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Identification of deposit types of natural corundum by PIXE

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ABSTRACT

Natural corundum, one of the most important exports of Thailand, is a rare, durable and valuable gemstone. The value of these precious stones is determined by their visual appearances, including brilliance, color, fire (light dispersion) and luster. Corundum is an allochromatic mineral whose trace element concentration depends on the origin and has influence on price setting. This work attempts to use an alternative method to identify the geological deposits of rubies and sapphires found in the Thai market which came from various countries, e.g., Africa, Cambodia, Myanmar, Sri Lanka, Thailand and USA. Interrelations between most important major trace elements are the main results of this work. Quantitative analysis of trace elements were performed by particle-induced X-ray emission (PIXE) technique, using 2-MeV proton beam generated and accelerated by the 1.7 MV tandem accelerator at Chiang Mai University. The trace elements of interest are Ti, Cr, Fe and Ga. We have found that the relationships between the ratios of trace element concentration can be used to classify the deposit type. Moreover, this method shows a clear separation between two main types of geological deposits, basaltic and metamorphic deposits, which further helps in determining the gemstone origin. For example, the gemstones from Cambodia, Thailand and the USA can be classified as the basaltic deposits with their high concentration in Fe but low in Ti, while the gemstones from Africa, Myanmar and Sri Lanka are metamorphic deposits because they have low Fe but high Ti concentrations. Both deposits required plots of pairs of trace elements and their ratios in population field appearance in order to distinguish their origins. The advantageous of these methods appear to be a new and a sustainable procedure for determining gemstone origins.

1. Introduction

Corundum is one type of gemstone which is actually a crystalline form of aluminum oxide (Al_2O_3) in hexagonal structure [1]. The gems from around the world are traded and treated by various methods to improve their quality in Thailand. These related industries create many jobs; hence the gem business has a substantial influence on the country's economy. Corundum is naturally colorless, but can exhibit different hues depending of the different trace elements incorporated during crystal formation and their chemical environment [2]. The red corundum is called ruby while the others ones are called sapphire. The hardness of corundum is second only to diamond, leading to its good resistance to abrasion and corrosion.

Normally, corundum can be classified to two main deposits on the basic of their geological activities. There are metamorphic deposits and basaltic (magmatic) deposits which differ in the trace element concentration inside the stone [3]. One of the remarkable factors is magma, the hot fluid flowing beneath the earth crust, which contains many dominant elements. According to the geological activity such as volcanic eruption, earthquake, and crust folding, these can lead the matter onto the outer crust and cool down to form basaltic rock or contact to the surrounding origin rock. On the one hand, the eruption magma, during cooling down process, can form to be corundum or aluminum oxide, if the composition and atmosphere are appropriate to recrystallize as a crystalline structure in the basaltic rock [4]. Thus, this deposit type is termed "basaltic" or "magmatic". On the other hand, for metamorphic types, this process occurs when magma has thermal contact with a neighboring rock beneath the earth crust, which is heated, deformed and recrystallized into a new structure. This corundum occasionally has a high content of Ti and low Fe because the recrystallization is indirectly formed by magma which differs from the basaltic process. Previous studies have reported that the

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population field appearance of trace element concentration can also indicate corundum's origin [5,6].

Ion beam analysis (IBA), as a non-destructive analytical method, is a powerful technique for the characterization of gemstones. Particle-induced X-ray emission (PIXE) is a simple and very sensitive analytical technique that can be used to identify and quantify trace elements [7]. Therefore, PIXE is the main characterization techniques used in the present investigation. The objective of the investigation was to establish a standard technique for the classification of the origin of corundum appearing in the Thai market.

