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Micro-PIXE analysis of trace element concentrations of natural rubies from different locations in Myanmar

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Abstract

The trace element concentrations found in geological samples can shed light on the formation process. In the case of gemstones, which might be of artificial or natural origin, there is also considerable interest in the development of methods that provide identification of the origin of a sample. For rubies, trace element concentrations present in natural samples were shown previously to be significant indicators of the region of origin [S.M. Tang et al., Appl. Spectr. 42 (1988) 44, and 43 (1989) 219]. Here we report the results of micro-PIXE analyses of trace element (Ti, V, Cr, Fe, Cu and Ga) concentrations of a large set ($n = 130$) of natural rough rubies from nine locations in Myanmar (Burma). The resulting concentrations are subjected to statistical analysis. Six of the nine groups form clusters when the data base is evaluated using tree clustering and principal component analysis. © 1997 Elsevier Science B.V.

1. Introduction

Traditionally, ruby of Myanmar comes from the Mogok district [3] 700 miles north of capital city of Yangon. In 1992, a new discovery of ruby was found in the Mong Hsu district [4–7] in the Shan state in north-eastern Myanmar. The authors acquired 135 samples of untreated rough natural rubies from nine locations. There are rubies from Mansi and Nayaseik from the Kachin state, Mohauk from near the Mogok stone tract region, Pyinmana in the southern part of the Mandalay Division, and Maingthauk, Pyinlon and Mong Hsu stones from the Shan state. The stones from Mong Hsu are listed in three groups: those found in Mong Hsu (Mong Hsu), those from a newly found deposit called Mong Hsu extension (Extension) [8] located 10 km north of Mong Hsu and finally those stones from the Mong Hsu main deposit which were found in host marble (Marble).

All the above rubies used in this study were found in metamorphic environments with different degrees of metamorphic overprint [6–9]. The complexity of the geology of Myanmar [10,11] and the diversity in the local geological environment lead to the large variability of the trace element concentrations found in these gemstones.

The mapping capability of the nuclear microscope was utilised to select areas free of inclusions or contaminations. The concentrations of the main trace elements (Cr, Ti, V, Fe, Cu and Ga) were then determined for all stones. Our aim was to determine whether trace element analysis is able to differentiate between rubies from different locations.

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2. Experimental

All the samples were mounted in resin, grounded and polished. Optical inspection was performed to find reasonably clean and inclusion free regions in all the rubies. Prior to the analysis, the samples were cleaned with acetone in an ultrasonic bath and carbon coated to prevent excessive charging.

The measurements were carried out using the nuclear microscope facility at the National University of Singapore [12]. A 1.9 MeV proton beam was focused down until a lateral resolution of 1–2 micron was achieved. The scan size in each sample was typically 200 μm. The current was kept below 500 pA to minimise dead time problems. RBS and PIXE spectra were simultaneously collected during all the measurements. The RBS data were taken with a detector placed at 160° with respect to the beam. PIXE spectra were measured with a SiLi detector of 150 eV resolution placed at 135°.

The data was stored in OMDAQ listmode files which allow off-line re-runs. This procedure allows the extraction of PIXE spectra from specific regions of the analysed area.

3. Data analysis

In the analysis the listmode files were used to generate elemental maps showing the intensity distribution of the X-rays from the main trace elements. This was done to exclude non-homogeneous regions so that finally spectra from homogeneous areas could be generated. The concentrations derived from these spectra are less biased by inclusions or surface contaminations of the gemstones [13]. Fig. 1 exemplifies and Table 1 shows the results of this procedure. After the analysis, 5 stones had to be discarded from the data base because a high level of surface contaminations prevented a meaningful analysis.

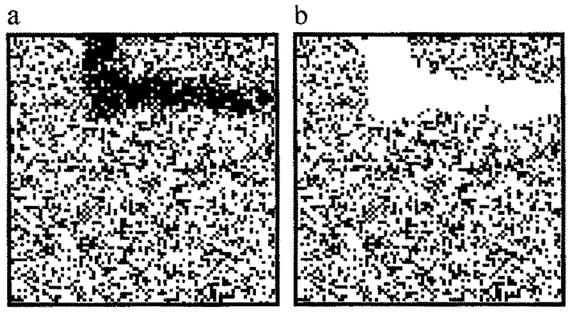

Fig. 1. (a) Elemental Fe map of Mong Hsu ruby showing Fe surface contamination in the upper right. Scan size was 200 μm. (b) Part of the map from (a) that is used to generate the PIXE spectrum.

Table 1
Concentrations of trace elements in weight-ppm from the PIXE spectra derived from the maps in Fig. 1a and b

	Fig. 1a	Fig. 1b
Ti	364 (6)	377 (6)
V	613 (10)	610 (9)
Cr	6493 (68)	6428 (30)
Fe	40 (2)	9 (2)
Cu	65 (3)	5 (3)
Ga	102 (5)	103 (6)

All final spectra were analysed using the data analysis package NUSDAN [14]. This program combines the backscattering simulation program RUMP [15] (for total charge determination) and the PIXE analysis code GUPIX [16]. The uncertainty of the derived concentrations was estimated to be ±10% from measurements of NBS glass standard (NBS 610).

