

The magmatic immiscibility between silicate-, brine-, and Fe-S-O melts from the porphyry (Cu-Au-Mo) deposits in the Carpathians (Romania): a review

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Abstract: The magmatic fluid phase immiscibility between salt-, silicate-, and Fe-S-O melts from Miocene porphyry Cu-Au-(Mo) deposits from Metaliferi Mountains and Eastern Carpathians in Romania is characterized based on ultrahigh temperature microthermometry (i.e. $\geq 900^{\circ}$ - 1100° C) and petrography of the fluid and melt inclusions assemblages, and was described first time two decades ago by the author, mainly in the potassic zone from some of these ore deposits, i.e. Deva, Roşia-Poieni, Tarnita, Bolcana, Rovina, Valea-Morii, Tălagiu in Metaliferi Mountains and Suplai-Măgura Neagră from Țibles massif in Eastern Carpathians. These data are reviewed here and new data and interpretations are added. There are five major types of fluid and melt inclusions in the investigated deposits (i.e. silicate melt, hydrous salt melt, vapor-rich, aqueous liquid-rich and globular (Fe-S-O) immiscible melt). The magmatic immiscibility between silicate-salt-(Fe-S-O) melt at $\geq 900^{\circ}$ - 1100° C and calculated pressure range from 0.3 and 12.8 kbars was documented in separate and/or coeval inclusions. Two main processes were involved in their generation: (1) direct exsolution from magma and (2) endogeneous autometasomatism. These processes started deep in the magma source and finished in the upper levels of the shallow intrusives in complex stratovolcanoes and/or calderas.

Keywords: hydrous salt melt, silicate melt, Fe-S-O melt, vapor-rich, aqueous liquid-rich, inclusion assemblages, petrography, microthermometry, immiscibility, porphyry copper deposit

1. Introduction

There are at least 14 known porphyry copper occurrences in the Metaliferi Mountains, Romania (Milu et al., 2004). The immiscibility between silicate melt and hydrous salt melt in these deposits from Metaliferi Mountains (Romania) was documented firstly in quartz by petrographic and microthermometric studies (Pintea, 1993, 1995, 1996, 1997). The silicate melt, hydrous salt melt and aqueous fluid inclusions are also coexistent with globular sulfide inclusions in magmatic-hydrothermal quartz in these deposits, so we can describe in reality immiscibility between silicate-saline-(Fe-S-O) melts and aqueous fluid phases (Pintea, 2002, 2009). The microthermometry shows that these processes took place first at very high P-T conditions ($\geq 900^{\circ}$ - 1100° C and 0.3-12.8 kbars) characterizing the endogenous stage of the magmatic-to-hydrothermal systems of the main

porphyry copper occurrences of Miocene mineralized intrusions in the area, i.e. Deva, Roşia-Poieni, Tarnița, Bolcana, Rovina, Valea-Morii and Tălagiu in Metaliferi Mountains, and also in Măgura Neagră-Suplai zone from Țibles massif in Eastern Carpathians (Pintea, 1996; Pintea et al., 1999a). Anyhow, many questions still remained, such as whether the immiscible phases were involved in the ore formation in these deposits, or perhaps they are conspicuous products of the complex magmatic-hydrothermal processes, including autometasomatism (Pintea, 2010). It is very probable that the salt melt was exsolved first, as homogeneous salt globules during the primary and secondary boiling processes (Burnham, 1979), and overprinted by fluid/melt-rock interaction in the brittle/ductile stress conditions or mafic magma mingling-mixing (e.g. Cloos, 2001). We assume that these processes produced multiple fluid and melt inclusions assemblages during quartz

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crystallization from the hydrosilicate-rich phases. In the mean time, it should be stressed that an evolved fluid phase of about 10 wt% NaCl split during the magmatic-to-hydrothermal transition (Burnham, 1979) in pairs of low density fluid phase and high salinity liquid containing up to 70 wt% NaCl, trapped in coeval inclusions (Bodnar et al., 1985). That is the consequence of the large immiscibility field in NaCl-H₂O system where vapor and liquid phases are coexistent (Cline and Bodnar, 1991; Heinrich, 2007; Bodnar, 2010). A superposition of the above mentioned processes can be documented sometimes in the same sample, in time-sequences of fluid inclusion generations (assemblages), but obviously was very difficult to find the exact pair of the fluid phases as snapshot of the fluid phase separation event(s). Nevertheless, there is a great progress now in the fluid phase equilibrium analysis by a new generation of analytical tools, theoretical and computer-software facilities (e.g. Harris et al., 2003; Heinrich et al., 2005; Driesner and Heinrich, 2007; Webster and Mandeville, 2007; Bodnar, 1995; 2010). The ore elements were complexed mainly as chlorides and precipitated from the hydrous salt melt as sulfides and oxides, depending on the initial S content and oxygen fugacity, which is in the range of magnetite-hematite buffer (Burnham and Ohmoto, 1980; Eugster, 1986). The increase of water content after its saturation in the silicate melt by the first and secondary boiling processes would change drastically the molten salt chemistry by more successive episodes of boiling and dilution. The (Fe-S-O) immiscible melts were also released as the main result of an autometamorphic process driven by the final magma crystallization at relatively ultrahigh P-T conditions ($\geq 900^\circ$ - 1100°C , 0.3 - 12.8 kbars), emphasized by Pinte (2010). The hydrothermal processes would be complicated even more by the addition of meteoric water, which would create a medium to low P-T ($\leq 650^\circ\text{C}$, 0.5-1 kbar) convective system centered on the protore zone and surroundings, enhancing the economic ore concentrations in veins and breccias by alteration processes (Pinte, 1996, and unpublished reports).

Fluid inclusion evidence of immiscibility at high P-T conditions between silicate melt and saline rich fluids in porphyry copper deposits (PCDs) and others silicate rocks was documented by many authors worldwide, and high homogenization temperatures of the brine

inclusions were reported by Ryabchikov, (1963), Roedder and Coombs (1967), Roedder (1970, 1981, 1984, 1992), Reyf and Bazeyev (1977), Wilson et al. (1980), Eastoe and Eadington (1986), Solovova et al. (1991), Frezzotti (1992), Pinte (1993, 1995, 1997), Lowenstern (1994), Yang and Bodnar, (1994), Reyf (1997), Campos et al. (2002), Kamenetsky et al. (2004), Fulignati et al. (2001, 2005), Kamenetsky (2006), Davidson and Kamenetsky (2007), Kamenetsky and Kamenetsky (2010), Li et al. (2011), Kodera et al. (2012, 2014). Magmatic immiscibility between silicate melt, salt melt and Fe-Cu sulfide melt was identified and described by Pinte (2002, and unpublished report) in the Upper Cretaceous porphyry Cu-Mo deposits from South Carpathian in Banat. Fluid-salt-melt evolution and the sources of fluids from high pressure magma chamber were described at Banská - Štiavnica magmatic-hydrothermal system in Western Carpathians (Naumov et al., 1996). Fluid-melt immiscibility in various P-T-X conditions was documented during experimental works related to chloride, silicate, sulfide, sulphate, borate fluids, e.g., Koster van Groos and Wyllie (1969), Shinohara et al. (1989), Ballhaus et al. (1994), Thomas et al. (2000), Martel and Bureau (2001), Veksler et al. (2002), Antignano and Manning (2008) and many others.

In this research, the author presents the most important petrographic and microthermometric data related to fluid and melt inclusions study “as they are” in a cluster of porphyry Cu-Au(Mo) deposits occurring in the Metaliferi Mountains (South Apuseni Mountains) and Magura Neagră-Suplai from Țibleș massif, which is situated in the Eastern Carpathians subvolcanic zone. Somehow, these data seem to make up an uncommon data set, suggesting very high P-T trapping conditions. These could be probably related to the specific geodynamics of the Eastern Carpathians and Apuseni Mountains during middle Miocene. A strong argument is based upon the published geothermometry (802° - 1416°C) and geobarometry (3.2 - 9.7 kbars) of the minerals formed from the magmatic processes originated in the mantle wedge above subducted slab in the Eastern Carpathians (e.g. Kovacs, 2002). The magmas and associated ore deposits from the Apuseni Mountains were formed during the middle Miocene extension (or post collision evolution of a metasomatized mantle lithosphere under asthenospheric upwelling) related to the decompression melting

in a high thermal regime (Roşu et al., 2004; Seghedi et al. 2010; Harris et al., 2013). High temperature up to 1000°C was suggested in the processes associated with subduction and postsubduction geotectonic settings worldwide (Richards, 2003, 2009; Li et al., 2011). Moreover, it was documented, at global scale, that the W-directed subduction processes, evolved in a very high thermal regime (Doglioni et al., 2009). The subduction in the Carpathians was W-directed, as mentioned by Seghedi et al. (2004).

Another explanation for these uncommon high T-P trapping conditions for the silicate and hydrous salt melt inclusions, probably more likely, could be related to the specific post-entrapment modifications or heterogeneous trapping mechanism, as suggested in the literature (e.g. Hall and Sterner, 1993; Li et al., 2009; Bodnar, 2003; Kamenetski and Danyusevski, 2005; Lerchbaumer and Audetat, 2012; and references therein).

2. Geological setting

The basement of Metaliferi Mountains from South Apuseni Mountains in Romania consists of complex Palaeozoic metamorphic rocks, Mesozoic ophiolites and sedimentary deposit, Upper Cretaceous-Paleogene and pre-Badenian magmatites and Miocene sedimentary deposits. The porphyry deposits are of Cu-Au(Mo)-types and clustered in the conventionally named “gold quadrilateral” (Ghiţulescu and Socolescu, 1941), associated or overprinted by low and high sulphidation epithermal Au-rich mineralization mainly with Au-tellurides, which mark the anomalous richness of Au in the area and also the enrichment of Cu (Fig. 1). The gold is known and exploited from immemorial times but real scientific investigations on the mineralogy, metallogeny and mining geology related to the epithermal and, later, on the porphyry copper mineralization were documented by Ghiţulescu and Socolescu (1941), Ianovici et al. (1977), Berbeleac (1985, 1988), Mitchell and Carlile (1994), Mârza (1999), Udubaşa et al. (2001), Vlad and Orlandea (2004), Seghedi et al. (2004), Roşu et al. (2004); Neubauer et al. (2005), and many others. The porphyry copper system described in the Țibleş massif situated in the Eastern Carpathians, specifically in the subvolcanic zone, shows many petrological and

geochemical features typical for a porphyry copper deposit (Udubaşa et al., 1983, Pintea et al., 1999a). Their fluid and melt inclusions microthermometry and petrography are comparable with those described in the Metaliferi Mountains, but the geological setting is different and still under debate (Udubaşa et al., 1984).

The host rock of the PCDs in the Metaliferi Mountains consisted of amphibole-, and biotite-andesite to quartz dioritic and microdioritic rocks in complex subvolcanic structures (Boştinescu, 1984; Berbeleac et al., 1995, Udubaşa et al., 2001). As a rule, in the stratovolcano edifice (or calderas) the latest intruded shallow body has been Cu-Au mineralized and the volcanic activity is a prerequisite in the development of the intrusions, these frequently being intruded at the bottom of the eruption cone. The main alteration products are related to the potassic, phyllic, propylitic and argillic facies and mineralization is typical of porphyry Cu-Au (Mo) described by Ianovici et al. (1977), Vlad (1983), Boştinescu (1984), Udubaşa et al. (2001), Roşu et al. (2001), Milu et al. (2004), Ivăşcanu, et al. (2003), Kouzmanov et al. (2005, 2006), among others. Typical quartz veins networks occur in all potassic zones of these deposits and host melt and fluid inclusions assemblages of various types (Fig. 2). Alternatively and/or complementary, the mineral assemblages from these deposits (Pintea, 2010) and similar ones worldwide could be formed as magmatic driven endogen (autometamorphic) products during the formation of the high temperature potassic and phyllic zones (Harris and Golding, 2002; Seedorff et al., 2005; Cathles and Shanon, 2007; Wilkinson and Cooke, 2011) (Fig. 3). The main mineralogical parageneses of the veinlets include quartz-bornite, quartz-magnetite, quartz – chalcopyrite - magnetite, quartz-pyrite, anhydrite-pyrite, etc. Quartz is present as small prismatic or doubly-terminated crystals occurring in some breccia zones.

The characteristic small veins have a coarse-grained texture and frequently form complicated cross-cutting systems with different ages and composition (Fig. 3, Fig 4). See also Damman et al. (1996), Milu (2004), Heinrich (2007), Kouzmanov et al., (2010) and references therein, for the complex relationships of veinlets cross-cutting.

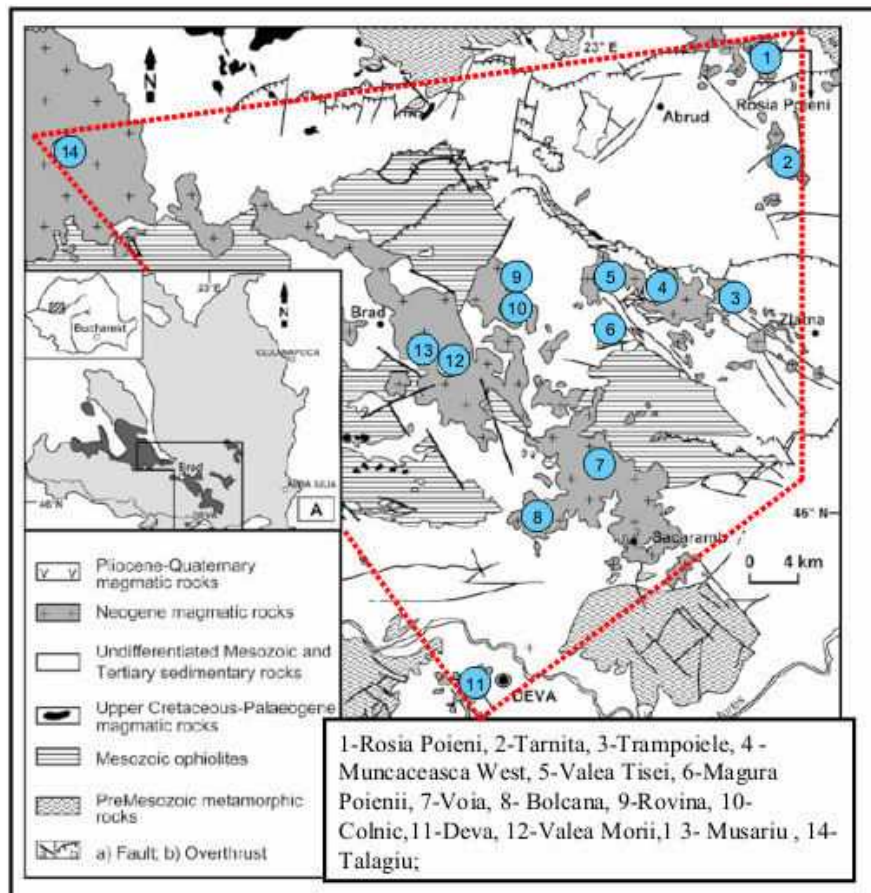


Fig.1. Cluster of Miocene porphyry Cu-Au-(Mo) deposits in the “Gold Quadrilateral” from Metaliferi Mountains (South Apuseni Mountains region - modified from Milu et al., 2004).

3. Methods

3.1. Sample collection and preparation.

The quartz samples were collected from outcrops, drill cores and from underground mines and open pits, specifically for each porphyry copper deposit. Generally they were separated from the characteristic vein networks from potassic zone, including breccia clasts by hammer crushing; then, doubly polished thin sections (e.g. Fig. 3) were prepared from faceted quartz crystals (3-15 mm length), or from quartz grains (1 to 5mm in size), and these were observed under the petrographic microscope. Totally, at least 100 thin polished sections (including wafers) were studied from the most representative quartz samples and used for petrography and microthermometry, as summarized in Table 1A.

3.2. Microthermometry

The micro-thermometric experiments were done in a Linkam TS 1500 stage installed and calibrated by the author in the Institute of Mineralogy and Petrography at ETH Zurich (as

“akademischer gast”, 1994). The system was adapted under a Leitz petrographic microscope equipped with a L32 (UTK 50) lens. For calibration, the melting points of $K_2Cr_2O_7$ (398°C), NaCl (801°C) and Au (1064°C) were used. For temperature higher than 200°C a correction value was added to the thermocouple readings using a calibration curve. The accuracy of recorded temperature ranged between 10° and 15°C for temperatures above 800°C.

The microthermometry was completed with additional measurements in a personal “home made device” used only between 20° up to 1100°C (Pintea, 1998- unpublished report). The heating procedure was selected as a function of the melt inclusion type. For silicate melt inclusion high heating and cooling rates 5° to 20°C/min and 50° to 100°C/min were used, respectively. For salt melt inclusions were recorded more than three melting points, and the heating rate was carefully selected. Consequently, around the melting point of each solid phase, the temperature was held for several



Fig. 2. Large prismatic quartz phenocrysts(QZ) from the potassic zone from the Rosia Poieni Cu-Au(Mo) deposit. An angular fragment of altered andesite (ABH) is covered by precipitated quartz crystals from a brecciated zone inside the deposit. They contains unique high temperature brine and vapor-rich inclusions assemblages related to multiple growth zones as depicted in Fig. 4.

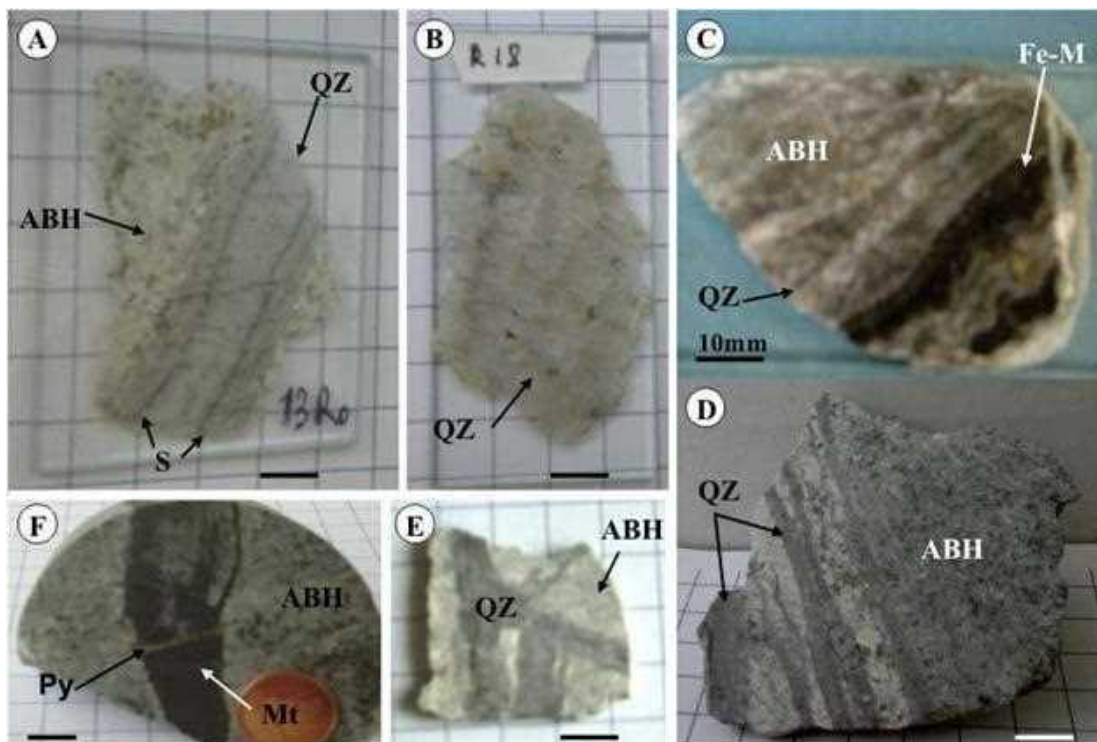


Fig. 3. Quartz vein sample as double polished thin sections (A- Rovina, B- Rosia Poieni) formed by coarse grain quartz and very thin veinlets with sulfide in a intense altered biotite-, and hornblende- andesite (ABH); C- Double polished thin section from Valea Morii PCD showing an alternate of quartz grain veinlets with altered andesite (ABH) and another Fe- rich metasomatic assemblage(Fe-M); D. Hand specimen of altered andesite (ABH) intersected by parallel multiple quartz veinlets; E. polished surface of a hand specimen with quartz veinlet intersection in altered andesite at Talagiu; F- magnetite (Mt) veinlets in the potassic zone from Bolcana PCD crosscut by late pyrite (Py) veinlet. Scale bar = 10 mm.

Table 1A. Summarized characteristics of the quartz samples showing immiscibility evidence between silicate-, salt-, and (Fe-S-O) melts from the porphyry copper system from Metaliferi Mountains and Țibles massif.

Ore deposit	Sample type	Location/alteration	Inclusion types	Distribution	Immiscibility-evidence type
Deva	quartz grains, faceted crystals (2-3mm)	veinlets, breccia	silicate glass hydrous salt melt $\pm$ aqueous liquid	random, in growth zones cluster, trails	a, b, c
Roșia Poieni	quartz grains, faceted crystals up to 15mm	potassic phyllic veinlets, druzes	silicate glass $\pm$ aq liquid; hydrous salt melt	trails in growth zones cluster	a, b, c
Tarnița	quartz grains	veinlets potassic phyllic	silicate glass hydrous salt melt	trails cluster	a, b, c
Bolcana	quartz grains	veinlets (magnetite-rich) potassic phyllic	silicate melt hydrous salt melt	in growth zones trail cluster	a, b, c
Rovina	quartz grains; faceted quartz crystals (2-3mm)	veinlets potassic	silicate glass hydrous salt melt	trail cluster	a, c
Valea Morii	quartz grains; faceted quartz crystals (2-5mm)	veinlets potassic phyllic	silicate glass hydrous salt melt	in growth zones trails cluster	a, b, c
Tălagiu	quartz grains	veinlets potassic phyllic propylitic	silicate melt silicate glass hydrous salt melt	in growth zones cluster trail	a, b, c
Țibles massif	quartz grains	veinlets aplites potassic phyllic propylitic	silicate silicate melt hydrous salt melt	cluster trail	a, b, c

Abbreviations: a-singular inclusion containing silicate glass + hydrosilicate melt; b-Coeval silicate melt or silicate glass with hydrosilicate melt; c-silicate melt released around salt melt $\pm$ vapor during the microthermometric runs.

Table 1B. EPMA analyses of the silicate melt inclusions associated with hydrous salt melt in quartz veins from the potassic zone from Deva porphyry copper deposit (Pinte, 1995).

Compound	P1	P2	P3	P4	P5	P6	P7
SiO ₂	71.57	72.61	73.86	74.02	76.21	76.86	72.55
Al ₂ O ₃	16.01	16.92	16.40	11.82	14.18	10.83	15.89
FeO	0.26	0.40	0.35	0.29	0.41	0.27	0.45
MnO	0.03	0.03	0.02	0.05	0.00	0.00	0.09
MgO	0.04	0.01	0.04	0.00	0.04	0.03	0.03
CaO	0.26	0.30	0.21	0.35	0.21	0.13	0.28
Na ₂ O	2.06	1.83	1.96	1.37	1.55	1.46	2.31
K ₂ O	4.98	3.88	5.34	3.50	4.00	3.49	5.01
Cl	0.35	0.36	0.34	0.28	0.23	0.19	0.34
Total	95.47	96.25	96.37	91.45	96.76	93.22	96.86
F, Cl=O	0.08	0.08	0.08	0.06	0.05	0.04	0.08
Total	95.40	96.17	96.29	91.39	96.71	93.18	96.78

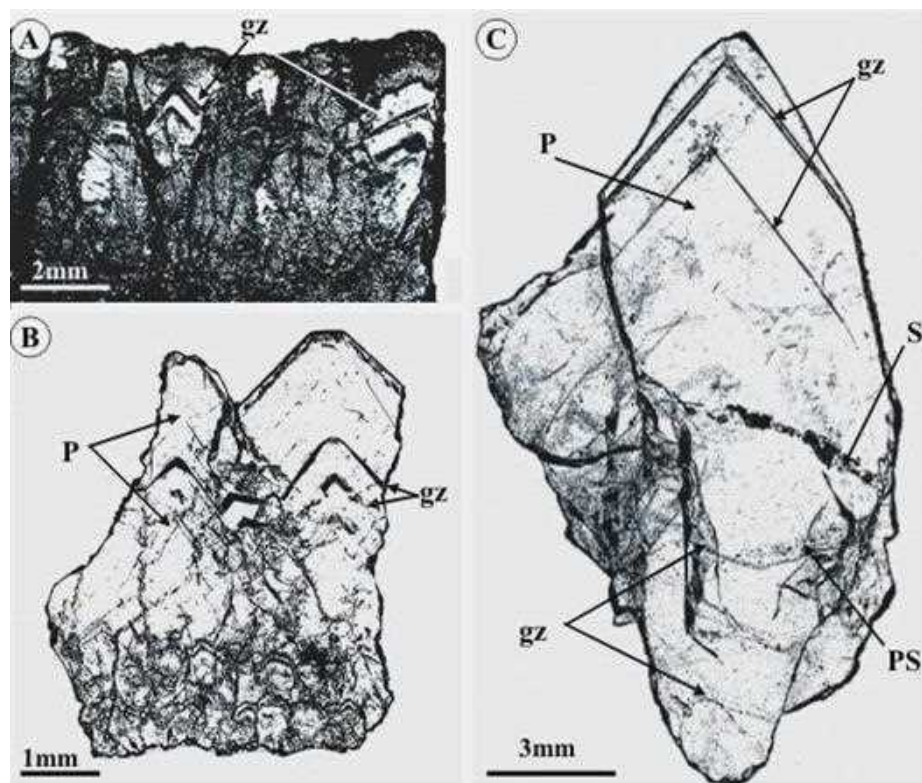


Fig. 4. Transversal sections in quartz grain veinlets (A, B) and monocrystalline-zoned quartz individual showing the distribution of silicate, saline, vapor rich and sulfide/oxide inclusions in Deva (A, B) and Rosia Poieni (C). All inclusions could be Primary (P), Pseudosecondary (PS) and secondary decorating growth zones(gz), cicatrized plain fissures as trails

minutes and the heating rate ranged between 5° and 10°C. Close to the melting or homogenization temperature a lower rate was used ranging between 2° and 5°C.

The duration of one complete run took sometimes several hours depending on the inclusion type; for brine inclusions, 30 to 50 minutes were enough to be heated up and then cooled down to room temperature. More than 500 microthermometric measurements were made especially on the hydrous salt-, and silicate melt inclusions. Because of the complex chemical composition and difficulty on the identification of the solid daughter phases the salinity was approximated only from halite melting points. To estimate salinity in w% NaCl eq the program SoWat¹ was used (Driesner and Heinrich, 2007), and all old data estimation for salinity were updated by using this software. The highest values are

¹ SoWat program was built-up by T. Driesner at ETH- Institute of Geochemistry and Petrology (Swiss) and SoWat stands for Sodium chloride-Water and is a model (almost an equation of state) for the properties of fluids in the H₂O-NaCl system. See the references list at the end of this paper.

representative for the hydrous salt melt inclusions, in which, at high temperature, the chloride liquid coexists with a silicate rich melt.

3.3. EPMA analyses

The glassy part of silicate melt inclusion brought onto the surface by polishing before the microthermometric experiments (only glass + small vapor bubble). Analyses were performed using a CAMECA SX-50 electron microprobe at the Institut für Mineralogie und Petrographie, ETH Zürich (Pintea, 1995). The microprobe is equipped with five crystal spectrometers and operated at an acceleration potential of 15 kV and a beam current of 10 nA on a Faraday cage, and a “spot” size of 1μ. Samples and standards were coated with 200Å of carbon. Glasses shown constant compositions (Table 1B) close to a normal granite, being similar with other chemical data for salt-silicate immiscibility documented in several granites worldwide by Reyf and Bazheyev, (1977); Harris, (1986); Frezzotti, (1992), or in the experimental study by Shinohara et al., (1989), Webster, (1997a), and many others.

3.4. Supplementary techniques.

During the last two decades the author used, in collaboration with different researchers, several complementary analytical methods such as SEM/EDS (Damman et al., 1996, Pintea, 1996), crush-leach technique for the bulk chemical analyses (Pintea, 1998, unpublished report), chlorine isotopic ratio (Pintea et al., 1999b), gas extraction by coupled GC-MS technique (Cună et al., 2001). All of these data are not the subject of this review but some of them were mentioned when necessary.

4. Fluid inclusion petrography

At room temperature conditions several types of melt and fluid inclusions were described, mainly based upon the mode of occurrence and the number and nature of trapped phases, as follows:

- *Silicate melt inclusions* (crystallized melt +/- glass +/- vapor bubble(s) +/- immiscible droplet of chloride rich fluid);
- *Silicate glass inclusions* (mainly glass + vapor bubble (s) +/- chloride rich fluid or only glass);
- *Hydrous salt melt inclusions* (multiple daughter phases such as chlorides, sulphates, sulphides/oxide +/- silicate+ vapor bubble);
- *Vapor - rich inclusions* (vapor mainly +/- liquid +/- solids);
- *Aqueous liquid - rich fluid inclusions* (liquid dominant +/- a vapor bubble);
- *Globular sulfide/oxide melt inclusions* (Fe-S-O) opaque globular solid phases.

In between, we can recognize various combinations where the ratios among solid, liquid and vapor phases are in any proportion as a result of heterogeneous trapping. All of the mentioned types of inclusions are primary, pseudosecondary (trapped generally as trails in recrystallized microcracks formed during the growth of the host mineral) and secondary, based upon phase relation, shape and distribution related to quartz microtexture. They are mono-, bi-, and multiphase fluid and melt inclusions according to the phase number at room temperature conditions. Because there are frequent growth zones and trails in the magmatic-hydrothermal quartz crystals or in quartz grains, a clear distinction between different temporal genetic types of fluid and melt inclusions was documented (e. g. Fig. 4).

4.1 Silicate melt inclusions. Silicate melt inclusions are characteristic of the quartz crystals which occur in short vein networks or in complex mineralogical association including pyrite, bornite, chalcopyrite, magnetite in some

breccia pipe bodies, for example at Deva porphyry Cu-Au (Mo) deposit (Boştinescu, 1983, unpubl report). It is necessary to note here that silicate glass remnants with or without other entrapped phases such as brine or vapor were described in all porphyry copper system from Metaliferi Mountains and they are characteristic not only for the high temperature processes but also for relatively low temperature hydrothermal events. Silicate glass remnants were found also as microinclusions in the opaque minerals by SEM/EDS (Nedelcu et al., 2003). Various in shape and size, this kind of inclusions occur as typical associations in crystal growth zones (Fig. 3, Fig. 5). Multiple growth zones can be recognized even in the single small crystal (1-3 mm), suggesting successive growing stages, but the PTX- conditions seem to be similar, according to Burnham's retreating-downward crystallization model (Burnham, 1979), which postulated that under the saturated carapace, the system is recovering its characteristics for each new explosive event, until extinct. As a result, it is apparent that the shallow body looks like a singular intrusion which shows precise PVTX-characteristics (Becker, 2008; Bodnar, 2010), but at the mineral scale, only the internal microtexture can reveal the real sequence of such complex processes. In other words, each small quartz veinlet is a micro-picture of the entire system. Cumulated, they composed the central stockwork, as the mineralized core of the porphyry copper system. The autometasomatic and remelting features complicated much more the picture and frequently is very difficult to say if the silicate glass inclusions are magmatic or metasomatic-hydrothermal product. Anyway, the magmatic silicate glass inclusions occur as isolated clusters or decorating the growth zone of the host mineral (Fig 5). The metasomatic-hydrothermal silicate glass inclusions occur mainly in healed microfissures, suggesting pseudosecondary and secondary origin. At room temperature conditions, they contain silicate glass and variable amounts (5-10% vol.) of globular saline phase. The glass phase is optically isotropic and colorless, and, during the microthermometric experiments up to 500°-600°C, no visible phase transition has been observed. In addition, the criteria enounced by Anderson (1991), concerning the hourglass inclusions and their magmatic significance, were also taken into account. However, in our case, they contain variable proportions of a chloride-rich phase and, consequently, the simple glass

Fig. 5. Microphotographs showing several kind of silicate glass inclusions, vapor-rich and hydrous salt melt inclusions in quartz from Deva (A, C, D, E, F,G, I) and Rosia Poieni (B,H) porphyry copper systems. G-glass, Cf-saline fluid, H-halite, V-vapor, Sc- another salt daughter phase, Hm-hematite, Kx- unidentified solid phases, Sh- probable anhydrite, O-opaques - pyrite, magnetite, bornite etc; Scale bar = 20 microns.



Fig. 6. Liquid - free hydrous salt melt - type inclusions at room temperature conditions from Deva Porphyry Cu-Au(Mo).Notations: Kxyz-multiple “daughter” salt microcrystals including halite,V- vapor, O-opaque. Scale bar in microns

plus vapor bubble inclusions, typical in many volcanic phenocrysts (Clocchiatti, 1975; Roedder, 1984), were difficult to be recognized in our studied samples.

This variable volumetric ratio between silicate melt and saline rich fluids in silicate glass inclusions is the result of heterogeneous trapping (Roedder, 1992). The initial mixture is formed by the silicate liquid and an exsolved chloride during magmatic to hydrothermal conditions (Fig. 5). Consequently, the fluid mixture is a sample of the growing medium from the potassic zone, where the quartz crystals occur together

with K-feldspar, biotite, amphibole and some metallic minerals such as pyrite, bornite, chalcopryrite, magnetite and hematite being a product of crystallization and not the initial fluid exsolved from the magma. The “hourglass” like shape of many of these inclusions suggest a decompression process supported by the high viscosity silicate-rich phase (the direct result is expressed by the unusual shape of the cavities) during explosive release episodes (brecciation processes, too), generating the multiple growth zones in the quartz crystals. Another explanation for the variable amount of chloride melt in the

silicate melt inclusion can be the necking-down after trapping in the recitrized microcracks. More features of this type of melt inclusions are the following:

- occasionally, in the decorated growth zones of quartz, silicate melt and/or salt melt occur, having constant proportion between the enclosed phases;
- at room temperature, the “chloride” side of these melt inclusions is a mixture of salt crystals and some silicate/sulphate rich phases (K-feldspar, anhydrite plus silicate glass identified by SEM/EDS analyses, see Fig 8 below); they are representative for the heterogeneous trapping, when variable quantities of chloride melt were exsolved from the silicate melt and enclosed in the same cavities;
- the frequent association with a “pure” fused salt inclusion, which, in turn, is primary and even pseudosecondary or secondary, suggests that the quantity of exsolved chloride melt was quite different, depending on various factors such as decreasing pressure-temperature conditions, or the fluid- rock interaction during autometasomatism;
- the quartz and fluid inclusion microtexture suggested that the evolution of the fluid phase proceeded by the separation of more and more chloride rich fluid, as the silicate magma crystallized, and by simultaneously and successive autometasomatic reactions between fluids and crystallizing minerals;
- a liquid H₂O-rich inclusion, mono-, or multiphase, is related to the remelting microtextures, in which a lot of globular Fe-rich (sulfide/oxide/silicate) phases can be recognized as a result of the autometasomatic processes. The monophasic liquid inclusions occur in characteristic associations in the quartz grains and probably are representative for the decompression process as it was described in volcanic environments and in the experimental run products (e.g. Martel and Bureau, 2001). In the mean time, the missing vapor bubble in the “superheated” aqueous fluids could be the consequence of metastability, also experimentally documented (Shmulovich et al., 2009). It is worth to emphasize that a H₂S phase could be released during these processes and perhaps this could be involved in the high sulfidation process overprinting the potassic and phyllic zones, for example at Roşia Poieni porphyry Cu-Mo(Au) deposit (Pinte, 2012).
- a special attention is required now to the presence of the globular silicate glass of

hydrosilicate gel or silicothermal fluid (Wilkinson et al., 1996) formed in the magmatic-to-hydrothermal conditions, ripened and then solidified (crystallized) as saccharoidal and comb quartz microtextures encountered as the very common quartz veinlets network in porphyry copper systems worldwide (e.g. Muntean and Einaudi, 2000; Harris et al., 2004; Vasyukova et al., 2008; Pinte, 2010; Vasyukova, 2011).

The chemical composition of the amphibole andesite, the rock type hosting the PCDs from Metaliferi Mountains, shows broad variation ranges of SiO₂ (57 - 63%), K₂O (0.8 - 1.9%) and Al₂O₃ (9 - 20%), as shown, for example, by Boştinescu (1984). In comparison, the chemical composition of the glass in the silicate melt inclusions from Deva PCD showed higher SiO₂ and K₂O contents and lower concentrations of MnO, MgO and CaO (Table 1 B). A preliminary conclusion is that the most part of the metallic elements were partitioned as chloride compounds in saline rich phase before being trapped in the quartz crystals as inclusions, thus the silicate melt enclosed is just a residual hydrosilicate including aqueous saline fluids, vapor and sulfide globules. It is worth noting that the chlorine content ranges between 0.14 to 0.36 %, according to our measurements, which is in agreement with the majority of chlorine content values measured on natural specimens and in experimental works, where immiscibility between silicate and hydrous salt melt was described (e.g. Metrich and Rutherford, 1992; Webster, 1997b; Shinohara, 1994; Signorelli and Carroll, 2000). Melt inclusions trapped in plagioclase phenocrysts from mineralized versus barren intrusion were used to characterize the calc-alkaline magmas associated with Valea - Morii PCD from Metaliferi Mountains (Grancea et al., 2001). Nevertheless, it is necessary to notice that there is not yet enough analytical data on all generation-types of silicate glass inclusions associated with brine, vapor-rich and sulfide/oxide minerals to give a complete petrological conclusion for the silicate melt trapped in the minerals from the porphyry copper systems of the Metaliferi Mountains and Ţibleş massif. There are also overprinted magmatic-autometasomatic stage(s) on mafic and felsic minerals that released large quantity of hydrosilicate phase containing salt-, (Fe-S-O)-melts and aqueous fluids globules, which decorated the old and new minerals phantom-microtextures (Pinte, 2010). The presence and

Fig. 7. Hydrous salt melt inclusions and vapor- rich inclusions in quartz veinlets from Rosia Poieni porphyry Cu-Au(Mo) deposit. A thin film of a liquid solution wetting the solid(s) and vapor phases. Notations: H- halite, Kxyz- multiple salt daughter phases including salt hydrates, sylvite , complex solid salt phase(s), sulphate and silicate phase(s), O-opaques, L- liquid, V-vapor, Hm- hematite (specularite). Scale bar in microns.

role of the hydrosilicate gel, silicothermal fluid or “heavy fluid” in the pegmatite and porphyry copper genesis is now under debate and it seems to be one of the main fluid/melt phase involved in mineral precipitation and alteration processes (Wilkinson et al., 1996; Williamson et al., 2002; Vasyukova, 2011; Thomas and Davidson, 2012).

4.2. Hydrous salt melt inclusion

The multiphasic inclusions are representative of the saline rich phases (named hydrosaline melt inclusions by Roedder, 1992), which have been exsolved from the silicate magma by immiscibility as a result of decreasing pressure conditions as well as of a complex chemical composition of the magma (Roedder, 1970; Cline and Bodnar, 1994; Harris et al., 2004). At room temperature, this kind of inclusions contains many solid daughter crystals, a vapor rich phase and variable amounts (zero to few %) of liquid phase. The solid phases include mainly halite, several anisotropic birefringent crystals, silicate minerals, opaques and unidentified mineral species (Fig. 6). The vapor phase is formed by aqueous vapor with small amounts of CO₂ detected by Raman spectroscopy and GC/MS (Pintea, 1996).

The hydrous salt melt inclusions can be primary in origin when they are distributed in growth zones or in random three-dimensional associations. Sometimes, they occur as specific isolated clusters associated with silicate melt inclusions shown in Fig. 5. Frequently, they are distributed in characteristic trails in healed microcracks, suggesting pseudosecondary and secondary origin. Often, they are associated with vapor rich inclusions (Fig.5; Fig. 7). Based upon the phase assemblage at room temperature conditions, the hydrous salt melt inclusions were classified in three main categories, as summarized in Pintea (2001). Saline melt inclusions contain obviously more than five solid daughter phases visible under the petrographic microscope, although a major problem arises here because many of them cannot be identified in this simple way and more analytical techniques were required, like SEM/EDS and PIXE (Damman et al., 1996). Additionally, SEM/EDS analyses were conducted in quartz grains from Deva and Roșia Poieni porphyry copper deposits, showed in Fig. 8 A; some specific spectra are showed in Fig. 8B.

Fig. 8A. Scanning electron microscope images showing several open microcavity from quartz (A, B, C, D, E, F, G, H, I, J, K, L, M, N, P, Q, R - Rosia Poieni; O-Deva) of the hydrous salt melt inclusions and vapor-rich inclusions filled by solid daughter phases identified by SEM/EDS (SEM JEOL JSM 840 at ETH Hönggerberg- HPT C107-8093 Zurich-1994) as halite (H), sylvite (Sy) feldspar (F), silicate glass remnant (SI), hematite (Hm), sulfides (PbS, Cpy-chalcopyrite and decrepitate mound (Dm) released during the open procedure of the microcavity.

Under the petrographic microscope and during the microthermometric runs, based upon specific melting points (e.g., Table 4) the daughter solid phases can be classified as follows:

- a. Transparent, pleocroic grains with blue-green or yellow-greenish birefringence color, which melted first during the microthermometric experiments. They were very sensitive to the laser beam in the Raman analyses, and released instantly a liquid phase (Dubessy pers.comm.);
- b. One or more transparent solid grains with orange or yellow birefringence color which melted obviously after halite dissolution;

- c. Two or three isotropic crystals, cubic-sharp and octahedral in shape which are the most important solid daughter crystals and are represented by halite, sylvite and K-Fe (Pb, Zn, Mn) Cl salt complex;
- d. One or more opaque grains of ore minerals. They can be real daughter crystals and they melted during the microthermometric runs (Table 4 and Fig. 12B), probably being chalcopyrite as was described experimentally by Mavrogenes and Bodnar (1994), or they remain undissolved after the vapor bubble disappearance, suggesting accidental trapping.

4.3. Aqueous vapor-, and liquid-rich inclusions contain a vapor-rich phase being almost monophasic or containing one or more solid transparent or opaque phases represented mainly by halite, hematite, magnetite or chalcopyrite and pyrite (Fig. 7). Obviously, these are associated with various types of melt inclusions as clusters or decorating the healed microcracks as “boiling assemblages”. The biphasic (liquid+vapor) type inclusions are related to the fluid phase evolution below 350°-450°C and could be primary in the former silicothermal fluid (now quartz) in a characteristic assemblage, sometimes containing a halite cube or opaque minerals (Pintea, 2010). They are abundant when the epithermal system overprinted the porphyry-type mineralization or are secondary, resulted by thermal decrepitation, necking-down of other inclusion types or during the recratization of the secondary microfissures. Epithermal mineralization overprinting the porphyry systems were described as low sulphidation-type at Valea Morii and Bolcana, or high sulphidation-type at Roşia-Poieni and Tălagiu (Pintea, 1996; André-Mayer et al., 2001; Milu et al., 2003; Milu et al., 2004; Kouzmanov et al., 2010; Cioacă, 2011).

4.4. Sulfide melt inclusions

These can be described as globular in shape and formed by pyrite, chalcopyrite, bornite and/or magnetite, occurring as trails, isolated or clustered in the quartz grains, in separate populations or combined assemblages with silicate glass, brine, aqueous and vapor rich inclusions. In fact, they are immiscible (Fe-S-O) melts with significations largely discussed for example by Larocque et al.(2000), Stavast et al.(2006), Nadeau et al., (2010) but can be produced also during the autometasomatic processes or remelting in hydrosilicate rich phases at high temperature and pressure indicated by their counterpart (silicate or saline) homogenization values, mentioned above. Although they cannot be studied by common microthermometry under the microscope, the meniscus-shaped separation at high temperatures could be a good indication that they were trapped in the liquid state (Pintea, 2002; 2010). They were described by their microtextural features as globular variations in quartz in transmitted and reflected light under the

microscope, suggesting the presence of Cu-rich pyrite, chalcopyrite, magnetite, pyrrhothite, monosulfide solid solution, intermediate solid solution, bornite etc (Fig. 9). They were described in many other porphyry copper deposits worldwide (e.g. Keith et al., 1997; Hattori and Keith, 2001; Landtwing et al., 2005; Halter et al., 2005; Shahabpour, 2006; Audetat and Pettke, 2006; Nadeau et al., 2010; Kamenetsky and Kamenetsky, 2010, the authors suggesting their importance for the ore deposit formation from the magmatic to the hydrothermal stages, no matter whether they are immiscible or fractionated sulfide/oxide phases.

5. Microthermometry

5.1. Silicate melt inclusion microthermometry

It was mentioned above that the silicate melt inclusions contain a clear, transparent and colorless glass and a small rounded vapor bubble. Generally they have small size and obviously are associated with salt melt inclusions and/or vapor inclusions (Fig 10). During the microthermometric experiments the disappearance of the vapor bubble was recorded. Unfortunately, the “pure” silicate melts are difficult to recognize because in almost 90 % of measured runs they contain in variable ratios salt melt and vapor mixtures around homogenization temperature (Fig. 11). Consequently, all silicate melt inclusions contain a few percent of chloride melt even when the homogenization temperature have values ranging between 970° and 1169°C for the measurements given in Table 2A. During cooling, the vapor bubble would nucleate at lower temperature, with 100°-200°C below homogenization value. The chloride globules remain as immiscible droplets in the silicate melt and the vapor bubbles have been renucleated around or inside the chloride phase at the same temperature as mentioned above. The wide range of both kinds of homogenization temperature recorded in the quartz crystals and quartz grains, especially from Deva porphyry copper deposit (Table 2B) shows that some of the higher **Thv** values suggest uncommon trapping conditions or, more probably, were affected by post-entrapment modifications, especially by thermal decrepitation and re-equilibration or heterogeneous trapping (see Discussion section).

Fig. 8B. Characteristic qualitative spectral diagrams printed for several open cavities analyzed by SEM/EDS depicted in Fig 8a. 1. K-feldspar, 2.complex chlorides and K- feldspar; 3. K-feldspar, Pb,Fe- chlorides; 4.K,Ca- feldspar, anhydrite, complex chlorides

Fig. 9. Opaque (Fe-S-O) immiscible melt globules in transmitted light in quartz from Miocene porphyry copper deposit. A- Rosia - Poeni; B, C (around 1300°C), E - Deva; D, F- Tibles; G,H- Valea Morii. Notations- globular sulphide, SM- silicate melt, LS- liquid sulphide, FG- (Fe-S-O) melt, BIAs- brine inclusion assemblages; V- vapor; black arrow in C indicated a liquid chloride (LC) globula inside the silicate melt. SG- silicate glass or restitic minerals (zircon or apatite -?) in plagioclase from Măgura Neagră – Suplai (Țibleș massif)- Pinte 2010). Scale bar in microns.

5.2. Hydrous salt melt inclusion microthermometry

In the liquid-free salt melt inclusions, at room temperature, it can be recognized a complex daughter phase assemblage and a vapor bubble which can occupy 40 to 50% volume in the cavities (Fig. 6). It should be noted that the volume estimations of the solid phases are in error because at room temperature the refractive index is close to the quartz host mineral and the contours of the cavities are not easy to follow, but on heating the contour becomes clear after several daughter phases melted on. During the heating experiments, the following phase transitions were recorded:

Tm₁, Tm₂ - The melting points of birefringent blue-green or yellow-greenish grains, which melted first one by one in all microthermometric experiments. The minimum melting temperature values suggests the presence of a hydrate Fe-chloride phase or another similar compound;

Tm₃ - The melting point for an isotropic crystal which was identified as sylvite or other K-rich chloride phase;

Tm NaCl - The dissolution point of halite daughter crystal;

Tm₄ - The dissolution temperature of another group of birefringent solid phases which melted after halite dissolution. They could be anhydrite, K-feldspar or other metal complex chlorides;

Tmo - The melting point of opaque minerals in liquid free hydrous saline melt inclusions. Frequently, they remain undissolved after the

disappearance of the vapor bubble. Exceptionally, “in-situ” transformation of an opaque solid phase (magnetite or hematite) during microthermometry, probably a Fe-chloride compound, was noted by Pintea (2009) especially in the samples from Bolcana and Tibles (Pintea, unpubl);

Tmg - At high temperature a silicate rich phase is formed mainly in liquid-free salt melt inclusions. This should be interpreted firstly as a result of dissolution of K-feldspar and other silicate phases formed as daughter crystals. Secondly, another source of silicate liquid phase could be the interaction of the saline fluid with the cavities wall. Nevertheless, this effect seems to be unimportant because the mutual solubility between silicate melt and chloride melt is low, for example anhydrous Na-Ca glasses containing 75% SiO₂ could dissolve a quantity of 0.66 to 2.3 % NaCl at temperature of 750° to 1400°C (Ryabchikov, 1963; Roedder and Coombs, 1967).

Thp - The temperature of vapor bubble disappearance in salt melt inclusions in which a silicate rich phase is coexistent with a chloride-rich melt. When a salt melt inclusion was heated up to around 1400°C a complex microthermometric behavior has been recorded (e.g. Fig 12A and microphotograph suite in Fig. 12B). The first solid phases dissolved between 60° to 215°C (Tm₁) or more. This is common for the blue-green birefringent daughter phase, probably represented by salt hydrates.

