

# Mineral inclusions in sapphire from the basalt-related deposit in Bo Phloi, Kanchanaburi, western Thailand: indication of their genesis

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## Abstract

The Bo Phloi gem field in Kanchanaburi Province, Western Thailand, is closely associated with Cenozoic basalts. Blue and yellow sapphire, black spinel, and minor zircon have been mined for over three decades. The mineral inclusions observed in sapphire samples are alkali feldspar, nepheline, hercynitic spinel, zircon, manganiferous ilmenite, silica-rich enstatite, almandine–pyrope garnet, monazite, calcite, sapphirine, biotite–phlogopite mica, and staurolite. Based on their geochemical affinity, these mineral inclusions can be categorized into two main groups: felsic alkaline and contact-metamorphic, which appear to have originated from different processes. These inclusions provide new evidence for proposing a bimodal genetic model. Felsic alkaline origin is evidenced by the occurrence of a felsic alkaline inclusion suite and the REE geochemistry of sapphire-associated zircon, which indicates that most of the sapphires crystallized from a high-alkali felsic melt (probably, in the lower crust). Contact-metamorphic origin is evidenced by the presence of a contact-metamorphic inclusion suite, suggesting that some of these sapphires might also have originated from metasomatized crustal rocks and a contaminated melt along the contact zone of a basaltic intrusion (probably, in the upper mantle or lower crust).

**Keywords:** Cenozoic basalt; basaltic sapphire; Bo Phloi gem deposit; genetic model

## Introduction

The Bo Phloi gem field of Kanchanaburi Province, Western Thailand (Fig. 1), is a well-known “basaltic” gem corundum deposit, which has supplied large quantities of good-quality blue sapphire and minor quantities of yellow sapphire to the world market. It used to be the biggest alluvial sapphire mine in Southeast Asia. In general, the Bo Phloi sapphires are found in secondary deposits derived from weathered alkali basalt that outcrops at Khao Lantom, near Bo Phloi city, and at Huai Maka of Ban Chong Dan, 6 km north of Bo Phloi city. Opencast mining in the Bo Phloi area is generally confined to a paystreak, a sapphire-bearing gravel bed normally about 3 m thick and lying at 13 to 15 m depth (Hansawek and Pattamalai, 1997). The gem-related Bo Phloi basalt is represented by dark dense fine-grained and porphyritic rocks. Megacrysts of clinopyroxene, black spinel, sanidine, olivine, and anorthoclase were often observed; besides, ultramafic nodules (especially spinel lherzolite) and gneissic xenoliths were reported (e.g., Srithai, 2005; Sutthirat, 2001; Sutthirat et

al., 1999). In addition, the megacrysts in the Bo Phloi basalt consist of nepheline, Al–Ti magnetite, and, most importantly, corundum (Pisutha-Armond et al., 1999, 2005). These basalts were geochemically classified as basanitoid by Vichit et al. (1978) and as nepheline hawaiite by Barr and Macdonald (1978, 1981) and Yaemniyom and Pongsapich (1982). Geochronologically, the Bo Phloi basalt was reported to have a K/Ar age of  $3.14 \pm 0.17$  Ma (Barr and Macdonald, 1981) and an  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $4.17 \pm 0.11$  Ma (Sutthirat et al., 1994).

In-depth studies of mineral inclusions in the Bo Phloi sapphires have been published by some researchers. Saminpanya (2000) reported a nepheline inclusion ( $\text{Ne}_{68.3}\text{Ks}_{28.6}\text{Q}_3$ ) and proposed a genetic model related to nepheline syenite. A cobalt-rich spinel inclusion was presented by Guo et al. (1994); consequently, they suggested a complex magma mixing process involving an alkali-rich felsic melt and a silica-deficient carbonatite melt in the lower crust for the formation of spinel and sapphire in this area. In addition, Pisutha-Armond et al. (1999, 2005) proposed a genetic model for the Bo Phloi sapphire, based on the information about “corsilzirspite” (a corundum + sillimanite + zircon + spinel assemblage) pebble found in the gem-bearing layer and inclusion suites (including alkali feldspar, zircon, monazite, hercynitic

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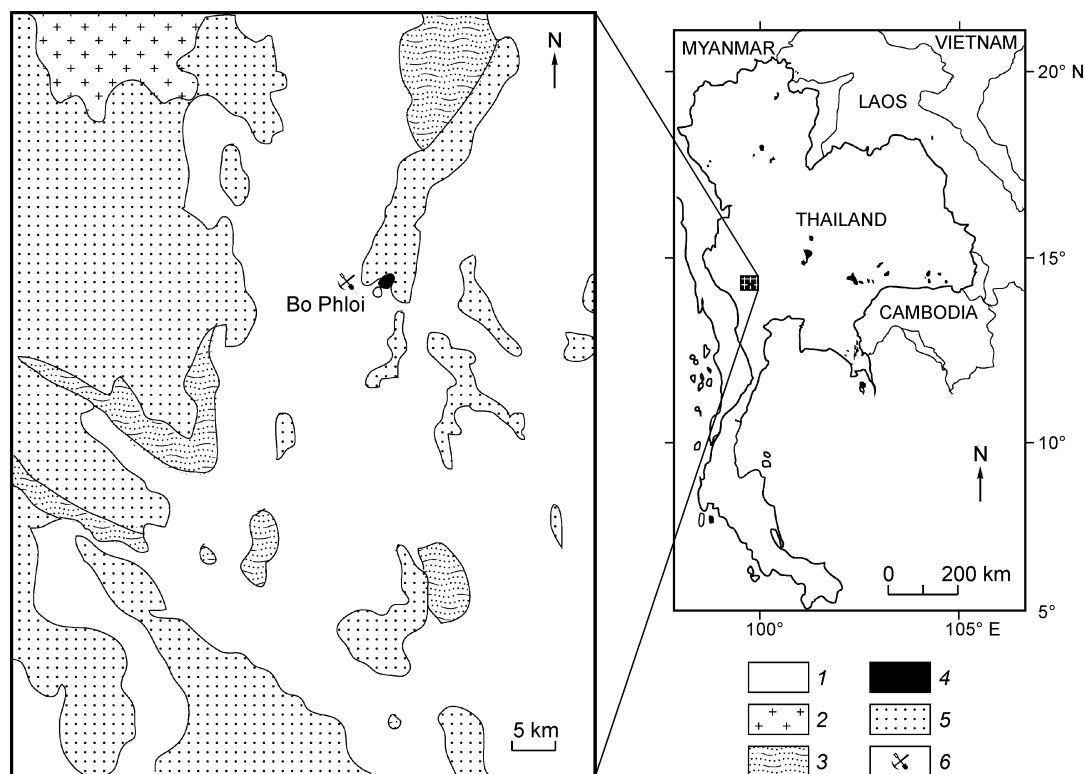


Fig. 1. Geological map in the vicinity of the Bo Phloi gem deposit, Kanchanaburi Province, western Thailand (modified after (Vichit et al., 1978)). 1, Tertiary sediments; 2, Mesozoic granite; 3, Precambrian complex; 4, Cenozoic basalt; 5, Paleozoic sequences; 6, main sapphire mining area.

spinel, niobium oxide, manganoan ilmenite, nepheline, pyrochlore (?), thorite (?), biotite (?), and calcite) observed in sapphires, which might have been produced by contact-metamorphic/metasomatic/contamination processes caused by interaction between a gabbroic melt and Al-rich crustal rocks. Although more mineral types of inclusions were mentioned in the last report, their mineral chemistries were not fully analyzed.

Therefore, this work is focused on a detailed study of mineral chemistry covering a full range of mineral inclusions in the Bo Phloi sapphire. Eventually, these mineral chemistries are used to constrain the crystallization conditions of the sapphires and their inclusions prior to proposing a more reliable genetic model.

## Material and methods

The Bo Phloi sapphires used in this study were recovered directly from local mines in the Bo Phloi gem field. The selected sapphires, a 2-mm concentrate, must represent the majority of stones from this gem field. More than 170 grains of the Bo Phloi sapphires which obviously contain a lot of mineral inclusions were selected for this study. They were subdivided by color into two main varieties: grayish brown and blue. Moreover, the grayish brown sapphires have two color shades: dark grayish brown (45 samples) and light grayish brown (48 samples), whereas the blue samples have blue (50 samples) and light blue (30 samples) shades (Fig. 2).

After the sampling, rough stones were examined under a binocular microscope to pick up suitable samples containing abundant inclusions before they were mounted in epoxy. The samples containing larger mineral inclusions were carefully polished until the inclusions were exposed. As most of the mineral inclusions observed in these sapphires are small (50  $\mu\text{m}$ ), it is certainly necessary to use a microscope with high magnification to observe their morphology.

Subsequently, the selected samples of each group were coated with carbon for analysis of the major components of the mineral inclusions using a JXA-8100 electron probe microanalyzer (EPMA) (JEOL) at the Department of Geology, Faculty of Science, Chulalongkorn University. The operating conditions were set at an accelerating voltage of 15.0 kV and about 24 nA beam current, with a focused beam (smaller than 1  $\mu\text{m}$ ). Mineral and pure oxide standards were selected for calibration. Counting times were set at 30 s for each element using suitable analytical crystals before ZAF correction was automatically carried out, and the results were reported in the form of percent oxides. The  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios of some iron-containing minerals were recalculated using the Droop equation (1987). In addition, the LA-ICP-MS technique was employed for the trace-element analysis of the zircon inclusion in this work. This technique was applied using a Perkin-Elmer ELAN 6000 ICP-MS coupled to a laser ablation microscope, based at GEMOC, Macquarie University, Sydney, Australia. Detailed descriptions of the instrumentation and analytical and calibration procedures can be found in Belousova et al. (2002).

