

МАКЕДОНСКО ГЕОЛОШКО ДРУШТВО

ВТОР КОНГРЕС

на

Геолозите на Република Македонија

**ЗБОРНИК НА ТРУДОВИ**



*Уредници:*

Јовановски, М. & Боев, Б

*Крушево, 2012*

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## ПРЕДГОВОР

Геолошката наука на територијата на Република Македонија има долга традиција, а е поврзана пред се со рударската активност. Познати се локалитети каде се најдени монети од бакарната и бронзената доба. Сочувани се траги на експлоатација на злато од речниот нанос на Коњска Река-Гевгелиско и на други места, од времето на Александар Македонски. Во источна Македонија рударењето било интензивно за римско време.

Први геолошки податоци на научна основа за територијата на Македонија се јавуваат во првата половина на XIX век, а првите печатени геолошки трудови за нашите простори се среќаваат кај А.Буче (1828-1870) и Виксенел (1842). Од крајот на XIX век па се до денес во зависност од интензитетот на истражувањата напишани се голем број на трудови од сите области на геологијата.

Активностите на стручните лица од областа на геологијата се изведуваат преку Македонското Геолошко Друштво кое е формирано во 1952 година.

Во 2008 година се одржа Првиот Конгрес на Геолозите на Република Македонија од кој излезе зборник со преку 50 научни трудови од кои добар дел беа подготвени од меѓународни тимови.

Во периодот помеѓу 2008 и 2012 година во нашата земја се изведоа голем број на активности во сите полиња на геологијата. Особено важни да се споменат се интензивните истражувања на металични и неметалични минерални сировини, регионалните, геохемиските и инженерско-геолошките, итн.

Вториот Конгрес на Геолозите на Република Македонија претставува сублимат на научните сознанија базирани на споменатите геолошки истражувања и испитувања кои се одвиваа на територијата на нашата земја во периодот од 2008-2012 година. Исто така, на конгресот е презентирани и дел од работата на колеги геолози од соседните земји, така да и овој пат со задоволство може да констатираме дека конгресот има меѓународен карактер.

## PREFACE

Geological science on the territory of Republic of Macedonia has long tradition, and is mainly connected to the mining activities. There are numerous localities where coins from copper and bronze age are found. Traces from exploitation of gold in the river Konjska-Gevgelija and other places are known, in the time of Alexander the Great. In eastern Macedonia the mining was very intensive during the Roman period.

First scientific geological data for the territory of Macedonia are found in the first half of XIX century, and the first printed papers for our region are found at A.Bue (1828-1870) and Viksenel (1842). From the end of XIX century until today, depending on the intensity of the investigations numerous publications are presented in all fields of geology.

The activities of geological scientists are performed in the frame of the Macedonian Geological Society which is formed in 1952.

In 2008 the First Congress of Geologists of Macedonia was held. Proceedings with over 50 papers were published. Numerous papers were prepared by international teams.

In the period between 2008 and 2012 investigations in all fields of geology were performed. Especially important to mention are the investigations of metallic and non-metallic mineral resources, regional, geochemical, engineering-geological, etc.

The Second Congress of Geologists of Republic Macedonia presents sublimates of scientific knowledge based on the mentioned geological investigations which were conducted in the period 2008-2012. Also, the congress presents part of the work of colleagues from neighboring countries, so with great pleasure we can once again confirm its international character.

**Претседател  
на организационен одбор**

**President  
of organizing committee**

Проф. д-р Милорад Јовановски

# MINERALOGY AND THE FLUID INCLUSION DATA OF THE BONČE TOURMALINE-BEARING PEGMATITE, THE SELEČKA MTS., REPUBLIC OF MACEDONIA

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## Abstract

The Bonče tourmaline-bearing pegmatite is situated approximately 150 km southern from Skopje, Republic of Macedonia, on the western slopes of the Selečka Mts. The Selečka Mts. belongs to the Eastern Pelagonian tectono-stratigraphic unit of the Dinaride-Hellenides. It comprises Precambrian ortho- and paragneisses, micaschists and amphibolites and hosts numerous pegmatites which differ according to their size, the mineralogical features, the internal structures and the fractionation degree. The Bonče pegmatite belongs to the group of simple pegmatites with simple mineralogy and weakly developed zonation. The wall zone comprise black-colored, up to 10 cm elongated prismatic tourmaline. According to chemical composition and XRD data tourmaline is determined as dravite. The pegmatite core is characterized by predomination of massive quartz. Textural features and fluid inclusion data suggest that the Bonče pegmatite formed as a result of subsequent crystallization from a granitic melt.