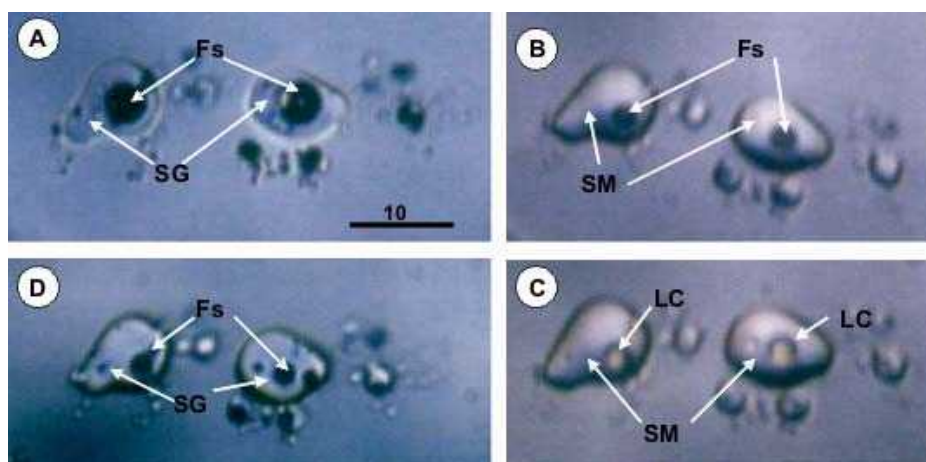


Fig. 10. Microthermometric cycle in complex silicate-hydrous salt melt inclusions in quartz from Deva porphyry Cu-Au(Mo) deposit. At room temperature conditions (A) the microcavities contains a rich silicate glass and a fluid formed by vapor- rich phase, a halite cube and some opaques. On heating the halite melted around 550°C and at 1085°C (B) the fluid bubble is more reduced in volume and contain silicate melt and a dark vapor bubble from which was released around 1267°C a yellow chloride melt (LC) surrounded by a vapor film (dark meniscus), (C). Back again to the room temperature (D) the fluid is redistributed in several small dark bubbles and the microcavities have changed their shape. The final homogenization temperature is imposible to be determined accurately because of the permanent immiscibility between the two trapped phases, the silicate melt and the hydrosilicate melt ,+/- vapor rich. Scale bar in microns.

Table 2A. Homogenization temperature measured in simple (glass + vapor) noted as Thv for vapor bubble disappearance in the silicate melt inclusions. Quartz sample from Deva porphyry Cu-Au (Mo) deposit, level-90 (quartz sample collected by S. Boştinescu).

Sample no.	Th _v , °C
D-90-1	1024
“	1050
“	1058
“	1060
“	1070
“	1075
“	1149
“	1150
“	1169
D-90-2	971
“	970
“	994
“	1013
“	1024
D-90-3	1070
“	1075
D-90-4	1149

Table 2B. Homogenization temperature in the silicate glass and hydrous salt melt inclusions trapped in two zones of the quartz crystal indicated with arrow from the selected area in the Fig 11 (ASZ). Thv- vapor bubble disappearance in the silicate glass inclusions (Fig 11.B) and Thp- vapor bubble disappearance in brine liquid-free inclusions from Fig 10.C). Quartz sample from Deva porphyry Cu-Au(Mo) deposit, level-90 (quartz sample collected by S. Boştinescu).

No.crt.	Th _v , °C	Th _p , °C
1	-	1363
2	-	> 1318
3	-	> 1345
4	-	> 1318
5	-	> 1318
6	-	1287
7	> 1365	-
8	> 1267	-
9	1222	-
10	1235	-
11	1232	-
12	1231	-
13	1231	-
14	-	1258
15	1229	-

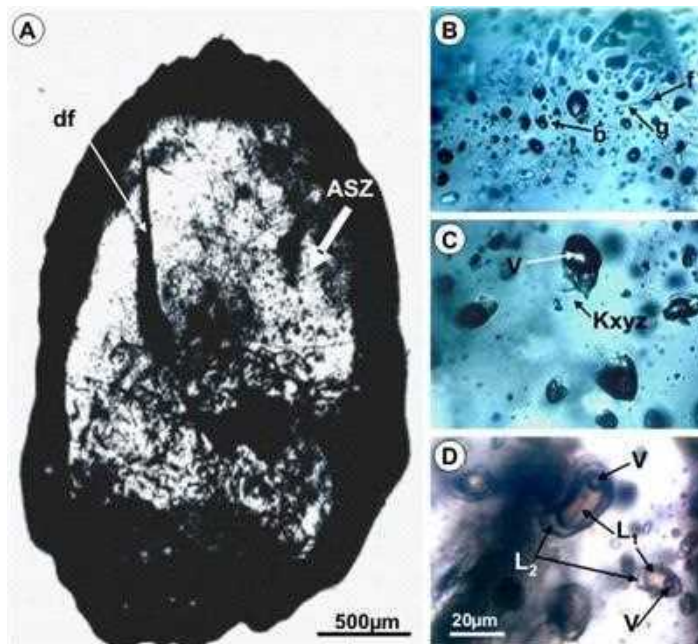


Fig. 11. Individual prismatic quartz crystal (A) double polished in thin section parallel to c axis and shown two distinctive primary assemblages formed by predominantly silicate glass inclusions pictured in (B), and liquid free hydrous salt melt inclusion assemblage in C at room temperature; (D), to high temperature > 1265°C showing three phase equilibrium between silicate melt, salt melt and a vapor bubble. Note that in the selected area indicated by white arrow (ASZ) the silicate glass decorated the border of the growth zone and brine inclusions are situated in the interior of the crystal but both are primary melt inclusions assemblages. df-fissure resulted after the microthermometric heating experiment around 1400°C.

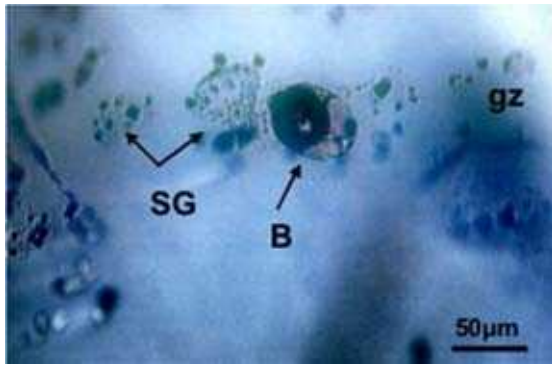


Fig. 12A Hydrous salt melt inclusion (B) trapped in a primary growth zone (gz) decorated with silicate glass inclusions (SG) from Deva porphyry Cu-Au(Mo). See the microthermometry sequences in this brine inclusion in Fig 12B below.

Fig. 12B. Microphotographs of a complete microthermometric cycle in a hydrous salt melt inclusion trapped in a primary quartz growth zone pictured in Fig 12A. a.25°C, b.243°C, c.386°C, d.450°C, e.504°C, f.594°C, g.599°C, h.648°C, i.840°C, j.1086°C, k.1219°C, l.1267°C, m.1284°C, n.1317°C, o.1394°C, p.1284°C, q.1062°C, r.25°C. $T_{mNaCl}=598^{\circ}C$, $T_{h(melt-V(melt))}=1347^{\circ}C$. Other melting temperature recorded for x ($T_{m1}=113^{\circ}C$), y ($T_{m2}=122^{\circ}C$, $288^{\circ}C$ -sylvite), z ($T_{m4}=602^{\circ}-840^{\circ}C$), $T_{mo}=1170^{\circ}C$ and renucleated at $1130^{\circ}C$. x,y- chloride hydrates-sylvite solid phase, z- silicate phase(s), and anhydrite-?, O- Fe,Cu sulphide-?, V-Vapor, L_1 - chloride liquid, L_2 - silicate liquid, g- sulphate globules-?, K- mixture of salt microcrystals renucleated at room temperature. Scale bar in microns. Experiment duration = 5h. Note: Above ca. $1100^{\circ}C$ the microcavity have been seriously damaged and their volume increased probably because the chloride liquid phase have dissolved quartz from the walls, and silicate melt liquid increased also in volume, but chloride part seem to be unchanged during the overheating steps. In this case it was estimated that immiscibility occurred at $1086^{\circ}C$, which could be considered as the real “heterogeneous” trapping temperature of the (L+V) chloride mixture and the silicate melt counterpart.

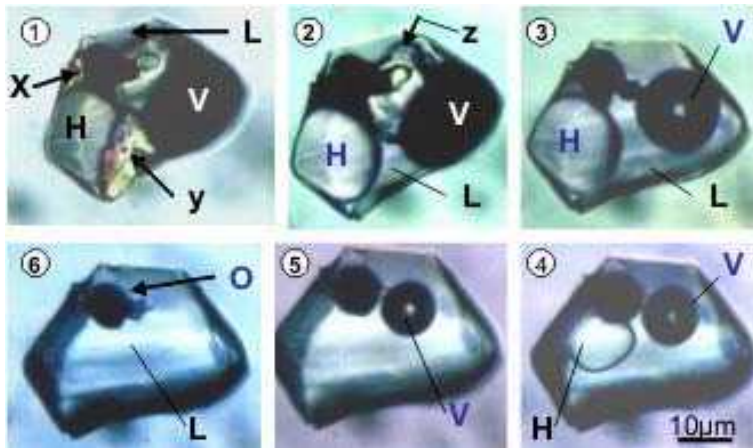


Fig. 13. Hydrous salt melt inclusion with liquid phase at room temperature from Roşia-Poieni porphyry Cu-Au(Mo) deposit, homogenized in “single phase state” in a completed microthermometric run. 1. 25°C, 2. 126°C, 3. 309°C, 4. 575°C, 5. 601°C, 6. 750°C, $T_m \text{ NaCl} = 585^\circ\text{C}$, $T_h \text{ (liquid + solid (s))} = 749^\circ\text{C}$; x,y- unknown solid phases, probably salt hydrates and/or complex salts, H- halite, V- vapor, O-opaque (Fe-S-O), L- liquid.

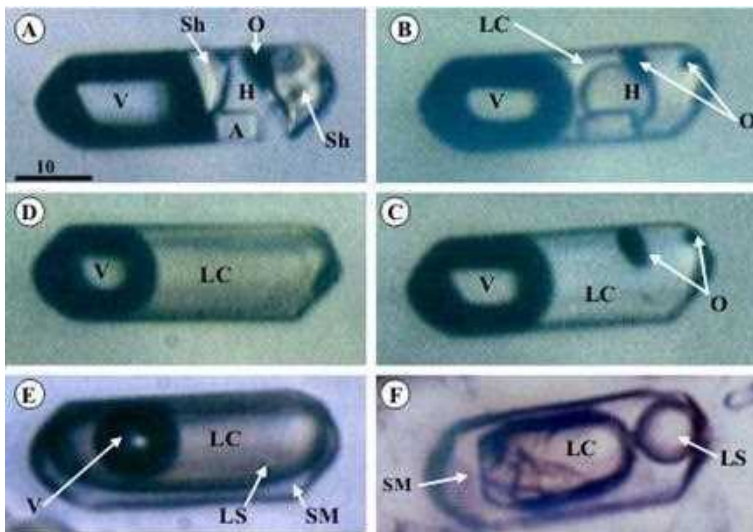


Fig. 14. Microthermometric sequences in hydrous salt melt inclusion from Deva porphyry copper deposit in which three liquid phases were present at homogenization temperature. A. 25°C, B. 551°C, C. 660°C, D. 1149°C, E. 1271°C, F. 1328°C, $T_m \text{ NaCl} = 593^\circ\text{C}$, $T_{mo} = 1130^\circ\text{C}$. At maximum value in F triple immiscibility is shown between silicate melt (SM)-salt melt (LC)-sulphate melt (LS), H- halite, V- vapor, O-opaque, Sh- salt hydrates, A- anhydrite. Scale bar in microns.

Fig. 15. Sequences of the second microthermometric run, repeated after 2 years in a liquid-free hydrous salt melt inclusion trapped in quartz crystal from Deva porphyry Cu-Au(Mo) deposit. a. 25°C, b. 220°C, c. 345°C, d. 678°C, e. 1305°C, f. 25°C, $T_{mh} = 555^\circ\text{C}$, $T_h = 1262^\circ\text{C}$. Notations: Kxyz- mixture of salt microcrystals with halite (H) dominant solid daughter phase, O-opaques, Ksp- feldspar, L_1 - salt melt released by melting of the salt mixture, L_2 - a tiny film of silicate melt released by melting the silicate phases, SMI- silicate glass inclusions formed in fissure probably during the first microthermometric cycle (indicated by dashed arrow in a) suggesting a slight leaking process (reequilibration) but the salt melt volume remains almost the same because this recrystallized and filled up the microcavity as in the starting moment (vol in a = vol in f) even if another small fissure (c) is formed in the second cycle (f).

Table 3. Melting temperatures of daughter solid phases and final homogenization temperature in liquid- free brine inclusions from Deva, Roşia Poieni (RP) and Valea Morii (VM) porphyry Cu-Au (Mo) deposits. **- ultrahigh pressure values (see explanation of Table 5). See text for notation explanations.

Deposit/ sample no.	Phase transition temperature (°C)								Salinity (wt% NaCl eq)
	Tm ₁	Tm ₂	Tm ₃	Tm _h	Tm ₄	Tm _o	Tm _g	Th _p	
Deva/1	88	189	272	583	658	1116	1209	1234	72
“	181	284	461	578	670	-	-	>1300	73
“	113	122	288	598	602	1170	1086	1347	74**
“	148	260	-	592	654	1136	1088	1326	73**
“	163	253	-	578	708	945	-	1354	71**
“	173	245	277	571	687	-	-	1219	70
“	120	-	-	571	707	1144	1151	1426	70**
“	130	277	324	589	696	1006	1326	1404	73**
“	90	216	316	587	607	1013	1345	1405	72**
“	130	223	374	588	704	1050	1345	1413	73**
“	184	256	362	570	665	1073	976	1170	70
“	130	276	362	581	674	1073	976	1322	71**
Deva/ 2	-	243	-	589	-	-	1224	1332	73**
“	120	175	268	575	643	932	-	1115	71
“	120	175	273	576	698	945	-	1160	71
“	170	271	276	569	698	739	1362	>1354	71**
R P/18	215	240	-	583	-	1010	-	1038	72
VM /1	90	-	256	495	830	976	1115	1151	59
“	133	-	285	531	908	1088	1115	1225	64
“	90	238	343	468	-	-	-	1133	56

The second solid phase which has almost the same optical properties (slightly greenish) dissolved at high temperature between 122°-284°C (Tm₂- probably sylvite when is isotropic). The next solid daughter crystal, assumed to be a complex (K, Fe, Mn - Cl) melted obviously between 256° to 461°C (Tm₃). On further heating, halite melted between 412° to 607°C (Tm NaCl) for the selected microthermometric runs in Tables 4 and 5. The latest transparent phases with yellow or orange color under cross polars were melted at temperature higher than 600°C, and sometimes around 900°C.

They might be represented by Fe-chloride, anhydrite or a silica-rich phase (K-feldspar, mica, quartz etc.). The liquid-rich phases appear in a wide temperature range between 976° to 1362°C and could be interpreted as the result of the silicate daughter phases dissolution and/or interaction between salt melt and inclusion walls. The melting of the opaque minerals took place in a wide range of temperature, between 890° and 1170°C as shown in the suite of selected values from Table 3 and Table 4. A more relevant phase transition, which was recorded usually in saline melt inclusions during

heating operations, is the formation of a silicate liquid rim around the salt melt droplet. A tiny film of silicate liquid phase start to appear at temperature near 1000°C or more, and the volume increased relative to the inclusion volume as a function of the partial homogenization temperature, i.e. temperature of the vapor bubble homogenization in the salt globule, Th_p. If this temperature is around 1400°C or even more, the silicate liquid phase can occupy more than 50% of the cavity volume. Perhaps some silicate-rich liquid is released by wall dissolution, but this is low and cannot exceed the mutual solubility limit. The volume increase of the cavity was only in the order of 5 - 10%, slightly more at the highest temperature in the stage. On further heating, the vapor bubble disappeared in a wide range of temperatures and, after that, in salt melt inclusions free of liquid at room temperature, the silicate-rich phase and a salt +/- sulfate globule coexisted (Fig 14). An opaque sulfide globule was often separated inside the silicate melt during the microthermometric run around 1300°C in many inclusions, especially in the quartz from Deva PCD (Pintea, 2002, e.g. Fig. 9 C). On cooling,

the vapor bubble nucleates first and, after that, one by one, the solid phases beginning with the solidification of the silicate glass around chloride melt + vapor phase. At the room temperature conditions all the initial phases should be present but the shape of the cavities and the arrangement of the phases is very different from the initial state before heating experiment (Fig 12B).

For the saline melt inclusions with liquid phase at room temperature, the microthermometric behavior is slightly different

from that presented above (see Fig. 13 as an example). They contain also a complex solid daughter phase assemblage, a vapor bubble and a small amount of liquid phase, but sometimes the birefringent phase is missing and the opaque grains remain (more undissolved after the vapor bubble disappears (Table 4).

The silicate liquid phase meniscus is seldom formed after homogenization temperature and commonly the vapor bubble disappeared before halite dissolution (i.e. halite homogenization).

Table 4. Microthermometric data for hydrous salt melt inclusions with small amount of liquid phase at room temperature in quartz sample from Roşia Poieni (RP), Bolcana (B), Valea Morii (VM), Talagiu (T), Țibleş Massif-Măgura Neagră-Suplai (Tb) porphyry copper deposits. See text for explanations.

Location /sample no.	Phase transition temperatures (°C)					Salinity (wt% NaCl eq.)
	Tm1	Tm3	Tmh	Thv	Tmo	
B/11	166	284	516	1094	890	62
“	-	-	550	1161	1081	67
“	175	274	574	1174	996	70
“	166	274	526	1074	929	64
“	175	275	574	1216	1158	70
“	173	235	534	1158	1098	65
B/17	130	275	549	817	-	67
“	132	270	571	842	-	70
RP/18	60	256	585	749	-	72
“	154	240	558	724	-	68
“	148	240	561	729	-	69
“	130	257	562	730	-	69
“	150	238	579	760	-	71
“	-	256	583	772	-	72
“	215	240	506	506	-	61
“	225	290	578	765	-	71
“	138	209	532	773	-	64
RP/25	170	296	455	1083	-	54
“	182	297	460	1136	-	54
“	130	-	412	665	-	49
“	137	-	422	676	-	50
“	95	-	541	753	-	66
“	150	-	549	775	-	67
VM/1	90	256	495	632	-	59
“	133	285	531	748	-	64
“	-	337	607	656	-	75
“	90	296	555	668	-	68
“	115	296	587	680	-	72
T/23	-	259	523	618	-	63
“	-	-	553	1037	-	67
Tb47	-	-	573	705	-	70
“	-	-	594	872	-	73
“	-	-	594	1070	-	73
“	-	-	565	830	-	69
“	-	-	519	682	-	63

Table 5. SoWat calculation showing the main characteristics of the trapped phases in the hydrous salt melt inclusions. The physical phase state (single phase state, L-liquid, V-vapor, H-halite) were observed at homogenization temperature values. For “single phase state” trapping was homogeneous, for L+V or V+H trapping was heterogeneous or the cavities have been decrepitated during the microthermometric runs or natural reheating.

No crt	Th _p , °C	P, kbar	Liquid		Vapor		Single phase		Initial fluid state
			W _L	D _L	W _V	D _V	W _S	D _S	
1	1262	12.8	-	-	-	-	68	1.2	single phase
2	1234	8.2	-	-	-	-	72	1.2	single phase
3	1219	6.3	-	-	-	-	70	1.2	single phase
4	1170	2.7	-	-	-	-	70	1.1	single phase
5	1115	2.0	71	1.1	10	0.4	-	-	V+L
6	1160	2.2	-	-	-	-	71	1.1	single phase
7	1038	1.6	-	-	-	-	72	1.1	single phase
8	1151	2.5	59	0.9	17	0.5	-	-	V+L
9	1225	7.0	-	-	-	-	64	1.1	single phase
10	1133	2.5	56	0.9	18	0.5	-	-	V+L
11	1094	2.2	-	-	-	-	62	1.0	single phase
12	1161	2.4	67	1.0	15	0.4	-	-	V+L
13	1158	2.4	-	-	-	-	65	1.0	single phase
14	817	1.0	-	-	-	-	67	1.0	single phase
15	842	1.0	-	-	-	-	70	1.0	single phase
16	749	0.7	-	-	-	-	72	1.1	single phase
17	724	0.7	68	1.1	0.8	0.2	-	-	V+L
18	729	0.7	69	1.1	0.8	0.2	-	-	V+L
19	730	0.7	-	-	-	-	69	1.0	single phase
20	760	0.8	71	1.1	0.8	0.2	-	-	V+L
21	772	0.8	-	-	-	-	72	1.1	single phase
22	506	0.3	61	-	0.1	0.1	-	-	V+H
23	765	0.8	71	1.1	0.9	0.2	-	-	V+L
24	773	1.0	-	-	-	-	64	1.0	single phase
25	1083	2.3	54	0.9	17	0.6	-	-	V+L
26	1136	2.5	54	0.9	18	0.6	-	-	V+L
27	665	0.9	-	-	-	-	49	0.9	single phase
28	676	0.9	50	0.9	2.3	0.3	-	-	V+L
29	753	0.9	66	1.0	1.3	0.2	-	-	V+L
30	775	0.9	66	1.0	1.3	0.2	-	-	V+L
31	632	0.7	-	-	-	-	59	1.0	single phase
32	748	0.9	-	-	-	-	64	1.0	single phase
33	656	0.5	75	1.3	0.2	0.1	-	-	V+L
34	668	0.6	68	1.1	0.4	0.2	-	-	V+L
35	680	0.6	-	-	-	-	72	1.2	single phase
36	618	0.6	-	-	-	-	63	1.1	single phase
37	1037	1.8	-	-	-	-	67	1.0	single phase
38	705	0.65	70	1.2	0.5	0.2	-	-	V+L
39	872	1.7	48	0.9	16	0.5	-	-	V+L
40	1070	1.6	73	1.1	6	0.3	-	-	V+L
41	830	1.0	69	1.1	2	0.2	-	-	V+L
42	682	0.8	-	-	-	-	63	1.1	single phase

Note : Ws-composition of single phase state in wt% NaCl eq.; Ds-single phase density in g/ccm; WL-composition of the liquid phase in wt% NaCl eq.; DL- liquid phase density in g/ccm; Wv- vapor phase composition in wt % NaCl eq.; Dv- vapor phase density in g/ccm. Note: For the inclusions labeled ** in Table 3 the density calculated values were 0 g/ccm, that is an uncertain significance, and these data will be probably avoided from further geological interpretation.

Table 6. Bulk crush-leach analyses of released fluid from quartz veins at Rosia Poieni porphyry Cu-Au(Mo) deposit (Pintea unpublished IGR-report arch. -1998). Sample No. 11* and 18* have been measured for $\delta^{37}\text{Cl}$ ratio, which ranged between -0.28‰ and -0.43 ‰, respectively (Pintea et al., 1999b)

Sample no.	Altitude (m)	KCl wt%	CaCl ₂ wt%	FeCl ₂ wt%	NaCl wt%	MgCl ₂ wt%
41	1060	24.17	24.33	24.81	13.88	12.81
8	1030	13.46	64.20	12.37	6.22	3.75
11*	1030	23.72	40.20	15.53	12.97	7.58
45	1030	13.06	25.30	52.63	5.08	3.93
16	1000	13.41	60.39	15.29	4.86	6.05
18*	1000	36.10	32.57	13.08	18.22	0.03
20	1000	39.51	25.66	10.99	17.51	6.33
43	985	26.61	40.75	19.30	6.24	7.10
29	970	17.00	35.93	32.85	6.54	7.68
31	970	19.64	43.06	24.55	7.68	5.07
33	970	28.67	39.86	12.84	8.96	9.67
27	970	26.90	44.65	16.01	8.35	4.09

This kind of homogenization is characteristic for the “halite trend solution” and an explanation for this trend is the precipitation of KCl-bearing halite prior to entrapment, mainly because of boiling processes (Cloke and Kesler, 1979; Quan et al., 1987). The selected values from Table 3 and Table 4 above come from a huge number (more than 500) of measurements (i.e. microthermometric cycles) and some of them (n=350) were projected recently in a Salinity-Homogenization temperature diagram (Pintea, 2012).

6. Discussion and conclusions

6.1. Melting and homogenization temperatures

The complex microthermometric behavior during the heating runs was recorded in liquid-free salt melt inclusions. There, the melting temperatures of almost all solid daughter phases were measured, including the formation of silicate liquid meniscus surrounding the salt melt, and also the opaques melting temperatures (e.g. Fig. 12B-j). These phases have the highest (excessive) final homogenization temperature in the salt liquid phase and show strong evidence of heterogeneous trapping (immiscibility). As the liquid content in the brine inclusions is more visible (Table 4) the number of melting points decreased and the opaque phase obviously could not be melted before the vapor bubble disappearance. Also, the liquid silicate meniscus is not visible at the homogenization temperature. The main questions that arised is if the melting temperature of the opaque phases recorded are the real precipitation temperatures of those

phases in the inclusions or have they already been entrapped in the solid state (as “micro-nuggets” or “step daughter minerals”). Opaque sulfide globules floating in the silicate melt inclusions coeval with salt melt inclusions were also observed, especially at highest homogenization temperatures (Pintea 2002, e.g. Fig. 9C). It is a common feature that during the alteration of the mafic phenocrysts as biotite, hornblende, pyroxene or during total feldspar destruction stage, a Fe-rich sulfide phase can be released and the globular appearance suggested the initial liquid phase state (Shahabpour, 2000). These minerals would be involved in the redistribution of ore elements together with silicate, saline and aqueous rich phases during the magmatic-to-hydrothermal processes and their study showed that they have great importance in developing economic ores (e.g. Keith et al., 1997; Hattori and Keith, 2001; Landtwing et al., 2005; Halter et al., 2005; Audetat and Pettke, 2006; Nadeau et al., 2010; Kamenetsky and Kamenetsky, 2010).

Another problem is related to the silicate liquid rim released around the salt melt from the silicate daughter minerals melted (dissolved) during heating. This can be the effect of the immiscibility of the two phases (trapped together in various proportions) or maybe the silicate liquid was generated by the reaction between the inclusion wall and the released salt rich fluid formed by the melting of the saline daughter phases inside the inclusion.

The first melting point is representative for several birefringent grains probably salt hydrates and then a slight birefringent phase occupies almost the same volume as the halite daughter

phase, probably a multiple salt phase. Sylvite is very difficult to be seen because of its small volume and high transparency. Anhydrite or even the silicate daughter phase cannot be identified by normal optical microscopy. Finally, only the temperature of the halite daughter phase dissolution can be precisely recorded, therefore, the system $\text{H}_2\text{O}-\text{NaCl}$ is obviously used to modeling the fluid phase equilibrium in brine inclusions. Nevertheless, as it is known, the composition of these is expressed as wt% NaCl equivalent and every evolution path (or snapshot) isochor-isopleth in a P-T plane is related to this system. This is a good approximation (e.g. Bodnar et al., 1985) but we do not have any data, yet, about the importance of the solubility of salt hydrates, (K, Fe, Mn)-Cl phase, KCl, anhydrite, quartz, micas, sulphide, oxide phases in the mother salty/silicate liquors of the hydrous salt melt inclusion. Moreover, the final homogenization temperature is higher than any liquidus temperature, considering the composition of the host magma, especially for the liquid-free saline inclusions in Table 3. Even if the salt-rich inclusions show re-equilibration after the high temperature homogenization runs (Fig. 12B, Fig. 14), the salt liquid + vapor is surrounded by the viscous silicate liquid and remain separated as immiscible phase, thus the temperature at the vapor bubble disappearance could be the trapping temperature, if the initial fluid was a homogeneous salt melt (Table 5). To justify immiscibility between silicate and salt melt, in this research, the microthermometric runs were obviously completed until the separate phases were coexistent and the liquid homogenization temperature (Thp) was used to calculate salinity using the new available software (e.g. Driesner and Heinrich, 2007). The microthermometric data from Table 3 suggest, firstly, that salt melt inclusions without visible liquid phase at room temperature conditions contain the most complete solid daughter phase assemblage. All of these phases dissolved during heating runs in the presence of a vapor phase and suggest homogeneous trapping, and they renucleated in reversed order when temperature in the stage decreased to the room conditions. Moreover, the petrographic observations showed a common distribution for the inclusions of primary origin (Roedder, 1984), and that salt melts are coexistent or trapped together with silicate melt. The salt melts floated as globules in the more dense silicate melt, taken into

account the low mutual solubility between these two melts. That is, during magma crystallization, salt melt will exsolve the first, and then, because of increasing water content, the chemistry of the salt melt would be drastically changed. This fact is illustrated in Table 4, showing the melting temperatures recorded in salt melt inclusions, where a variable amount of water is present as a liquid film visible at room temperature. In these inclusions, many of the solid daughter phases are missing and/or the opaque phases remains undissolved after the vapor bubble disappearance, and also the silicate liquid phase is not released during heating runs. Probably, when only salt is exsolved from magma, much more metal comes out as chloride complexes and probably precipitates as oxides and sulphides depending on the initial S content of the melts and on the oxygen fugacity controlled by hematite-magnetite (HM) buffer (Eugster, 1986, Burnham and Ohmoto, 1980). The presence of magnetite and hexagonal red flakes of hematite (specularite) is a common fact in salt melt inclusions from PCDs (Roedder, 1981; Fig. 7, Fig. 5 this study). During the microthermometric runs in the salt liquid-free inclusions, these generally melted and renucleated constantly on decreasing temperature. But they remained undissolved in the hydrous salt melt inclusions, where a film of liquid solution is visible. The ultrahigh Thp values recorded in our sample from the porphyry Cu-Au(Mo) deposits from Metaliferi Mountains could be related also to many factors such as post-entrapment modification of the microcavities by necking-down, stretching, thermal decrepitation and leakage-in or out during reequilibration (Hall and Sterner, 1993; Audetat and Günther, 1999; Bodnar, 2003). On the other hand, the stability of vapor bubbles of the hydrous salt melt inclusions could be influenced probably by their chemistry. For example, Webster and Mandeville (2007) emphasized recently that the high temperature homogenization in brine inclusions, i.e. the persistence of the vapor bubble to high temperatures, could be done by the presence of the CaCl_2 and MgCl_2 when the fluid were exsolved from mafic melts, which in their turn were subjected to large ranges of P-T conditions. This interpretation is concordant with the bulk crush-leach analyses of the solutions extracted from quartz, sampled at Roşia Poieni (Table 6, Pintea-unpublished) and Țibles (Pintea et al., 1999a) porphyry copper

systems, where the predominant chlorides are CaCl_2 , FeCl_2 , and not NaCl , as was obtained by microthermometry of the individual hydrous salt melt inclusions. More recent analyses by LA-ICP-MS in complex brine inclusions and vapor-rich ones as well, from the Western Carpathians (Kodera et al., 2012; 2014) showed unusual proportions of Fe-K-Na-Cl (i.e. $\text{FeCl} > \text{KCl} > \text{NaCl}$).

6.2. Fluid-melt immiscibility in porphyry copper genesis

The milestone orthomagmatic model elaborated by Burnham (1979) postulated that a granodioritic magma containing 3.0 wt% H_2O has been emplaced in a subvolcanic environment and undergone cooling to below solidus temperature, under the saturated carapace, labeled “ S_1 ” in his famous Fig 3.5a. These picture sequences are then reloaded and discussed everywhere the orthomagmatic model is invoked (see recent data of Becker et al., 2008, Bodnar, 2010). The inner temperature in that model is fixed at 1025°C and the line 1000°C is the limit of the melt with the solidifying carapace where biotite and hornblende start to crystallize in the outer zones, releasing silica, which leads to the crystallization of quartz (Burnham, 1979). Some of this quartz will be accumulated in the vein networks, which are formed outward by a sequence of explosion and brecciation of the retreated-downward saturated carapace. This is why we assumed that the small quartz grains protruded in the dilating endocinetic fissures (veinlets) contain multiple overgrowth zones (Pinte, 2009). Moreover, in the Burnham’s model (1979) was evidenced that the second boiling process (resurgent boiling) is characterized by the reaction H_2O -saturated melt $\rightarrow$ crystal + vapor, which involved a pressure increase under the carapace as cooling and crystallization proceeded. The inner pressure can reach any value (i.e. $\rightarrow \infty$) and would be very high mainly in isolated small pockets of H_2O -saturated magma. Despite the fact that our homogenization temperature is far away from the liquidus temperature used by Burnham in his model, the pressure calculated from these are in accord with the assertion made above. So we can explain these ultrahigh P-T data in several ways and one of these is the stress conditions under the saturated carapace inside the liquid magma batch which can be recharged by ultrahot silicate liquids from underlying mafic magma coming from different depths generated first in the

MASH zone (Cloos, 2001; Campos et al., 2002; Richards, 2003). A strong argument in favor of this recharging process with high P-T fluids is based on the fact that for hydrous salt melt inclusions, the saline rich melt is always surrounded by the viscous silicate melt as immiscible phase, so that, during the high temperature microthermometry, the saline rich phase cannot change its initial volume and the measured T_{hp} seems to be correct (Fig. 14). Even in the picture sequences from Fig. 15, where a small crack is filled with silicate melt inclusions (SMI) it is evident that the chloride phase has not leaked around because the silicate liquid acted as a protector wall and the saline phase remained in constant volume and recrystallized and refilled the cavity as it was initially, before starting the microthermometric experiment. Another plausible explanation for the accuracy of our data in terms of P-T trapping conditions is the fact that the highest values are characteristic for the sample coming from Deva porphyry copper system, which occurred near the South Transylvanian fault system that, as the Western fissure in the Andes (Campos et al., 2002) is a deep fault system developed during subduction in the back arc region. Even the geological profile at Deva porphyry is suggestive for this tectonics as it looks like a narrow dyke (Ivășcanu, et al., 2003) probably ascended through a deep fault system. Therefore, it is possible that the quartz grains in the veinlets from the Deva stockwork (high pressure breccia body at -90 m level underground) mentioned by Boștinescu (1983, unpublished report) originate from different depths, as suggested by the high P-T conditions (Table 2, Table 3). By using the SoWat software (Driesner and Heinrich, 2007), it was possible to find out that the majority of the hydrous salt melt inclusions contain, at the homogenization temperature, a single homogeneous liquid phase (Table 5). Other hydrous salt melt inclusions show liquid (L) and vapor (V) coexistence, which could be an indication of boiling at the trapping moment, when vapor and liquid were enclosed heterogeneously in the same cavity. Rarely, vapor and solid halite crystals were trapped together; this is the case presented recently by Muntean and Einaudi (2000) for the porphyry-Au deposits in the Maricunga belt (Chile) and by Kodera et al. (2012), in the Western Carpathians, for the same type of the deposit. In both mentioned examples, only high salinity brine inclusions were coexistent with vapor-rich

inclusions in trails, and there is no mention of immiscibility between fluid and the silicate melt, as in our case study. In our interpretation, the hydrous salt melt inclusions are the result of heterogeneous trapping at different depth, below the actual porphyry systems as the calculated pressure suggested (Table 5). Additionally, it was emphasized (Pintea, 2009), based upon microtextural evidences, that adjacent quartz grains contain different kinds of fluid and melt inclusion assemblages suggesting that they were crystallized at different depths and brought together in the same fractures by successive fluid flushing events. Alternatively, the quartz grains in the veinlets recrystallized from the hydrosilicate gel (silicothermal fluids) or “heavy fluid” as was emphasized by Vasyukova et al. (2008) and Vasyukova (2011).

The ultrahigh P-T ($\geq 900^\circ$ -1100°C and 0.3-12.8 kbars) data reported in this research could be related to the metasomatised lithospheric mantle above the asthenospheric wedge (802°-1416°C, 3.2-9.7 kbars) in a W-directed subduction environment in the Eastern Carpathians (Kovacs, 2002; Seghedi et al., 2004; Doglioni et al., 2009) and to the extension and partial melting of the mantle source and metasomatism in the Apuseni Mountains (Richards, 2009; Harris et al., 2012). These data and settings suggest the separation of hydrous salt, silicate, sulfide and aqueous fluids by immiscibility from the partially molten mafic rocks at the base of the Earth crust. In this respect, at magmatic to hydrothermal transition concomitantly with the second boiling process and fluid phase separation, a wide range of autometasomatic and remelting features were also described in these two regions (Pintea, 2010). Moreover, data about high pressure at magmatic temperature come out from high density water-rich inclusions study from central Slovakia, in Western Carpathians (Naumov et al., 1996). The authors mentioned a water pressure of 5.6 to 15-17 kbars at 800°-900°C, during magma crystallization. However, these high pressure values were questioned by Davidson and Kamenetsky (2007), and they argued that “the presence of single-phase aqueous bubbles in melt inclusions is a metastability effect”. The metastable superheated solutions were studied by isochoric experimental runs in synthetic fluid inclusions synthesized at 7.5 kbars and 530°-700°C, and demonstrated that “natural solutions can reach high levels of superheating” (Shmulovich et al.,

2009). Also, the presence of silicate globules as (re)melting products in the porphyry copper deposits from Metaliferi Mountains and Eastern Carpathians (e.g. Țibleș massif), as well as their formation in many experimental studies (e.g. Antignano and Manning, 2008) are strong arguments that our microthermometric records could be the real trapping P-T conditions for silicate melt and hydrous saline inclusions assemblages (Table 2, 3, 4 and 5). Anyhow, the excessive values labeled * * in Table 3, probably would be avoided from further interpretation, these being related mostly of post-entrapment processes. Therefore, there still remain a lot of debatable issues regarding the fluid/melt separation and evolution during the porphyry copper genesis in the studied regions of the Carpathians.

In summary, the silicate and hydrous salt melt inclusions study from the porphyry Cu(-Au,-Mo) deposits of the Metaliferi Mountains and Țibleș massif in the Eastern Carpathians (Romania) presented in this review could be summarized as follows:

- The evidence of liquid magmatic immiscibility between silicate melt and salt melt is based on the contemporary occurrence of inclusions within the quartz crystals. The phases in the inclusions include silicate melt, hydrous salt melt, (Fe-S-O) globules and water-rich fluids trapped in various proportions in separate and/or coeval inclusions.
- The temperature of vapor bubble disappearance in silicate glass inclusions and the temperature of the silicate liquid rim formation surrounding the salt melt globule, seem to be the real trapping temperatures of the melt inclusions, mostly in the interval 1000°-1100°C. Nevertheless, they seems to have a reasonable geological meaning only if we assume that they were trapped from different magma batches, where ultrahigh P-T mafic influx invaded the MASH zone, from which the andesitic melt was segregated, then ascended and crystallized by retreating downward, as it was postulated by Burnham's model. An exception is the case of Deva porphyry copper deposit, which is emplaced close to the South-Transylvanian deep fault system, as is the Western fissure in the Andes, where porphyry copper system were also developed and show similar characteristics of the fluid and melt inclusions (Campos et al., 2002). The multiple stages of the porphyry copper evolution, starting deep in the Earth's

crust were emphasized by many authors, worldwide, e.g., Richards (2003, 2009) and Cloos (2001).

- Usually, quartz crystals are zoned because of the retreating downward crystallization process and the mixture of silicate melt, salt melt + vapor were exsolved sequentially during magma emplacement in the inner part of the shallow intrusives where the ore is located. This is composed of myriads of small veins in a brittle structure, filled up with quartz - pyrite, quartz - magnetite - chalcopyrite, quartz - bornite - chalcopyrite, and is associated with the potassic alteration in the host rock, consisting of K-feldspar, biotite, magnetite; the potassic alteration may be obliterated by subsequent alteration mineral characteristic for the phyllic, propylitic or argillic alteration facies.

- The saline melts can be sometimes considered as metal solvent solution because in most microthermometric runs, depending on the water content, the opaque daughter minerals were dissolved during heating and reprecipitated on cooling; otherwise they remained undissolved or became globular opaque melt phases at very high temperature, i.e. around 1300°C.

- Alternatively or complementary, the silicate melt, and hydrous salt melt inclusions plus vapor- and liquid-rich inclusions seem to be the products released by the reaction between a supercritical fluid(?), which separates in low and high salinity fluid phases, and the crystallizing magmatic minerals during the autometasomatic and remelting processes. The high P-T ($\geq 900^\circ\text{C}$, 0.3-12.8 kbars) conditions of such processes would be correlated with the existence of a "mafic nucleus" mixed or mingled with the felsic melt in intermediate magma chambers and recycled by autometasomatism, as subtle mechanism of porphyry-copper deposits generation inside the shallow subvolcanic structures. In these processes, the fluid phases were transported by hydrous silicate melts (silicothermal fluids-Wilkinson et al., 1996, "heavy fluid"-Vasyukova, 2011) and trapped in crystallized quartz in magmatic to hydrothermal conditions; globular sulfide were released in the mean time and benefited the ore deposit metal content.

- In many PCDs from Metaliferi Mountains and Țibles massif in Eastern Carpathians, a meteoric water-dominated convective system was recognized being centered on the "protore" zone and surroundings, composed by veins, breccias, stockworks, where the primary ore deposit

(spatially corresponding with the potassic alteration zone) was altered, transported and reprecipitated as epithermal products of high sulfidation and/or low sulfidation type.

- The ultrahigh P-T ($\geq 900^\circ\text{C}$ -1000°C, 0.3-12.8 kbars) magmatic immiscibility, discussed in this paper, was generated in specific geodynamic conditions during the middle Miocene extensional regime in the Apuseni Mountains, which caused decompression melting in a geotectonic setting modified by clock-wise rotation of the intra-Carpathian blocks coupled to the asthenosphere upwelling and a higher thermal regime (Roșu et al., 2004; Seghedi et al., 2010; Harris et al., 2013). The genesis of the Măgura Neagra-Suplai porphyry copper system from Țibles Mountains in Eastern Carpathians is still under debate (Udubașa et al., 1984; Pinte et al., 1999a).

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FLUIDS IN THE EARTH CRUST AND UPPER MANTLE: AN ATLAS OF THE FLUID AND MELT INCLUSIONS FROM ROMANIA

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Abstract. The geological history of the Romanian territory spanned ca. 2.0 Ga from the Proterozoic to the present time (Balintoni 2000). There are plenty of geological events where one or more fluid/melt phases were involved during their formation time. Metamorphic, magmatic and sedimentary rocks were generated during Wilson cycles characterized by various fluid mixtures trapped as carbonic, aqueous and melts inclusions in petrogenetic and hydrothermal or evaporate ore minerals. A complex fluid assemblage can also be encountered in the upper mantle peridotite nodules and in the high to low grade metamorphic rocks in all crystalline chains of the Carpathians. In this work the fluid and melt inclusions trapped in mineral formed during various geological processes and ages from Carpathian area from author's collection are presented, based mainly upon petrography and microthermometry.

1. Introduction

The main goal of this paper is to present in an atlas form the principal fluid and melt inclusions types and assemblages from mineral growth in various geological conditions and time period from Romania, based upon the personal author's collection. Magmatic-hydrothermal and sedimentary deposits are well represented by many fluid and melt inclusions types, related to the most important ore deposit from the Eastern Carpathians, Metaliferi Mountains, North Apuseni Mountains and South Carpathians in the Banat region. Igneous and hydrothermal processes are related to the Alpine subduction zones and to the magmatism of late Cretaceous and Neogene age, to which the most productive events of the studied areas are associated (Borcoş et al., 1998).

Hydrous silicate melt and aqueous-carbonic fluids evolved in shallow subvolcanic or plutonic rocks generating huge geochemical anomalies as associated ore deposits, including porphyry copper, skarn and epithermal ore deposits and occurrences, many of them being of economic interest from immemorial times (Borcoş and Udubaşa, 2012). Complex silicate melt inclusions were described inside the shallow magmatic – hydrothermal systems from Moldova-Nouă, Oraviţa, Birtin and Vlădeasa granite – pegmatite complex (Pinte, 1991b; Pinte 2012 and

unpublished data). Complex fluid phase immiscibility between hydrous salt melt–silicate and Fe-S-O phases was documented in the Miocene porphyry copper system from Metaliferi Mountains and Țibles massif in the subvolcanic zone of the Eastern Carpathians (Pintea, 1993c; 1995b; 1996b; 2014a). Silicate glass and multiphase aqueous inclusions were described in the bipyramidal quartz phenocrysts from Roșia Montană, “Laleaua Albă” and Dănești-Piatra Roșie dacite or plagioclase from the Bătarci hyalodacitic rocks from Oaș Mountains. Glass “foam-like” silicate melt inclusions were described in the Dej tuff formation (Pintea, 2013).

Epithermal fluids were studied mostly in the gangue minerals (quartz, calcite, anhydrite, gypsum, barite etc) but also in ore minerals such as enargite and wolframite (Bailly, com pers) and sphalerite (Pintea, 1995a). Greisens-like fluids were evolved during the Variscan emplacement of the Highiş massif and they are characterized by a saline rich liquid phase trapped as primary, pseudosecondary and secondary fluid in quartz from veins and druses (Pintea, 2002 unpublished). Generally, the metamorphic fluids trapped in the quartzite fissures systems from the Carpathian crystalline chain, including amphibolite facies rocks, contain also saline rich fluids and $\text{CO}_2\text{-H}_2\text{O} \pm \text{CH}_4 \pm \text{N}_2$ fluid assemblages. (Pintea, 1987, unpublished data). Complex fluid inclusion assemblages were described in quartz from the REE-Mo mineralization at Jolotca ore deposit, belonging to Ditrău alkaline massif metallogenetic prospect (Pintea, 1991b; Pintea and Diamond, 1994).

Evaporite minerals from various sedimentary environments, including the recent and ongoing process such as saline crust generation around saline lakes and above salt mining prospects, contain mostly monophasic liquid inclusions (Pintea, 2008b). The diagenetic processes up to anchizone facies shown complex fluid and solid fluid inclusion assemblages trapped mostly in salt diapire bodies in Transylvania basin and outer Carpathians. Carbonic fluids (CO_2 , CH_4) were found in halite from Badenian salt deposits, while liquid hydrocarbons and methane was found in the “Maramureș diamond” quartz crystals in fissures within the upper Cretaceous carbonaceous flysch from north Romania (Pintea, 1995a).

The methods used by the author during about 25 years of work on fluid and melt inclusions in Romania started with microscopic petrography and continued by low and high temperature microthermometry (Pintea, 1995a; 1998, unpublished), crush-leach techniques coupled with selective ion devices and AAS, CG-MS (Cuna et al., 2001) for gas extraction, SEM-EDS, PIXE, Raman microspectroscopy (Pintea, 1996b) and chlorine isotope measurement (Pintea et al., 1999b). Significant benefits were gained by working, visiting and collaborating with various European laboratory from Lvov, Zurich, Amsterdam, Nancy, Utrecht and Univ. “Babes-Bolyai” - Physics department; INCTDIM and “Raluca Ripan” Chemical and Physical Institutes in Cluj - Napoca. SEM-EDAX analyses were carried out using the facilities of the Geological Institute of Romania and METAV in Bucharest. Based upon these data, it is concluded that there is still much work to be done to characterize the diversity of Fluid and Melt Inclusions assemblages trapped in minerals within the geological history of the Romania’s environment.

2. General principles and techniques of the fluid and melt inclusion study.

“From simple optical techniques to the use of particle accelerators, no stone has been left unturned in the search for analytical perfection” stated T.J. Shepherd and A.H. Rankin (1998) to argue the exceptional evolution of fluid and melt inclusion research in the last few decades. This started from the 1970s, when the first Chaixmeca microthermometric stage (Poty et al., 1976) became commercially available, followed by USGS (Were et al., 1979), Linkam (Shepherd, 1981; Esposito et al., 2012), Leitz 1350 (e.g. Tissot and Rodriguez, 1999; Amorim et al., 2012) and the Vernadsky stage (Zappuný et al., 1989). Nowadays, these were completed by HDAC (hydrothermal diamond anvil cell - Basset et al., 1993; Schmidt et al., 1998) or internally heated

pressure vessel for “in situ” observations at high T and P conditions (Gondé et al., 2011). Fluid and melt inclusion petrography and microthermometry are *fundamental* and precede any further investigation or sophisticated analytical technique (Weisbrod, 1979; 1984).

2.1. Fluid and melt inclusion petrography. The general philosophy of the fluid and melt inclusion study is based on the natural entrapment of representative samples from the melt and/or fluid, from which their mineral hosts crystallized or precipitated. After being trapped, it is assumed that they recorded the initial PVTX – time as the unique snapshot of the entrapment conditions. Relative to the entrapment time, there are *primary inclusions*, formed during crystal growth and arranged following internal growing zones or random isolated distribution. The *pseudosecondary inclusions*, trapped during the rehealing of internal microfractures, formed during crystal growth, while the *secondary inclusions*, which decorated the microfissure planes, formed after the crystal growth had ceased. Based upon the nature and number of phases present at room temperature conditions, the fluid and melt inclusion are monophasic (liquid, gas or glass), biphasic (liquid + gas, glass+ vapour), triphasic (liquid + gas + solid; glass + vapour + solid) and multiphase. The first step in this study starts with the optical microscopy, when fluid and melt inclusions are identified, described and classified, according to the “golden rules” stated by Roedder (1984) as follows (Bodnar, 2003a):

1. *The inclusions trapped a single, homogeneous phase;*
2. *The inclusions represent an isochoric (constant volume) system;*
3. *after trapping, nothing has been added to, or removed from, the inclusions.*

Commonly, there is little chance for a fluid or melt inclusion to *follow strictly* these petrographic rules because of many perturbations, which can occur after their sealing. During petrogenesis, several post entrapment processes must be recognized and, amongst them, decrepitation, necking-down and stretching are the most common (Roedder, 1984). Heterogeneous trapping (two or more phases trapped simultaneously in the same cavity) and post-entrapment re-equilibration processes are also recognised frequently (Stern et al., 1995; Audétat and Gunther, 1999; Bodnar, 2003b; Steele-McInnis et al., 2011). In the last few years a plenty of papers deal with the *in* or *out* movement of several chemical compounds from the fluid inclusions, such as H₂O, H₂, Cu, Na (Hall and Stern, 1993; Li et al., 2009). The most important achievement of the petrographic method is the introduction of the concept of fluid and melt inclusion assemblages (**FIAs** - Goldstein and Reynolds, 1994; **MIAs** - Bodnar and Student, 2006) which delineate a homogeneous group of fluid/melt inclusions having almost the same PVTX-t characteristics related to a specific internal feature of the host microtexture such as growth zone or microfissure planes (e.g. Chi et al., 2003). Microtexture internal feature are analysed by the OM/CL and/or SEM/CL techniques which help to elucidate significant relationships between fluid/melt inclusions and their occurrence and distribution in their hosts (e.g., van den Kerkhof and Hein, 2001), although simply optical microscopy is still useful for studying the growing characteristics of these minerals (Pintea, 2010). Size, shape and distribution of fluid inclusions are analysed with various techniques including the spindle stage (Anderson and Bodnar, 1993; Bakker and Diamond, 2006) or 3D imaging by x-ray-fluorescence - micro- tomography (Ménez et al., 2001) and multimodal nonlinear microscopy using coherent anti-Stokes - Raman – scattering (CARS- Burrus et al., 2012). Fluid phase evolution in various fluid system is performed by synthetic fluid/melt

inclusion techniques, for determination of phase equilibria properties, fluid - rock interaction or the physical and chemical data of model fluid systems (e.g. Bodnar and Sterner, 1987; Bodnar, 1989; Simon et al., 2007).