2. Experimental procedures

Prior to IBA, samples surface, of worldwide corundum including known and unknown deposit types, are cleaned from stains and small particles by washing in ethanol in an ultrasonic bath. After that, the samples are closely observed and micrographied at 10× magnification through an optical microscope. The elemental compositions of the gemstone samples are analyzed by PIXE technique with a 2 MeV proton beam generated from a Cs-sputter ion source using the 1.7 MV tandem accelerator system at Chiang Mai University [8]. The beam is collimated to ~1 mm diameter, and the beam current at the sample was kept below 10 nA. The vacuum in the chamber is $\sim 1 \times 10^{-6}$ torr. Samples are mounted on a small bolt with a piece of carbon tape and then skewed onto the sample holder. During measurement, energetic protons collide and penetrate into the sample at a depth of ~25 μm (calculated by SRIM code [9]) and induce characteristic X-ray emissions in all directions. The X-rays are detected by a Si(Li) detector placed at 120° to the beam direction. An ORTEC multichannel analyzer card connected to a personal computer is used for data accumulation. In order to reduce the count rate caused by impurities of elements with low atomic numbers, a 74 μm mylar foil with a 0.38% relative hole area is placed in front of the detector as an absorber. An electron shower generated by an electron gun is applied to reduce the bremsstrahlung effects caused by the charge build-up on such insulating targets. Each measurement is taken for approximately 10 min. Trace element concentrations are calculated using GUPIX-WIN software [10] and are reported as parts per million (ppm). The procedure for quality control of our detections system was comprised of several steps [11]. Prior to X-ray measurements, Si(Li) detector was calibrated using X-rays from a ^{109}Cd radioactive source. In PIXE measurement, SRM 610 standard reference material (National Institute of Standards and Technology, 2005), consisting of trace elements in a glass matrix, was analyzed. The measurement demonstrated the accuracy of the experimental set-up to be within ±8%. In addition, resolution of the detector system can be achieved from the full width at half maximum (FWHM) of the Fe Kα peak at 6.4 keV of type 304 stainless steel sample. The resolution of the detection system was estimated to be 180 ± 10 eV.

3. Results and discussion

