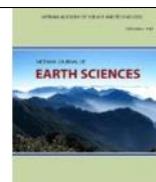




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## Trace elements and oxygen isotopes of gem spinels in marble from the Luc Yen - An Phu areas, Yen Bai province, North Vietnam

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### ABSTRACT

Trace elements investigated by electron microprobe analysis (EMPA) have been combined with oxygen isotopic composition of pink, red and other colored spinels (blue, purple, brown, orange, lavender) hosted by marbles and found in placers from Luc Yen and An Phu deposits, Yen Bai province, North Vietnam. The deposits are those from Nuoc Ngap, Cong Troi, Bai Son and different placers from the An Phu area. Trace elements such as Fe-Zn-Cr-V in red and pink gem spinels permit to separate those from Cong Troi and those from the others deposits of the An Phu area. Spinel from Cong Troi have low to extremely low Zn (< 500 ppm) and high Fe contents (3,000 to 16,000 ppm) while those from An Phu area are Zn-rich (up to 11,000 ppm). Iron is the dominant element for the other colored spinels whereas Zn, Cr and V contents are extremely variable. The Bai Son blue spinel is Fe-rich (5,000 to 7,200 ppm) with some V (950 to 1,830 ppm), Cr (270 to 480 ppm), Co (240 to 400 ppm) and Ni (550 to 950 ppm). The O-isotope composition of the whole spinels ranges between 12.1 and 24.2‰ (n = 25). Within each deposit, the range of  $\delta^{18}\text{O}$  values for red, pink and colored spinels is usually similar. However, the red and pink spinels from An Phu present two distinct sets of  $\delta^{18}\text{O}$  values, respectively between 13.2 to 17.0‰ (n = 7) and  $22.5 < \delta^{18}\text{O} < 24.2$  (n = 5). Those from Cong Troi are from 14.8 to 17.7‰ (n = 3) and their range overlaps that of An Phu. The use of O-isotopes is not useful for distinguishing between the deposits, but the low to extremely low Zn content of the Cong Troi spinels is a discriminant. The variation of  $\delta^{18}\text{O}$  values ( $12.1 < \delta^{18}\text{O} < 24.2$ ‰) of the whole spinels indicates that the oxygen isotopic compositions of the metamorphic fluids were probably buffered by the local  $\delta^{18}\text{O}$  values of the impure host marbles.

*Keywords:* marble; gem spinel; trace elements; oxygen isotopes; geographic origin; Luc Yen - An Phu; Vietnam.

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### 1. Introduction

Gem spinels have compositions close to  $\text{MgAl}_2\text{O}_4$  *sensu stricto* and the color depends

on the incorporation in various proportions of bivalent and/or trivalent chromophores ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , Cr and V) in the octahedral and tetrahedral sites of the crystal structure. Spinel offers a wide palette of colours extending from pink

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to red, violet to purple tinges, orange brown to yellow, and also cobalt blue (Figure 1). World-famous and economic deposits of Cr-V-bearing red and pink spinels occur in Himalayan and East African marbles that have undergone high-temperature metamorphism (Pardieu & Hughes 2008; Giuliani et al., 2017). Vietnam is the main producer of gem spinels found in primary (marble type) and secondary (placer) deposits. Spinel is exploited in small-scale mines and the most significant deposits are found in North Vietnam along the Red River Shear Zone (Huong et al., 2012; Pham et al., 2013). Vietnamese spinels have been investigated by different authors in terms of geological setting as for the discovery of the Lang Chap deposit in the Tan Huong-Truc Lau area (Malsy et al., 2012), gemmology (Pham et al., 2014), trace elements chemistry (Pham et al., 2004; Malsy&Klemm, 2010; Kleišmantas&Daukšyte, 2016; Giuliani et al., 2017) and genesis (Hauzenberger et al., 2001; Chauviré et al., 2015).



**Figure 1.** Spinel on the gem market of Luc Yen. A, B, C- Several gem cut coloured spinels. D- Three of rough sky blue spinels from Bai Son area. Photographs: Pham Van Long

The present study describes the use of trace elements and oxygen isotopic ratios ( $^{18}\text{O}/^{16}\text{O}$ ) of lattice oxygen in pink and red spinels as well as other coloured varieties, to provide a gem geographic identification. This study differs from the previous paper devoted to the characterization of pink and red spinels hosted by marbles worldwide (Giuliani et al., 2017), when considering the following issues:

(i) an update of spinel mining activities and types of deposits in the Luc Yen - An Phu areas; (ii) trace elements combined to oxygen isotopes exclusively to Vietnamese gem spinels; (iii) an in-depth discussion of the data to precise that the O-isotope composition of spinel is not useful in discriminating their geographic origin while trace elements are relevant for indicating their mine origin.

## 2. Geological setting

The primary spinel deposits are located in the Himalayan mountain belt which formed during Tertiary collision of the Indian plate northward into the Eurasian plate. They are spatially related to ruby deposits hosted by platform carbonate series metamorphosed to the amphibolite facies (Garnier et al., 2008). The marble units are intercalated generally with biotite-garnet-sillimanite or -kyanite gneisses, and granitoids. Marble paragenesis consists of calcite, dolomite, spinel, forsterite, clinohumite, apatite, margarite, pargasite, chlorite such as sheridanite-clinoclone,  $\pm$  graphite,  $\pm$  pyrite,  $\pm$  pyrrhotite (Garnier et al., 2008). In Vietnam, the primary deposits occur in the Lo Gam tectonic zone in the Thac Ba and An Phu metasedimentary sequences of Cambrian age, comprising marble and overlying biotite-garnet-sillimanite gneiss and schist (Figure 2). The Lo Gam zone is limited by two left-lateral faults which belong to the Red River Shear Zone, and is intruded by granitoids of Triassic age (Garnier et al., 2005). Spinel (Spl) occurs either as crystals disseminated in marble (Figure 3A, C) or impure marbles associated with mostly calcite (Cal) - dolomite (Dol), forsterite (Fo), clinohumite (Chu), pargasite (Figure 3E), phlogopite (Phl) and chlorite (Figure 3B, D). Hauzenberger et al. (2001) obtained a minimum temperature of about 700°C for the formation of spinel based on the mineral assemblage Chu-Cal-Fo-Dol-Spl at water-rich fluid composition. Such temperature conditions are different from those defined for gem ruby (Crm) formation

