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# $CO_2-H_2S-COS-S_8-AlO(OH)$ -bearing fluid inclusions in ruby from marble-hosted deposits in Luc Yen area, North Vietnam

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#### Abstract

Fluid inclusions have been studied in rubies from marble-hosted deposits in the Luc Yen mining district, North Vietnam. Raman and Infrared spectroscopy combined with microthermometry investigations on primary and secondary fluid inclusions provided evidence of  $CO_2-H_2S-COS-S_8-AIO(OH)$ -bearing fluids with native sulphur and diaspore daughter minerals, without visible water. Diaspore appeared as a nonvisible film of  $2-3 \mu m$  coating the wall of the fluid inclusion cavity and native sulphur was generally nucleated during Raman irradiation. The presence of diaspore and COS in the fluid inclusions indicates that water was present in the paleofluid. The mole fractions of  $H_2O$  and  $CO_2$  are around  $10^{-2}$  and the expected concentration of water in the fluid inclusions is in the 1-10 mol.% range. Crush-leach identified sulphates and chlorides that are assigned to the presence of anhydrite and Na–Ca–Cl salts found by SEM in the ruby crystals. The  $CO_2$ -rich inclusions which do not coexist with an aqueous phase by immiscibility process demonstrate that ruby grew from this  $CO_2$ -rich and water-poor fluid at equilibrium with Na–Ca–Cl salts. Thermal reduction of evaporitic sulphates based on an initial assemblage of anhydrite, calcite and graphite, originating from the metamorphism of organic matter is proposed to explain the original fluid chemistry of these marble-hosted

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rubies. The marbles acted as a closed system and the carbonic composition of the parent fluids in ruby indicates that aluminium can be transported in CO<sub>2</sub>-rich fluids at high P-T.

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#### 1. Introduction

Marble-hosted deposits are the most important sources of high-quality rubies in Southeast Asia (Hughes, 1997). Rubies originating from these deposits may show excellent quality with intense colour and high transparency, and may reach very high carat prices on the gem market (Ward, 1998). Primary deposits occur in Tajikistan (Turakuloma deposits), Afghanistan (Jegdalek), Pakistan (Hunza valley), Azad Kashmir (Nangimali), Nepal (Chumar, Ruyil), Myanmar (Mogok, Mong Hsu), North Vietnam (Luc Yen) and South China (Yunnan province). All the deposits are hosted by metamorphosed platform sedimentary series that are intruded by granites and pegmatites (Jegdalek, Hunza valley, Mogok). The timing of ruby deposition relative to metamorphism and magmatism is unknown. The most common genetic model described for these deposits is the regional metamorphism of limestones and shales (Okrush et al., 1976; Hughes, 1997). At Mogok, Kammerling et al. (1994) proposed a metasomatic model for the origin of ruby with the mixing of fluids from metamorphic and magmatic sources. Fluid mixing is a possible hypothesis but has not as yet been confirmed by geochemical studies.

Fluid inclusion studies of rubies are poorly documented. Peretti et al. (1996) reported preliminary microthermometric data on fluid inclusions in ruby samples originating from Mong Hsu. They reported multiphase volatile, CO2-rich fluid inclusions containing Al-hydroxide minerals. Delaigue (1999) and Dao and Delaigue (2000) characterised the gas composition of fluid inclusions in Vietnamese rubies by Raman spectroscopy: CO<sub>2</sub>, native sulphur and diaspore were found in the cavities. In addition, Hoàng Quang et al. (1999) documented CO<sub>2</sub>-H<sub>2</sub>S mixtures by Raman microprobe and microthermometry. These studies emphasize the uncommon composition of the fluid inclusions, which require further study to determine the nature, composition and origin of fluids involved in ruby formation.

In the present paper, we present detailed microthermometric, Raman and Infrared spectrometric data on fluid inclusions in rubies from marbles in the Luc Yen mining district. The composition of the fluids involved in the deposition of ruby was also quantified by a crush-leach technique. The data will be discussed with respect to the formation of ruby at amphibolite metamorphic conditions.

## 2. Geological setting

Gem quality Vietnamese rubies and pink sapphires have been mined since 1987 in the Luc Yen and Yen Bai mining districts (Yen Bai Province, Fig. 1). Ruby is found either in primary deposits hosted by Cambrian metasediments or in placer concentrations within quaternary sediments lying in karst depressions and valley terraces. The primary deposits are linked with the formation of the sinistral Red River shear zone (Phan Trong et al., 1997; Phan Trong et al., 1999). The Red River fault system constitutes the Day Nui Con Voi metamorphic belt (DNCV) formed by high grade sillimanite-biotite garnet gneiss and micaschists. These gneisses contain various leucosome and leucocratic magmatic dikes. Marbles and amphibolites are locally interlayered within the garnet micaschists.

Deformation occurred under upper amphibolite facies conditions (P=4-6.5 kbars and T=650-750 °C, Leloup et al., 2001) coeval with crustal partial melting and the emplacement of leucocratic melts. The melts have yielded <sup>40</sup>Ar/<sup>39</sup>Ar ages from micas and K-feldspar of between 40 and 23 Ma (Harrison et al., 1996), and phlogopite from a Luc Yen rubybearing marble yielded an <sup>40</sup>Ar/<sup>39</sup>Ar age of 33 Ma. Petrographic data indicate decompression from 6.5 kbars during left-lateral shearing at a temperature around 700 °C (Leloup et al., 2001). <sup>40</sup>Ar/<sup>39</sup>Ar data have shown that the DNCV was above 450 °C until 27 Ma, and started to cool from above 350 °C to below 150 °C between 25 and 22 Ma. Considering



Fig. 1. Geological map showing the major tectonic domains of the Red River shear zone with the location of the main ruby deposits (adapted from Phan Trong and Hoàng Quang, 1997).

the P-T-t deformation path determined for the Red River shear zone by Leloup et al. (2001) at between 32 and 27 Ma (the age of ruby formation), the pressure was in the range of 3–5 kbars and the temperature between 500 and 600 °C.