PIXE spectra demonstrates that corundum consists of aluminum as the main matrix element and other trace element are found as impurity such as Si, K, Ca, Ti, V, Cr, Fe, Zn, and Ga. As shown in Table 1, blue sapphires and dull white sapphires from Sri Lanka and ruby from Mogok contained the high concentration of Ti (>300 ppm) but low of Fe (<4200 ppm) compared to another types. As explained above, the low quantity of Fe indicates that both sapphires are from metamorphic deposits. On the other hand, other sapphires such as sapphires from Bang Kha Cha (Thailand), Pailin (Cambodia), Montana (USA) and ruby from Bo rai (Thailand) contain high concentrations of Fe (>5000 ppm) but low of Ti

Table 1
Concentrations of Ti, V, Cr, Fe and Ga in each type of corundum, in parts per million (ppm) by weight as measured by PIXE technique.

Label	Type of corundum	Deposits	Number of samples	Trace elements concentrations (ppm)														
				Ti			V			Cr			Fe			Ga		
				Mean	Std	LOD	Mean	Std	LOD	Mean	Std	LOD	Mean	Std	LOD	Mean	Std	LOD
(1)	Blue sapphire	Sri Lanka	10	372	306	20	<	–	33	78	96	14	4119	8311	20	50	14	24
(2)	Blue–green sapphire	Bang Kha Cha, Thailand	10	134	110	16	<	–	20	160	178	13	6860	3759	24	154	70	61
(3)	Yellow sapphire	Montana, USA.	10	210	165	21	<	–	22	313	208	15	11288	9330	36	63	36	46
(4)	Dark blue sapphire	Pailin, Cambodia	10	221	224	22	<	–	23	90	64	13	4629	2654	24	98	88	25
(5)	Dull white sapphire	Sri Lanka	19	449	533	11	<	–	17	29	22	8	1230	1051	5	69	44	9
(6)	Ruby	Bo rai, Thailand	10	146	70	19	<	–	22	2220	935	23	4510	886	30	<	–	38
(7)	Ruby	Mogok, Myanmar	10	828	595	9	182	59	24	2712	1349	14	56	46	6	43	9	13
(8)	Light blue–green sapphire	Unknown	10	61	10	14	<	–	14	196	232	9	6456	2081	16	42	11	16
(9)	Dark blue–green sapphire	Unknown	4	186	149	14	<	–	11	34	13	10	5095	1356	12	98	25	16
(10)	Green–blue sapphire	Unknown	3	103	44	13	<	–	17	28	23	10	3620	491	13	108	26	18
(11)	Blue sapphire	Unknown	10	226	134	14	<	–	20	82	74	9	897	433	13	71	41	22
(12)	White sapphire	Unknown	11	516	420	12	<	–	24	25	12	11	898	419	9	60	17	16
(13)	Pink sapphire	Unknown	13	328	209	15	42	34	21	392	378	12	5886	9645	13	51	22	18
(14)	Pale yellow sapphire	Unknown	3	116	85	12	<	–	19	58	36	10	1339	380	6	28	15	14
(15)	Pink sapphire	Madagascar	11	61	20	14	<	–	15	3185	1623	8	1850	842	12	29	17	12
(16)	Light green sapphire	Africa	5	353	430	12	<	–	19	124	149	9	6959	2556	9	86	67	13
(17)	Dark blue sapphire	Africa	4	1623	786	16	128	46	42	294	114	17	3936	724	17	50	27	15
(18)	Green sapphire	Africa	7	355	254	15	<	–	22	342	193	11	10914	3908	15	160	91	19
(19)	Green–blue sapphire	Africa	3	77	21	11	<	–	10	11	16	10	8163	1774	9	130	59	15
(20)	Yellow–green sapphire	Africa	2	518	161	11	<	–	24	229	264	8	9192	4076	13	96	19	5

