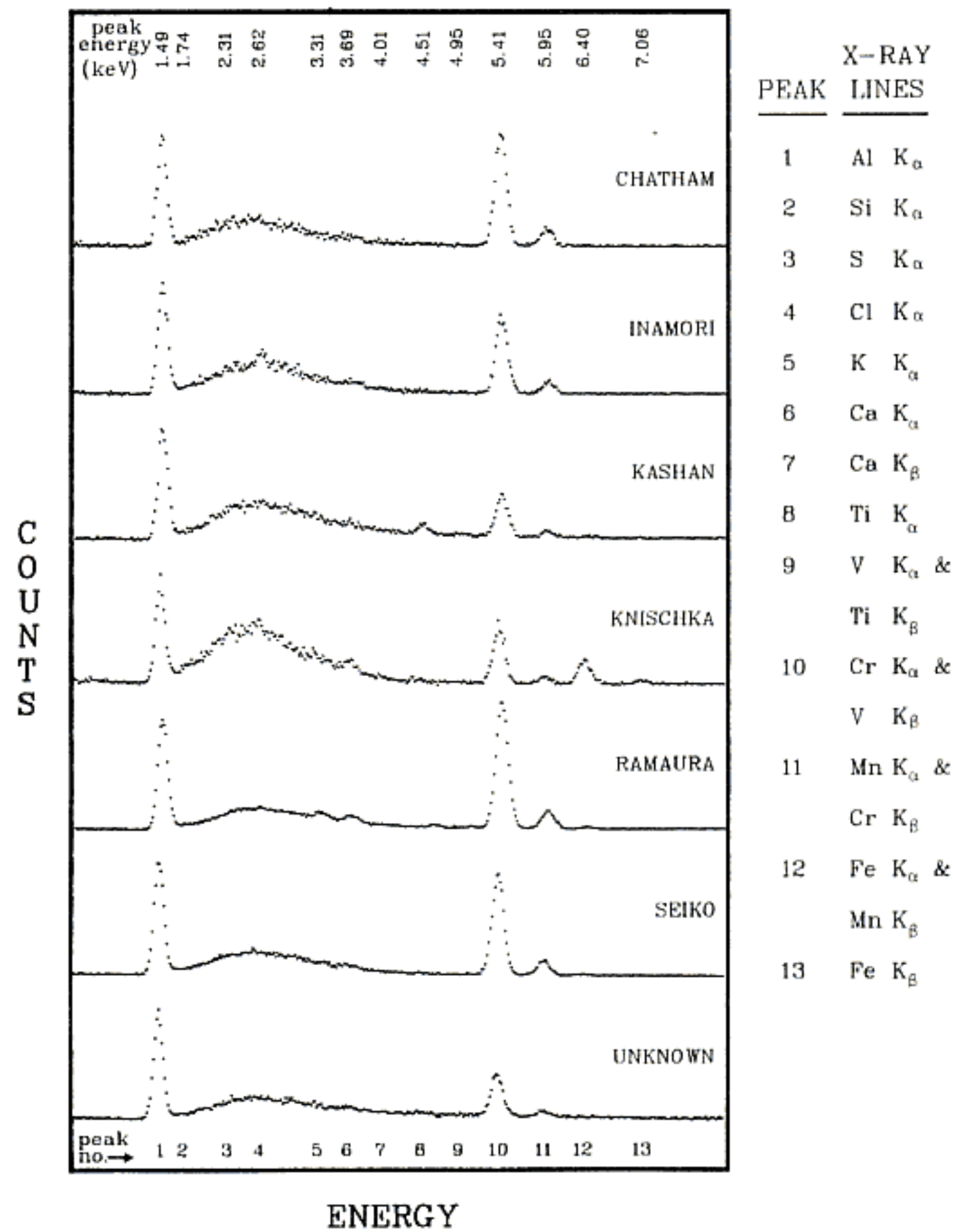


FIG. 2. X-ray spectra of seven synthetic rubies produced by different manufacturers.

five synthetics possessed identical gemological features and hence were believed to be of the same origin.

All the samples were cleaned with acetone before they were mounted on the sample ladder for measurement.

### QUALITATIVE OBSERVATIONS

Figure 1 shows the x-ray spectra of seven natural rubies from the various mentioned sources, and Fig. 2 also shows seven spectra of synthetics produced by different manufacturers. By comparing these two groups of spectra, one can readily conclude that synthetic rubies generally contain fewer and lower concentrations of impurities than do their natural counterparts. Most of the natural samples were found to contain more than ten trace elements with observable concentrations. Aside from Cr, these trace elements included Si, Cl, S, K, Ca, Ti, V, Mn, Fe, and Ga. On the other hand, our measurements also revealed that the Chatham, Inamori, Seiko, and "Unknown" synthetic samples contained no significant amount of any trace element except chromium. The Knischka sample had a relatively high iron concentration, and all the Kashan synthetics exhibited a prominent titanium peak.

