Analysis of Burmese and Thai Rubies by PIXE

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Trace element analysis of 60 Burmese and Thai rubies by using the technique of proton-induced x-ray emission was carried out. It was found that the Burmese rubies contained higher concentrations of all impurities except iron. Our results also reveal that vanadium and iron are useful indicators for Burmese and Thai ruby attribution. The Thai rubies have high contents of iron and very low concentrations of vanadium. On the other hand, all the Burmese rubies examined contain significant amounts of vanadium, and their iron contents are, on the average, four times lower than those in the Thai rubies.

Index Headings: **Proton-induced x-ray emission; Gemstones.**

INTRODUCTION

Burma and Thailand are the major sources of natural rubies. One of the two methods which have been used to distinguish the Burmese ruby from the Thai ruby is the examination of their colors. Colors of Burmese rubies range from pale pinkish red to deep red, and some fine-quality but rare Burmese rubies have a vivid "pigeon's blood" color.[1] Thai rubies exhibit color variations from strongly violet to deep crimson[2] but typically have brownish to purplish overtones. Identification of these rubies by their colors can be subjective and may not always be reliable. The other method employed by gemologists and experienced gem dealers is to look at the ruby inclusions by using a microscope. Many Burmese rubies contain crystalline inclusions of rutile, spinels, or calcite rhombs;[3] some exhibit short rutile needles arranged in prismatic patterns,[4] while others have a growth structure with a "heatwave effect" appearance.[4] The most common inclusions in Thai rubies are subhexagonal to rounded opaque metallic grains of pyrrhotite, yellowish hexagonal platelets of apatite, and reddish brown almandite garnets.[5,6] These inclusions are usually surrounded by circular feathers and polysynthetic twinning planes.[7] Excellent illustrations and discussion of inclusions in gemstones can be found in a recent book by Gubelin and Koivula.[8] While a conclusive identification can usually be achieved by examining the inclusions, problems may still arise from the lack of characteristic inclusions or the absence of any inclusion in some rubies.

The characteristic color and inclusion of rubies from a certain source are obviously linked to the source's geology. Most Burmese rubies are mined mainly in and around the Mogok region. The geology of this area is very complex, comprising mainly high-grade metamorphic schists and gneisses, granite intrusives, and the ruby-bearing metamorphic marble. Rubies from this region are chrome-rich, and this factor is believed[1] to give rise to the "pigeon's blood" color. The majority of the Thai rubies are mined from alluvial deposits in the Chanthaburi-Trat district. These secondary gem deposits come from weathered basaltic dykes formed in the early and middle Tertiary Orogenic period[9] and have an iron-rich nature. The brownish to purplish overtones of the Thai rubies have been attributed to their characteristically high concentrations of iron.[2]

Since some Burmese and Thai rubies cannot be identified by either color or inclusions, there is a need to search for additional criteria by which to distinguish them. This article reports the results of our attempt to develop such criteria by deploying the technique of proton-induced x-ray emission to analyze quantitatively the contents of chromium and iron as well as other trace elements in a sizable quantity of Burmese and Thai rubies.

EXPERIMENTAL

The measurements were made with the use of 2 MeV protons produced from the 2.5 mV Van de Graaff accelerator at the National University of Singapore. The proton beam was collimated with a set of diaphragms that gave a beam spot of 4 mm diameter at the target position. Throughout the experiment, the proton beam was maintained at an average value of about 8 nanoamperes. A Si(Li) detector with a sensitive area of 36 mm^2 and a 0.007-mm-thick beryllium window was used for obtaining the x-ray spectra. The detector was placed outside the sample chamber against a 0.036-mm-thick hostaphan window of the chamber and at an angle of 90° to the beam. A manually operated sample ladder of 220 mm total displacment length was used for sample mounting. Ten samples can be mounted on the ladder simultaneously. The samples were supported with adhesive tape that was free from interfering impurities. The counting time for each sample was 150 s.

The Samples. A total of 60 samples were studied. Twenty-nine of them were Burmese rubies purchased from several ruby wholesale markets in Thailand. The rest were obtained directly from gem cutters in Chanthaburi and hence were believed to be rubies mined around that area. The samples were examined by two of the authors, Tay and Retty (gemologists and experienced gem dealers), prior to the experiment. The origins of the majority of the samples could be identified by their colors and inclusions. Thirty-one of these showed a medium dark purple-brownish red color—a typical color for Thai rubies. Among these thirty-one samples, twenty-eight had characteristic Thai ruby inclusions such as crystal pyrrhotite and polysynthetic twinning planes. The other twenty-nine samples exhibited Burmese ruby characteristics, displaying a light-to-medium pinkish red color and containing rutile needles, spinel crystals, or heat-wave-