Primary ruby deposits are found within and outside the DNCV range (Fig. 1): (1) in the DNCV, ruby occurs in marble lenses interlayered with amphibolites within the garnet micaschists and gneiss. These marbles represent boudins of the limestone and mudstone that were sheared and metamorphosed during the activity of the shear zone (Leloup et al., 2001). Microgranites and pegmatite veins are spatially associated with the interlayered marbles and amphibolites



Fig. 2. SEM images of solid and fluid inclusions in ruby (R). (A) Phlogopite (Ph) and apatite (Ap)-solid inclusions trapped during the growth of ruby crystal (Bai Da Lan mine). (B) Opened fluid inclusion developed around a pyrite crystal (Py), containing phlogopite (Ph) from the Minh Tien mine. (C) Zircon (Zr) and rutile (Ru) inclusions in ruby (Luc Yen). (D) Opened fluid inclusion in ruby, containing prismatic diaspore (Di) from the An Phu mine.

(e.g. Tan Huong mine, Yen Bai district) but there is no direct relationship between corundum mineralization and magmatic rocks in the field. (2) Outside the DNCV, in the Lo Gam metamorphic zone, ruby is found in thick Cambrian marble units overlying micaschists. The Luc Yen mining district comprises the following ruby mines, from South to North (Fig. 1), respectively: Bai Dá Lan, An Phú, Minh Tien, Nuóc Ngap, Luc Yen and Khoan Thong.

In the Luc Yen mining district, in addition to carbonates (calcite, dolomite), marbles may contain graphite, phlogopite, ruby and pink sapphire, spinel, forsterite, pyrite, rare pyrrhotite, rutile, dravite and margarite (Pham Van, 1996). Four kinds of ruby occurrences have been found in the marbles: (i) disseminations with phlogopite, dravite, pyrite and graphite, (ii) in veinlets with calcite, phlogopite, pyrite, margarite and dravite, (iii) in fissures with graphite, pyrite and margarite, (iv) in pockets with calcite, dravite, pyrite, margarite, graphite and phlogopite. In the ruby crsytals, many solid inclusions have been identified by microscopy and SEM/EDS analyses (Hoàng Quang et al., 1999): phlogopite and apatite (Fig. 2A), pyrite (Fig. 2B), calcite, rutile and zircon (Fig. 2C), margarite, diaspore (Fig. 2D). Also, Dao et al. (1996) noticed diamond inclusions in the Luc Yen rubies and Dao and Delaigue (2000) found anatase, graphite, muscovite, monazite, nepheline and titanite. Diamond is not stable under the conditions estimated for ruby formation and must be considered as inherited.

#### 3. Samples and analytical techniques

Rubies for fluid inclusion study were selected exclusively from deposits within the Lo Gam zone (Fig. 1), the mines at Bai Dá Lan, An Phu, Minh Tien, Luc Yen and Khoan Thong, respectively. All the samples were collected from the different ruby occurrences in marbles and the majority of the crystals exhibit a regular prismatic shape. The rubies and pink sapphires range in colour from a low to moderate saturation of purplish red to purplish pink through reddish to pinkish purple.

The fluid inclusion study was performed on doubly polished plates  $150-200 \mu m$  thick. Microthermometric measurements were obtained using a USGS heating-freezing stage mounted on a Leitz microscope

equipped with a UMK50 Leitz objective at the CRPG/ CNRS (Vandœuvre). The stage was calibrated using natural compounds (pure water triple point at 0.01 °C, critical point of pure H<sub>2</sub>O: 374.1 °C) and synthetic fluid inclusions (CO<sub>2</sub> triple point: -56.6 °C; H<sub>2</sub>O– NaCl eutectic composition: -21.2 °C; H<sub>2</sub>O–KCl eutectic composition: -10.7 °C). The stage was optimised to give a reproducibility of 0.1 °C for the melting temperature of pure CO<sub>2</sub> and pure water.

The composition of selected inclusions was measured using a Labram Jobin-Yvon Raman microspectrometer at the UMR G2R (Vandœuvre). The excitation radiation was the 514.5-nm line of an Ar<sup>+</sup> green laser (2020 Spectra-physics) that delivered 10– 20 mW at the sample surface. Ruby is strongly fluorescent under this excitation and a Leitz  $\times$  100 oil objective was used to decrease the fluorescence contribution of the host crystal.

Qualitative analysis of the solid phases contained in the crystal rubies and in opened fluid inclusions was performed by A. Kholer, at the University Henri-Poincaré (Vandœuvre), on a Hitachi S2500 SEM, operating at an accelerating voltage of 20 kV.

Micro-FTIR spectroscopy Infrared absorption spectra were obtained in the frequency range 4000–600 cm<sup>-1</sup> from room temperature to 350 °C, at the LEM-ENSG (Vandœuvre). They were recorded with a Bruker IFS 88 Fourier transform infrared (FTIR) microspectrometer equipped with a Globar source and a MCT detector and a heating stage (®Linkham). The beam size was 60  $\mu$ m and the spectral resolution was 4 cm<sup>-1</sup>. Spectra were recorded with a transmitted and nonpolarised IR beam.

Chemical analysis of the fluid inclusions was carried out using a bulk crush-leach method as described in Banks et al. (2000). The samples were crushed to a grain size of approximately 1-2 mm and any contaminating grains were removed by picking under a binocular microscope. The samples were cleaned by boiling and rinsing several times in 18.2-M $\Omega$  milli Q water and dried prior to analysis. Between 0.5 and 1 g of the cleaned sample was crushed to a fine powder in an agate pestle and mortar. During crushing, the gases (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S,...) were released to the atmosphere and thus only the contents of the aqueous phase remained. The sample was then transferred to a sample container and approximately 5 ml of milli Q water added to redissolve the dried salts. The solution was filtered through a 0.2- $\mu$ m nylon filter prior to analysis. Analysis of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> was carried out by ion chromatography on the water leaches along with analysis of Na<sup>+</sup>, K<sup>+</sup> and Li<sup>+</sup> by flame emission spectroscopy at the University of Leeds.