The most striking fact revealed by our measurements was that all the synthetic samples contained no observable amount of vanadium, and yet this element was detected in all of the natural rubies, except some of those from Thailand and India. The vanadium detection limit of our experimental setup was 20 ppm in the absence of titanium.

Another interesting observation was that all the syn-

thetic rubies had low concentrations of iron, except the Knischka sample. However, all the Thai rubies and some of the Sri Lanka samples contained a much larger amount of iron than did the rest of the natural rubies.

### QUANTITATIVE ANALYSIS

The quantitative analysis of the spectra was achieved in the same manner reported earlier,<sup>9</sup> with the use of the program AXIL<sup>17</sup> (Analysis of X-ray spectra by Iterative Least-squares fitting; Version 04) to obtain the intensi-

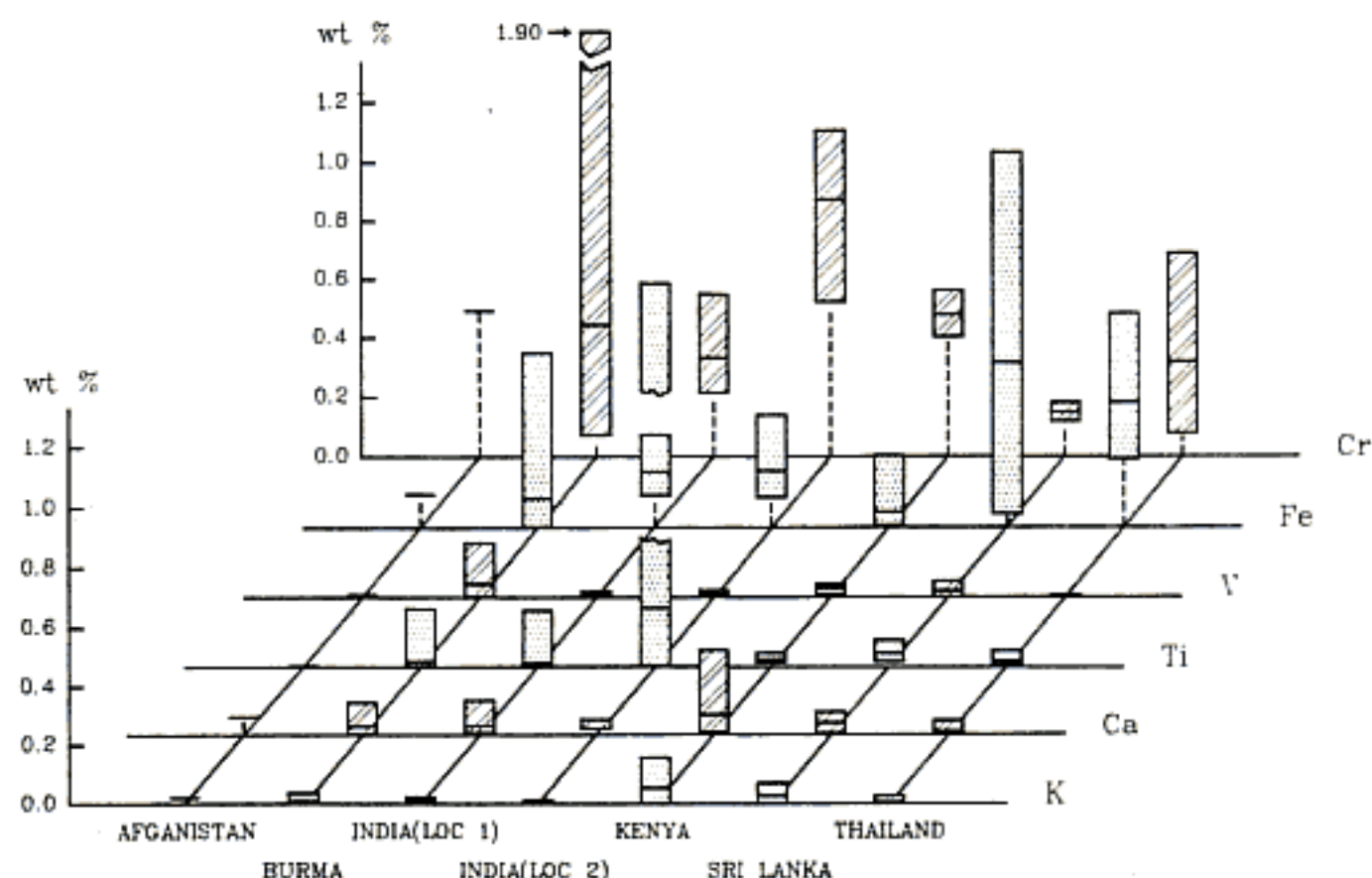


FIG. 3. Ranges of concentrations of the trace elements K, Ca, Ti, V, Fe, and Cr observed in 133 natural rubies from seven different sources. The mean concentration is indicated by the line within the bar.