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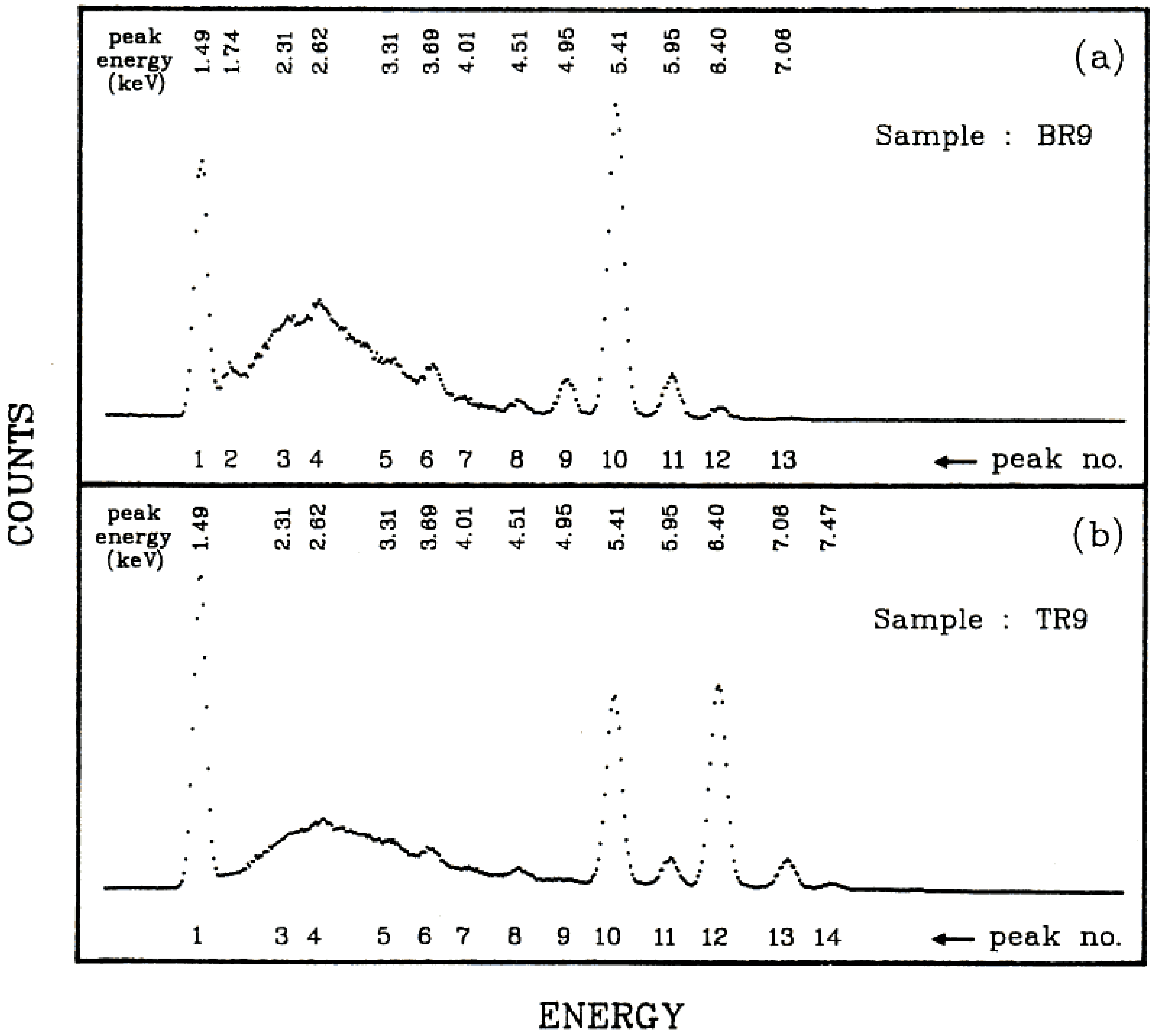

PEAK	X-RAY LINES
1	Al K_α
2	Si K_α
3	S K_α
4	Cl K_α
5	K K_α
6	Ca K_α
7	Ca K_β
8	Ti K_α
9	V K_α + Ti K_β
10	Cr K_α + V K_β
11	Mn K_α + Cr K_β
12	Fe K_α + Mn K_β
13	Fe K_β
14	Ni K_α

FIG. 1. Typical x-ray spectra of the Burmese (a) and the Thai (b) rubies obtained by 2 MeV proton excitation.

effect inclusions. Hence, of the sixty samples, three could not be definitely identified by their inclusions. All samples were cleaned with acetone to remove any surface contamination before they were placed in the sample chamber for measurement.

Qualitative Characteristics. Over ten trace elements were observed in varying concentrations in all of the samples studied. The more prominent ones were Cr and Fe. Those present in less abundance but in most samples were Si, S, Cl, K, Ca, Ti, V, and Mn. An observable amount of Ga was found in many samples. Other elements detected in some of the rubies included Ni, Cu, and Zn. Figure 1a and 1b show, respectively, the typical x-ray spectra of the Burmese and the Thai rubies. The striking differences between them are the apparent presence of the V K_α peak in the former and the relatively high Fe K_α line in the latter.

