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Geographical origin classification of gem corundum using elemental fingerprint analysis by laser ablation inductively coupled plasma mass spectrometry

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ABSTRACT

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to study source identification by using elemental fingerprint analysis combined with the use of multivariate statistical analysis of gem corundum samples with different colors (red, blue, purple, yellow) from six countries (Kenya, Madagascar, Nigeria, Tanzania, Cambodia and Thailand). With LA-ICP-MS, the element concentrations in the samples were calculated using NIST 612 standard glass reference material as the external standard, with Al being used as the internal standard. The optimum conditions of laser ablation, i.e., 9 mJ laser power, 100% laser energy, a spot size of 200 μm and a repetition rate of 20 Hz, were selected to improve the signal intensities. The multivariate data analysis, including principal component analysis (PCA) and linear discriminant analysis (LDA) was used for classification study of samples. Two categories of gem corundum were analyzed including the gem corundum of the same color and the gem corundum of different colors. In the case of gem corundum of the same color classification, the LDA provided good scatter plot that could differentiate rubies between South East Asia and African countries and blue sapphires from Madagascar and Nigeria. For the classification of gem corundum with different colors, the LDA with the use of normalization factor was effective for the identification of the origin of corundum samples with 80% accuracy.

1. Introduction

Gem corundum is considered as one of the most precious stones, by which its cost depends on color, clarity, size and cut. In addition, its geographic origin is one of the most important factors affecting the price and value [1–3]. The ability to classify the source of gem corundum is therefore needed. As the elemental compositions of samples reflect their geographic origins, fingerprinting techniques based on elemental compositions and multivariate statistical analysis can be used for geographic identification of samples [4–7]. Suitable elements that reflect the link with geological origin must be selected to have discriminating potential for that particular product.

Various techniques have been reported to provide elemental fingerprint information. Particle induced X-ray emission/proton induced gamma-ray emission (PIXE/PIGE) was used for analysis of large collection of emeralds from various places [8]. The elemental database obtained was then applied to infer the origin of several ancient emeralds set on historical jewels. Moreover, micro PIXE was employed for the determination of trace element concentrations in ruby samples [9]. Trace element concentrations of 130 natural rough rubies from nine locations in Myanmar were reported. Further, the techniques were used to examine element concentrations in gold alloys [10]. Laser induced breakdown spectrometry (LIBS) was employed for characterization of the jewelry products [11]. Energy-dispersive X-ray fluorescence analysis was also applied to determine trace element contents of rubies and sapphires [12]. The aforementioned techniques, however, either are time-consuming or provide insufficient detection limits.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been successfully reported to provide element concentrations for jewelry and gemstones applications [1,13–18] including the investigation of beryllium diffusion in yellow and orange sapphires [19,20]; source identification of sapphires [1,15,16]; and elemental fingerprint analysis of diamond [17,18]. Guillong and Günther studied 25 sapphire samples from five different locations using LA-ICP-MS [1]. The use of statistical methods could separate five groups of sapphires from each other. However, sources and colors of these gemstones were not given in their work. Peucat et al. used the Ga/Mg ratio from LA-ICP-MS technique to define the two major types of blue sapphires [21]. The ratio was high for magmatic sapphires, whereas metamorphic sapphires exhibited lower ratios. The 31 diamonds originating from four different mines were studied by Moens et al. using LA-ICP-MS [17]. Nine

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Table 1
Operating conditions for LA-ICP-MS.

Laser ablation: CETAC LSX-500	
Laser wavelength	266 nm
Crater diameter	200 μm
Repetition rate	20 Hz
Laser shot	600
Laser power	9 mJ
Sampling scheme	Spot analysis
Carrier gas flow rate	1 L min^{-1} (He)
ICP-MS: Perkin Elmer ELAN 6000	
Torch	Fassel type with alumina ceramic injector
Rf generator frequency	40 MHz
Rf power	1050–1400 W
Nebulizer gas flow rate	0.9 L min^{-1}
Coolant gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	0.9 L min^{-1}
Scanning mode	Peak hopping
Isotopes monitored (m/z)	^{9}Be, ^{10}B, ^{24}Mg, ^{27}Al, ^{29}Si, ^{42,43,44}Ca, ^{45}Sc, ^{49}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{54,57}Fe, ^{59}Co, ^{63}Cu, ^{64,66,67}Zn, ^{71}Ga, ^{72}Ge, ^{85}Rb, ^{88}Sr, ^{120}Sn, ^{121}Sb, ^{138}Ba, ^{140}Cs, ^{153}Eu, ^{208}Pb, ^{232}Th, ^{238}U, ^{232}Th^{16}O

elements (Al, Hg, Na, Ni, Pb, Sb, Sn, Ti and Zn) were selected for fingerprinting purpose and different pattern recognition techniques were used in order to classify the data.