which occurred during retrograde metamorphism ( $620 < T < 670^{\circ}\text{C}$ ; Garnier et al., 2008). The main equilibrium reaction between corundum and spinel during prograde metamorphism is the following:  $\text{Crn} + \text{Dol} \rightarrow \text{Spl} + \text{Cal} + \text{CO}_2$ . This reaction explains why gem corundum and spinel are generally not associated in the same outcrop. In addition, in situ U/Pb dating of zircons included in spinel from An Phu (Garnier et al., 2005) indicated a crys-

tallization age during the Permian (256 Ma) with a reopening of the U/Pb system in the Early Triassic (232 Ma). These two ages contrast with the U/Pb ages of 38 Ma found for zircons included in ruby from the same area. This discrepancy signifies that at least two metamorphic episodes occurred in the Indochina block before the Himalayan orogeny, and most likely some of the spinels are older than the associated rubies.

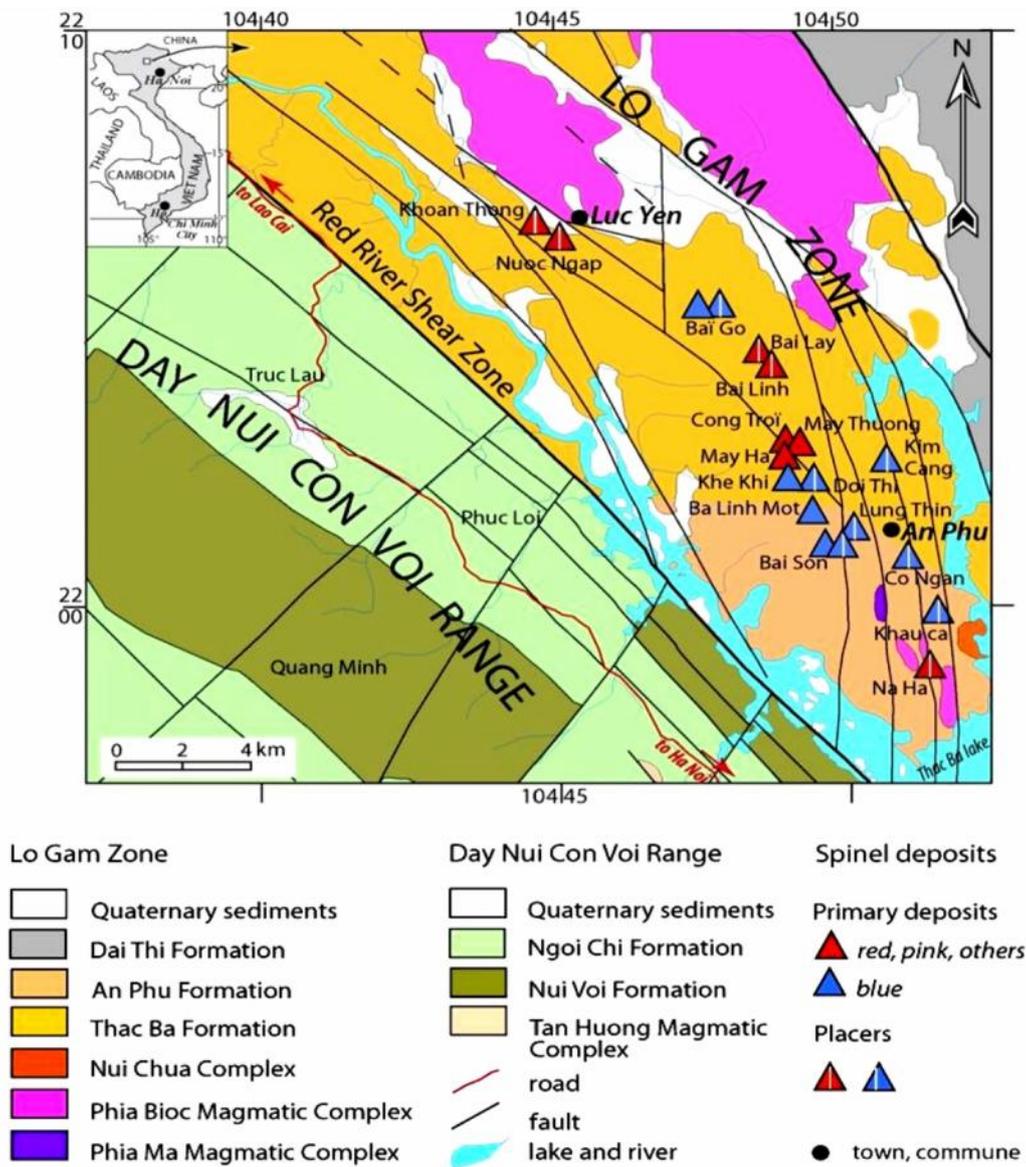
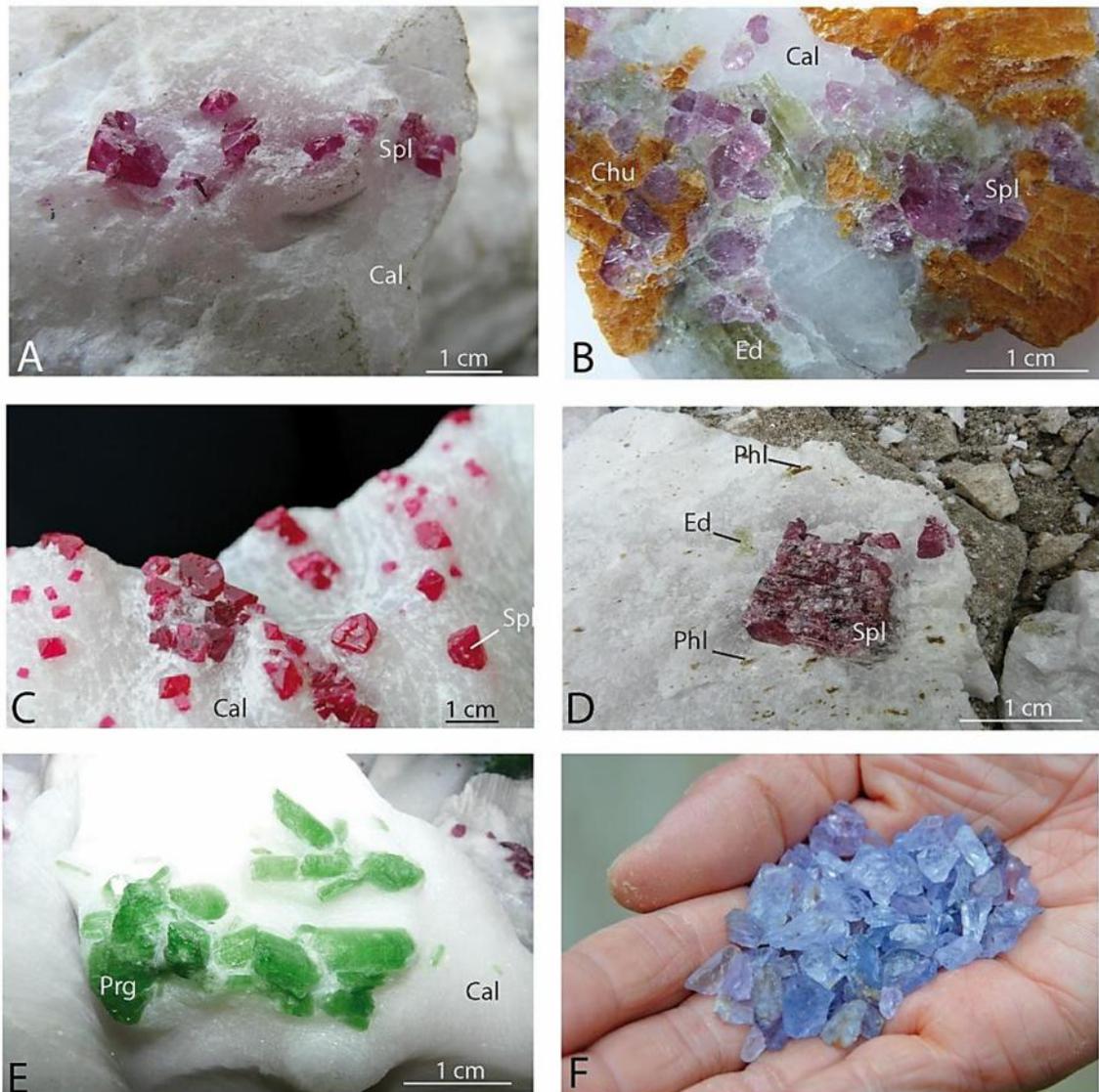