The existence of the V K_α peak in all the spectra of the Burmese rubies is obvious by visual inspection, despite the presence of the interfering Ti K_β line. On the other hand, all except one of the Thai rubies have very low vanadium contents, and none of their spectra show a distinct V K_α peak.

Generally, the Thai rubies have higher iron concentrations than the Burmese rubies. However, their ranges of concentration do overlap. For a qualitative analysis of the spectra, it is convenient to compare the Fe K_α intensity with the intensity of the neighboring Cr K_α line. The intensity ratio $R = I(\text{Fe } K_\alpha)/I(\text{Cr } K_\alpha)$ is below 0.3 for more than two-thirds of the Burmese samples. Over two-thirds of the Thai rubies, however, have R values greater than 0.7. The frequency distribution of such intensity ratios for each of the two groups of samples is shown in Fig. 2. It can be seen that no Burmese sample has an $I(\text{Fe } K_\alpha)/I(\text{Cr } K_\alpha)$ ratio greater than 0.7.

The only Thai sample that was found to contain a relatively high vanadium concentration was also found to have the lowest iron content of all the Thai rubies. In fact, the x-ray spectrum of this sample exhibits the typical feature observed in the spectra of the Burmese rubies. This sample is also one of those which cannot be attributed definitely by its color and inclusions. Therefore, it is highly possible that the sample is of Burmese origin. It is not uncommon that gemstones are brought from Burma to Chanthaburi, because gem trading is much more active there. If this particular sample is indeed a Burmese ruby, then our results show that the distinction between the Burmese ruby and the Thai ruby can be based on their vanadium and/or iron contents.

Quantitative Analysis. The program AXIL[10] (Analysis of X-ray spectra by Iterative Least-squares fitting, version 04) was used on a PRO350 DEC microcomputer to determine the integrated counts of the x-ray peaks. The factors for converting the integrated counts to concentrations were obtained by means of calibration standards. Since rubies are corundum and contain 96–99%[11]