Previous works focus only on simple case, which is the classification of gem corundum of the same color. Nonetheless, the classification of gem corundum with different colors is also useful when in the lack of known samples with the same color to create separation pattern. In this work, two categories of gem corundum were analyzed including the gem corundum of the same color and the gem corundum of different colors. Linear discriminant analysis (LDA) was used for classification study of the samples. This work illustrates the first attempt to differentiate the source of gem corundum of different colors. The criteria for selection of suitable elements for classification purpose were also discussed.

2. Experimental

2.1. Instrumentation

A 266 nm Nd:YAG laser ablation system (LSX 500, CETAC Technologies, Omaha, NE, U.S.A.) coupled to an inductively coupled plasma quadrupole mass spectrometer (ICP-MS, Elan 6000 Perkin Elmer/Sciex, Toronto, Canada) was employed. A laser beam with the maximum energy of 9 mJ was focused onto the sample placed inside an ablation cell to skin off the sample surface producing fine particles. Helium (1.0 L min^{-1}) was used as a carrier gas to sweep the obtained particles out of the ablation cell because He gas can spread particles away from the sampling position faster than the other gases [22]. The He gas containing particles was transported through a 1 m Tygon® transfer tube having an internal diameter of 3.2 mm. An argon carrier gas flow (0.9 L min^{-1}) was merged with the helium stream at approximately 5 cm before entering the ICP-MS torch. The operating parameters for LA-ICP-MS are detailed in Table 1. Data reduction was performed using the method reported by Longerich et al. [23].

2.2. Corundum samples

Fifty eight natural gem corundum from six locations, four from Africa (Kenya, Madagascar, Nigeria and Tanzania) and two from Asia (Cambodia and Thailand) were provided by the Department of Mineral Resources, Ministry of Natural Resources and Environment, Thailand. These samples were analyzed for their elemental fingerprints by LA-ICP-MS. The description of the samples is summarized in Table 2. All corundum samples were cleaned with 10% hydrochloric acid and ethanol (Merck, Germany) in order to remove dust and other remnants on surfaces of the samples. In this work, SRM NIST 612 (glass reference material) was used for quantification purpose, because no commercial reference standards for elements in gem corundum were available.

Table 2
Details of the gem corundum samples.

Gem corundum ID	Origin	Location	Color
KY 01 – KY 06	Kenya	John Saul	Red
MD 01 – MD 05	Madagascar	Andranondambo	Dark blue, blue
MD 06 – MD 13	Madagascar	Andilamena	Dark red, red, pink
NG 01 – NG 11	Nigeria	Mabira	Dark blue, blue
TZ 01 – TZ 08	Tanzania	Umba River Valley	Yellow, purple
TZ 09 – TZ 18	Tanzania	Tunduru	Pink
CB 01 – CB 06	Cambodia	Pailin	Red, purple
TH 01 – TH 04	Thailand	Bo Rai	Red

2.3. Multivariate processing of data

For multivariate processing of data, the SPSS software package (version 16.0, SPSS Inc.) was used. Factor analysis including principal component analysis (PCA) and linear discriminant analysis (LDA) were performed for the classification of gem corundum samples according to their origins. A matrix was constructed with rows representing gem corundum samples and columns representing elemental concentrations from LA-ICP-MS. The data matrix consisted of 14 columns (concentration of B, Si, Zn, Ga, Sn, Mg, Ti, V, Cr, Fe and 58 rows (the numbers of sample from six locations)).

3. Results and discussion

3.1. Elemental fingerprint analysis by LA-ICP-MS

With the selected LA-ICP-MS operating conditions as indicated in Table 1, the limits of detection for 28 elements are summarized in Table 3. Fifty eight natural gem corundum samples were ana-

Table 3
Limits of detection in gem corundum samples measured by LA-ICP-MS.