2.2. Analytical techniques. In fluid and melt inclusion analysis two groups of methods are generally used function of complexity of the chemical content and trapping conditions. These are destructive and non-destructive methods which using single or bulk chemical analyses, respectively. Theoretically, the analysis of any given inclusion should be complete (Roedder, 1990): The major solvent H_2O and/or CO_2 , the major solute ions Na, K, Ca, Mg, Cl, SO_4 and HCO_3 , the minor solute ions Al, Fe, B, Ba, Br, Mn, NH_4 , P, F, and Si, metals with high atomic mass such as Au, Ag, U, also pH and Eh, other species of elements with variable valences Fe, Mn, S (SO_4^{2-}), H_2S , HS^- , and C (CO_2 , CH_4 , CO , C_xH_y , H_2CO_3 , HCO_3^-), the organic compound when present (acetate, oxalate, amino acids, etc), others gaseous species (H_2 , He, N_2 , O_2 , Ar), the isotopic ratio of the major elements (H, C, N, O, S and also Sr, Ar, He). It must remind that these components participate in variable mixtures from an inclusion to another function of their origin, but the quantity of material available for chemical analysis is about 10^{-9} to 10^{-13} g in each of them (Shepherd and Rankin, 1998). Therefore, it is not an easy operation to do this in normal chemistry or physical laboratory facilities. For this reason, the majority of preparation techniques and even analytical methodologies were adapted for such low available sample-quantity for analysis.

2.2.1. Non-destructive analyses. The most important analytical tool in this group is represented by microthermometry from the lowest temperature i.e. -190°C to $+700^\circ\text{C}$ for fluid inclusions and up to 1500°C for silicate melt inclusions in several commercially microthermometric stages mentioned above. These elaborated techniques allow us to determine the main PTX data of the fluid/melt phases included. They are completed by micro-spectroscopic methods such as micro-Raman (e.g. Dubessy et al., 1989; Frezzotti et al., 2012), FTIR and UV fluorescence, PIXE (proton induced X-ray emission), PIGE (proton induced gamma ray emission) or more sophisticated synchrotron X-ray fluorescence microanalysis (SXFMA). These methods are capable of analysing the elemental and molecular species, polyatomic gaseous species and polynuclear ones, in solution for single unopened inclusion (Roedder, 1990; Shepherd and Rankin, 1998). Other methods of this category are: Transmission electron microscopy (TEM) used for nanoscale structures and fluid inclusion shape, Confocal Laser Scanning Microscopy and Atomic- Force Microscopy (AFM) which are used for 3D images of fluid inclusion cavities and bubbles (Chi, et al., 2003; Bodnar, 2003a). Estimation of the viscosity and water content of silicate melt using homogenization measurements were delineated by Thomas (1994) in silicate melt inclusions from granites and rhyolites. PVTX evolution of crystalline melt inclusions during heating and cooling were determined by Student and Bodnar (1996), using available phase equilibrium data for the hydrous haplogranite system (albite-ortoclase-quartz-water).

2.2.2. Destructive methods. They were the first techniques used in fluid inclusion study (e.g. Roedder et al., 1963; Petrichenko, 1973) and consist of extract the fluid inclusion content, opening the microcavities during mechanical crushing, or decrepitation by heating in vacuum or even opened in atmospheric conditions in the case of evaporites (halite). There are techniques suitable only for volatile analyses, such as GC (gas-chromatography)-MS (mass spectrometry), Gas Chromatography (GC) or simply gas (G)

- mass (M) - spectrometry (S) especially for high hydrocarbons. Modern “crush-leach” analyses based upon the protocols designed by Roedder et al., (1963), Weisbrod and Poty (1975), Botrell et al., (1988); Banks and Yardley (1992), Halbauer (1997) are used for solute ion analysis in conjunction with atomic absorption spectrometry (AAS), Ion Chromatography (IC), ICP-OES, ICP-MS, selective ionic electrodes (SIE) and capillary electrophoresis (CE). By these combined methodologies, a wide variety of chemical compounds can be analysed, including Na, K, Li, Rb, Ca, Mg, Fe, Mn, Zn, Cu, Pb, (Al), Ba, Sr, Cl, Br, F, B and SO_4^{2-} , and also REE (Shepherd and Rankin, 1998). All the techniques mentioned above are bulk analyses, thus they involve the opening of several hundreds or thousands of inclusions mixed together in the leachate solutions and the results characterizes several generation of fluid inclusions related to different processes. This approximation was avoided by the new generation of high- technology methods based upon laser technique which are able to analyse the content of one single inclusions and the advantage is now described in many papers (e.g. Heinrich et al., 2003; Mason et al., 2008; Pettke et al., 2012). There are three method based on laser ablation technique (Shepherd and Rankin, 1998): laser-ablation-inductively-coupled plasma mass spectrometry (LA-ICP-MS), laser ablation coupled plasma atomic emission spectroscopy (LA-ICP-AES), and laser ablation emission spectroscopy (LA-AES). This are in situ sampling analysis of major, trace and isotopic analyses by opening the cavity with a pulsed laser beam (Heinrich et al., 2003). The methods involving the single fluid or melt inclusions analysis are now calibrated (e.g. Pettke, 2008; Jackson, 2008; Pettke et al., 2012) and used routinely in many fluid inclusion laboratories worldwide. SEM/EDS techniques involving mechanical opening, coating and analysed in high vacuum chambers are used to identify daughter solid mineral in transparent and opaque minerals, as well (Halterbauer, 1983; Nedelcu et al., 2003), the composition of the evaporate mound released by thermic decrepitation (Kontak, 2004) and the crio - technique used mainly for the evaporate minerals (halite) which work in two variants; Crio-SEM/EDS (Ayora and Fontarnau, 1990) and ESEM/EDS (Timofeeff et al., 2000). Electron probe microanalyzer (EPMA) is used routinely to analyse the chemical composition of silicate melt inclusions after these were re-homogenized in the microthermometric stage, in muffle furnace or high pressure vessels. These results are used in petrochemistry and petrologic investigations in all petrogenetic minerals from ultramafites to felsic rocks (e.g. Clocchiatti, 1975; Sobolev, 1996; Danyushevsky et al., 2002; Thomas, 2003; Blundy et al., 2006; Naumov et al., 2013 among others). Quantitative microanalysis of entire silicate and sulphide melt inclusion by excimer Laser-ablation inductively-coupled-plasma-mass spectrometry (LA-ICP-MS) has been applied by Halter et al., 2004 in a suite volcanic rocks and subvolcanic Farallon Negro Volcanic Complex from Argentina. The authors used silicate melt from pyroxene, amphibole, plagioclase and quartz together with sulphide melt trapped in amphibole to evaluate the accuracy of this technique. The quantification of the inclusion composition is performed by using an internal standard which corrects for the crystallization of the host mineral onto the inclusion wall upon cooling and consequently it is not necessary to pre-homogenize the melt inclusions content before analyses (Halter et al., 2005). Secondary ion mass spectrometry (SIMS) is frequently used for isotopic and halogen content of silicate melt inclusions (e.g. Hauri et al., 2002, Thomas, 2003). Petrography and microthermometry of silicate melt inclusions from eruptive, subvolcanic and plutonic rocks were treated on many published articles

and book chapters as following: Sorby, 1858; Clochiatti, 1975, Takenouchi and Imai, 1975; Roedder, 1979; Li, 1994; Lowenstern, 1995; Frezzotti, 2001 Bodnar and Student 2006, and related endogene process such as fluid-melt or melt-melt immiscibility (Roedder, 1992; Frezzotti, 1992; Naumov et al., 1996; Davidson, 2004; Heinrich, 2007; Webster and Mandeville, 2007; Kamenetsky, 2006; Kamenetsky and Kamenetsky, 2010; and many others)

3. Data interpretation and applications.

After a complete chemical analysis, the data are interpreted based upon the evolutionary topology of the model - systems for which a large range of experimental data are known, i.e. H_2O , CO_2 , (Dubessy, 1994; Diamond, 2003ab); H_2O - NaCl (Bodnar et al., 1985; Bodnar and Vityk, 1994; Bodnar, 2003c; Driesner and Heinrich, 2007); H_2O - CO_2 (e.g. Sterner and Bodnar, 1991; Diamond, 1994); H_2O - CO_2 - NaCl (Schmidt and Bodnar, 2000); H_2O - NaCl - KCl (Chou, 1987; Sterner et al., 1988); CO_2 - CH_4 - N_2 (Van den Kerkhof, 1988). The chemical composition of the silicate melt inclusions are projected in the common petrologic diagrams and also using fluid-melt equilibria in specific diagrams of the vapour saturated silicate melt- CO_2 - H_2O or vapour saturated silicate melt- NaCl - KCl - H_2O systems (Student and Bodnar, 1996; Steele - MacInnis et al., 2011). Oil-bearing fluid inclusions in carbonate cement, “Marmarosh diamond” quartz crystals as single inclusions were analysed by microthermometry (e.g. Godstein and Reynolds, 1994; Pinteá, 1995; Jones and Macleod, 2000) to determine the minimum trapping temperature and the gas composition derived by confocal microscopy and P-V-T- simulation. Thermal decrepitations, GC-MS, $\mu\text{FT-IR}$, μRaman spectroscopy were used with microthermometry to calibrate high precision curves from synthetic hydrocarbon inclusions in halogenide and sulphate crystals at low temperatures (Pironon, 1990). Fluid phase evolution at elevated P-T conditions in the water - oil mixtures were used to study the interaction of natural petroleum and hydrothermal fluids in the range of 180 – 500°C and 1-150MPa (e.g. Balitsky et al., 2009). A combination between time-of - flight-mass spectrometry - SIMS and GC-MS analyses were applied on single oil-bearing fluid inclusions from fluorite veins (Siljeström, 2011).

Nowadays, Fluid and Melt inclusions are not simple geothermometers or geobarometers anymore but they became (mainly because of their abundance in the majority of terrestrial and extraterrestrial minerals crystallized from melt and precipitated from solution and also because of the tremendous technical analytical advance *from* (of) the last decades), the most valuable source of information about the initial geochemical media of the rocks and mineral formation. In fact, they are part of the rocks and minerals and must be studied together with their hosts in any magmatic, metamorphic and sedimentary environment. From the beginning (e.g. Sorby, 1858, Zirkel, 1893; Vogelsang, 1869; Deicha, 1955; Bakker, 1999; Zhili et al., 2008) following the evolution in the last 150 years (Touret, 1984), their practical applications could be summarized, for the purpose of the atlas topic, *based upon the main authors and milestone works*, as follows: **magmatic petrology** (i.e. Roedder, 1979; Roedder, 1992; Frezzotti, 1992, 2001; Touret and Frezzotti, 1993; Yang and Bodnar, 1994; Student and Bodnar, 1996; Sobolev, 1996; Naumov et al., 1996, 2013; Larocque et al., 2000; Kamenetsky et al., 2002; Danyushevsky et al., 2002; Thomas, 2003; Bodnar, Student,

2006; Kamenetsky, 2006; Mason et al., 2008; Hansteen and Klügel, 2008; Kamenetsky and Kamenetsky, 2010; Steele-Maccinnis et al., 2011); **volcanism** (e.g. Clocchiatti, 1975, Takenouchi and Imai, 1975; Lowenstern, 1995; 2003; Webster and Mandenville, 2007; Anderson, 1991; Pintea, 2013; Blundy et al., 2006); **porphyry-copper types and pegmatites** (e.g. Roedder, 1971; Nash, 1976; Bodnar, 1995; Thomas et al., 2000; Campos et al., 2002; Student and Bodnar, 2004; Williams-Jones and Heinrich, 2005; Heinrich et al., 2005; Heinrich, 2005, 2006, 2007; Halter et al., 2005; Bodnar, 2010; Audetat and Simon, 2012; Pintea, 2014a); **hydrothermal ore deposits** (e.g. Bodnar et al., 1985a; Roedder and Bodnar, 1997; Bailly et al., 1998; Brown, 1998; Wilkinson, 2001; Kesler, 2005; Heinrich, 2005; Kouzmanov et al., 2010; Kouzmanov and Pokrovski, 2012; Bodnar et al., 2014); **fluid and multiphase solid inclusions in metamorphic rocks** (e.g. Touret, 1977, 2001; Frezzotti and Ferrando, 2007; Cesare et al., 2009; Van den Kerkhof et al., 2014); **sedimentary and oil-bearing fluids** (e.g. Petrichenko, 1973; Roedder, 1984a; Shepherd et al., 1985; Robert and Spencer, 1995; Lowenstein et al., 1998; Pironon, 1990; Jones and Macleod, 2000; Dubessy, 2004; Balitsky et al., 2009; Kovalevich, Vovnyuk, 2010); **upper mantle and subduction zone fluids** (e.g. Roedder, 1965; Pintea and Mârza, 1989; Varela, 1997; Chalot-Prat and Arnold, 1999; Scambeluri and Philippot, 2001; Harlov, 2014); **fluids in planetary systems** (Bodnar, 2005; Madden, 2005); **fluid and melt inclusions books, short courses, computer programs and workshop proceedings** (e.g. Pomârleanu, 1971, 1975, 2007; Pomârleanu and Neagu, 2003; Ermakov and Dolgov, 1979; Hollister and Crawford, 1981; Roedder, 1972; 1984; Shepherd et al., 1985; De Vivo and Frezzotti, 1994; Bakker, 1999; Samson et al., 2003; Bakker, 2003; Bakker and Brown, 2003; Webster, 2006; Driesner and Heinrich, 2007; Van den Kerkhof and Sosa, 2012; Bodnar et al., 2013; Yardley and Bodnar, 2014; Hurai et al., 2015).

Important web links: The “world of fluid inclusions” at [www.geology.wisc.edu; Bodnar's Fluid's Research Lab Web Site-](http://www.geology.wisc.edu/Bodnar's%20Fluid's%20Research%20Lab%20Web%20Site-); [Ron Bakker's Home Page - University of Leoben](http://www.leoben.ac.at/~ronbakker/); [Linkam Scientific Web; Site IMA Home Page](http://www.sciencelinks.org/LinkamScientificWeb/Site/IMAHomePage) and link to [Working Group on Inclusions in Minerals](http://www.geopetro.ethz.ch/); Geo-Petro-ETH Zurich- http://www.geopetro.ethz.ch; Fluid Inclusion Technologies, Inc-<http://fittulsa.com>; <http://rruff.geo.arizona.edu>.

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Figures

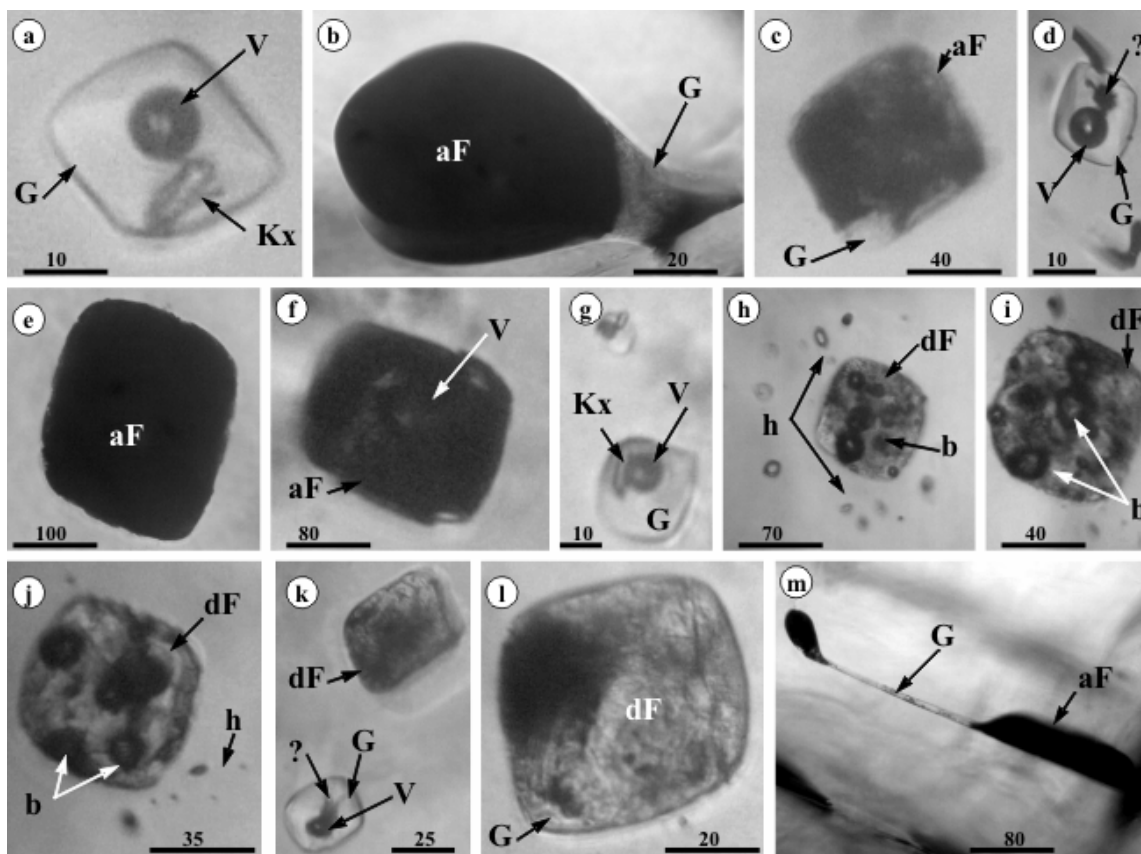


Fig. 1. Silicate melt inclusions types in bipyramidal quartz phenocrysts extracted from the bentonites from Valea Chioarului (Maramureş County). **a, d, g, k**, - three-phase inclusions with glass (G) + vapor (V) + solids (Kx- transparent quartz or feldspar microcrystal, ?-unidentified); **b**- altered “foam-like” hourglass inclusion (aF), G-glass; **c, e, f, m** - altered glass “foam - like” inclusions; **h, i, j, k, l** - decrepitated “foam-like” glass inclusions (dF). Total homogenization temperature recorded in six silicate glass inclusions ranged between 845°-1045°C, and the solid microcrystals melted between 550°-990°C (Pintea, unpubl. data). Scale bar in μm .

Fig. 2. Overgrowth zonation in plagioclase from Bătarci hyalodacite (e.g. Jude, 1977) decorated with silicate melt inclusions, F-feldspar, gz- oscillatory growth zones, SM- silicate melt inclusions (Bătarci Valley, Oaş Mountains).

Fig. 3. Internal sieve microtexture (ST) containing multiple silicate melt inclusions (SM) formed in a dissolved feldspar microcrystal during a subsequent magmatic melt influx, overgrowth with new feldspar (F) zone equilibrated with the Bătarci hyalodacite groundmass(Bătarci Valley, Oaş Mountains). Crystal host interference imaging, electron microprobe analysis, petrography and microthermometry of the silicate melt inclusions are the favorites in study of sieve-texture significance in magmatic-volcanic processes (e.g. Stewart and Pearce, 2004; Pintea et al., 2003; Blundy et al., 2006).

Fig. 4. Trellis type ilmenite lamellae exsolution microtexture features in the Bătarci hyalodacite containing silicate melt inclusions. ilm-ilmenite, sm- silicate melt, s- sulfide. (Bătarci Valley, Oaş Mountains) (e.g. sphenitization described by Udubaşa, 1984).

Fig. 5. Immiscible Fe-S-O melt assemblage trapped in plagioclase phenocrysts from Batarci hyalodacite. IFM- immiscible opaque globules, F- plagioclase, HD- hyalodacite (Larocque et al., 2000; Pintea, 2002).

Fig. 6. Silicate melt and solid microinclusions in the Batarci hyalodacite. **a, c, d, e, g** - silicate melt inclusions; **b**- silicate glass inclusion; **e, h, i, j, k**- solid microinclusion, probably several generation of restitic apatite microcrystal sometimes with early silicate melt inclusion pictured in **k**; **K**- apatite, zircon or plagioclase solid microcrystal (undefined), **R**- restitic microcrystal or simply glass inclusions (**e, g, j**); **O**- opaque (Fe-S-O immiscible melt); **G**-glass, **V**-vapor, **SG**- silicate glass inclusion. (Bătarci Valley, Oaş Mountains). Scale bar in μm .

Fig. 7. Fluid and melt inclusions in quartz xenoliths, phenocrysts and fragments from Săpânța caldera (Pintea, 2014b). **a, b, c, d, e, f, g, n, t**- silicate melt inclusions; **d, g, h, i, j, k, m, o, p, q, r, s, u, v, w** – vapor rich inclusions, **l**- quenched from 1000°C in the high temperature microthermometric stage, three grain sublimated from the vapor-rich phase; **G**-glass, **Gm**- mafic silicate glass, **Ks**- silicate solid phase, **Kx**- salt mineral phase (halite, and others), **V**-vapor, **H**-halite, **O**-opaque, **f**- fissure, **Kxy**-undetermined, **Q**-presumably β -quartz. Scale bar in μm .



Fig. 8. Silicate melts inclusions in quartz and feldspar phenoclasts from “Laleaua Alba” dacite quarry from Baia Mare region. Macroporphyrlic dacite nucleus with quartz, biotite, amphiboles and pyroxene surrounded by quartz andesite with pyroxene, amphibole and biotite; gabbros xenoliths are quite frequent too (Kovacs, 2002). The majority of primary melt inclusions were thermally decrepitated and late-hydrothermally altered by the volatile rich phases associated with the mafic magma pulse and magma mixing processes. Decrepitated and remelting features show characteristic halos around primary melt inclusions and melted and deformed edges in a plastic state during the reheating processes (Pintea, 1986). Generally, they cannot be homogenized in the heating stage at 1 bar pressure only up to 950°C - 1100°C (e.g. 986°C, $n = 3$; biphasic silicate melt inclusions in zircon embedded in plagioclase homogenized at 923°C - Pintea, 2006). The primary silicate melt changed the initial vapor/melt ratio and so the homogenization values are characteristic for the re-equilibration conditions. SG- silicate glass, MK- microcrystal, V-vapor, SGG- secondary silicate glass globule, mf- microfissures; ASG- altered glass inclusion, IFM- (Fe-S-O) melt, k – the dashed arrow indicates the separation of new silicate glass inclusions from the principal inclusions during the natural reheating process; Comprehensive geochemistry and geothermometry of the silicate melt inclusions from the Laleaua Alba dacite was recently published by Naumov et al., 2014. Scale bar in μm .

Fig. 9. Silicate glass inclusions in quartz and feldspar phenoclasts from Dănești-Piatra Roșie dacite. Dacite lava dome produced by mingling/mixing between mafic /ultramafic melt and rhyolitic magma matrix located near Baia Sprie and Cavnic areas (Kovacs, 2002). They also contain ultrabasic xenoliths with Mg-hastingsite amphibole, probably the primary metallic source of the epithermal ore deposit in the region as globular sulfide/oxide as immiscible melt of (Fe-S-O) type. **a** - Quartz phenoclast(QP) containing silicate glass inclusions (SGI), **c**- silicate melt inclusions (SMI) in plagioclase, SG- silicate glass; **b, d, e, f, g, h, i, j, k, l, m, n, o**- silicate glass inclusions (SG) containing glass (G), vapor (V), Kx- undetermined solid phase, RF- natural remelting feature; Silicate melt inclusions(G +V ± solid) homogenized between 700-1000°C (n= 172) in quartz (e.g. one reliability test for one inclusion ranged between 730-780°C, n= 15) and from 800-1060°C (n= 22), in plagioclase; n - number of measurements (Pintea, 2006). Geochemistry and petrologic significances of the silicate melt inclusions from Dănești dacite were published by Grancea et al., 2003. Scale bar in μm

Fig. 10. Thinly white silicate glass globules (WSG) in reddish colored silicate glass matrix (RSG) in the dacite groundmass from Piatra Roșie-Dănești dacitic extrusive rocks. (Pintea, 2010). Scale bar in μm .

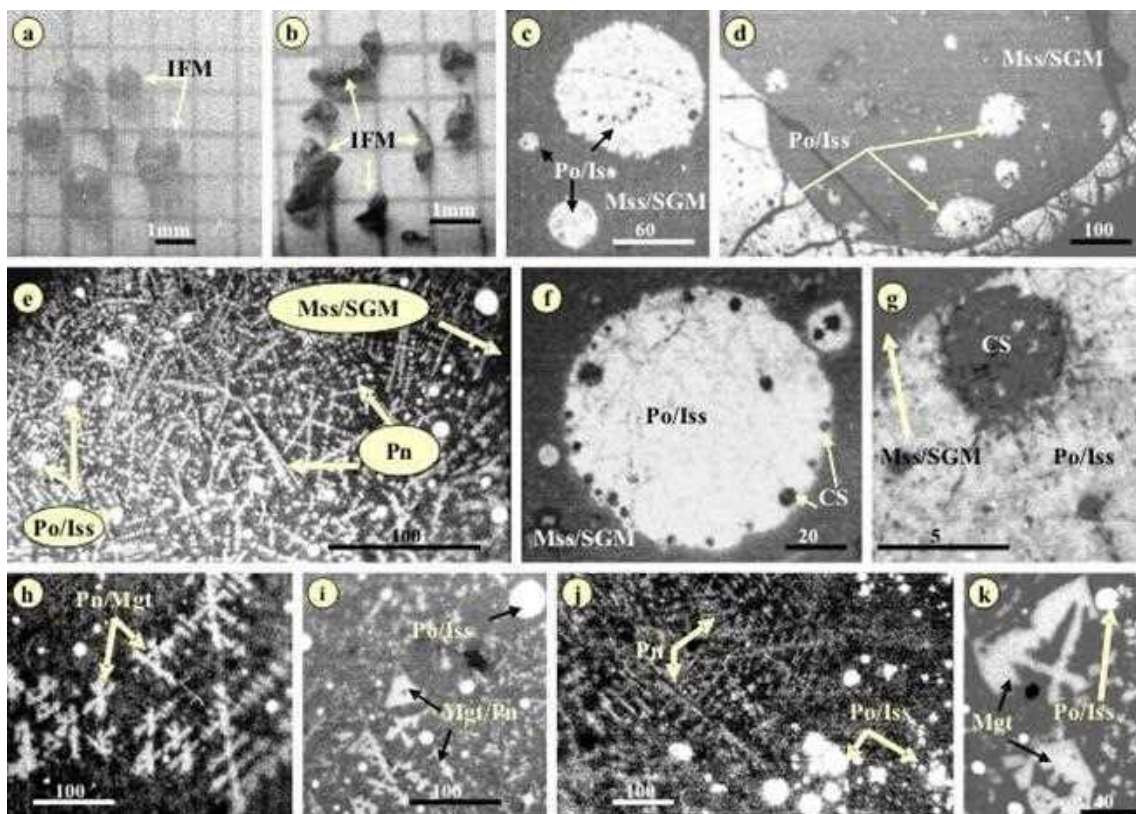


Fig. 11. Globular sulfide melt from Dănești - Piatra Roșie dacite (Maramureș county). **a**-perfect spherical globules collected from a dry outcrop of the dacitic lava dome near Dănești village; **b**- elongate shaped (Pelee's tears-like); **e, h, i, j, k**- microphotographs in reflected light suggesting the presence of monosulfide solid solution (Mss) an/or intermediate solid solution (Iss), pyrrhotite (po) magnetite (mgt) and pentlandite-like dendrites (pn), and another immiscible compound as black globules (CS) inside the Mss or Iss, all embedded probably in mafic glass matrix (SGM); their identification is based upon textural features in reflected light microscopy and comparative literature data (e.g. Desborough et al., 1968; Kelly and Vaughan, 1983; Stone and Fleet, 1991; Guo et al., 1999; Craig, 2001; Török et al., 2003; Etschmann et al., 2004); **c, d, f, g**- under high magnification in reflected light the globular phases embedded in presumable pyrrhotite, Mss or Iss, a second immiscible Cu-Fe sulfide phase formed mainly at the border of the host globules, based upon optical reflectivity and comparative references data (e.g. Ranjarni and Naldrett, 1978; Ballhaus et al., 2001, Baker et al., 2001). This interpretation is only qualitative there are no analytical data yet, but the trace distribution of Sc, Ni, Co (which presumably are relate the immiscible silicate melt) was used to separate the subvolcanic bodies in the region, as suggested many years ago by Rădulescu and Dimitrescu(1982). Scale bar in μm .

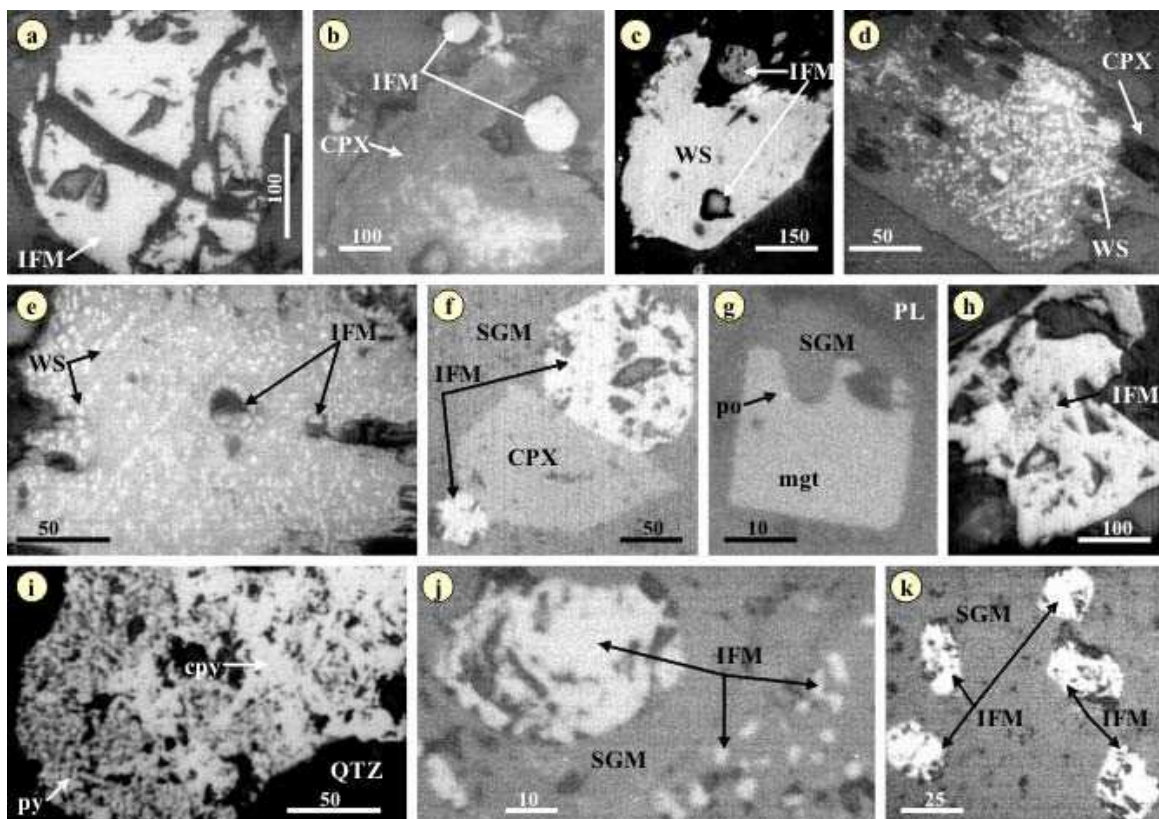


Fig. 12. Globular sulfide (IFM) from Dănești - Piatra Roșie dacite trapped in pyroxene (CPX) and glass matrix pictured in **a, b, f, g, h, j, k**; **c, d, e** - microphotographs showing a sulfide film (decrepitated mound-WS) wetting the host mineral surface after experimentally heating around 1000°C; **i**- chalcopyrite (cpy) exsolution from pyrite (py) during the autometasomatism in quartz grain from Valea Morii porphyry copper deposit (Apuseni Mountain, Romania). Scale bar in μm.

Fig. 13. “Foam-like” glass inclusions types in quartz phenocrysts from “Dej Tuff” formation, Transylvania basin, Romania. Quartz phenocrysts (QP) containing glass foam inclusions (SGF) partially decrepitated in **a.** and **b.**, **c.** - clear “bubble-free” glass inclusions; **d.**, **e.**, **i.**, **k.**- natural reheated glass foam inclusions revealing silicate foam microtexture; **g.**- biphasic glass inclusions (SGI) with glass+ contraction bubble; **f.** cluster of primary glass foam inclusions in sanidine, some of them contain contraction bubble ; **l.**, **m.**, **n.**,- silicate glass inclusions bubble-free which shown obviously homogeneous foam microtexture above 500°C, and they homogenized on further heating in the stage (minimum trapping temperature). It should be noticed that during repeated microthermometric cycles some of them lost all bubbles and become “real” “bubble-free” silicate glass inclusions. (Pintea 2005a; 2006; Pintea, 2013); Scale bar: a, b, c- 250 µm; d, e, f, g, h, i, j, k, l, m, n – in µm.

Fig. 14. More microtexture features of the glass foam inclusions from Dej tuff trapped in quartz phenoclasts. **a.** Foam glass inclusion(F) surrounded by decrepitation halo(?), developed in the stage during heating, cannot be homogenized; **b.** Glass + contraction bubble (+ CO₂-?) and microlites (m); **c.** Partly devitrified foam glass inclusion (F); **d.** Multiphase glass inclusion containing glass (G), opaque globule (O) and probably another droplet of immiscible silicate melt (mafic-g); **e.** Foam glass inclusion with one contraction bubble and an attached solid phase (cb+s) surrounded by an unknown ellipsoidal halo (reequilibration- ?); **f.** Elongated secondary glass foam inclusion (F), partially decrepitated showing several ripened-? bubbles(b); **g.** Empty void(dv) left behind after complete decrepitation of a glass foam inclusion; **h.** Glass foam inclusion partially decrepitated containing glass(G), fissure (f) and bubbles (b); **i., j.** Typical partially decrepitated glass foam inclusion which never homogenized during the heating procedure in the stage. (Pintea, 2013). Scale bar in μm .

Fig. 15. Glass foam inclusions in quartz from ignimbrites (Măgura Ciceului) with various natural reheated microtextures. **a.** Silicate glass (G) and microlites (m); **b, c, f, g-** contracted (? - menisci) clear silicate glass bubble-free at room temperature (the same type as in Fig 4); **c-** Voids (dv) formed after decrepitation of two glass foam inclusions, f- microcracks; **d.** Silicate glass with contraction rim (?) contain contraction bubble(cb) and a solid grain (s); **h.-** Slightly decrepitated glass foam inclusions with contraction bubble(cb) and another small bubble(b); **i.** Decrepitated glass foam inclusion with a silicate glass (G) surrounding concentrically bubbles (b); **j.** Partially decrepitated glass foam inclusion contain contracted (?) silicate glass, disrupted foam (dF), f- microfissure; **k.** Elongated glass foam inclusions with contracted bubble containing a solid grain(s) in contracted silicate glass (G), b- bubbles. (Pintea, 2013). Scale bar: μm (a, d, e, f, g = 40 μm).

Fig. 16. Microthermometric cycle in silicate foam-like inclusions from quartz phenoclast from the Dej tuff collected at Măgura Ciceului ignimbrite outcrop. During heating it seems that two silicate phases were separated formed by a rim of silicate melt (m_1) around the silicate foam (F). **a.** 25°C, **b.** 332°C, **c.** 616°C, **d.** 814°C, **Th=831°C**, **e.** 834°C. The first observable change in silicate glass inclusion was mentioned around 300°C by Clocchiatti, 1975, when ephemeral cracks were formed or the glass seem to be separated from the cavity wall in the still solid state. Our observation suggests that the separation menisci are still there around the homogenization temperature (see Fig. 17). Scale bar in μm .

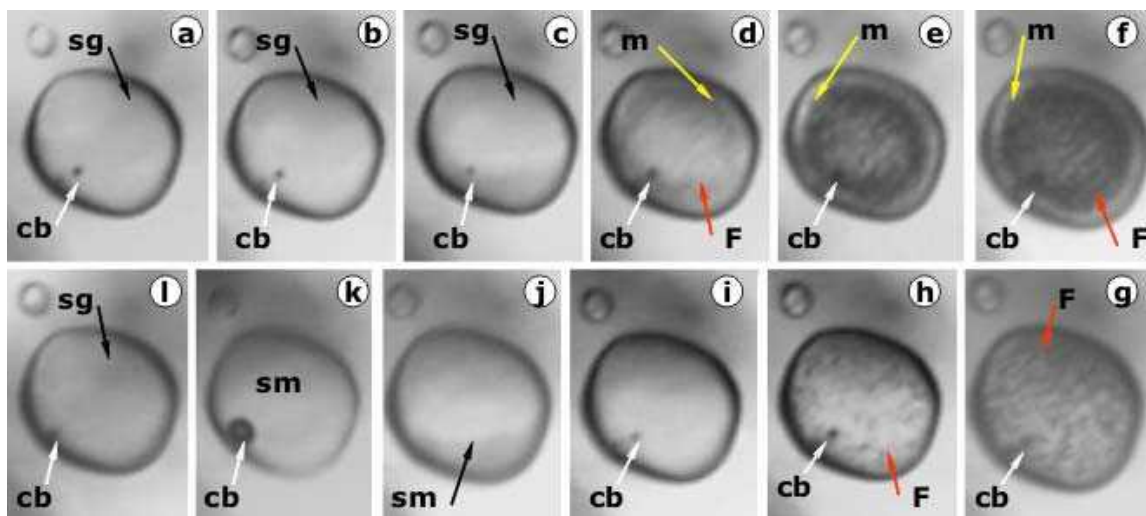


Fig. 17. Complete microthermometric cycle of silicate foam-like inclusion in quartz phenoclasts from Jichisul de Sus. A second silicate phase was developed during heating as an immiscible rim around the silicate foam (**d, e, f**) which disappeared on further heating before final bubble homogenization (**j**). Such kind of immiscibility between two silicate melt phases was envisaged by Rădulescu (1979) as a possible process for ignimbrite genesis **a.** 25°C, **b.** 390°C, **c.** 477°C, **d.** 550°C, **e.** 570°C, **f.** 578°C, **g.** 580°C, **h.** 710°C, **i.** 721°C, **Th=818°C**, **j.** 823°C, **k.** 581°C, **l.** 25°C. Scale bar in μm .

Fig. 18. Replicated microthermometric cycle in the silicate foam-like inclusion (homogeneous foam) from Jichisul-de Sus in quartz phenoclasts showing a large contraction bubble at starting temperature in **a.** and homogenized first at **Th= 882°C**. In the second cycle this homogenized at **Th=848°C**. This seem to be a common feature of the silicate foam-like inclusion, as it was documented by Pintea (2013) in a lot of microthermometric cycles from inclusions trapped in phenoclasts from the Dej tuff. **a.**25°C, **b.**219°C, **c.**396°C, **d.**546°C, **e.**569°C, **f.**601°C, **g.**744°C, **h.**784°C, **i.**859°C, **j.**879°C, **k.**881°C, **l.**639°C, **m.**585°C, **n.**517°C, **o.**471°C, **p.**662°C, **g.**720°C, **r.**761°C, **s.**853°C, **t.**713°C. Scale bar in μm .

Fig. 19. Microthermometric cycle in a partial decrepitated silicate foam-like inclusion (heterogeneous foam) in quartz phenoclast from Jichişul de Sus. **A.** Starting at 25°C with a silicate glass (sg) + bubbles (bb) mixture it homogenized completely at 913.5°C, but still showing meniscus (m) suggesting silicate melt immiscibility. In the replicated cycle the final homogenization increased at 919.5°C because of the initial decrepitated state. **A.**25°C, **B.**914°C, **Th=913.5°C**, **C.**582°C, **D.**619°C, **E.**928°C, **Th=919.5°C**, **F.**547°C. Scale bar in μm

Fig. 20. Silicate melts inclusions in fluorapatite from Tibles massif. Fluorapatite euhedral phenocrysts are associated with phlogopite, rutile, quartz and metallic minerals (Kovacs et al., 1982), formed by reaction between the monzogranodiorite host magma and embedded Paleogene sedimentary material (Edelstein et al., 1981- Geological Map of the Tibles Mountains- unpubl. report). The silicate melt inclusions contain several solid transparent phases (Kxyz-undetermined), probably silicate, carbonates and chlorides etc, in a glassy matrix (G). Opaque O, are also present. Homogenization tentative failed around 850°C, because thermic decrepitation (Pintea, 1998, unpubl.). Calculated formulae based upon chemical composition of Tibles fluorapatite is $\text{Ca}_5(\text{PO}_4)_3[\text{F}_{0.73}\text{Cl}_{0.25}(\text{OH})_{0.02}]$ (Kovacs et al., 1995). The sample described occurred in the N-E part of Tibles Massif on the Izvorul Mesteacănului Valley. Scale bar in μm .

Fig. 21. Brine and vapor rich inclusions in fluorapatite phenocrysts from Tibles massif. Primary isolated or random distributed and pseudosecondary and secondary fluid inclusions parallel to the cleavage planes and microfissures are representative for high salinity high temperature saline fluids. They are fluid separated during magma crystallization and fluid-rock high-Mg metasomatic processes. L-liquid, V-vapor, H-halite, Sc- carbonate, O- opaque, kx- transparent solid phase. Halite melting temperature shown 30- 40 wt% NaCl eq and Th > 400-600°C, indicating fluid phase immiscibility at high temperatures (Pintea, 1998; Kovacs et al., 1995). Scale bar in μm .

Fig. 22. Plan deformation features in quartz from Măgura-Neagră - Suplai porphyry - type ore deposit suggesting post “shock” events related to variable UHPT conditions supported probably during exhumation processes (argued by thermochronology, fission track” and (U-Th)/(He). Similar features are characteristic also in the Miocene porphyry copper deposits from Apuseni Mountains (e.g. Deva, Valea Morii, Talagiu etc) and were also described by CL at Butte porphyry system (Rusk et al., 2005, their Fig.2G). e.g. others similar features between Țibles porphyry copper system with Butte were mentioned by Udubașa et al., 1984. **a, b, c, d, e, f, g, h, i, j, k, m, n, o** – planar elements (cracks) probably structural controlled in quartz similar to the shocked quartz frequently described in the high pressure environment (e.g. Langenhorst, 2002; Trepmann and Spray, 2006). Solid microinclusions in quartz, probably titanite in **l** and zircon in **p**.

Fig. 23. Silicate – brine assemblages in the Măgura-Neagră–Suplai mining district (Țibles massif). Kxyz-undetermined solid transparent microminerals, undifferentiated vapor and opaque solid phases, together trapped in sm-silicate melt (now glass-G). Associate aqueous fluid inclusions, vapor rich (k) and/or brine (l) seem to be contemporaneous at high temperatures. Homogenization temperature exceeded frequently 1000°C, the silicate melted around 600-900°C, and salt mineral melted around 500°C (Pintea, 1998; Pintea et al., 1999).

Fig. 24. Silicate-brine inclusion assemblages in quartz from Măgura-Neagră-Suplai mining district (Țibles massif). Frequently the brine inclusions are liquid-free at room temperature suggesting the existence of salt melt at trapping conditions. Kxyz- salty and silicate daughter minerals undifferentiated, but obviously halite is the dominant transparent solid. Vapor (V) and opaque (O) were separated after trapping inside the microcavities. G-glass. Variable homogenization temperature between 1000-550°C, salinity between 60 - 80 wt % NaCl eq. suggesting single fluid phase separation by decompression in a magmatic - to - hydrothermal transition (Pintea, 1998; Pintea et al., 1999a); Scale bar 10 μ m.

Fig. 25. Brine and vapor-rich inclusions in quartz from Măgura-Neagră-Suplai mining district from Țibles massif. Complex salt daughter minerals including halite (H), sylvite sometimes anhydrite (Cs) are noted as Kx, Kxyz ; Sc- presumably carbonate rich salt; O- opaque, L-liquid, vapor (V), O- opaque frequently undifferentiated at room temperature (V+O). Intermediate to low temperature homogenization by vapor bubble disappearance between 400 – 600°C, or by halite homogenization at low than 450°C showing variable salinity between 30 and 70 wt% NaCl eq. More data in tables 1 an 2 (Pintea et al., 1999a). Scale bar in μm .

Fig. 26. Complex silicate melts plus brine inclusions in pargasite from the high temperature magnezian skarn from Țibles massif. More than 40 minerals were described for the first time in relation with the wide temperature processes from the contact between quartz monzodiorite and Oligocene sedimentary rocks mainly described in the Saci transversal (Udubaşa et al., 1981). V-vapor, Kd- silicate mineral, Ks- saline daughter phase, G-glass, ?-unknown, O-opaque. Microthermometric experiments (Pintea, 1998 and unpubl.) indicated very high final homogenization temperatures ($\geq 960^{\circ}\text{C}$) in good accord with experimental published data for pargasite formation in the presence of diopside, forsterite, spinel, nepheline, anorthite and silicate melt between $995\text{-}1103^{\circ}\text{C}$ and 1.2-8 kbars (e.g. Holloway, 1973). Scale bar in μm .

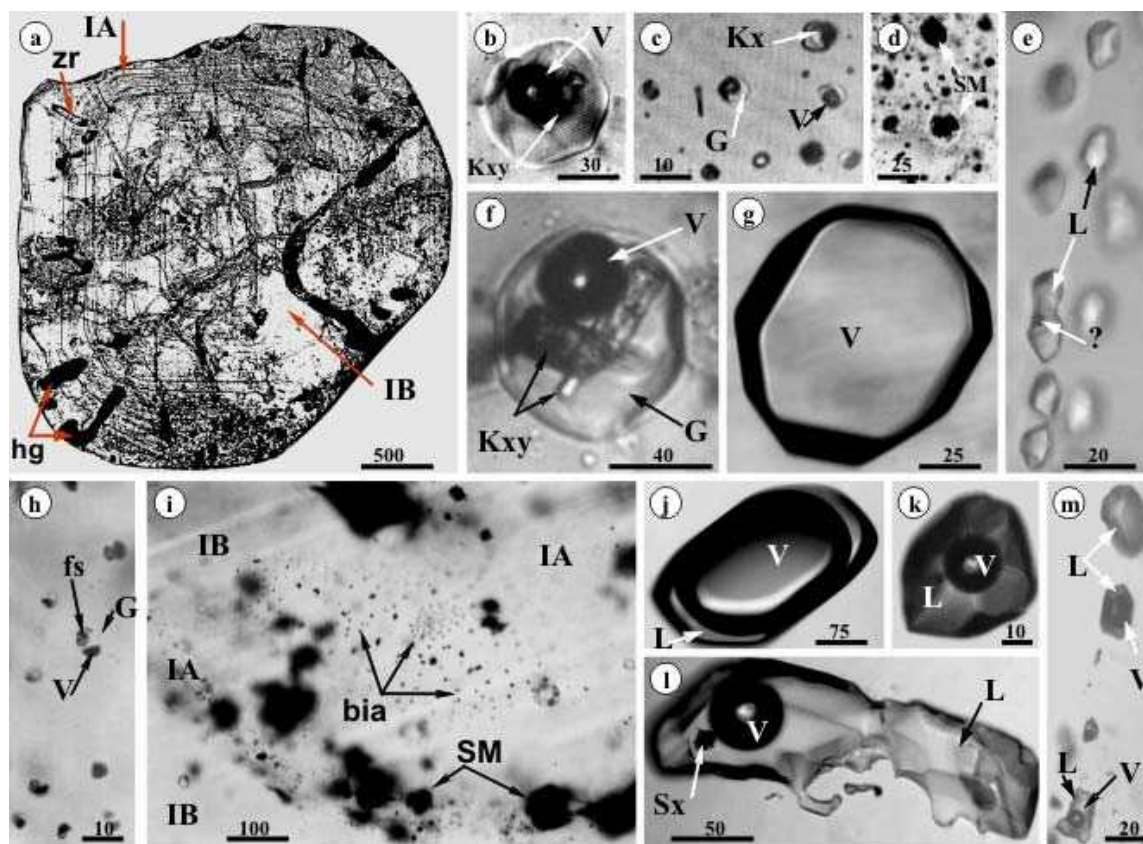


Fig. 27. Silicate melt and fluid inclusions in quartz phenocrysts from Roșia Montană. **a.**-Transversal double polished thin section on typical β -quartz crystal from Roșia Montană dacite showing oscillatory zoned feature of a thin resorption layer- IA and a wide growing zone- IB. Specifically they contain various silicate melt-, fluid inclusions and sometimes embedded solid inclusions as zircon-zr, and hourglass inclusions - hg; **b.** and **f.**- Silicate melt inclusions containing glass (G), vapor (V) and daughter solid phases (Kxy); **d.**- Completely altered silicate melt inclusions with characteristic decrepitation halos formed by secondary fluid inclusions; **e.**- Monophasic liquid (L) rich inclusion +/- vapor (V) in epithermal quartz; **g.** Vapor (V) rich inclusion looking empty at room temperature conditions, but during microthermometry a special kind of phase transition were recorded (see Fig. 116). **h.** - Brine (fs) trapped in silicate glass inclusions (G-glass, V-vapor); **i.** - Brine inclusions assemblage (bia) formed "in situ" in a large zone (IB) of β -quartz from decrepitated silicate melt inclusions (SM) in a subsequent decompression stage; **j.** **k.**- Biphasic vapor – rich and liquid – rich inclusions in epithermal quartz phenocrysts (L-liquid, V-vapor); **l.**- Three phase fluid inclusion in epithermal quartz trapped frequently a liquid (L), vapor (V) and accidentally a solid grain phase of carbonate, silicate or sulfate, but never a real daughter saline (halite) mineral; **m.**- Biphasic fluid inclusions with variable phase ratios between vapor (V) and liquid (phase) in a secondary trail in magmatic quartz formed "in situ" around decrepitated silicate melt inclusions (Pintea, 1999; Pintea, Iatan, 2013). Scale bar in μm .

