HYDROSILICATE AQUEOUS -, AND VAPOR - “MELT” INCLUSIONS IN SOME SPECIFIC ROCKS AND MINERALS FROM ROMANIA

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Motto: “Terminology that is readily applicable to a one-component system, such as “gas”, ”liquid”, ”boiling” and critical point, can be very misleading when applied to complex multicomponent system” (Roedder and Coombs, 1967).

Abstract. The paper deals with uncommon aqueous-, and vapor-rich “melt” inclusions from various rocks and minerals from Romania. It is envisaged that complex hydrosilicate ± chloride ± carbonate ± sulphate ± phosphate ± CO_2 ± CH_4 fluid/melt was released from deep, intermediate and shallow environments during subduction processes in the Carpathian zone. Heterogeneous fluid inclusions of silicothermal fluids containing liquid/melt±vapor±solid(s) were formed in quartz and ore minerals from epithermal systems, pegmatites and sedimentary rocks. In porphyry copper systems (Upper Cretaceous and Miocene terrains from Romania) the counterparts of silicate melt -, and brine inclusions as vapor-rich “melt” inclusions are representative for the released fluid/melt phases during magma crystallization and endogenous metasomatic processes.

Keywords: hydrosilicate vapor “melt” inclusions, epithermal ores, pegmatites, porphyry copper, sedimentary rocks, Carpathians

Introduction

In specific geological conditions (e.g. epithermal veins and breccias, granitic pegmatites, porphyry copper systems, sedimentary salty rocks, etc) the ubiquitous vapor-rich inclusion, aqueous multiphase, and vapor bubbles in brine or melt inclusions are represented at room temperature conditions by a mixture of low temperature alkali-hydrosilicate ± chloride ± sulfate ± carbonate “melt”- like with consistency of glycerin (10^2 Pa·s) which at room temperature conditions seems to be a certain fragile solid phase (*e.g.* Thomas and Davidson, 2012, and references therein; Wilkinson et al., 1996, 2015). Generally, an opaque bubble could be seen under the transmitted light microscope. These bubbles are isolated or randomly distributed as primary inclusions but frequently are present along other melt or fluid inclusion types (*i.e.* aqueous - liquid biphasic, brine or melt inclusions) in crystal growth zones or cicatrized microfissures (trails) being the counterpart assemblages of the boiling or immiscibility processes, formed mainly by heterogeneous trapping.

Hydrosilicate melt in vapor - rich “melt” inclusions

An open cavity on the surface of a polished slide from a conspicuous quartz pseudomorphose after halite from a brecciated salty rock (Marginal folds nappe, Vrancea zone in Romania) showed that the opaque bubble visible in transmitted light is formed by a solid carapace of an empty inner space which probably contained a vapor or liquid immiscible phase rich in CO_2 and CH_4 (Nuţu and Vaselli, 2015; Fig. 1). Generally, it is presumed that in many cases the vapor bubble inside the brine and silicate melt inclusions could be assigned to a second immiscible phase instead of a pure gaseous volatile phase (*e.g.* Pintea, 2014, 2016; Pintea et al., 2017). A hydrous rind around the vapor bubble in silicate melt inclusion as a reaction product between gas and silicate melt during cooling was noted by Lowenstern (1993) in quartz from rhyolites erupted at the Valley of Ten Thousand Smokes, Alaska. Amazing graphite rim covering the gas bubble containing traces of CO_2, N_2 and CH_4 in two-phase (L+V) aqueous fluid inclusion (H_2O-NaCl) in coarse quartz veins from BIF-hosted iron ores from Krivoy Rog, Ukraine was detected by Raman spectroscopy (Sośnicka et al., 2015). Biphasic aqueous bubbles in silicate melt inclusions formed by shrinkage or heterogeneous trapping were described as aqueous fluid inclusions formed at various pressure conditions in volcanic environments worldwide (Davidson et al., 2005; Kovalenker et al., 2006; and reference therein). In Romania such complex aqueous bubble in silicate melt inclusions were described in quartz phenocrysts from “Laleaua Alba” dacite by Naumov et al. (2014) and elsewhere by Pintea (2010, 2016). Generally, they have relatively low homogenization temperatures (< 100^o up to around 300-350^{o}C) and show specifically “bubble collapse” phenomena during quenching