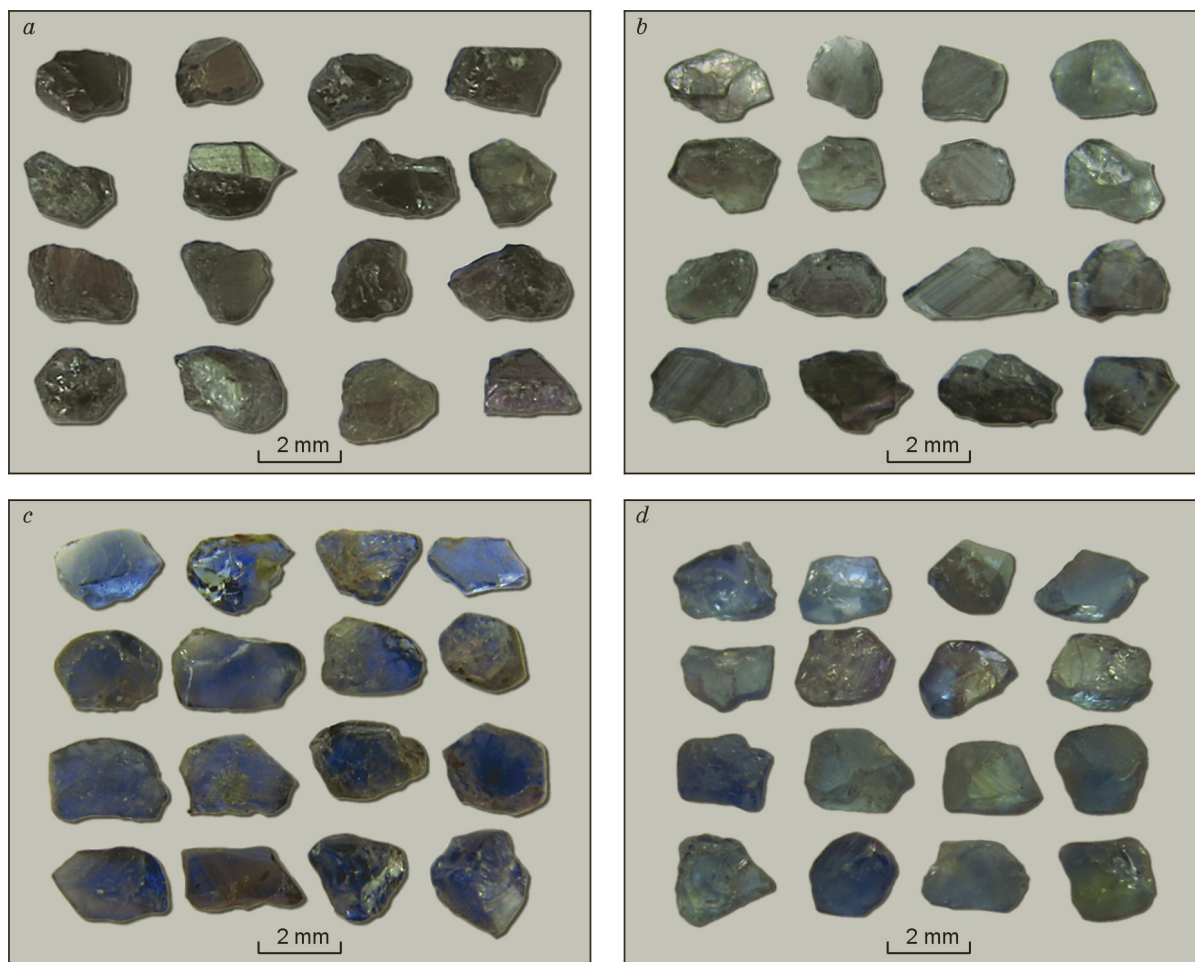


Fig. 2. Four varieties of the Bo Phloi sapphire samples used in this study: (a) dark grayish brown; (b) light grayish brown; (c) blue; and (d) light blue.

## Results

The mineral inclusions found in each sample group under study are summarized in Table 1. Some photomicrographs and BSI images of the mineral inclusions are shown in Fig. 3. Representative EPMA of these inclusions are presented in Tables 2–7. Details of each mineral inclusion are reported below.

### Feldspar

Feldspar is the most common mineral inclusion in all the color varieties of the Bo Phloi sapphires (Fig. 3a); however, it was more often found in the blue varieties (both blue and light blue). Representative EPMA analyses of the feldspar inclusions obtained from all the color varieties of the Bo Phloi sapphires are summarized in Table 2 for comparison. The ternary diagram for the Ca–Na–K atomic proportion (Fig. 4) shows that the compositions of all the feldspar inclusions found in these Bo Phloi sapphires plot as the Na-rich or albite component with a low to moderate K content and a low Ca content. Based on these compositions, they are clearly classified as alkali feldspar. In fact, Na-rich alkali feldspar (albite) inclusions of similar chemical composition were previously

detected in the blue and brown varieties of the Bo Phloi sapphire by Pisutha-Arnond et al. (1999). However, the feldspar inclusions in the dark grayish brown sapphire are slightly more sodic than those in the light grayish brown and light blue sapphires, whereas those in the blue sapphires appear to have a K-rich composition. Hence, three groups of feldspar inclusions can be distinguished (see the ternary diagram in Fig. 4); the first group ranges within the compositions  $\text{Ab}_{70-77}\text{Or}_{9-23}\text{An}_{6-14}$ , which are inferred from all the analyses in the dark grayish brown sapphires and one sample in the light blue sapphire. The second group ( $\text{Ab}_{52-63}\text{Or}_{28-35}\text{An}_{3-14}$ ) is from the inclusions found in all the light grayish brown, some light blue, and some blue sapphires. The third group ( $\text{Ab}_{42-45}\text{Or}_{42-49}\text{An}_{7-14}$ ) clearly belongs to the blue sapphires only. It seems likely that the formation of the blue sapphire is rather related to a K-rich environment, whereas that of the grayish brown sapphire is related to a Na-rich one. The light blue and light brown sapphires appear to be a transition between the former and the latter environments.

### Nepheline

Nepheline inclusions are found in almost all the varieties of the Bo Phloi sapphires except the light blue ones. Repre-

Table 1. Summary of mineral inclusions in the Bo Phloi sapphires

Mineral group	Mineral inclusion	Grayish brown sapphire		Blue sapphire	
		Dark grayish	Light grayish	Blue	Light blue
		(45 samples)	(48 samples)	(50 samples)	(30 samples)
Silicates	Zircon	***	**	**	**
	Feldspar	**	**	***	***
	Nepheline	**	***	**	—
	Enstatite	***	**	**	—
	Garnet	**	*	—	—
	Sapphirine	—	*	*	—
	Mica	*	—	—	—
	Staurolite	—	*	—	—
Oxides	Spinel	***	***	—	—
	Ilmenite	**	—	—	**
Carbonates	Calcite	*	—	—	—
Phosphates	Monazite	***	—	—	—

Note. \*\*\* Often found; \*\* found; \* rarely found; — not found.

sentative EPMA of the nepheline inclusions are summarized in Table 3. All the nepheline analyses show a high sodium content ( $\text{Na}_2\text{O} \sim 14\text{--}18\%$ ), and their atomic proportions are normal for nepheline chemistry, though one inclusion in a blue sapphire sample (3BA3g) is slightly more potassic ( $\text{Na}_{5.238}\text{K}_{1.969}\text{Al}_{0.581}\text{Al}_{8.073}\text{Si}_{8.044}\text{O}_{32}$ ). A similar composition of the nepheline inclusions in the Bo Phloi sapphires was previously reported by Pisutha-Armond et al. (1999) and Saminpanya (2000). In general, the nepheline inclusions observed in the Bo Phloi sapphire have a chemical composition similar to that of nepheline from nepheline syenite (Deer

et al., 1992) which is associated with low-temperature feldspar of the albite–microcline series. Moreover, nepheline is the most typical mineral in alkaline rocks. Therefore, this evidence implies that the sapphire formed in a silica-poor (undersaturated) and alkali-rich (Na and K) environment.

### Spinel

Spinel inclusions are commonly observed in the grayish brown sapphires. Their chemical compositions (Table 4) vary within narrow ranges of 58–60%  $\text{Al}_2\text{O}_3$ , 34–36% FeO, and

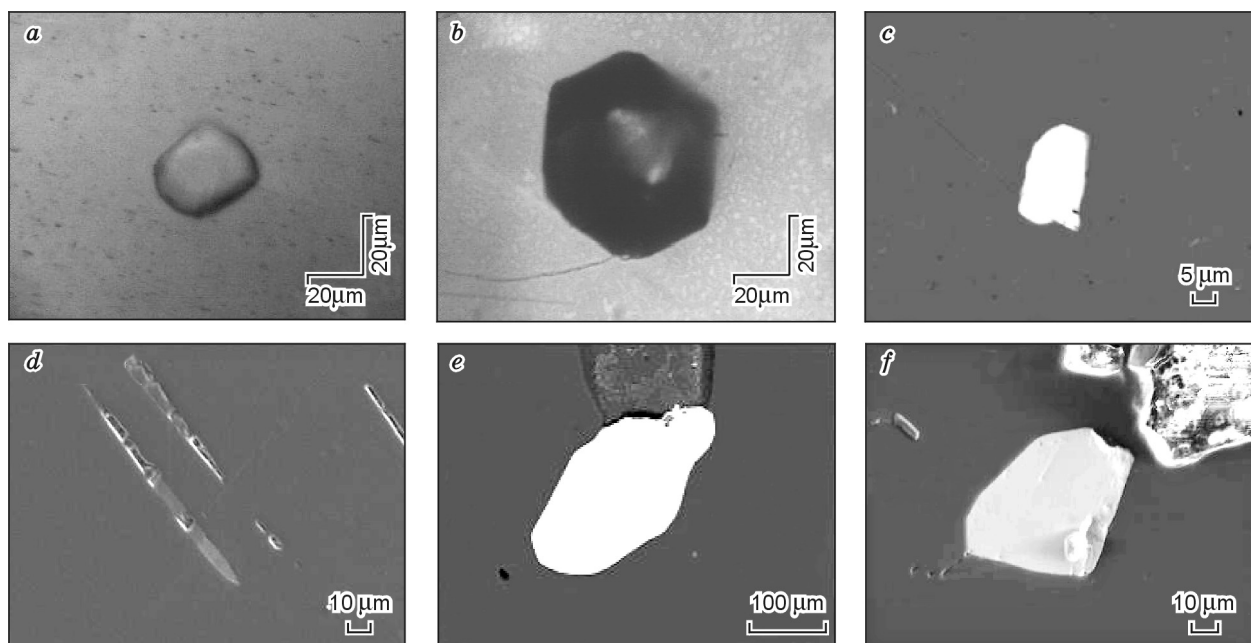


Fig. 3. Photomicrographs of (a) feldspar and (b) spinel; and back scattered electron images (BSI) of (c) spinel, (d) ilmenite, (e) zircon, and (f) monazite inclusions found in dark grayish brown sapphires.