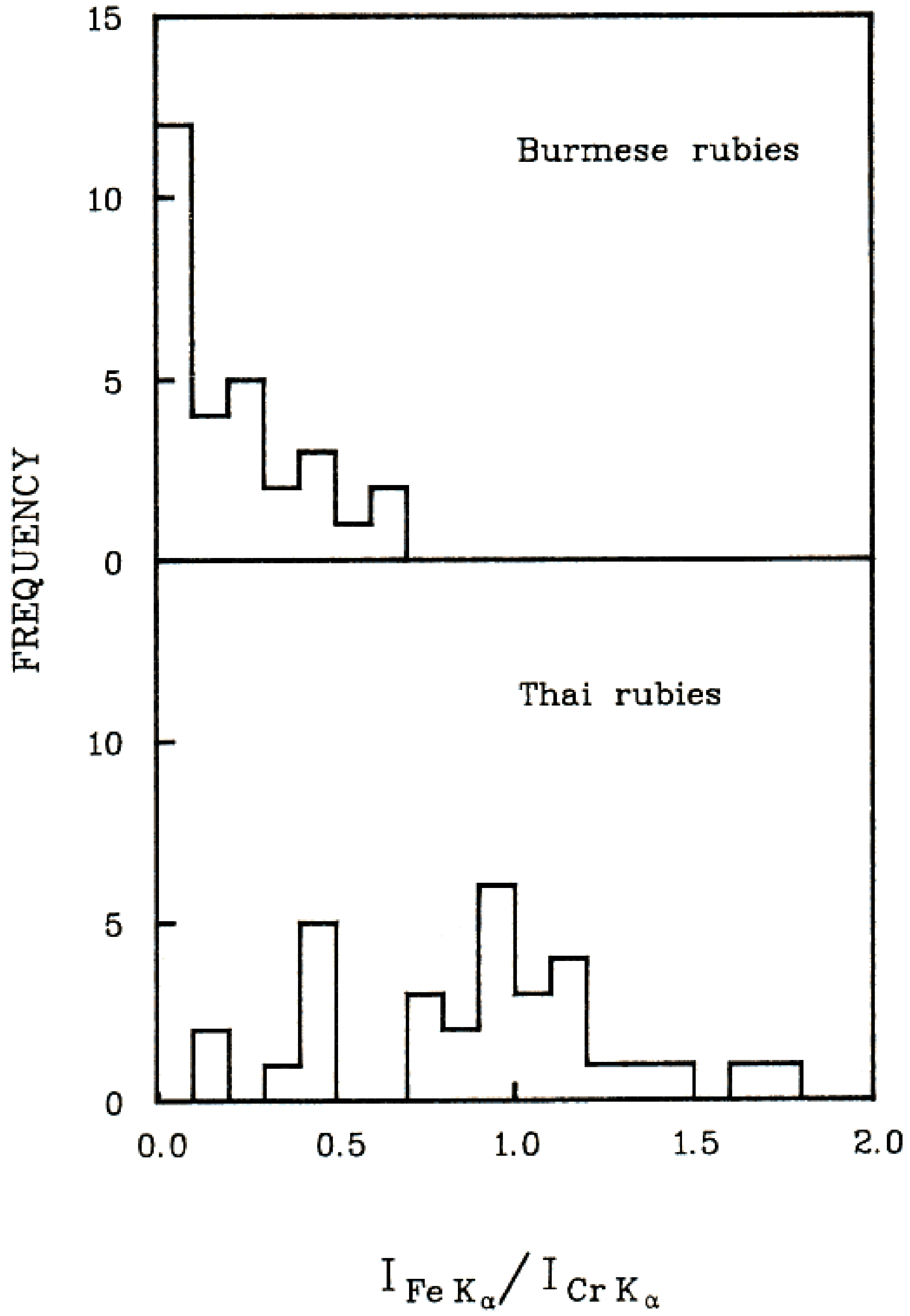

FIG. 2. Frequency distributions of the Fe K_α intensity to Cr K_α intensity ratio for the Burmese and the Thai rubies.

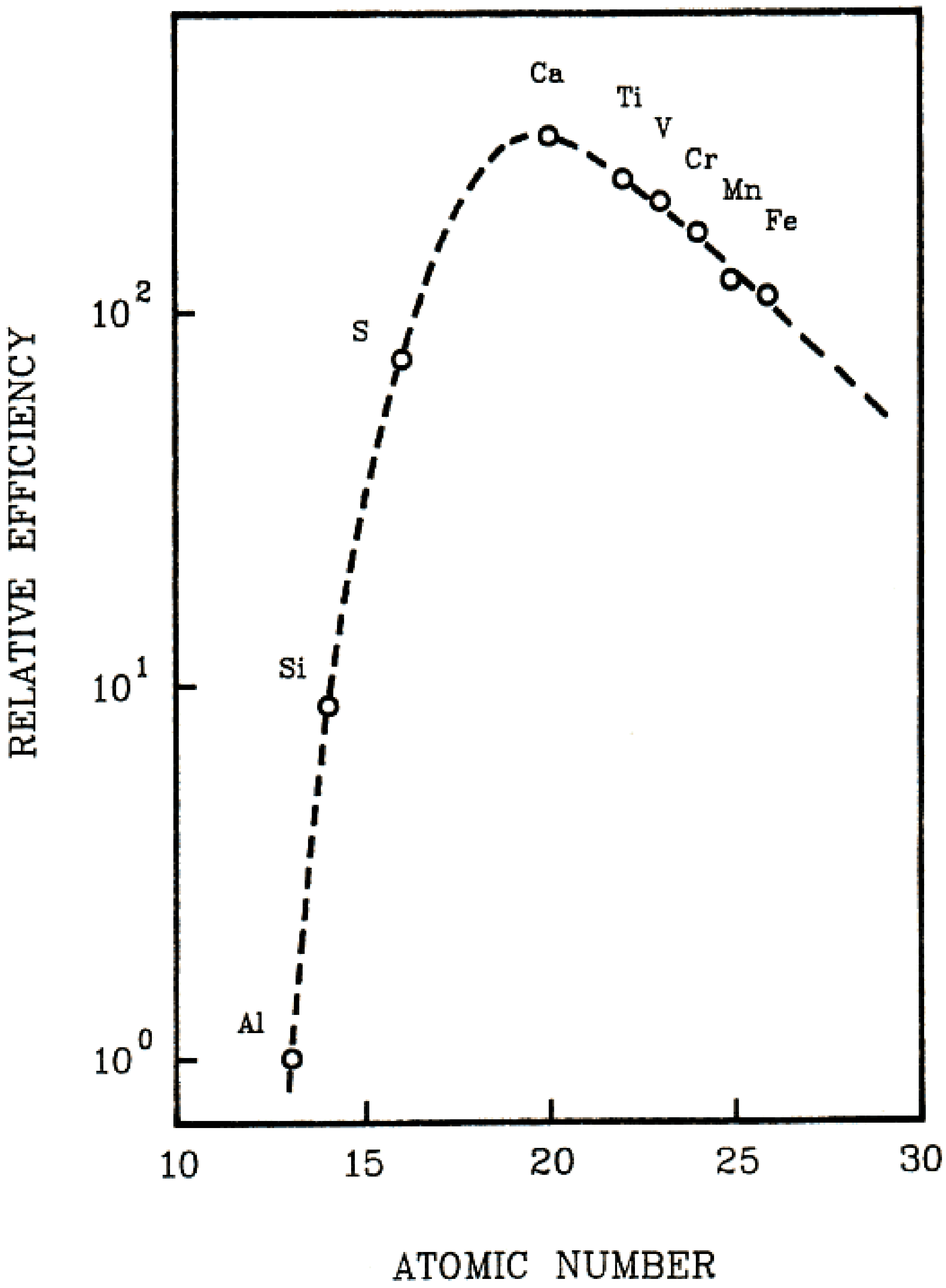

FIG. 3. Relative detection efficiency curve obtained with calibration standards.