Elements	Limit of detection	Unit
Be	0.2	mg kg^{-1}
B	1.0	mg kg^{-1}
Mg	0.2	mg kg^{-1}
Al (Al_2O_3)	0.00006	wt.%
Si	10	mg kg^{-1}
Ca	34	mg kg^{-1}
Sc	0.2	mg kg^{-1}
Ti	0.8	mg kg^{-1}
V	0.3	mg kg^{-1}
Cr	0.1	mg kg^{-1}
Mn	0.1	mg kg^{-1}
Fe	2	mg kg^{-1}
Co	0.03	mg kg^{-1}
Cu	0.1	mg kg^{-1}
Zn	0.2	mg kg^{-1}
Ga	0.04	mg kg^{-1}
Ge	0.1	mg kg^{-1}
Rb	0.02	mg kg^{-1}
Sr	0.01	mg kg^{-1}
Sn	0.02	mg kg^{-1}
Sb	0.02	mg kg^{-1}
Ba	0.01	mg kg^{-1}
Pb	0.02	mg kg^{-1}
Th	0.003	mg kg^{-1}
U	0.002	mg kg^{-1}
Th (ThO)	1.5	mg kg^{-1}
Ce	0.004	mg kg^{-1}
Eu	0.008	mg kg^{-1}

Table 4
Elemental concentrations of 58 natural gem corundum samples ($n = 3$).