Table 2. Representative EPMA of feldspar inclusions in the Bo Phloi sapphires

	Grayish brown sapphire				Blue sapphire			
	Dark grayish		Light grayish		Blue		Light blue	
	1C4ia2-1	1C4ib2	3LGC1g-3	3LGC3c	3BD3a	3BD1a	3LBA2g	3LBB6a
SiO <sub>2</sub>	63.84	63.69	64.81	64.00	65.60	63.55	63.09	65.88
TiO <sub>2</sub>	0.05	0.05	0.06	0.01	0.01	0.02	0.03	0.04
Al <sub>2</sub> O <sub>3</sub>	22.14	22.18	26.30	26.20	21.50	20.50	21.80	19.56
FeO	0.05	0.05	0.38	0.10	0.04	0.05	0.06	0.07
MnO	0.03	0.02	0.09	0.03	0.00	0.00	0.03	0.01
MgO	0.01	0.00	0.05	0.00	0.05	0.01	0.00	0.01
BaO	0.03	0.02	N.a.	N.a	N.a.	N.a	0.07	0.00
CaO	2.69	2.71	1.96	2.01	2.59	1.62	2.07	0.83
Na <sub>2</sub> O	8.32	8.38	4.39	5.11	4.31	5.11	7.20	7.57
K <sub>2</sub> O	1.66	1.61	3.93	3.45	6.52	8.59	5.60	6.50
Total	98.82	98.71	101.97	100.91	100.62	99.45	99.95	100.45
Formula 8(O)								
Si	2.853	2.850	2.794	2.786	2.908	2.895	2.841	2.947
Ti	0.002	0.002	0.002	0.000	0.000	0.001	0.001	0.001
Al	1.166	1.170	1.337	1.344	1.124	1.101	1.157	1.031
Fe	0.002	0.002	0.014	0.004	0.002	0.002	0.002	0.003
Mn	0.001	0.001	0.003	0.001	0.000	0.000	0.001	0.000
Mg	0.000	0.000	0.003	0.000	0.003	0.001	0.000	0.001
Ba	0.001	0.000	–	–	–	–	0.001	0.000
Ca	0.129	0.130	0.091	0.094	0.123	0.079	0.100	0.040
Na	0.721	0.727	0.367	0.431	0.371	0.451	0.628	0.656
K	0.095	0.092	0.216	0.192	0.369	0.499	0.321	0.371
Total*	4.970	4.973	4.827	4.853	4.899	5.029	5.054	5.050
Atomic %								
Na	76.3	76.6	54.5	60.2	43.0	43.8	59.9	61.5
Ca	13.6	13.7	13.5	13.1	14.2	7.7	9.5	3.7
K	10.0	9.7	32.1	26.7	42.8	48.5	30.6	34.8

Note. N.a., Not analyzed.

3–6% MgO, whereas the other components are negligible. Based on these chemical analyses, most of them fall within the spinel–hercynite series. The average chemical formula of these spinel inclusions could be expressed as  $(\text{Fe}_{6.343}\text{Mn}_{0.111}\text{Mg}_{1.647}\text{Zn}_{0.008})(\text{Si}_{0.002}\text{Ti}_{0.025}\text{Al}_{15.635}\text{Cr}_{0.011}\text{Fe}_{0.369})\text{O}_{32}$ . Hercynitic spinel inclusions of similar composition were also detected in the Bo Phloi sapphires by the previous investigators (Pisutha-Arnond et al., unpublished results; Saminpanya and Sutherland, 2011). The detailed compositions of these hercynitic spinel inclusions, however, differ from that of a cobalt-rich spinel inclusion found in the Bo Phloi sapphires, as previously reported by Guo et al. (1994, 1996).

#### Ilmenite

Ilmenite inclusions are relatively rare in all the varieties of the Bo Phloi sapphires. Some selected chemical analyses of ilmenite inclusions (Table 4) show a similar composition in

both the dark grayish brown and light blue varieties. Their compositions vary in ranges of 49–50% TiO<sub>2</sub>, 35–41% FeO, and 6–10% MnO with traces of MgO, except one inclusion in a light blue sample (3LBA2d) with relatively low TiO<sub>2</sub> (45.73%), low FeO (27.64%), and higher MnO (17.59%) contents. The average chemical formula of these ilmenite inclusions can be expressed as  $(\text{Fe}_{1.36}, \text{Mn}_{0.45})^{2+}\text{Fe}_{0.19}\text{Ti}_{1.86}\text{O}_3$ . Substitution of  $\text{Mn}^{2+}$  at divalent sites should, therefore, be classified as manganiferous ilmenite; besides, a small amount of  $\text{Fe}^{3+}$  may occur both at divalent and tetravalent sites.

#### Pyroxene

Pyroxene inclusions are found in both the grayish brown and blue sapphires. In general, the chemical composition of this pyroxene is fairly similar in both varieties; it is composed

Table 3. Representative EPMA of nepheline inclusions in the Bo Phloi sapphires

	Grayish brown sapphire				Blue sapphire	
	Dark grayish		Light grayish		Blue	
	2A7ia	1A3ia	3LGC4c-2	3LGC12f	3BA3g	3BC3a-2
SiO <sub>2</sub>	42.43	42.54	43.44	42.86	42.20	40.49
TiO <sub>2</sub>	N.a.	N.a.	0.03	0.08	0.05	N.a.
Al <sub>2</sub> O <sub>3</sub>	35.80	35.32	34.36	36.06	35.94	34.48
FeO	0.00	1.33	0.35	0.15	0.43	4.39
MnO	0.04	0.02	0.03	0.00	0.00	0.49
MgO	0.02	0.02	0.00	0.00	0.04	0.05
CaO	2.58	2.56	0.31	0.30	0.52	0.53
Na <sub>2</sub> O	15.66	15.17	15.53	17.88	14.17	14.68
K <sub>2</sub> O	4.54	4.52	5.61	3.54	8.10	5.48
Total	101.06	101.49	99.65	100.88	101.44	100.57
Formula 32(O)						
Si	8.032	8.055	8.326	8.085	8.044	7.883
Ti	–	–	0.004	0.011	0.007	–
Al	7.987	7.881	7.762	8.018	8.073	7.911
Fe	0.000	0.211	0.056	0.024	0.068	0.715
Mn	0.006	0.003	0.006	0.000	0.001	0.080
Mg	0.006	0.006	0.000	0.000	0.011	0.013
Ca	0.523	0.519	0.063	0.060	0.106	0.111
Na	5.746	5.568	5.771	6.541	5.238	5.539
K	1.096	1.091	1.371	0.852	1.969	1.360
Total*	23.396	23.334	23.359	23.591	23.516	23.611
ΣR	7.888	7.697	7.268	7.512	7.419	7.120

Note. ΣR = (2Ca + Na + K). N.a., Not analyzed.

of 60–65% SiO<sub>2</sub> and 31–35% MgO (Table 5). The recalculated formulae of the pyroxene inclusions have significantly high Si and slightly low Mg contents, though they are consistent with enstatite composition. However, the total number of cations, on the basis of six oxygen atoms, in all the analyses is less than four. This suggests the presence of a vacancy at the cation sites. Excess of Si<sup>4+</sup> and the substitution of Mg<sup>2+</sup> by Al<sup>3+</sup> may lead to the compensation of charge at the cation sites by such a vacancy. If we consider the chemical compositions in Table 5, the amount of excess atomic Si is almost equal to the number of vacancies in the enstatite structure. This study demonstrates that excess Si incorporation into the M site in the enstatite structure is charge-balanced by absences of atomic Mg<sup>2+</sup>.

The occurrence of Si-rich enstatite inclusions implies that their host sapphires might have crystallized from contaminated melts at the zone of contact of crustal materials (Si- and Al-rich) and mantle-derived basaltic magma (Mg source) (Arndt and Goldstein, 1989; Hawkesworth and Kemp, 2006; Hofmann, 1997; Shen et al., 2009).

### Garnet

Garnet inclusions are mainly observed in the grayish brown sapphire. Their chemical compositions (Table 6) fall in narrow ranges of 42–43% SiO<sub>2</sub>, 23–25% Al<sub>2</sub>O<sub>3</sub>, 20–21% MgO, and 13% FeO. Their atomic proportions fall within the range of the almandine–pyrope series with high Mg/(Mg + Fe<sup>2+</sup>) ratios ranging between 0.72–0.73 Mg (richer toward the pyrope end-member), which are similar to those of a garnet inclusion in Bo Rai ruby (0.87 Mg#) (Saminpanya and Sutherland, 2011) and a garnet xenocryst in Nong Bon ruby-related basalt (Sutthirat et al., 2001); both are ruby deposits situated in Eastern Thailand near the Thai–Cambodia frontier. However, the garnet inclusions in the Bo Phloi sapphires appear to be lacking the Ca component (Fig. 5); their end-member components are of composition Py<sub>72.30–75.45</sub>Alm<sub>24.50–27.53</sub>Gro<sub>0.05–0.17</sub>, which indicates a mantle source.