TABLE II. Average concentrations (in wt % w.r.t. Al<sub>2</sub>O<sub>3</sub>) of K, Ca, Ti, V, Cr, and Fe in 160 natural and synthetic rubies from 14 different sources. The values in parentheses are one standard deviation of the mean concentration.

Origin	Quantity	K	Ca	Ti	V	Cr	Fe
Natural							
Afghanistan	1	0.018	0.063	0.004	0.010	0.490	0.109
Burma	40	0.010 (010)	0.030 (022)	0.021 (032)	0.046 (035)	0.439 (314)	0.098 (122)
India (Loc 1)	28	0.009 (006)	0.033 (024)	0.013 (035)	0.011 (005)	0.359 (084)	0.182 (065)
India (Loc 2)	10	0.006 (004)	0.036 (012)	0.200 (402)	0.009 (006)	0.870 (213)	0.187 (083)
Kenya	10	0.053 (047)	0.069 (091)	0.026 (013)	0.031 (012)	0.476 (051)	0.049 (069)
Sri Lanka	5	0.027 (028)	0.044 (030)	0.046 (032)	0.019 (022)	0.148 (029)	0.545 (459)
Thailand	39	0.006 (006)	0.013 (011)	0.019 (011)	0.002 (002)	0.314 (111)	0.413 (108)
Synthetic							
Chatham	7	... <sup>a</sup>	0.008 (004)	0.004 (002)	...	0.528 (087)	0.006 (003)
Inamori	2	...	0.007 (002)	...	...	0.303 (003)	...
Kashan	6	0.012 (010)	0.030 (023)	0.034 (016)	...	0.163 (075)	0.031 (019)
Knischka	1	...	0.011	0.005	...	0.247	0.159
Ramaura	5	0.008 (006)	0.010 (008)	0.002 (001)	...	0.329 (286)	0.037 (046)
Seiko	1	...	0.005	0.002	...	0.386	0.006
Unknown	5	...	0.006 (006)	0.007 (001)	...	0.179 (013)	0.004 (004)

<sup>a</sup> Below detection limit.

ties of the x-ray peaks and a set of calibration standards to measure our system's detection efficiencies for various elements relative to that of aluminium. Table II shows the average concentrations (in wt % w.r.t. Al<sub>2</sub>O<sub>3</sub>) of those elements that appear to have some relationship to the samples' origin. The values enclosed in the brackets are one standard deviation of the mean concentration. These values reflect the range of concentration variation among samples of the same origin. The actual extent of variation of each of these elements is also shown in Fig. 3 for the natural rubies and in Fig. 4 for the synthetic specimens.

The mean chromium concentrations varied considerably for the natural as well as the synthetic rubies. The range extended from 0.15 wt % to 0.87 wt %. However, the concentration variation of this element among samples of the same origin was surprisingly small in many cases. For example, among the seven Chatham synthetics, the lowest chromium concentration was 0.45 wt % and the highest was 0.66 wt %. This observation suggests that the concentration of chromium could be used as an indicator to separate rubies of some sources from those of others.

The Burmese rubies had the highest mean vanadium concentration among all the natural samples. One of them

contained as much as 1800 ppm. Thai specimens, on the other hand, had the smallest mean vanadium concentration. While the absence of vanadium in a ruby does not imply that the ruby is a synthetic, the presence of vanadium in a ruby is a strong indication that the ruby is a natural one.

It is obvious that source identification cannot be based on the concentration of a single trace element. But the concentrations of several trace elements together could be used to derive useful information. Suppose a ruby is found to be very rich in iron content (say, in the region of 4000 ppm); then our results suggest that it is either from Sri Lanka or Thailand. If the ruby also contains less than 1500 ppm of chromium and more than 100 ppm of vanadium, the ruby is very likely to be a Sri Lanka ruby.

## DISCUSSION

Undoubtedly, PIXE is a useful and fast technique for gemstone identification. The results of our investigation show that the origin of a ruby has some bearing on the concentrations of certain trace elements. Vanadium and iron concentrations are good indicators for separating natural rubies from synthetics. Others, such as the concentrations of chromium, titanium, calcium, and potassium, can in some cases be of help in source identification. In principle, it would be useful and desirable to build up a data base on trace-element concentrations by examining a large number of samples of known origins. This approach may, however, lead to a more perplexing problem in separating synthetic rubies from the natural ones in the future, as the synthetic stone manufacturers could modify the compositions of their products.