Note: Mean = mean value concentration; Std = standard deviation; LOD = Limit of detection; < = below limit of detection.

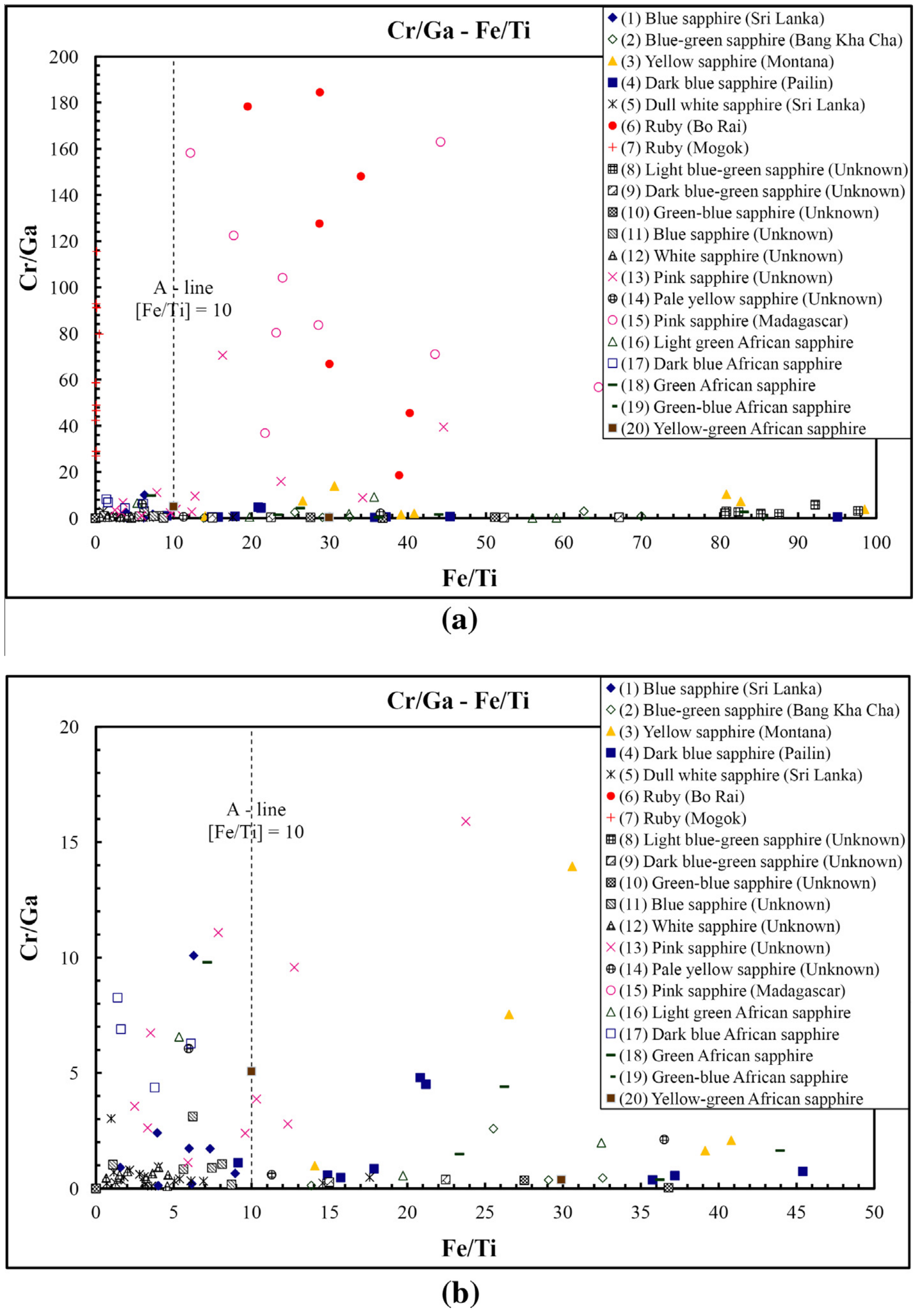

Fig. 1. The relation between the ratio of Cr/Ga and Fe/Ti concentrations; (a) overview of the relation and (b) enlarging of the area near the A-line.

concentrations than those from the metamorphic deposits. These rubies and sapphires are categorized as basaltic deposits. This confirms that different sapphire origin tends to be correlated with different concentrations of trace elements. The standard deviations of trace elements are quite large due to the very wide range of data above the detection limit, which agrees very well with the findings of Calligaro et al. [12]. However, we need to use further analysis method for classifying the other sapphires or rubies.

The trace element concentrations extracted from the recorded PIXE spectra are plotted in the subsequent graphs and their fingerprint were distinguished as follows; Fig. 1 shows the relation between Cr/Ga and Fe/Ti concentration ratios. It is clearly seen that the points from different deposit of corundum located at different areas. We notice from the A-line that those points with Fe/Ti above 10 belong to basaltic deposits and those less than 10 belong to metamorphic deposits. In this manner, the A-line in Fig. 1 acts like a boundary between the two deposits. For example, pink sapphires from Madagascar, which have Fe/Ti > 10, are from basaltic deposits. It is also interesting to note that the data points belonging to metamorphic deposits are clustered more than basaltic deposits according to their specific condition of formation. In this case, the sapphire and ruby of unknown origin can be characterized by this relation like the blue (11) and white (12) sapphires that could be ascribed to a metamorphic type. In addition, dark-blue African sapphire (17) also occurs in the metamorphic condition, which difference from another type of African sapphire. It might be because each territory containing the sapphires has been undergone different geological activities. On the other hand, other unknown deposit's corundum are the basaltic deposit type, including light blue–green sapphire (8), dark blue–green sapphire (9), green–blue sapphire (10), light green African sapphire (16), green African sapphire (18), green–blue African sapphire (19), and yellow–green