### Sapphirine

Sapphirine is a comparatively rare inclusion in the Bo Phloi sapphire. A few sapphirine inclusions with acceptable compo-

Table 4. Representative EPMA of spinel and ilmenite inclusions in the Bo Phloi sapphires and a published analysis of a spinel inclusion in Thai sapphire

	Spinel					Ilmenite			
	This study				(Saminpanya and Sutherland, 2011)	This study			
	Grayish brown sapphire					Grayish brown sapphire		Blue sapphire	
	Dark grayish		Light grayish			Dark grayish		Light blue	
	1B3ia2-1	1B3ia1	3LGD4b	3LGD4c		BPEP13-SP1	2DGA3c	2DGA3c-2	3LBA2a-1
SiO <sub>2</sub>	0.03	0.01	0.00	0.00	0.40	0.00	0.02	0.05	0.00
TiO <sub>2</sub>	0.07	0.15	0.17	0.18	N.a.	49.45	49.45	49.63	45.73
Al <sub>2</sub> O <sub>3</sub>	59.52	59.25	58.34	58.78	56.70	0.46	1.30	0.76	6.90
Cr <sub>2</sub> O <sub>3</sub>	0.16	0.00	0.02	0.07	0.80	N.a.	N.a.	N.a.	N.a.
FeO	35.39	35.98	36.14	35.19	35.30	41.02	41.02	35.79	27.64
MnO	0.22	0.24	0.98	0.88	0.90	6.88	6.88	10.80	17.59
MgO	5.85	5.90	4.19	3.76	6.70	0.69	0.69	0.53	0.98
ZnO	0.14	0.00	0.02	0.03	N.a.	0.04	0.04	n.a.	n.a.
CaO	0.00	0.00	0.00	0.00	N.a.	0.00	0.00	0.00	0.00
Total	101.36	101.53	99.85	98.89	100.80	98.55	99.40	97.56	98.84
Formula	32(O)					6(O)			
Si	0.007	0.001	0.000	0.000	0.090	0.000	0.001	0.003	0.000
Ti	0.011	0.026	0.029	0.032	–	1.917	1.893	1.931	1.713
Al	15.570	15.510	15.635	15.825	15.032	0.028	0.078	0.047	0.405
Cr	0.028	0.000	0.004	0.013	0.142	–	–	–	–
Fe <sup>2+</sup>	6.157	6.106	6.482	6.627	6.162	1.566	1.547	1.422	0.904
Fe <sup>3+</sup>	0.412	0.577	0.391	0.097	0.478	0.202	0.199	0.127	0.248
Mn	0.041	0.045	0.189	0.169	0.171	0.300	0.297	0.473	0.742
Mg	1.934	1.953	1.419	1.282	2.247	0.053	0.052	0.041	0.073
Zn	0.023	0.000	0.003	0.004	–	0.002	0.002	–	–
Ca	0.000	0.000	0.000	0.000	–	0.000	0.000	0.000	0.000
Total*	24.183	24.218	24.151	24.049	24.323	4.069	4.067	4.043	4.084
ΣR <sup>2+</sup>	8.155	8.105	8.093	8.083	8.581	1.921	1.897	1.935	1.718
ΣR <sup>3+</sup>	16.028	16.113	16.059	15.966	15.742	2.148	2.169	2.105	2.366

Note. ΣR<sup>2+</sup> = Fe<sup>2+</sup> + Mn + Mg + Zn + Ca. ΣR<sup>3+</sup> = Si + Ti + Al + Cr + Fe<sup>3+</sup>. N.a., Not analyzed.

sitions are obtained in this study (Table 6). In addition, the composition of the sapphirine inclusions found in Bo Na Wong ruby from Eastern Thailand (Saminpanya and Sutherland, 2011; Sutthirat et al., 2001) is displayed in this table for comparison. As shown in the table, the sapphirine inclusions in the Bo Phloi sapphire contain 2.07–2.41 Si p.f.u. and 7.68–9.04 Al p.f.u., with a narrow range of the Mg/(Mg + Fe<sup>2+</sup>) ratios (0.98–0.99). Their Mg/(Mg + Fe<sup>2+</sup>) values are slightly higher than those of the sapphirine inclusions in the Bo Na Wong ruby.

Sapphirine is a comparatively rare mineral, which typically occurs in high-grade alumina-rich silica-poor regional and contact-metamorphic rocks (Deer et al., 1992). Sapphirine was also observed as an inclusion in ruby from Bo Rai (Koivula and Fryer, 1987) in Eastern Thailand. In addition, Sutherland and Coenraads (1996) and Sutherland et al. (1998) reported sapphirine coexisting with spinel in pink sapphire and ruby

from basaltic terrains from Australia. These authors suggested a crystallization temperature of 780–940 °C for the aggregates and reactions with the host magma at over 1000 °C. Therefore, the presence of the sapphirine inclusions reported in this study indicates that some of the Bo Phloi sapphires might have crystallized under conditions of high-temperature regional or contact metamorphism.

#### Mica and staurolite

Mica and staurolite inclusions are observed only in the grayish brown sapphire varieties; however, their softness and perfect cleavage give rise to a poorly polished surface. Only a few analyses are acceptable and shown in Table 6. The major compositions of the mica inclusions seem to fall within the biotite–phlogopite range. In general, biotite–phlogopite is formed under a wide range of temperature and pressure

Table 5. Representative EPMA of pyroxene inclusions in the Bo Phloi sapphires

	Grayish brown sapphire				Blue sapphire	
	Dark grayish				Light grayish	Blue
	2DGA7c-3	2DGB2a-2	2DGB9c-2	2DGB10e-1	3LGC8b-1	3BC2a
SiO <sub>2</sub>	65.23	60.30	61.43	61.30	64.53	64.73
TiO <sub>2</sub>	0.00	0.03	0.03	0.02	0.02	0.02
Al <sub>2</sub> O <sub>3</sub>	0.21	0.09	0.20	0.62	0.31	0.15
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.04	0.00	0.07	0.04	0.00
FeO	0.86	3.26	6.36	5.93	1.46	1.30
MnO	0.01	0.00	0.00	0.01	0.00	0.03
MgO	33.13	35.69	30.93	31.21	32.58	31.75
NiO	0.00	0.01	0.00	0.00	N.a.	0.05
CaO	0.01	0.02	0.00	0.03	0.01	0.00
Na <sub>2</sub> O	0.00	0.02	0.00	0.01	0.03	0.01
K <sub>2</sub> O	0.01	0.01	0.01	0.02	0.01	0.00
Total	99.45	99.47	98.97	99.22	98.99	98.05
Formula 6(O)						
Si	2.163	2.046	2.110	2.098	2.157	2.179
Ti	0.000	0.001	0.001	0.000	0.001	0.000
Al	0.008	0.003	0.008	0.025	0.012	0.006
Cr	0.000	0.001	0.000	0.002	0.001	0.000
Fe	0.024	0.092	0.183	0.170	0.041	0.037
Mn	0.000	0.000	0.000	0.000	0.000	0.001
Mg	1.638	1.805	1.584	1.592	1.624	1.593
Ni	0.000	0.000	0.000	0.000	–	0.001
Ca	0.000	0.001	0.000	0.001	0.000	0.000
Na	0.000	0.001	0.000	0.001	0.002	0.000
K	0.000	0.001	0.000	0.001	0.000	0.000
Total*	3.833	3.952	3.886	3.889	3.837	3.818
Vacancy	0.167	0.048	0.114	0.111	0.163	0.182
Si <sub>excess</sub>	0.163	0.046	0.110	0.098	0.157	0.179

Note. Enstatite formula = (Mg, Fe, Al, Si<sub>excess</sub>)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> = (M2)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>. N.a., Not analyzed.

conditions; besides, it occurs abundantly in many contact- and regionally metamorphosed sediments. Among intrusive igneous rocks, it is especially common in granites, granite–pegmatites, and nepheline syenites (Deer et al., 1992).

Staurolite has been identified as a mineral inclusion in the Bo Phloi sapphire for the first time in this study (Table 6). In general, staurolite is a crucial assemblage of intermediate–high-grade metamorphic rocks. It is also a common constituent of regionally metamorphosed medium-grade argillaceous sediments, which typically develops in rocks rich in alumina (Deer et al., 1992). In addition, occurrence of staurolite was reported as an intergrowth with orthopyroxene and spinel in ultrahigh-temperature Al–Mg granulite (Belyanin et al., 2010). Therefore, the presence of the staurolite inclusion in the Bo Phloi sapphires indicates that they possibly crystallized under high-temperature metamorphic conditions.

### Zircon

Zircon is a very common inclusion in all the color varieties of the Bo Phloi sapphire. Its chemical composition (Table 7) varies within a narrow range of about 33–34% SiO<sub>2</sub>, 62–66% ZrO<sub>2</sub>, and a slightly wider range of 1.37–3.50% HfO<sub>2</sub>. The zircon inclusions in the blue sapphires have a slightly higher Hf content than the zircon inclusions in the grayish brown sapphires, particularly the zircon inclusions in sample 3BC9a-1 (up to 3.50% HfO<sub>2</sub>). However, they show rather uniform chemical compositions, as plotted in the Si–Zr–Hf ternary diagram (Fig. 6) and clearly show an increase in the Hf contents of the zircon inclusions in the light grayish brown sapphire toward those in the dark grayish, light blue, and blue sapphire, respectively; besides, high Hf content is present in zircon inclusions within blue sapphire from Huai Sai, Laos



Table 6. Representative EPMA of garnet, sapphirine, mica, and staurolite inclusions in the Bo Phloi sapphires and some published data for comparison

	Garnet			Garnet xenocryst		Sapphirine		Mica		Staurolite
	Bo Phloi		Bo Rai	Nong Bon	Bo Phloi	Bo Na Wong	Bo Phloi	Bo Phloi	Bo Phloi	
	Dark grayish	Light grayish	(Saminpanya and Sutherland, 2011)	(Suthirat et al., 2001)	Light grayish	(Suthirat et al., 2001)	Dark grayish	Dark grayish	Light grayish	
	2DGB1a	3LGD6c-3	BREPI-GRT1	NB-5A	3LGD6d-2	3BB8b-1	NWEP-9	NWEP9-SPR3	1A31a2-1	3LGC9b-1
SiO <sub>2</sub>	42.07	42.80	41.90	40.62	20.87	18.32	13.79	13.80	36.21	28.67
TiO <sub>2</sub>	0.01	0.01	N.a.	0.52	0.06	0.04	0.00	N.a.	2.83	0.00
Al <sub>2</sub> O <sub>3</sub>	25.14	23.88	23.40	22.48	56.50	67.94	62.91	62.90	28.28	58.92
Cr <sub>2</sub> O <sub>3</sub>	0.04	0.04	N.a.	0.05	0.00	0.00	0.24	0.20	N.a.	0.03
FeO	13.58	13.32	7.70	14.08	0.38	0.47	3.07	3.10	10.18	0.31
MnO	0.01	0.02	0.20	0.37	0.01	0.00	0.21	0.20	0.07	0.00
MgO	20.00	20.68	18.20	16.34	20.95	13.30	18.99	19.00	13.38	12.04
NiO	N.a.	N.a.	N.a.	N.a.	N.a.	N.a.	N.a.	0.50	N.a.	N.a.
CaO	0.07	0.03	8.40	5.35	0.02	0.05	0.11	0.10	0.00	N.a.
Na <sub>2</sub> O	N.a.	N.a.	0.40	N.a.	0.06	0.00	N.a.	N.a.	0.07	N.a.
K <sub>2</sub> O	N.a.	N.a.	N.a.	N.a.	0.04	0.00	N.a.	N.a.	6.34	N.a.
Total	100.94	100.78	100.20	99.81	98.89	100.12	99.32	99.80	97.35	99.97
Formula	24(O)				20(O)				24(O)	48(O)
Si	5.942	6.046	5.975	5.944	2.407	2.069	1.620	1.618	5.456	7.657
Ti	0.001	0.001	–	0.057	0.005	0.004	0.000	–	0.320	0.000
Al	4.185	3.975	3.933	3.877	7.682	9.043	8.710	8.689	5.021	18.544
Cr	0.005	0.004	–	0.006	0.000	0.000	0.022	0.019	–	0.005
Fe <sup>2+</sup>	1.604	1.573	0.580	1.553	0.036	0.044	0.261	0.222	0.309	0.069
Fe <sup>3+</sup>	0.000	0.000	0.339	0.170	0.000	0.000	0.040	0.082	0.974	0.000
Mn	0.002	0.003	0.024	0.046	0.001	0.000	0.021	0.020	0.009	0.000
Mg	4.212	4.356	3.869	3.565	3.604	2.239	3.326	3.320	3.005	4.793
Ni	–	–	–	–	–	–	–	0.047	–	–
Ca	0.010	0.005	1.283	0.839	0.003	0.006	0.014	0.013	0.000	–
Na	–	–	0.111	–	0.012	0.000	–	–	0.019	–
K	–	–	–	–	0.006	0.000	–	–	1.218	–
Total*	15.962	15.963	16.114	16.057	13.757	13.406	14.014	14.029	16.331	31.068
ΣR <sup>2+</sup>	1.616	1.581	1.887	2.437	0.040	0.050	0.296	0.302		
ΣR <sup>3+</sup>	4.191	3.980	4.271	4.110	7.687	9.047	8.772	8.789		
Mg/(Mg + Fe <sup>2+</sup> )	0.72	0.73	0.87	0.70	0.99	0.98	0.93	0.94		