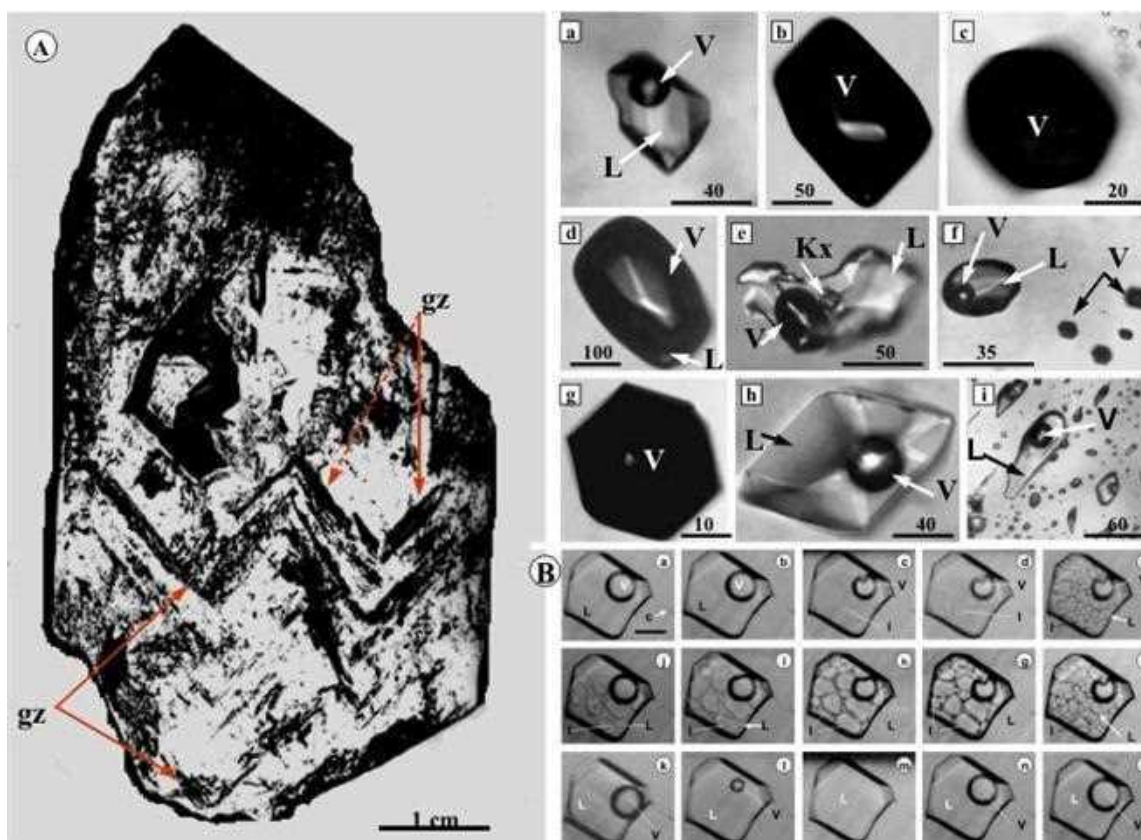


Fig. 28. Typical aqueous fluids trapped in epithermal quartz from Roșia Montană. **A.** Double terminated prismatic quartz crystal with parallel double zonation (gz). **a, h.-** Primary biphasic fluid inclusion with vapor (V) and liquid (L); **b, c, d, g.-** Isolated vapor-rich inclusions containing a vapor phase (V) and a film of liquid (L); Presumably boiling event recorded by pairs of aqueous- rich (L+V) and vapor- rich (V), trapped in a restricted zone; **j.-** Pseudosecondary biphasic (L+V) assemblage in epithermal quartz. **B.** Sequences shown the complete microthermometric cycle, typical for aqueous-rich inclusions in the epithermal quartz from Roșia Montană, first recorded with an original microthermometric stage, working between -196 to +750°C (Pintea et al., 1992). **a. and o.** +25°C, **d.** - 40°C (Tf), **e.** -20.8°C (Te), **k.** -0.2°C (Tmi), **m.** +221.5°C (Th), salinity = 0.35 wt% NaCl eq. **b. c. f. g. h. i. j. l. n.** intermediate temperatures; the fine capillary (*c* in **a.**) had no visible influence on microthermometry; Notations: L- liquid, I-ice, V- vapor; Scale bar = 20μm.

Fig. 29. Roşia Montană melts and fluid inclusion feature in β - quartz phenocrysts. **A, B, C, D-** multiphase glass inclusion formed by heterogeneous trapping or in situ fractionation after thermic decrepitation (e.g. **B** from Pintea and Iatan, 2013); M_1+M_2 reproducible homogenization temperature around 1050°C was determined by microthermometry (Pintea, 2003). **E.-** Recrystallized melt inclusions along a resorption layer. **a, b, c, d, e** - Duplicated low-T microthermometry in low density vapor- rich inclusion trapped in hydrothermal quartz from Roşia Montană. **a.** +25°C (L-liquid rim, V- vapor phase), **b.** to -196°C (S-sublimated gas phase, I-ice), **c.** +25°C (Liquid + Vapor), **d.** -196.7°C (ice + sublimated grains), **e.** + 25°C. In this fluid inclusion, and similar ones the liquid phase have a salinity of 0.71 wt % NaCl eq, and homogenized between 362 -373.8°C for n= 10 determinations. (Pintea, 1999). Review on melt inclusion study from Roşia Montană magmatic quartz phenocrysts were published by Naumov et al., 2013. Scale bar in μm .

Fig. 30. Multiple growth zones (gz) in quartz coarse grain in veinlets from Deva porphyry copper deposit (A, B, C, D- level -450, Pinte 1996, 2014a) Generally, they are decorated by silicate (SM), hydrous saline melt inclusions (B) and vapor rich inclusions (V). More than 20 growth zones could be counted for small quartz veinlets of max 10 mm wide and zonation could be the result of the retreating downward crystallization, mafic influx, autometamorphism, dissolution or diffusion. Complex imaging methodology by using SEM-CL technique was applied to decipher episodes in porphyry copper genesis based upon zonation and trace element distribution (e.g. Penniston-Dorland, 2001; Landtwing et al., 2005; Rusk et al., 2004). Microtextural feature on quartz zonation from Deva porphyry copper also in Ivășcanu et al., 2003. Scale bar: 100μm.

Fig. 31. Immiscible silicate melt (G) and hydrous salt melt (Fs) trapped together (**a, b, d, e, f, g, h**) and/or coeval inclusions (**c, i, k, l**) decorating quartz growth zones in quartz from Deva porphyry copper deposit. These are common feature of immiscibility when two fluid/melt phases were trapped in various proportion in the host mineral (Roedder, 1992), documented also by large P-T range, e.g. $\geq 900^{\circ}\text{C}$ and 0.3 to 12.8 kbars (Pintea, 1996b; 2014a). Scale bar: 10 μm .

Fig. 32. Compositional variation at room temperature between silicate melt (now glass) and the hydrous saline melt in individual complex inclusions trapped in quartz from Deva porphyry copper deposit. **a, b, c, e, h, i, j, l, m, n, o**- hydrous salt melt; **d, f, k**, - complex silicate melt (now glass) inclusions and hydrous salt melt. G-glass, V-vapor, O-opaque, Kxyz- solid phase association, Fs-hydrous salt melt. Scale bar: 10µm.

Fig. 33. Individual hydrous salt melt inclusions without liquid phase at room temperature condition formed in quartz as primary, pseudosecondary or secondary inclusions in quartz grain from veinlets from Deva porphyry Cu-Mo (Au) ore deposit. **a, b, c, d, e, f, g, h, i, k, l, m, o, q, r, t, w, x, y**, - hydrous saline melt inclusions; **n, p, s, u, v**- vapor rich inclusions; kxyz- multiple solid daughter mineral association. Amongst them halite, anhydrite, sylvite, complex K, Fe, Mg, Ca – chlorides and K-feldspar were positively identified by microthermometry and SEM/EDS (Pintea, 1996b; 2014a). Complete microthermometry was firstly documented up to 1500°C (Pintea, 1993ac, 1996ab, 1997, 1998-unpubl., 2001ab, 2014a), showing multiple immiscibility between silicate-sulfide-salt-sulfate liquid phases and vapor. Scale bar: 10µm (n to y).



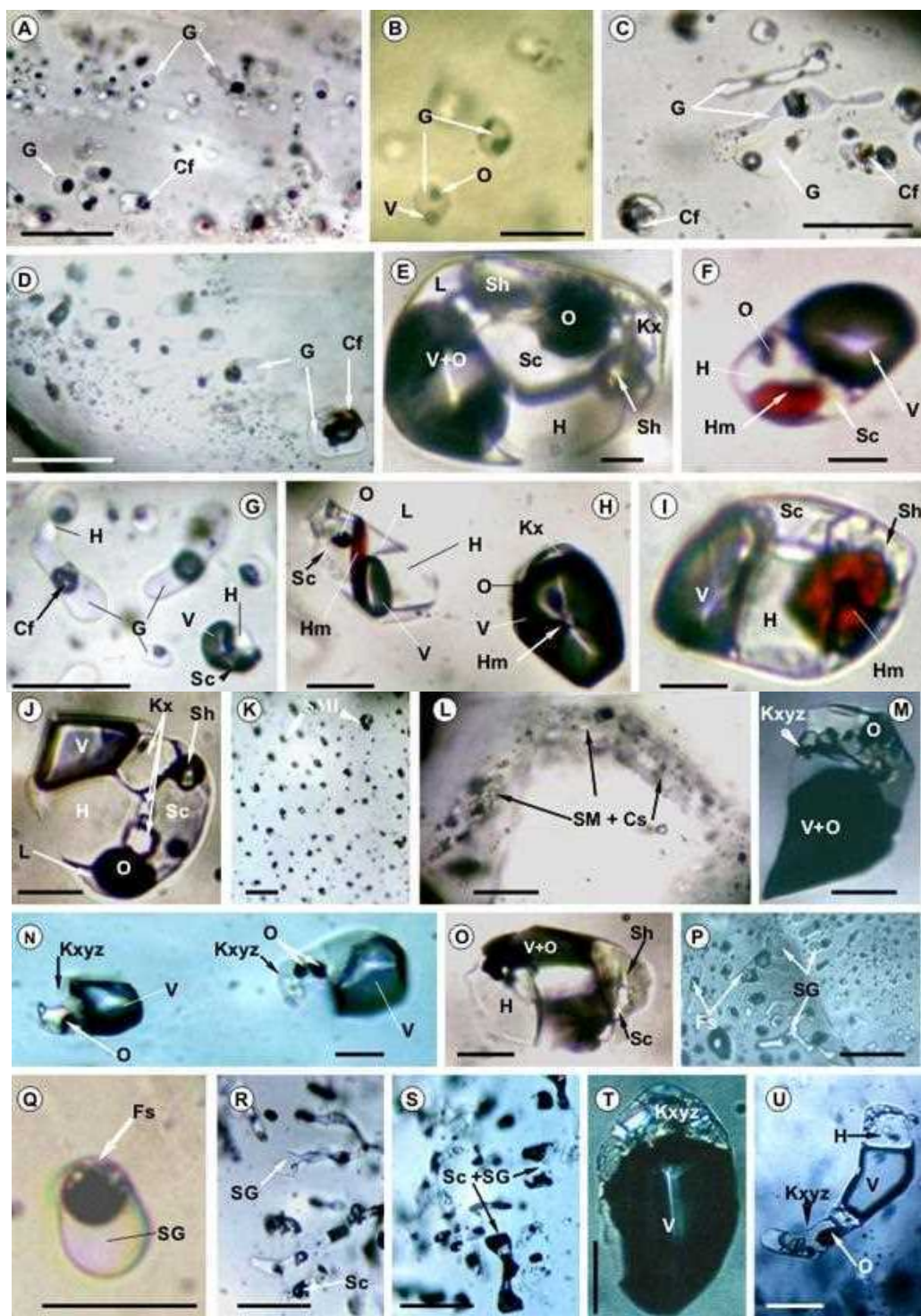


Fig. 34. Coloured microphotographs showing several kind of silicate glass inclusions, vapor-rich and hydrosaline melt inclusions in quartz from Deva (A, C, D, E, F, G, I) and Rosia Poieni (B, H) porphyry copper systems. G-glass, Cf- saline fluid, H-halite, V-vapor, Sc- another salt daughter phase, Hm- hematite, Kxyz- unidentified solid phases, Sh- unknown, O-opaque solid phases (pyrite, magnetite, bornite etc (Pintea, 2014a); Scale bar: 20 μm.

Fig. 35. Longitudinal sections through the prismatic quartz crystals from potassic zone - brecciate veinlets during overprinting by high-sulfidation stages from Roşia Poieni porphyry copper deposit (**a, b, c, d**). Early potassic quartz veins were fragmented and (re) cemented by high sulfidation mineralization described as pebble dike by Kouzmanov et al., 2010. Quartz is multiple zoned (gz) and decorated with primary fluid inclusions (vapor - rich and brine) and intersected by pseudosecondary (PS) and secondary (S) trails. Microthermometry and LA-ICP-MS analyses were published by Damman et al., 1996, Pintea, 1996; Pettke et al., 2001; Ivăşcanu et al., 2001; Heinrich et al., 2005, Kouzmanov et al., 2010. Scale bar in μm .

Fig. 36. Fluid and brine inclusions trapped in quartz from Roşia Poieni porphyry Cu-Au (Mo) deposit. **a, c, d, e, g, k-** brine inclusions containing halite (H), Kxyz- transparent salt and silicate solid daughter phases, O-opaque, V-vapor, L-liquid; **b, f, h, i, j-** vapor-rich inclusions with vapor-V, Hm-hematite, O-opaque (py, cpy), L- liquid, Kxyz- salt and/or silicate solid daughter phases. Scale bar in μm .

Fig. 37. Vapor-rich and multiphase (brine) inclusions in prismatic quartz crystals from Roşia Poieni porphyry Cu-Au (Mo) deposit; **a, c, g, m-** vapor rich inclusions with vapor-V, Ks- chloride daughter phase, O-opaque, Hm-hematite, Ksx- others salt/silicate phases. **b, d, e, f, h, i, j, k, l, o-** brine inclusion containing H-halite, Ks- complex (K, Fe, Mg, Ca – chloride), O-opaque, Ksx- other solid transparent daughter phases (chloride or silicate), **n-** coeval vapor-rich and brine inclusion trapped from a boiling episode (Damman et al., 1996; Pintea 1996b; Pintea, 2000; 2001ab; Heinrich, 2007). Scale bar in μm .

Fig. 38. Various fluid and solid inclusion types in quartz from Roşia Poieni porphyry Cu-Au (Mo) deposit; **a, c, d**- biphasic with solid remnants (Kr) and vapor (V); **b, g, l**- vapor rich, V-vapor, rt- rutile, H-halite; **f, j, k, m**- brine, H-halite, O-opaque, Ksy, Kxs- daughter solid phases association (chloride, sulphate, silicate; **e, h, i**- unknown globular (S) and dendrites (arborescent- nc) feature in microfissures (possible liquid/solid hydrocarbons or sulfide or native Cu). “Crush-leach” solution analyzed by Mass Spectrometry at department of geochemistry of Utrecht University (VG SIRS 24 EM mass spectrometer), showed chlorine isotopes ranges between -0.6 and -0.3‰ relative to the SMOC (Pintea et al., 1999b; Pintea, 2014a). Scale bar in μm .

Fig. 39 Coeval association (**a**) of the liquid-rich (L), vapor (V) and brine inclusion containing variable content of liquid (L), vapor (V), halite (H), other chloride (Ks), V-vapor and opaque-O; **b, c, d, f, g** – vapor rich inclusions with V-vapor, L-liquid, O-opaque, rt- rutile, Hm-hematite; **e**- decrepitated and recrystallized brine inclusion showing multiple daughter phases association including halite (H), V-vapor, and opaque-O. All inclusions were hosted by quartz crystals from Roşia Poieni porphyry Cu-Au (Mo) deposit. Scale bar in μm ; **c, f, g**-10 μm .

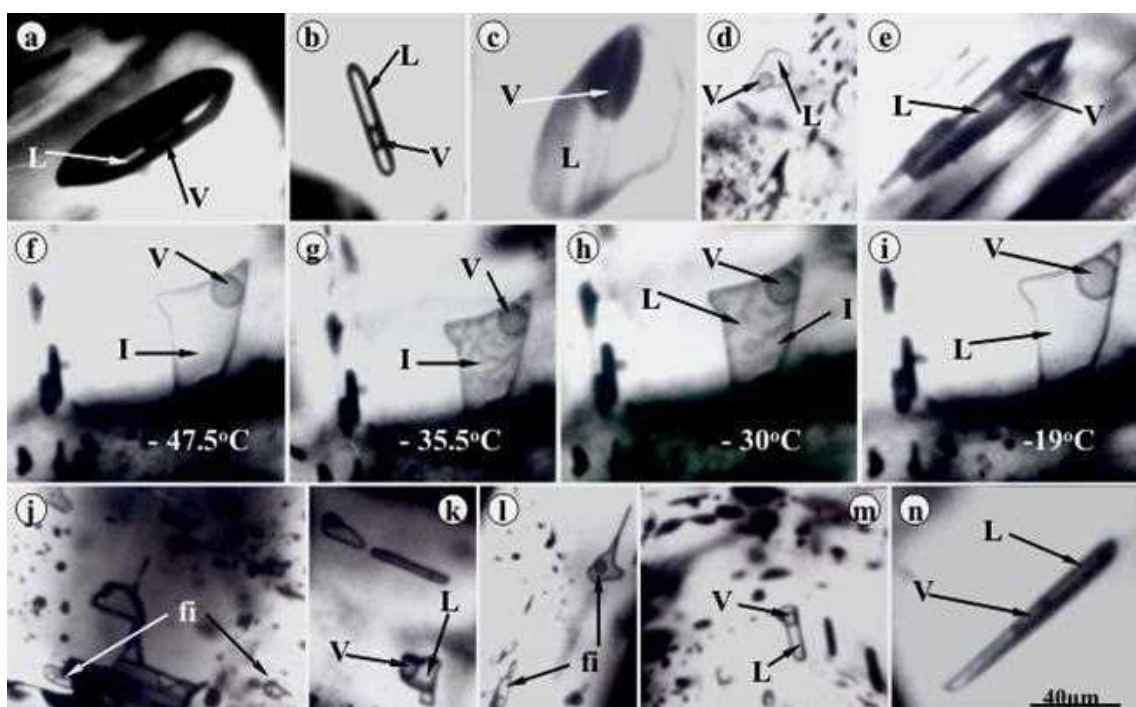


Fig. 40. Fluid inclusions trapped in enargite-luzonite from high-sulfidation epithermal overprinting from the Roșia-Poieni porphyry Cu-Au(Mo) deposit (L. Bailly, com. pers., 2002); **a, b, c, e, n**- primary liquid-rich inclusions, L-liquid, V-vapor; **d, j, l, m**-pseudosecondary fluid inclusions (fi) with liquid (L) and vapor (V) phases; **f, g, h, i**-microthermometric sequences at indicated temperatures, I-ice, V-vapor, L-liquid. From 29 determinations Th (homogenization temperatures) = 243-284°C and salinity = 4.03-14.15 wt% NaCl eq. (Pintea, 2008a; 2012). Scale bar from n in all microphotographs.

Fig. 41. Fluid-, brine-, vapor-rich and solid microcrystals from Tarnița porphyry copper deposit (belonging to the Roșia Montană-Roșia Poieni-Bucium-Tarnița caldera zone from Metaliferi Mountains, (e.g. Popescu and Neacșu, 2012); **a, b, d, h, i, k, n, p, q, u, w**- vapor rich inclusions; **c, g, f, m, o, r, s, v, x, y, z** – brine inclusions; **c, e** - microcrystals sometimes with attached brine; **j, l, m, t**- coeval brine(B) and vapor-rich inclusions. V-vapor, H- halite, O-opaque, Ks, Kx- anhydrite, silicate or other solids, L-liquid. Microthermometry: brine inclusions frequently floating in silicate melt at Th=885°-969°C, salinity=68 wt%NaCl eq., P=1.1-1.5kbars (Pintea, unpubl.); Scale bar 10μm.

Fig. 42. Magmatic hydrous silicate-, and hydrous saline melt inclusions from quartz grains in veinlets from the Bolcana porphyry Au-Cu (Mo) –Metaliferi Mountains; **a, c, d, u**- restitic solid microcrystals or glass inclusions; **b, e, h**- brine inclusions; **f, g, i, j, k, l, m, n, o, p, q, r, s, t**- silicate melt inclusions (SM) often coeval with vapor-rich (V) and/or brine (B) inclusions. Generally, silicate melt inclusions are completely recrystallized after trapping and their petrography and microthermometry encountered by many difficulties (Student and Bodnar, 2004). V-vapor, H-halite, Ks, Kx-solid salt or silicate daughter phases. Scale bar: 10µm.

Fig. 43. Fluid inclusion types trapped in the quartz veinlets from the potassic zone of the Bolcana porphyry Au-Cu (Mo) deposit (Metaliferi Mountains); **a, i, j, l, r**- vapor-rich inclusions; **b, d, e, f, g, h, k, o, p, q, s, t**- brine inclusions; **c, m, n**- aqueous liquid-rich inclusions. H-halite, cpy- chalcopyrite, O-opaque, L-liquid, V-vapor, Ks, Kx, Ksx- solid salt and/or silicate daughter phases, An- anhydrite, ?- unknown. Scale bar: 10µm. Petrography and microthermometry were published (e.g. Pintea, 1996a, Milu and Pintea, 2001; Cioaca, 2011; Dénes et al., 2014). Scale bar: 10µm.

Fig. 44. Fluid and melt inclusions types from the deep potassic zone of the Bolcana porphyry Cu-Au (Mo) deposit. Alteration and mineralization associations described from the column of F4 drill-hole (Milu et al., 2003). **a, b, c, d, e, f**- silicate melt inclusions (SM); **g, h, i, n, r, t**- vapor rich inclusions; **i, j, k, m, o, p, s, u, v, w**- brine inclusions (B); V-vapor, G-glass, H-halite, O-opaque, L-liquid, Hm-hematite, Ks, Kx - other solid daughter phases (complex chloride, anhydrite, silicate). Scale bar: 10µm.

Fig. 45. Fluid and solid inclusions types from Bucuresci-Rovina porphyry copper deposit (from Metaliferi Mountains - Boştinescu, 1984); **a, c, e, g, h, i, j, l, m, n, p, r, s, t, v, w, y**- brine inclusions; **b, d, f, k, o, u, x**- vapor-rich inclusions; **z**- solid microcrystal, sometimes with attached brine. Informative microthermometry (Pintea, 1996b and unpubl. data): Th= 598-1017°C, 0.6-1.6 kbars, 56-70 wt% NaCl equiv. Scale bar: 10µm.

Fig. 46. Fluid inclusions types from Valea Morii porphyry Cu-Au (Mo) deposit (Metaliferi Mountains); **a, b-** solid microcrystals with brine; **c, d, f, g, h, j, k, l, o, p, s, t, u-** brine inclusions; **e, i, m-** vapor rich inclusions; **n, p, r-** coeval brine(B) and vapor rich (V) inclusions; V-vapor, H-halite, Rx- solid remnants, Ks, Kx, Ksx- other solid daughter phases, O-opaque. Petrography and microthermometry were documented by Pintea, 1996b; André-Mayer et al., 2001; Nedelcu et al., 2001; Kouzmanov et al., 2003). Silicate melt inclusions in plagioclase were studied by Grancea et al., 2001. Scale bar: 10µm.

Fig. 47. Fluid and melt inclusions types from the endogenous (autometasomatism- Roşu et al., 2001, Pintea, 2010) zone from the Valea-Morii – Barza underground (Spiros adit; Nedelcu sample courtesy); **a, d, h, m, o** – brine inclusions; **b, d, h, m, o**- silicate melt inclusions, **v**- vapor – rich inclusions; **c, f, i, j, p, q, r, s, u**,- coeval inclusions of different phases as opaque-vapor, brine (B)- silicate melt (SM), vapor-liquid, sulfide – vapor; V-vapor, L- liquid, H-halite, O-opaque, x-unknown, Ks, Kx- solid daughter phases, G-glass. Microthermometry (Pintea, 2014, unpubl.): 420-1060°C, 0.2-1.5 kbars, 44-73 wt% NaCl eq. Scale bar: 10 µm.

Fig. 48. Fluid and melt inclusions from Bolcana, Valea Morii and Tălagiu trapped in quartz and anhydrite; **a, b, c** - coeval silicate melt and brine assemblages (BIA) as heterogeneous mixtures, rejuvenated after microthermometry up to 1000°C (Bolcana-Pintea, unpubl.); **f, g**- heterogeneous inclusions containing silicate glass and brine from quartz at Valea Morii porphyry Cu-Au(Mo) deposit (microthermometry: Th=665°C, Salinity = 63 wt% NaCl eq., P = 0.7 kbars- Pintea, 2008a); **d, e** - brine inclusions from quartz and **h, i, j, k, l** fluid inclusions types in anhydrite from Talagiu porphyry Cu-Au(Mo) deposit; V-vapor, G-glass, Fs-brine, SC- another salt or silicate solid daughter phases, L-liquid, Kx, Ky-unknown, H-halite, O-opaque. Scale bar: 10µm.

Fig. 49. Internal (re)crystallized microtexture features in the quartz grains from veinlets in the potassic zone of the Tălagiu porphyry Cu-Au (Mo) deposit. Tiny silicate melts (SM) and brine (B) inclusions are the main components decorating the growth zones. Because their small size are very difficult to be study by petrography and microthermometry (e.g. Student and Bodnar, 2004); Scale bar in μm .

Fig. 50. Fluid and melt (solid) inclusions from Tălagiu porphyry Cu-Au(Mo) deposit; **a**- unknown dendrites feature (nc) formed by (sulphides, native copper, possible solid hydrocarbons or phosphate phases -?; **b, f, j**- complex melt inclusions (mi) including brine, silicate glass (g), silicate globules (Sg) and vapor (V); **c, e, h, i, k, l, m**- brine inclusions without liquid phase at Troom conditions; **d**- vapor-rich inclusion; **g**- coeval (boiling) brine and vapor-rich inclusions; V-vapor, H-halite, L-liquid, Ks, Kx- other solid daughter phases (complex chloride, sulphate, silicate), O- opaque. Scale bar in μm . Petrography and microthermometry were documented by Pintea, et al., 1992; Pintea, 1996 – unpubl.; Stovold, 2009 – unpubl. (web item 21035474). Traces of CO_2 , CH_4 , and H_2S were detected by CG/MS in quartz and anhydrite (Cuna et al., 2001); Scale bar in μm .

Fig. 51. Melt and fluid inclusions types inherited in a rounded quartz-veinlet fragment (xenoliths) from propylitic andesite suggesting the collapse of the volcanic edifice after Tălagiu porphyry copper system genesis, overprinted by high-sulphidation mineralization (Pintea, 2012- unpubl.); **a, e, k**- complex silicate melt (SG) and fluid (FSO); **b, h, j**- vapor rich inclusions; **c, f, g, i**- brine inclusions, **d**- coeval (boiling) brine (B) and biphasic aqueous (Aq) inclusions; V-vapor, L-liquid, O-opaque, Ksx, Ks, Kxyz- other solid daughter phases (complex chloride, sulphate, silicate). Microthermometry (Pintea, 2012-unpubl.): Th = 618-1037°C, P= 0.5-2.2 kbars, salinity = 52-81 wt % NaCl eq. Scale bar in μm .

Fig. 52. Fluid and melt inclusion types from quartz sampled from drill-holes S1 (DI Roatei – Larga , M. Borcoş- sample courtesy), L1, L2 (Larga –Trâmpoiele; L. Nedelcu –sample courtesy) from Larga-Trâmpoiele porphyry Cu-Au(Mo) deposit in the Zlatna zone (Pintea, 1998- unpubl.); **a, d, i, k, l**- vapor – rich inclusions; **b, c, f, g, j, m, o, p, r, s, t**- brine (B) inclusions; **h**- silicate melt inclusion (SM); **e, n**- coeval brine (B) and vapor rich (V) inclusions; **u**- globular opaque (sulphide); V-vapor, O-opaque, H-halite. Scale bar: 10µm.

Fig. 53. Primary melt inclusion assemblages (mi) decorating growth zones in quartz grains in veinlets from Moldova Nouă Upper Cretaceous porphyry Cu-Mo (Au) deposit (**a, b, c, d, e**). Some of these features could be generated by grain boundary dynamic recrystallization (in a similar way as in experimental run product of several analogues, (i.e. Schmatz and Urai, 2008). It is suggested that immiscible fluid globules were dispersed in a hydrosilicate matrix formed by metasomatic reactions between supercritical fluids and crystallizing country rocks during stock formation. Their generation is possibly related to the hydrosilicate recrystallization processes (e.g. Vasyukova, 2011) showing internal euhedral zonation (phantom) and isolated or trail of inclusions in the former grain boundaries; **f**- the petrography and microthermometry is difficult to be done especially because their small size (obviously less than 10 μ) and are completely recrystallized (e.g. Student and Bodnar, 2004). Scale bar: 50 μ m.

Fig. 54. Fluid and melt inclusions types from the Moldova Nouă (Suvorov) porphyry Cu-Mo (Au) deposit; **a, i**- Recrystallized quartz grain microtexture decorated by silicate melt inclusion assemblages (mi); **b, e, f, h**- vapor rich inclusion containing complex fluid mixture (fc) of ($\text{H}_2\text{O} + \text{CO}_2$), suggested by the presence of a second bubble or solid hydrate at low temperature; **c, d, e, g, j, k**- solid microcrystals (kp) and silicate glass inclusions (G); **b, j, k**-opaque globular sulphides (O); V-vapor, H-halite. Scale bar: 50 μm .

Fig. 55. Silicate melts inclusion types from Upper Cretaceous porphyry Cu-Mo (Au) deposits. **a, c, d, e, f, g**- Oravița (Nicolae adit); **b, h, i, j, k, l**- Moldova Noua; V-vapor, H-halite, Kx, Ksx, Kxyz, Ks-other solid daughter phases (i.e. chloride, silicate, sulfate), G-glass, O-opaque, L-liquid, B-brine (L+V+H+O); Microthermometry of the complex inclusion from **e** indicated Th=925°C, salinity=52 wt% NaCl eq, P=1.8 kbars and the opaque phases melted completely at Tm= 909°C, becoming an immiscible opaque phase stable up to 1037°C where the experiment was stopped (Pintea in Roșu et al., 2002-unpubl.). Scale bar 10 μm.

Fig. 56. Silicate melt and fluid inclusion types from garnet and quartz from the potassic zone or the Moldova Noua porphyry Cu-Mo (Au) deposit; **a, b, c, d**- glassy, vapor-rich and brine inclusions from garnet; **e, i, k, l, m, q, t, u, z**- aqueous rich + vapor inclusions; **g, h, n, o, p, v, w, x, y**- brine inclusions; **f, j, r**- opaque dominated inclusions; O-opaque, B-brine, G-glass, H-halite, V-vapor, L-liquid, ks, kx, ksx, ksxy- other daughter solid phases, kc-chalcopyrite or nantokite(?), rt- rutile, ?- vapor bubble or solid at Troom; V/L- carbonic vapor rich or liquid carbonic phase at Troom (?), (e.g. Rusk et al., 2008). Scale bar in μm . Microthermometry of brine inclusions from Moldova Nouă and other porphyry Cu-Mo (Au) deposits (Pomârleanu and Întorsureanu, 1986; Pintea, 2002; Pintea in Roşu et al., 2002- unpubl.), evidenced Th between 350° and up to 1050°C, salinity = 32 - 76 wt% NaCl eq., P= 0.1-1.9 kbars, suggesting boiling episodes and sulfide/oxide-silicate-chloride magmatic immiscibility. Endogenous metasomatism is also emphasized (Pintea, 2010).Scale bar: 10 μm .

Fig. 57. Fluid and melt inclusions types in quartz grains from Sasca-Montana porphyry Mo-Cu deposit (Upper Cretaceous); **a, b, c, d, e, f, g, h, i, j**- silicate melt inclusions; g-silicate glass, kx-solid daughter phases (silicate, possible chloride, anhydrite etc); **k, l, m**- fluid and melt inclusions; B- brine and aqueous biphasic inclusions, rt- rutile needles, V-vapor. Scale bar: 10µm.

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Fig. 59. Hydrous silicate melt and brine inclusions trapped in miarolitic smoky quartz from Vlădeasa granite (North Apuseni Mountains, upper Cretaceous); **a, d, f, g, h, i, k, m**- completely crystallized silicate melt; **b, c, j, l** - brine inclusions; V-vapor, G-glass, Kf- orthoclase, H-halite, Sy-sylvite, Kx- other solid daughter phase (chloride, silicate, sulfate), O- opaque, L-liquid; Microthermometry under microscope at 1 bar, indicated Th= 979-1083°C (n=10; Pintea, 2012); Scale bar 10µm.

Fig. 60. Fluid inclusions types from zoned miarolitic quartz crystals from Vlădeasa granite; **a, d, e, g, j, k, n, q, r, s**- S₁-type brine inclusions (Pintea, 1991b; 1993b); **b, c, h, l, o, t**- S₂ type brine inclusion (Pintea, 1993); **f, m, p, u**- vapor rich inclusions; **i**- liquid rich inclusion; L-liquid, V-vapor, Mgt-magnetite, u-unknown, H-halite, Sy-sylvite, T-tourmaline (rutile-?). Microthermometry (Pintea, 1993a, 1995a, 2012) aqueous rich inclusions : Th (L) = 295-372°C, salinity = 1-6 wt % NaCl eq.; vapor - rich inclusions: Th (V) = 363-414°C, salinity= 2wt% NaCl eq.; S₁-brine: Th (L) = 570-1070°C, salinity = 41-74 wt% NaCl eq., P = 0.6-2.3 kbars; S₂ brine: ThV=179-405°C, TmH = 420°C, salinity = 46 wt % NaCl eq., P= 7.9kbars. Scale bar in μm .



Fig. 61. Vapor-, high density(?) aqueous liquid and brine inclusions in recrystallized pegmatitic quartz from Vlădeasa granite; **a, b, e, f**- vapor rich fluid inclusions; **c, d, g, h**- decrepitated high density (?) aqueous- liquid inclusions; **j**- silicate glass (G) with aqueous or carbonic fluid (L+V); **k, l**- biphasic liquid – rich, **i, n**- brine inclusions, **n**- (re) crystallized silicate melt inclusion (SM). Scale bar: 10 μm .

Fig. 62. Microthermometric replicated cycles of brine inclusion microthermometry in quartz from miarolitic quartz from Vlădeasa granite; I cycle: **a.** 25°C, **b.** 267°C, **c.** 496°C, Thv=513°C, **d.** 533°C, TmH=553°C (salinity = 67 wt% NaCl eq.), **e.** 556°C, **f.** 344°C, **g.** 196°C, **h.** 25°C; II cycle: **i.** 25°C, **j.** 261°C, Thv=511°C, **k.** 515°C, TmH=553°C (salinity= 67 wt% NaCl eq.), **l.** 25°C; Calculated trapping P= 0.7kbar; L-liquid, O-opaque, H-halite, ms- solid salt mixture, sm-salt melt, V-vapor; Thv- vapor bubble disappearance temperature, TmH- halite melting temperature. There are three homogenization mode of the brine or hydrous salt melt inclusions: **1.** by vapor bubble homogenization after halite melting temperature; **2.** by halite final homogenization after bubble disappearance temperature and **3.** simultaneous homogenization temperature of vapor bubble and halite phases (details in Bodnar et al., 1985; Pinte, 1993a; Becker, 2008; Becker et al., 2008; Lecumberri-Sanchez et al., 2012). Scale bar in μm .

Fig. 63. Quartz eyes (Qtz) from endogenous metasomatized quartz-monzonite from Birtin-dyke (Upper Cretaceous- Ștefan et al., 1982); B- brine, Fi- biphasic aqueous inclusions, G-glass, V- vapor-rich inclusions, O-opaque. Microthermometry: Th= 339-1004°C, salinity= 39-74 wt% NaCl eq., P=0.1-1.3 kbars (Pintea, 2012 unpubl.). Scale bar in μm .

Fig. 64. Silicate melts and brine inclusions types from quartz veinlets and biotite from the Birtin-dyke (Upper Cretaceous). **a, b, c, d, e, g, h, i-** brine inclusions in quartz; **f-** silicate glass (G) + vapor inclusions in biotite (Bi); V-vapor, O-opaque, H-halite, L- liquid, Kx, Kxy, Kxyz-other solid mineral daughter phases (chloride, sulfate, silicate), O-opaque, Hm-hematite. Scale bar: 10µm.

Fig. 65. Fluid and melt inclusions types from quartz related to the Highis granite massif (Hercynian) from Apuseni Mountains; **a, b, c, e, f, g, h**- brine inclusions; **d, n, p, v**- vapor rich inclusions, **i, j, k, l, m, o, r, s, t, u**- silicate melt inclusions; V-vapor, L-liquid, H-halite, O-opaque, kx, ks- other solid daughter phases (chloride, silicate), g-glass, Brine inclusions microthermometry: Th =193-298°C, salinity= 31-38wt% NaCl eq; Bulk crush leach analyses: NaCl= 25.20-46.90 wt%; KCl= 11.18-27.00 wt%, CaCl₂= 13.36-42.33, MgCl₂=0.07-2.96, FeCl₂=2.80-23.07 wt% (Pintea, 2003-unpubl.); Scale bar:5µm.

Fig. 66. Silicate melt inclusion types from quartz phenocrysts in rhyolitic- dyke sample G5 (M. Tatu-sample courtesy) from the Highiş massif; **a, b, c, d, e, f, g, m, n**- silicate remnants; **j, o, q, r, s, t, u**- microthermometric experiments showing the exsolution of multiple fluid bubbles during heating up to 1100°C at 1 bar pressure condition under the microscope (Pintea, in Rosu et al., 2002-unpubl.); frequently the unheated silicate melt inclusion shown similar features with the experiments, suggesting natural reheating (endogenous remelting); **gr**- glass remnants (glass + microcrystal), **O**-opaque, **V**-vapor, **g**-silicate glass, **Ks, Kx**- daughter phases (chloride, silicate, opaque); Scale bar: 10µm; **h, i, k, l**- 200µm.

Fig. 67. Brine inclusion microthermometry in quartz from Bolcana porphyry Cu-Au (Mo) deposit showing the sudden formation of FeCl_2 (?) phase from magnetite around 816°C. Pictures **A**, **B** take at indicated temperatures; L-liquid, V-vapor, Mt-magnetite, S-opaque. Microthermometry (Pintea, 2009): Th (L) = 901°C, P= 1.1 kb, salinity=72 wt% NaCl eq. Scale bar 10µm.

Fig. 68. Sequential microphotographs in brine inclusions from Roşia Poieni porphyry Cu-Au (Mo) deposit. Selected values: **1.** 25°C, **4.** 133°C, **11.** 302°C, **15.** 530°C, **19.** 712°C, **21.** 363°C, **24.** 25°C. Th (L) = 712°C (corrected by Sowat), P = 0.8kb, salinity = 64 wt% NaCl eq. Tmhalite = 532°C. Pintea, 1998, unpubl.). Scale bar 20µm.

Fig. 69. Microphotographs showing features of the brine inclusion cycled in Fig. 68 before and after the microthermometric experiment, at 25°C. This is a typical microcrack in quartz from Roşia Poieni porphyry Cu-Au (Mo) deposit with coeval brine and vapor-rich inclusions defining so called “boiling assemblage” (see also Heinrich et al., 2005).

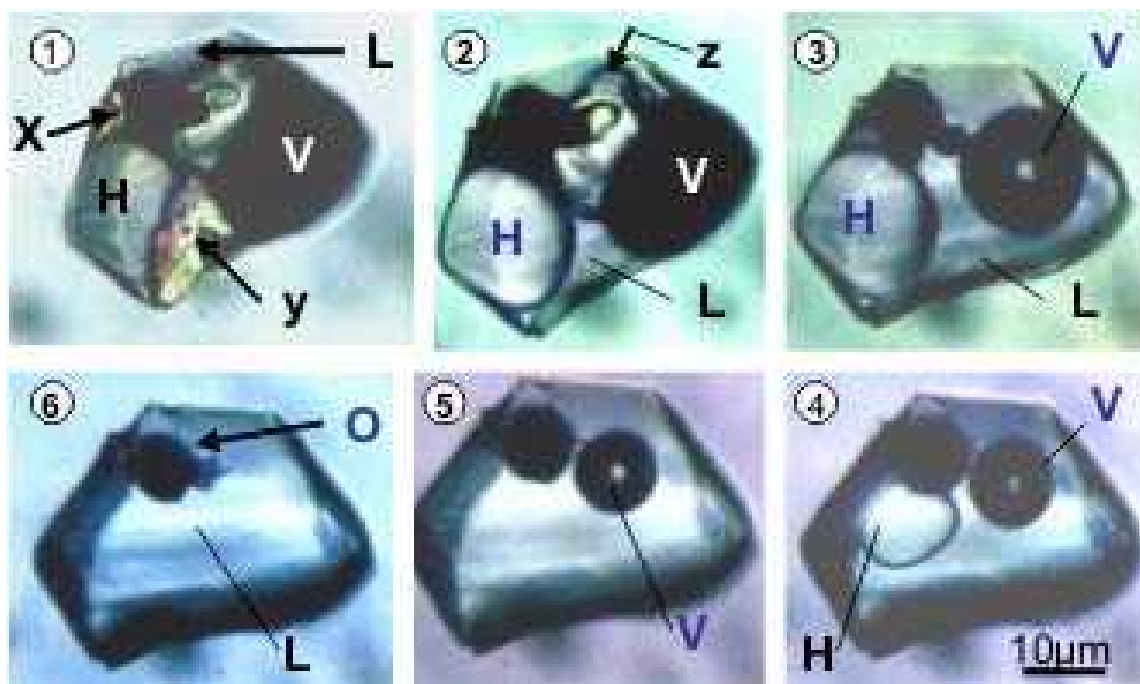


Fig. 70. Hydrous salt melt inclusion with liquid phase at room temperature from Roşia-Poieni porphyry Cu-Au (Mo) deposit, homogenized in “single phase state” in a completed microthermometric run. **1.** 25°C), **2.** 126°C, **3.** 309°C, **4.** 575°C, **5.** 601°C, **6.** 750°C, Tm NaCl=585°C, Th (liquid + solid (s)) = 749°C; x,y-unknown solid phases, probably salt hydrates and/or complex salts, H- halite, V- vapor, O-opaque (Fe-S-O), L- liquid (Pintea, 2014a).

Fig. 71. Sequential Linkam-overlaid microphotographs showing a complete microthermometric cycle of the typical hydrous salt melt inclusion (without liquid phase at room temperature) in quartz from Deva porphyry Cu-Au(Mo) deposit; H-halite, Kx,y,z- other solid daughter phases, O-opaque, V-vapor, LC- salt melt, SM-silicate melt, Scale bar around 35 μ .

Fig. 72. Sequences of the first (**a** to **h**) and the second (**i** to **n**) microthermometric run, repeated after 2 years in a liquid-free hydrous salt melt inclusion trapped in quartz crystal from Deva porphyry Cu-Au(Mo) deposit; **a.** 25°C, **b.** 187°C, **c.** 349°C, **d.** 597°C, **e.** 589°C, **f.** 561°C, **h.** 450°C, **i.** 25°C, **j.** 220°C, **k.** 345°C, **l.** 678°C, **m.** 1305°C, **n.** 25°C, T_{mh}= 555°C, T_{h(L)}=1262°C. Notations: Kxyz- mixture of salt microcrystals with halite (H) dominant solid daughter phase, O- opaque, Ksp- feldspar, L₁- salt melt released by melting of the salt mixture, L₂- a tiny film of silicate melt released by melting the silicate phases, SMI-silicate glass inclusions formed in fissure probably during the first microthermometric cycle (indicated by dashed arrow in **a**) suggesting a slight leaking process (re-equilibration) but the salt melt volume remains almost the same because this recrystallized and filled up the microcavity as in the starting moment (vol in **a** = vol in **f**) even if another small fissure (**c**) is formed in the second cycle (**f**). (Pintea, 1993ac; 2014a). Scale bar in µm.

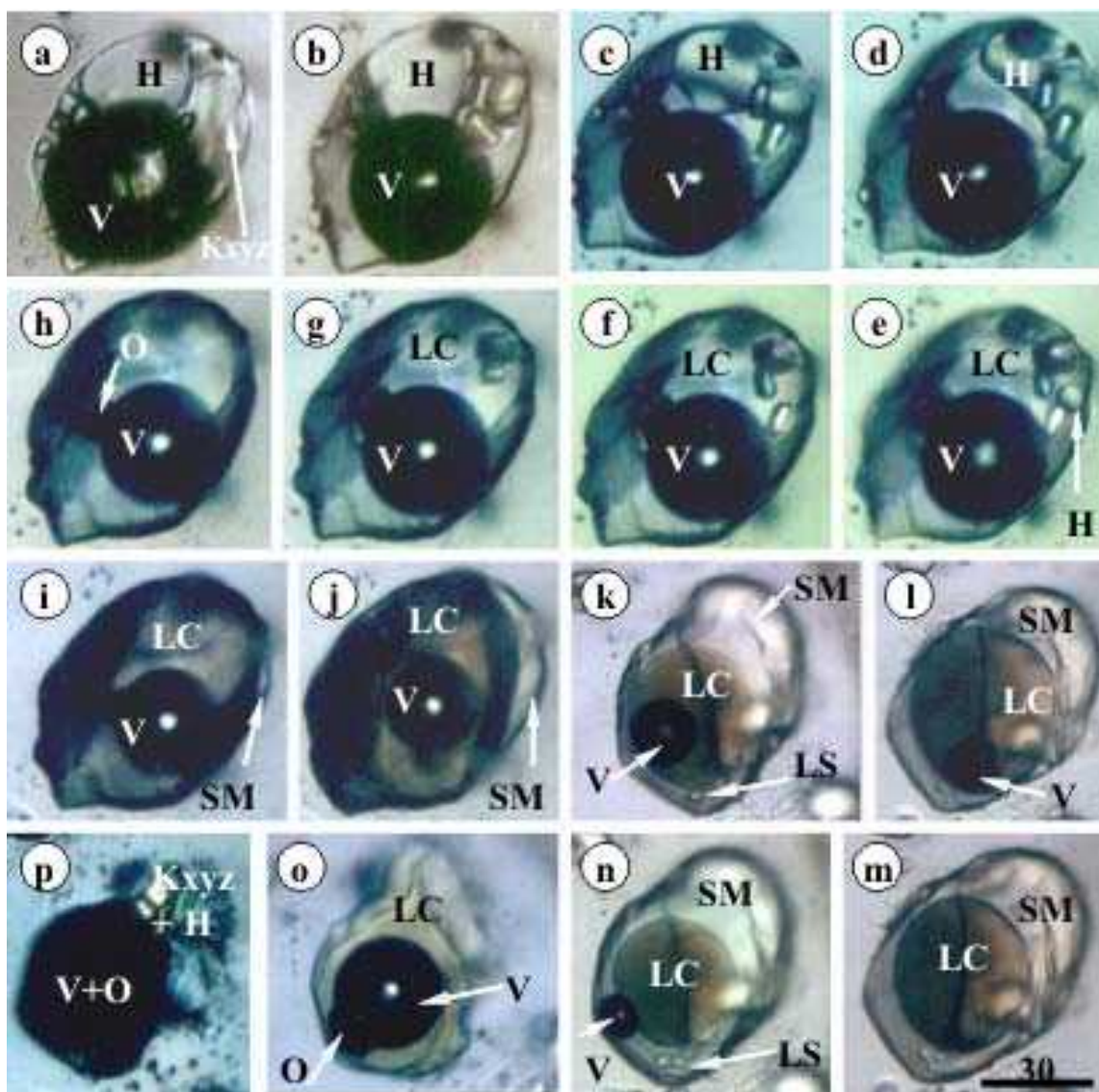


Fig. 73. Sequence of microphotographs showing the complete microthermometric cycle in a hydrous salt melt inclusion trapped in a primary quartz growth zone from Deva porphyry Cu-Au(Mo) deposit (Pintea, 1995b, 2014a modified) **a.** 25°C, **b.** 243°C, **c.** 450°C, **d.** 504°C, **e.** 594°C, **f.** 599°C, **g.** 648°C, **h.** 840°C, **i.** 1086°C, **j.** 1219°C, **k.** 1284°C, **l.** 1317°C, **m.** 1394°C, **n.** 1284°C, **o.** 1062°C, **p.** 25°C. $T_{mNaCl}=598^{\circ}\text{C}$, T_h (melt- V (melt))= 1347°C . Other melting temperature recorded for x ($T_{m1}=113^{\circ}\text{C}$), y ($T_{m2}=122^{\circ}\text{C}$, 288°C -sylvite), z ($T_{m4}=602^{\circ}\text{C}$ - 840°C), $T_{mo}=1170^{\circ}\text{C}$ and renucleated at 1130°C . x, y- chloride hydrates-sylvite solid phase, z- silicate phase(s), and anhydrite-?, O- Fe,Cu sulphide-?, V-Vapor, L₁- chloride liquid, L₂-silicate liquid, g- sulphate globules-?, K- mixture of salt microcrystals renucleated at room temperature.. Experiment duration = 5h. Note: Above ca. 1100°C the microcavity have been seriously damaged and their volume increased probably because the chloride liquid phase have dissolved quartz from the walls, and silicate melt liquid increased also in volume, but chloride part seem to be unchanged during the overheating steps. In this case it was estimated that immiscibility occurred at 1086°C , which could be considered as the real “heterogeneous” trapping temperature of the (L+V) chloride mixture and the silicate melt counterpart (see also Steele-MacInnis and Bodnar, 2013). Scale bar μm .