#### 4. Fluid inclusion study

Fluid inclusion investigations were performed on 25 ruby samples representative of the ruby-hosted marbles from the Luc Yen mining district. In each ruby set, the same population of texturally primary and secondary carbonic fluid inclusions dominated. Three main types of fluid inclusions were recognized in the samples on the basis of their respective chronology:

# 4.1. Type A $CO_2-H_2S-COS-S_8-AlO(OH)$ -bearing fluid inclusions (primary)

Type A inclusions occur as isolated or oriented clusters present throughout, from the core to the rim of the crystals (Fig. 3A). They are best observed in longitudinal sections, with sizes between 20 to 200  $\mu$ m. Type A inclusions display two kinds of morphol-



Fig. 3. Photomicrographs of fluid inclusions in ruby. (A) Primary type A inclusion in colour zoned ruby, containing a liquid phase composed of  $CO_2$ ,  $H_2S$  and COS (L). (B) Type B inclusion capped by a crystal of calcite (Ca), containing a carbonic liquid phase (L) and a globule of native sulphur (S) nucleated during Raman experiment. (C) Two-phase type C inclusion occurring along fracture planes; respectively, liquid (L) and vapour (V) phases. (D) Isolated type A inclusion containing diaspore crystal (Di) and a carbonic liquid phase (L).

ogy: (i) euhedral negative crystals with polygonal (Fig. 2B) or square outlines found in planes parallel to the basal pinacoid c (0001). Fluid cavities are often developed around solid inclusions identified by SEM/ EDS as pyrite, phlogopite and apatite (Fig. 2A,B); (ii)

flat or broad tubes sometimes capped by mineral inclusions. They may contain rare crystalline solids such as plagioclase, calcite, rutile, phlogopite, diaspore and sulphur determined by SEM/EDS or Raman spectrometry.



Fig. 4. Raman spectra of the different phases analysed in fluid inclusion cavities from ruby. (A) Diaspore and glassy sulphur detected in the same fluid inclusion. The peaks of sulphur are obtained during Raman irradiation of the liquid phase. The intensity of the peak increased rapidly and the nucleated sulphur phase remained stable at room temperature. The diaspore spectrum corresponds to the nonvisible diaspore film of 2-3 µm thick, which coats the wall of the fluid inclusion cavity. (B) Raman spectra of rutile (Ru) and calcite (Ca) found as solid inclusions in a fluid inclusion cavity. Diaspore spectrum corresponds to the nonvisible diaspore film wetting the wall of the fluid inclusion cavity.

Diaspore is found either as very rare solid inclusions, as prismatic crystals with a length up to 15 µm (Fig. 3D) or as a nonvisible film,  $2-3 \mu m$  thick, coating the wall of the whole inclusion cavity. The film of diaspore is considered as a daughter phase, based on the criteria defined by Roedder (1984), and was found in 70% of the fluid inclusions analysed by Raman spectrometry. Diaspore was identified by its Raman lines at 331 and 448 cm<sup>-1</sup>, respectively (Fig. 4A,B). The mid-infrared adsorption spectra at room temperature shows (Fig. 5): (i) the stretching peak of  $CO_2$  at 2350 cm<sup>-1</sup>, (ii) the two-characteristic peaks of diaspore at 1991 and 2121 cm<sup>-1</sup> with the OH-stretching vibration between 2600 and 3500 cm<sup>-1</sup> and combination bands of  $CO_2$  between 3580 and 3700 cm<sup>-1</sup>. In addition, the two weak contribution bands at 3277 and  $3411 \text{ cm}^{-1}$  could be assigned to liquid water in low concentration.

Native sulphur is present at room temperature, as very rare solid globules in the inclusions but it is commonly nucleated from a nonvisible thin layer during laser irradiation.  $S_8$  was identified by its characteristic peaks at 220 and 462 cm<sup>-1</sup> (Fig. 4A).

Type A inclusions are commonly two-phase fluids (liquid and vapour carbonic phases) but may sometimes be associated in a single growth zone with single phase carbonic-rich inclusions. The volumetric fraction of the carbon dioxide-rich liquid in the carbon dioxide-rich phase shows degrees of filling (Flc) ranging between 60% and 100%.

Final-melting temperatures of solid CO<sub>2</sub> (TmCO<sub>2</sub>) are between -57.4 and -63.8 °C (Fig. 6), lower than the triple point for CO<sub>2</sub> (T = -56.6 °C) indicating the presence of other gas species. The important variation of TmCO<sub>2</sub> between -57.4 and -62.3 °C (Luc Yen samples) overlaps the TmCO<sub>2</sub> ranges defined for rubies from the other mines. Melting of a solid between -79 and -95 °C was observed in some of these inclusions, which can be attributed to the melting of solid mixtures between CO<sub>2</sub>-H<sub>2</sub>S (Dubessy et al., 1984). Raman spectrometry confirmed the presence of H<sub>2</sub>S and the absence of N<sub>2</sub>, SO<sub>2</sub>, CH<sub>4</sub> and CO in the volatile phase (limit of detection around 1 mol.% for these peculiar samples and analytical conditions). H<sub>2</sub>S, identified by its Raman peak at 2603 cm<sup>-1</sup>, was found in variable amounts between 3.3 and 13.5 mol.% (Table 1). Homogenisation temperature of CO<sub>2</sub> (ThCO<sub>2</sub>) always occurred to the liquid  $(L+V \rightarrow L)$  at temperatures between 14.8 and 33.9 °C. There is no correlation between the distribution of ThCO2 values and the fluid inclusion location within the ruby crystal. The histograms for ThCO<sub>2</sub> (Fig. 7) show an asymmetrical distribution with a major mode between 25 and 35 °C, and a few ThCO2 values between 15 and 20 °C (Luc Yen samples). No correlation between ThCO<sub>2</sub> and the H<sub>2</sub>S content of inclusions was found, contrasting



Fig. 5. Infrared spectrum obtained on a diaspore-bearing primary fluid inclusion (type A). The OH band on peak 3100 cm<sup>-1</sup> and adsorption peaks at 1991 and 2121 cm<sup>-1</sup>, respectively, correspond to IR diaspore wave numbers. The acute peak at 2350 cm<sup>-1</sup> is attributed to CO<sub>2</sub>.