Figure 2. Location of the spinel deposits from the Luc Yen area in northern Vietnam (modified from Garnier 2003)



**Figure 3.** Spinel in marble. A- Pink spinels (Spl) disseminated in a calcitic (Cal) marble from Cong Troi, Luc Yen area. B- Spinel (Sp) associated with clinohumite (Chu), edenite (Ed) in a calcitic marble (Cal) from An Phu quarries. C- Crystals of red spinel around 1 cm across in a marble from Luc Yen. D- Pinkish spinel associated with phlogopite (Phl) and edenite (Ed) in a marble from Cong Troi. E- Pargasite (Prg) in a saccharoidal marble from An Phu. F- Pale blue spinel from the Luc Yen area. Photographs A-B-D-E: G. Giuliani/IRD; C-F: V. Pardieu/GIA. Mineral abbreviations after Kretz (1983)

### 3. Spinel mining activities in Luc Yen district

Gem spinels, rubies and sapphires were discovered in Luc Yen in 1987 (Pham et al., 2013). Today, the deposits which extend between Luc Yen and An Phu localities are found either in marble or placers (Figure 4).

*Primary deposits* concern the Cong Troi mining district where spinels occur in different colours (red, pink, brown, violet) and the Bai son mine where spinel is blue. These deposits are characterized by crystals of spinel widespread in dolomitic marble with

sometimes a Ca- and Mg-Si-rich paragenesis such as dolomite, calcite, phlogopite, forsterite, clinohumite and edenite-pargasite (Figure 3), and sulphides and graphite. Spinel, edenite-pargasite and phlogopite are distributed in bands and strips parallel to the foliation

of the marbles. The crystals vary in size from 1x1 cm to 3x3 cm, and present the common octahedral habit and its red to brownish red colour. The biggest crystals are usually translucent to opaque and are used only as mineralogical collection samples.



**Figure 4.** Views of spinel mining in the Luc Yen and An Phu areas. A- The Cong Troi spinel mining quarry and camp. B- Opening of a spinel-bearing alluvial in a rice field. C- Mining spinels in colluvial soil and sediments. D- Prospecting spinel in a rice field. E- Gem spinel mining in a karst formed in marble. Photographs: V. Pardieu

The spinel and pargasite mining activities are focused in the Cong Troi area since 2000s

(Figure 4A). In 2009-2010, the mining licences in the region were allocated to a local com-

pany for exploiting white marble intended for export. They started to carry out drilling operations in the area, so the exploitation of gems by local people was suspended up to late 2010. Currently, there are two or three different groups of miners with a total of twenty people are working at the mine site. The spinel mining area is often spread over a large area and covers the whole Cong Troi mountain from the base to the top. The spinels in the Cong Troi area present different colours, but the most common ones are brownish red, reddish brown, brown, purple, pink, and purplish pink. The size varies from 1×1 mm to 50 × 50 mm (Figure 3A, D). The crystals present the octahedral habit with spinel twin law.