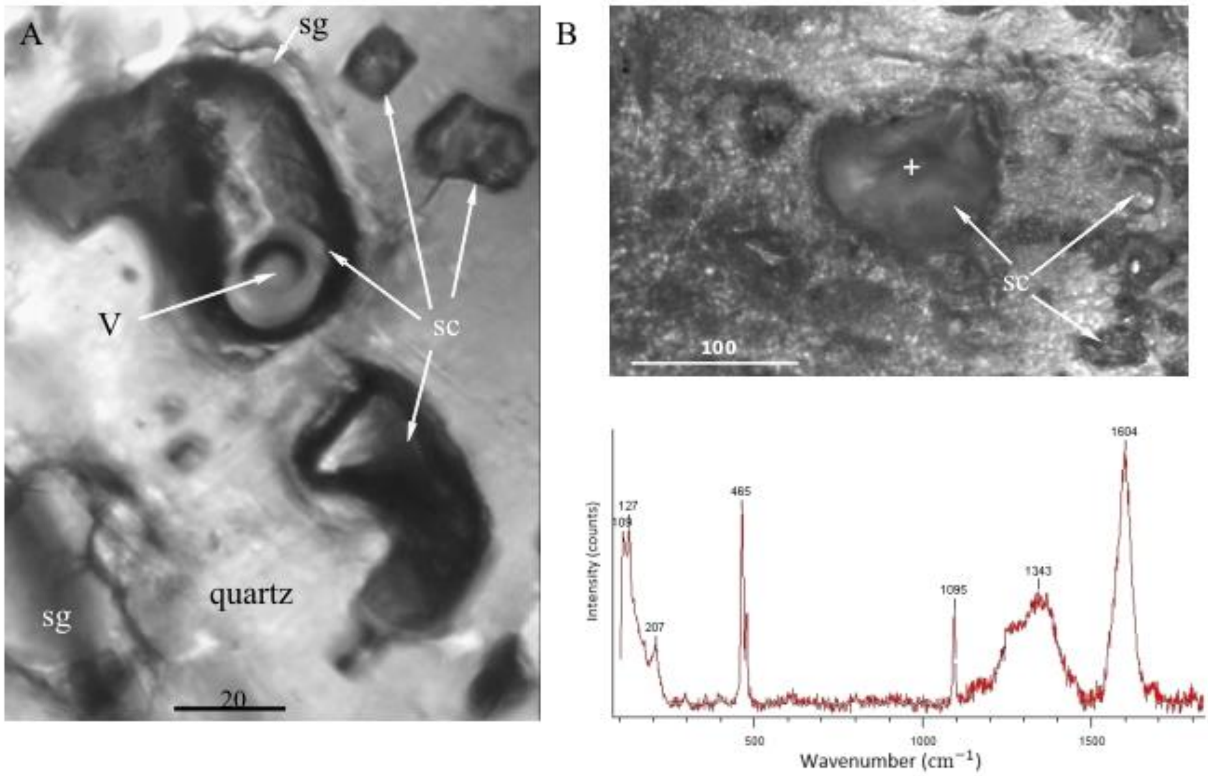

Fig. 1. A. Low-temperature alkali-hydrosilicate melt inclusions in quartz pseudomorphose after halite in a sedimentary brecciate salty rocks (Marginal fold nappe, Vrancea zone, Romania). During polishing a small hole (**V**) was opened at the inclusion surface showing the real content of the presumed vapor-rich inclusion. But, in short time, around 2-3 days, the content disintegrated in air suggesting metastability, perhaps a kind of foam assemblage (or hydrate microtexture) formed by a melt (now glass) and gas bubbles (CO_2, CH_4 etc). **B.** Based upon preliminary Raman spectroscopy (e.g. Raman spectra enclosed) it is presumed that inclusions are silicate-carbonate melt (**sc**) occurring together with another glassy counterpart inclusions (**sg**), suggesting immiscibility. During heating microthermometry several small bubbles formed around 200ºC and then homogenized on further heating near 400ºC (i.e. inclusion formation temperature). Scale bar in µm.