Fig. 6. Histograms of melting temperatures of the solid carbonic phase (TmCO<sub>2</sub>, °C) in the different fluid inclusion types. Samples V232c and Viet1 originated from the ruby market of Luc Yen.

with the work of Bény et al. (1982) for the CO<sub>2</sub>– $H_2S$ -bearing fluid inclusions trapped in fluorite and quartz from Sierra de Lujar (Spain). The molar volume of the CO<sub>2</sub>+ $H_2S$  phase, deduced from the homogenisation temperature with reference to the CO<sub>2</sub>– $H_2S$  system, is around 200 cm<sup>3</sup>/mol, (Bierlein and Kay, 1953; Mironova et al., 1974). It is worth noting that COS molecules were identified by their Raman line at 857 cm<sup>-1</sup>. The melting temperature of glassy sulphur nucleated during laser irradiation was between 120 and 150 °C with a maximum value of 300 °C (Fig. 8).

The occurrence of water in fluid inclusion was checked by different methods: (i) firstly, optical examination does not show any rim of water even in flat or angular parts of the inclusions; (ii) secondly, during microthermometric freezing-heating runs, no nucleation of clathrate was observed contrary to the observation made by Touray and Guilhaumou (1984) in visible water-bearing  $CO_2-H_2S$  inclusions; (iii) thirdly, infrared spectra were obtained during heating experiments between 23 and 350 °C on one rare inclusion, which contains a visible diaspore crystal (Fig. 5). Two points are considered: (i) the presence

Ruby mines	Inclusion types	Samples	Micro	thermometry		Raman data					
			Flc	TmCO <sub>2</sub>	ThCO <sub>2</sub>	CO <sub>2</sub>	$H_2S$	COS	Native sulphur	Diaspore	
Luc Yen	А	V.5.1	100	-61.3	16.5L	87.9	12.1	+	+		
	А	V.5.1.1	100	-61.8	15.1L	90.4	9.6		+	+	
	С	V.5.2	100	-61.0	13.9L	91.2	8.8	+	+	+	
	А	V.1.1	100	-60.1	22.4L	93.8	6.2	+	+	+	
	С	V.1.2	75	- 59.7	29.3L	92.0	8.0	+	+		
	А	V.1.4	90	-60.2	23.5L	93.3	6.7	+		+	
	А	V.2.1	65	-62.0	33.9L	86.5	13.5	+	+	+	
	В	V.3.2	100	-57.8	22.8L	+	+				
	В	V.4.1	40	-62.6	28.8V	+	+		+	+	
An Phu	С	V.6.2	85	- 59.9	28.5L	96.1	3.9	+	+	+	
Khoan Thong	А	K.1.1	90	- 59.9	30.9L	96.7	3.3	+			

 Table 1

 Microthermometric and Raman data of the selected types of fluid inclusions from the studied rubies

Flc: volumetric fraction of the carbonic-rich liquid in the carbon-rich phase;  $TmCO_2$ : melting temperature of  $CO_2$ ;  $ThCO_2$ : homogenisation temperature of  $CO_2$ , vapour state (V) and liquid state (L). All temperatures in °C. Composition of  $CO_2$  and  $H_2S$  in mol.%. +: Detected native sulphur, diaspore or COS by Raman spectrometry.

of water in the cavity which should be under the form of liquid water at room temperature and as a component of the CO<sub>2</sub> phase at high temperature (T>200 °C) after the nonvisible homogenisation; (ii) the release of water by corundum following the reaction 2AlO(OH)  $\rightarrow$  Al<sub>2</sub>O<sub>3</sub>+H<sub>2</sub>O.

With respect to the first point, the OH-stretching band assigned to diaspore does not facilitate any identification of liquid water located along the wall of the inclusion at room temperature, although some weak bands, at 3277 and 3411 cm<sup>-1</sup>, respectively, could be assigned to liquid water. During heating, at 200 and 350 °C, these weak bands disappear (Fig. 5). This feature is compatible with the homogenisation of the fluid inclusion, with all the water incorporated in the CO<sub>2</sub>-rich single phase. In these conditions, the infrared band of free-water should be at 3854, 3750 and 3676 cm<sup>-1</sup>, respectively. The CO<sub>2</sub> combination bands at 3580 and 3700  $\text{cm}^{-1}$  do not facilitate the identification of water dissolved into the carbon dioxide-rich phase. In spite of these difficulties, water if present will be likely at low concentration.

With respect to the second point, the infrared spectrum of diaspore evolves during heating experiments, mainly by a modification of the shape of the OH-stretching band (Fig. 5). The intensity ratio between the diaspore bands in the  $1800-2200 \text{ cm}^{-1}$  range and the CO<sub>2</sub> absorption band decreases slightly in intensity. This would be eventually the beginning of

the transformation of diaspore into corundum. However, during heating experiments up to 450 °C on other inclusions, visible diaspore remained stable. This indicates the slow kinetics of transformation with respect to the experimental times and further experimental work is obviously required.