Al_2O_3, our calibration standards were made with the use of Al_2O_3 powder as the matrix. Several standards were prepared in duplicate, each containing 2–3% of two or three of the following elements and compounds : Si, S, $CaCO_3$, TiO_2, V_2O_5, CrO_3, MnO_2, and Fe_2O_3. The elements and compounds used to prepared the standards were of AR grade and in fine powder form. They were mixed thoroughly with the Al_2O_3 matrix and some starch before being hydraulically pelletized at 190,000 psi. These calibration standards weighed about 1 gram each and had a diameter of 12 mm. Starch was used as a binder. It was found that an aluminum oxide pellet could crack easily if less than 10% starch was added. We had made an experimental investigation and found that adding up to 25% of starch in making the standards would not result in any significant effect on the calibration. The calibration curve obtained with the standards is shown in Fig. 3. It is a plot of relative detection efficiency of the system vs. atomic number. Aluminum is taken as the reference and assigned a relative efficiency of 1.

Tables I and II give the concentrations of those trace elements observed in most of the samples. Other minor trace elements observed, namely Ni, Cu, Zn, and Ga, were not included in these tables, since they were present only in some of the samples and in relatively low concentrations. The sample that has a high content of vanadium and was originally presumed to be a Thai ruby is now included in the Burmese group and labeled as sample BR30 in Table I. The concentrations are expressed in wt % with respect to Al_2O_3. The average concentration for each element is also shown. These results show that, on the average, the Burmese rubies contain higher concentrations of all impurities except iron. In addition to vanadium, which has already been mentioned, silicon and chromium are also present, at significantly higher concentrations in the Burmese rubies than in the Thai rubies. However, concentrations of these elements vary substantially among individual samples within each species.

The element Ga was observed in 19 Burmese samples, with concentrations varying from 0.003% to 0.010%. Among the Thai samples, only 6 showed the presence of Ga in concentrations between 0.001 and 0.003%.

A two-dimensional plot of vanadium concentrations and iron concentrations in the Burmese and the Thai rubies is presented in Fig. 4. This plot clearly shows that data obtained with the Thai rubies form a cluster in the region bounded by $C_v = 0.02$ and $C_{Fe} = 0.2$ (dotted line).

DISCUSSION

Our results reveal some important characteristics of the Burmese and the Thai rubies. A selection of 60 samples is deemed sufficient for establishing a preliminary

TABLE I. Trace elements in the Burmese rubies (in wt % w.r.t. Al_2O_3).

Sample	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
BR1	1.091	0.072	0.064	0.035	0.051	0.021	0.062	0.627	0.005	0.075
BR2	0.645	0.010	0.043	0.023	0.030	0.016	0.086	0.708	0.012	0.019
BR3	0.877	0.054	0.048	0.013	0.039	0.026	0.112	0.406	0.011	0.026
BR4	1.084	0.026	0.073	0.027	0.042	0.017	0.040	0.342	0.006	0.020
BR5	0.727	0.010	0.036	0.010	0.029	0.008	0.023	0.386	0.003	0.012
BR6	0.804	0.004	0.032	0.005	0.034	0.013	0.016	0.631	0.009	0.006
BR7	0.653	0.005	0.029	0.003	0.024	0.007	0.029	0.489	0.007	0.015
BR8	0.363	0.000	0.017	0.006	0.017	0.011	0.055	0.412	0.006	0.031
BR9	0.549	0.022	0.028	0.006	0.019	0.012	0.045	0.469	0.007	0.026
BR10	0.994	0.004	0.071	0.020	0.039	0.017	0.057	0.353	0.006	0.028
BR11	0.016	0.087	0.019	0.026	0.042	0.005	0.024	0.148	0.003	0.046
BR12	0.046	0.028	0.015	0.011	0.016	0.003	0.006	0.082	0.001	0.056
BR13	0.152	0.042	0.024	0.005	0.018	0.033	0.019	0.275	0.004	0.089
BR14	0.007	0.013	0.009	0.005	0.008	0.006	0.027	0.233	0.002	0.074
BR15	0.188	0.152	0.037	0.038	0.114	0.020	0.015	0.103	0.002	0.057
BR16	0.000	0.011	0.004	0.004	0.008	0.098	0.012	0.076	0.001	0.068
BR17	0.111	0.007	0.008	0.005	0.009	0.015	0.003	0.077	0.002	0.082
BR18	0.045	0.021	0.013	0.009	0.015	0.014	0.043	0.070	0.000	0.068
BR19	0.036	0.031	0.011	0.007	0.017	0.008	0.029	0.134	0.003	0.065
BR20	0.094	0.041	0.046	0.013	0.031	0.017	0.051	0.820	0.010	0.262
BR21	0.001	0.193	0.043	0.005	0.053	0.063	0.041	0.686	0.012	0.075
BR22	0.251	0.088	0.081	0.026	0.054	0.026	0.059	0.632	0.014	0.451
BR23	0.324	0.057	0.038	0.013	0.035	0.013	0.048	0.726	0.003	0.241
BR24	0.028	0.022	0.083	0.035	0.064	0.018	0.047	0.751	0.022	0.338
BR25	0.731	0.157	0.096	0.024	0.099	0.037	0.182	2.262	0.062	0.581
BR26	0.197	0.030	0.038	0.005	0.056	0.011	0.026	0.333	0.006	0.242
BR27	0.127	0.015	0.017	0.001	0.063	0.008	0.025	0.613	0.011	0.107
BR28	0.247	0.167	0.034	0.011	0.043	0.010	0.039	0.494	0.014	0.116
BR29	0.057	0.009	0.007	0.003	0.044	0.013	0.086	0.620	0.012	0.079
BR30	0.093	0.009	0.013	0.010	0.019	0.196	0.136	1.903	0.043	0.293
Avg.	0.351	0.046	0.036	0.013	0.038	0.025	0.048	0.529	0.010	0.122