**Key words:** pegmatite, tourmaline, fluid inclusions, microthermometry, Raman microspectroscopy

## INTRODUCTION

The Bonče pegmatite is situated approximately 150 km southern from Skopje, Republic of Macedonia, on the western slopes of the Selečka Mts. which represents a part of the Eastern Pelagonian tectono-stratigraphic unit of the Dinaride-Hellenides (Fig. 1). The Pelagonian Massif exposes Precambrian crystalline basement made of ortho- and paragneisses, micaschists and amphibolites and hosts numerous pegmatites, which differ according to their size, the mineralogical features, the internal structures and the fractionation degree (e.g. Ivanov et al., 1966; Zebec & Radanović-Gužvica, 1992; Jovanovski et al., 2003).

The Bonče pegmatite is characterized by simple mineralogy comprising up to 10 cm long prismatic black colored tourmaline crystals embedded within massive quartz matrix.

Generally pegmatites are related to the late stage of magmatic crystallization. While the importance of volatiles and incompatible elements enriched melts is generally accepted, there are still numerous open questions about the mechanism of their deposition. The majority of authors consider

that water-saturated magmas are responsible for the principal mineralogical characteristics of pegmatites (e.g. Burnham & Nekvasil, 1986; Nabelek et al., 2010). Contrary, London et al. (1989) and London (1990) explain the formation of pegmatites by disequilibrium crystallization from water unsaturated magmas, emphasizing the role fluxing elements such as B, F, P and F.

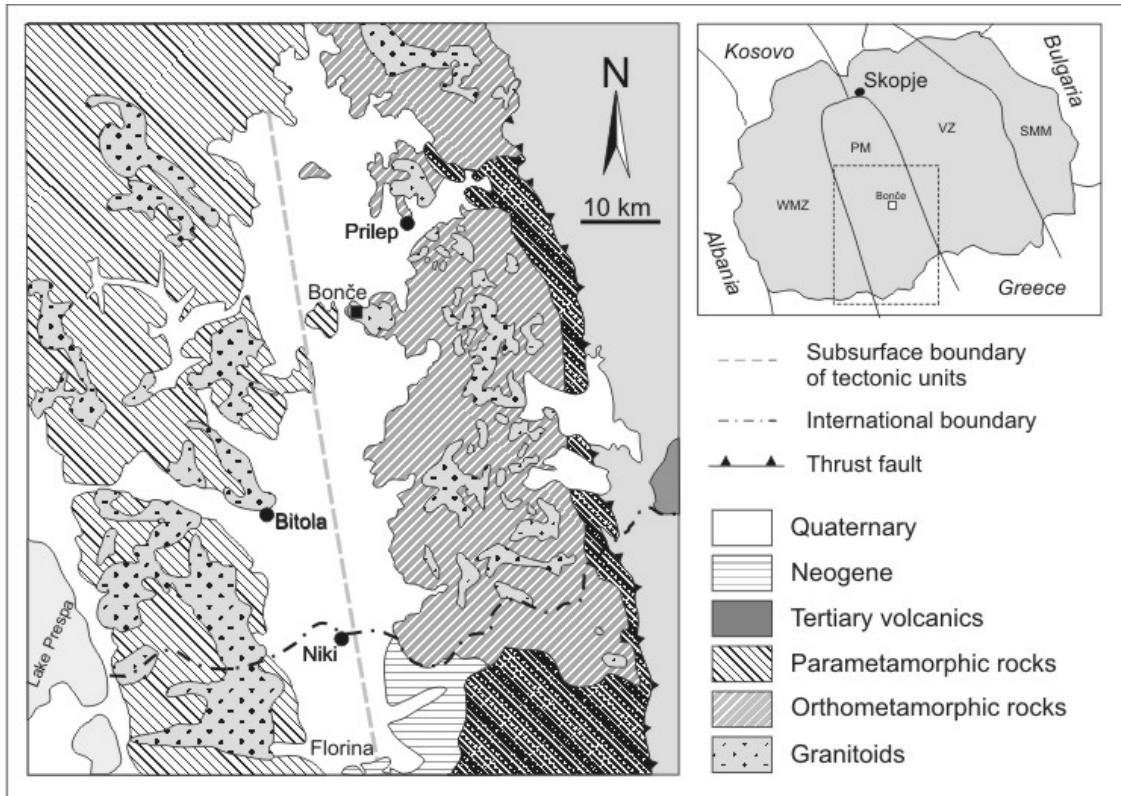
## EXPERIMENTAL SECTION

Mineralogical phase analyses (X-ray powder diffraction, XRD) were performed on Philips PW 3040/60 X'Pert PRO powder diffractometer (45 kV, 40  $\mu$ A) with CuK $\alpha$  monochromatised radiation ( $\lambda=1.54056$  Å) and  $\theta$ - $\theta$  geometry. Area between 4 and 63° 2 $\theta$ , with 0.02° step, was measured with 0.5° primary beam divergence. Compound identifications were based on computer program X'Pert High Score 1.0B and literature data.