Trace-element analysis of some natural and synthetic rubies using the energy-dispersive x-ray fluorescence method<sup>5</sup> and by neutron activation<sup>8</sup> has been reported in the literature. Our results are in good agreement with those published.

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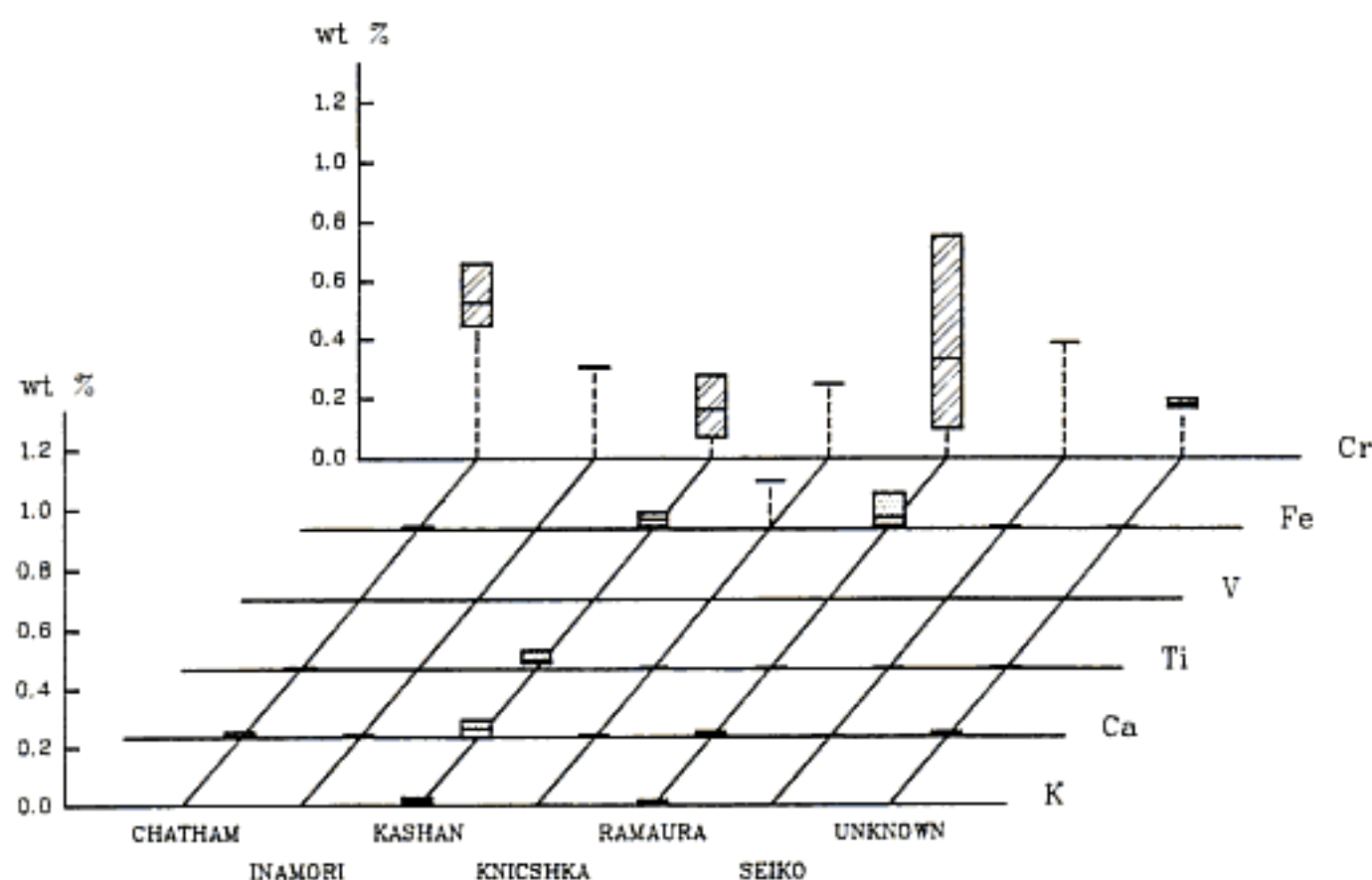


FIG. 4. Ranges of concentrations of the trace elements K, Ca, Ti, V, Fe, and Cr observed in 27 synthetic rubies produced by seven manufacturers. The mean concentration is indicated by the line within the bar.

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