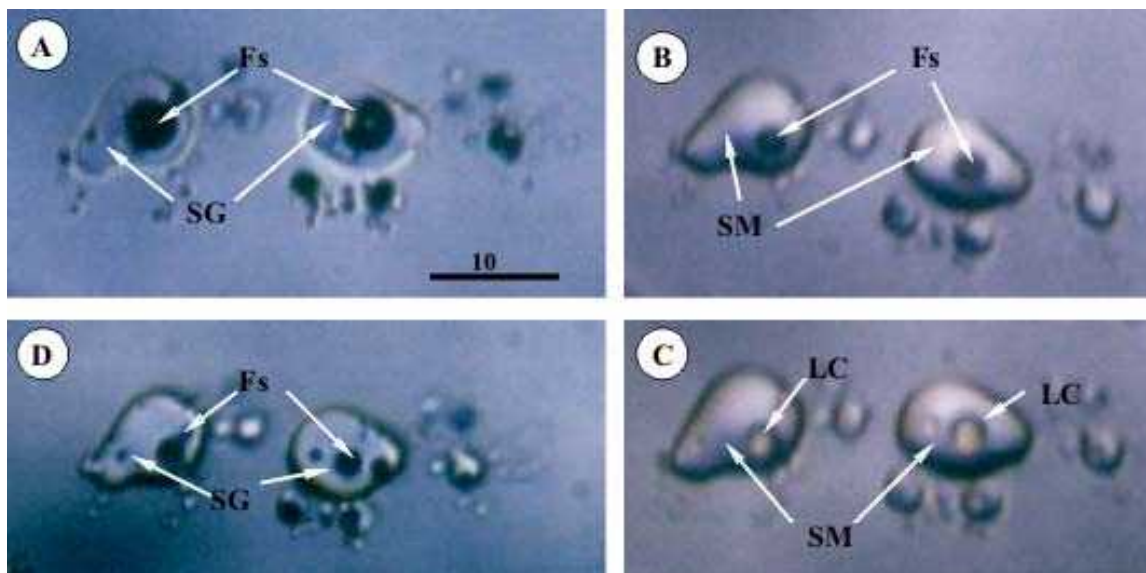


Fig. 74. Sequence of microphotographs showing HT-microthermometry in complex silicate-hydrous salt melts inclusions in quartz from Deva porphyry Cu-Au (Mo) deposit. At room temperature conditions (**A**) the microcavities contains a rich silicate glass and a fluid formed by vapor- rich phase, a halite cube and some opaque. On heating the halite melted around 550°C and at 1085°C (**B**) the fluid bubble is more reduced in volume and contain silicate melt and a dark vapor bubble from which was released around 1267°C a yellow chloride melt (LC) surrounded by a vapor film (dark meniscus), (**C**). Back again to the room temperature (**D**) the fluid is redistributed in several small dark bubbles and the microcavities have changed their shape. The final homogenization temperature is impossible to be determined accurately because of the permanent immiscibility between the two trapped phases, the silicate melt and the hydrosilicate melt, +/- vapor rich. Scale bar in microns (modified from Pintea, 2014a). It should be emphasized that the silicate melt rim appearance in hydrous salt melt inclusions depicted in **Fig 73i**, and the first appearance o the salt melt rim in silicate melt inclusions from this sequence in **B** could be the maximum “normal” trapping temperature of hydrous salt melt inclusions in the porphyry copper systems as already was proved experimentally by Burnham (1979) and reloaded by Becker, 2008 ; Bodnar, 2010. More recently, magmatic control on porphyry copper genesis was published by Audetat and Simon, 2012. Scale bar in μm .

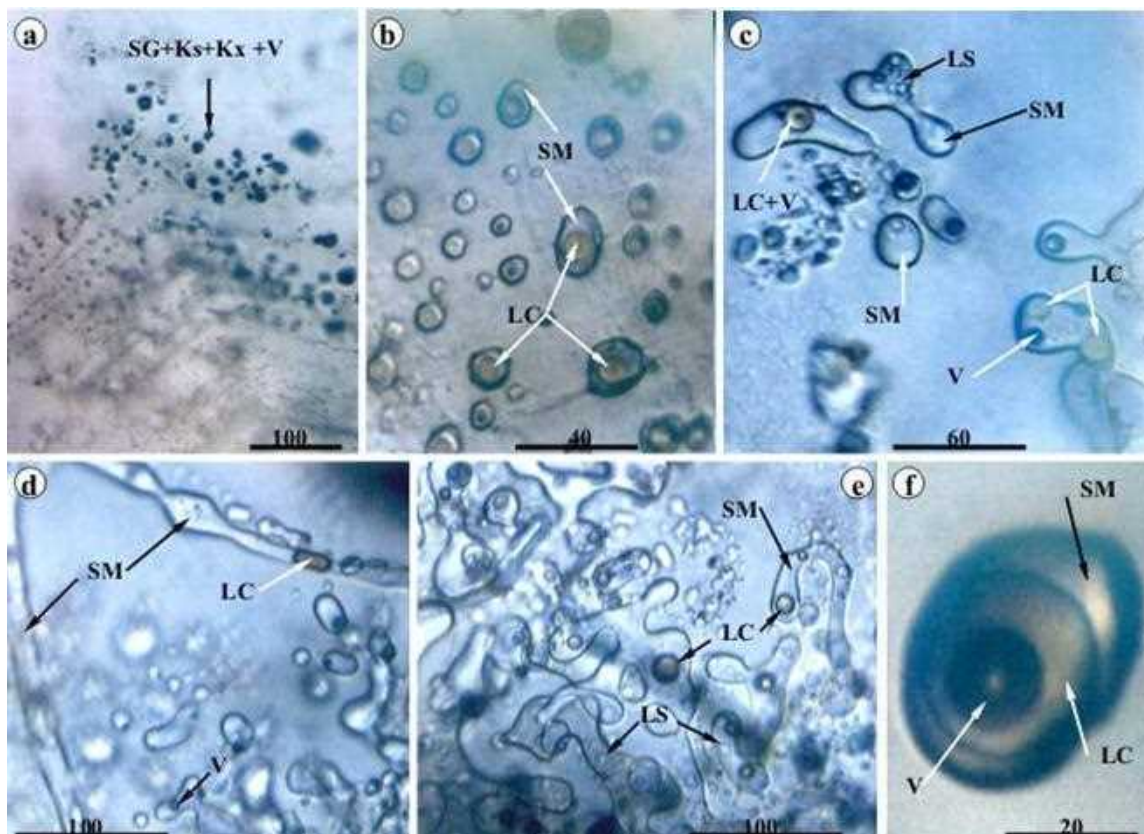


Fig. 75. Coeval silicate melt and hydrous salt melt inclusions in zoned quartz from veinlet of the Deva porphyry Cu-Au(Mo) deposit; **a.** complex silicate melt- salt melt inclusions formed by silicate glass (SG), salt crystal (Ks), silicate (sulfate) daughter phase (Ks) and vapor; **b, c, d, e, f-** silicate - salt melt immiscibility depicted around 1300°C; SM-silicate melt, LC-salt melt, LS-sulfate melt (?), V-vapor. Scale bar in µm.

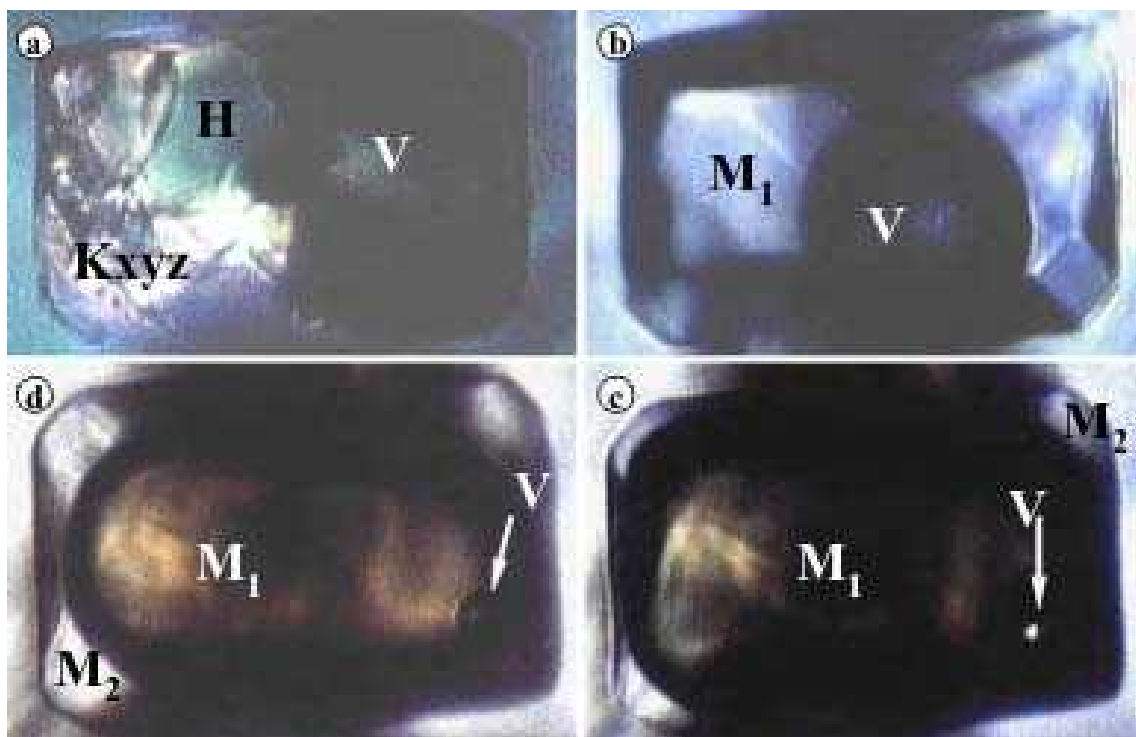


Fig. 76. Rectangle shaped (high pressure form-?) hydrous salt melt inclusion without liquid phase at Troam showing HT immiscibility in quartz from Deva porphyry Cu-Au(Mo) deposit; V-vapor, H-halite, Kxyz-other solid daughter phase including complex chloride, silicate, sulfate), M₁- salt melt, M₂-silicate melt; **a.** 25°C, **b.** 641°C, **c.** 1170°C, **d.** 1226°C. Microthermometry: Th (L) = 1234°C, P=8kb, salinity=72 wt% NaCl eq. (Pintea, 1994a, unpubl.). Inclusion size=70µm.

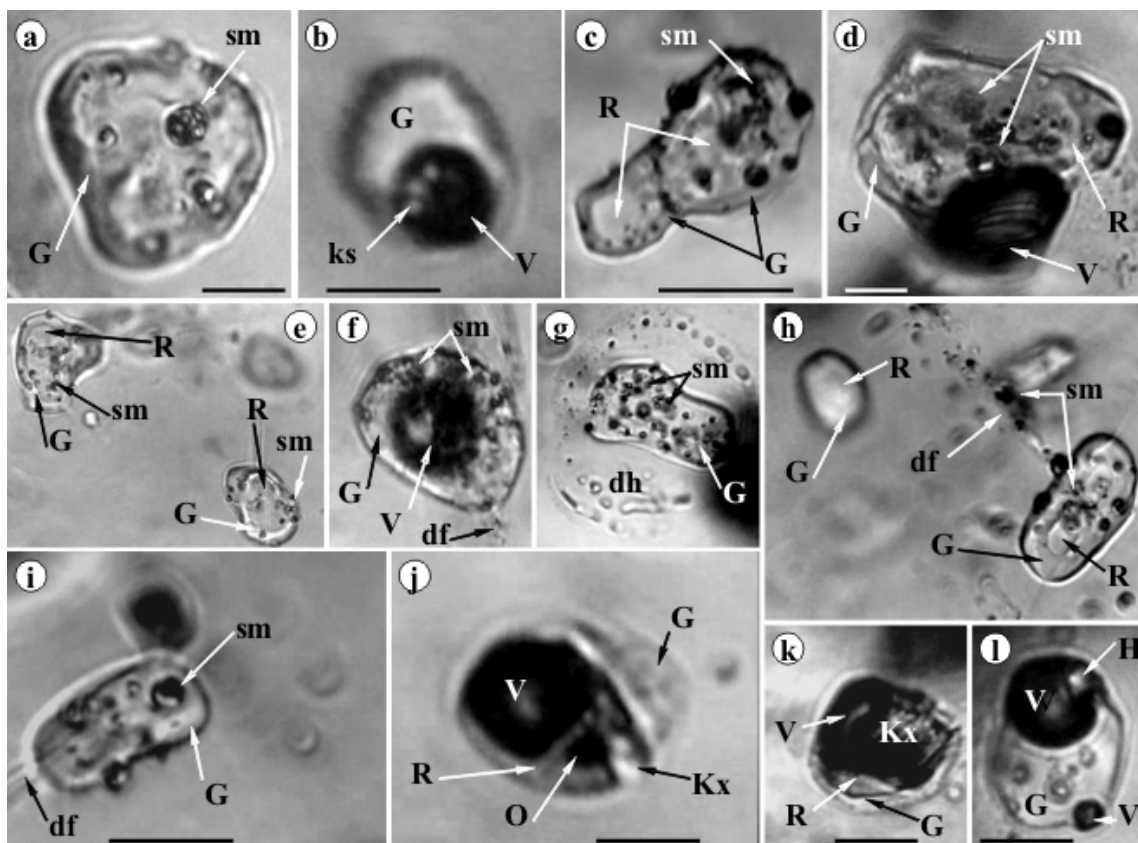


Fig. 77. Experimentally re-melted features in silicate melt inclusions from Upper Cretaceous porphyry Mo-Cu (Au) occurrence from Oravița (Nicolae adit); **a, c, e, g, h, i**- immiscible saline droplets exsolved from silicate melt depicted around 1000°C; **b, d, f, j, k, l**- two phase silicate melt inclusion (glass + vapor) and separate immiscible globules exsolved around 1000°C; G-glass, sm-silicate melt, R-restitic glass (unmelted), dh/df-decrepitation halo/fissure, O-opaque, Kx- other daughter solid phase (silicate, chloride). Scale bar 10µm.

Fig. 78. Microthermometric sequences in two contemporaneous silicate melt inclusions (assemblage) in plagioclase from Danesti-Piatra Rosie dacite showing different internal features during heating up around 1100°C; a, b, c, d- homogeneous silicate foam-like inclusion; e, f, g, h- silicate melt inclusion; cb= contraction bubble, G-glass, b- erratic bubbles, Kx- daughter silicate, SM- silicate melt. **a.** 25°C, **b.** 1048°C, **c.** 1080°C, **d.** 25°C, **e.** 25°C, **f.** 1047°C, **g.** 1094°C, **h.** 25°C. Scale bar: 10µm

Fig. 79. Three phase silicate melt inclusion (glass + crystal + vapor) showing uncommon high temperature disappearance of the vapor bubble, suggesting heterogeneous trapping. Nevertheless the recent published data on contemporaneous silicate melt inclusions in quartz from Laleaua Alba dacite (Naumov et al., 2014) suggested very deep trapping conditions (about 30 km $\approx$ 8kb). Moreover xenocrystic pyroxene geothermometry from acidic rocks indicate high temperature values up to 1416°C, suggesting magma mixing by hot mafic magma influx (Kovacs, 2002; Pintea 2007; 2008a). Scale bar cca 20 µm.

Fig. 80. Microthermometry of an silicate melt remnant in β -quartz crystal from Roşia Montană dacite dome (Metaliferi Mountains). The inclusion contain at room temperature in **a.** silicate glass (G), a vapor phase as multiple bubbles (V) and solid silicate phases (kx) and opaque (O). During heating procedure in the stage around 1400°C, the phase disappeared one by one and now contains only silicate melt (SM), a vapor bubble (V) and remaining glass in **b.** and **c.** which melted completely at 1370°C showed in **d.** (uncorrected temperature, see Pintea and Iatan, 2017). This behavior is uncommon and trapping temperature cannot be estimated, but this seems to be the initial temperature of a new melt influx. The new overheating magma influx induced overgrowth of the β -quartz phenocrysts, after homogenization of the mafic and felsic melt during decompression (Pintea and Iatan, 2013). Such high temperature fluid and/or melt phases seem to be extracted from the astenospheric mantle wedge in postcollisional environment followed by an extensional regime as was emphasized in the Miocene volcanism from Metaliferi Mountains (Harris et al., 2013). Scale bar in μm .

Fig. 81. Aqueous fluid inclusions (monophase and biphasic) in various Neogene epithermal deposits from Carpathians (Romania). **1.** Herja (low sulfidation); **2, 4.** “Cucu” crater in Harghita Mountains, **3.** Baia Sprie (low sulfidation), **5, 9.** Tălagiu (possible high sulfidation fluids overprinting the porphyry copper system); **6, 7, 8, 9, 10.** Roșia Montană Au-Ag epithermal deposit (Gold Quadrilateral- Metaliferi Mountains). V-vapor, L-liquid, ?- unknown solid daughter phase. Scale bar in μm .

Fig. 82. Fluid inclusions types in quartz from Herja epithermal ore deposit (Baia Mare mining district); **a, k, l**- biphasic fluid inclusions; **b, e, f, h, m, n**- multiphase fluid inclusions; **c, d, g, i, j**- vapor-rich inclusions; **o**- monophasic liquid inclusions; As it was pointed out by Damian (2003) that the Herja low sulfidation ore deposit could be related at depth with a subvolcanic body activated as a porphyry copper - like system, suggesting that the early fluid were high- salinity ones, as now proved by the presence of solid phases precipitated (?) in the fluid inclusions in quartz (this Figure). The salinity estimated by Pintea (1995a; 1996b) ranged between 4.9 to 19.5 wt % NaCl eq at temperatures between 175°C and 370°C. Moreover it is suggested that the early mineralization stage was characterized by high temperature values as indicated by the S-isotope compositions of coexisting pyrite-galena pairs between 417±75°C and 320±70°C. The famous stibnite and sulphosalt parageneses including “plumosite” probably crystallized below 220°C (Pomârleanu 1971; Cook and Damian, 1997); L-liquid, Lc-CO₂ liquid, kx, kxy- solid phases (silicate, carbonate, sulfate), V-vapor. Scale bar in µm.

Fig. 83. Typical aqueous biphasic ($\pm$ carbonic fluid) fluid inclusions from Baia Sprie epithermal ore deposit containing dawsonite as solid daughter (?) phase.; L-liquid, Lc- liquid carbonic rim, V-vapor, D-Dawsonite – $\text{NaAl}(\text{CO}_3)(\text{OH})_2$. Despite metastability during heating in the stage under the microscope, it is considered a real daughter phase formed in inclusions after trapping of Al- rich carbonaceous alkaline solution in low T-P epithermal environments (e.g. Coveney and Kelly, 1971) or in granitic-pegmatites formations by Sîrbescu and Nabelek (2003) at relatively high T ($\sim 340^\circ\text{C}$) and P(2.7 kbars). Generally a CO_2 - rich phase is necessary present as a thin rim of liquid CO_2 around the vapor bubble at Troom conditions (Nedelcu and Pintea, 1993; Pintea, 1995a; 1996b). Scale bar $40\mu\text{m}$.

Fig. 84. Pseudosecondary parallel alignments (overgrowths) decorated with aqueous-rich biphasic fluid inclusions in epithermal quartz from Baia Sprie ore deposit. V-vapor, L-liquid. Scale bar in μm .

Fig. 85. Pseudosecondary trail containing coeval vapor-rich (V) and liquid-rich (L) fluid inclusions representing a presumptive boiling episode during quartz crystallization in the main vein from Baia - Sprie ore deposit (level X). There are many episodic boiling and effervescence or evaporation stages in the “Main Vein” from Baia Sprie (e.g. Manilici et al., 1965, Pomârleanu et al., 1985; Nedelcu and Pinte, 1993) precipitating successive mineral parageneses all together suggesting the characteristic ore elements distribution with precipitation height column (cca 800m): (Au-Ag) on the top, (Pb-Zn) and (Pb-Zn-Cu) $\pm$ Bi $\pm$ W intermediate depth to the bottom, deposited between 150-360°C, rarely more, and 0 to 21.0 wt % NaCl eq. (Manilici et al., 1965; Pinte, 1995a; Grancea et al., 2002). Mixed fluids (magmatic and meteoric) with low salinity (4.6-6.4 wt% NaCl eq) and intermediate Th between 154° and 240°C was estimated in wolframite for primary biphasic fluid inclusions (Bailly comm. pers, 2001; Bailly et al., 2002). Scale bar in μ m.

Fig. 86. Overgrowths zones in quartz decorated with multiphase (L+V+solids) fluid inclusions in the second crystallization stage from the “Main Vein” of the Baia Sprie epithermal system (Nedelcu and Pinte, 1993; Pinte, 1995a; 1996b). L-liquid, V-vapor, Kx- crystal (silicate, carbonate, sulfate or silicate glass-?). Scale bar in μ m.

Fig. 87. Presumptive magmatic vapor-rich fluid inclusions as pseudosecondary parallel alignment in a microfissure plane in quartz from Baia Sprie – “Main Vein”. V- vapor, Kx- sublimated solid phase (silicate or carbonate). Scale bar in μm .

Fig. 88. Coeval presumptive magmatic vapor- rich inclusions trails with aqueous biphasic fluid inclusions in the same microfissure plane in epithermal quartz from Baia Sprie ore deposit. V-vapor, Kx- solid condensate (silicate or carbonate), L-liquid. Scale bar in μm .

Fig. 89. Individual presumptive magmatic vapor-rich inclusions types (**a, b, c, d, e, f, g, h, i, j, k, l**) trapped in epithermal quartz in the “Main Vein” from Baia Sprie ore deposit. Recent (Pintea, 2014b) petrographic and microthermometric evidences suggested a deep source of silicate- rich vapor phase as it was envisaged by Wyllie and Ryabchikov, (2000) in the join $\text{NaAlSi}_2\text{O}_6$ - KAlSi_3O_8 - H_2O at 2GPa and 700°C, where the silicate content in the vapor increase from ~30 wt% in the $\text{NaAlSi}_2\text{O}_6$ - H_2O boundary system to ~60 wt% for vapor coexisting with both jadeite and muscovite; Chalot-Prat F., Arnold M.(1999) documented immiscibility between carbonate and silicate melts at mantle depth in the Persani Mountains quaternary alkaline magmatism. V-vapor, Kx-solid (silicate, carbonate, sulfate), L-liquid, ?- unknown. Scale bar in μm .

Fig. 90. Primary and pseudosecondary microtexture features in zoned epithermal quartz from “Main Vein” of Baia Sprie ore deposit; **a, b, h**- coeval liquid -, and vapor-rich inclusions; **c, d, e, f, g, i**- growth zones decorated by biphasic aqueous inclusions with variable orientation in the same horizontal plan section; gz- growth zone, orz- horizontal perpendicular growth zone, vrt- vertical parallel growth zones in horizontal plane-view, aqb- aqueous fluid inclusion, V- vapor, L-liquid.. (similar feature mentioned also in Heinrich, 2007, fig 1c). Scale bar in μm

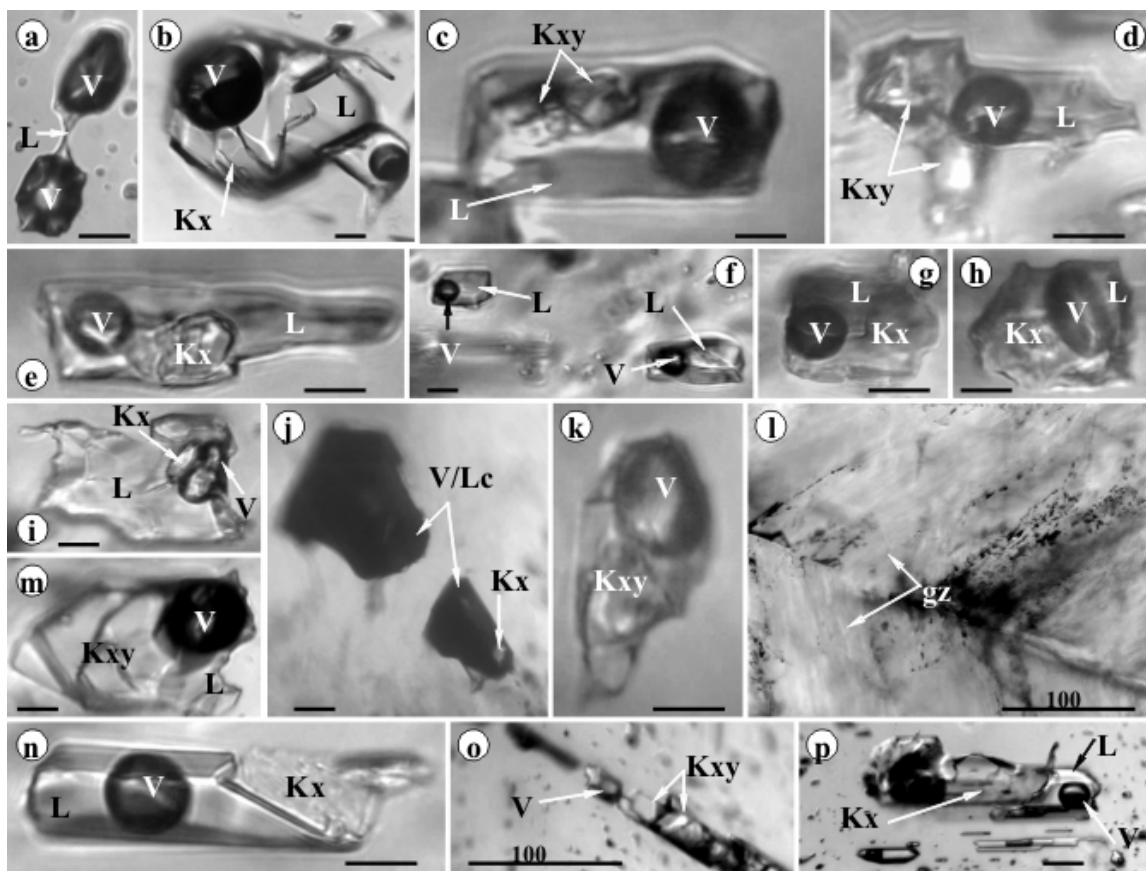


Fig. 91. Vapor - rich inclusion (a, j), biphasic (f) and multiphase (b, c, d, e, g, h, i, k, m, n, o, p) fluid inclusions (in quartz growth zone of the second mineralization stage (Nedelcu and Pintea, 1993; Pintea, 1995a; 1996b) of the “Main Vein” from the Baia Sprie epithermal ore deposit; l. diedral growth zones; V- vapor, L-liquid, Lc- CO₂-liquid rim, Kx, Kxy – solid phases (silicate, carbonate, sulfate); These solid phases are characteristic trapped phases in fluid inclusions from all epithermal ore deposit from Baia Mare mining district suggesting complex fluid phase composition (primary and secondary silica and carbonate) probably responsible for intensive adularization and silicification processes (Giuşcă, 1960, Manilici et al., 1965; Stanciu, 1984). Scale bar in µm.

Fig. 92. Aqueous fluid inclusion microthermometry from Baia Sprie hydrothermal quartz. **a.**+25°C, **b.**-79°C, **c.**-28°C (Te), **d.**intermediate, **e.** -11.4°C (Tmi), **f.**-7°C, **g.** +25°C, **h.** to **i.** Th= +250°C (first fluid inclusion criometry in Romania – I. Pinteá in Nedelcu et al., 1987, unpubl. report IGG; Pinteá, 1995a, 1996b); L-liquid, V-vapor, I-ice, Scale bar in μm .

Fig. 93. Aqueous fluid inclusion microthermometry from Baia Sprie hydrothermal quartz. **a.**+25°C, **b.**-63°C, **c.**-28°C, **d.**-25°C, **e.**-23.8°C, **f.** -19.8°C, **g.** to **h.** T_{mi} =-4.6°C, **i.**+130°C, **j.**+167°C, **k.** to **l.** Th=+250°C, salinity =7.31wt % NaCl eq (Bodnar ,1993) (modified from Pintea, 1995a).Scale bar 15µm.

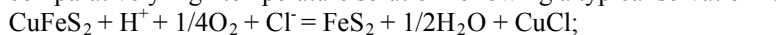
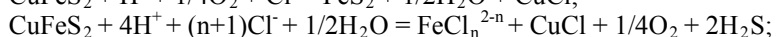
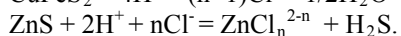
Fig. 94. Solid-bearing liquid-rich inclusions in epithermal quartz from Cavnic Pb-Zn-Cu deposit (Baia Mare mining district); **a, b, c, h, j, r, t, u-** liquid rich with insoluble solid phases (silicate, carbonate); **g, i, l, o, p, r, s, u, w-** liquid-rich with possible soluble solid phases (rounded unknown salt-? etc); **d, m-** liquid – rich with dawsonite; **e, f, n, x-** multiple solid and vapor (no liquid at room temperature); **kx, kxy, kxyz-** insoluble solid phases; **ks-ksx-** possible soluble solid phases; **kb-** biotite-like flakes embedded in another solid phase (glass-?); **L-**liquid, **V-**vapor, **Lh-**liquid hydrocarbon (?), **D-** dawsonite. The nature and origin of the solid phases are unknown yet but some of them could be precipitate from the silicate rich magmatic vapor phases (Pintea, 2014b), others were formed before trapping during fluid-rock interaction processes as alteration products. There is not mention yet about the halite daughter phase in these fluid inclusions (Pintea, 2012). Scale bar in μm ; **d-** 20 μm , **w-**10 μm .

Fig. 95. Solid and fluid inclusions in Cavnic-Bolduț sphalerite; **a, b**- globular sulphides (immiscibility-?); **c, d, o, p, t**- biphasic fluid inclusions; **g, n**- biphasic fluid inclusions showing oscillatory stria (varves-?) on the cavity walls (see Roedder, 1972); **e, f, i, j, k, l, s**- liquid rich inclusions with unknown solid phases; **h, u, v**- vapor (?) rich like fluid inclusions; **m, o, r**- multiple solid microinclusions; **S**- sulfide, **x**- unknown solid phase, **o**-opaque, **c**- capillary with liquid (?), **L**-liquid, **V**- vapor, **?**- unknown. Scale bar in μm .

Fig. 96. Aqueous biphasic fluid inclusion microthermometry from Cavnic-Bolduț sphalerite (Baia Mare mining district); **a.**+25°C, **b.**-70°C, **c.**-22.5°C, **d.**-14°C, **e.**-11°C, ($T_{mi} = -9^{\circ}\text{C}$, salinity = 12.85 wt% NaCl eq), **f.**+162°C, **g.**+20°C, **h.** $T_h = +214^{\circ}\text{C}$. Scale bar in μm (Pintea, 1995a; 1996b). Scale bar in μm .

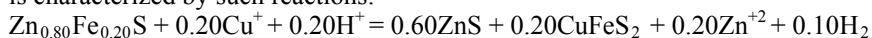
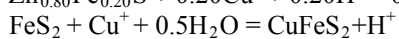
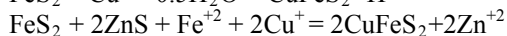
Fig. 97. Solid and multiphasic fluid inclusions in sphalerite quartz paragenese from Căvnic-Bolduț (Kelemen vein) epithermal Pb-Zn-Cu ore deposit; **a.** quartz containing an opaque grain coprecipitated with sphalerite; **b, c** – aqueous biphasic and multiphase fluid inclusions (the rounded solid phase suggest a soluble included salt, but halite daughter phase was not identified yet, by microthermometry- Pintea, 2012); L- liquid, V-vapor, kx- solid (soluble-?) entrapped or daughter phases(?), ky- silicate, carbonate grains. Scale bar in μm .

Fig. 98. Chalcopyrite “disease” in sphalerite and fluid and solid inclusions in paragenetic epithermal quartz crystal; **a.** tubular fluid inclusion trapped in a typical dusty “chalcopyrite disease” microtexture in sphalerite; contemporaneous fluid inclusions and opaque sulphides in **b** sphalerite and **d** in paragenetic quartz; **c.** coprecipitated microtexture of chalcopyrite in sphalerite. Coprecipitation was suggested during experimental work by Kojima (1990) to explain the intimate association of chalcopyrite in sphalerite. It was noticed that “it is likely that the typical “chalcopyrite disease” textures are generated from a comparatively high temperature solution following a typical solvation reaction such as (Kojima, 1990):



Notations: sph- sphalerite, cpy-chalcopyrite, L-liquid, V- vapor, ?-unknown, O-opaque, aqb- aqueous biphasic (L+V) fluid inclusions. Scale bar: 100 µm.

Fig. 99. Bimodal chalcopyrite “disease” in sphalerite from Cavnic-Boldut (Kelemen vein) Pb-Zn-Cu epithermal ore deposit suggesting a replacement process (Barton and Bethke, 1987) through a fracture dusted with chalcopyrite, cross-cutting a primary oscillatory growth zone in sphalerite. Replacement process in chalcopyrite disease microtexture was introduced by Barton and Bethke, 1987 and further discussed by Sugaki et al., 1987; Bortnikov et al., 1991. Replacement of the FeS from sphalerite with CuFeS₂ was suggested by Barton (1987) and Eldrige et al., (1988) showed experimentally that the process is characterized by such reactions:



The presence of copper in sphalerite Cavnic samples is suggested for example in Fig. 95e by the triangular opaque daughter phase formed inside the aqueous epithermal fluid and also by some isolated rounded blebs from Fig. 95a,b,c in sphalerite or in paragenetic quartz in Fig. 97a and Fig. 98d. Notations: cpy-chalcopyrite, bl-sphalerite, gz-growth zones. Scale bar in μm .

Fig. 100. Chalcopyrite “disease” partially oriented (coprecipitated) parallel to the oscillatory growth zone in sphalerite up to complete replacement (right down side of the picture); bl- sphalerite, cpy-chalcopyrite. Scale bar in μm .

Fig. 101. Intimate chalcopyrite “disease” microtexture by coprecipitation (?) in the yellow-brown sphalerite from Coranda-Hondol epithermal ore deposit (Metaliferi Mountains). Scale bar in μm .

Fig. 102. Pseudo-3D image feature in sphalerite by lattice coprecipitation or replacement with chalcopyrite tiny blebs. Coranda – Hondol epithermal ore deposit (Metaliferi Mountains). cpy-chalcopyrite, bl-sphalerite. Scale bar in μm .

Fig. 103. Discontinuous coprecipitation or replacement of chalcopyrite blebs in sphalerite from Coranda-Hondol epithermal ore deposit (Metaliferi Mountains); cpy-chalcopyrite, bl- sphalerite. Scale bar in μm .

Fig. 104. Various focuses of transmitted light microscopy onto the natural growing face of sphalerite from Coranda-Hondol epithermal ore deposit, showing the real half- shaped precipitated chalcopyrite blebs. The “lamellar-colomorphic” microtexture of chalcopyrite blebs is suggestive for precipitation in free voids in sphalerite already formed perhaps by resorption with reaction of acidic Cu- rich fluid related a mafic influx inside the magma chamber below. Coranda-Hondol ore deposit formation is caused mainly by the fluid escaped during the subvolcanic intrusion event in the Cretaceous sedimentary formations, and several magmatic successive events (even a porphyry- type mineralization was suggested by the presence of enargite-luzonite association on the “Avram brook” zone) (Udubaşa et al., 1979). Sx- chalcopyrite blebs (?), bl-sphalerite. Scale bar in μm .

Fig. 105. Aqueous biphasic fluid inclusions trapped in a yellowish growth zone of sphalerite from Coranda-Hondol ore deposit, associated with isolated sulphides blebs (chalcopyrite-?). Sx- sulfide blebs (chalcopyrite-?), L-Lichid, V-vapor. Scale bar in μm .

Fig. 106. Plan deformation features, solid-, melt and fluid inclusions types in the brecciated subvolcanic rock fragment pervasive hydrothermally altered from Coranda-Hondol open pit (Metaliferi Mountains); **a**, **b**, **c**, **e** - plan deformation paralel fractures (pdf) in quartz grain (pdf) similar to the features described in high pressure impact rocks (shocked quartz), e.g. Langenhorst (2002); Trepman and Spray (2003). They are very characteristic also in quartz from veinlets of porphyry copper deposit from Eastern Carpathians (e.g. Tibles massif) and Metaliferi Mountains, probably related to a strong decompression during exhumation (see also Fig. 22 and Fig. 109); **d**, **f**, **k**- opaque solid microcryst (O) isolated or agglutinated grain association; **h**, **l**, **n**, **p**- restitic solid mineral probably apatite (R-?) and rutile (R-?, rt), kx- silicate remnants or new dentritic; **i**, **j**, **o**- silicate melt inclusions containing brine (B), vapor (V) and glass (g); g.- recrystallized quartz phenocrysts (hqtz); **m**- decrepitated silicate melt inclusion (dh); **q**- brine inclusion association (B). Scale bar in μm .

Fig.107.

Fig. 107. Silicate melt and fluid inclusions types from β -quartz phenocrysts (2-3 mm) from quartz andesite (Săcărâmb type, e.g. Udubaşa et al., 1976) from Bocşa epithermal ore deposit (Metaliferi Mountains); **a.**- growth zoning in β -quartz phenocrysts; **b, c, d, f, j, q, u**- hydrothermally altered silicate melt inclusions; **e, g, m, n, o, p, t**- brine inclusions; **h, s, v**- vapor rich inclusions; **k, l**- silicate glass inclusions; **i**- opaque inclusion; **r** secondary aqueous biphasic fluid inclusions; gz- growth zone, dh- decrepitated halo, ag.- altered silicate glass; L-liquid, H-halite, V- vapor, kx- other daughter(?) solid phase, zr- zircon. The microthermometry of the brine inclusions (L+H+V) suggested salinity between 30 and 50 wt% NaCl eq., and final homogenization temperature of $\geq 400^\circ$ and 600°C . Their metallogenetic signification is very hard to be interpreted because many of them are secondary (and pseudosecondary) and perhaps formed “in situ” as alteration product of former silicate melt inclusions (Pintea, 2000- IGR unpubl. report). Scale bar in μm .

Fig. 108. Fluid inclusion types in epithermal quartz from Leopold upper level from Bocşa epithermal ore deposit (N Săcărâmb, Metaliferi Mountains); **a, l, h, j**.- possible hydrocarbons inclusions with pyrobitumen (?); **b, c, g, i**- multiphasic fluid inclusions; **d, f**- monophasic aqueous liquid inclusions; **i, k**- vapor rich inclusions; **P**-pyrobitumen(?), **x, y, z**,- unknown solid phases, **L**-Liquid, **Lh**- liquid hydrocarbons, **V**- vapor. Scale bar in μm .

Fig. 109. Microtexture features, solid and fluid inclusions types in aplitic quartz veins from Toroioaga massif (Maramureş Mountains); **a, b**- plan deformation microcracks system in quartz grains; **c, d, e, f, h, j, k, p, r, w**- brine inclusions; **g**. l.- biphasic fluid inclusions; **m, s, t, v, x**- vapor rich inclusions; **u**- coeval vapor-rich and brine inclusions; **q, t**- silicate melt inclusions; **n. o.** recrystallized acicular phase (tourmaline-?); **V**- vapor, **L**-liquid, **H**- halite, **ksx**- another soluble solid daughter phase, **kx**- unknown solid phase, **A**- aqueous fluid inclusion, **B**- brine inclusions, **T**- tourmaline, **o**- opaque, **SM**- silicate melt (glass $\pm$ crystals). Silicate melt inclusion microthermometry showed $T_h \geq 951^\circ\text{C}$ and coeval brine inclusions indicated 50-52 wt % NaCl eq. and T_h between 827°C - 974°C suggesting magmatic immiscibility (Pintea, 2014-PN 09210501 - IGR unpubl.). Scale bar in μm .

Fig. 110. Presumably magma mixing/mingling process suggested by the crystallized silicate melt inclusion containing brownish-dark mafic microminerals in acidic (white) silicate melt (now glass) in quartz and plagioclase phenocrysts from “Laleaua Albă” dacite (Baia Mare mining district); **a, b, d, e, f, g, i, o-** multiphasic silicate melt inclusions; **d, h, k, l** - probable two contrasting melt as a result of heterogeneous trapping (better evidenced in complex silicate melt inclusions from Roșia Montană β -quartz phenocrysts showed in Fig.29 A, which homogenized around 1050°C- Pintea and Iatan, 2013); **m-** isolated Fe-S-O melt globule in plagioclase; Magma mixing/mingling was argued from Laleaua Alba dacite based upon the presence of sieve microtexture in feldspar phenocrysts and xenocrysts, coronas with orthopyroxene around quartz (Kovacs, 2002) and also by recent EMPA analyses of isolated mafic solid minerals (biotite, amphibole) inclusions in quartz and plagioclase or K-feldspar and analyses of acidic silicate melt inclusions which shown distinctive ranges of SiO₂ content (Naumov et al., 2014). Notations: m- mafic minerals, o-opaque, V-vapor, g- glass, r- restitic apatite, ?- unknown. Scale bar in μm .

Fig. 111. Magmatic vapor phases in the contraction vapor bubbles from silicate melt inclusions in quartz and plagioclase from “Laleaua Albă” dacite (Baia Mare mining district); **a.** three-phasic aqueous fluid bubble in silicate glass inclusion. Biphasic inclusions (L+V) in the same silicate melt inclusion types measured by Naumov et al., 2014 showed salinity of 0.5 wt% NaCl eq, density of 0.84 g/cm³ and Th=225°C, the author suggesting a minimum trapping pressure of about 8kbars for 800°C formation temperature; **b.** (-122°C), **c.**(-50°C), **d.**(-56.2°C), **e.**(25°C), **f.**(-90°C), **g.**(-55°C), **h.**(-55.3°C)- CO₂-rich secondary and pseudosecondary fluid inclusions at indicated temperatures; **j, k, l, m, n, o, p, q, r-** contraction vapor bubbles in silicate melt inclusions sometimes with solid and a tiny film of liquid CO₂ at room temperature conditions; **i-**association of silicate melt and vapor-rich inclusions in a secondary or pseudosecondary microcrack in quartz. Note: CO₂ rich inclusion pictured in **b** and **c** homogenized in vapor phase at +25.3°C, from **f** and **g** Th= +23.6°C, from **d** and **e** Th= +21.2°C (Pintea, 1998 unpubl; Pintea, 2014b). The calculated trapping pressure, based upon CO₂ density value of about 0.2 g/cm³ give around 0.4 kbars which means ≤1.5 km depth formation conditions, which suggest that the “Laleaua Alba” dacite was re-crystallized very close to the surface being brought out by hot magma influx (1100°-1200°C) from initial deep source (20-30 km). The vapor bubble content (soluble minerals and silicate, carbonate, sulfate solid phases) for unaltered silicate melt inclusions could be used successfully in magmatic vapor characterization and exploration purposes as it was documented elsewhere by Kamenetsky et al., 2002. Notations: df- decrepitation microfissure system oriented parallel to the C-axis of quartz, ks- soluble daughter phase (?), V-vapor, L-liquid, Sc- solid CO₂, kx- other daughter (?) solid phase (silicate, carbonate), Lc- CO₂- liquid film, SM- silicate melt inclusions. Scale bar in μm (b, c, j, k, l, m, n, o, p, q, r- 10μm).

Fig. 112. Fluid and “melt” inclusions types in epithermal quartz crystals collected during “Field application” of the Geol. Soc. of Romania, Baia Mare branch (22-23 09.1990), from Hudin massif, near Arcer peak (Țibleș Mountains); **a, b, d, f, i, k, l, m, p, u, v**- multiphasic inclusions with various ratio between solid, liquid and vapor phases; **c, r**- hydrocarbons fluid inclusions (pyrobitumen-?); **e, g, j, o, t**- vapor-rich inclusions; **h, i, n, s**- aqueous biphasic fluid inclusions; **q**- brine inclusion (?); **Fi**- fluid inclusions, **o**-opaque, **kx, ks**- unknown solid daughter(?) phases, **L**-liquid, **Lc**- CO₂-liquid rim, **Lh**- liquid hydrocarbon, **P**-pyrobitumen-?, **?**- unknown, **V**- vapor, **H**-halite(?). Scale bar: 10μm; **i. s.**- 100μm.

Fig. 113. Microsolid-, and fluid inclusions in remelted sphalerite (i.e. low-Fe yellow sphalerite-Udubaşa et al., 1983) from metamorphic upper Precambrian Rodna-Guşet Pb-Zn mineralization (Făget adit); **a. f.**- aqueous biphasic fluid inclusions; **c, d, g, h, i, k, m, o, u, x**-vapor rich inclusions; **b, c, d, j, l, q, r, s, t, v, w, y**- solid microinclusions (Pintea et al., 2021 - preliminary Raman analyses- Rruff data base- sugested the presence of Fizelyite- $\text{Ag}_5\text{Pb}_{14}\text{Sb}_{21}\text{S}_{48}$, Germanite- $\text{Cu}_{13}\text{Fe}_2\text{Ge}_2\text{S}_{16}$), Corkite- $\text{PbF}_3(\text{SO}_4)(\text{PO})_4(\text{OH})_6$ and possible zircon- ZrSiO_4 microcrysts, noted in the pictures undifferentiated by **zr**); **m, q, r, s, w**- others solid daughter (?) phases. Other notations: V-vapor, L-liquid, x-unknown, d_h-decrepitated halo. Scale bar in μm .

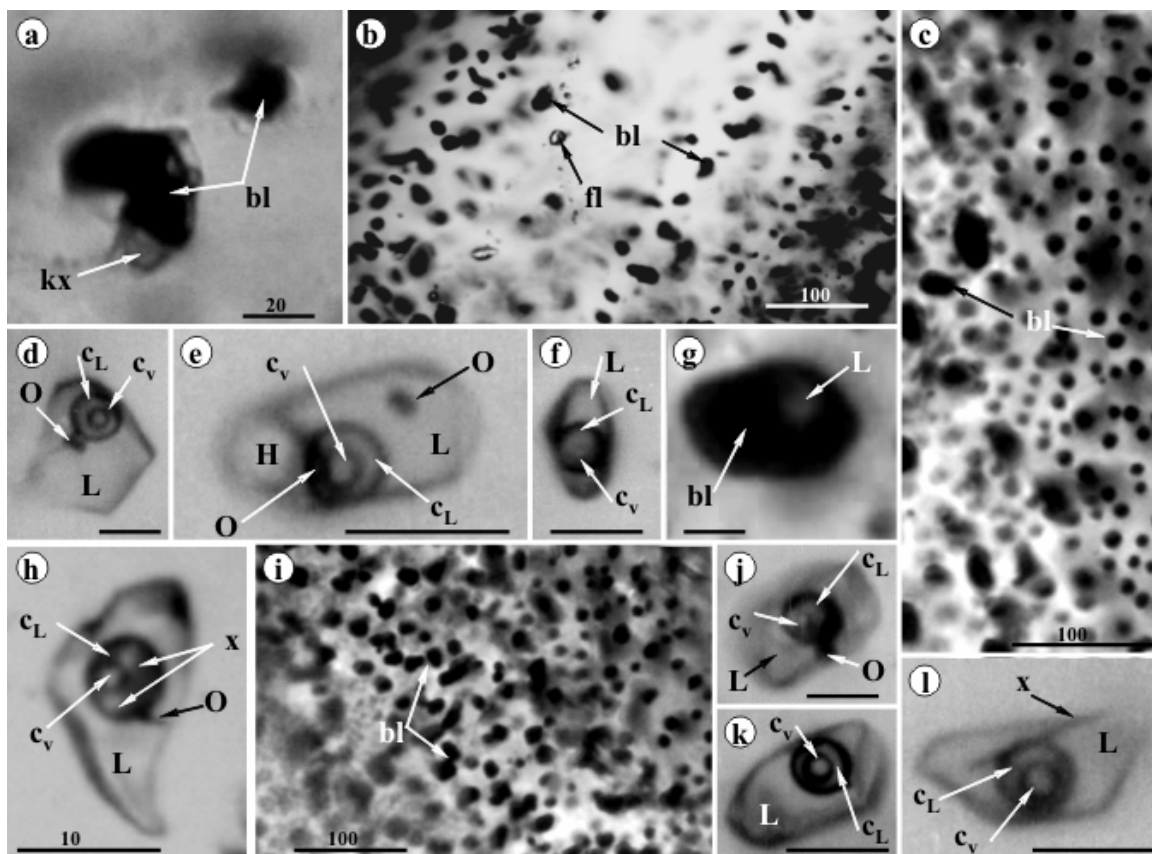


Fig. 114. Sphalerite globules (remelted) and CO₂- rich aqueous fluid inclusions in quartz from Blazna-Guşet metamorphic Pb-Zn mineralization (Faget adit); **a, g**, solid sphalerite globules (flakes) trapped together with liquid and others microsolid phases; **b, c, i**- sphalerite and fizelyite (?) flakes and blebs in trails of the recatized microcracks in quartz; **d, e, f, h, k, l**- CO₂- rich multiphasic fluid inclusion types in the same quartz samples; fl- fluid inclusions; bl- sphalerite, kx- other solid phases, H- halite, c_L- CO₂- liquid, c_V-CO₂ gas, L- aqueous liquid, O-opaque, x- unknown; (modified from Pintea 2012). Remobilization of sulphides as remelted product during metamorphism is a critical feature encountered in many metamorphic Pb-Zn ore deposits (e.g. Frost et al., 2002). Scale bar in µm; d, e, f, g, j, k, l- ca 10µm.