Blue spinel is found in the white marble along Bai Son valleys. The blue spinels from placer are generally of gem quality (Figure 1D), however the blue spinel crystals found in marble are often in dull coloured, of low transparency, and not of gem quality. Spinel is associated with phlogopite, clinohumite and sometimes pyrite. The pargasite crystals present prismatic and elongated shapes. The colour of the amphibole varies from green, light green to yellow green but the crystals are not transparent. They can form groups of crystals with a size between 0.5 × 2 cm to 1.5 × 5 cm.

*Placer deposits* are mined along the streams or alluvial by local farmers (Figure 4B to D). Spinel is generally of gem-quality and used for gem cutting. They exhibit red, brownish red, pink, purple, sea blue, and sky blue colours (Figure 3F). The red, brownish red and pink spinels are found in An Phu, Minh Tien, and Khoan Thong areas (Figure 2), and pink and purple spinels are found in the Cong Troi area. Sea blue spinel is mined in Co Ngan area located at about 5 km north of An Phu commune and sometimes in Bai Son. Sky blue colour spinel is only found in Bai Son and Lung Thin area in an underground development about 5-8 m deep, where a blue spinel of 97 cts was recovered.

Mining is carried out along the streams of Cong Troi, Nuoc Ngap (An Phu area) and sometimes in the removing spoil tips of old mining areas such as in Minh Tien, Khoan Thong, Bai Chuoi areas producing light blue spinel. In some places, the local people mined in karst or caves formed in white marbles (Figure 4E; Cong Troi 2, Cong Troi 3, May Thuong and May Ha deposits).

#### 4. Analytical Techniques

For this study, 32 crystals of spinels collected from primary and secondary deposits of Cong Troi, An Phu commune, Nuoc Ngap and Bai Son (see Tables 1 and 2 for the type of deposit) were used for examination through EMPA (n = 32, and 220 analysis) and oxygen isotopes analyses (n = 25). Spinel samples were collected by the authors from different field work programs.

EMPA data of the spinels were obtained using the CAMECA SX100 facility at the University of Lorraine, Nancy, France. The operating conditions were the following: accelerating voltage of 15 kV for Mg, Al and Fe, beam current 20 nA, raster length 0.05 μm, collection time 20 s; and accelerating voltage of 25 kV for the other trace elements, beam current 100 nA, raster length 0.05 μm, collection time of 30 s for Ti, Mn and Zn and 60 s for Ca, V, Cr, Co and Ni. Mineral and synthetic standards used were Mg (olivine), Al (corundum), Fe (hematite), Ti and Mn (manganese titanite), V (V-SX9 metal), Cr (chromite), Co (Co metal), Ni (NiO alloy) and Zn (sphalerite). The detection limits for trace elements in mass percentage ratio (ppm) were 37 for Ti, 60 for V, 30 for Cr, 130 for Mn, 90 for Co and Ni, and 180 for Zn. Data reduction was performed with the PAP program (Pouchou and Pichoir, 1991).

Oxygen isotope analyses were performed on different coloured spinels at S.U.E.R.C Glasgow (Scotland) using a modification of the laser-fluorination technique (see Giuliani et al., 2005). Data are reported in the conventional δ<sup>18</sup>O notation as per mil (‰) relative to

the Vienna Standard Mean Ocean Water (V-SMOW).

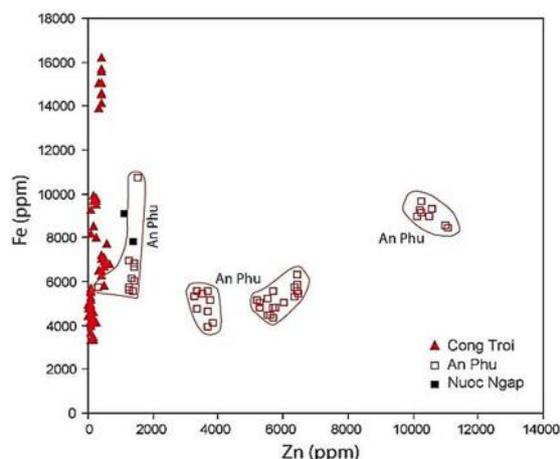
## 5. Results

### 5.1. EMPA analysis

Representative EMPA data of spinels are reported in Table 1. The highest concentrations in trace elements were obtained for Cr, V, Fe and Zn whereas Ti and Mn contents were low to very low and sometimes below the detection limits. Co and Ni were only detected in blue spinels. The chemical variations between pink to red spinels (variety 1) with other colours (variety 2) will be examined separately.

*Variety 1:* The pink and red spinels are characterized by the presence of Fe, Cr and V. Zn is not a chromophore but its concentration is very high for some spinels from An Phu (up to 11,000 ppm). The Zn vs. Fe diagram discriminates the spinels from Cong Troi from those of An Phu and Nuoc Ngap (Figure 5). The spinels from Cong Troi are Fe-rich and

Zn-poor. They show a vertical trend starting from 3,000 and going up to 16,000 ppm of Fe but with very low Zn contents (Zn < 500 ppm). On the contrary, the An Phu spinels present four chemical fields. They are Zn-rich and with Fe values between 4,000 and 11,000 ppm.