Microthermometric measurements of fluid inclusions were performed on double polished ~0.5 mm thick, transparent mineral wafers. Measurements were carried out at

Linkam THMS 600 stage mounted on an Olympus BX 51 microscope using 10x and 50x Olympus long-working distance objective lenses for visible light. Two synthetic fluid inclusion standards (SYN FLINC; pure H<sub>2</sub>O and mixed H<sub>2</sub>O-CO<sub>2</sub>) were used to calibrate equipment. The precision of the system was  $\pm 2.0^{\circ}\text{C}$  for homogenization temperature, and  $\pm 0.2^{\circ}\text{C}$  in the temperature range between  $-60$  and  $+10^{\circ}\text{C}$ .

Raman microspectroscopy for identification of fluid inclusions content was used to characterize the solid and vapour components of the fluid inclusions. Both-side polished samples were analyzed by HORIBA Jobin Yvon Labram Raman spectrometer operating at 514.5 nm with a laser power of 20 mW. Compounds identifications were based on literature data.



**Figure 1.** Geological setting of the Bonče tourmaline-bearing pegmatite, Republic of Macedonia (after Most, 2003). WMZ – Western Macedonian zone; PM – Pelagonian massif; VZ – Vardar zone; SMM – Serbo-Macedonian massif.

## GEOLOGICAL SETTING

The Pelagonian tectonostratigraphic unit is a ca. 420 km long and 60 km broad NNW-SSE striking part of the central Hellenides (Fig. 1). Granitoids intruded the Precambrian crystalline basement made of ortho- and paragneisses, micaschists and amphibolites during: I) Upper Carboniferous and II) Late Permian – Early Triassic magmatic events (Most, 2003). According to the QAP classification, Pelagonian granitoids range from granite to quartz-diorite, but are mainly granodioritic in composition (Dumurdzanov, 1985). A sedimentary sequence, comprising carbonate and clastic rocks, was deposited during Triassic and Jurassic time. The geological structure of Pelagonian zone is mostly con-

sequence of polyphase tectonometamorphic events during the convergence of the Apulian and European plates between Upper Jurassic and Upper Tertiary time (Most, 2003).

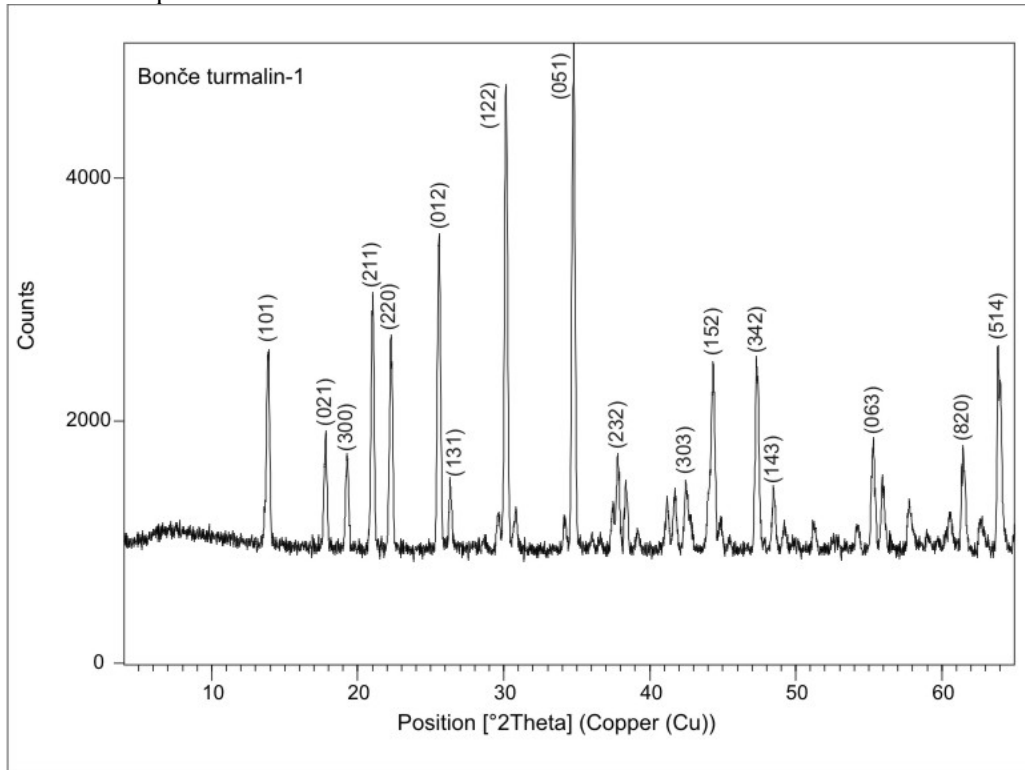
The Bonče pegmatite is one of the numerous pegmatite occurrences on within the Eastern Pelagonian zone. The pegmatites vary in size from a few decimeters wide and tens of meters long to larger bodies tens of meters wide by hundreds of meters long. They differ according to the mineralogical features, the internal structures and the fractionation degree. Beside tourmaline-bearing (Bonče and Dunje localities), the most interesting are those enriched in uranium and thorium mineralization (Alinci and Crni Kamen localities; e.g. Ivanov et al.,