Corundum	Color	Concentration ($mg\,kg^{-1}$)									
		B	Si	Zn	Ga	Sn	Mg	Ti	V	Cr	Fe
KY 01	Red	16 ± 1.0	821 ± 46	<0.2	228 ± 9	0.4 ± 0.01	94 ± 5	188 ± 16	26 ± 2.3	1917 ± 118	12 ± 3
KY 02	Red	16 ± 1.9	762 ± 95	1.3 ± 0.4	178 ± 10	0.4 ± 0.02	221 ± 52	631 ± 196	22 ± 1.4	2009 ± 198	7 ± 3
KY 03	Red	14 ± 3.2	574 ± 41	2.2 ± 1.0	171 ± 11	0.2 ± 0.04	289 ± 152	1493 ± 1188	18 ± 2.8	1584 ± 225	11 ± 13
KY 04	Red	9 ± 1.4	575 ± 61	1.2 ± 0.5	162 ± 5	0.2 ± 0.02	178 ± 22	539 ± 104	22 ± 0.8	2044 ± 165	9 ± 3
KY 05	Red	10 ± 1.5	523 ± 36	0.8 ± 0.2	193 ± 17	0.3 ± 0.03	109 ± 30	201 ± 64	47 ± 9.5	1562 ± 196	14 ± 3
KY 06	Red	8 ± 0.8	428 ± 14	0.7 ± 0.1	166 ± 2	0.2 ± 0.03	124 ± 16	212 ± 24	16 ± 0.8	1307 ± 33	10 ± 1
MD 01	Dark blue	11 ± 1.3	399 ± 5	0.8 ± 0.1	137 ± 10	1.7 ± 1.09	22 ± 6	380 ± 116	9 ± 1.7	0.4 ± 0.05	1539 ± 186
MD 02	Dark blue	10 ± 0.9	386 ± 32	0.7 ± 0.2	134 ± 2	2.7 ± 0.71	28 ± 5	263 ± 21	9 ± 0.2	0.4 ± 0.03	1446 ± 13
MD 03	Dark blue	11 ± 1.0	400 ± 14	<0.2	84 ± 1	0.5 ± 0.02	4 ± 0.3	64 ± 6	5 ± 0.1	0.5 ± 0.03	539 ± 7
MD 04	Blue	10 ± 1.9	450 ± 44	0.3 ± 0.01	90 ± 3	0.5 ± 0.04	20 ± 4	60 ± 2	4 ± 0.2	0.6 ± 0.09	762 ± 45
MD 05	Blue	9 ± 0.2	401 ± 26	0.5 ± 0.1	64 ± 0.4	3.1 ± 2.09	14 ± 2	204 ± 104	7 ± 1.3	0.5 ± 0.14	936 ± 48
MD 06	Dark red	2 ± 0.7	429 ± 43	<0.2	45 ± 1	0.2 ± 0.01	56 ± 6	109 ± 15	37 ± 1.5	7591 ± 155	1953 ± 52
MD 07	Dark red	3 ± 0.4	387 ± 34	0.5 ± 0.1	37 ± 1	0.2 ± 0.01	53 ± 1	103 ± 1	42 ± 0.3	11,951 ± 193	2578 ± 40
MD 08	Purplish red	3 ± 0.2	381 ± 34	<0.2	42 ± 1	0.2 ± 0.02	49 ± 15	90 ± 28	41 ± 4.1	1377 ± 276	1906 ± 92
MD 09	Purplish red	3 ± 0.8	378 ± 58	0.5 ± 0.2	36 ± 1	0.2 ± 0.01	47 ± 0.1	85 ± 3	34 ± 0.2	1869 ± 25	1752 ± 252
MD 10	Purplish red	3 ± 0.5	465 ± 26	0.5 ± 0.1	53 ± 1	0.2 ± 0.06	32 ± 2	48 ± 2	41 ± 0.7	1584 ± 52	2655 ± 67
MD 11	Purplish red	3 ± 0.8	487 ± 62	0.7 ± 0.1	45 ± 1	0.3 ± 0.01	31 ± 0.2	48 ± 2	38 ± 0.8	2005 ± 63	2926 ± 78
MD 12	Purplish pink	2 ± 0.5	458 ± 23	<0.2	38 ± 1	0.3 ± 0.03	29 ± 1	56 ± 2	36 ± 0.8	744 ± 15	1705 ± 56
MD 13	Purplish pink	3 ± 0.9	600 ± 63	<0.2	35 ± 1	0.3 ± 0.06	41 ± 4	69 ± 7	20 ± 1.0	944 ± 57	1678 ± 66
NG 01	Dark blue	8 ± 1.2	381 ± 27	1.6 ± 0.3	95 ± 1	1.1 ± 0.2	14 ± 1	1597 ± 346	1 ± 0.1	0.4 ± 0.05	2254 ± 48
NG 02	Dark blue	8 ± 1.6	377 ± 4	0.8 ± 0.1	205 ± 1	0.3 ± 0.02	2 ± 0.2	153 ± 38	2 ± 0.1	0.4 ± 0.04	1702 ± 49
NG 03	Dark blue	10 ± 1.6	446 ± 24	1.9 ± 0.3	121 ± 3	0.3 ± 0.01	14 ± 0.8	51 ± 5	3 ± 0.2	0.6 ± 0.1	1978 ± 49
NG 04	Light blue	10 ± 0.8	458 ± 44	2 ± 0.5	149 ± 4	4.4 ± 1	2 ± 0.6	1586 ± 376	0.5 ± 0.03	0.7 ± 0.04	1743 ± 91
NG 05	Light blue	7 ± 1.0	511 ± 30	1 ± 0.7	111 ± 8	0.5 ± 0.1	7 ± 5	322 ± 114	6 ± ±2	2 ± 0.2	1358 ± 87
NG 06	Light blue	9 ± 1.4	538 ± 90	0.6 ± 0.1	98 ± 3	0.2 ± 0.03	3 ± 0.2	80 ± 23	6 ± 0.04	0.6 ± 0.1	1361 ± 59
NG 07	Light blue	9 ± 1.2	443 ± 24	0.6 ± 0.1	94 ± 1	0.2 ± 0.02	4 ± 1	98 ± 5	8 ± 0.2	5 ± 0.1	1251 ± 33
NG 08	Light blue	6 ± 1.1	404 ± 30	1.8 ± 0.6	122 ± 1	0.4 ± 0.01	13 ± 2	1028 ± 309	11 ± 0.4	1 ± 0.1	1357 ± 53
NG 09	Light blue	6 ± 0.3	434 ± 37	1.2 ± 0.5	119 ± 9	0.3 ± 0.03	6 ± 0.7	116 ± 62	3 ± 1	1 ± 0.7	1134 ± 45
NG 10	Light blue	5 ± 0.6	453 ± 13	1 ± 0.4	134 ± 4	3.2 ± 1	3 ± 1	627 ± 247	3 ± 0.2	1 ± 0.06	2507 ± 53