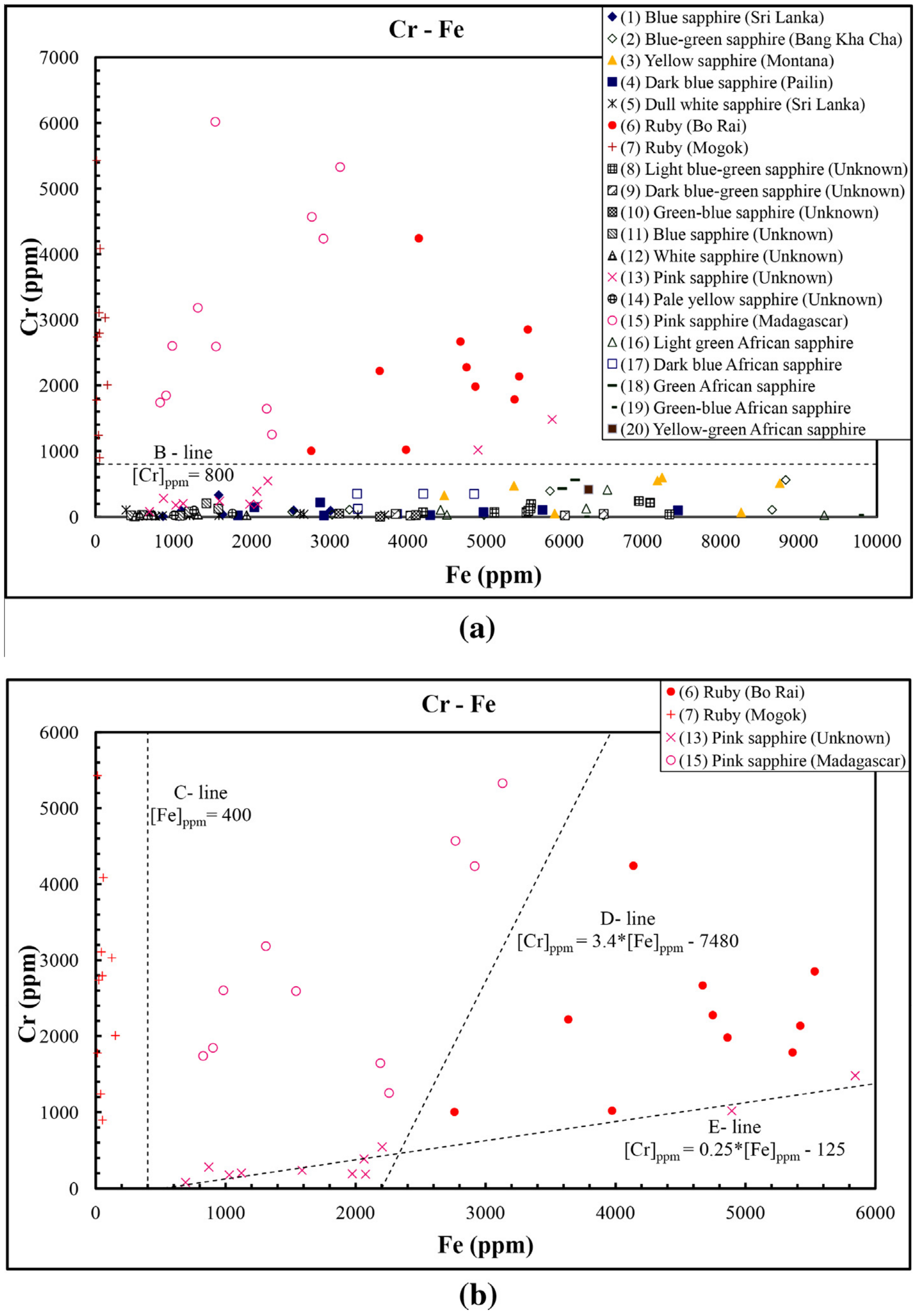

Fig. 2. The relation between the Cr and Fe concentrations; (a) overview of the relation and (b) comparison of the red and pink sapphire.

African sapphire (20). However, the pale yellow sapphire (14) and pink sapphire (15) cannot be classified using this relation.

Fig. 2(a and b) are the relation between the Cr and Fe concentration. Evidently the red tone corundum is distinguished from the non-red tone corundum by the B-line in Fig. 2(a) because of the Cr concentration. In Fig. 2(b), the pink sapphires from Madagascar (15) lie between the C-line and D-line, in other words, between Mogok (7) and Bo rai origins. Besides, these sapphires contain high Cr concentration which should be called ruby. It is worth pointing that the data belonging to pink sapphires from unknown deposit is settled along the E-line (the corresponding equation is shown in Fig. 2(b). All data supports that Cr is the main cause of the red color in both ruby and pink sapphire – which confers a different red tone for each origin depending on its concentration.