# 4.2. Type B $CO_2-H_2S-COS-S_8-AlO(OH)$ -bearing fluid inclusions (pseudo-secondary)

Type B inclusions appear as small clusters in crystals or isolated and mainly related to small intragranular fractures. Fluid inclusions planes are related to micro-cracks and subsequent healed fractures during crystal growth. Based on the criteria defined by Roedder (1984), these fluids are pseudo-secondary. At room temperature, Type B inclusions are single or two-phase (liquid and carbonic phases) with degree of filling (Flc), between 40% and 100%. Inclusions have variable sizes (from 20 up to 125 µm) and variable shapes close to negative crystal. Some of the negative crystals are capped by mineral inclusions (mainly calcite; Fig. 3B) at one end and contain calcite, rutile and daughter crystals of diaspore and native sulphur, determined by Raman spectrometry. Final-melting temperatures of the solid  $CO_2$  are between -57.1and -63.3 °C (Fig. 6). ThCO<sub>2</sub> occurred to liquid between 13 and 32.8 °C and to vapour between 16.6 and 33.1 °C (Fig. 7). The density of CO<sub>2</sub>-H<sub>2</sub>S



Fig. 7. Histograms of homogenisation temperatures of the  $CO_2$ -rich phase (Th $CO_2$ , °C) in the different fluid inclusion types. Samples V232c and Viet1 originated from the ruby market of Luc Yen. V: homogenisation in vapour. Otherwise homogenisation occurred in liquid.

inclusions is varying erratically from vapour to liquid in the same crystal. Raman analyses, in selected inclusions, revealed that the carbonic phase contained CO<sub>2</sub>, H<sub>2</sub>S and COS (Table 1). Glassy sulphur was identified by its peaks at 219 and 462 cm<sup>-1</sup>. The melting temperature of glassy sulphur occurred between 160 and 170 °C (Fig. 8). 4.3. Type C  $CO_2-H_2S-COS-S_8-AlO(OH)$ -bearing fluid inclusions (secondary)

They occur along healed fractures planes which cross-cut several crystal limits and have an elongated (Fig. 3C) or rounded morphology. Irregular or crescent shapes are also present which are interpreted as



Fig. 8. Histogram of dissolution temperatures of glassy native sulphur (S<sub>8</sub>) in types A and B inclusions.

product of textural re-equilibration. Their size ranges from 10 to 100  $\mu$ m. At room temperature, they contain one or two phases and the volumetric fraction of the carbonic-rich liquid in the carbon-rich phase is between 35% and 100%.

TmCO<sub>2</sub> is between -57.1 and -62.5 °C (Fig. 6) and ThCO<sub>2</sub> varies from 16.2 to 29.1 °C to liquid (Fig. 7). Clathrate and ice nucleation were checked during freezing but were not observed. Selected type C fluid inclusions were analysed by Raman spectrometry (Table 1): besides the dominant constituent CO<sub>2</sub>, H<sub>2</sub>S was detected in variable amounts of between 3.9 and 8 mol.%. COS and diaspore were also identified as well as glassy sulphur S<sub>8</sub> by its Raman lines at 219 and 462 cm<sup>-1</sup>, respectively.

### 5. Crush-leach results

The results for the crush-leach analysis of fluid inclusions in rubies from Vietnam are presented in Table 2. The main feature is the presence of salts, despite water not being observed in fluid inclusions. The amounts of salts are quite low. Chloride is generally the dominant anion but  $SO_4^2$  and  $NO_3^-$  are present at only slightly lower concentrations but either may be the dominant species in some cases. As for water,  $SO_4^2$  and  $NO_3^-$  were not detected in the fluid inclusions. Subsequent controls were made using other ruby crystals of exactly the same origin. Crystals were broken and observed under SEM. Masses or crystals, 10 to 50 µm large were found either in

Table 2

Crush-leach analyses of fluid inclusions in rubies and spinels (as analysed in ppb)

Ruby mines	Mineral	Na	Κ	Li	F	Cl	Br	$NO_3$	$SO_4$
Khoan Thong	spinel	238	161	5.8	192	876	4.3	494	763
Khoan Thong	ruby	99	70	0.7	126	371	1.9	455	118
Luc Yen	ruby	251	137	2.5	30	784	3.3	379	1778
An Phu	ruby	132	40	0.9	nd	779	3.3	663	229
Bai Dà Lan	ruby	223	193	1.1	nd	651	3.3	309	106
Quy Chau	spinel	375	160	1.8	nd	1576	11.2	369	553
(Doi San)	-								

nd: Not detected. The data correspond to concentrations in the leachates. Because of the nature of the fluid inclusions, the reported values cannot be normalised to come from fluid inclusions. The analyses are not complete and the charge balance cannot be documented.

cavities or at the borders of fluid inclusions as well as in the form of solid inclusions in the crystals. SEM analysis revealed Ca and S indicating that these crystals were anhydrite. In addition, Ca, Na and Cl were identified as anhedral crystals, which appear to be located around the cavities. Regarding the presence of NO<sub>3</sub><sup>-</sup>, analytical replicates (three times) were performed to control and avoid any possible contamination. Nitrate concentrations were the same in all analyses. For the moment, no nitrate crystal has been detected by SEM. Fluoride was not detected in some samples (<10 ppb in solution) and bromide concentration is only at a few ppb level.

# 6. Discussion

# 6.1. Sulphur-bearing fluid inclusions in the $CO_2$ - $H_2S-COS-S_8-AlO(OH)$ system

Two stages of fluid circulation have been established during the crystallisation of ruby. The first stage is represented by primary (type A) and pseudo-secondary fluid inclusions (type B). The second stage corresponds to secondary fluids trapped along healed fractures (type C). Microthermometry and Raman spectrometry of the fluids for the two stages enabled the same fluid composition to be recognized: CO<sub>2</sub>-H<sub>2</sub>S-COS-S<sub>8</sub>-AlO(OH)-bearing fluid without visible water. The absence of any significant evolution in the fluid composition during the later stage, and whatever the ruby occurrence in marbles may be, suggests that the host-rock acted as a closed system with no contribution from external fluids. Variations in the density of type B fluid inclusions are interpreted to result from the fluctuation of pressures associated with successive localised micro-fracturing.