1966; Bermanec et al., 1988; 1992) as well as pegmatites with a peculiar Ca-enriched mineral assemblage with unique occurrence of up to 2 meters long epidote crystals (Čanište locality; Bermanec et al., 2001). The Bonče lens-shaped and up to 5 m wide pegmatite body cuts Precambrian gneisses. The internal zonation is weakly developed, with predomination of tourmaline in the wall zone and massive quartz within the core.

## RESULTS AND DISCUSSION

### *Mineralogy and chemical composition of tourmaline*

The tourmaline unit cell parameters, calculated with the least-square refinement program UNITCELL (Holland & Redfern, 1997) on the basis of XRD patterns (Fig. 2) are following:  $a = 15.961(0)$  Å,  $c = 7.189(7)$



**Figure 2.** X-ray diffraction pattern of tourmaline from the Bonče pegmatite.

**Table 1.** The results of classical wet chemical analysis, calculated formula and distribution of the key cation sites for tourmaline from the Bonče pegmatite.

CHEMICAL COMPOSITION (WT. %)										
SiO <sub>2</sub>	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O
34.49	0.57	8.75	33.06	7.12	0.24	1.99	5.75	2.09	0.39	3.18
STRUCTURAL FORMULA (ATOM. %)										
Si <sup>4+</sup>	Ti <sup>4+</sup>	B <sup>3+</sup>	Al <sup>3+</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	OH <sup>-</sup>
5.652	0.070	3.000	6.386	0.878	0.033	0.349	1.405	0.664	0.082	3.476
DISTRIBUTION OF IONS ON KEY SITES										
	B site		B <sup>3+</sup>				3.000			
	T site		Si <sup>4+</sup>				5.652			
			Al <sup>3+</sup>				0.348			
	T site		Al <sup>3+</sup>				6.000			
	Y site		Al <sup>3+</sup>				0.038			
			Ti <sup>4+</sup>				0.070			
			Fe <sup>3+</sup>				0.878			
			Mg <sup>2+</sup>				1.405			
			Fe <sup>2+</sup>				0.033			
	X site		Ca <sup>2+</sup>				0.349			
			Na <sup>+</sup>				0.664			
			K <sup>+</sup>				0.082			