Note. ΣR<sup>2+</sup> = Fe<sup>2+</sup> + Mn + Mg + Ca. ΣR<sup>3+</sup> = Ti + Al + Cr + Fe<sup>3+</sup>. N.a., Not analyzed.

Table 7. Representative EPMA of zircon inclusions in the Bo Phloi sapphires and some published data for comparison

	Bo Phloi								Bo Phloi alluvial zircon	Ban Huai Sai
	Grayish brown sapphire				Blue sapphire				(Sutthirat, 2001)	(Sutherland et al., 2002)
	Dark grayish		Light grayish		Blue		Light blue			
	1B3ib2	2DGC6a-REE2	3LGC1c-1	3LGC1d	3BC9a-1	3BC13a	3LBA7a	3LBC9a		
SiO <sub>2</sub>	33.08	32.49	34.22	33.08	34.14	34.44	34.10	33.83	31.57	31.23
ZrO <sub>2</sub>	64.65	65.57	64.04	66.18	62.40	63.36	64.91	65.13	68.42	64.02
HfO <sub>2</sub>	1.62	1.75	1.37	1.59	3.50	2.40	2.39	2.33	0.81	3.58
Al <sub>2</sub> O <sub>3</sub>	0.12	0.01	0.00	0.02	0.17	0.05	0.10	0.02	0.00	0.01
CaO	0.01	0.00	0.02	0.01	0.00	0.02	0.02	0.00	0.00	N.a.
FeO	0.06	0.06	0.03	0.00	0.04	0.06	0.02	0.05	0.00	0.06
Total	99.54	99.87	99.68	100.87	100.25	100.33	101.54	101.35	100.80	98.90
Formula 4(O)										
Si	1.013	0.998	1.038	1.004	1.036	1.040	1.023	1.019	0.968	0.981
Zr	0.966	0.982	0.947	0.979	0.923	0.933	0.949	0.956	1.023	0.980
Hf	0.017	0.018	0.014	0.016	0.036	0.025	0.024	0.024	0.008	0.038
Al	0.004	0.000	0.000	0.001	0.006	0.002	0.004	0.001	0.000	0.000
Ca	0.000	0.000	0.001	0.000	0.000	0.001	0.001	0.000	0.000	–
Fe	0.002	0.001	0.001	0.000	0.001	0.002	0.001	0.001	0.000	0.002
Total*	2.002	2.001	2.001	2.000	2.002	2.002	2.001	2.001	2.000	2.001
Atomic %										
Si	50.8	49.9	51.9	50.2	51.9	52.1	51.2	51.0	48.4	49.1
Zr	48.4	49.1	47.4	49.0	46.3	46.7	47.6	47.8	51.2	49.0
Hf	0.8	0.9	0.7	0.8	1.8	1.2	1.2	1.2	0.4	1.9

Note. N.a., Not analyzed.

(Sutherland et al., 2002). The Bo Phloi zircon inclusions in this study obviously have a higher HfO<sub>2</sub> content than Bo Phloi alluvial zircons (Sutthirat, 2001), which implies different origins of both types of zircon. Wark and Miller (1993) reported that the Hf content in the zircon can roughly reflect the degree of differentiation of the parental melt; e.g., the high abundances of Hf in the Bo Phloi zircon inclusions suggest that the host sapphire was derived from a highly evolved source material.

In this study, a suitable zircon inclusion (sample 1B3ib2), observed in dark grayish brown sapphire, was selected for analyses of trace-element and rare-earth element (REE) contents, because this inclusion had a good oval shape, large size (200 μm), and no fracture (Fig. 3e). The LA-ICP-MS technique was employed for the trace-element analysis of the zircon inclusion in this work. The REE contents of the zircon inclusion were normalized to those of chondrite (values from Taylor and McLennan, 1985) and plotted together with those of zircons in various rock types (data from Belousova et al., 2002 in Fig. 7). Moreover, trace-element analyses of zircon in a zircon + sapphire + nepheline + hercynitic spinel assemblage and of zircon in “corsilzirspite” gravel (unusual rock comprising corundum, sillimanite, zircon, and spinel), found

in the Bo Phloi alluvial gem-bearing layer (unpublished results of Pisutha-Armond), are plotted for comparison in the same figure. The chondrite-normalized pattern of the Bo Phloi zircon inclusion appears to be similar to those of the Bo Phloi zircons from the assemblage and from the “corsilzirspite” gravel. In addition, all the patterns of the Bo Phloi zircons show a positive Ce anomaly, a negative Eu anomaly, and a rapid rise toward heavy REE, which is similar to the patterns of zircon from syenite pegmatite rocks. This suggests that the Bo Phloi zircons might have crystallized from relatively evolved and oxidized melts such as granitoid or syenite pegmatite, in which most of Eu is expected to be in divalent state. In addition, these Bo Phloi chondrite-normalized REE patterns match the REE pattern of type 4 zircon (Fig. 7), published by Nemchin et al. (2010), who reported that such zircon may be associated with some felsic and granitic source representing very late differentiation of primitive mafic magmas.

#### Other mineral inclusions

Apart from the mineral inclusions reported above, other minerals such as monazite and calcite were identified in these

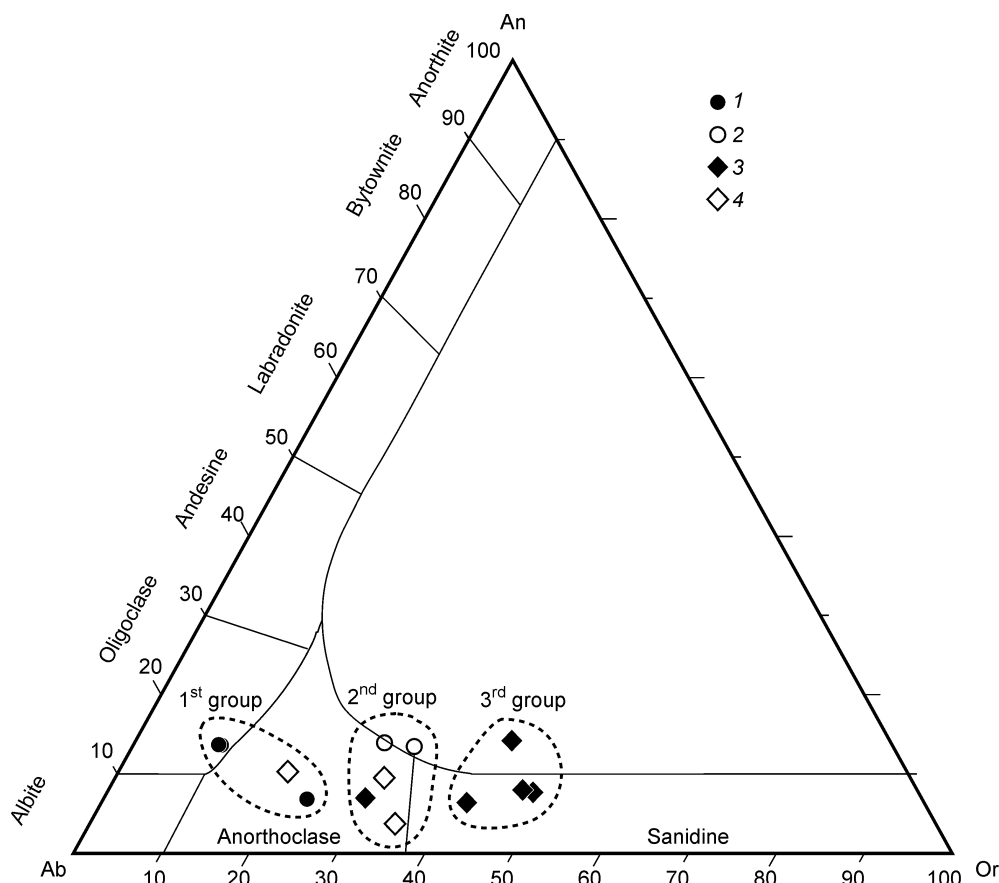


Fig. 4. Ternary Ca–Na–K plots of alkali feldspar inclusions in the Bo Phloi sapphires. 1, dark grayish brown sapphires; 2, light grayish brown sapphires; 3, blue sapphires; 4, light blue sapphires.

sapphire samples. Monazite inclusions were also reported from basaltic sapphires such as the Cyangu District in SW Rwanda (Krzemnicki et al., 1996), Thailand and Cambodia (Intasopa et al., 1998), and Huai Sai in Laos (Singbamroong and Thanasuthipitak, 2004); however, all these previous works were characterized by the application of the Raman technique. Monazite usually occurs as a rare accessory mineral in granitic rocks, syenitic rocks, and granitic pegmatites with great enrichment in Ce, La, and Nd (Deer et al., 1992). Calcite is also recognized as an inclusion in the Bo Phloi sapphires. As stated earlier, calcite inclusions were reported in the Bo Phloi sapphire by Pisutha-Arnond et al. (unpublished results). Calcite may occur in certain alkaline igneous rocks, notably some nepheline syenites (Deer et al., 1992). Therefore, the find of calcite inclusions in this study may support the nepheline syenite origin of the Bo Phloi sapphire.