Fig. 115. Two types of FIAs of the system H₂O-CO₂-NaCl trapped in (re)crystallized quartz veins from the REE-MoS₂ mineralizations of the NW Ditrău massif (Mesozoic) of the Jolotca mining prospect; **a, b, c, j, i, h, g, k, l, n, o, p, q, r, s, t, u, v, w, x, y, z, b', c', e', f', g', k', m'**- complex carbonic - rich type; **d, e, f, m, d', h', g', l'**- brine type. Firstly, described by I. Pintea in the Jolotca epithermal prismatic euhedral quartz (750 Jolotca- main adit) and presented by Pomârleanu et al., 1984 (unpubl.) and further data from 21 Jolotca - adit, presented by Pintea, 1991a, 1995a, 1996b; Pintea and Diamond, 1994 (unpubl.), mentioned in Fall et al., 2007; Notations: L₁- aqueous liquid, L₂- CO₂- liquid, Kx- unknown (KCl-?), H- halite, V- gas. Pictured at ≤+10°C in the microthermometric stage, under the microscope. Scale bar in µm.



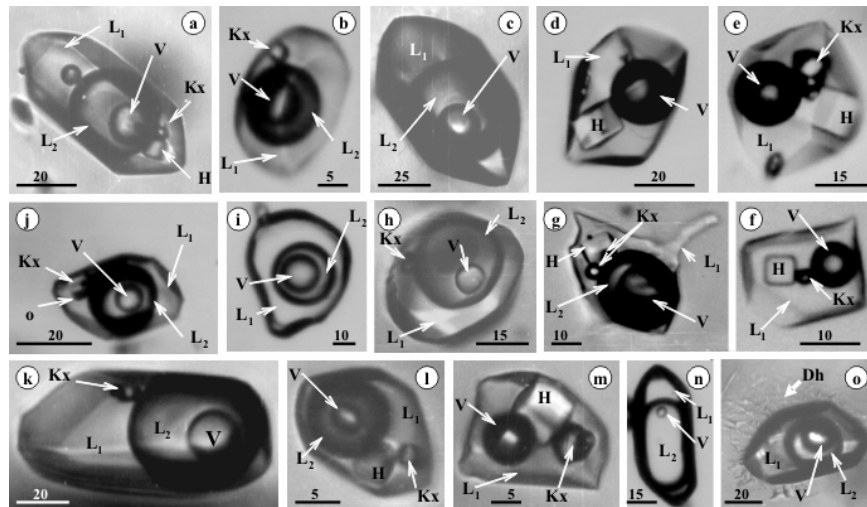


Fig.116. Microthermometric cycle in a gaseous inclusion (presumably empty at Troom), trapped in epithermal quartz. At temperature room condition in **a.** the microcavity look like empty but when was cooled down to -170°C, in **b.** three grains of solid were sublimated (s) . The first solid grain melted in **c.** between -112° and -94°C (H₂S) , **d.** the second melted around -84°C (CH₄) and in **e.** the ultimate grain melted sharply at -56.6°C (CO₂) , in **f.** back to room temperature the fluid inclusion contain a presumably pure and invisible gas mixture of CO₂-CH₄-H₂S, no liquid phase was detected by microthermometry in this fluid inclusion type (modified from Pintea and Iatan, 2013); V- vapor, S- sublimated gas mixture; Scale bar: 30 µm.

Fig. 117. Clathrate ($\text{CO}_2 5\frac{3}{4}\text{H}_2\text{O}$) microthermometry in $\text{CO}_2\text{-H}_2\text{O-(CH}_4\text{)}$ fluid inclusion trapped in epithermal quartz from Jolotca REE-MoS₂ mineralization (Mesozoic Ditrau alkaline massif); Complete freezing was noted at -91.3°C , and during reversal heating the solid CO_2 melted at -57.6°C and clathrate melted at $+11.8^\circ\text{C}$. On further heating the complete CO_2 homogenization was recorded at $+19.7^\circ\text{C}$; c- clathrate, L₁- aqueous liquid rim, L₂- CO_2 -liquid, V-gas. (Pintea, 1991a, 1995a, 1996b). Scale bar in μm

Fig. 118. Complete microthermometric cycle of CO₂-H₂O-(CH₄) fluid inclusion trapped in the epithermal quartz from Jolotca REE-MoS₂ mineralization (Mesozoic Ditrău alkaline massif); Complete freezing was noted between -96.6°C and -121.9°C, and during reversal heating the TmCO₂ solid = -57.7°C, Tm clathrate recorded at +10.1°C and Th CO₂ = +16.1°C; **a.** +9.8°C, **b.** -17.8°C, **c.** -35.7°C, **d.** -77.8°C, **e.** -121.9°C, **f.** -84.8°C, **g.** -73.4°C, **h.** -72.2°C, **i.** -67.2°C., **j.** -65.2, **k.** -57.7°C, **l.** -43.3°C, **m.** -36.8°C, **n.** -19°C, **o.** -8.6°C, **p.** -3.3°C, **q.** +3.5°C-, **r.** +9°C, **s.** +15.6°C, **t.** +17.7°C; L₁- aqueous liquid rim, L₂- CO₂-liquid, V- gas, Cs- solid CO₂, c- clathrate, x- unknown. (Pintea, 1991a, 1995a, 1996b); Scale bar in µm.

Fig. 119. Microthermometry of the carbonic-brine fluid inclusion containing more than one solid phase (daughter-?) in the euhedral hydrothermal quartz from Jolotca mining district (Mesozoic Ditrău massif); **A.**+25°C, **B.**-intermediate, **C.**-70°C, **D.**-101.9°C, **E.**-intermediate, **F.**-74.5°C, **G.**-59.8°C, **H.**-17°C, **I.**-2.5°C, **J.**+9.7°C ; kx-unknown, H-halite, L₁- aqueous liquid, L₂-CO₂ liquid, V- gas, h- hydrohalite (?), c- clathrate, Cs- solid CO₂.(compiled from Pintea, 1991a, 1995a,1996b). Scale bar in μm.

Fig. 120. Total homogenization temperatures in CO₂-H₂O fluid inclusions trapped in euhedral quartz crystals from Jolotca REE-MoS₂ mineralization (Mesozoic Ditrău massif). **A.** +13°C, **B.** ≥ 40°C (ThCO₂= -2° to = +31.5°C), **C.** Th= 275°-280°C, **D.** +10°C (n=38, Pintea, 1991a, 1995a, 1996b); L₁- aqueous liquid, L₂- CO₂ liquid, V- vapor. Scale bar in μm.

Fig. 121. Two immiscible silicate melt (now glass) trapped in heterogeneous silicate melt inclusions from nefeline syenite from Ditrău Mesozoic alkaline massif; **a, e, g, h, i, k-** immiscible silicate glass inclusions; **b, c, d, f, j, l-** multiphasic silicate glass inclusions; V- vapor, g₁- white glass (syenitic melt); g₂- dark gray glass (mafic silicate melt); m- mafic daughter microminerals; kx- unknown; Two or three magmatic events were envisaged to interact each others during Triassic/Jurassic time represented by syenitic and ultramafic rocks (gabbroic) and their interaction formed complex petrologic products during the genesis of the Ditrău massif (e.g. review in Fall et al., 2007). Such kind of heterogeneous silicate melt inclusions pictured in this figure are pristine samples to study silicate melt unmixing or magma fractionation processes. Scale bar 10µm.

Fig. 122. Silicate melt inclusion types in zircons from granitoidic rocks from South Carpathians (zircons courtesy T.Berza); **a, b, c, f, g**- biphasic silicate glass inclusions; **d, h**- Partially remelted (unhomogenized) silicate melt inclusions; z- zircon, sm- silicate melt inclusion, g-glass, Kxy- remelted daughter microcrystals (partially); V-vapor. More microthermometry in Table 3 (Pintea in Berza et al., 2007-unpubl.). Scale bar in μm .

Fig. 123. Silicate melt inclusions in zircons from Neogene volcanic rocks (Dej Tuff, Dănești and Laleaua Albă dacite; Roșia Montană and Săcărâmb dacite and andesites (some sample courtesy L.Robu); **a, b, d, h**- multiphasic silicate melt inclusions; **c, e, g**- biphasic glass inclusions, **f**- monophasic silicate glass inclusion; **z, z_o**- zircons, **z_i**- inherited zircon, **ap**- apatite, **sm**- silicate melt inclusion, **g**- glass, **kx**- microcrystal(s), **V**- vapor. Microthermometry: **a**. Th= 923°C and **g**. Th= 783°C, generally homogenization temperatures in silicate glass inclusions ranged between 552°C-990°C (Pintea in Berza et al., 2007-unpubl.). Scale bar in μm.

Fig. 124. Fluid inclusion types in volcanic - exhalative native sulfur from Gura Haitii open pit from Călimani caldera (sample courtesy I. Seghedi, 1982); **a, b, c, d, e, j, m, n, v, w, x, y, b', c'**- vapor rich inclusions; **f, g, h, i, l, o, p, r, z, a'**- decrepitation features of the vapor rich inclusions; **q, s, t, a'**- sulfur melt-like inclusions (?); **V**- vapor, **S**- unknown; Pristine droplets of immiscible subcritical fluid - sulfur were described as globular inclusions in plagioclase from Petricelu andesitic apophysis (Balintoni, 1970) and worldwide as spherules in acidic crater lakes (e.g. Mason et al., 2001). Our crushing experiments on Călimani volcanic sulfur, under the microscope, shown mainly H₂O vapor in the vapor-rich inclusion type (Pintea, 2007- unpubl.). Scale bar in μm.



Fig. 125. Fluid inclusion types in the epithermal (geothermal) quartz crystals from Cucu and Vârghiș volcanic environments (Harghita Mountains- sample courtesy I. Seghedi, 1992); **a, h, m, o, r**- aqueous biphasic fluid inclusions; **b, c, d, f, g, i, k, l, n, p, q**- vapor-rich inclusions; **e**. heterogeneous liquid inclusion(?); **j**- multiphasic fluid inclusion(?); L-liquid, V- vapor, Lh- liquid hydrocarbon(?), x- undetermined solid, ?- unknown. Microthermometric cycle (Pintea, 1992- unpubl.): **r**. +25°C; **s**. -70°C; **t**. -21°C; **u**. -15°C; **v**. +200°C; **w**. +230°C (Th); T_{mi}=-9.5°C (salinity = 13.4 wt% NaCl eq., P= 26 bar). Frequently, the vapor bubbles from biphasic liquid-rich inclusions seem to have a CO₂-liquid rim around its. This could be a feature of the magmatic fluids trapped in geothermal quartz. Blamey and Norman (2001) noticed that the most primitive or most magmatic fluid contain: 7-8 wt% NaCl eq., 5-6 mol % CO₂, 0.5 – 1 mol% CH₄, 0.01-0.02 mol % H₂S and N₂/Ar>400. Nevertheless, it seems that the fluid phases trapped in the Cucu and Vârghiș quartz crystals have mixed origin being contaminated with meteoric fluids containing also liquid hydrocarbons and/or pyrobitumen, otherwise a characteristic feature in the majority of the Neogene epithermal ore deposits from Carpathians. More data on petrography and microthermometry from Harghita Mountains (Sântimbru-Băi) in Pintea and Laczko, 2005). Scale bar in μm.

Fig. 126. Silicate melt remnants and fluid inclusions types in olivine and pyroxene peridotitic nodules brought out by Plio-Pleistocene alkali basaltic volcanism from the Perșani Mountains (Bogata Valley, SE Transylvania Basin); **a, h, k, p, a', b', h'**- dark-brown silicate glass inclusions vs. spinel like microinclusions (primary); **f, g, i, q, s, j'**- immiscible silicate glass and sulfide globules (secondary); **b, c, e, j, l, m, n, o, r, t, u, v, w, x, y, z, c', d', f', g', j'** - carbonic fluids ± silicate glass ± sulfide (multiphasic, mainly secondary); **g₁**- dark-brown (ultramafic) silicate glass vs spinel microcrystal, **g, g₂**- white silicate glass(alkali basaltic), **c_L**- liquid CO₂, **c_V**- gas CO₂, **c**- carbonic fluid phases, **V**- vapor, **dh**- decrepitation halo, **kx**- silicate daughter phases, **sg**- silica globules, **s**- sulfide; Reequilibration features of the pure carbonic (sometimes dark sulfide globules) and multiphasic carbonic ± silicate were described at ca 3-4 kb (12-15 km) and 1100°-1200°C in the volcanic conduit (Pintea and Mârza, 1989). Immiscibility between calcicarbonatitic and silicate melts in veinlets cross-cutting the peridotitic nodules from Persani Mountains basaltic andesites were documented by Chalot-Prat and Arnold, 1999. Scale bar in μm. ⇨

Fig. 127. Primary “en chevron” relict microtexture in Badenian halite from Slănic Prahova (Băile Baciului mining prospect); **a.** internal dihedral zonation growth bands decorated with monophasic and biphasic liquid - rich inclusions; **b.** - distribution of monophasic liquid inclusions in the growth zone; L- liquid, V- vapor, kx- diagenetic solid phase (recrystallized). New hypothesis on the genesis of the halite from Transylvania Basin, petrography and microthermometry of fluid inclusions in halite from Ocna Dej and Slănic Prahova were published by Balintoni and Petrescu, 2002; Pomârleanu and Mârza, 2003; Har et al., 2006, respectively. Scale bar in μm .

Fig. 128. Sedimentary microtexture remnants of monophasic fluid inclusion associations in the Badenian recrystallized (partially) halite from Ocna Dej and Slanic Prahova salt mining prospects. **A. C. D.**- rectangular sedimentary relicts = primary growth zones in halite; **E. F. G. K. L.**- isolated groups of former rectangular growth zones in halite; **B. E. I. J.**- isolated liquid - rich liquid inclusions surrounded by halos. L- liquid, V- vapor (compiled from Pintea, 2005; 2008). The rounded corners of the primary “negative crystal” cavities is suggestive for equilibrium internal zones of the halite during recrystallization (in accord with NaCl equilibrium shape simulated by G. Barkema and M.Holzer, <http://www.lassp.cornell.edu/-unpubl>), and generally they contain the “unique” mother sample of the seawater (as liquid inclusions) used for paleotemperature estimation and chemistry evaluation of the precipitation marine/lagunar conditions (e.g. Petrichenko, 1977; Roedder, 1984a; Goldstein and Reynolds, 1994; Zimmermann, 2001; Kovalevich and Vovnyuk, 2010). Scale bar in μm .

Fig. 129. “Diagenetic” fluid inclusion types in Badenian halite from Ocna Dej and Slănic Prahova mining prospects; **a, b, c, d, f, g, i, j, k, l, m, n, o, p-** liquid rich inclusions with solid(s) and immiscible liquid (?) or gas droplets/bubbles; **e, h, q-** vapor (gas)- rich fluid inclusions; L- aqueous liquid, s- sulphate minerals (mainly anhydrite) and other crystallized microcrystals, d- dendritic (argillaceous) grains (agglutinated), Lh- droplets or bubbles of liquid/gas hydrocarbons (?). Scale bar: 100µm for all.

Fig. 130. Multiphase fluid (melt) inclusions in langbeinite from Tazlău potassium and magnesium salt deposit prospect; **1, 3, 4, 9, 10, 11, 13-** multisolid(s) with bitumen droplets; **2, 5, 6, 7, 8, 12, 14, 15, 16-** multisolids(s) with vapor (gas) $\pm$ bitumen droplets, Sx, Sy, Sz- salt/sulfate microminerals, S- sylvite (?), P- bitumen droplets, KF- potassium-magnesium dominant solid phase (?), V- vapor/gas. Host mineral description and genesis of K-Mg salt from Tg - Ocna - Găleanu -Tazlău were made by Rădulescu, 1960, Paucă, 1966, Stoica and Gherasie, 1981 and others. Scale bar in μm .

Fig. 131. Microtexture features and fluid inclusion types in recrystallized salt at laboratory conditions (pure H₂O, T_{room} and ambient pressure) from Tazlău mining prospect (Pintea, unpubl); **a**- recrystallized mineral association containing halite (H) and probably langbeinite (Kx); **b, j**- microtexture in langbeinite (?) and dihedral zonation in halite, respectively; **c**- biphasic fluid inclusion in recrystallized langbeinite (?); **d, e, f, g, h, i, k**- liquid dominated fluid inclusions in the associated recrystallized halite; Scale bar in μm ; d. e. f. g. h. j. k.- 100 μm .

Fig. 132. Fluid inclusion types and microtexture features of the recrystallized halite crust around Cojocna old mining district (sampled by I. Pinteà at 30.09. 2003); **a, b, d, f, g, h-** monophasic and biphasic liquid-rich inclusions; **c, e-** microtextural features; L-liquid, H-halite, V-vapor, chs- dihedral growth zone (“chevron” microtexture); Microthermometry: **i.** +29.5°C; **j.** intermediate; **k.** +31.5°C = Th (Pinteà, 2003 and unpubl.). Scale bar in μm .

Fig. 133. The trapping temperature estimation by vapor bubble nucleation and homogenization, directly under the microscope (Pintea, 2005b; 2008b) in primary fluid inclusion in halite from Slănic Prahova mining prospect (Băile Baciului); **a.** -5.5°C, **b.** -20.4°C, **c.** +2.3°C, **d.** +10.1°C; L-liquid, V-vapor. Homogenization by vapor bubble recovery in monophasic liquid inclusion in evaporate minerals (Roedder, 1971; Petrichenko, 1973), was revised and applied for paleotemperature estimation in sedimentary basins by Golstein and Reynolds, 1994, Roberts and Spencer, 1995; Lowenstein and Brown 1998, among others. An ultimate high-tech method using laser pulse is used to generate vapor bubble in monophasic metastable liquid inclusions in various minerals (Krüger et al., 2007). Scale bar in μm .

Fig. 134. Microthermometric cycle of primary monophasic liquid inclusion showing decrepitation after second homogenization in halite from Slanic Prahova salt mining prospect; **a.** -12°C, **b.** +14.3°C (Th₁), **c.** -4.5°C, **d.** +5.3°C, **e.** -90°C, **f.** -70°C, **g.** -25°C, **h.** +25°C, **i.** +25°C after final homogenization at +101.8°C (Th₂); hydrohalite melted around ±0.1°C; L-liquid, V-vapor, Hh-hydrohalite. Completed microthermometry on several chloride salts-water systems from laboratory-grown halite was presented by Davis et al., 1990. Scale bar in µm.

Fig. 135. Completed microthermometric cycle of the monophasic liquid inclusions in the recrystallized halite around a fossilized tree (*Sequoia* sp.- I. Petrescu comm. pers. - 1988) from Ocna Dej mining prospect (Transylvania Basin); **a**.-4.3°C, **b**.-8.5°C, Th= +14.1°C (upper left); Th= +16.9°C (down right); **c**.-44°C, **d**.-22.4°C, Tmi= -21.8°C, **e**.-12°C, **f**.-8.6°C, **g**.-2.2°C, TmHh= ± 0.1°C, **h**. +4.3°C; L- liquid, V-vapor, I-ice, Hh- hydrohalite (compiled from several cycles - Pintea, 2005b; 2008b). Scale bar in µm.

Fig. 136. Fluid inclusion types in the “Marmarosh diamond” quartz crystals from Bocicioiu Mare (Maramures district, Romania) from Neocomian-Albian argillaceous black shales from the Transcarpathian flysch (quartz sample courtesy V.Ghiurcă in Pintea and Ghiurcă, 1991 unpubl., Pintea, 1995a); **a**, **b**- quartz crystal host; **c**, **g**, **h**- monophasic liquid hydrocarbon inclusions, **i**, **a'**, **b'**- carbonic gas-rich inclusions; **d**, **e**, **f**, **j**, **m**, **n**, **p**, **r**, **s**, **t**, **u**, **v**, **w**, **x**, **y**, **z**, **c'**- multiphase hydrocarbon inclusions; **k**- aqueous biphasic liquid-rich inclusions; Symplified microthermometry (example): **c'**.+25°C, **d'**. to **e'**.- around +300°C, **f'**.-120°C (TmCH₄= -82.4°C), **g'**.+25°C; generally hydrocarbon liquid- rich inclusions containing CH₄ bubble homogenized between +60 to +600°C and CH₄ solid melted between -66° and -82,1°C (Pintea, 1995a). Coeval aqueous rich inclusions shown Te= -21°C, Tmi=- 4.5 to -5.6°C (7-9 wt% NaCl eq.), Th= 150°-250°C ; Pt(corrected)= 0.5-1.0 kbars (Pintea, 1995); Banerjee and Ghiurcă (1997) identified in the “Marmarosh Diamond” quartz crystals by FTIR absorption spectroscopy the presence of H₂O, CO, CO₂, H₂S, CH₂, CH₃ and CH₄; dq- quartz specimen, Fi- fluid inclusions, Lh-liquid hydrocarbons, cg- carbonic gas, b- bitumen, V- vapor, L-liquid, I-ice, sc- solid CH₄. Experimentally work on synthetic oil-water mixtures at high P and T shown similar behavior between 180°-500°C and 1-150MPa (e.g. Balitsky et al., 2009). Microthermometry of liquid hydrocarbon-CH₄ gas + H₂O are useful for hydrocarbon identification and eventually for study oil migration and maturation during burial history of the country rocks, but not for determining fluid inclusions trapping conditions. For that purpose, the coeval aqueous-rich inclusions seem to be a good geobarometer in conjunction with external data offered by the geothermal gradients (e.g. Pintea, 1995) or tectonobarometers and (re)equilibration features of fluid inclusions (e.g. Vityk et al., 1996); More data about “Marmarosh diamond” quartz crystals and their fluid inclusions in Jarmolowicz-Szulc, 2003; Jarmolowicz-Szulc et al., 2006, among others. Scale bar in µm.



Fig. 137. Fluid inclusion types in quartz from Măgura Țebeș epithermal ore deposit (Caraci-Măgura Țebeș volcano-subvolcanic structure (Jude, 2012; sample courtesy S. Boștinescu); **a, b, j**- liquid- rich fluid inclusions; **c, g, h, i, k, l, n**- vapor- rich inclusions; **d**. boiling assemblage; **m**.- vapor- rich vs. liquid hydrocarbon inclusion; **e, f**.- microcrack types in quartz,; L-liquid, V-vapor, P- pyrobitumen (?), Ks,?- unknown solid phases, Lp- liquid hydrocarbon (?). Scale bar in μm .

Fig. 138. Oscillatory zoning in β -quartz phenocrysts from Măgura Sturzii dacite-rhyolite subvolcanic structure from Bârgau zone (Bistrița Năsăud county); **a, j**- oscillatory growth zones; **b, c, d, e, f, i, h, g, j, k**- altered silicate melt inclusions (ag); **l, m, n, o, p, r**- secondary fluid inclusions associated with altered silicate melt inclusions; q.- vapor - rich inclusions; dg- hydrothermally altered silicate melt inclusions, fc- microfissures oriented to c quartz axis, G- glass, mf- decrepitation microcracks, x- micromineral inclusion, PS- pseudosecondary, sh- “sweet” silicate glass halo, g- silicate glass globule, L- liquid, H- halite, V- vapor, kx- unknown solid. Scale bar in μm .



Fig. 139. a, b, c, d, e, f, g- Partially remelted features in silicate melt inclusions like those pictured in Fig 138, heated up to 1050°C in the stage under the microscope, at 1 bar pressure (Pintea, unpubl.) in β -quartz phenocrysts from Măgura Sturzii subvolcanic dacite-rhyolite structure (Bărgau Mountains); V-vapor bubbles, G- glass, fc- microfissures oriented along the c axis of β -quartz phenocrysts, kx- recrystallized microminerals, sd- “sweet” decrepitation halo. Fluid inclusion microthermometry in Papp et al. (2003). Scale bar in μm .

Fig. 140. Variety of silicate melt inclusions in plagioclase phenocrysts from andesitic (white) volcanic rocks (lava flow) from Cetățeaua Hill (Dumbrava village, Cluj county); **a, b, d, e, f', g', j', k', l', m'** - silicate glass inclusions (mostly biphasic); **f, h, i, j, k, l, m, n, o, q, s, t, u, v, x, y, z, b', c', d', h', j'** - multiphase crystallized melt inclusions; **e, r, a'** - micromineral inclusions; **g** - secondary solid granular inclusions; **p** - coeval (immiscibility) silicate glass inclusion and crystallized melt inclusion; **w** - secondary liquid(?) inclusions; **G** - glass, **V** - vapor, **kx, kxs, ksx, kxy, kxyz** - unknown solid phases, **O** - opaque, **zr** - zircon. Petrologic data from Ștefan et al., 1985. Scale bar in μm .

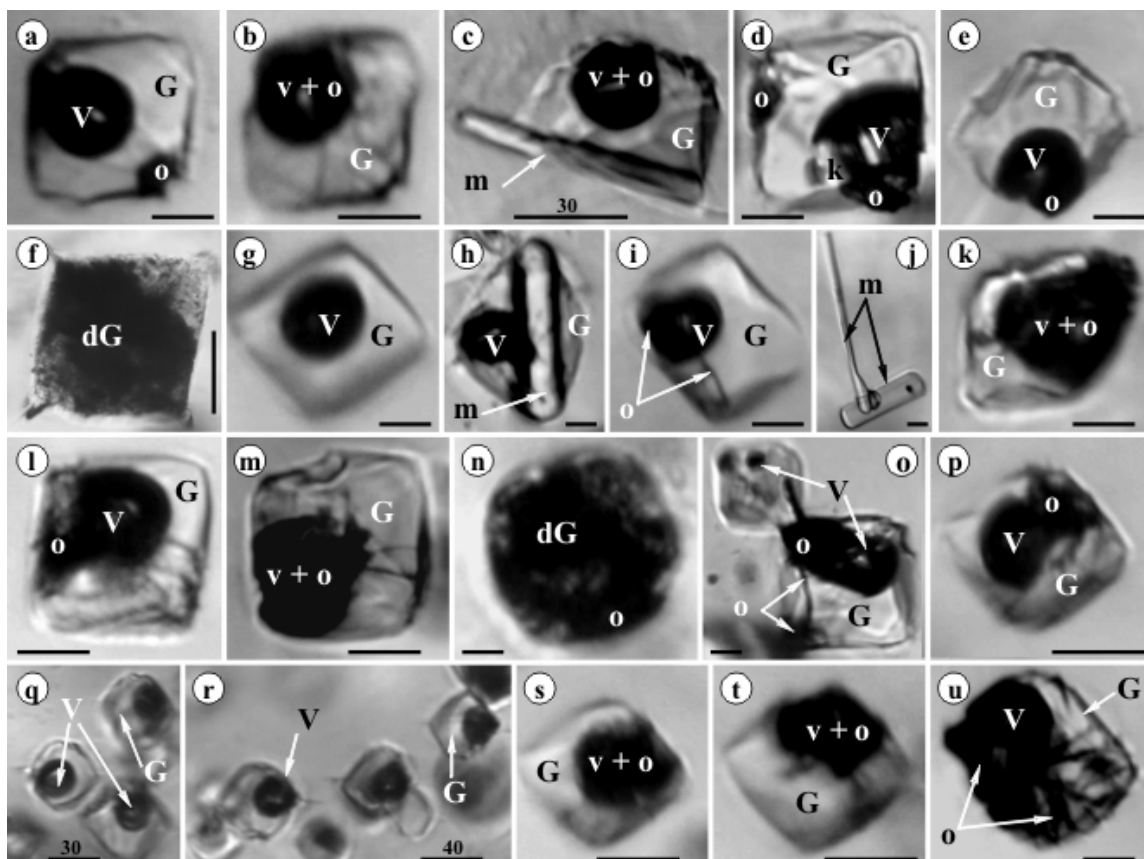


Fig. 141. Silicate melt inclusions types trapped in quartz (**a, b, c, d, e, f, g, h, i, j, k, l, n, o, p, q, r, s, t, u**) and feldspar (**m**) from Ulmoasa dacite collected from Ulmoasa Valley close to the confluence with Baita Valley on the right side (Baia Mare region, Maramureș county). Notations: **V** - vapor, **G** - silicate glass, **dG** - devitrified silicate glass, **O** - opaque, **m** - microsolid (mainly apatite). Scale bar in μm .

Fig. 142 Liquid monophase-, (a, b, c, d) – biphasic-, (i, l, m, p, q, r, w, x, y) and triphase-, (e, f, g, h, j, k, n, o, s, t, u, v) fluid inclusions in barite nodules from the bentonite Valea Chioarului mining prospect (geol. V. Todoran, 1997 - sample courtesy). Notations: L-liquid, H- halite, V- vapour. Homogenization temperature in un-stretched biphasic fluid inclusions ranged between 154° and 240°C (n = 30). Rarely, triphase fluid inclusions (n=4) showed Th= 263-330°C, with estimated salinity of 30-34 wt% NaCl eq., and formation pressure between 28 and 96 bars from a boiling fluid vent evolved under seawater down to 1000m. Scale bar: 10µm (Modified from Pintea, 2016).

Fig. 143. Various filling ratio in fluid inclusions trapped in barite nodules from Valea Chioarului mining district suggesting heterogeneous mixtures of the trapped boiling fluid. Vapor-rich + liquid $\pm$ halite $\pm$ unknown solid phases: **a, b, c, g, h, i, j, k, l, q**; Biphasic: **d, e, f, o, r, t, w, y**; Monophase liquid: **n, u, v, x**; Liquid + unknown solid (s): **m, s**. Scale bar in μm .

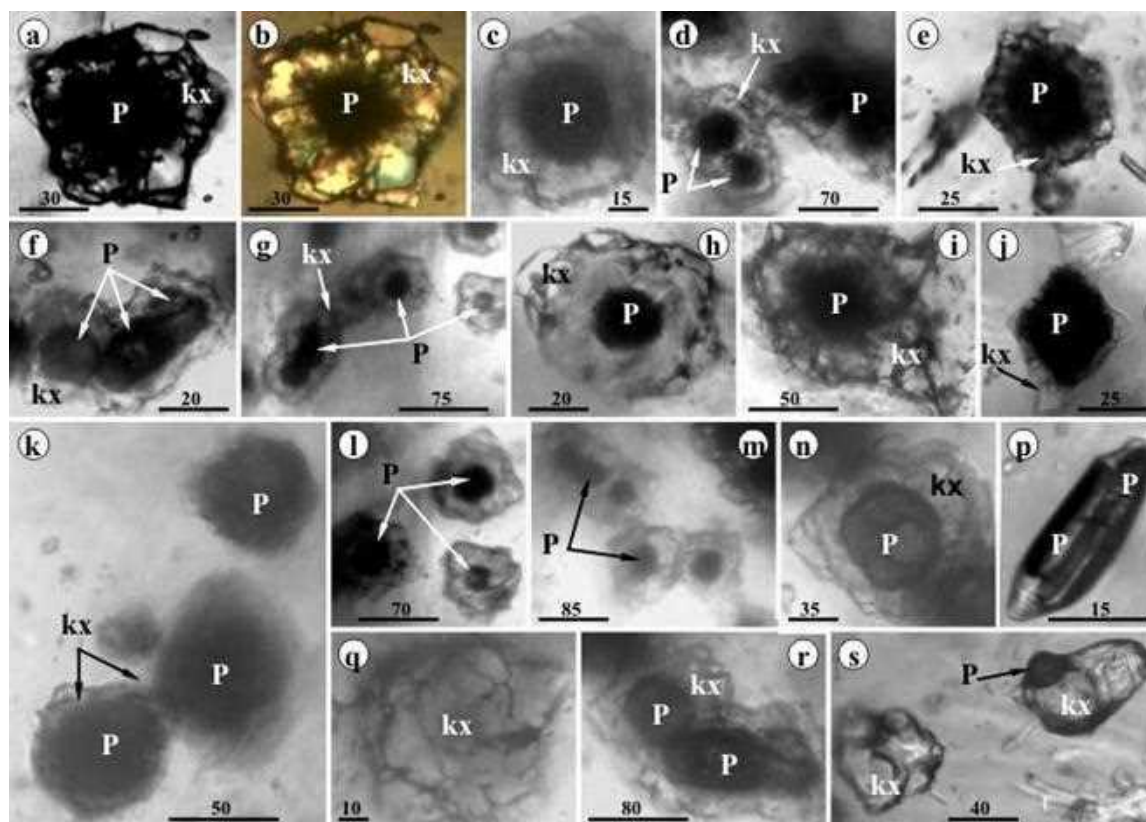


Fig. 144. Presumable recrystallized (solidified) multiphasic (?) fluid inclusions during barite diagenesis and bentonite formation in the Valea Chioarului mining district.
P, kx - unknown solid phases. Scale bar in μm .

Fig.145

Fig. 145. Crystalline and amorphous solid microinclusions trapped accidentally in the barite nodules from Valea Chioarului mining district. They are also trapped in fluid inclusion as pictured in **p**. Scale bar in μm .

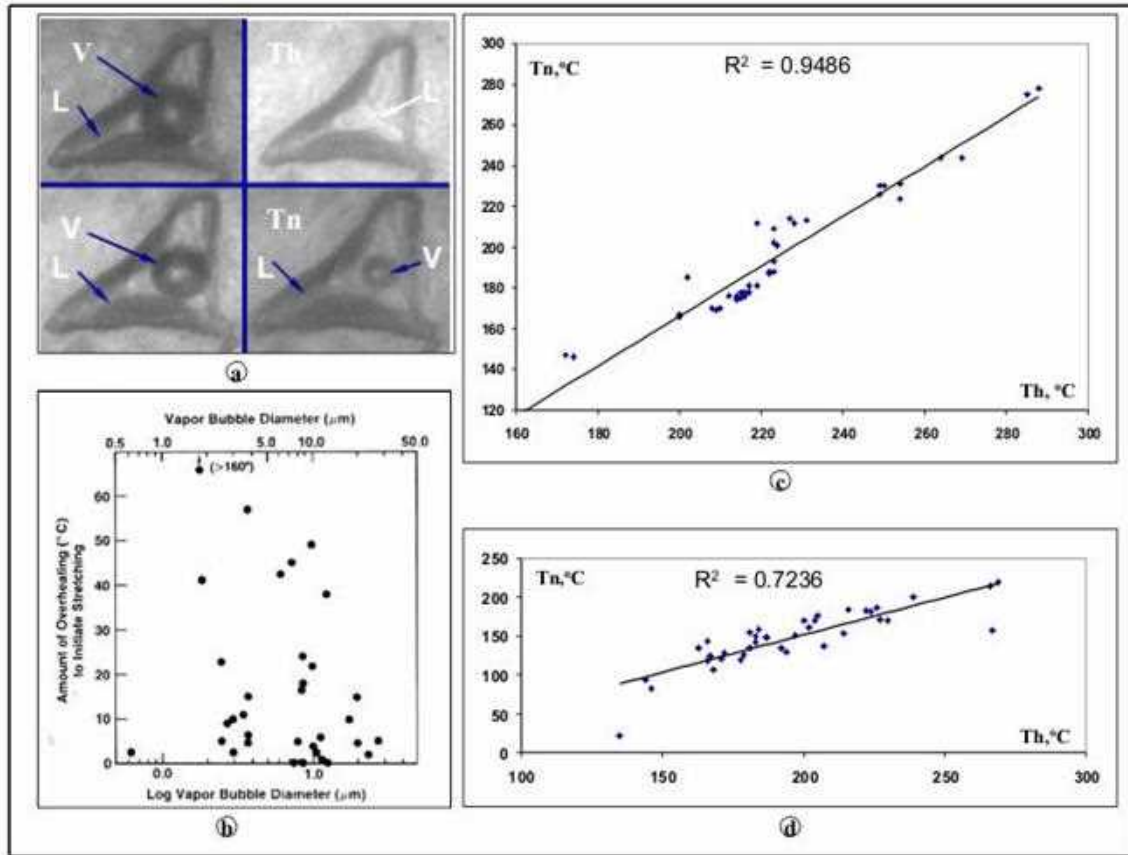


Fig. 146. Validation of homogenization temperature in presumable unstretched fluid inclusions from barite nodules from Valea Chioarului by using final liquid homogenization temperature value (Th) versus renucleation temperature value (Tn) of the vapour bubble during normal quenching in the microthermometric stage under the microscope (a). The stretching of fluid inclusions during microthermometry was tested by Ulrich and Bodnar (1988) by calculating the overheating amount necessary to induce stretching of fluid inclusion in barite at 1 atm confining pressure (b). Our data set (c) shown a very good correlation between Th and Tn comparable with similar measurements made in synthetic fluid inclusions in quartz measured by Schmulovich et al., 2009 (d). Tentatively, it is considered that based upon such data consistency the fluid inclusions in barite were unstretched during microthermometry and the homogenization temperature are the minimum formation temperature of the barite nodules from Valea Chioarului (Pintea, 2016). Notations: L-liquid, V-vapor.

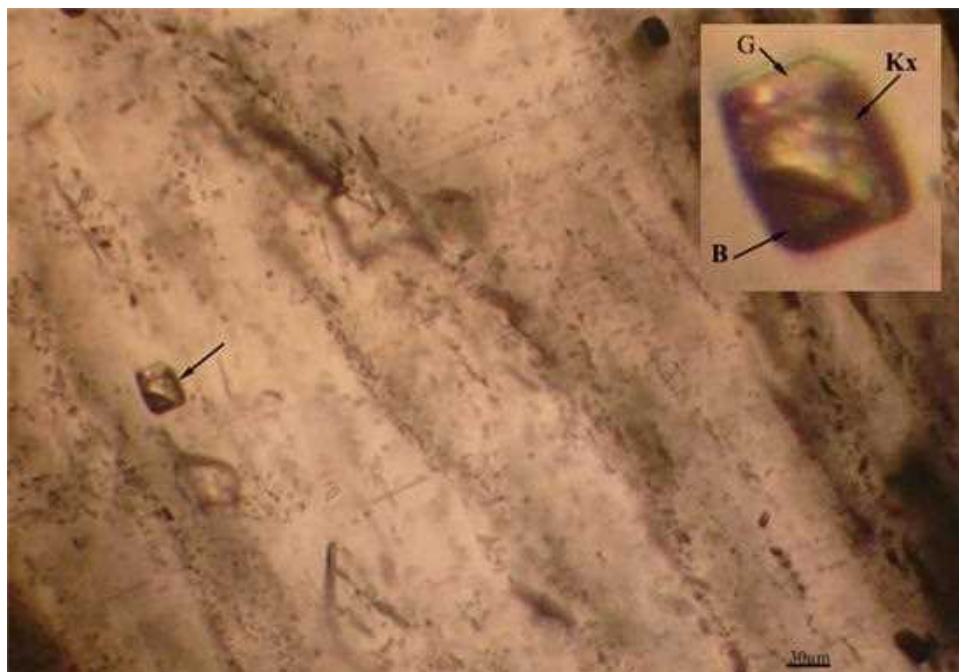


Fig. 147. Multisolid inclusion in oriented exsolution microtexture in almandine garnet from Lotru Metamorphic Suite (sample courtesy G. Săbău), unlocalized; arrowed inclusion in medallion: G-glass, B-vapor bubble, Kx – crystallised phases.

Fig. 148. Two microtextural features in almandine garnet from Lotru Metamorphic Suite (unlocalized, sample courtesy G. Săbău. A. lination with rutile elongated microcrystal and B. central sieve texture with multiphase solid inclusions. Scale bar in μm.

Fig. 149. Remelted features of zircon inclusions in almandine garnet from Lotru Metamorphic Suite (unlocalized), sample courtesy G. Săbău. Notations: zr. – zircon, sg- silicate glass, V- vapor bubble, sm- silicate melt, rt- restitic rutile, rte- exsolved rutile rod. Scale bar in μm .

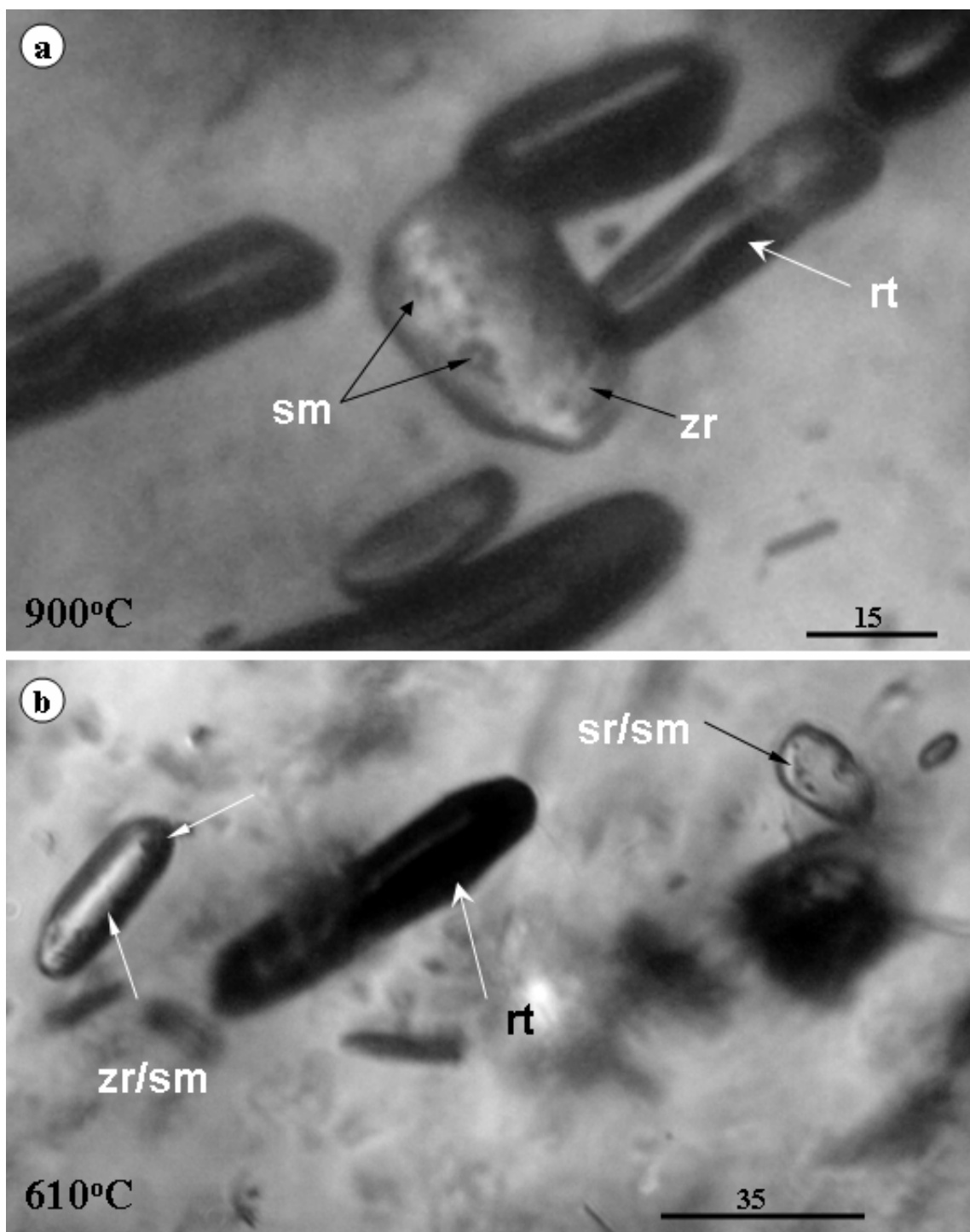


Fig. 150. Rounded (partially dissolved) rutile rods and zircon “xenocrysts” in garnet at indicated temperatures. Some of them have silicate melt (glassy) inclusions-?. Preliminary data (one recorded measurement indicated bubble homogenization between 875-939°C (not shown in the pictures). Notations: rt- rutile rods, zr-zircon, sm- silicate melt. The microthermometry data are similar with the P-T estimation of Săbău and Massone, (2003) from coexisting garnet-clinopyroxene. Unlocalized almandine, sample courtesy G. Săbău).

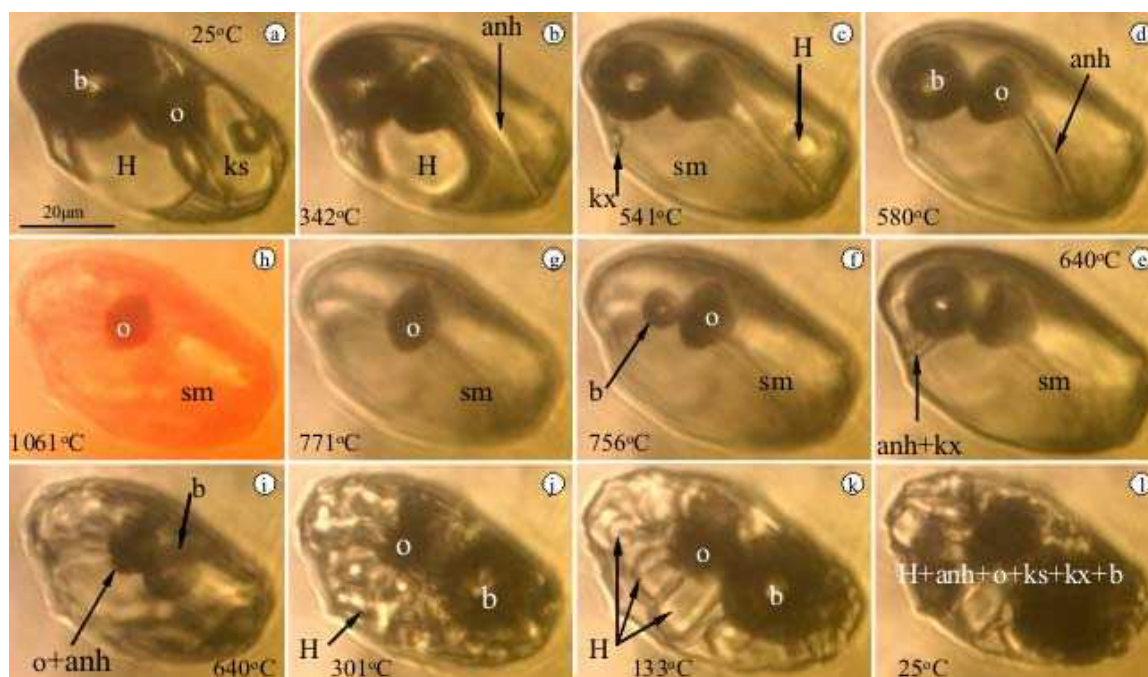


Fig. 151. Anhydrite microthermometry of brine inclusions in quartz from Roşia Poieni porphyry Cu-Au-(Mo)- Pintea et al., 2019. **a.** 25°C, **b.** 342°C, **c.** 541°C, **d.** 580°C, **e.** 640°C, **f.** 756°C, **g.** 71°C, **h.** 1061°C, **i.** 640°C, **j.** 301°C, **k.** 133°C, **l.** 25°C; Tm1= 66-238°C, TmH= 543°C, Tmanh= 723°C, Th= 770°C, Tmax= 1062°C; Tmo> 1062°C, T= 770, P= 907.48 bar, Ws= 66.0109 wt % NaCl eq., d= 1.064, x=0.4, single phase state; Notations: b-bubble, o-opaque, H-halite, ks-other salt daughter minerals, anh-anhydrite, kx-unidentified; scale bar in microns; Tm-anhydrite almost fitted to the experimental data in the Albite-Quartz-Anhydrite-H₂O system (Ducea et al., 1999).

Fig. 152. Homogeneous - brine inclusion microthermometry in quartz from Moldova Noua porphyry Cu-Mo-(Au). **a.** 25°C, **b.** 229°C, **c.** 377°C, **d.** 164°C, **e.** 134°C, **f.** 25°C; T_{mH}=298°C, T_h=363°C, P=136.265 bar, W_s=37.5702 wt% NaCl eq., d=1.02705g/ccm, x=0.16, single phase state; Notations: L-liquid, H-halite, cs- clathrasil, b- vapor bubble, o-opaque (chalcopyrite ?), sl- liquid sulphide globulae, s-unknown solid; scale bar in microns (Pintea et al., 2019).

Fig. 153. Hydrosaline melt – silicate melt immiscibility in quartz from Bolcana porphyry Cu-Au-Mo deposit. (Pintea et al., 2019). **a.** 25°C, **b.** 517°C, **c.** 897°C, **d.** 943°C, **e.** 1048°C, **f.** 547°C, **g.** 265°C, **h.** 25°C; notations: of-ore fluid, kx- solid, sg- silicate glass, sm- silicate melt, mc- salt melt, b- bubble, o-opaque; scale bar in microns.

Fig. 154. Hydrosaline melt inclusion microthermometry, Bolcana porphyry Cu-Au-Mo deposit (B4-3). **a.** 25°C, **b.** 487°C, **c.** 539°C, **d.** 569°C, **e.** 735°C, **f.** 908°C, **g.** 925°C, **h.** 1095°C, **i.** 882°C, **j.** 756°C, **k.** 208°C, **l.** 25°C; T_{mH}= 575°C, T_{mKx}= 645°C; T_{nky}= 902°C, T_{mky}= 1028°C, T_{nxo}= 786°C; T_h≥ 1095°C, P= 1897.36 bars, W_s= 70.6299, d= 1.05291, single phase state; Notations: ks- saline minerals, b+O= bubble + opaque, kx,ky,kz- unidentified solids, xo- oxide (magnetite or hematite), sm-salt melt, gs-globular sulfide; s-sulfide; T_m-melting temperature, T_n- nucleation temperature; T_h- homogenization temperature; P= pressure, W_s-salinity; scale bar in microns.