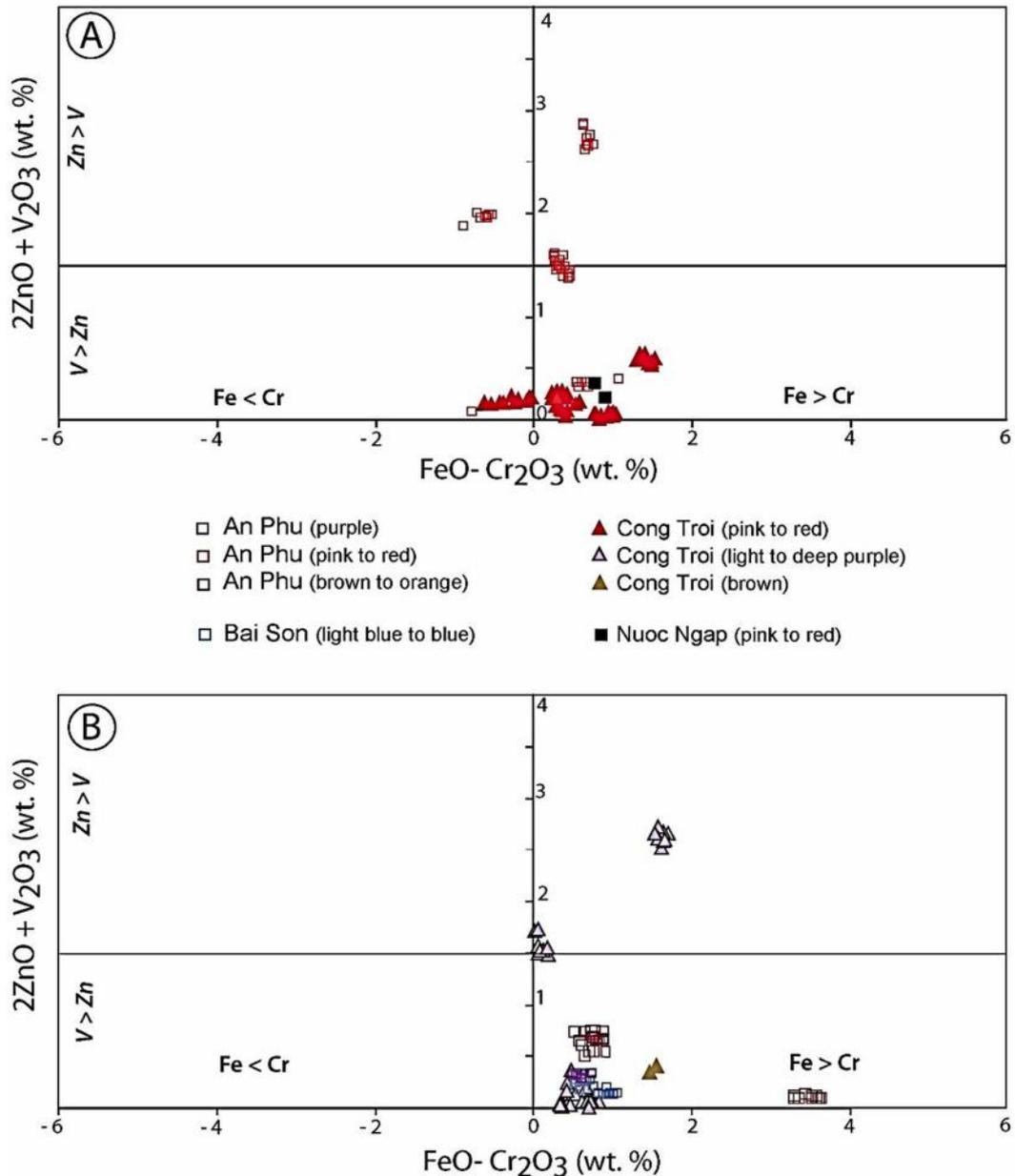
**Figure 5.** Zn vs. Fe (in ppm) diagram for pink and red spinels from the mining sites of Cong Troi, An Phu and Nuoc Ngap

**Table 1.** Representative electron microprobe analyses of pink, red and coloured spinels from An Phu, Cong Troi, Bai Son and Nuoc Ngap deposits