Natural fluid inclusions reported in corundum from different deposits generally contain pure CO<sub>2</sub>-bearing fluids: (i) in metamorphic environments, pure CO<sub>2</sub>bearing fluids were documented in corundum from gem gravel in granulite facies rocks in Sri Lanka (De Maesschalck and Oen, 1989); (ii) in pegmatite deposits from the Kerala district in India, Menon et al. (1994) reported pure CO<sub>2</sub>-inclusions in sapphire, (iii) in basaltic environments, Coenraads (1992) identified silicate glass inclusions in New England corundum, (iv) in U–Th–hibonite–corundum-bearing skarns from granulites of South-East Madagascar, Rakotondrazafi et al. (1996) documented free-water nearly pure CO<sub>2</sub>. Nevertheless, Peretti et al. (1990) described CO<sub>2</sub>-rich fluids in the Kashmir blue sapphires contained in metasomatised pegmatites, and Srithai and Rankin (1999) found silicate melt inclusions, hypersaline brines coexisting with a CO<sub>2</sub>-rich vapour phase in sapphires from basalt deposits in Thailand.

Natural fluid inclusions in the C–O–H–S system containing only CO<sub>2</sub>, H<sub>2</sub>S,  $\pm$  (H<sub>2</sub>O) and S<sub>8</sub> have been formerly described only from two geological occurrences: (i) in fluorite and quartz samples from F–Pb veins hosted within dolomitic horizons from a calcareous unit of Triassic age in Spain (Touray and Tona, 1974; Bény et al., 1981, 1982; Guilhaumou, 1982), (ii) in halite from salt beds affected by thermal metamorphism by dolerite sills in the Siberian platform (Grishina et al., 1992). Now, similar fluids, but containing also diaspore and COS, have been found for the first time in rubies hosted by marbles in North Vietnam.

# 6.2. Water

The presence of water is a key problem with respect to the transport of aluminium, even over small distances, and to the growth of corundum. Its presence and estimated amount are based on fluid inclusion composition, mineral paragenesis and phase equilibrium in the  $H_2O-CO_2$ -salt systems.

Water was not identified neither by optical microscopy nor by any phase transition. However, in carbonic fluids, small quantities of H<sub>2</sub>O could be present at room temperature in the form of a film wetting the wall of the inclusion cavities. Under the 1  $\mu$ m spatial resolution of an optical microscope, concentration of water in a spherical CO<sub>2</sub>-fluid cavity with a radius of 100  $\mu$ m, a CO<sub>2</sub> density of 0.7 g cm<sup>-3</sup> and with a water film 1  $\mu$ m thick, would be 0.11 as a mole fraction. This value represents the highest H<sub>2</sub>O concentration expected in the fluid considering that the largest inclusions in rubies are up to 200  $\mu$ m in size. In addition, the nonobservation of water in angular shaped parts of the inclusions indicates a much lower water content.

Diaspore crystals ( $\alpha$ AlOOH) were visible by optical microscopy and identified by Raman spectroscopy and are very rare. By contrast, nonvisible diaspore crystals coating the wall of the inclusion cavities were identified in 70% of the inclusions by Raman and infrared spectroscopy. The P-T conditions for the formation of ruby estimated for the Red River shear zone by Leloup et al. (2001), between 32 and 27 Ma, are 3-5 kbars and 500-600 °C. Such conditions correspond to the field of corundum stability and thus diaspore cannot coexist with corundum (Fig. 9). During cooling of the inclusion, any water present will react with the host corundum to produce diaspore at a temperature, which depends on the activity of water. The fluid intersects an isowater activity curve of the diaspore-corundum equilibrium between 150 and 250 °C: diaspore nucleates and incorporates water. Therefore, any liquid film of water present in the inclusion will be very thin. An estimation of the water content of the fluid is based on the incorporation of water in diaspore during cooling. Considering a maximum thickness of the diaspore coating of 2  $\mu$ m, for a fluid inclusion of 100-µm radius (CO2 density of  $0.7 \text{ g.cm}^{-3}$ ), the water content would be 10 mol.%. In the remaining 30% fluid inclusions of type A, no diaspore film was identified. This could correspond to fluctuation of fluid composition at a very low water activity that did not allow the formation of the daughter diaspore during cooling.

Diaspore was previously identified by infrared spectroscopy (Smith and Surdez, 1994; Smith, 1995; Smith et al., 1997) and optical microscopy (Peretti et al., 1995; 1996) in other rubies from marble-hosted deposits (Mong Hsu in Myanmar and in Nepal). It was found in a variety of occurrences including coating, irregular veins and as tiny crystals included in corundum, which were interpreted as a late corundum transformation into diaspore below their equilibrium curve (Smith, 1995).

The water content can also be determined from molecular equilibrium in the C–O–H–S system. In Vietnamese rubies, occurrence of COS in primary and secondary fluid inclusions indicates that water was present in the fluid. Because COS is involved in the following chemical equilibrium:  $CO_2 + H_2S \Leftrightarrow COS + H_2O$ , the low value of the equilibrium constant (T=300 °C, log K=-3.3; T=400 °C, log K=-2.8; T=500 °C, log K=-2.5) calculated from Ohmoto and Kerrick (1977) allows an estimation of the water content from the equation:

$$\frac{f_{\rm H_2O}}{f_{\rm CO_2}} = \frac{f_{\rm H_2S}}{f_{\rm COS}}K$$



Fig. 9. Pressure versus temperature diagram of the  $Al_2O_3-H_2O$  system (following the equation: 2 diaspore = corundum +  $H_2O$ ) as a function of the activity of  $H_2O$  (a $H_2O$  from 0.001 to 1) for temperatures in the ranges 50–500 °C and for pressures in the range 0.5–7.5 kbars (calculated from the thermocalc of Powell and Holland).