## Discussion

A wide variety of mineral inclusions in the Bo Phloi sapphires has been discovered in this study. These inclusions are alkali feldspar, nepheline, hercynitic spinel, zircon, manganiferous ilmenite, silica-rich enstatite, almandine–pyrope garnet, monazite, calcite, sapphirine, biotite–phlogopite mica,

and staurolite. Most of these inclusions appear to have been incorporated into their host sapphires during their formation, because they seem to have an equilibrium mutual grain contact with the host sapphires without a reaction rim or resorbed outline (Fig. 3). Hence, they must provide valuable information about the chemical environment, physical conditions, and geologic processes during the initial host sapphire crystallization before they were brought to the surface via basaltic eruptions. Alkali feldspar, zircon, and nepheline are the predominant inclusions, while Si-rich enstatite, hercynitic spinel, manganiferous ilmenite, monazite, almandine–pyrope garnet, sapphirine, biotite–phlogopite mica, staurolite, and calcite are found occasionally. Based on their geochemical affinities, such mineral inclusions can be categorized into two groups: alkaline magma-related and metamorphic-related mineral suites. Each group of inclusions may give clues to the parental rocks of their host sapphires.

The alkaline-related inclusion suite comprises alkali feldspar, nepheline, zircon, manganiferous ilmenite, monazite, and, probably, calcite, which are likely to be mineral phases crystallized from alkaline felsic magma. The composition of the alkali-feldspar inclusions appears to range from Na-rich (albitic) feldspar in the grayish brown variety to K-richer feldspar in the blue variety. This variation seems to be consistent with the composition of the nepheline inclusions,

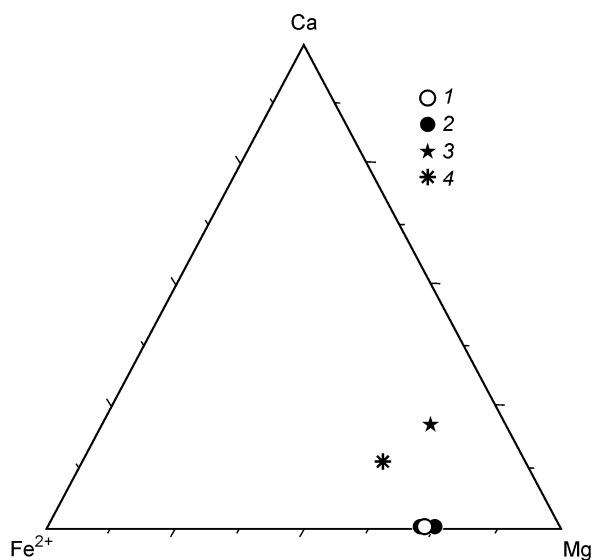


Fig. 5. Ternary Ca–Fe<sup>2+</sup>–Mg plots of garnet inclusions in the Bo Phloi sapphires and published data of ruby-related garnets from eastern Thailand for comparison. 1, light grayish brown sapphires; 2, dark grayish brown sapphires; 3, garnet inclusions in Bo Rai ruby (Saminpanya and Sutherland, 2011); 4, garnet xenocryst in Nong Bon ruby-related basalt (Sutthirath et al., 2001).

in which the Na-rich nepheline is found in the grayish brown variety, while slightly K-rich nepheline occurs in the blue variety only. In fact, both minerals are known as typical constituents of nepheline syenite (Deer et al., 1992; Wilkinson and Hensel, 1994).

Apart from the alkali-feldspar and nepheline inclusions, the chemical composition of the zircon inclusions indicates the formation of the Bo Phloi sapphire from highly evolved felsic melts. Moreover, the chondrite-normalized REE patterns of these zircon inclusions show a positive Ce anomaly and Eu depletion, similarly to those in the patterns of zircon from syenite–pegmatite rocks (Belousova et al., 2002). Furthermore, manganiferous ilmenite generally occurs in igneous rocks and in some s which may have an anomalous content (Deer et al., 1992). Hence, the presence of manganiferous (without anomalous Nb) ilmenite inclusions in the Bo Phloi sapphires (particularly, in the blue variety) also favors a felsic-melt origin. In addition, the existence of monazite (as well as Nb oxide; Pisutha-Armond et al., 1999) inclusions in these sapphires supports the origin from a highly evolved melt, as they are common accessory minerals in felsic rocks. Based on the occurrences of this mineral inclusion suite, the majority of the Bo Phloi sapphires appears to have crystallized from a highly evolved alkali-rich silica-poor melt such as syenitic magma.

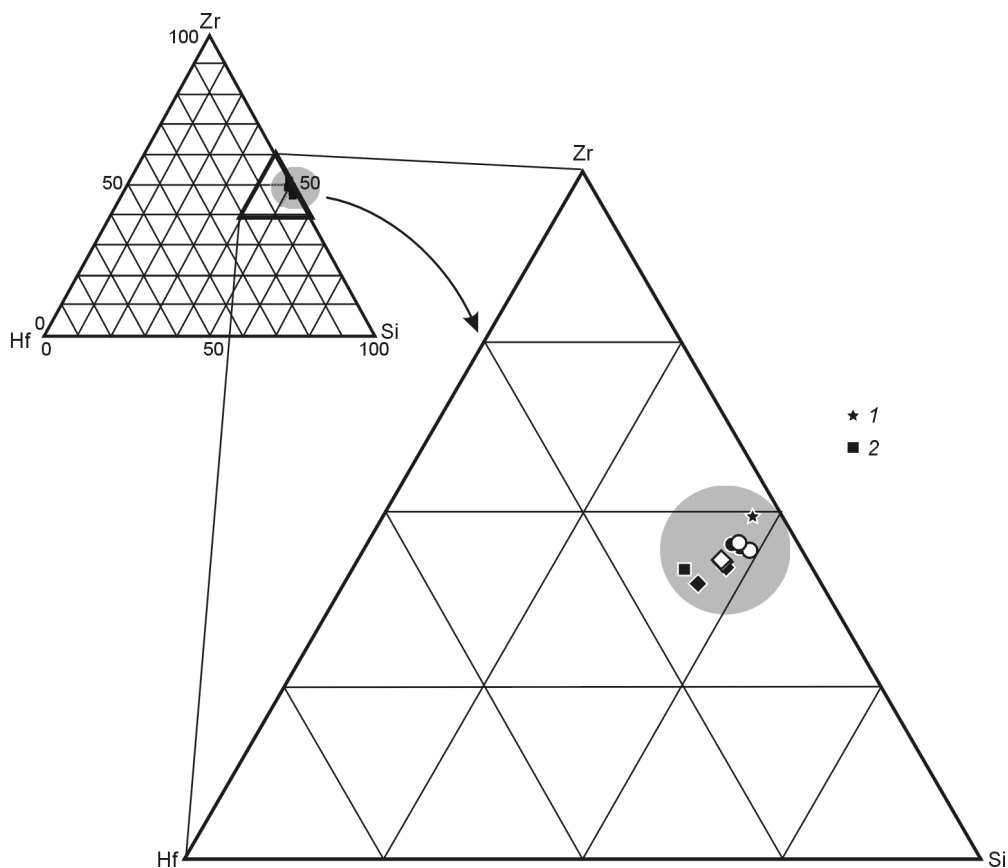


Fig. 6. Ternary Si–Zr–Hf plot of zircon inclusions in the Bo Phloi sapphires and alluvial zircon (Sutthirath, 2001) from the same deposit as well as zircon inclusions from Ban Huai Sai sapphire, Laos (Sutherland et al., 2002). 1, alluvial zircons in Bo Phloi sapphire (Sutthirath, 2001); 2, zircon inclusions in Ban Huai Sai sapphire (Sutherland et al., 2002). See Fig. 4 for other designations.

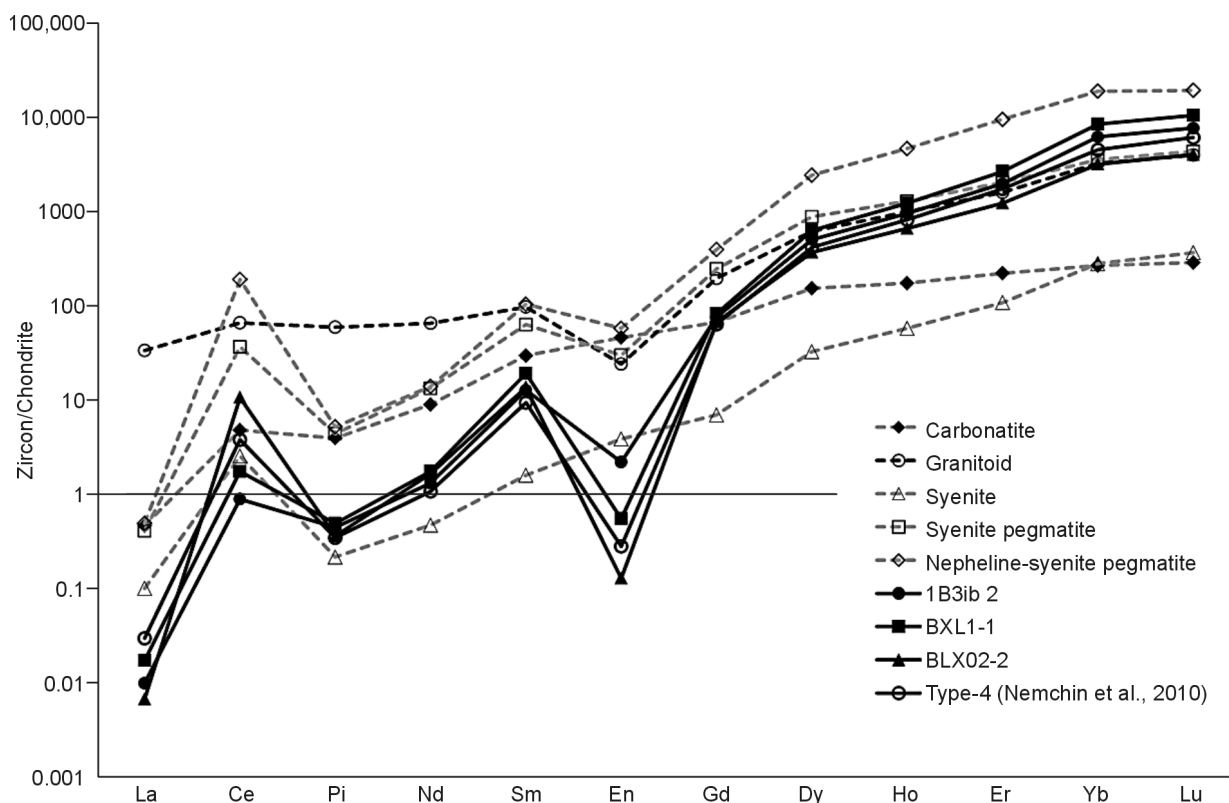


Fig. 7. Chondrite-normalized REE patterns of a zircon inclusion (sample 1B3ib2, filled circles) as well as zircon in a zircon + sapphire + nepheline + hercynite spinel assemblage (sample BLX02-2, filled triangles) and zircon in “corsilzirspite” gravel (sample BXL1-1, filled squares), both from the Bo Phloi deposit, compared with patterns of zircons from various rocks (data from Belousova et al., 2002 and Nemchin et al., 2010).