NG 11	Light blue	7 ± 1.5	522 ± 9	0.8 ± 0.2	125 ± 1	0.9 ± 0.3	2 ± 0.2	291 ± 87	3 ± 0.1	1 ± 0.1	2633 ± 21
TZ 01	Yellow	5 ± 0.6	435 ± 82	<0.2	33 ± ±0.4	0.2 ± 0.02	21 ± 0.3	42 ± 0.2	13 ± 0.2	41 ± 2	3975 ± 71
TZ 02	Yellow	4 ± 05	403 ± 32	<0.2	22 ± 1	0.2 ± 0.01	21 ± 4	80 ± 8	6 ± 0.2	8 ± 0.7	3873 ± 138
TZ 03	Yellow	5 ± 0.7	435 ± 36	<0.2	14 ± 0.4	0.3 ± 0.06	21 ± 2	111 ± 3	12 ± 0.5	13 ± 1	3372 ± 140
TZ 04	Reddish purple	5 ± 0.4	403 ± 76	0.5 ± 0.1	52 ± 2	0.2 ± 0.04	21 ± 4	42 ± 2	17 ± 0.8	621 ± 17	2816 ± 143
TZ 05	Reddish purple	4 ± 1.0	476 ± 87	0.6 ± 0.1	50 ± 2	0.3 ± 0.03	21 ± 0.6	55 ± 8	141 ± 6	739 ± 27	881 ± 59
TZ 06	Reddish purple	4 ± 0.8	469 ± 31	0.6 ± 0.2	45 ± 2	0.3 ± 0.03	21 ± 4	96 ± 17	82 ± 4	736 ± 46	953 ± 47
TZ 07	Purple	4 ± 0.5	437 ± 43	<0.2	51 ± 1	0.3 ± 0.02	21 ± 2	70 ± 1	15 ± 0.2	222 ± 6	1502 ± 19
TZ 08	Purple	4 ± 0.4	395 ± 34	<0.2	56 ± 1	0.2 ± 0.02	21 ± 0.5	59 ± 2	22 ± 0.3	237 ± 6	1560 ± 32
TZ 09	Purplish Pink	4 ± 0.4	426 ± 32	0.5 ± 0.02	64 ± 2	1.1 ± 0.7	24 ± 4	145 ± 60	15 ± 1	484 ± 74	362 ± 15
TZ 10	Purplish pink	3 ± 0.8	469 ± 20	0.8 ± 0.02	79 ± 0.5	0.3 ± 0.03	49 ± 3	122 ± 1	124 ± 5	392 ± 9	579 ± 15
TZ 11	Pink	4 ± 1.1	427 ± 12	0.4 ± 0.01	19 ± 0.4	0.3 ± 0.02	47 ± 4	52 ± 5	5 ± 0.2	528 ± 4	1495 ± 51
TZ 12	Pink	3 ± 0.5	450 ± 42	<0.2	14 ± 0.3	0.2 ± 0.01	27 ± 1	71 ± 5	6 ± 0.02	511 ± 11	944 ± 18
TZ 13	Light yellow	8 ± 1.2	340 ± 15	<0.2	38 ± 1	0.5 ± 0.08	35 ± 1	17 ± 2	3 ± 0.3	0.4 ± 0.02	240 ± 8
TZ 14	Light yellow	6 ± 1.8	459 ± 95	<0.2	14 ± 3	35 ± 2.7	55 ± 11	20 ± 5	2 ± 0.7	0.4 ± 0.1	208 ± 83
TZ 15	Light yellow	5 ± 0.8	361 ± 11	<0.2	48 ± 2	14 ± 6	59 ± 15	25 ± 6	3 ± 0.1	0.5 ± 0.04	200 ± 19
TZ 16	Light yellow	8 ± 2.3	694 ± 59	<0.2	78 ± 3	25 ± 11	21 ± 5	6 ± 2	3 ± 0.2	0.4 ± 0.1	134 ± 50
TZ 17	Light yellow	4 ± 0.9	587 ± 30	0.5 ± 0.01	80 ± 2	233 ± 22	45 ± 3	41 ± 20	3 ± 0.2	0.5 ± 0.06	183 ± 21
TZ 18	Light yellow	5 ± 1.6	517 ± 107	1.5 ± 0.02	29 ± 1	0.4 ± 0.1	97 ± 30	172 ± 12	2 ± 0.2	0.6 ± 0.16	234 ± 13
CB 01	Purplish red	3 ± 1.3	611 ± 14	0.8 ± 0.1	25 ± 1	0.3 ± 0.01	182 ± 8	94 ± 0.5	5 ± 0.3	634 ± 36	1471 ± 58
CB 02	Purplish red	3 ± 0.9	583 ± 40	0.6 ± 0.2	19 ± 0.2	0.2 ± 0.01	192 ± 2	96 ± 1	11 ± 0.4	1943 ± 114	1700 ± 79
CB 03	Dark purple	3 ± 0.9	585 ± 71	1.5 ± 0.1	23 ± 0.4	0.2 ± 0.02	258 ± 4	320 ± 3	30 ± 0.8	2258 ± 36	2253 ± 54
CB 04	Dark purple	3 ± 1.1	611 ± 15	1.5 ± 0.4	29 ± 0.7	0.3 ± 0.02	271 ± 11	328 ± 6	25 ± 1.5	611 ± 34	2091 ± 66
CB 05	Dark purple	2 ± 0.7	500 ± 40	1.9 ± 0.2	27 ± 0.1	0.2 ± 0.03	238 ± 8	343 ± 7	42 ± 0.7	1294 ± 89	3537 ± 18
CB 06	Dark purple	2 ± 0.5	559 ± 28	1.1 ± 0.2	23 ± 0.5	0.1 ± 0.02	218 ± 4	213 ± 4	25 ± 0.5	825 ± 13	2346 ± 69
TH 01	Purplish red	5 ± 1.0	537 ± 44	1.8 ± 0.4	29 ± 0.2	0.2 ± ±0.01	279 ± 3	291 ± 2	26 ± 0.2	4960 ± 107	1794 ± 92
TH 02	Purplish red	4 ± 0.8	561 ± 45	1.7 ± 0.2	27 ± 0.6	0.2 ± 0.02	229 ± 7	205 ± 4	20 ± 0.04	2579 ± 113	2025 ± 19
TH 03	Purplish red	3 ± 0.9	607 ± 100	1.4 ± 0.2	24 ± 0.5	0.3 ± 0.01	220 ± 5	182 ± 11	18 ± 2	2242 ± 52	1862 ± 148
TH 04	Purplish red	5 ± 0.3	608 ± 23	1.2 ± 0.2	23 ± 0.2	0.3 ± 0.02	217 ± 4	187 ± 1	24 ± 0.4	1840 ± 21	1867 ± 38