4. Results

Table 2 shows the means and the ranges of concentrations for the principal trace elements. The number of samples for each location and typical detection limits are also given.

The results show that large variations of the trace element concentrations are present between stones from different locations and also in stones from one locality. Only one element, Ga, has a consistent concentration distribution throughout all groups of stones, closely following a standard distribution.

However, some elemental concentrations seem to differentiate stones from different locations. The V concentration separates the Marble and Mansi rubies (concentration below 124 ppm) from Pyinmana (concentrations above 147 ppm). The Ti concentrations are higher in Marble (concentration above 147 ppm) than in Nayaseik (concentration below 124 ppm).

Table 2
Number of samples, means, ranges and typical detection limits (DLs) of concentrations in weight-ppm for the nine locations

	No. of samples	Ti	V	Cr	Fe	Cu	Ga
Extension	8	508 (1325-34)	107 (172-76)	4060 (5729-2267)	41 (52-33)	< DL (5- < DL)	80 (87-66)
Mansi	20	424 (1116-41)	76 (124-30)	502 (895-112)	613 (1347-19)	9 (27- < DL)	120 (180-52)
Maingthauk	6	203 (487-48)	224 (322-67)	1648 (2746-308)	76 (110-46)	35 (146- < DL)	92 (127-33)
Marble	5	631 (1133-147)	84 (120-43)	13626 (20597-9479)	13 (17-10)	< DL (9- < DL)	65 (74-55)
Mong Hsu	45	849 (3571-67)	358 (1003-87)	4868 (12729-1346)	38 (125-7)	15 (85- < DL)	76 (122-29)
Mohauk	6	42 (158-13)	129 (214-84)	1338 (1950-749)	380 (453-259)	251 (669-85)	89 (117-66)
Nayaseik	3	75 (124-38)	144 (223-61)	1750 (2323-1048)	40 (45-36)	< DL	46 (54-40)
Pyinmana	20	267 (1260-102)	338 (630-147)	3812 (7503-1085)	100 (213-32)	2 (24- < DL)	70 (124-31)
Pyinlon	17	202 (310-96)	413 (662-105)	4373 (8298-1598)	112 (220-43)	74 (127-31)	61 (120-29)
Detection limit		3	5	5	2	2	2

The Cu concentration can be used as a discriminator between the rubies from Mohauk and Pyinlon (concentration above 31 ppm) and Nayaseik, Marble, Mansi, Pyinmana and Extension (concentrations below 27 ppm). The Fe concentration can tentatively be used to divide the rubies in three sets, those below 17 ppm (Marble), those between 32–220 ppm (Extension, Nayaseik, Maingthauk, Pyinmana and Pyinlon) and those higher than 259 ppm (Mohauk). The Cr concentration also divides the rubies in three groups, those below 895 ppm (Mansi), those between 1048–8298 ppm (Extension, Nayaseik, Pyinmana and Pyinlon) and those above 9479 ppm (Marble). The Ga concentrations are lower in Nayaseik (concentration below 55 ppm) than in Extension and Mohauk (concentration above 66 ppm).

Tree clustering analysis [17] is used to assess whether the rubies will form clusters according to the location of origin. In this analysis a distance between any two stones is defined as the average difference between their standardised elemental concentrations. Initially, each individual stone will be taken as a cluster. From there they will join into bigger clusters according to their distance, until they merge into one. The criteria to determine the joining of the clusters in each iteration is called the amalgamation rule, here the weighted pair group average is chosen.

The result is shown in Fig. 2. The rubies from Nayaseik were not included in this analysis because there are only three specimens. The Mansi, Mohauk, Extension and Marble rubies form distinct clusters, whereas the Pyinmana and Pyinlon rubies scatter in smaller groups. The ten stones that do not cluster are

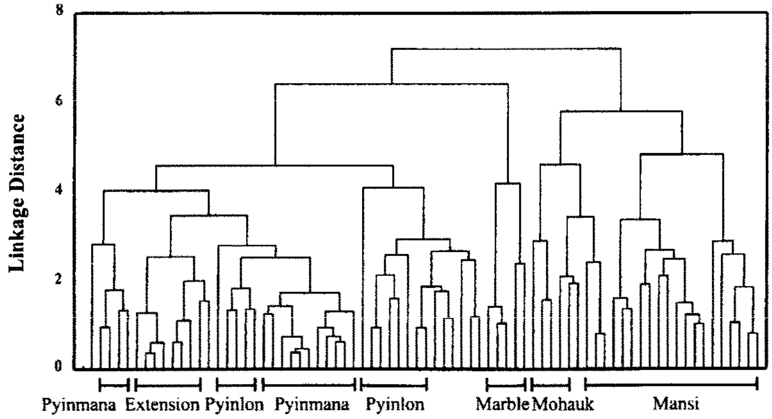

Fig. 2. Tree clustering diagram for hierarchical cluster analysis for the locations Mansi, Mohauk, Marble, Extension, Pyinmana and Pyinlon. The abscissa represents each stone and the ordinate gives the similarity between concentration as explained in the text.