criterion to differentiate rubies from these two regions. The main question is exactly where the line of boundary in Fig. 4 should be. The level of confidence in any boundary established can be increased only by further study of more samples. Nevertheless, vanadium and iron are definitely useful indicators for distinguishing the Burmese ruby from the Thai ruby.

Trace element analysis has been used for many years

TABLE II. Trace elements in the Thai rubies (in wt % w.r.t. Al_2O_3).

Sample	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
TR1	0.000	0.011	0.017	0.005	0.012	0.011	0.002	0.292	0.004	0.412
TR2	0.085	0.003	0.012	0.006	0.008	0.013	0.002	0.517	0.009	0.309
TR3	0.028	0.005	0.007	0.004	0.006	0.011	0.002	0.382	0.006	0.274
TR4	0.036	0.053	0.007	0.003	0.004	0.009	0.002	0.231	0.005	0.339
TR5	0.097	0.000	0.003	0.002	0.004	0.009	0.002	0.263	0.004	0.298
TR6	0.014	0.002	0.004	0.002	0.003	0.010	0.001	0.379	0.007	0.255
TR7	0.015	0.010	0.007	0.004	0.005	0.007	0.000	0.366	0.006	0.421
TR8	0.017	0.014	0.011	0.004	0.007	0.017	0.003	0.226	0.002	0.344
TR9	0.054	0.006	0.007	0.004	0.008	0.009	0.001	0.242	0.006	0.420
TR10	0.096	0.015	0.011	0.004	0.017	0.012	0.003	0.322	0.006	0.387
TR11	0.084	0.024	0.012	0.006	0.011	0.017	0.001	0.233	0.003	0.387
TR12	0.091	0.022	0.013	0.003	0.011	0.027	0.002	0.299	0.004	0.530
TR13	0.122	0.045	0.017	0.010	0.020	0.032	0.005	0.373	0.007	0.506
TR14	0.216	0.066	0.024	0.007	0.017	0.026	0.003	0.290	0.003	0.426
TR15	0.345	0.072	0.042	0.021	0.035	0.052	0.003	0.449	0.009	0.532
TR16	0.232	0.065	0.053	0.012	0.035	0.012	0.002	0.687	0.010	0.496
TR17	0.212	0.062	0.047	0.011	0.041	0.045	0.007	0.441	0.012	0.712
TR18	0.156	0.114	0.029	0.009	0.021	0.024	0.002	0.267	0.006	0.487
TR19	0.385	0.097	0.037	0.017	0.018	0.049	0.005	0.254	0.005	0.526
TR20	0.448	0.080	0.035	0.027	0.050	0.018	0.001	0.263	0.008	0.509
TR21	0.133	0.025	0.020	0.004	0.015	0.025	0.002	0.570	0.009	0.349
TR22	0.146	0.003	0.017	0.006	0.011	0.022	0.001	0.223	0.007	0.612
TR23	0.000	0.003	0.004	0.003	0.009	0.013	0.003	0.297	0.006	0.529
TR24	0.000	0.019	0.022	0.006	0.013	0.022	0.000	0.207	0.007	0.531
TR25	0.053	0.013	0.015	0.006	0.020	0.014	0.002	0.273	0.006	0.387
TR26	0.024	0.009	0.011	0.005	0.008	0.017	0.003	0.210	0.005	0.448
TR27	0.000	0.009	0.004	0.000	0.012	0.031	0.007	0.408	0.009	0.629
TR28	0.011	0.004	0.008	0.004	0.010	0.013	0.002	0.398	0.005	0.550
TR29	0.060	0.006	0.004	0.004	0.006	0.008	0.000	0.392	0.005	0.275
TR30	0.063	0.009	0.014	0.011	0.010	0.018	0.003	0.338	0.004	0.428
Avg.	0.108	0.029	0.017	0.007	0.015	0.020	0.002	0.336	0.006	0.444