Fig. 155. Hydrosaline melt inclusion microthermometry from Bolcana porphyry Cu-Au-Mo (Pintea et al., 2019). **a.** 225°C, **b.** 361°C, **c.** 438°C, **d.** 640°C, **e.** 761°C, **f.** 868°C, **g.** 936°C, **h.** 1081°C, **i.** 729°C, **j.** 405°C, **k.** 208°C, **l.** 25°C; T_{mh}= 464°C, T_{mds}= 716°C, T_{mo}= 936-1025°C, T_{no}= 644°C, T_{nds}= 609°C; T ≥ 1081°C, P= 2331.66 bar, W_s= 55.0043 wt% NaCl eq., d= 0.883646 g/ccm, x_{NaCl}= 0.27, V+L phase state. Notations: L-Interstitial liquid phase, sk-salt crystals, b-bubble, anh-anhydrite, s-sulphide, o-oxide (magnetite and or hematite), sm-salt melt, gs-globular liquid sulfide, kx-unknown solid, scale bar in microns.

Fig. 156. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (Pintea et al., 2019). **a.** 25°C, **b.** 366°C, **c.** 545°C, **d.** 753°C, **e.** 863°C, **f.** 881°C, **g.** 891°C, **h.** 658°C, **i.** 556°C, **k.** 507°C, **l.** 27°C; T_{mH}= 554°C, T_{hV}= 889°C, T_{nV}= 778°C, T_{nH}= 538°C, T_{nfinal}= 207°C; T=889°C, P=1246.21 bar, Ws=67.5962 wt% NaCl eq., d= 0.773078 g/ccm; single phase state; Notations: B+O bubble + opaque, ks-saline daughter phases, s-sulfide, sl-liquid sulfide, anh-anhydrite, kx – unknown phase, clathrasil (?), gs-globular sulfide; scale bar in microns.

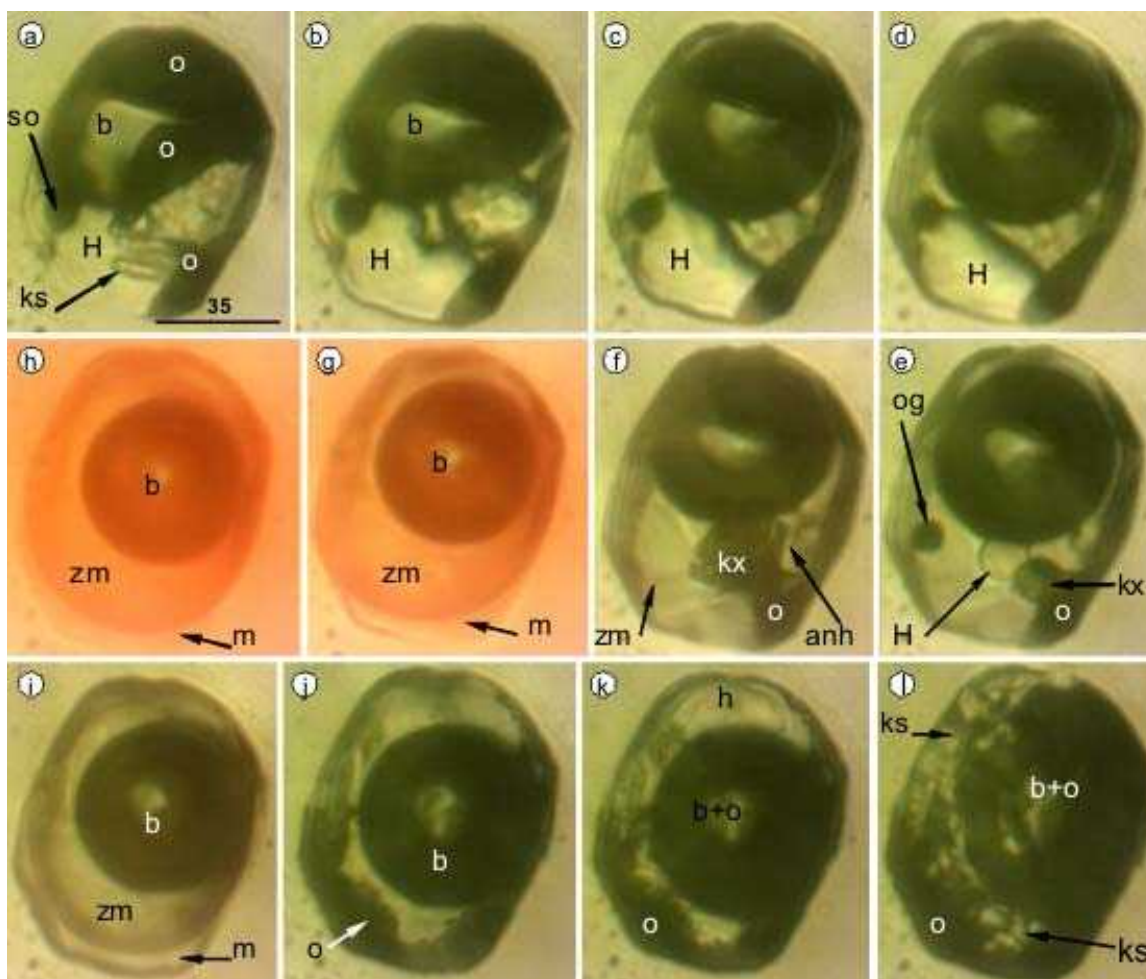


Fig. 157. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (Pintea et al., 2019). **a.** 25°C, **b.** 285°C, **c.** 443°C, **d.** 553°C, **e.** 609°C, **f.** 828°C, **g.** 1003°C, **h.** 1033, **i.** 870°C, **j.** 560°C, **k.** 319°C, **l.** 25°C. Microtermometry: $T_{mH}=612^{\circ}\text{C}$, $T_{mog}=786^{\circ}\text{C}$, $T_{mo}=1000^{\circ}\text{C}$, $T_h \gg 1037^{\circ}\text{C}$; $T_{fmenisci}=1000^{\circ}\text{C}$, $T_{no}=574^{\circ}\text{C}$; if $T_f=1037^{\circ}\text{C}$ $P=1312.53$ bar, $W_s=75.9472$ wt% NaCl eq., $d=1.102$ g/ccm, $x_{NaCl}=0.5$. Notations: so-solid opaque, H-halite, o-another opaque, b- bubble, ks- soluble minerals,og-globular opaque (liquid),anh-anhydrite, zm- hydrosilicate liquid, m- silicate melt,. Scale bar in microns.

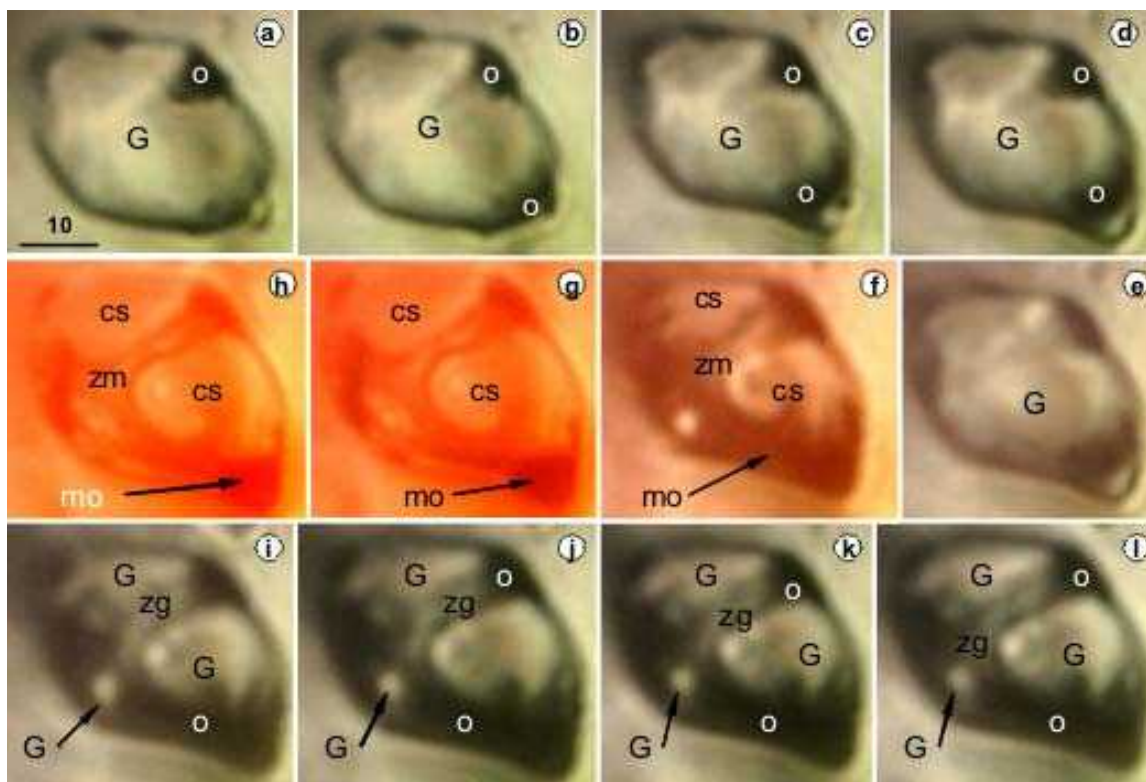


Fig. 158a. Hydrosilicate glass inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit. **a.** 25°C, **b.** 266°C, **c.** 537°C, **d.** 584°C, **e.** 837°C, **f.** 931°C, **g.** 1007°C, **h.** 1015°C, **i.** 760°C, **j.** 502°C, **k.** 206°C, **l.** 25°C; TmG= 546°C (start melting), Ti~ 808°C (immiscibility); Notations: G-glass, o-opaque, cs- other salt, zm- hydrosilicate melt (clathrasil), mo- opaque melt; scale bar in microns.

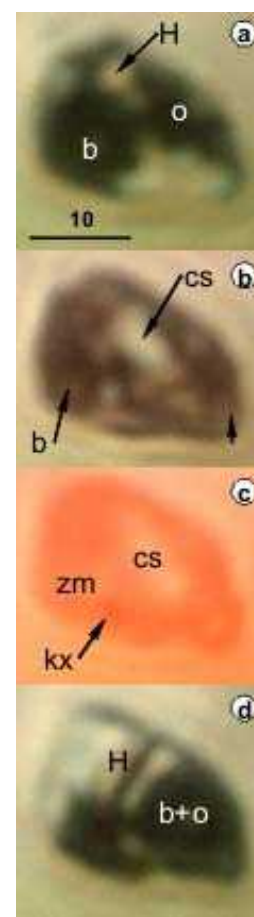


Fig. 158b. Coeval hydrosaline melt inclusion microthermometry. **a.** 429°C, **b.** 827°C, **c.** 1015°C, **d.** 206°C; Microthermometric data: TmH= 573°C, Th=992°C, P=1482.11 bars, Ws= 70.341 wt% NaCl eq., d= 1.05842 g/ccm, xNaCl=0.41, Tmk= 1011°C, Tnb= 832°C, Tno= 712°C, TnH=344°C, Tnks=159°C; Notations: H-halite, o-opaque, b-bubble, cs- salt melt (or other melt?), zm- hydrosilicate melt (cathrasil), kx-anhydrite; scale bar in microns.

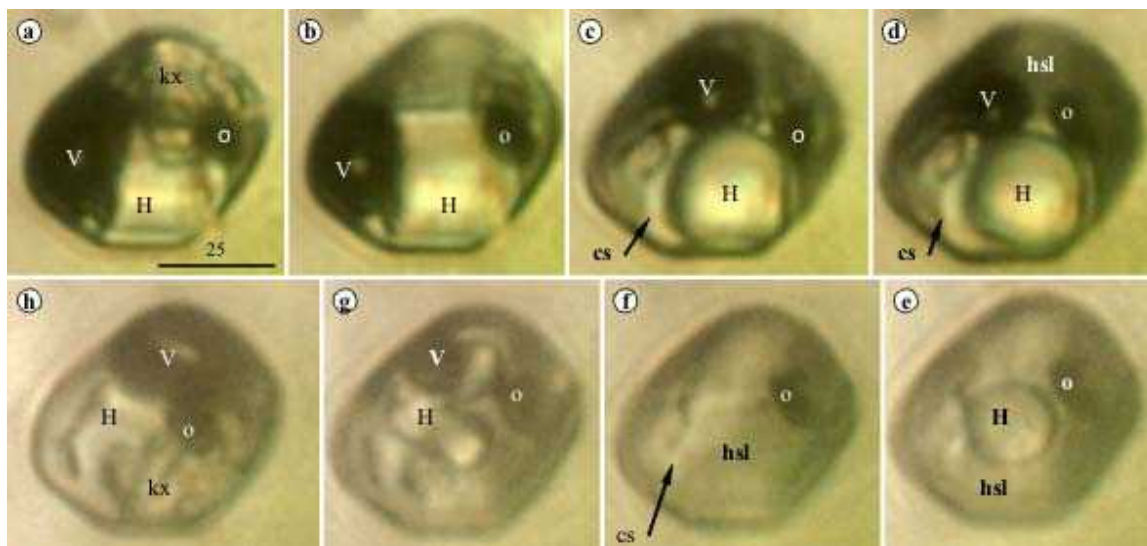


Fig. 159. Hydrosaline melt inclusion microthermometry from Vlădeasa miarolitic quartz pegmatite (Zarna Valley). **a.** 25°C, **b.** 164°C, **c.** 274°C, **d.** 360°C, **e.** 450°C, **f.** 507°C, **g.** 362°C, **h.** 41°C; Microthermometry: Th(L+H)= 451°C, Th (L)= 511°C, P= 807.231 bar, Ws= 61.152 wt% NaCl eq., d= 1.2168, xNaCl= 0.32, Tn(V+H)= 375°C, Tn_{kx}= 43°C, single phase state. Notations: V- vapor, kx- unidentified solid(s), H-halite, o-opaque, hsl- hydrosaline melt, cs- clathrasil, scale bar in μm.

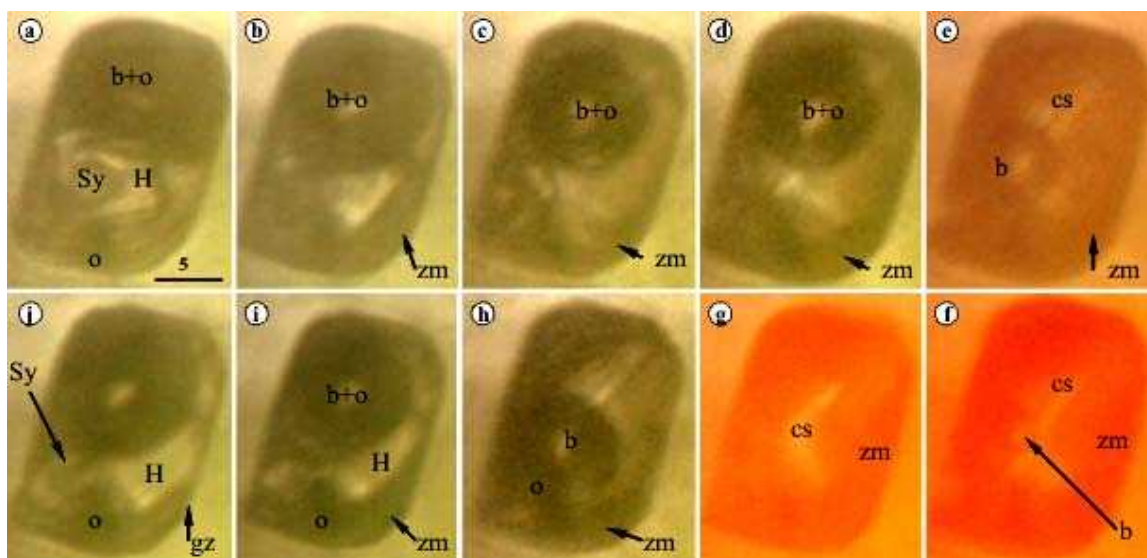


Fig. 160. Hydrosaline melt inclusion microthermometry in quartz from Vlădeasa miarolitic pegmatite. (Zarna Valley). **a.** 40°C, **b.** 157°C, **c.** 465°C, **d.** 683°C, **e.** 935°C, **f.** 992°C, **g.** 1004°C, **h.** 650°C, **i.** 190°C, **j.** 25°C; Tm_l= 100°-149°C, Tm_H=450°C, Th=1004°C, Tn_V=953°C, P=2099.57 bar, Ws=53,177 wt% NaCl eq., d=0.8769 g/ccm, xNaCl=0.26, single phase state; Notations: Sy-sylvite, b-bubble, o-opaque, H-halite, cs-clathrasil, zm- hydrosilicate liquid, gz- hydrosilicate glass; scale bar in microns.

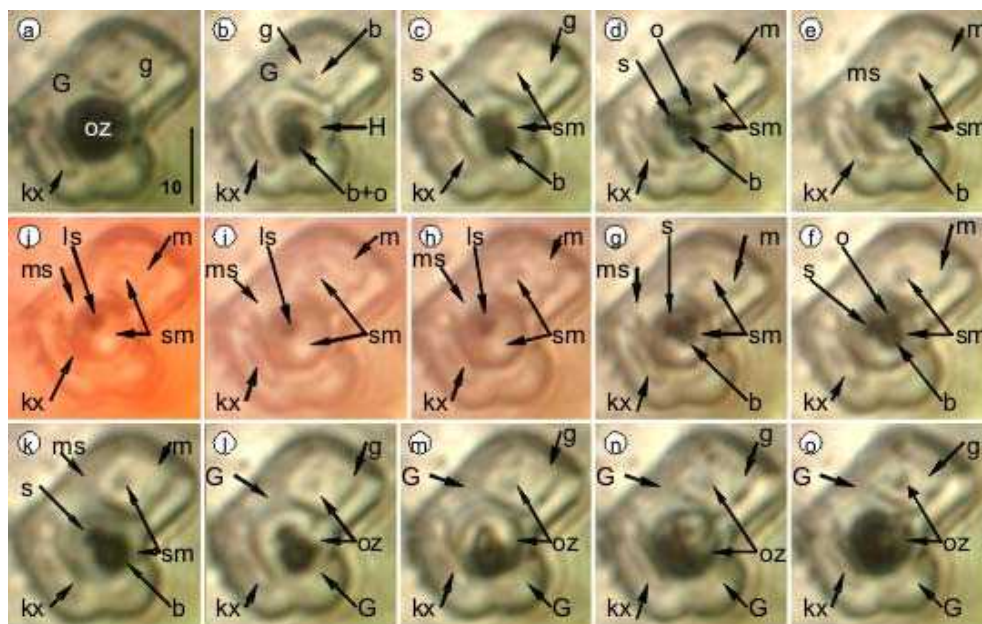


Fig. 161. Hydrosilicate-hydrosaline melt inclusion from Moldova Noua porphyry Cu-Mo-Au deposit (Pintea et al., 2019). **a.** 25°C, **b.** 337°C, **c.** 405°C, **d.** 689°C, **e.** 708°C, **f.** 775°C, **g.** 830°C, **h.** 918°C, **i.** 939°C, **j.** 988°C, **k.** 661°C, **l.** 369°C, **m.** 259°C, **n.** 187°C, **o.** 25°C; Microthermometry: T_{mH}= 401°C, T_h= 892°C, P= 1784.59 bar, W_s= 47.2345 wt% NaCl eq., d= 0.831571 g/ccm, x_{NaCl}=0.21, single phase state: (L+V); Notations: ks-solid, xg-glass, sg-silicate glass, of-ore fluid, sm-silicate melt, mc- salt melt, s- solid sulfide, gs- liquid sulfide, m- magnetite, h-halite, hs- hydrous salt crystal; scale bar in microns.

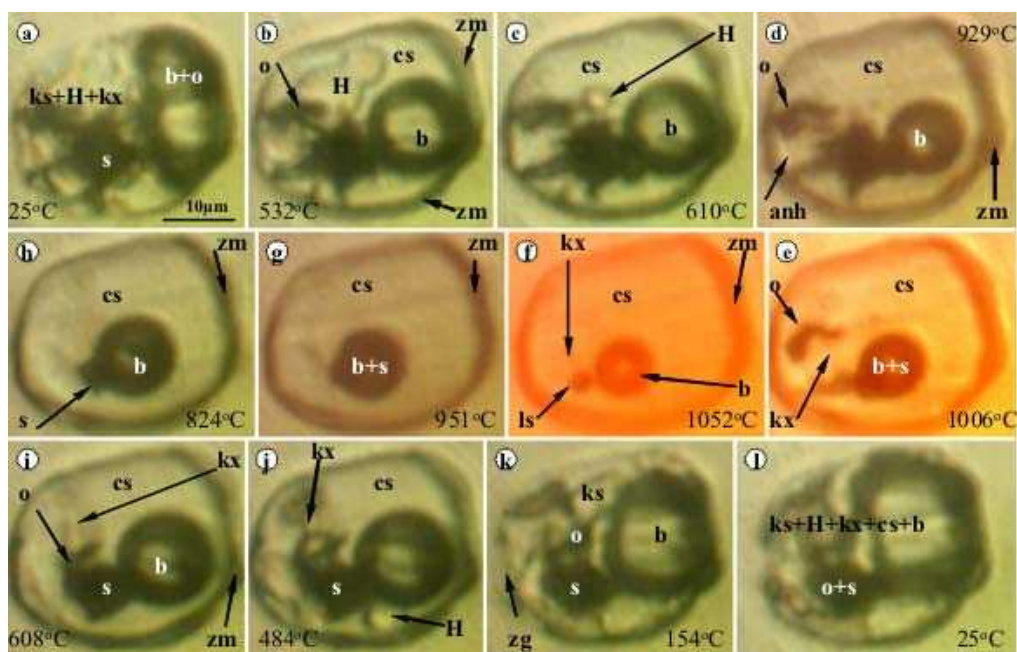


Fig. 162. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (Pintea et al., 2019). **a.** 25°C, **b.** 532°C, **c.** 610°C, **d.** 929°C, **e.** 1006°C, **f.** 1052°C, **g.** 951°C, **h.** 824°C, **i.** 608°C, **j.** 484°C, **k.** 154°C, **l.** 25°C; Microthermometry: T_{mH}=611°C, T_{mo}= 1017°C, T_h ≥1052°C, T_{no}= 657°C, T_{nH}= 495°C, (T_m anhydrite = 987°C in the followed cycle), T_{mKx}≥1040, T_f≥1052°C, P=1364.37 bar, W_s=75.8046 wt% NaCl eq., d=1.09793, x_{NaCl}= 0.5; Notations: s-sulfide (chalcopyrite?), liquid sulfide, H-halite, ks-other salt, b-bubble, cs- cathrasil (?), zg- hydrosilicate glass, o-opaque; scale bar in microns.

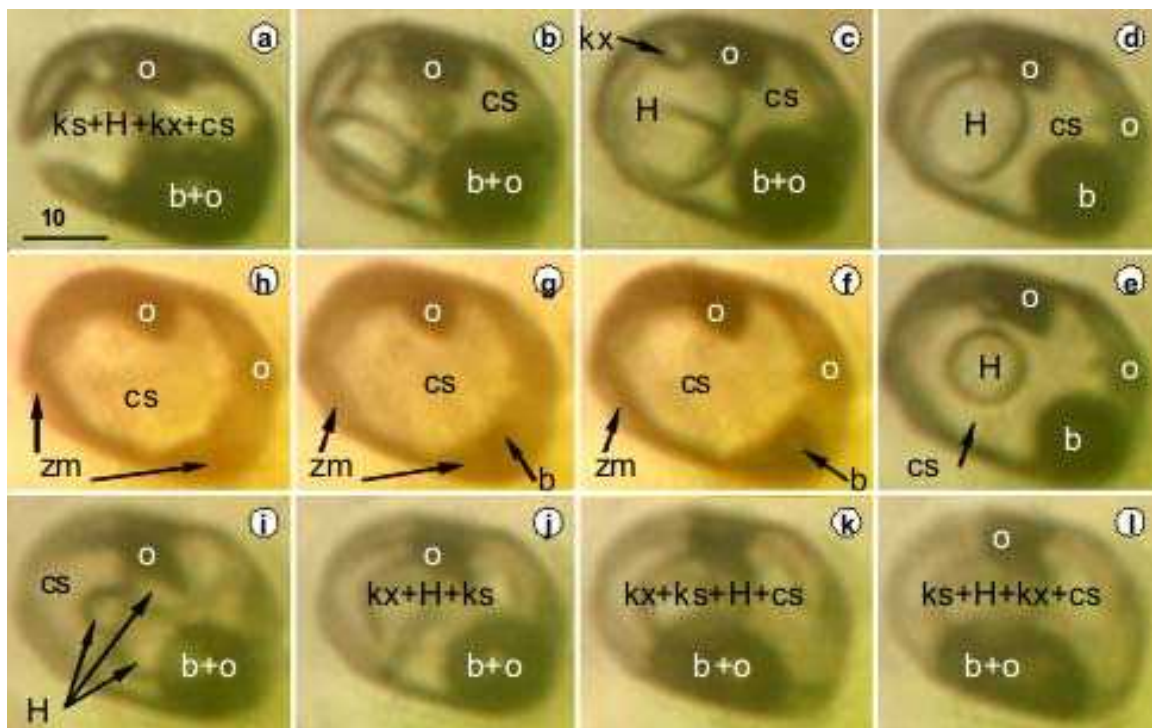


Fig. 163. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposi.(ROV- 1A). a. 25°C, b. 348°C, c. 402°C, d. 507°C, e. 545°C, f. 789°C, g. 816°C, h. 828°C, i. 433°C, j. 238°C, k. 155°C, l. 101°C; $T_{m1}=258^{\circ}\text{C}$, $T_{mH}=562^{\circ}\text{C}$, $T_h=825^{\circ}\text{C}$, $P=1009.37$ bar, $W_s=68.7515$ wt%NaCl eq., 1.07986 g/ccm, $x=0.41$, single phase state. Notations:H-halite, kx-other salt, kx-anhydrite (?), b-bubble, o-opaque undifferentiated, cs-clathrasil, zm- hydrosilicate liquid; scale bar in microns.

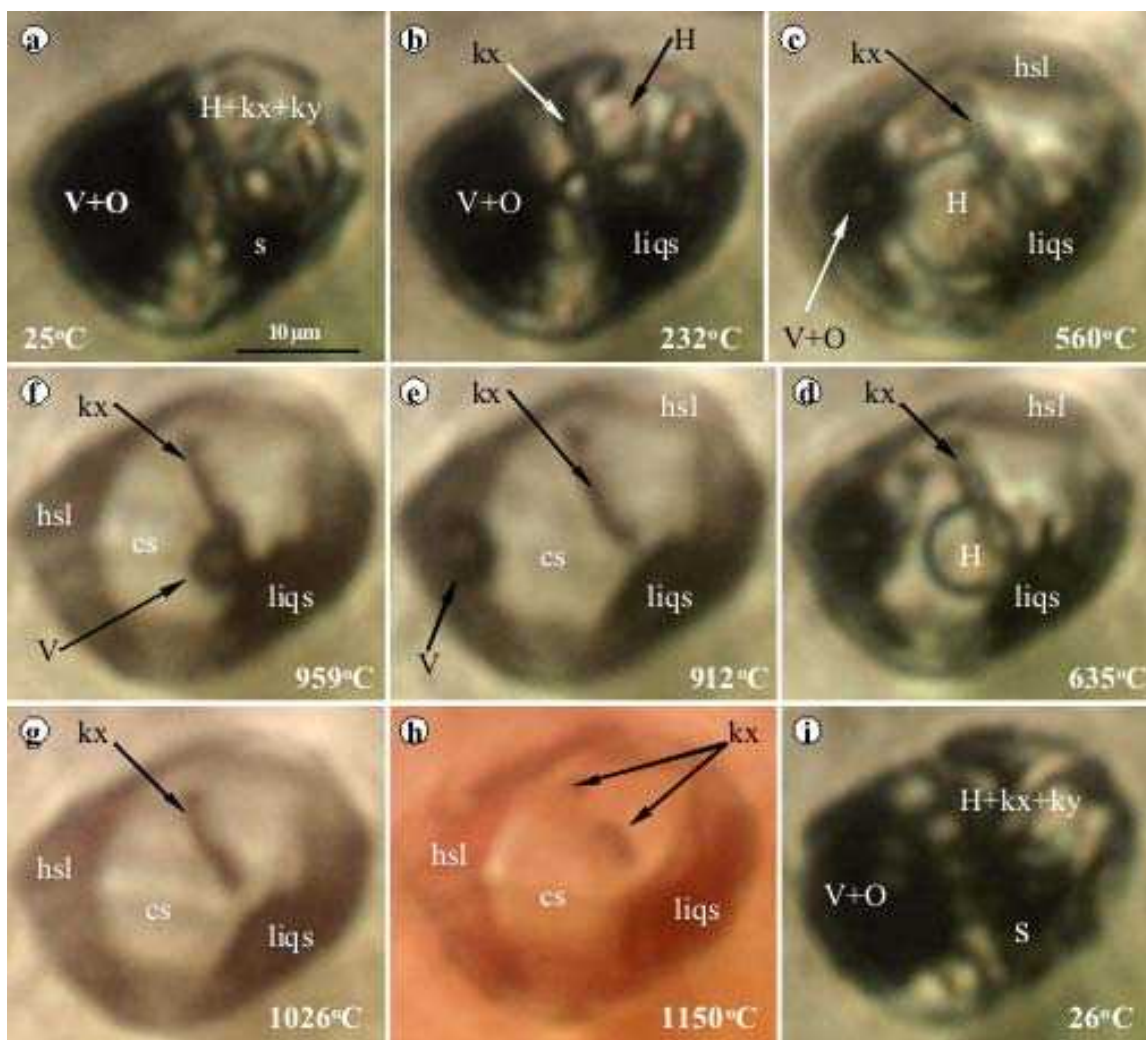


Fig. 164. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposit, the same in **Fig 163**, after two years, modified by stretching(?). Microthermometry: $T_mH= 659^{\circ}C$, $T_h (L)= 989^{\circ}C$, $P= 863.021$ bar, $W_s= 82.5287$ wt% NaCl eq., $d= 1.18199$, $x_{NaCl}= 0.60$, single phase state. Notations: V- vapor, H-halite, kx, ky- unknown, hsl- liquid hydrosaline, cs- clathrate, liqs- liquid sulfide, s- sulfide, o- opaque.

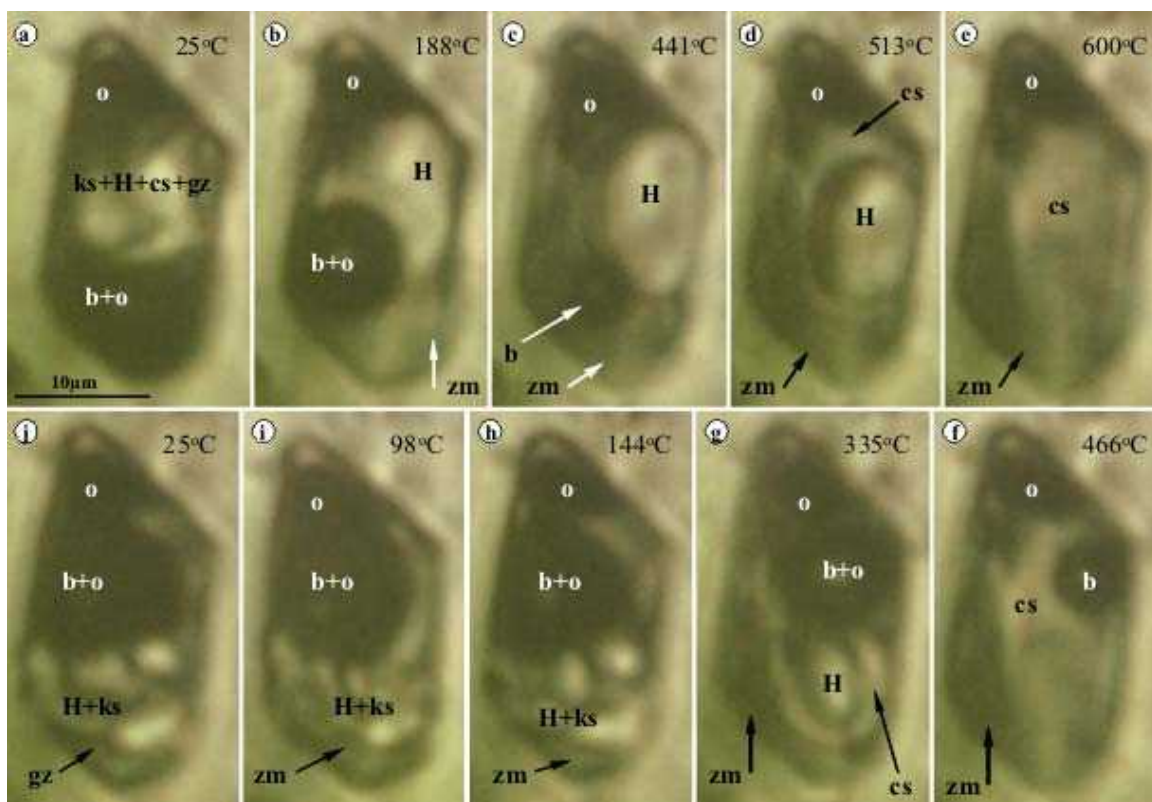


Fig. 165. Hydrosaline melt inclusion from Tălagiu porphyry Cu-Au-Mo deposit (Pintea et al., 2019). **a.** 25°C, **b.** 188°C, **c.** 441°C, **d.** 513°C, **e.** 600°C, **f.** 466°C, **g.** 335°C, **h.** 144°C, **i.** 98°C, **j.** 25°C; Microthermometry by halite homogenization: T_{mks} = 161°C, T_{hV} = 512°C, T_{mH} = 599°C (formation temperature), P = 1628.25 bar, W_s = 72.5583 wt% NaCl, d = 1.33906 g/ccm, x_{NaCl} = 0.4, single phase state; Notations: ks- soluble salt, H- halite, cs- clathrasil, b-bubble, o-opaque, zm- hydrosilicate liquid (melt), gz- transparent glassy crust-?; scale bar in microns.

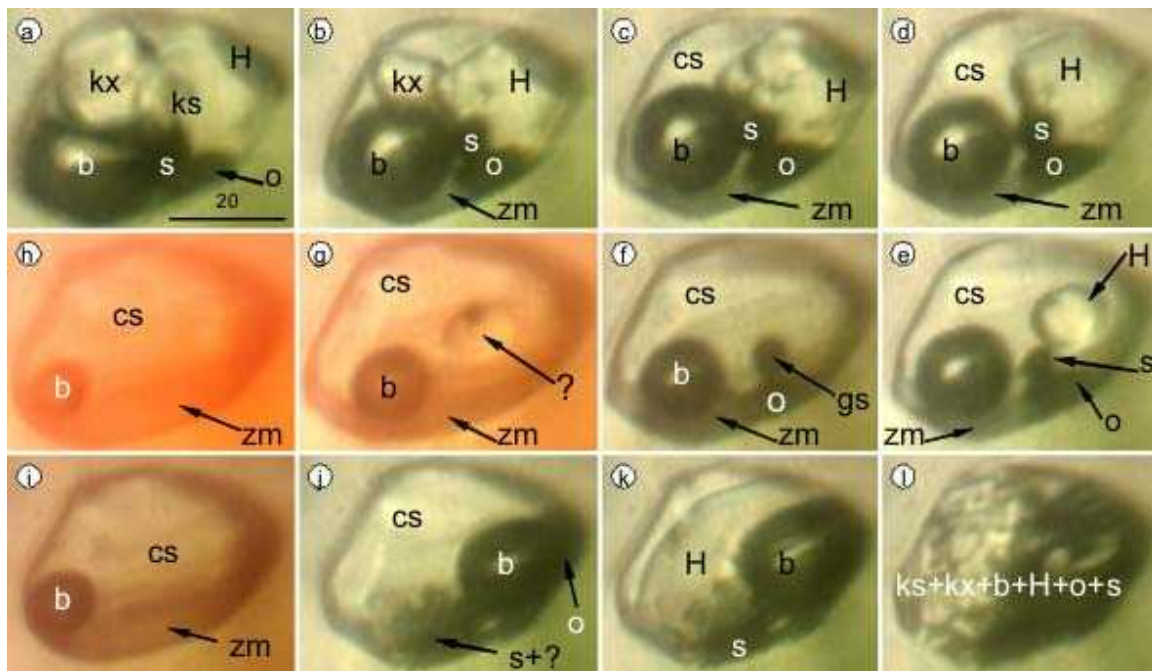


Fig. 166. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry copper Cu-Au-Mo deposit (VM520-1-1). **a.** 25°C, **b.** 284°C, **c.** 377°C, **d.** 523°C, **e.** 650°C, **f.** 863°C, **g.** 1006°C, **h.** 1083°C, **i.** 997°C, **j.** 594°C, **k.** 237°C, **l.** 25°C; Microthermometry: T_{mH} = 652°C, T_{mo} = 1031°C, $T_h \geq 1083^\circ\text{C}$, P = 1077.71 bar, W_s = 81.5662 wt%NaCl eq., d = 1.1409, x_{NaCl} = 0.6; Notations: b- bubble, s-sulphide, H-halite, ks-other salt;o-opaque, cs-clathrasil (?), zm- hydrosilicate melt, ?-unknown, scale bar in microns.

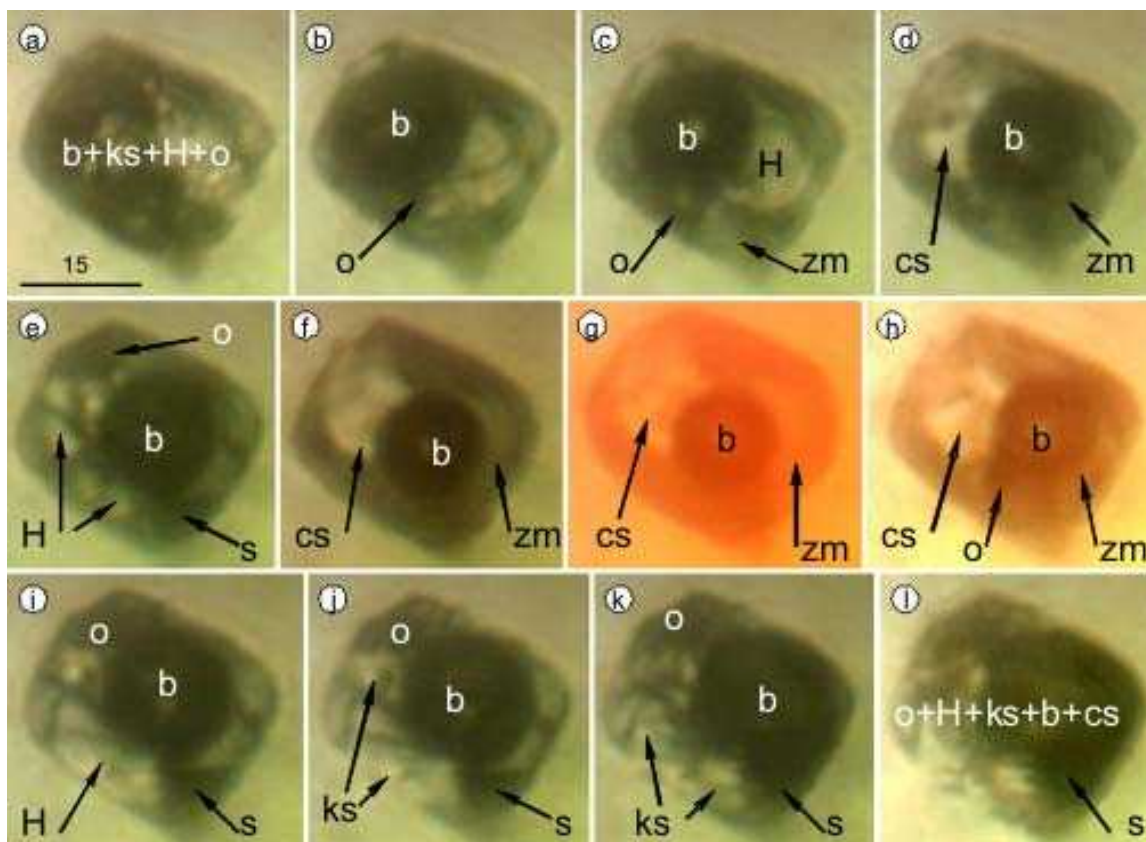


Fig. 167. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (VM-520-1-3). **a.** 25°C, **b.** 149°C, **c.** 297°C, **d.** 466°C, **e.** 737°C, **f.** 971°C, **g.** 1060°C, **h.** 880°C, **i.** 443°C, **j.** 216°C, **k.** 150°C, **l.** 106°C, $T_{m1} = 206^{\circ}\text{--}365^{\circ}\text{C}$, $T_{mH} = 662^{\circ}\text{C}$, $T_{nH} = 456^{\circ}\text{C}$, $T_{nz} = 107^{\circ}\text{C}$, $T_h \geq 1060^{\circ}\text{C}$, $P = 1141.65$ bar, $W_s = 79.7607$, $d = 1.13109$, $x = 0.6$, Notations: b-bubble, H-halite, Ks-other salt daughter phases, o-opaque, cs-clathrasil (?), zm-hydrosilicate gel., s-sulphide, scale bar in microns.

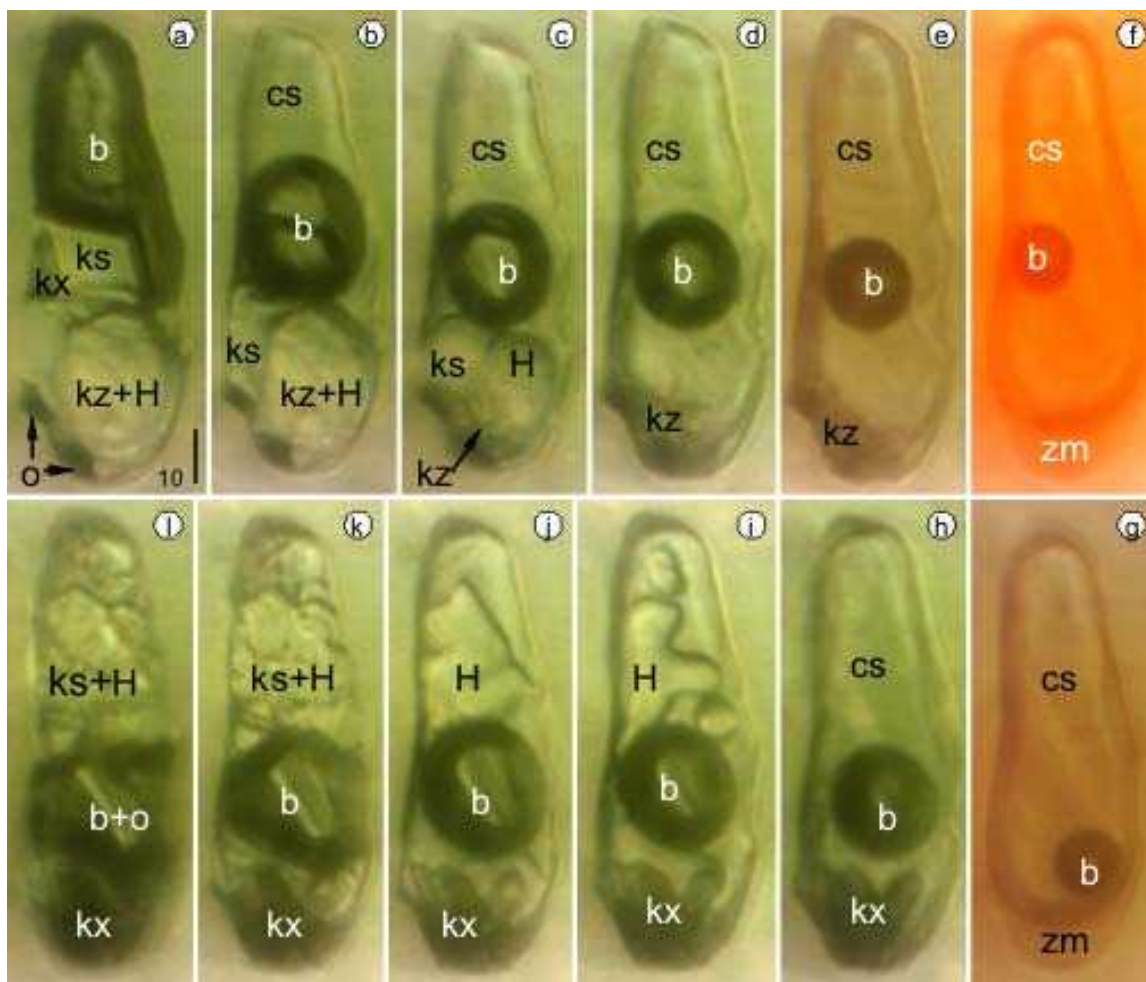


Fig.168. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (VM-520-2-1). **a.** 25°C, **b.** 373°C, **c.** 553°C, **d.** 651°C, **e.** 934°C, **f.** 1047°C, **g.** 997°C, **h.** 644°C, **i.** 495°C, **j.** 248°C, **k.** 152°C, **l.** 54°C; Tmks= 366°C, TmH= 624°C, Tmkx= 989°C, Tnh= 526°C, Tmax≥1050°C, P= 1245.21 bar, Ws= 77.6515 wt% NaCl eq., d= 1.11454, xNaCl= 0.52; Notations: H-halite, Kx-anhydrite?, ks-other salt, o-opaque, cs-clathrasil (?), zm-hydrosilicate liquid, b-bubble; scale bar in microns.

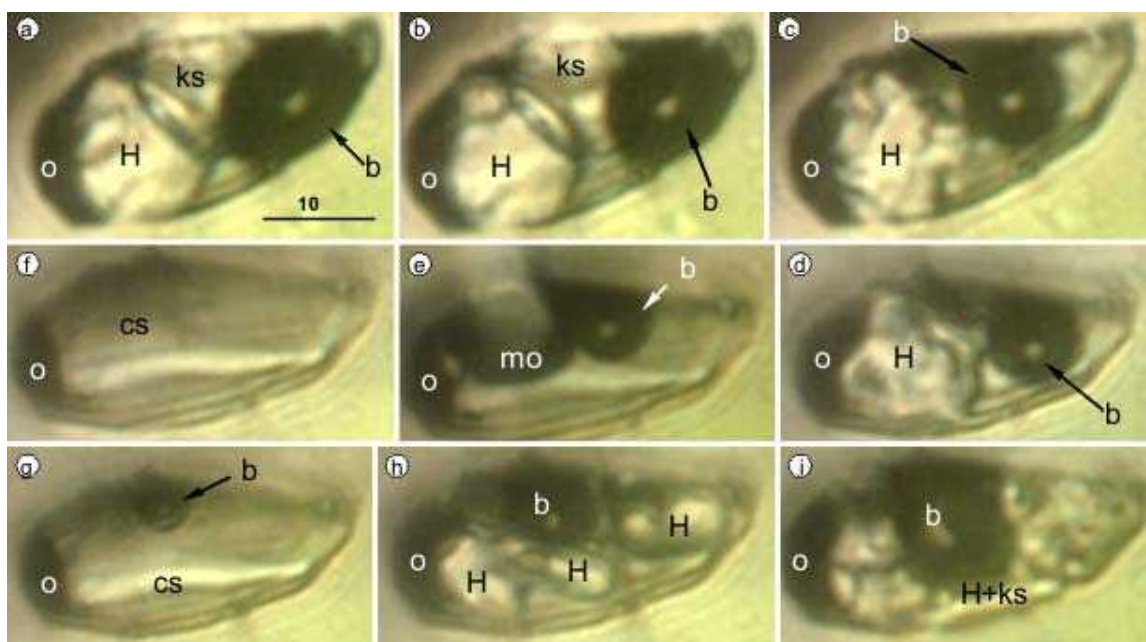


Fig. 169. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (VM-520-6). **a.** 25°C, **b.** 131°C, **c.** 278°C, **d.** 354°C, **e.** 502°C, **f.** 567°C, **g.** 629°C, **h.** 430°C, **i.** 25°C; TmH=550°-562°C; Tmo~600°C, Th=618°C, TnV=573°C, TnH=431°C, T=618°C, P= 497.215 bar, Ws= 68.7515 wt% NaCl eq., d= 1.19284, xNaCl=0.41, single phase state; Notations:H-halite, ks- other salt, b- bubble, o-opaque, cs- clathrasil (?), mo-opaque globulae; scale bar in microns.