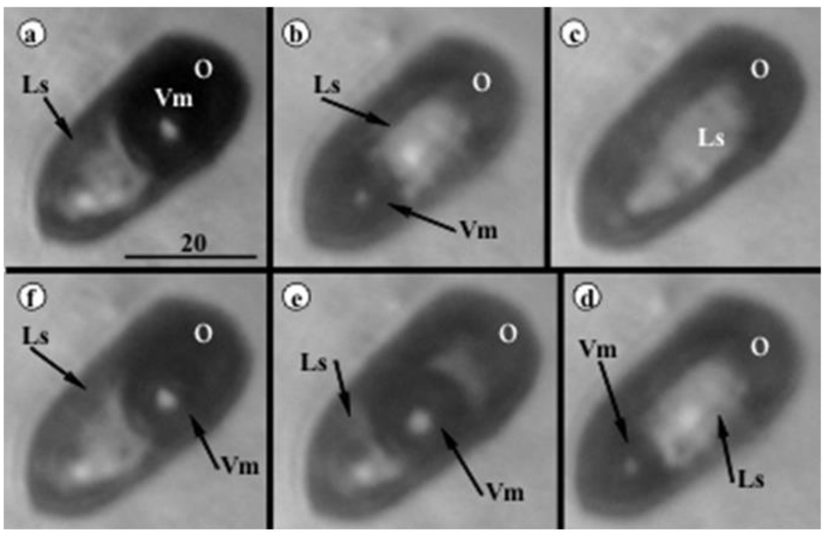

Fig. 2. Microthermometric sequence (from **a** to **f**) for a hydrosilicate – chloride – carbonate - sulphate - CO_2 biphasic inclusion from pegmatitic quartz from Vlădeasa granite (Upper Cretaceous). During heating-quenching cycles (multiple and reproducible) the presumed solidified low temperature hydrosilicate glass (**Ls**) was liquefied between 221-237ºC marked by the releasing of the internal vapor-rich bubble (the second immiscible phase). On further heating **Vm** was consumed completely in the liquid hydrosilicate phase at 299ºC. During quenching **Vm** renucleated at 277ºC and the hydrosilicate liquid phase (**Ls**) solidified between 237º and 197ºC. At 197ºC bubble (**Vm**) suddenly collapsed suggesting a contraction phenomenon reminding the bubble collapse during normal freezing experiment in the microthermometry of the aqueous biphasic inclusions. Notations: **Ls**-hydrosilicate glass/gel phase, **Vm**- immiscible vapor-“melt” bubble, **o**- Fe-rich amorphous opaque phase. Scale bar in µm.

under the microscope reminding the freezing moment during criometry of the aqueous biphasic fluid inclusions (Fig. 2). Besides the bubble and liquid, these inclusions often contain a lot of solid phases which remain unmelted during heating, similar to the colloidal-silica inclusions in chalcedony (Prokofiev et al., 2016). Uncommon fluid inclusions were mentioned in porphyry copper systems by Roedder (1971) and also by Rosasco and Roedder (1979) in Brasilian pegmatite quartz where the authors measured homogenization temperatures between 92-113°C for vapor bubble + aqueous phase, and 95-152°C for presumed liquid "H_2S" droplets from various individual inclusions and finally suggested that they could be immiscible liquid hydrocarbons, possibly with some H_2S in solution. The presence of hydrosilicate-chloride-carbonate-sulfate-CO_2-vapor-rich "melt", "hydrosilicate gel" (Vasyukova, 2011) or "silicothermal fluid" (Wilkinson et al., 1996) is suggested by the presence of multiple solid microphases which remain unmelted during microthermometry in quartz from epithermal ore deposits in Eastern Carpathians and Metaliferi Mountains or in Carpathian metamorphic environments mentioned long time ago by Pomârleanu (1971), Murariu and Dumitrescu (1976), Pintea (1991) in Udubașa et al., 1991, IGR report - from Udubașa et al., 2003), suggesting heterogeneous trapping.