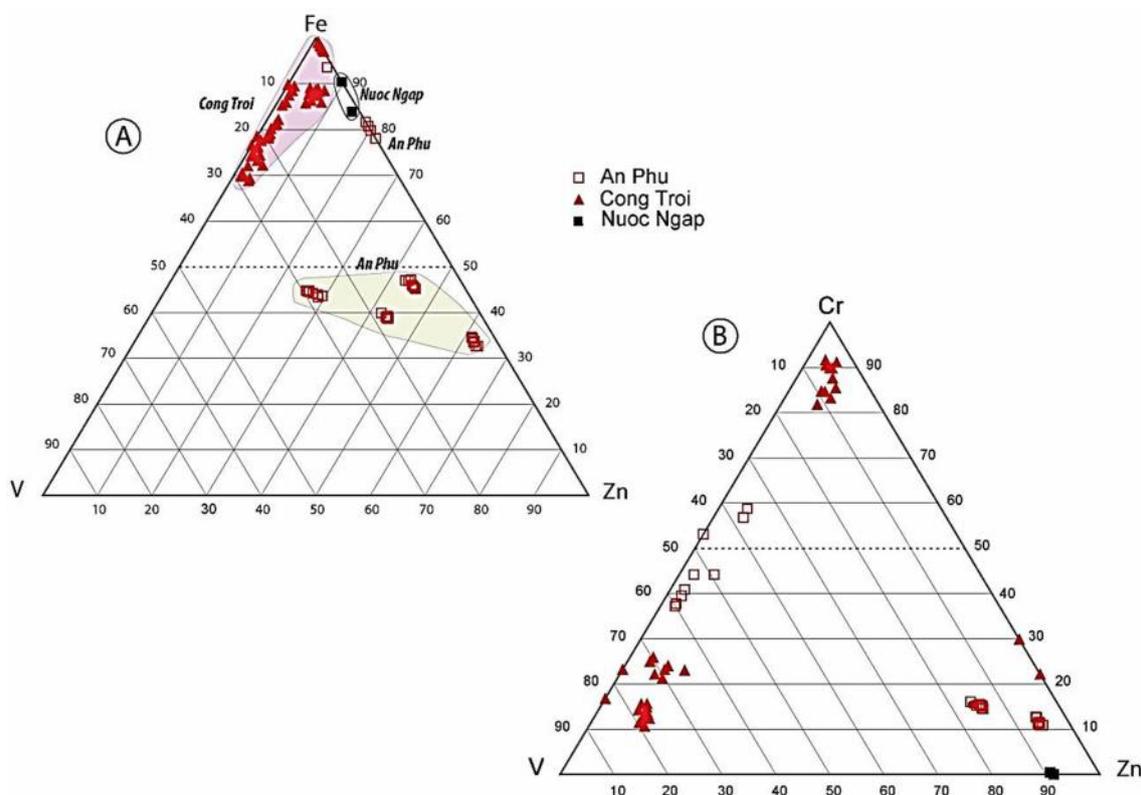
Deposit	Type of deposit	Sample	Colour	MgO	Al <sub>2</sub> O <sub>3</sub>	FeO	TiO <sub>2</sub>	Oxides (weight %)			ZnO	CoO	NiO	Total
								V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO				
An Phu	primary	AP4	red	27.64	70.86	0.57	0.00	0.00	0.18	0.00	0.04	0.00	0.00	99.29
	placer	VIET1	red	27.55	70.25	0.55	0.02	0.37	1.15	0.00	0.80	0.00	0.00	100.69
	"	VIET2	pale red	27.56	71.10	0.41	0.02	0.52	0.12	0.00	0.48	0.00	0.00	100.21
	"	VIET3	red	27.92	70.64	0.92	0.00	0.10	0.23	0.01	1.27	0.00	0.00	101.08
	"	VIET8	pale pink	28.34	70.91	0.48	0.01	0.16	0.17	0.00	0.66	0.00	0.00	100.73
	"	ANP5	lavender	27.77	71.61	0.66	0.01	0.05	0.05	0.01	0.12	0.00	0.00	100.28
	"	VIET23	purple to brown	27.39	71.69	0.79	0.00	0.00	0.00	0.01	0.32	0.00	0.00	100.20
An Phu	placer	VIET24	purple to brown	25.97	71.89	3.41	0.00	0.01	0.10	0.02	0.05	0.00	0.00	101.5
	placer	VIET27	brownish to orange	27.74	71.46	0.57	0.01	0.01	0.57	0.09	0.28	0.00	0.00	100.7
Cong Troi	placer	VIET9	pink	27.36	72.62	0.97	0.00	0.00	0.01	0.00	0.02	0.00	0.00	100.98
	primary	CT1	pink	28.54	70.75	0.50	0.01	0.20	0.06	0.01	0.00	0.00	0.00	100.13
	"	CT4	pink	28.12	70.34	1.41	0.02	0.52	0.10	0.01	0.05	0.00	0.00	100.71
	"	VIET31	pink	27.70	71.83	0.41	0.02	0.25	0.18	0.00	0.01	0.00	0.00	100.41
	"	VIET33	pink	27.43	71.32	0.58	0.00	0.04	1.13	0.02	0.06	0.00	0.00	100.58
	"	VIET1	pale purple	28.97	71.27	0.48	0.00	0.09	0.01	0.01	0.00	0.00	0.00	100.9
	placer	VIET11	purple	28.33	70.58	0.57	0.01	0.17	0.51	0.00	0.67	0.00	0.00	100.8
	"	VIET14	purple	28.41	71.55	0.73	0.00	0.06	0.02	0.00	0.00	0.00	0.00	100.8
	"	VIET15	deep purple	27.03	70.95	1.58	0.00	0.00	0.01	0.01	1.31	0.00	0.00	100.9
	"	VIET16	pale purple	28.89	72.19	0.39	0.00	0.03	0.01	0.00	0.00	0.00	0.00	101.5
Bai Son	primary	VIET32	dark brown	28.10	70.88	1.45	0.02	0.41	0.09	0.01	0.00	0.00	0.00	101.0
	placer	VIET19	pale blue	27.52	72.36	0.75	0.00	0.00	0.01	0.00	0.34	0.00	0.00	101.0
	"	VIET20	purple	28.10	71.13	0.90	0.01	0.14	0.07	0.00	0.00	0.00	0.00	100.4
Nuoc Ngap	placer	VIET21	blue	27.88	72.95	0.51	0.01	0.14	0.07	0.01	0.02	0.05	0.12	101.8
	placer	V41a1	pinkish	27.14	71.11	0.91	0.02	0.01	0.01	0.09	0.12	0.00	0.00	99.41
		V41a2	pink	26.56	71.89	0.78	0.02	0.02	0.01	0.10	0.17	0.00	0.00	99.53

The FeO-Cr<sub>2</sub>O<sub>3</sub> vs. 2ZnO + V<sub>2</sub>O<sub>3</sub> diagram (Figure 6A) shows that the chemical fields of spinels from Cong Troi and Nuoc Ngap plot mainly in the Fe>Cr and V>Zn boxes. Some samples of Cong Troi and An Phu plot in the box of Fe<Cr. The Cong Troi spinels have higher Cr (between 70 and 9,000 ppm) than V

(between 70 to 3,670 ppm). The ternary diagram Fe-V-Zn (Figure 7A) corroborates these different chemical trends and also discriminates their geographic origin. The ternary diagram Cr-V-Zn (Figure 7B) confirms the chemical differences between spinels from Cong Troi, An Phu and Nuoc Ngap.