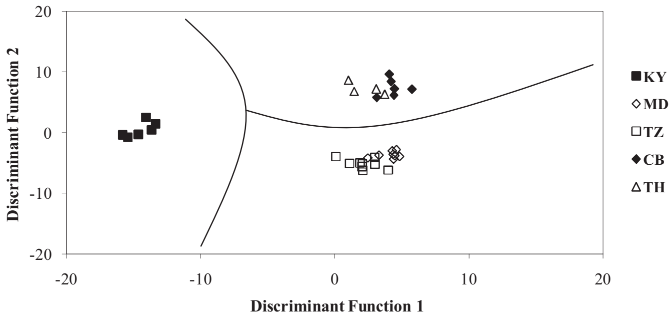

Fig. 1. LDA analysis of 33 rubies from five locations (Kenya, Madagascar, Tanzania, Cambodia and Thailand) using the concentration values of B, Si, Zn, Ga, Sn, V, Mg, Ti, Cr and Fe.

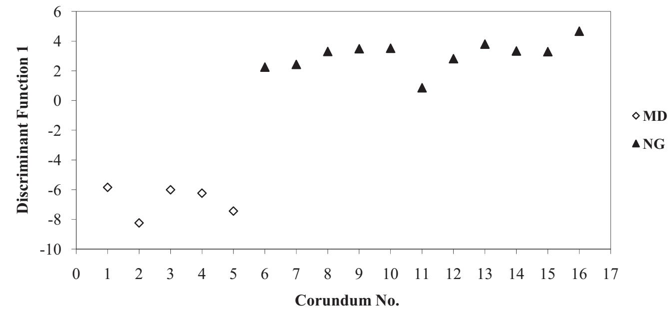

Fig. 2. LDA analysis of 16 blue sapphires from two locations (Madagascar and Nigeria) using the concentration values of B, Si, Zn, Ga, Sn, V, Mg, Ti, Cr and Fe.

lyzed for the element concentrations. Only some elements, which were found in the higher concentrations than the detection limits, were quantified as summarized in Table 4. The concentrations of 10 elements (B, Si, Zn, Ga, Sn, Mg, Ti, V, Cr and Fe) are possible to be used for classifying source of origin of the gem corundum samples. However, the Zn concentration in gem corundum in some location regions was not detectable or lower than the detection limits. Among these elements, B, Si, Zn, Ga and Sn are not the main coloring elements, whereas Mg, Ti, V, Cr and Fe are involving in the color of gem corundum [2,24,25]. Multivariate data analysis was performed for classification study of samples. Two statistical methods, i.e., factor analysis and linear discriminant analysis, were employed.

3.2. Origin classification of gem corundum samples

To classify the origin of samples by the SPSS statistical technique, the values of variables (concentrations) in every case (sample) must be available. So, the concentration values of less than the detection limits were replaced with zero to complete statistical process. In this study, the gem corundum samples from all six sources were not of the same color, therefore the study of source identification was divided in two parts, i.e., classification of gem corundum of the same color; and classification of gem corundum of different colors. As some trace elements can influence on the colors of gem corundum, e.g., Fe and Ti on blue in blue sapphire; Ti and V on purple in purple sapphire; Cr on red in ruby; and Fe and Mg on yellow in yellow sapphire, classification of gem corundum with color giving elements must be careful.