Results and discussions

Recent non-destructive Raman spectroscopy analyses (Fig. 3) indicate specific vibrational stretching lines and bands which could be assigned for SO_4^{2-}, HCO_3^-, CO_3^{2-}, P_2O_5 or PO_4^{3-} molecules detected in the vapor-rich type inclusions from pegmatite quartz from Vlădeasa granite (upper Cretaceous), Miocene porphyry copper systems from Metaliferi Mountains, quartz from xenoliths brought out by alkaline basaltic andesite rocks in the Igniş Mountains, quartz and sphalerite from Cavnic mining prospect from Maramureş district (Romania). Sulphates, carbonates, phosphates, quartz, dawsonite and other solid phases were envisaged by optical microscopy during microthermometry of such heterogeneous aqueous inclusions (Pomârleanu, 1975, 2007; Pintea, 1995, Grancea et al., 2002, a.m.o.). Questioned many years ago by Roedder and Stalder (1981) in several volcanic environments from USA, the vapor-rich inclusion characterizing a "pneumatolisis" process (*i.e.* vapor-phase crystallization) are nowadays described as hydrosilicate vapor-"melt" or hydrothermal gel solution in pegmatites from Transbaikalia, Russia, Volhin in Ukraine, Tin Mountain from South Dakota (USA), Ehrenfriedersdorf (Germany), Rønne granite and pegmatite in Norway (*e.g.* Touret et al., 2007; Sîrbescu and Nabelek, 2003, Thomas and Davidson, 2012) or in porphyry copper deposits from South America (*e.g.* Davidson and Kamenetsky, 2001; Kamenetsky et al., 2004; Wilkinson et al., 2015).

Experimental works on Na_2O-K_2O-Al_2O_3-SiO_2-H_2O system at various PTX-conditions suggest that three immiscible highly concentrated alkali silicate aqueous fluid can be generated at temperature as low as 450°C up to 900°C and pressure of 0.1-0.2 GPa in equilibrium with quartz and K-feldspar or synthetic granite compositions (Veksler et al., 2002, 2006). A hydrosilicate liquid (HSL) was released from water and alkali rich silicate melt (Na_2O-SiO_2-H_2O+NaF+NaCl+Ta) around 600°C, and special mass transfer and metal transport properties were assigned to this unconventional fluid phase by Smirnov et al. (2012). Kotelnikova and Kotelnikov (2010) studied immiscibility in sulfate-bearing fluid system at high P and T and suggested that fluid phases exolved at magmatic stage undergo unmixing by decreasing temperature between 180-200°C. The occurrence of such a complex immiscibility in silicate melt containing alkalies and carbonates with volatile phases including F, Cl, S, P and CO_2 it seems to be conditioned by the high activity of the alkalies in the alkali-aluminosilicate melts (Panina and Usoltseva, 2004).

Conclusions

Published data worldwide and our recent microthermometry and Raman spectroscopy in various samples from geological formations in Romania allowed us to (preliminary) conclude that vapor-rich inclusions and heterogeneous aqueous inclusions are representative for a complex hydrosilicate ± chloride ± carbonate ± sulfate ± phosphate (and Fe-rich) supercritical fluid phase originating from deep upper mantle and mid crustal environment released from various melt types (batches) during magmatic flare-up or metamorphism (metasomatic) associated with the subduction processes of different ages in the Carpathians. Alternatively, they could be representative for successive phase separation process related to specific stage of melt evolution in magma chambers and volcanic conduits such as magma mixing, mingling or assimilation. The separation of vapor, liquid and multiple microsolid phases in these inclusions (*i.e.* vapor-rich or aqueous-rich) took place after trapping during decreasing temperature and pressure and their homogenization temperature recorded by microthermometry is not their original