The syenitic origin agrees with the genetic model for the Bo Phloi sapphire and other basaltic sapphires proposed by the previous researchers. For example, Saminpanya (2000) proposed a nepheline syenite origin of the Bo Phloi sapphires based on the presence of nepheline inclusions. Moreover, Guo et al. (1996) reported ilmenite inclusions, together with feldspar, zircon, uraninite, and Fe, Cu sulfide inclusions, in common basaltic sapphires and hypothesized an alkaline granitic or syenitic liquid origin. This also agrees with the previous genetic models for common basaltic sapphires, originally derived from felsic rather than mafic melts (Coenraads et al., 1990, 1995; Izokh et al., 2010; Sutherland and Schwarz, 2001) (most likely, syenitic melts; probably, within upper mantle to lower crust) (e.g., Aspen et al., 1990; Upton et al., 1999).

The metamorphic inclusion suite found in the Bo Phloi sapphires comprises Si-rich enstatite, almandine–pyrope garnet, sapphirine, staurolite, biotite–phlogopite mica, and, probably, hercynitic spinel. Although the metamorphic inclusions are comparatively rarer than the alkaline-related inclusions in the Bo Phloi sapphires, their presence is especially noteworthy, as most of these phases (except hercynitic spinel) have never been recorded as inclusions in the Bo Phloi basaltic sapphires before. These mineral inclusions provide further strong evidence for the previously proposed genetic model for the Bo Phloi sapphire, related to the contact-metamorphic reaction of basaltic magma and crustal rocks.

The presence of the Si-rich enstatite inclusions in the Bo Phloi sapphires may be crucial evidence for a hybrid metasomatic reaction between basaltic magma and crustal materials (e.g., alkaline felsic rocks or other crustal rocks), as their composition is, most likely, derived from both types of source material. In addition, this Si-rich enstatite has a rather high Al content, probably originating from the crustal source. The crystallization of Si-rich enstatite, therefore, may be a result of contamination in the zone of contact between mafic mantle magma and crustal rocks that are rich in both silica and alumina. Furthermore, the occurrence of almandine–pyrope garnet with a pyrope-rich end-member indicates a deep-seated source (most likely, mantle or lower crust).

The presence of sapphirine, staurolite, and biotite–phlogopite inclusions in the Bo Phloi sapphire is further evidence that the host sapphire formed in high-temperature contact-metamorphic environments. Even though hercynitic spinel can occur in both metamorphic and magmatic rocks (Deer et al., 1992), the occurrence of hercynitic spinel inclusions in the Bo Phloi sapphire, in which their compositions are similar to those of the hercynitic spinel in the “corsilzirspite” gravel (Pisutha-Arnond et al., 1999, 2005), points, at least in some cases, to a contact-metamorphic origin of alumina-rich crustal rock. This evidence suggests that the Bo Phloi sapphires might also have crystallized from metasomatic reactions and contaminated melt of basaltic magma rising from the mantle and crustal rocks. Under such contact-metasomatic conditions,



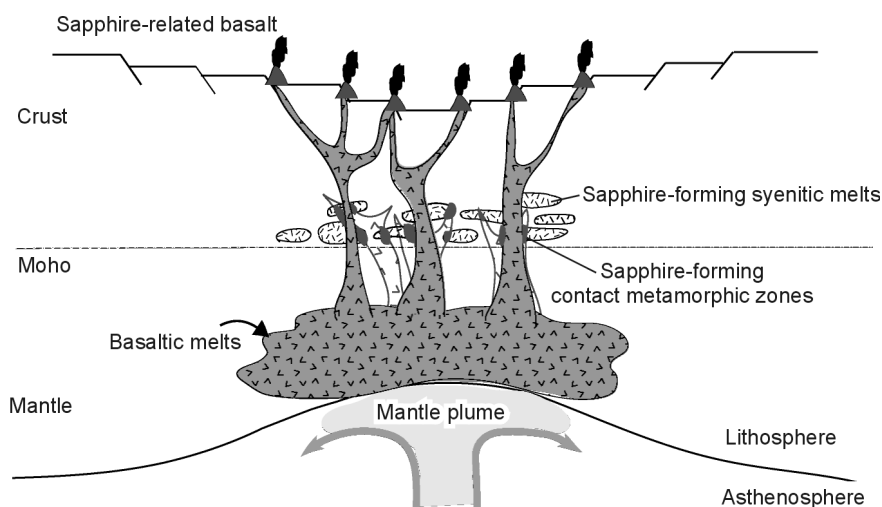


Fig. 8. Bimodal genetic model of the Bo Phloi sapphire formation, including syenitic melt-related and contact metamorphic-related origins.

desilicification of the crustal materials might have occurred. As a result, sapphire, along with those metamorphic mineral suites, might have crystallized from the metasomatized rocks and contaminated melt at or near the contact zone. The metamorphic origin of the Bo Phloi sapphires also agrees with the contact-metamorphic/metasomatic/contaminated gabbroic model proposed earlier by Pisutha-Arnond et al. (1999, 2005), which is based on the discovery of the “corsilzirspite” gravel in the sapphire-bearing gravel bed in the Bo Phloi gem field.

Referring to the above evidence and discussion, it is reasonable to propose a bimodal genetic model for the Bo Phloi sapphire formation: (1) syenitic-melt origin, when the sapphires crystallized from highly evolved melts of alkaline felsic composition, derived from mafic crustal material with a low degree of partial melting, and (2) contact-metamorphic origin, when the sapphire originated from the metasomatized crustal rocks and contaminated melt at the zone of contact of basaltic intrusions. This is also consistent with the data by Peucat et al. (2007), who found that the trace-element signatures of the Bo Phloi sapphires overlapped both magmatic and metamorphic fields. The bimodal genetic model for the formation of the Bo Phloi sapphire is illustrated by Fig. 8. As shown in this figure, both the basaltic melt and felsic alkaline melt were generated as a result of decompression stress. Rifting and thinning of lithosphere in the Bo Phloi area and the Southeast Asian region might have developed initially and led to an enormous pressure release. Meanwhile, expansion of hot asthenosphere took place. Subsequently, basaltic magma may have been formed by such upwelling asthenosphere in the upper mantle beneath this region during the crustal extension. At the same time, the felsic alkaline melt (i.e., syenite) might also have formed as a result of low-degree partial melting of the mafic layer in the lower crust owing to crustal thinning and/or a mantle plume. Hence, the Bo Phloi sapphires might have crystallized from such early syenitic melts, whose slow cooling began shortly afterward. Later, larger areas of both felsic alkaline melt and basaltic melt were formed, which then caused an uprising of basaltic melts from

the upper mantle to form contact zones with the lower crustal rocks above the mantle plume in this area. The syenitic melt-related sapphires still crystallized episodically, while basaltic intrusions from the upper mantle to the lower crust might have caused additional formation of so-called “contact-metamorphic sapphire” from such a contact zone and contaminated melts. This is strongly confirmed by the find of the “corsilzirspite” gravel in the Bo Phloi mine (unpublished results of Pisutha-Arnond), which may represent the main contact-metamorphic sapphires. Afterward, the alkaline basaltic magma rose from deep-seated mantle and carried mantle xenoliths (e.g., spinel lherzolite, suggested by Srithai, 2005; Sutthirath, 2001; Sutthirath et al., 1999), xenocrysts (e.g., pleonastic spinel, diopside pyroxene, Al–Ti-rich magnetite, and zircon, reported by Pisutha-Arnond et al., 1999; Saminpanya and Sutherland, 2008), and xenoliths of crustal rocks (including sapphires crystallized from the felsic alkaline melts and contact-metamorphic zones formed earlier and during the time of eruption to the surface).

## Conclusions

The detailed analysis of the mineral chemistry of inclusions in the Bo Phloi sapphires carried out in this study has revealed unique mineral inclusion suites relevant to the origin of their host sapphires. The mineral inclusions found in the Bo Phloi sapphires illustrate a wide range of mineral phases: alkali feldspar, nepheline, hercynitic spinel, zircon, manganiferous ilmenite, silica-rich enstatite, almandine–pyrope garnet, monazite, calcite, sapphirine, biotite–phlogopite mica, and staurolite. Moreover, the trace-element study of a representative zircon inclusion in the Bo Phloi sapphire reveals a typical positive Ce anomaly and Eu depletion of chondrite-normalized REE patterns, which conclusively demonstrate that this zircon inclusion crystallized from syenitic magma. Based on the mineral chemistry of the inclusions in these sapphires, they appear to belong to at least two distinct mineral groups: felsic

alkaline and contact-metamorphic, which were likely to originate from different environments. A “bimodal genetic model” is, therefore, proposed based on such strong evidence for “syenitic-melt” and “contact-metamorphic” origins of the Bo Phloi sapphires.