3.2.1. Gem corundum of the same color classification

The multivariate statistical analysis was applied to classify the location of gem corundum samples of the same color. As listed in Table 2 the yellow sapphires were from only one source, which is in Tanzania region. However, the red and the blue were from more than one country. Thirty three rubies were from Kenya, Madagascar, Tanzania, Cambodia and Thailand. Sixteen blue sapphires were from Madagascar and Nigeria. Principal component analysis (PCA) was applied to the concentrations of the color and non color giving elements, clear separation pattern was not obtained between the samples of various origins (see Fig. S1 in supplementary data). Therefore, another statistical method, linear discriminant analysis (LDA) was employed. This method maximizes the ratio of between-class variance to the within-class variance in any particular data set thereby guaranteeing maximal separability [26]. Linear discriminant analysis of 33 rubies from five locations (6 from Kenya, 8 from Madagascar, 9 from Tanzania, 6 from Cambodia and 4 from Thailand) is presented in Fig. 1, which was plotted between the score of linear combination of 10 elements (B, Si, Zn, Ga, Sn, V, Mg, Ti, Cr and Fe) of each sample calculated from discriminant functions 1 and 2. This score plot shows good separation of Kenya rubies from the other samples. In addition, the Madagascar and Tanzania rubies showed lower value in scale of discriminant function 2 as compared with those of Cambodia and Thailand rubies. This LDA plot illustrated the potential of this pattern for classification of rubies between South East Asia and African countries. On the other hand, when compared this LDA technique with PCA technique (see Fig. S1 in supplementary data) in the same case, better classification in term of the scattering within and between groups was achieved with LDA. With LDA, the within group scatter was low whereas the between group scatter was high.

Similar to rubies, 10 elements were used to classify the origin of blue sapphires by LDA analysis. The concentrations of 10 elements (B, Si, Zn, Ga, Sn, V, Mg, Ti, Cr and Fe) were used to construct the LDA plot of 16 blue sapphires from two locations (Madagascar and Nigeria). As this case consists of only two groups (countries), 10 elements were calculated to only one discriminant function. Fig. 2 shows the relationship between blue sapphire number and score of discriminant function 1. The values of discriminant function 1 of Madagascar (between −8 and −6) were clearly different from those of Nigeria blue sapphires [1–5]. Therefore, the LDA function from these 10 elements can be used for the differentiation of the blue sapphires from these two locations. This LDA method gave better classification of blue sapphires over the PCA method (see Fig. S2 in supplementary data).

3.2.2. Gem corundum of the different color classification

The ability to differentiate the origin of the gem corundum with different colors is useful when in the lack of samples with the same color. Therefore, the aim of this part was to construct the pattern for identifying the origin of gem corundum samples that have different colors in the same mapping. Both PCA and LDA techniques were applied to the concentration values of the elements. Nonetheless, with PCA clear separation pattern was not obtained (see Figs. S3 and S4 in supplementary data). Therefore, only the separation patterns obtained from the LDA technique are illustrated as shown in Figs. 3 and 5.

Using the non color giving elements, which are B, Si, Zn, Ga and Sn, for LDA statistical method, the LDA of 58 gem corundum from six different locations (6 from Kenya, 13 from Madagascar, 11 from Nigeria, 18 from Tanzania, 6 from Cambodia and 4 from Thailand), the score plot of each source is scattered and not suitable for use with unknown samples (see Fig. S5 in supplementary data). Consequently, the linear discriminant fingerprint of B, Si, Zn, Ga, Sn, Mg, Ti, V, Cr and Fe as both non and color giving elements of six locations (6 from Kenya, 13 from Madagascar, 11 from Nigeria, 18 from Tanzania, 6 from Cambodia and 4 from Thailand) of 58 gem corundum samples was constructed and the LDA pattern is shown in Fig. 3 showing the three groups as follows:

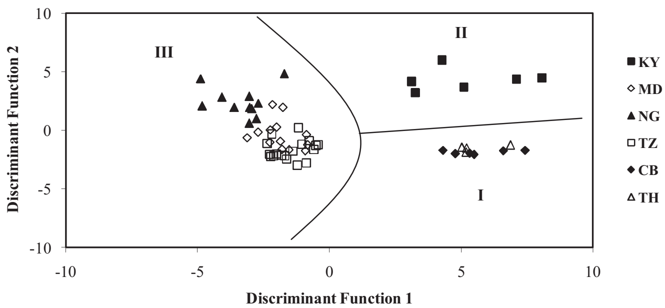

Fig. 3. LDA analysis of 58 gem corundum samples from six locations (Kenya, Madagascar, Nigeria, Tanzania, Cambodia and Thailand) using the concentration values of B, Si, Zn, Ga, Sn, V, Mg, Ti, Cr and Fe.