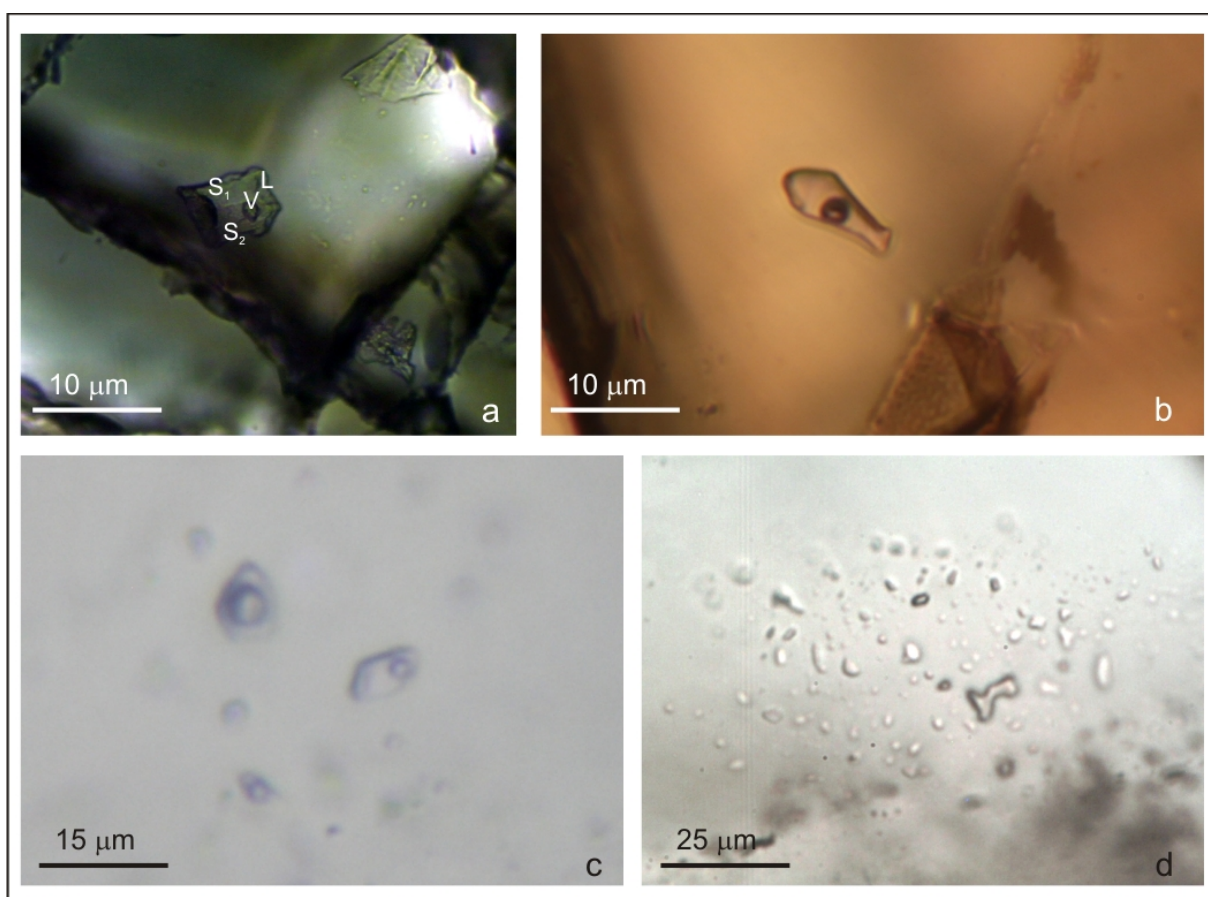
$\text{\AA}$ , and  $V = 1586.21(4) \text{\AA}^3$ . According to the  $a$  vs.  $c$  ratio (Donnay & Barton, 1972) as well as to the results of classical wet chemical analysis (Table 1) and classification proposed by Henry et al. (2011) tourmaline from the Bonče pegmatite is classified as dravite with general formula of  $\text{NaMg}_3\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$ . The structural formula and the key cation sites calculated on the basis of  $B=3$  *apfu* are listed in Table 1.