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## References

- Arndt, N.T., Goldstein, S.L., 1989. An open boundary between lower continental crust and mantle: its role in crust formation and crustal recycling. *Tectonophysics* 161 (3–4), 201–212.
- Aspen, P., Upton, B.G.J., Dickin, A.P., 1990. Anorthoclase, sanidine and associated megacrysts in Scottish alkali basalts; high-pressure syenitic debris from upper mantle sources? *Eur. J. Mineral.* 2 (4), 503–517.
- Barr, S.M., Macdonald, A.S., 1978. Geochemistry and petrogenesis of Late Cenozoic alkaline basalts of Thailand. *Geol. Soc. Malaysia Bull.* 10, 21–48.
- Barr, S.M., Macdonald, A.S., 1981. Geochemistry and geochronology of late Cenozoic basalts of Southeast Asia: Summary. *Geol. Soc. Am. Bull.* 92 (8), 508–512.
- Belousova, E.B., Griffin, W.L., O'Reilly, S., Fisher, N.I., 2002. Igneous zircon: trace element composition as an indicator of source rock type. *Contrib. Mineral. Petrol.* 143 (5), 602–622.
- Belyanin, G.A., Rajesh, H.M., Van Reenen, D.D., Mouri, H., 2010. Corundum + orthopyroxene ± spinel intergrowths in an ultrahigh-temperature Al–Mg granulite from the Southern Marginal Zone, Limpopo Belt, South Africa. *Am. Mineral.* 95 (1), 196–199.
- Coenraads, R.R., Sutherland, F.L., Kinny, P.D., 1990. The origin of sapphires; U–Pb dating of zircon inclusions sheds new light. *Mineral. Mag.* 54 (374), 113–122.
- Coenraads, R.R., Vichit, P., Sutherland, F.L., 1995. An unusual sapphire–zircon–magnetite xenolith from the Chanthaburi Gem Province, Thailand. *Mineral. Mag.* 59 (3), 465–479.
- Deer, W.A., Howie, R.A., Zussman, J., 1992. *An Introduction to the Rock-Forming Minerals*, 2nd ed. Longman, Essex; Wiley, New York.
- Droop, G.T.R., 1987. A General Equation for Estimating  $\text{Fe}^{3+}$  Concentrations in Ferromagnesian Silicates and Oxides from Microprobe Analyses, Using Stoichiometric Criteria. *Miner. Mag.* 51 (361), 431–435.
- Guo, J., Griffin, W.L., O'Reilly, S.Y., 1994. A cobalt-rich spinel inclusion in a sapphire from Bo Phloi, Thailand. *Miner. Mag.* 58 (391), 247–258.
- Guo, J., O'Reilly, S.Y., Griffin, W.L., 1996. Corundum from basaltic terrains: a mineral inclusion approach to the enigma. *Contrib. Mineral. Petrol.* 122 (4), 368–386.
- Hansawek, R., Pattamalai, K., 1997. Kanchanaburi sapphire deposits, in: Dheeradolok, P., Hinthong, C., Chaodumrong, P., Putthapiban, P., Tansathien, W., Utharoon, C., Sattayarak, N., Nuchanong, T., Techawan, S. (Eds.), *Proc. of Int. Conf. on Stratigraphy and Tectonic Evolution of Southeast Asia and the South Pacific (Geothai '97)* (19–24 August 1997). Department of Mineral Resources, Bangkok, p. 717.
- Hawkesworth, C.J., Kemp, A.I.S., 2006. Evolution of the continental crust. *Nature* 443 (7113), 811–817.
- Hofmann, A.W., 1997. Mantle geochemistry: the message from oceanic volcanism. *Nature* 385 (6613), 219–229.
- Intasopa, S., Atichat, W., Pisutha-Arnond, V., 1998. Inclusions in Corundum: A New Approach to the Definition of Standards for Origin Determination, Science and Technology for Gem and Jewelry Industry [in Thai]. Thailand Research Fund.
- Izokh, A.E., Smirnov, S.Z., Egorova, V.V., Tran Tuan Anh, Kovyazin, S.V., Ngo Thi Phuong, Kalinina, V.V., 2010. The conditions of formation of sapphire and zircon in the areas of alkali-basaltoid volcanism in Central Vietnam. *Russian Geology and Geophysics (Geologiya i Geofizika)* 51 (7), 719–733 (925–943).
- Koivula, J.I., Fryer, C.W., 1987. Sapphirine (not sapphire) in a ruby from Bo Rai, Thailand. *J. Gemmol.* 20 (6), 369–370.
- Krzemnicki, M.S., Hänni, H.A., Guggenheim, R., Mathys, D., 1996. Investigations on sapphires from an alkali basalt, South West Rwanda. *J. Gemmol.* 25 (2), 90–106.
- Nemchin, A.A., Grange, M.L., Pidgeon, R.T., 2010. Distribution of rare earth elements in lunar zircon. *Am. Mineral.* 95 (2–3), 273–283.
- Peucat, J.-J., Ruffault, P., Fritsch, E., Bouhnik-Le Coz, M., Simonet, C., Lasnier, B., 2007. Ga/Mg ratio as a new geochemical tool to differentiate magmatic from metamorphic blue sapphires. *Lithos* 98 (1–4), 261–274.
- Pisutha-Arnond, V., Wathanakul, P., Intasopa, S., 1999. New Evidence on the Origin of Kanchanaburi Sapphire [in Thai]. Final Report Submitted to the Thailand Research Fund (TRF).
- Pisutha-Arnond, V., Intasopa, S., Wathanakul, P., Griffin, W.L., Atichat, W., Sutthirath, C., 2005. Sapphire xenocrysts in basalt from the Bo Phloi Gem Field, Western Thailand, in: Wannakao, L., Youngme, W., Srisuk, K., Lertsirivorakul, R. (Eds.), *Proc. of Int. Conf. on Geology, Geotechnology and Mineral Resources of Indochina (GEOINDO 2005)* (Khon Kaen, 28–30 November 2005). Khon Kaen, pp. 338–344.
- Saminpanya, S., 2000. Mineralogy and origin of gem corundum associated with basalt in Thailand. Dissertation. The University of Manchester, United Kingdom.
- Saminpanya, S., Sutherland, F.L., 2008. Black opaque gem minerals associated with corundum in the alluvial deposits of Thailand. *Aust. Gemmol.* 23 (6), 242–253.
- Saminpanya, S., Sutherland, F.L., 2011. Different origins of Thai area sapphire and ruby, derived from mineral inclusions and co-existing minerals. *Eur. J. Mineral.* 23 (4), 683–694.
- Shen, B., Jacobsen, B., Lee, C.-T.A., Yin, Q.-Z., Morton, D.M., 2009. The Mg isotopic systematics of granitoids in continental arcs and implications for the role of chemical weathering in crust formation. *PNAS* 106 (49), 20,652–20,657.
- Singbamroong, S., Thanasuthipitak, T., 2004. Study of solid mineral inclusions in sapphires from Ban Huai Sai area, Laos by Raman spectroscopy. *Chiang Mai J. Sci.* 31 (3), 251–263.
- Srithai, B., 2005. Petrography and mineral chemistry of ultramafic xenoliths from Bo Phloi basalt, Kanchanaburi, Thailand, in: Wannakao, L., Youngme, W., Srisuk, K., Lertsirivorakul, R. (Eds.), *Proc. of Int. Conf. on Geology, Geotechnology and Mineral Resources of Indochina (GEOINDO 2005)* (Khon Kaen, 28–30 November 2005). Khon Kaen, pp. 358–364.
- Sutherland, F.L., Coenraads, R.R., 1996. An unusual ruby–sapphire–sapphirine–spinel assemblage from the Tertiary Barrington volcanic province, New South Wales, Australia. *Mineral. Mag.* 60 (401), 623–638.
- Sutherland, F.L., Schwarz, D., 2001. Origin of gem corundums from basaltic fields. *Austral. Gemmol.* 21 (1), 30–33.
- Sutherland, F.L., Hoskin, P.W.O., Fanning, C.M., Coenraads, R.R., 1998. Models of corundum origin from alkali basaltic terrains: a reappraisal. *Contrib. Mineral. Petrol.* 133 (4), 356–372.
- Sutherland, F.L., Bosshart, G., Fanning, C.M., Hoskin, P.W.O., Coenraads, R.R., 2002. Sapphire crystallization, age and origin, Ban Huai Sai, Laos: age based on zircon inclusions. *J. Asian Earth Sci.* 20 (7), 841–849.
- Sutthirath, C., Charusiri, P., Farrar, E., Clark, A.H., 1994. New  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology and characteristics of some Cenozoic basalts in Thailand, in: *Proc. of Int. Symp. on Stratigraphic Correlation of Southeast Asia*. Bangkok, pp. 306–321.
- Sutthirath, C., Droop, G.T.R., Henderson, C.M.B., Manning, D.A.C., 1999. Petrography and Mineral Chemistry of Xenoliths and Xenocrysts in Thai Corundum-Related Basalts: Implications for the Upper Mantle and Lower

- Crust beneath Thailand, in: Proc. of Symp. on Mineral, Energy, and Water Resources of Thailand: Towards the Year 2000. Chulalongkorn University, Bangkok, pp. 152–161.
- Sutthirat, C., 2001. Petrogenesis of mantle and crustal xenoliths and xenocrystals in basaltic rocks associated with corundum deposits in Thailand. Dissertation. The University of Manchester, United Kingdom.
- Sutthirat, C., Saminpanya, S., Droop, G.T.R., Henderson, C.M.B., Manning, D.A.C., 2001. Clinopyroxene-corundum assemblages from alkali basalt and alluvium, eastern Thailand: constraints on the origin of Thai rubies. *Mineral. Mag.* 65 (2), 277–295.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell, Oxford–Melbourne.
- Upton, B.G.J., Hinton, R.W., Aspen, P., Finch, A., Valley, J.W., 1999. Megacrysts and Associated Xenoliths: Evidence for Migration of Geologically Enriched Melts in the Upper Mantle beneath Scotland. *J. Petrol.* 40 (6), 935–956.
- Vichit, P., Vudhichativanich, S., Hansawek, R., 1978. The distribution and some characteristics of corundum-bearing basalts in Thailand. *J. Geol. Soc. Thai.* 3 (1), 1–38.
- Wark, D.A., Miller, C.F., 1993. Accessory mineral behavior during differentiation of a granite suite: monazite, xenotime and zircon in the Sweetwater Wash pluton, southeastern California, U.S.A. *Chem. Geol.* 110 (1–3), 49–67.
- Wilkinson, J.F.G., Hensel, H.D., 1994. Nephelines and analcimes in some alkaline igneous rocks. *Contrib. Mineral. Petrol.* 118 (1), 79–91.
- Yaemniyom, N., Pongsapich, W., 1982. Petrochemistry of the Bo Phloi basalt, Kanchanaburi Province, in: *Proceedings of The Annual Technical Meeting*, Department of Geological Science, Chiang Mai University, pp. 19–52.

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