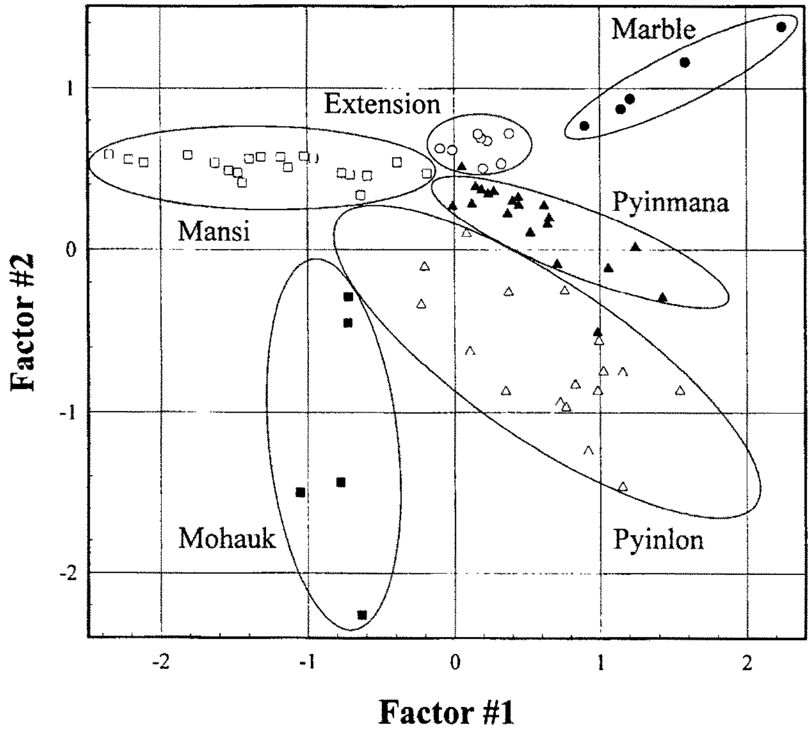

Fig. 3. Results of factor analysis of Cr, V, Cu and Fe for six locations. One stone from Mohauk group is not plotted at (−1.5, −6.2).

from Pyinmana (5), Pyinlon (4) and Mohauk (1). An attempt to include the Mong Hsu and Maingthauk rubies is unsuccessful because no clustering is observed at all.

Factor analysis can be applied to the analysis of multidimensional noisy data sets to find a structure that otherwise would not be seen. The aim of this analytical technique is to reduce the number of variables necessary to describe the data [18].

In a first attempt, we performed factor analysis on the complete set of data without clear results. Because there are no internal correlations for the Mong Hsu and Maingthauk groups, these were removed from further analysis. The Nayaseik stones were also removed due to the small size of the group.

The result of factor analysis of the remaining set is presented graphically in the Fig. 3. Two significant factors were found. The first one had a high loading on Cr and Fe, while the second one had a high loading on Cu.

Nearly all rubies form clusters which can be labelled by location. The trace elements included in this analysis are Cr, V, Fe and Cu. Ga and Ti are not used because Ga concentrations are distributed homogeneously among all the rubies, while Ti concentrations are found to have large variations (see Table 2).

5. Conclusion

One hundred and thirty rubies from nine different Myanmar locations have been analysed using the nuclear microprobe. PIXE elemental maps were used to select contamination free regions, from which the most abundant trace element concentrations are obtained. Large variations of concentrations could be observed between the groups and within the groups as well.

However certain concentrations can be used to differentiate between specific regions of origin. Lower V concentrations are present in the Marble and Mansi rubies than in those from Pyinmana. The Cu concentration is high in the rubies from Mohauk and Pyinlon than in those from Nayaseik, Marble, Mansi, Pyinmana and Extension. The Fe content divides the rubies in three sets. The lowest concentration are found in Marble, higher concentrations are found in stones from Extension, Nayaseik, Maingthauk, Pyinmana and Pyinlon and the highest Fe abundance is seen in stones from Mohauk. The Cr concentration also divides the rubies in three groups, the first (Mansi), the second (Extension, Nayaseik, Pyinmana and Pyinlon) and the third (Marble).

The concentrations have been statistical evaluated using tree clustering and factor analysis. The result of tree clustering analysis shows that clusters exist, correlating the stones with regions of origin in six of nine groups. Factor analysis confirms this result.

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