### Fluid inclusion studies

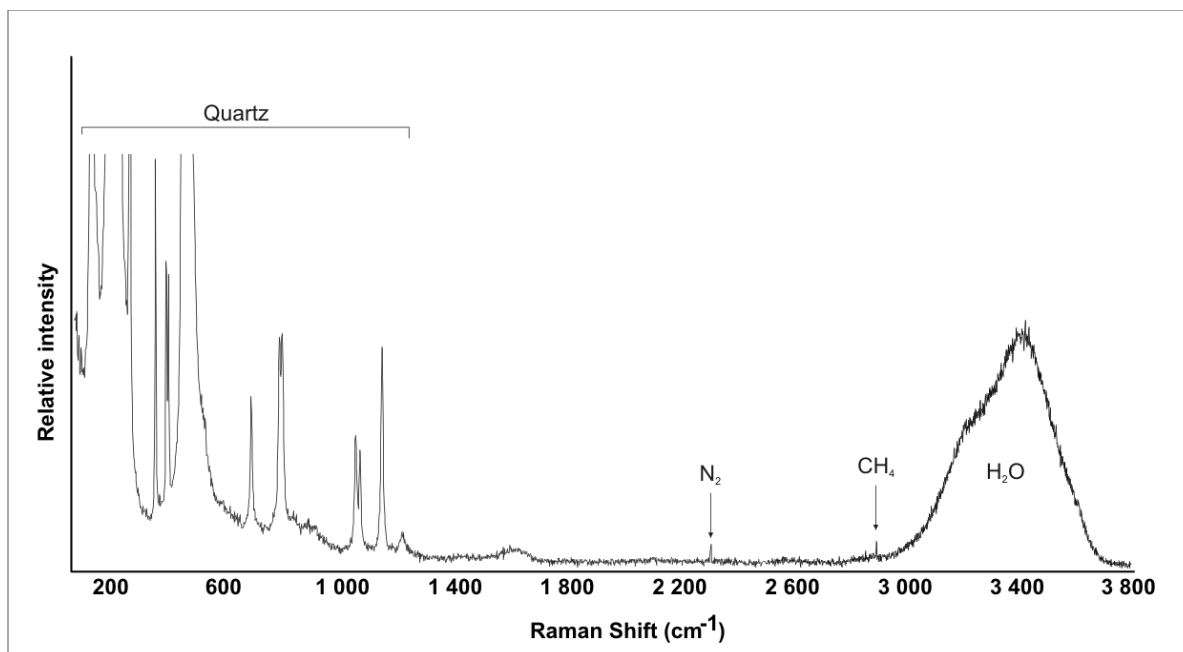
Fluid inclusions from tourmaline crystals were classified as either primary or secondary according to the criteria proposed by Roedder (1984). Primary fluid inclusions are sub-rounded to irregular in shape and up

to 25  $\mu\text{m}$  in size. Usually these inclusions occur in individual clusters or isolated. Based on the number of phases primary tourmaline-hosted fluid inclusions could be subdivided into two additional sets: 1) polyphase (L+V+S) and 2) two-phase (L+V) inclusions.

Polyphase inclusions comprise up to 50 vol. % of solid phases, highly saline aqueous solution and vapor bubbles (Fig. 3a). Solid phases are usually transparent and inactive in Raman spectra. According to Raman microspectroscopy data the vapor bubbles contain only water vapor. Total homogenization occurs by the vapor phase disappearance at temperature higher than 450°C.



**Figure 3.** Photomicrographs of representative primary fluid inclusions from the Bonče tourmaline-bearing pegmatite: a) hydrosaline (L+V+S<sub>1,2</sub>) inclusion recorded within tourmaline; b) two-phase (L+V) inclusion hosted by tourmaline; c) two-phase inclusion (L+V) within the massive quartz core; d) clusters of monophasic inclusions hosted by the massive quartz core.



**Figure 4.** Raman spectrum of the vapor bubble from two-phase inclusion hosted by quartz reveals the presence of H<sub>2</sub>O, N<sub>2</sub> and CH<sub>4</sub>.

Two phase inclusions contain liquid and vapor phase at room temperature (Fig. 3b). Degree of fill (F) varies between 0.70 and 0.85. Eutectic temperature (T<sub>e</sub>) around -52°C suggests CaCl<sub>2</sub> and NaCl as dominant dissolved salts. The final ice melting temperature (T<sub>m ICE</sub>) has been measured between -7.0 and -8.0°C, and clathrate melting temperature between 9.5 and 10.0°C. Total homogenization (T<sub>H</sub>) spans from 145 to 200°C by vapor-bubble disappearance. Raman microspectroscopy revealed the presence of water, nitrogen and methane. Salinity estimated from the ice melting and clathrate melting temperatures ranges from 4.2 to 4.8 wt.% NaCl equ.

Fluid inclusions from the massive quartz core show irregular to rounded shape and range in size up to 25 μm (Fig. 3c). They occur either isolated or in clusters of 5 to 10 inclusions arranged in three-dimensional, non-planar arrays. Inclusions mostly comprise two phases (liquid and vapor) and have degree of fill between 0.6 and 0.85. Raman microspectroscopy revealed the traces of N<sub>2</sub> and CH<sub>4</sub> within the vapor phase (Fig. 4). Eutectic temperature (≈ -52°C) suggests Ca-Na-Cl system. The final ice melting temperatures range from -3.4 to -8.1°C (salinity between 5.6 and 11.8 wt.% NaCl equ.). Temperatures of homogenization into a liquid phase were recorded within the wide range between 173 and 400°C.

The clusters of monophase inclusions point to the resorption and partial recrystallization of silica-rich melt inclusions within quartz host (Fig. 3d). According to Raman microspectroscopy monophase inclusions contain only water.

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