An estimate of the  $H_2S/COS$  mole fractions is around 6. Considering an average equilibrium constant of around  $10^{-3}$  in this interval range, it is reasonable to estimate a mole ratio of  $H_2O$  and  $CO_2$ to be around  $10^{-2}$ . Therefore, the expected concentration of water in the fluid inclusions is around 1 mol.%.

The low content of water in fluid inclusions leads to the possibility of an aqueous liquid phase at equilibrium with the CO<sub>2</sub>-rich phase. If this was the case, the absence of water-rich inclusion could be due to selective trapping of the CO<sub>2</sub>-rich phase by ruby. The possibility of immiscibility can be discussed with respect to the H<sub>2</sub>O-CO<sub>2</sub>-NaCl system at 500 °C and at few kbars. The topology of the H<sub>2</sub>O-CO<sub>2</sub>-NaCl system (Fig. 10) shows a one-phase field (Fl) near the H<sub>2</sub>O corner (S-L-G-CO<sub>2</sub>-H<sub>2</sub>O), a Halite + aqueous phase with low  $CO_2$  content (H + L'') along the  $H_2O-$ NaCl edge of the triangle (S-L-H), a Halite + CO<sub>2</sub> rich phase (H+G'') located near the CO<sub>2</sub>-NaCl part of the triangle  $(G-CO_2-H)$ , a two-fluid phase field (L'+G') limited by the GL tie-lie and a loop towards the H<sub>2</sub>O corner and the three-phase field in the middle of the diagram (triangle H-G-L). Coexistence of a CO<sub>2</sub>-rich fluid with a water-rich fluid implies that the

minimum water content of the CO<sub>2</sub>-rich phase is given by point G. According to the data of Shmulovich, at 500 °C and 5 kbar, the water content of fluid G will be around 35–40 mol.% (Frantz et al., 1992; Shmulovich and Plyasunova, 1993; Shmulovich and Graham, 1995, 1999; Shmulovich, personal communication). This value is much higher than the water content estimated to be in fluid inclusions. Therefore, the low water concentration in the fluid inclusions ( $\ll$ 10 mol.%) completely rules out the immiscibility process and therefore the coexistence of an H<sub>2</sub>O-rich fluid phase. The identification of halite and other salts (anhydrite, a calcium chloride, a nitrate) in some ruby crystals demonstrates the coexistence of this CO2-rich fluid with these salts. Finally, this discussion confirms that ruby grew from a CO<sub>2</sub>-rich and water-poor fluid. In addition, this implies that host-marbles were an almost closed system, which was not penetrated by external water-bearing fluids during the growth of ruby and would suggest no aluminium income from pelitic rocks around the marbles. Such a conclusion is common in metamorphic marbles: many authors have found important isotopic gradients between marbles and their immediate surrounding rocks, indicating a very low permeability between both (Valley, 1986).



Fig. 10. Phase equilibria and fluid immiscibility in the system  $H_2O-CO_2-NaCl$  at 500 °C and few kbars (modified from Shmulovich and Graham, 1999). See text for explanations. Points : H=halite, L= liquid, S= position of the NaCl-saturation, G= gas with constant composition (at fixed *P* and *T*). FI = field of homogeneous one fluid phase; L'+G'= the two-fluid immiscible field, H+L''= the stability field of halite + NaCl-saturated fluid with very low CO<sub>2</sub> contents, H+G''= the stability field of halite + NaCl-saturated fluid with high CO<sub>2</sub> concentrations. Dashed lines: tie-lines for different fluid compositions.

#### 6.3. Possible role of evaporites

An important result of crush-leach data from fluid inclusions is the identification of sulphate. SEM study demonstrated the existence of rare crystals and masses of anhydrite widespread throughout the ruby. Anhydrite was not visible in the ruby plates. Indeed, the high refractive indices of Vietnamese rubies (e =between 1.759 and 1.762; *o* = between 1.768 and 1.770; Kane et al., 1991) and irregularities on the surfaces of inclusions do not permit good optical observations. The presence of chloride in the leachate (371 < Cl < 876 ppb) is explained by the Na–Ca–Cl salts found by SEM in the ruby crystals. The presence of  $Cl^-$  and especially  $SO_4^2$  – still points to the possibility of an evaporite contribution for these elements. The presence of evaporitic levels or lenses intercalated within limestone and mudstone sequences is a common feature in platform series. In the Cambrian formation of Luc Yen, anhydrite levels have not been

described up to now but anhydrite was found in the ruby crystals.

The presence of nitrate in the leachate is unusual. As for Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> is tentatively assigned to small nitrate crystals, currently unidentified. Nitrogen is present mainly under three chemical forms in sediments:  $NO_3^-$ ,  $N_2$  and  $NH_4^+$ . Ammonium results from the chemical biodegradation of the proteins of the organic matter in anoxic environments. It can be stabilised in clays and feldspaths and then in muscovite, biotite and feldspaths and released in the form of N<sub>2</sub> during metamorphism (Dubessy and Ramboz, 1986; Dubessy et al., 1989). Some heterocyclic nitrogen may be released as N2 also during catagenesis (Tissot and Welte, 1980). The too low redox state of the system attested by the presence of  $H_2S$  and  $S^\circ$  in fluid inclusions makes unlikely the oxidation of  $N_2$  into  $NO_3^-$ . In oxidising sedimentary environments, organic matter is degraded into nitrate and nitrite. However, the concentration of these chemical species remains low. The last occurrence of nitrate is that developed in evaporitic lakes (Hardie, 1984) where nitrate can be associated with chloride and sulphate. We propose that the nitrates as well sulphate, sodium, calcium and chloride are relicts of nonmarine evaporite crystals preserved locally in the marbles and consequently in the ruby.