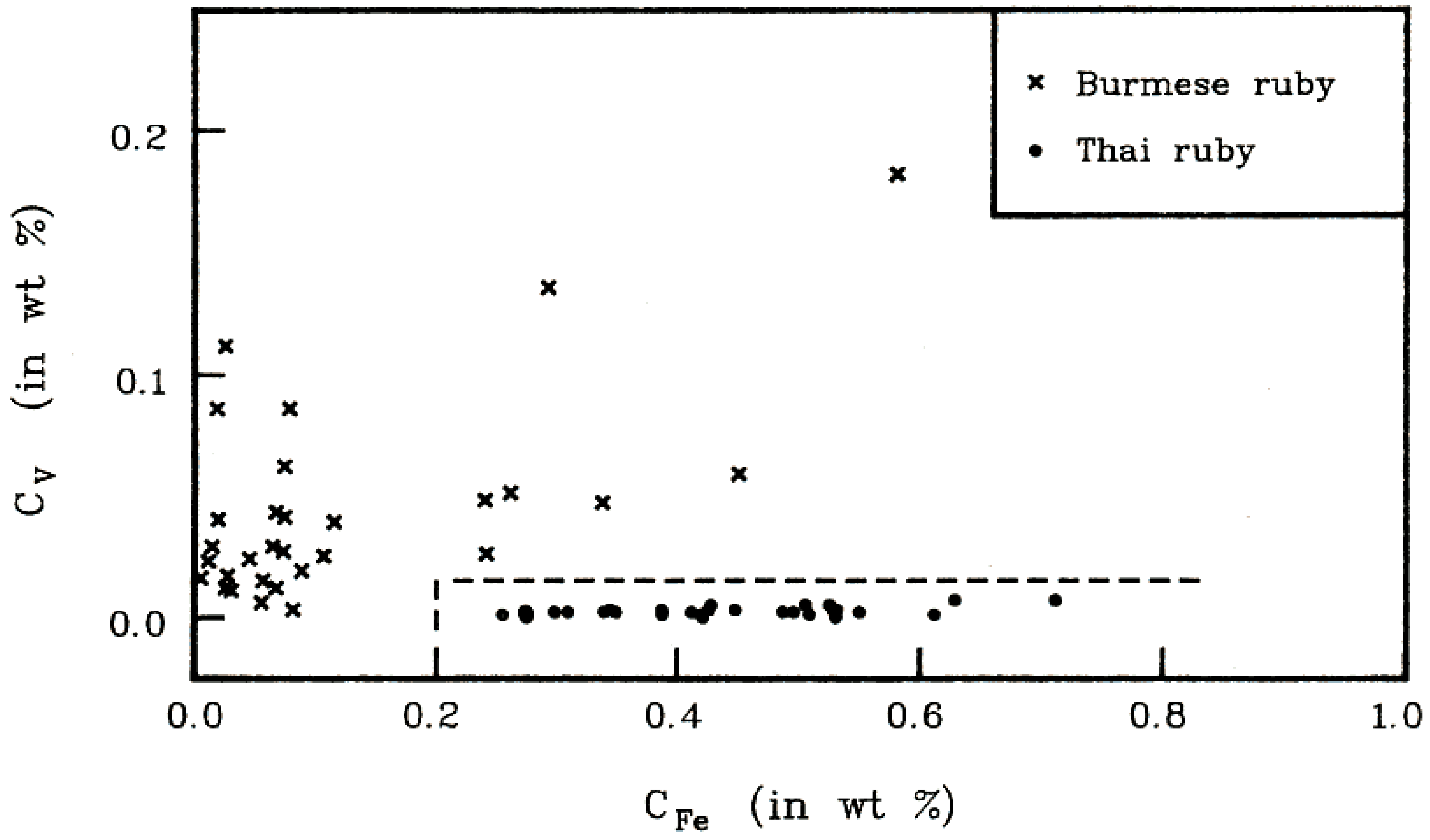

FIG. 4. Two-dimensional plot of vanadium concentrations and iron concentrations in the Burmese and the Thai rubies.

for gemstone identification, but mainly to distinguish natural stones from synthetic ones. Techniques which have so far been employed include neutron activation[12] and fluorescent x-ray analysis using scanning electron microscopes[13] or electron microprobes.[14] PIXE has been a well-established technique for elemental analysis for over a decade and has been applied in a great variety of studies, including the study of geologic materials.[15] To our best knowledge, however, this is the first time it has been used for gemstone analysis. It has an advantage over electron microscopy, in that there is no need to apply a conductive coating to the sample, and the surface of the sample need not be highly polished and flat. An advantage which PIXE has over neutron activation is that it does not render the sample radioactive.