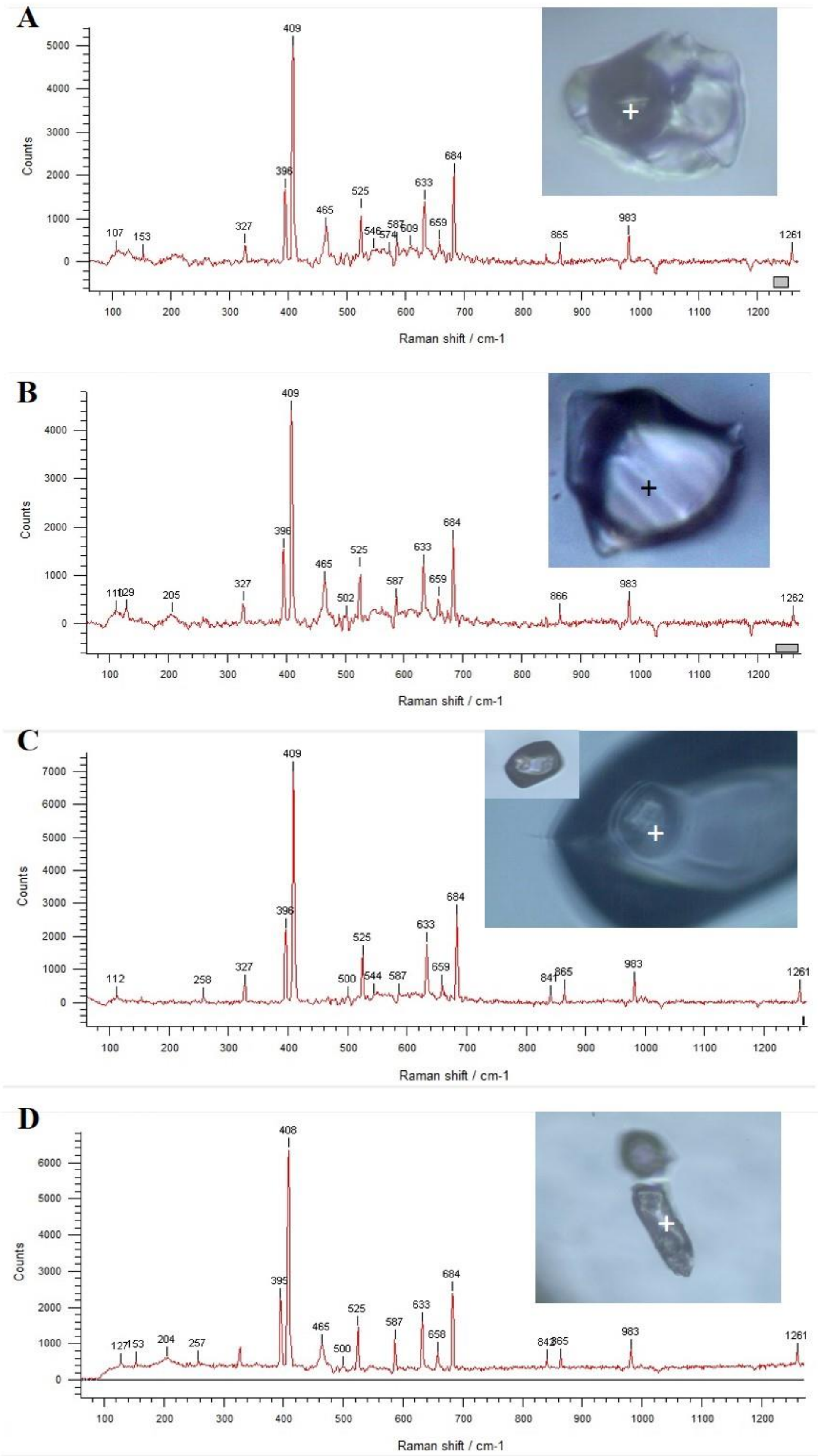

Fig. 3. Raman spectra in some selected samples from Carpathian zone (Romania). **A.** Vlădeasa pegmatite quartz; **B.** Quartz from Roșia Poieni porphyry copper deposit; **C.** Săpânța quartz xenolith (Pintea, 2014 - Fig. 1h); **D.** Quartz from Cavnic-Bolduț mining prospect. Measurements were performed at Romanian Geological Institute in Bucharest by a Raman Renishaw spectrometer equipped with a Leica DM 2700M and 50x objective lense. Excitation was provided by two laser types: 532 nm with resolution of 1200l/mm to 1800l/mm and 785 nm with resolution of 1200l/mm, respectively. Laser time exposure ranged between 5 to 15 sec and counting time from 1 to 55. Fluid inclusion length around 60 µm.

formation temperature. Moreover, it was demonstrated by experimental microthermometry in the H_2O-NaCl (Bodnar et al., 1985) or H_2O-CO_2 (Sterner, 1992) systems that the final homogenization temperature in the vapor phase could be underestimated suggesting exsolution from magmas (or metamorphism) at much higher temperatures comparatively to their homogenization values recorded under the microscope.

Anyhow, it is worth noting that the interpretation of the microthermometric data in the H_2O-NaCl, H_2O-CO_2 and other well studied model systems is the most important tool in fluid phase applications and interpretations in various geological setting mentioned above, and still remaining the best proxy in fluid geochemistry and geothermobarometry, also taking into account the inherent post-entrapment modifications.

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