Elemental sulphur, hydrogen sulphide and COS were present in the fluid during the growth of ruby. H<sub>2</sub>S and elemental sulphur may be produced by the reduction of sulphate by Grishina et al. (1992) or by the oxidation of sulphur species present in the fluid by Bény et al. (1981, 1982). However, in the Luc Yen area, the alternative of a connection between sulphurrich fluids and the remobilization of sulphur deposits of diagenetic origin is not suitable. Indeed, sulphur deposits are not described in the Cambrian formations and sulphide concentrations were not observed in the marbles. In the Siberian platform example, a succession of carbonate-anhydrite and halite beds were intruded by dolerites. The H<sub>2</sub>S, COS and orthorhombic or glassy S<sub>8</sub> in the CO<sub>2</sub>-inclusions originated from the partial dissolution and reduction of anhydrite by organic carbon (Grishina et al., 1992). In Luc Yen, graphite is a common accessory mineral in the rubybearing marbles. The  $\delta^{13}$ C-values of graphite in the Luc Yen and Yen Bai ruby districts show mixing of carbon from biogenic carbonate and reduced organic matter sources (Giuliani et al., 1999). Graphite found in the ruby-bearing marbles exhibits several alteration features resulting from the interaction of a fluid with the graphitised organic matter: the shape and the surface of the graphite crystals observed under scanning electron microprobe show smooth borders and cavities with dentritic shapes connected to each other with residual bridges that are evidences of dissolution reactions (Fig. 11). The possible chemical reactions based on an initial assemblage of anhydrite, calcite and graphite originating from organic matter are tentative explanations for the fluid chemistry found in these marbles:

$$\begin{split} & \text{CaSO}_{4(\text{anhydrite})} + 3/2\text{C}_{(\text{graphite})} \\ & \rightarrow \text{S}^{\circ}_{(\text{fluid})} + \text{CaCO}_{3(\text{calcite})} + 1/2\text{CO}_{2(\text{fluid})} \\ & \text{CaSO}_{4(\text{anhydrite})} + \text{C}_{(\text{graphite})} + \text{H}_2\text{O} \\ & \rightarrow \text{H}_2\text{S}_{(\text{fluid})} + \text{CaCO}_{3(\text{calcite})} + \text{CO}_{2(\text{fluid})} \end{split}$$

These reactions have the advantage in explaining (i) the presence of rare anhydrite masses within the ruby



Fig. 11. SEM images of the graphite flakes from the ruby-bearing marbles. (A) Crystal of graphite showing evidences of dissolution (arrows). (B) Enlargement of a dissolution zone characterised by cavities with dendritic shapes connected by residual bridges.

crystals, (ii) the formation of native sulphur found as daughter orthorhombic crystals and glasses in fluid inclusions, (iii) the formation of carbon dioxide from graphite, (iv) the corrosion of graphite, and (v) the consumption of water. In addition, thermal reduction of sulphate will explain the exclusive presence of calcite in the ruby-bearing veins or lenses and deposition of pyrite with:  $7H_2S + 4Fe^{2+} + SO_4^{2-} \rightarrow 4FeS_2$  (pyrite)  $+ 4H_2O + 6H^+$  or  $Fe^{2+} + H_2S \rightarrow 2H^+ + FeS_2$ . The absence of nitrogen in fluid inclusions shows these nitrate crystals were stable not ungoing reduction reaction by graphite in contrast to anhydrite. This point is not clarified as well as the redox reactions in the system  $C-N_2-NO_3-CO_2-H_2S-SO_4^{2-}-H_2O$  at 500– 600 °C and a few kilobars.

In the absence of evidence for fluid immiscibility (as modelled by the system H<sub>2</sub>O-CO<sub>2</sub>-NaCl), the presence of primary CO<sub>2</sub>-rich inclusions demonstrates that the ruby grew from a water-poor fluid. Thus, aluminium has been transported in a CO2-rich fluid at high P-T conditions. This is in accordance with the preliminary experiments carried out by Banerjee, Seward and Suleimenov in Zürich (Seward, personal communication) showing a solubility of AlCl<sub>3</sub> (anhydrous) in a pure and dry supercritical  $CO_2$  medium (T=500 °C and P=800 bars) of up to about 20 ppm. In these conditions, the source of Al<sub>2</sub>O<sub>3</sub> may originate from the host-marbles. Such proximal origin was already demonstrated to be the aluminium source of ruby from the deposit of Nangimali (Azad Kashmir) where the Al<sub>2</sub>O<sub>3</sub> content  $\sim 1000$  ppm in the marbles is sufficient for the formation of ruby (Pêcher et al., in press). The transport properties of other elements by CO<sub>2</sub>-rich fluids would deserve to be studied experimentally as shown by the solubility of SiCl<sub>4</sub> in supercritical CO<sub>2</sub> (Suleimenov et al., 2000).

### 7. Conclusions

The conclusions from this study of primary fluid inclusions in ruby by microthermometry, Raman and infrared spectrometries, and crush-leach analysis are the following:

 Primary fluid inclusions in ruby corresponds to a CO<sub>2</sub>-H<sub>2</sub>S-COS-S<sub>8</sub>-AlO(OH)-bearing fluid containing daughter minerals such as diaspore and native sulphur. The estimation of the water content of the fluid, based on the incorporation of water in diaspore during cooling, is less than 10 mol.%.

- (2) Immiscibility in the fluid system is ruled out and finally, ruby grew from a CO<sub>2</sub>-rich and water poor fluid which probably coexisted with relicts of evaporitic mineral (halite, anhydrite, nitrate).
- (3) The marbles acted as a closed system and the carbonic composition of the parent fluids of ruby indicate that aluminium can be easily transported in CO<sub>2</sub>-rich fluid at high P-T.
- (4) The presence of H<sub>2</sub>S, COS, and S<sub>8</sub> in fluid inclusions is interpreted as the result of thermal reduction of sulphates based on an initial assemblage of anhydrite, calcite and graphite originating from organic matter. The stability of nitrate found by crush-leach analysis requires further studies.

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