**Figure 6.** FeO - Cr<sub>2</sub>O<sub>3</sub> vs. 2ZnO + V<sub>2</sub>O<sub>3</sub> (in wt %) diagram for A: pink and red spinels, and B: other coloured spinels from Cong Troi, An Phu, Nuoc Ngap and Bai Son mines



**Figure 7.** Chemical ternary diagrams for pink and red spinels from Cong Troi, An Phu and Nuoc Ngap. A: Fe-V-Zn ternary diagram that discriminates amongst the different deposits. B: Cr-V-Zn ternary diagram for each spinel deposit

*Variety 2:* The chemical compositions of coloured spinel reported in Table 1 are presented in Figure 6B. Iron is the dominant element whereas Zn, Cr and V contents are extremely variable. The Bai Son blue spinel is Fe-rich (5,000 to 7,200 ppm) with some V (950 to 1,830 ppm), Cr (270 to 480 ppm), Co (240 to 400 ppm) and Ni (550 to 950 ppm). Purple spinels from An Phu are characterized by  $Fe > Zn > V > Cr$  whereas light to deep purple ones from Cong Troi are Fe-rich but with extreme variation in Zn (a few to 10,100 ppm), and with Cr up to 6,350 ppm and V up to 1,300 ppm. Brown to orange spinels from An Phu have  $Fe > Zn$  with extremely variable Cr and V contents (Table 2) whereas dark brown spinels from Cong Troi are Zn-free but with concentrations in Fe, V and Cr of respectively, 14,500, 2,800 and 600 ppm.

## 5.2. Oxygen isotope analyses

The O-isotope composition of Vietnamese spinels from primary and secondary deposits ranges between 12.1 and 24.2‰ ( $n = 32$ ; Table 2). Spinel can be classified heuristically into two distinct sets of  $\delta^{18}O$  values (Figure 8):

(i) The first  $\delta^{18}O$  set, between 12.1 and 18.6‰ ( $n = 19$ ) includes red, pink and coloured spinels: (i) the pink and red spinels from the primary and placer deposits of Cong Troi and An Phu have  $\delta^{18}O$  values in the range of respectively, 14.7 to 17.7‰ ( $n=3$ ) and 13.2 to 17‰ ( $n=7$ ); (ii) the other coloured spinels from Cong Troi have  $\delta^{18}O$  values between 15.5 and 18.6‰ ( $n = 3$ ) whereas those of An Phu are in the range 14.2‰ to 14.9‰ ( $n = 4$ ). The Bai Son blue dark spinel has a relatively low O-isotopic composition of 12.1‰.

(ii) Spinel from the second set of  $\delta^{18}\text{O}$  value sare characterized by higher values ( $19 < \delta^{18}\text{O} < 24.2\text{‰}$ ,  $n = 13$ ): (i) the pink to red spinels from An Phu ( $22.5 < \delta^{18}\text{O} < 24.2$ ,  $n = 5$ ); (ii) the coloured spinels, either orangey or brown, from An Phu have a  $\delta^{18}\text{O}$  range between 21.2 and 24.1‰ ( $n = 5$ ). The Bai Son light blue and purplish spinels have O-isotopic values in the range 19.4 to 22.7 ( $n = 2$ ) and a single Cong Troi purple spinel has a value of 22.6‰.

## 6. Discussions

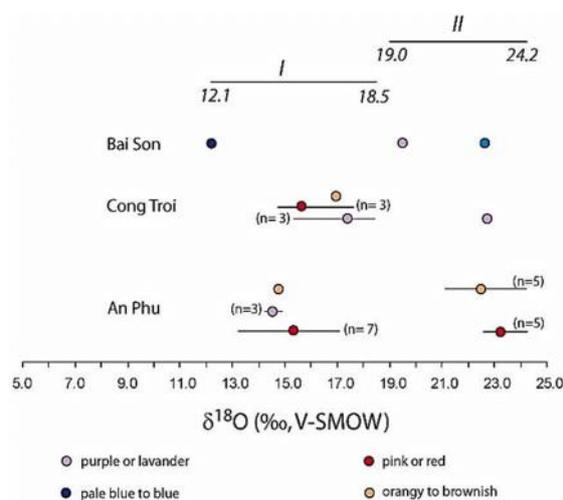
The use of trace elements such as Fe, Zn, Cr and V allowed to characterize the geographic origin i.e. the mine locality or mining district, of the red and pink spinels (*variety 1*) from Cong Troi, An Phu and Nuoc Ngap (Figure 6A and 7A). The low to extremely low Zn content of the Cong Trois pinels is a discriminant compared to other deposits. On the contrary, the O-isotope composition of spinels is not useful for geographical origin determination because the range of  $\delta^{18}\text{O}$  values from Cong Troi (14.7 to 17.7‰,  $n = 3$ ) overlaps the first range of  $\delta^{18}\text{O}$  values from An Phu (13.2 to 17.0‰,  $n = 7$ ).

As regards spinels of variety 2, they are Fe-rich ( $\text{Fe} > \text{Cr}$ ) and present variation in the content of Zn and V. To the contrary of variety 1, the spinels from Cong Troi are enriched in Zn and V (with  $\text{Zn} > \text{V}$ ) while those of An Phu are depleted (with  $\text{V} > \text{Zn}$ ).

The blue spinels from Bai Son have a chemical field that is similar to the purple ones from An Phu or Cong Troi (with  $\text{V} > \text{Cr}$ ) but they contain Co and Ni. The spinels present highly variable O-isotope compositions between 12.7 and 22.7‰. Chauviré et al. (2015) assumed that the cobalt blue colour is due predominantly to  $\text{Co}^{2+}$  substituting for  $\text{Mg}^{2+}$  in the spinel structure even if iron is more abundant. To the contrary, shades of paler blue in spinel with insignificant Co contents are due to electronic transitions in Fe (D'ippolito et al., 2015). Huong et al., (2012)

have shown that: (i)  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  were located in the octahedral site of  $\text{Al}^{3+}$  in the spinel structure; and (ii)  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  ions contributed to colour variation.