Fig. 3 shows the relationship between the ratio of Ti/V and Fe/Ga concentrations. This relation clearly demonstrates the separation, as shown by F-line, of corundum of different origins and confirms the result in Fig. 1; however, where the data points are slightly grouped together in the same area such as Sri Lanka sapphires and Bang Kha Cha sapphires. We found the remarkable result that the Bo rai ruby data are aligned along the G-line which also clearly fingerprint their origin.

As a result, we have found that the separation of deposit types of corundum need to consider the relation of the ratio of trace elements. For example, the relation between the concentration ratio of Cr/Ga and Fe/Ti can distinguish the basaltic deposit and metamorphic deposit. Moreover, the other relation of element or the ration of element can make the fingerprint of corundum origin and track the unknown deposit type. The result shows the good plausibility and

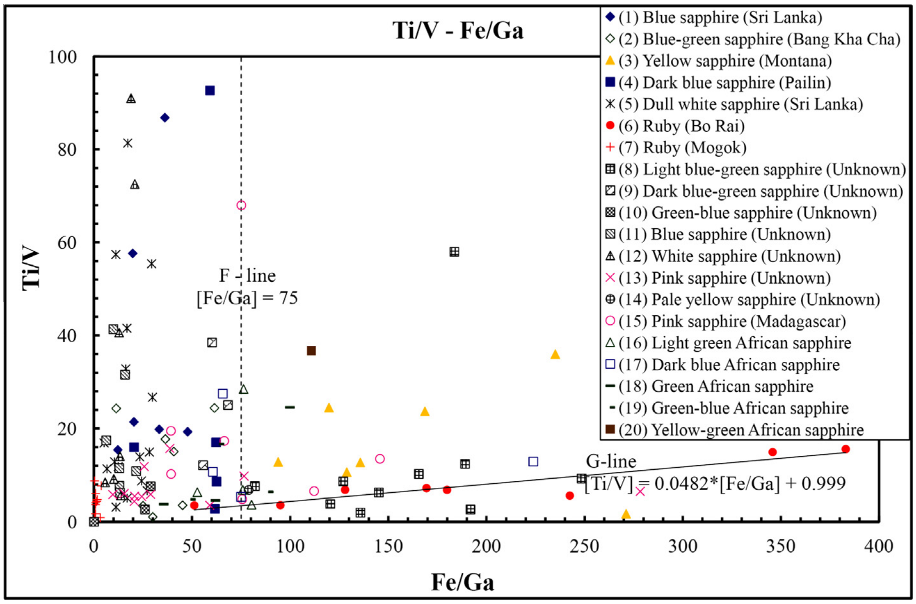

Fig. 3. The relation between the ratio of Ti/V and Fe/Ga concentrations.

conforming to literatures [13–15]. This alternative method will be beneficial for indicating the origin of all corundum whereas most efficient methods reported earlier [16,17] rely on geological or chemical approaches that require a strong expertise. Gemologist can also apply our method in combination with conventional approach to straighten up the confidence on the gems origin. It is important to note that our findings are based on the measurement of about 10–15 samples for each origin. However the statistical significance of our results has to be improved by increasing the number of samples.

4. Conclusion

PIXE is an appropriate technique for detecting trace elements in quantities of a few ppm. Using this, we have found that basaltic deposits (Thailand, Cambodia, Madagascar, and the USA) have high Fe and low Ti, while metamorphic deposits (Sri Lanka and Mogok) have low Fe and high Ti. Basaltic deposits required plots of pairs of trace elements and their ratios in population field appearance to be able to distinguish their origins. It is interesting that Bo rai of Thailand and Pailin of Cambodia cannot be distinguished due to similarity of geological appearance. Therefore, the method cannot distinguish the corundum from the identical geological origins. The other important finding is that we can identify the type corundum of unknown deposits by comparing them against the groups established with corundum of known deposit types. Since price of gemstone are very affected by their origin, this work could be applied as reasonable grading on the deposit type of corundum leading to identifying the origin. The confidence of customer will be increased if the alleged provenance can be verified using a scientific method.

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