Being a nondestructive technique, PIXE is very suitable for gemstone identification. The simplicity in sample preparation (requiring just cleaning and mounting) and the simultaneous multielement analyzing capability are its major advantages. In addition, its sensitivity is good. Concentrations in ppm level can easily be measured for many elements. However, like electron microscopy, PIXE can be used to study only the surface layers and not the interior of gemstones. Near-surface inclusions might sometimes result in misleading bulk concentration for a particular element.

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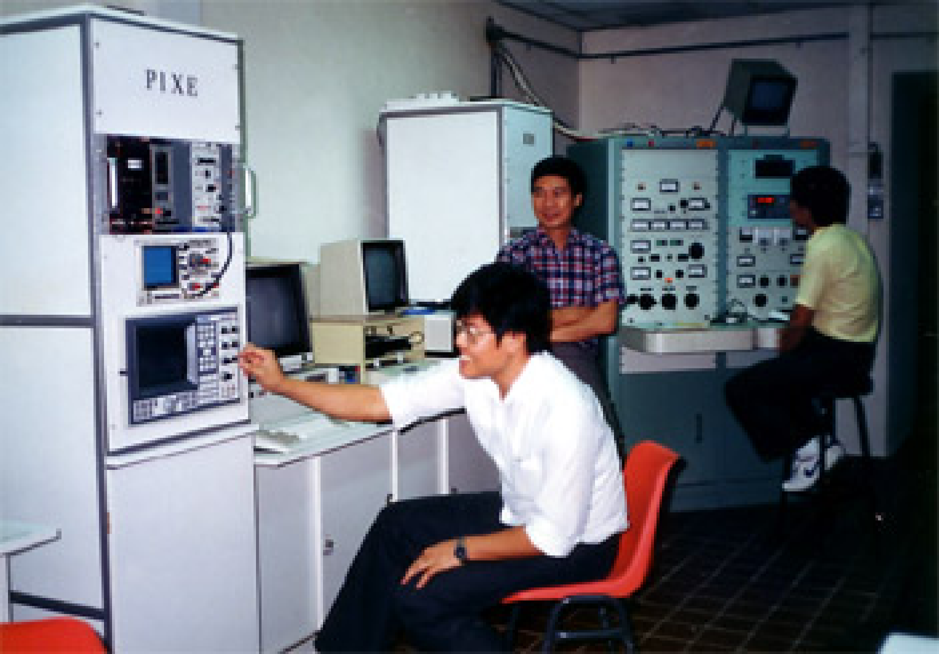
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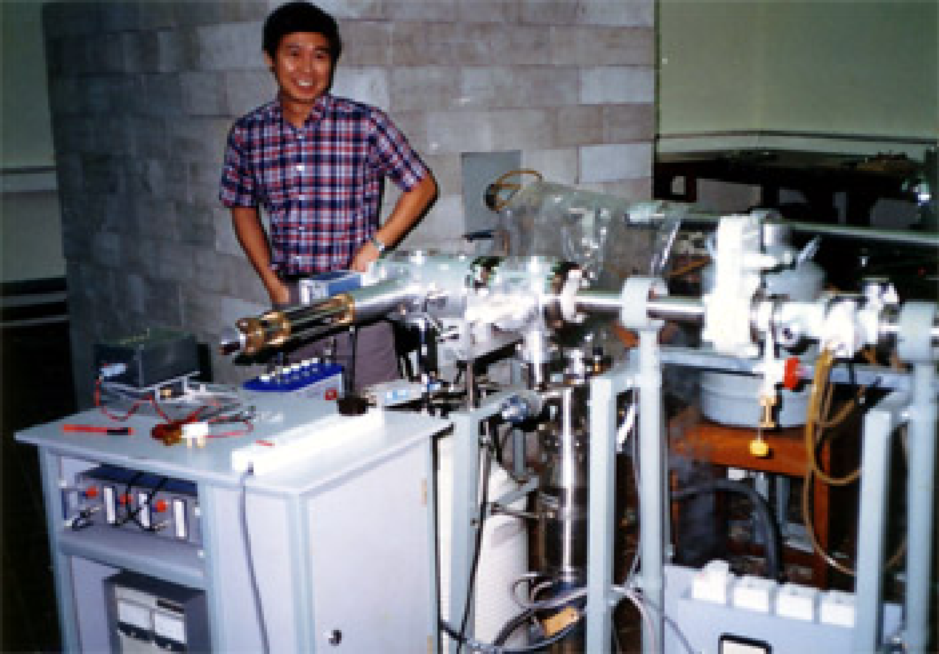


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