Within each deposit, the range of  $\delta^{18}\text{O}$  values for red, pink and coloured spinels is similar indicating that O-isotope compositions are independent of the nature of the chemical elements incorporated in the spinel structure. The  $\delta^{18}\text{O}$  values of spinel from variety 2 overlap those of variety 1 for An Phu and Cong Troi (Figure 8), except for one purple spinel of Cong Troi which has a  $\delta^{18}\text{O}$  value of 22.6‰.



**Figure 8.** Distribution of the  $\delta^{18}\text{O}$  values (‰, V-SMOW) of spinels in marble from the Cong Troi, An Phu and Bai Son deposits. Numbers enclosed in parentheses are the number of analyses

Spinel are considered to be of metamorphic origin (Hauzenberger et al., 2001; 2014; Garnier 2003; Giuliani et al., 2017) but their O-isotope composition is highly variable ( $12.1 < \delta^{18}\text{O} < 24.2\text{‰}$ ). Spinel is either disseminated in the marble or associated with other minerals such as clinohumite, phlogopite, pargasite, chlorite (Table 2) but the  $\delta^{18}\text{O}$  value of spinel is independent of the colour of the crystal and the nature of its paragenesis. The O-isotope variability is probably related to the initial O-isotopic composition of the host marble. The

$\delta^{18}\text{O}$  values for spinel (and/or ruby)-bearing marbles from the Lo Gam zone range between 18 and 27.1‰ (Garnier, 2003; Garnier et al., 2008). The depletion in oxygen-isotope values for the majority of these marbles cannot be related to batch or Rayleigh decarbonation processes of marble during metamorphism, because the observed isotopic variations are too large (see the discussion in Valley, 1986). It is more likely that the O-isotope heterogeneity of the impure marbles is linked to their heterogeneous compositional chemistry and oxygen

isotopic ratios acquired during sedimentation and diagenesis of the protolith. Additionally, the study of Yuiet al. (2008) has shown that the O-isotope fractionation  $\delta^{18}\text{O}_{(\text{cc-sp})}$  between co-existing calcite and spinel, at Mogok in Myanmar, was 3.1 and 4.0‰ (n = 2 samples). Such O-isotope fractionation between calcite and spinel could explain the observed variation of O-isotopes for these spinels and current study on spinel in marbles worldwide indicates that the O-isotope fractionation is around 3.6‰ (manuscript in preparation).

**Table 2.** Oxygen isotope composition (in ‰, V-SMOW) accompanied by the V/Cr ratio and Zn content of spinels from An Phu, Cong Troi and Bai Son deposits

Deposit	Type of deposit	Sample	Colour	Mineral assemblage in the marble	$\delta^{18}\text{O}$	V/Cr	Zn
					(V-SMOW) (‰)		(ppm)
An Phu	alluvial	ANP1	reddish		14.3	na	na
		ANP2	reddish to pinkish		16.2	"	"
		ANP3	pink		14.4	"	"
		ANP4	pinkish		13.2	"	"
		ANP5	lavender		14.5	0.97	1080
		VIET1	red		23.8	0.31	6358
		VIET2	pale red		22.5	5.26	3588
		VIET3	red		22.8	0.47	10,488
		VIET5	light red		15.3	-	1390
		VIET7	pale pink		24.2	na	na
		VIET8	pale pink		22.9	0.96	5543
		VIET23	purple to brown		22.4	0.03	2624
		VIET24	purple to brown		21.3	0.09	362
		VIET27	brownish to orange		24.1	0.02	2162
		VIET28	brownish to orange		21.2	na	na
VIET29	dark orange		22.9	"	"		
VIET30	dark orange		14.8	"	"		
An Phu	primary	Apa	deep purple	pargasite, clinohumite	14.9	"	"
		AP2	pale purple	forsterite, edenite, graphite	14.2	"	"
		AP4	red	edenite	16.8	0.03	321
		V41a	pale pink	pyrite, graphite	17.0	na	na
Cong Troi	placer	VIET9	pink		17.7	-	175
		VIET11	purple		22.6	0.31	5632
		VIET14	purple		15.5	5.81	0
		VIET15	purple		18.5	0.10	10,560
		VIET16	pale purple		18.6	2.90	0
		VIET31	pale pink	no associated mineral	14.7	1.2	72
		VIET32	dark brown	clinohumite	17.0	5.54	40
VIET33	red	no associated mineral	14.8	0.08	460		
Bai Son	placer	VIET19	pale blue		22.7	-	2624
		VIET20	purple		19.4	1.81	0
		VIET21	blue		12.1	5.28	102

## 7. Conclusions

The EMPA and oxygen isotope ratio analyses of gem spinels from Luc Yen -An Phu areas have shown that: (i) the use of trace el-

ements such as Fe-Zn-Cr-V in red and pink gem spinels permits to discriminate the geographic origin of Cong Troi and An Phu deposits; (ii) on the contrary, the O-isotope composition of spinels is not useful in this re-

gard. Indeed, the  $\delta^{18}\text{O}$  range of values for spinels from Cong Troi overlaps that of An Phu but the low to extremely low Zn and high Fe contents of spinels from Cong Troi compared to An Phu permit to discriminate these two main Vietnamese deposits; (iii) the variation of  $\delta^{18}\text{O}$  values ( $12.1 < \delta^{18}\text{O} < 24.2\text{‰}$ ) of spinel indicates that the oxygen isotopic composition of the metamorphic fluids were probably buffered by the local  $\delta^{18}\text{O}$  values of the impure host marbles.

Future work combining more analysis of trace elements and O-isotopes on spinels from Cong Troi with its considerable quantity of blue spinels, An Phu and other Vietnamese deposits will improve the preliminary chemical and O-isotope database presented in this work.

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