- *group I*: South East Asia area where the borders are connected including Cambodia and Thailand.
- *group II*: only one country, i.e., Kenya.
- *group III*: Africa area including Madagascar, Nigeria and Tanzania.

Therefore, the new fingerprint patterns were required for complete classification of the gem corundum in group I and group III countries. For classifying gem corundum from two countries in the first group, the ratio of Si and B concentrations were investigated and shown to be able to distinguish the Cambodian and the Thai gem corundum as shown in Fig. 4. Silicon and B were the suitable elements to create the ratio for classifying the origin because both elements are the non color giving elements. Moreover, the concentration values of these two elements were found in significant levels in every sample (higher than the detection limit). The use of the ratio of some elements or isotopes to differentiate gem corundum from different locations or different source rocks was reported earlier by other investigators [1,21]. As illustrated in Fig. 4, the ratio of Si and B concentrations was higher in the case of Cambodia gems when compared with those of Thailand. Nonetheless, poor precision was obtained which may be caused by heterogeneity of the samples.

For classifying gem corundum from three countries in the third group (African area), the concentration data were normalized before subjecting to LDA technique. Four new variables were then obtained by normalization factor with average concentration of B and Sn from the following equations:

$$\text{normalization factor} = \{[B] + [Sn]\}/2$$
$$Si_1 = [Si]/\text{normalization factor}$$
$$V_1 = [V]/\text{normalization factor}$$
$$Zn_1 = [Zn]/\text{normalization factor}$$
$$Ga_1 = [Ga]/\text{normalization factor}$$

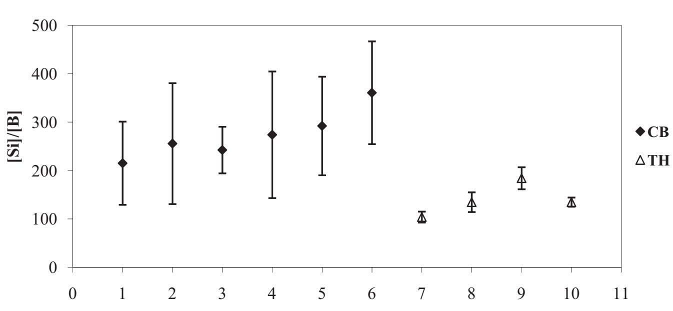

Fig. 4. Ratio between Si and B concentrations of Cambodia and Thailand gem corundum ($n = 3$).

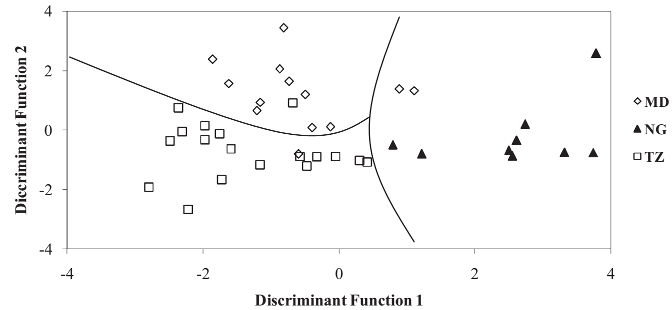

Fig. 5. LDA analysis of African gem corundum samples from three locations using the conscentration values of Si, V, Zn, Ga and the normalized values of Si_1, V_1, Zn_1 and Ga_1.

B and Sn were selected to be incorporated in the normalization factor as B and Sn showed highest factor loading score in each component of PCA analysis (results not shown here). With four new variables, LDA using concentrations of Si, V, Zn, Ga and their normalized concentrations was performed as shown in Fig. 5. This LDA pattern can be used for the identification of the country origin of corundum samples with 80% accuracy. Separation between the countries was not perfect which may be likely due to the similar compositions in geological appearance of the countries where in the nearby location.

4. Conclusions

This work illustrates successful attempt to use elemental fingerprint data obtained by LA-ICP-MS combined with the use of LDA for source identification of gem corundum. Two categories of gem corundum were analyzed including gem corundum of the same color and gem corundum of the different colors. For the same color group, the LDA mapping can separate rubies between South East Asia and African countries and blue sapphires from Madagascar and Nigeria. For the classification of gem corundum with different colors, the LDA with the use of normalization factor was effective for the identification of the corundum origin with 80% accuracy.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.06.010.

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