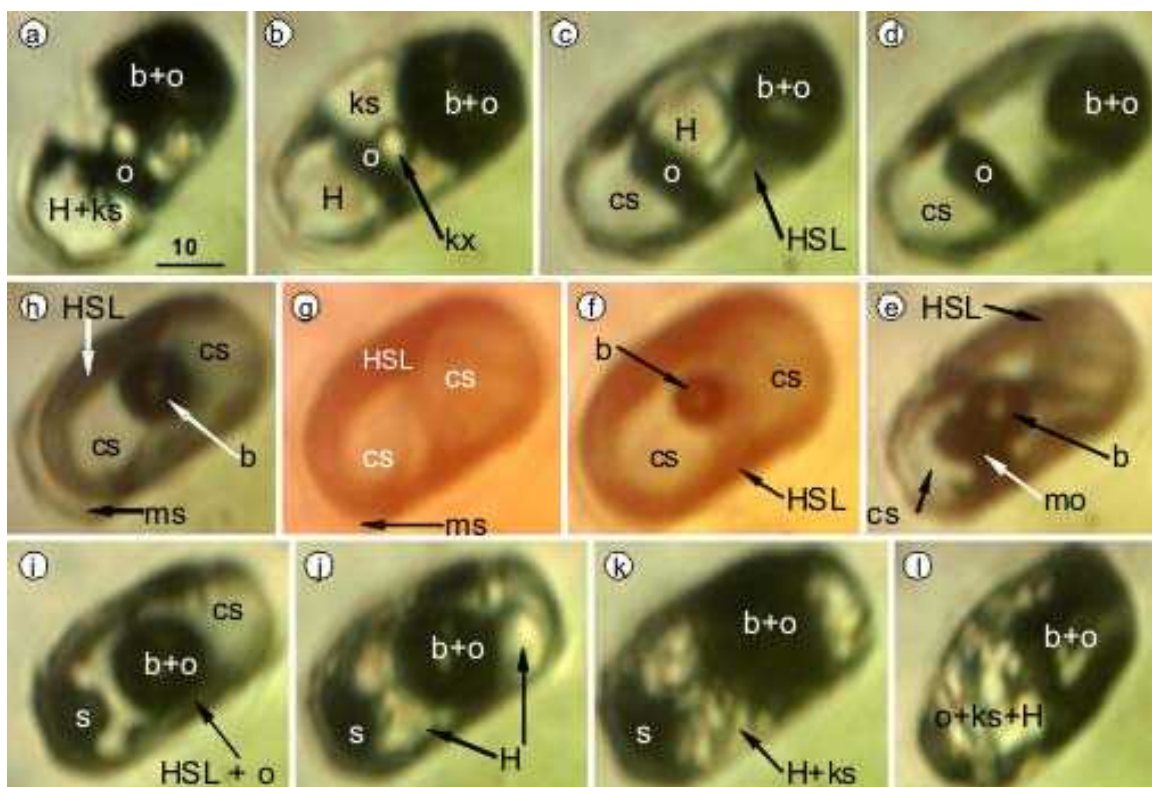


Fig. 170. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (VM-520-20-4bis). **a.** 25°C, **b.** 193°C, **c.** 438°C, **d.** 562°C, **e.** 840°C, **f.** 979°C, **g.** 1083°C, **h.** 842°C, **i.** 541°C, **j.** 378°C, **k.** 213°C, **l.** 25°C; $T_mH=577^\circ\text{C}$, T_{mkx} (anhydrite?)= $982^\circ\text{--}988^\circ\text{C}$, $T_{mo}\sim 1050^\circ\text{C}$, $T_h=1077^\circ\text{C}$, $P=1790.97$ bar, $W_s=70.9187$ wt% NaCl eq., $d=1.05572$ g/ccm, $x_{NaCl}=0.43$, single phase state; $T_{nb}=977^\circ\text{C}$, $T_{no}=705^\circ\text{--}583^\circ\text{C}$, $T_{nH}=402^\circ\text{C}$, $T_{nKs}=100^\circ\text{--}95^\circ\text{C}$; Notations: T_m - melting temperature, T_n -renucleation temperature, b- bubble, o- opaque, H-halite, ks, kx, ky- other salt including anhydrite, s- sulphide (chalcopyrite ?), cs-cathrasil (?), zm-hydrosilicate melt, ms- silicate melt; scale bar in microns; Note: salt melt is floating in zm coated with silicate melt; (zm- hydrosilicate-carbonate-sulphate-chloride-fluoride liquid).

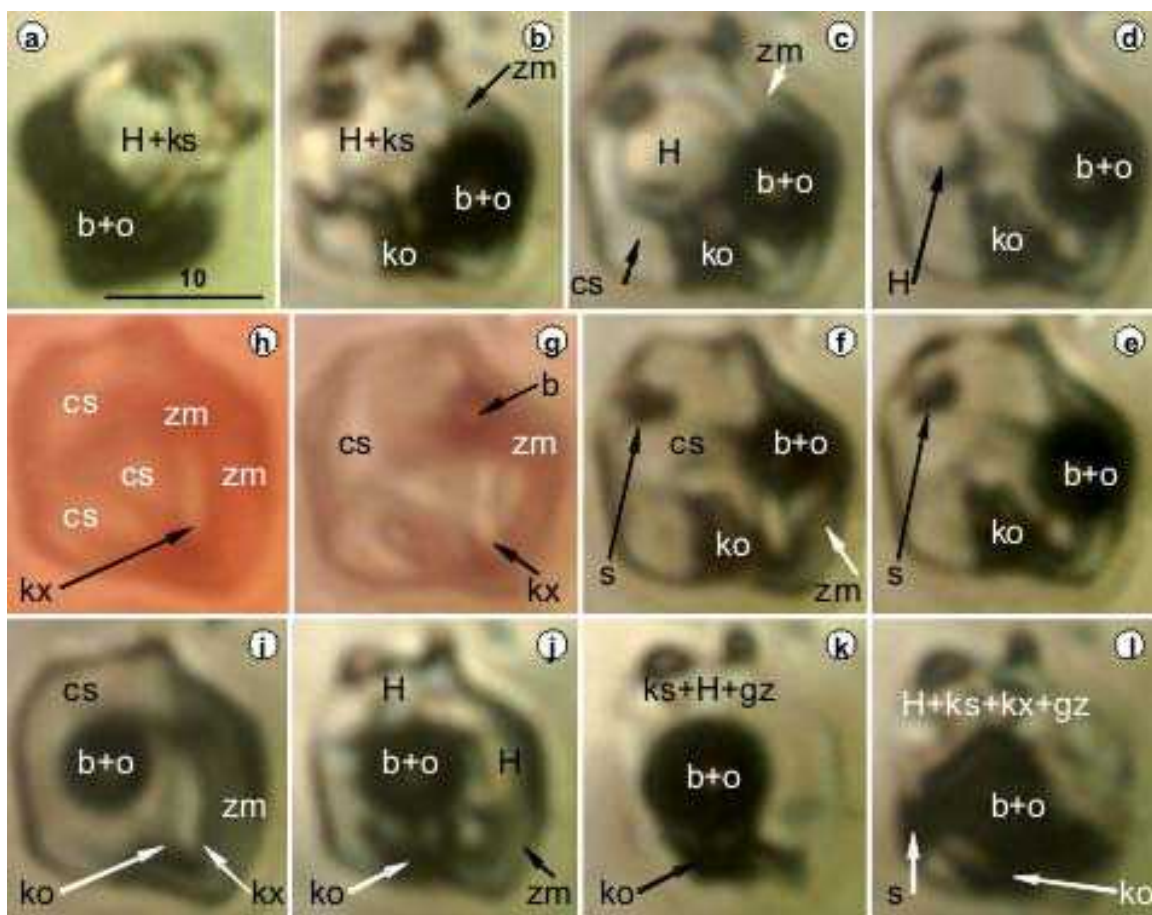


Fig. 171. Hydrosaline melt inclusion microthermometry. Valea Morii porphyry Cu-Au-Mo deposit (VM-520-20-5bis- second cycle). **a.** 25°C, **b.** 220°C, **c.** 344°C, **d.** 531°C, **e.** 616°C, **f.** 813°C, **g.** 1006°C, **h.** 1083°C, **i.** 780°C, **j.** 429°C, **k.** 109°C, **l.** 25°C; Microthermometric data: $T_mH = 553^\circ\text{C}$, $T_{ms} = 980^\circ\text{C}$, $T_nH = 451^\circ\text{C}$, $T_h = 1076^\circ\text{C}$, $P = 2002.72 \text{ bar}$, $W_s = 67.4519 \text{ wt\% NaCl eq.}$, $d = 1.0255 \text{ g/ccm}$, $x_{\text{NaCl}} = 0.38$, $T_{nb} = 1039^\circ\text{C}$, $T_{mko} = 1017^\circ\text{C}$, $T_{nko} = 690^\circ\text{C}$; first cycle microthermometric data: $T_{mks} = 207^\circ\text{--}248^\circ\text{C}$, $T_{mgz} = 393^\circ\text{C}$, $T_{mkx} = 1004^\circ\text{C}$, $T_{nks} = 109^\circ\text{C}$; Notations: H-halite, ks-other salt, b-bubble, o-opaque, ko-another opaque, zm- hydrosilicate liquid, cs-clathrasil (?), s- sulphide, kx-anhydrite(?), gz-glassy zm, s-sulphide (chalcopyrite?), scale bar in microns.

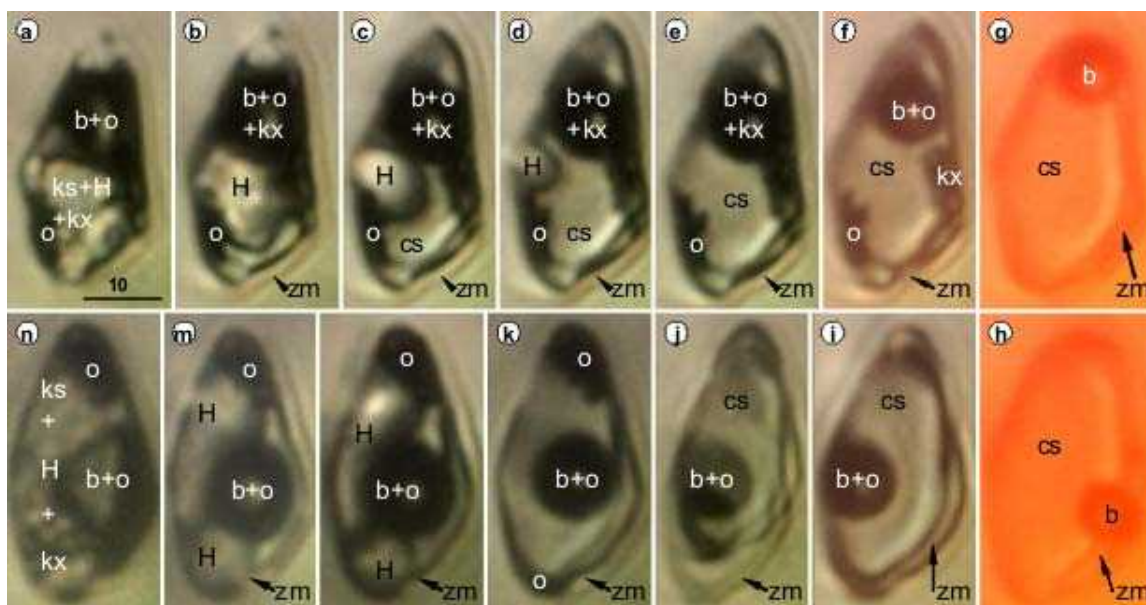


Fig.172. Hydrosaline melt inclusion microthermometry. Valea Morii Cu-Au-Mo deposit (VM-520-26-4). **a.** 25°C, **b.** 289°C, **c.** 565°C, **d.** 604°C, **e.** 613°C, **f.** 871°C, **g.** 1049°C, **h.** 1101°C, **i.** 826°C, **j.** 695°C, **k.** 561°C, **l.** 413°C, **m.** 205°C, **n.** 25°C; Microthermometric data: $T_{mH} = 613^{\circ}\text{C}$, $T_{mkx} = 1007^{\circ}\text{C}$, $T_{mo} = 1001^{\circ}\text{C}$, $T_{h \geq 1001^{\circ}\text{C}} = 1499.67$ bar, $W_s = 76.0892$ wt% NaCl eq., $d = 1.09311$ g/ccm, $x_{NaCl} = 0.5$; $T_{nH} = 422^{\circ}\text{C}$, $T_{nks} = 151^{\circ}\text{C}$; Notations: b- bubble, o-opaque, H-halite, ks-other salt, kx- anhydrite, cs- clathrasil (?), zm- hydrosilicate melt; scale bar in microns.

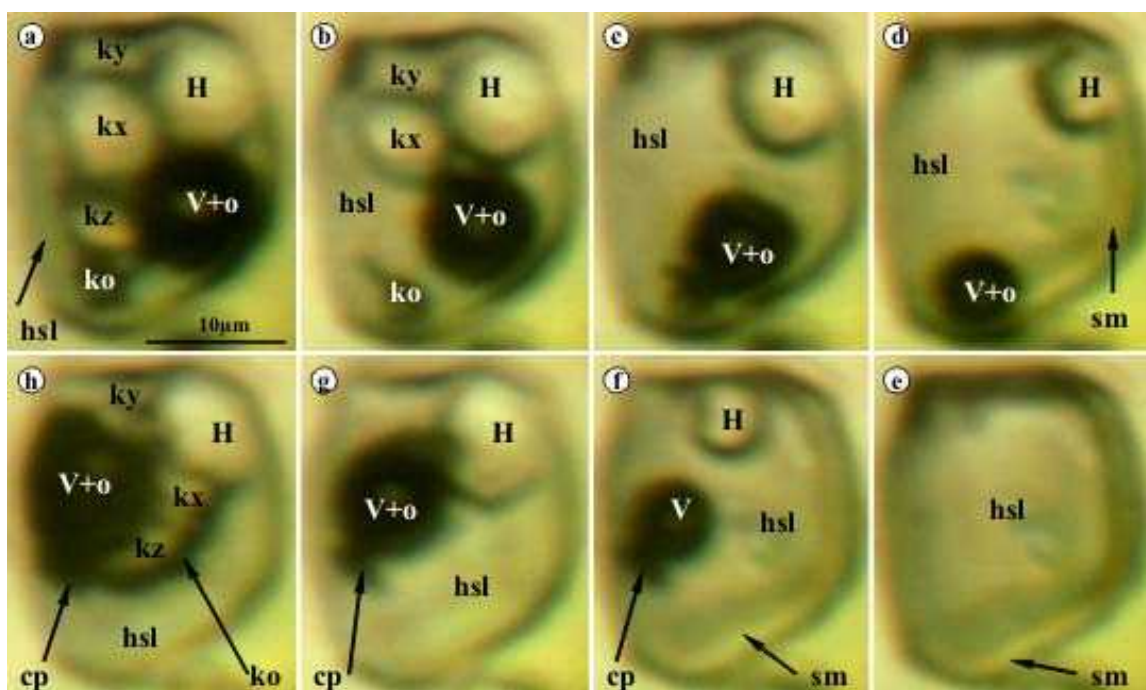


Fig. 173. Hydrosaline melt inclusion microthermometry. Pseudosecondary assemblage. Rovina porphyry Cu-Au deposit. (ROV Ia pseudosecondary) **a.** 27°C, **b.** 135°C, **c.** 200°C, **d.** 312°C, **e.** 424°C, **f.** 309°C, **g.** 129°C, **h.** 60°C; Microthermometric data: $T_{mkz} = 89^{\circ}\text{C}$, $T_{mky} = 180^{\circ}\text{C}$, $T_{mkx} = 302^{\circ}\text{C}$, $T_{mH} = 363^{\circ}\text{C}$, $T_{h(L)} = 416^{\circ}\text{C}$, $T = 416^{\circ}\text{C}$, $P = 219, 154$ bar, $W_s = 43.033$ wt% NaCl eq., $x_{NaCl} = 0.19$, single phase state. Notations: kx, ky, kz, - undetermined salt, H-halite, V-vapor, o, ko-opaque, cp- chalcopryrite, hsl- hydrosaline melt, sm- hydrosilicate melt.

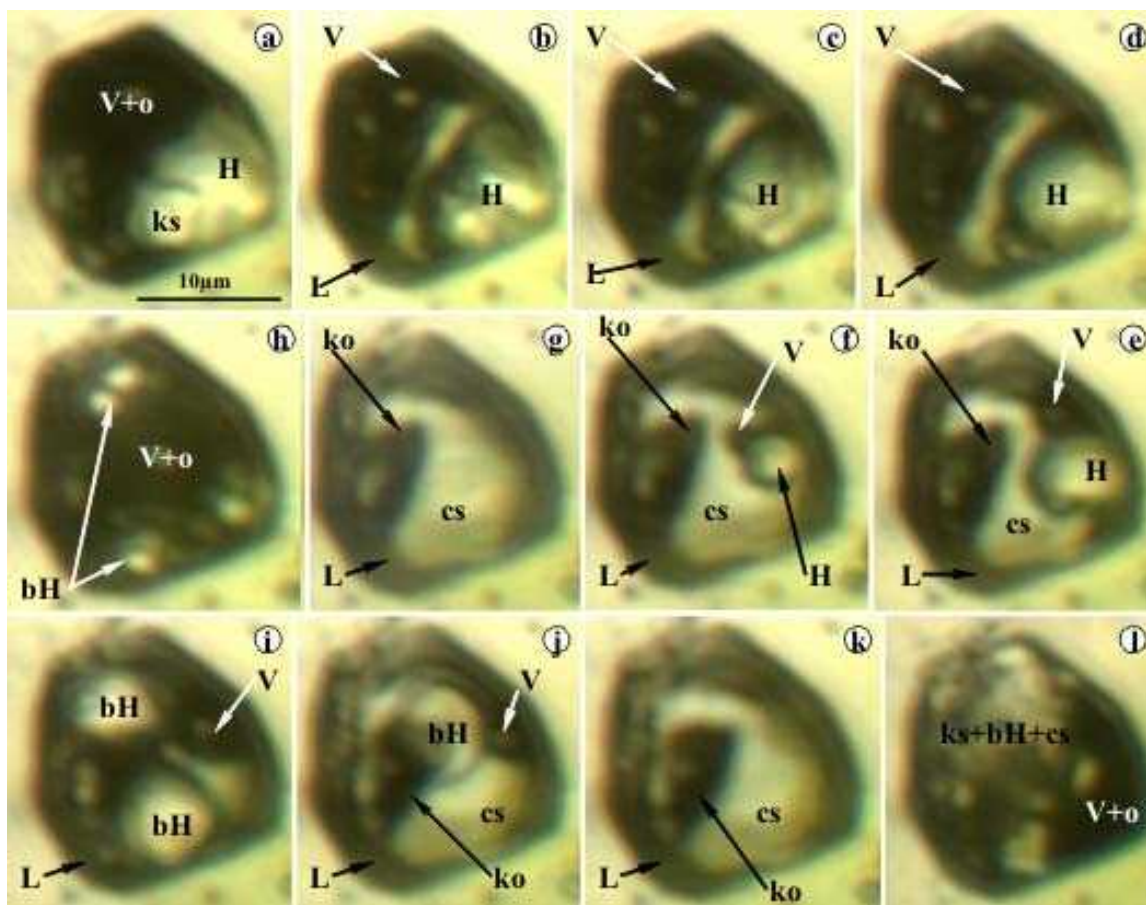


Fig. 174. Hydrosaline melt inclusion microthermometry, double cycled by halite homogenization. Tarnița porphyry Cu-Au. (T-Ta-I-8-1a), Pintea et al., 2020. **a.** 23°C, **b.** 408°C, **c.** 426°C, **d.** 485°C, **e.** 528°C, **f.** 542°C, **g.** 561°C, **h.** 365°C, **i.** 477°C, **j.** 525°C, **k.** 550°C, **l.** 29°C; Microthermometric data- (1 cycle): Th(L+H)= 545°C, Th(L)= 549°C. TnV= 508°C, TnH= 396°C), d= 1.21804 g/ccm, Ws= 66.2987 wt% NaCl eq., - (2cycle): TmbH= 499°C, Th(L+H)= 544°C, Th(L)= 549°C, TnV= 508°C, TnH= 429°C, Tnks= 211°C, Tnko= 371°C; d= 1.21681 g/ccm, Ws= 66.1548wt% NaCl eq., Notations: V- vapor (Fe-rich phase), opaque, ko- another opaque (pyrrhothite), H-halite, ks- another salt, bH- burst halite, cs- clathrasil, L- hydrosaline melt.

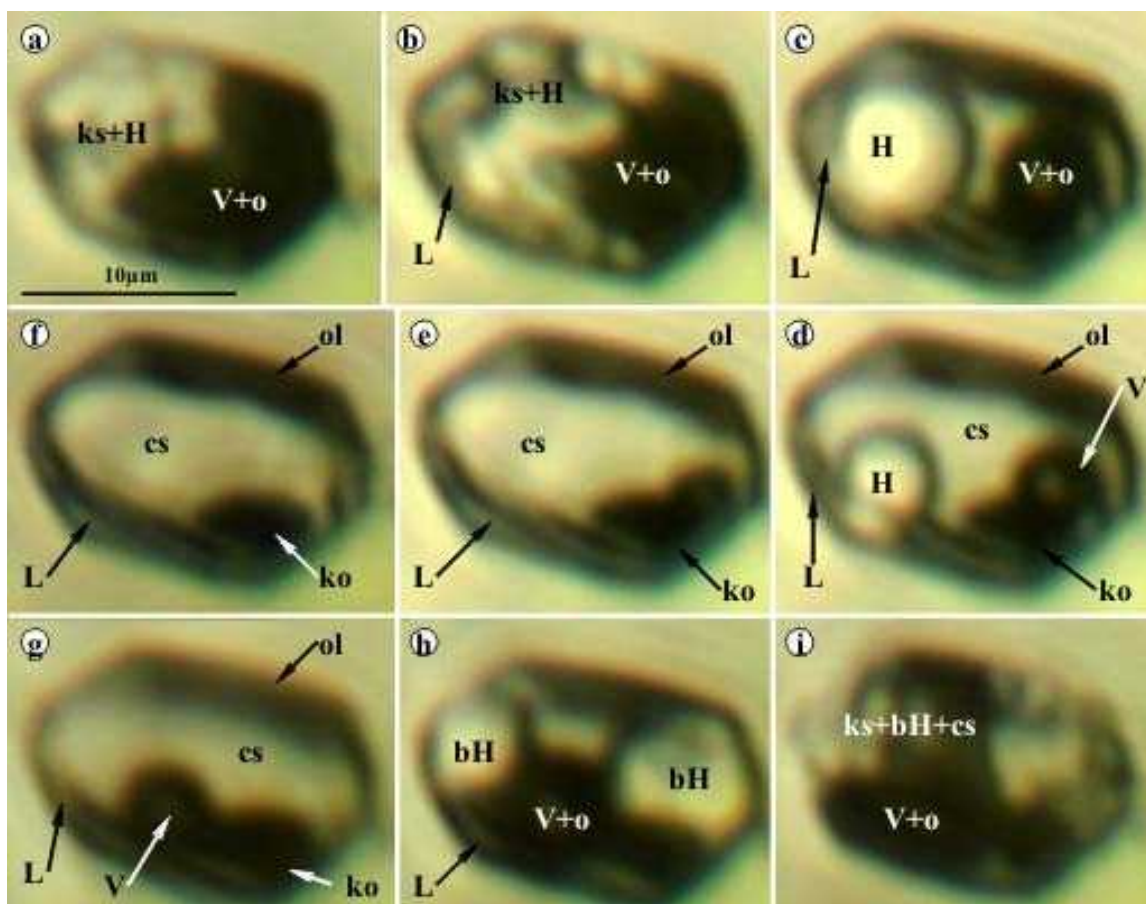


Fig. 175. Hydrosaline melt inclusion microthermometry, double cycled. Tarnița porphyry Cu-Au-Mo deposit. (T-Ta-I-6g). Pintea et al., 2020. **a.** 24°C, **b.** 243°C, **c.** 517°C, **d.** 590°C, **e.** 636°C, **f.** 696°C, **g.** 535°C, **h.** 307°C, **i.** 27°C. Microthermometric data: Tmks= 103°C; 242°C; 286°C, TmH= 611°C, Th(L)= 683°C, TnV= 657°C (1 cycle); 612°C (2 cycle), TnH 489°C (2 cycle): Tnks= 94°C, T= 683°C (2 cycle), P=505.773bar, Ws= 75.8046 wt% NaCl eq., d= 1.24775 g/ccm, xNaCl= 0.5, single phase state. **Notations:** H-halite, ks- another salt, V-Fe-rich vapor "melt" phase, o- opaque undifferentiated (oxide, sulfide), cs-clathrasil, L-hydrosaline melt, ko- opaque sulfide, ol- opaque liquid, bH- bursted halite.

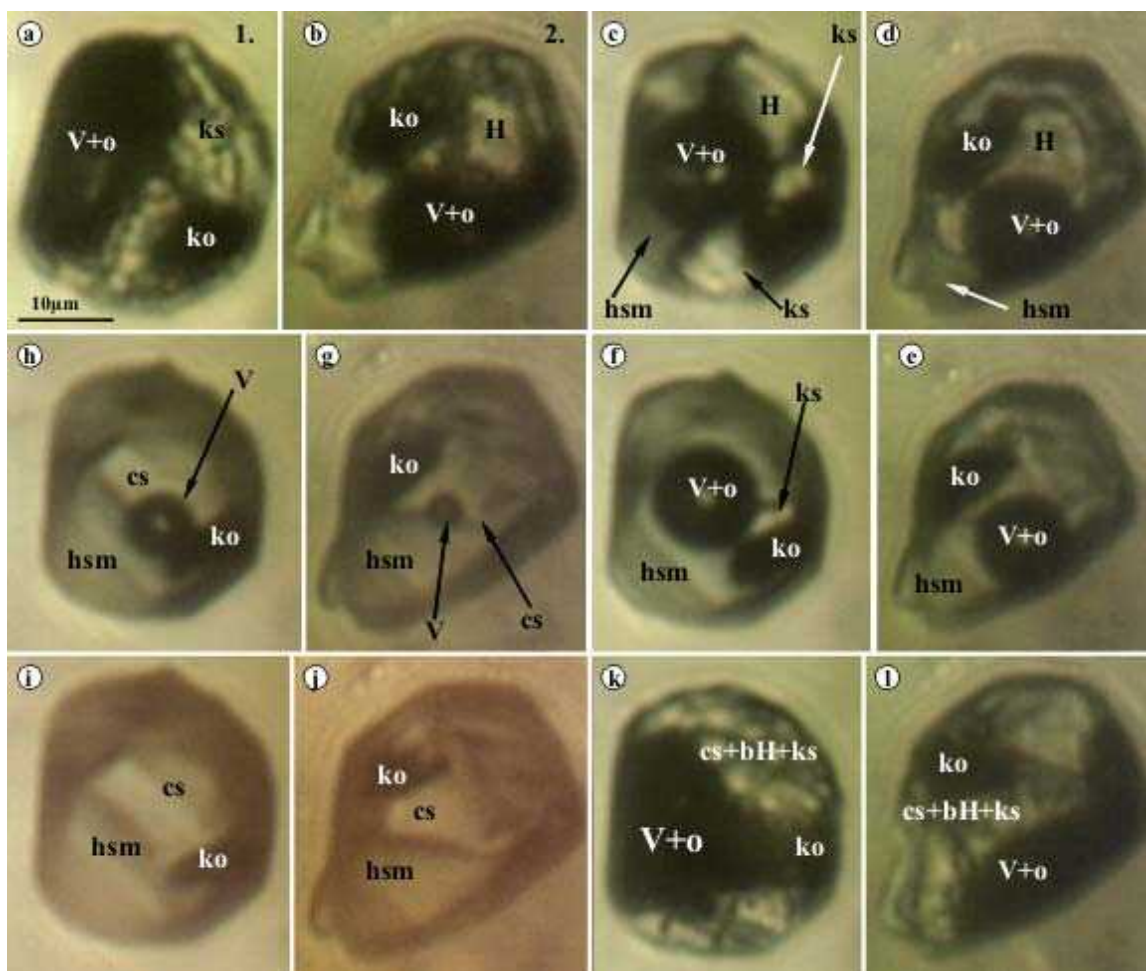


Fig. 176. Two Hydrosaline melt inclusion microthermometry, cycled in tandem. (Rovina porphyry Cu-Au-Mo deposit. (Ro-H4-2c). **a,b.** 23°C, **c,d.** 326°C, **e,f.** 409°C, **g,h.** 857°C, **i,j.** 931°C, **k,l.** 24°C; Microthermometric data: **1.** Tm1= 252°C, Tm2= 489°C, TmH= 599°C, Tms=591°C (anhydrite), Th(L)= 922°C, TnV= 839°C, Tq= 573°C-567°C, TnH= 383°C; P=1329.96bar, Ws= 68.318 wt% NaCl eq., xNaCl= 0.40, d= 1.0513g/ccm, single phase state. **2.** Tm2= 422°C, TmH= 522°C, Tms= 603°C (anhydrite) Th(L)= 866°C, TnV= 779°C, TnH= 471°C; P= 1180.54 bar, Ws= 67.3076 wt% NaCl eq, d= 1.0513 g/ccm, xNaCl= 0.38, V+L state; Notations: V- vapor (Fe-rich phase), o opaque, ko- another opaque, H-halite, bH- bursted halite, ks-another salt (anhydrite and others), hsm- hydrosaline melt, cs-clathrasil.

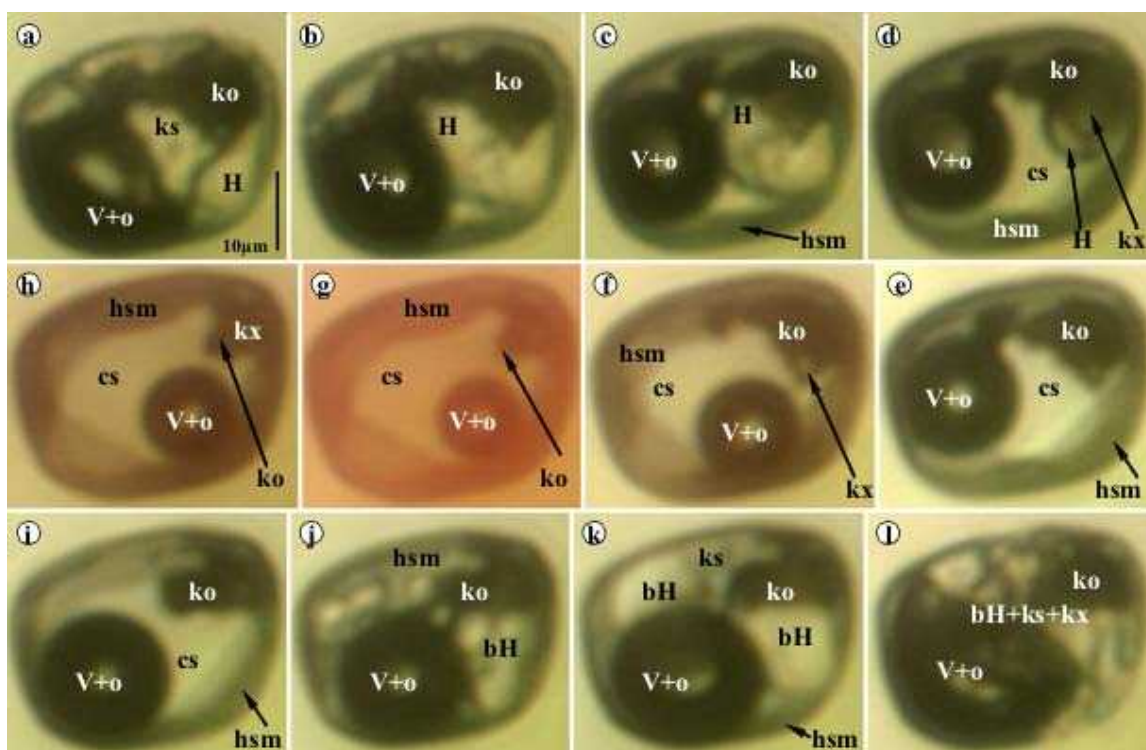


Fig. 177. Homogeneous hydrosaline melt inclusion microthermometry in quartz from Rosia Poieni porphyry Cu-Au-Mo deposit.(RP18new-9f). **a.** 36°C, **b.** 196°C, **c.** 351°C, **d.** 538°C, **e.** 678°C, **f.** 939°C, **g.** 1071°C, **h.** 995°C, **i.** 325°C, **j.** 303°C, **k.** 159°C, **l.** 27°C; Microthermometric data: TmH= 566°C, Th(L) ≥ 1071°C, P= 1869.38 bar, Ws= 69.3295 wt% NaCl eq., d= 1.04274 g/ccm, xNaCl= 0.41, TnbH= 318°C, Tns= 74°C, single phase state; Notations: V-vapor, o- opaque (Fe- rich phase), Ko- another opaque (oxide, sulfide), kx- anhydrite?, H-halite, ks- another salt, hsm- hydrosaline melt, cs- clathrasil, bH- bursted halite.

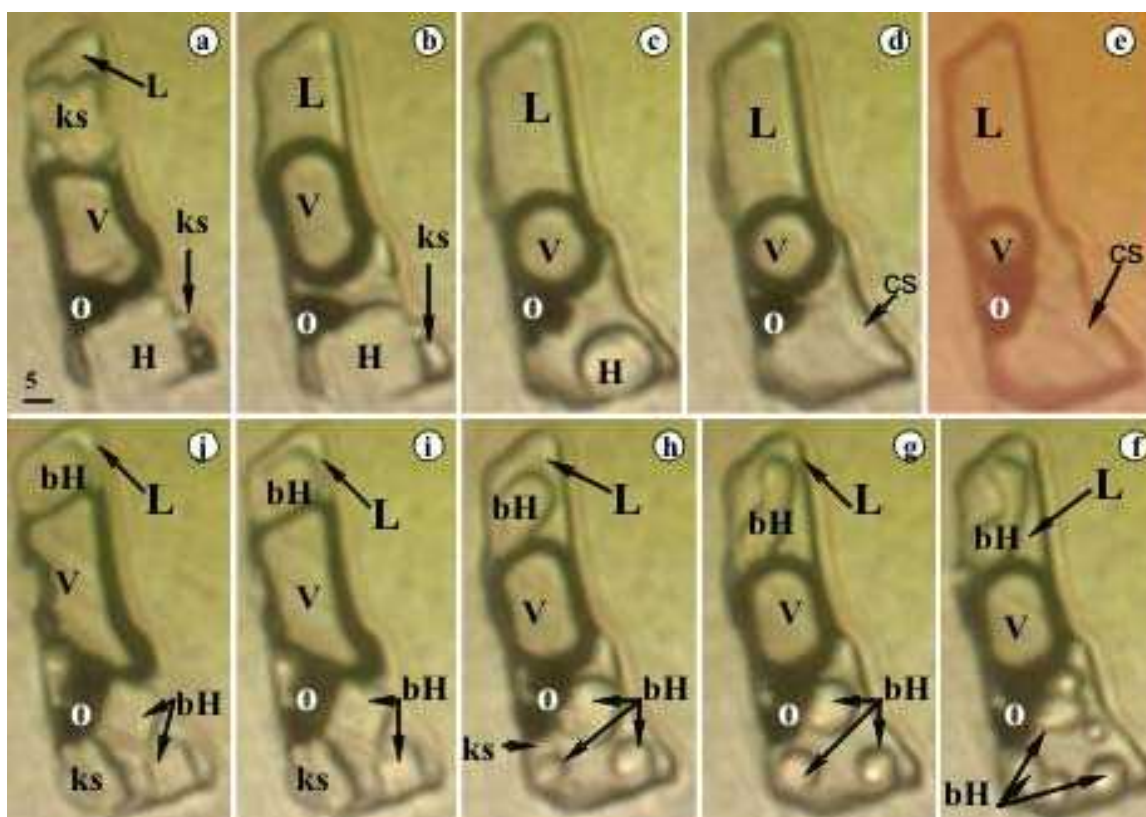


Fig. 178. Hydrosaline melt inclusion microthermometry. Rosia Poieni porphyry Cu-Au-Mo deposit.(RP-18re-3-4). **a.** 25°C, **b.** 172°C, **c.** 542°C, **d.** 656°C, **e.** 1014°C, **f.** 313°C, **g.** 294°C, **h.** 94°C, **i.** 50°C, **j.** 30°C; Microthermometric data: $T_{mks}=145^{\circ}\text{C}$, $T_{mH}=572^{\circ}\text{C}$, $T_h(L)\geq 1014^{\circ}\text{C}$, $P=1572.1\text{ bar}$, $W_s=70.1965\text{ wt\% NaCl eq.}$, $d=1.05434\text{ g/ccm}$, $x_{\text{NaCl}}=0.4$, (V+L) phase state; Notifications: H-halite, Ks-other salt, o-opaque, V-vapor, bH- bursted halite, L-hydrosaline liquid, cs-clathrasil.

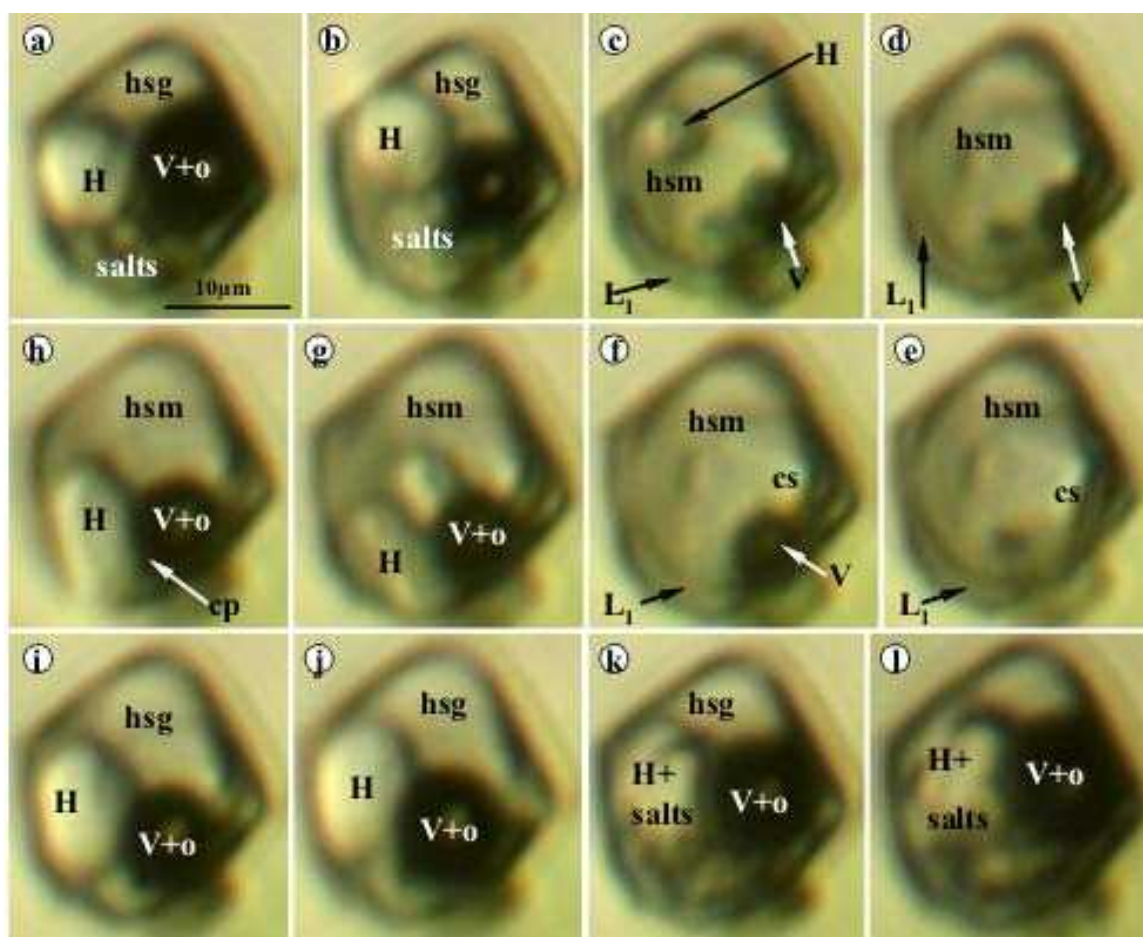


Fig. 179. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposit. (Rov-Ih pseudosecondary). **a.** 27°C, **b.** 139°C, **c.** 334°C, **d.** 358°C, **e.** 423°C, **f.** 309°C, **g.** 238°C, **h.** 185°C, **i.** 158°C, **j.** 100°C, **k.** 70°C, **l.** 28°C; Microthermometric data: T_{m1} = 115°C, T_{mH} = 353°C, $T_{H(L)}$ = 401°C, T_{nV} = 322°C, T_{nH} = 253°C, T_{nsalt} = 78°C, T = 401°C, P = 192.137bar, W_s = 42.2285 wt% NaCl eq., d = 1.03857 g/ccm, x_{NaCl} = 0.18, single phase state. Notations: H-halite, hsg-hydrossilicate (carbonate-sulphate-phosphate) glass?, salts-unidentified salt phases, hsm- hydrosaline melt, V-vapor, o-opaque, cp-chalcopyrite, cs-clathrasil, L1- silicate-(carbonate-sulphate-phosphate) liquid phase.

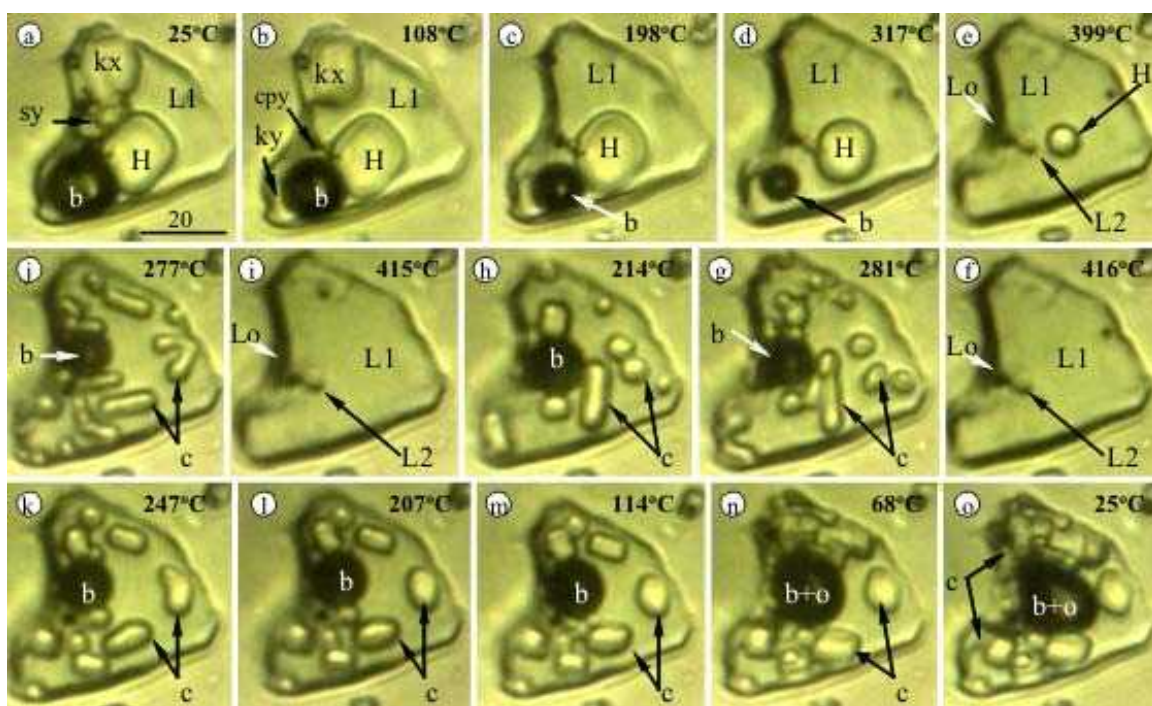


Fig 180. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposit, double cycled with formation of second liquid salt phase (Ro-H1).Pintea et al., 2021. Microthermometric data: **Cycle 1:** ThV=375°C;TmH= 410°C,Tn (H+b)= 306°C; **Cycle 2:** ThV= 377°C, TmH= 406°C, Tm intermediate = 274°C; 324°C; 349°C; 382°C;Tn (H+b)= 303°C, Tnlast= 101°C; 81°C; Notations: sy-sylvite, kx-second salt unknown, ky-third salt unknown, cpy-chalcocopyrite, b-bubble, H-halite, L1- liquid salt, Lo- opaque liquid, o-opaque solid, c- “conglomerate salt”; scale bar in μm .

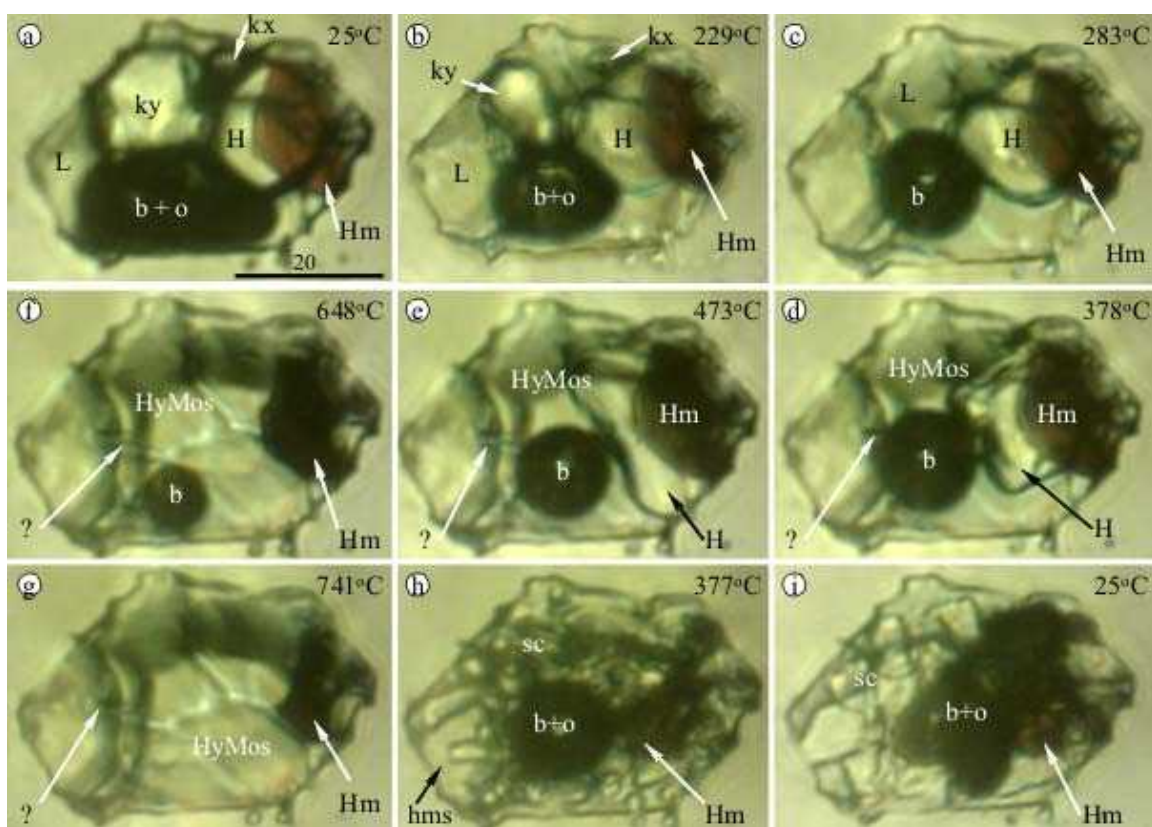


Fig. 181. Hydrosaline melt inclusion microthermometry with specularitic hematite. Rovina porphyry Cu-Au-Mo deposit. (Ro-H8-1); Pintea et al., 2021. $T_mH = 555^\circ\text{C}$, $T_h(L) = 717^\circ\text{C}$, $P = 724.398$ bar, $W_s = 67.7405$ wt% NaCl eq., $d = 1.10995$ g/ccm, $x_{\text{NaCl}} = 0.4$, single phase state. Notations: L-saline aqueous solution (brine), b-bubble, o- opaque, kx,ky-unknown, H-halite, Hm-hematite, HyMos- hydrous molten salt, sc-“conglomerate”- salt. Scale bar in microns.

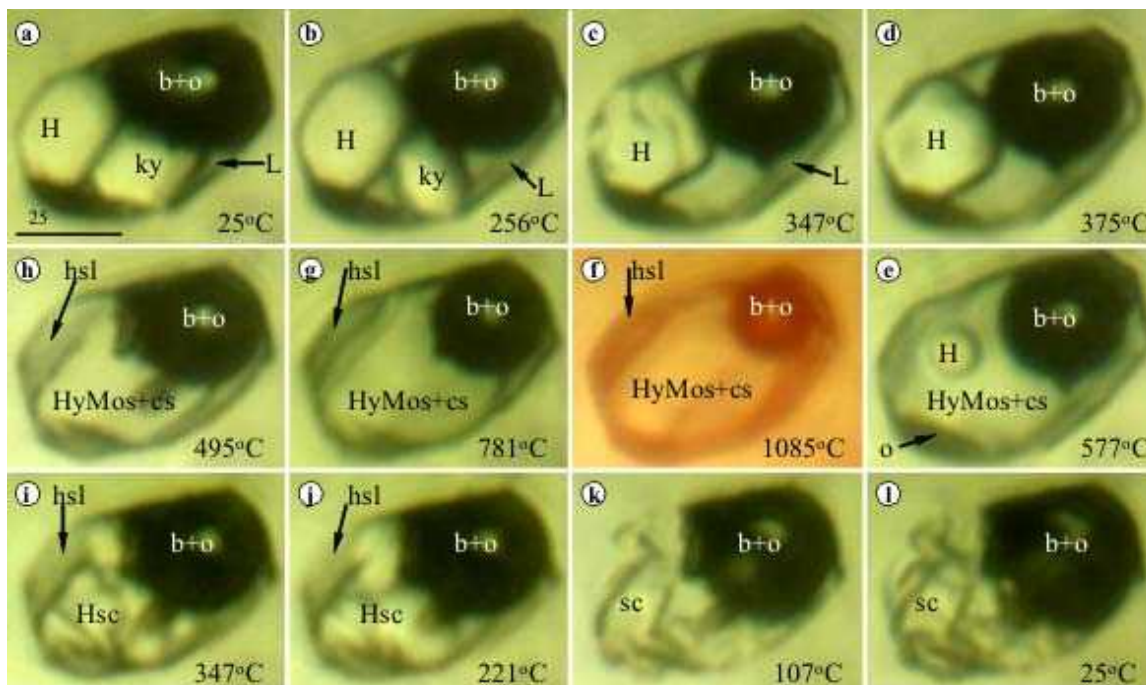


Fig. 182. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposit (Ro-H19-1), Pinteá et al., 2021. Microthermometric data: $T_m H = 585^\circ\text{C}$, $T_h(L) \geq 1085^\circ\text{C}$, $P = 1743.83$ bar, $W_s = 72.0732$ wt% NaCl eq., $d = 1.06448$ g/ccm, $x_{\text{NaCl}} = 0.4$, V+L phase state, $T_n H = 392^\circ\text{C}$, $T_{m\text{new}} = 966^\circ\text{C}$ (crystallised from around 642°C probably by reaction of mixed salt liquid and opaque Fe-rich phase initially adhering to the wall inclusion, not shown in the pictures), T_{n2} (zeolite?) = 105°C . Notations: H- halite, ky- unknown, b- bubble, o- opaque, L- brine, cs₁ clathrasil, HyMos- hydrothermal molten salt, Hsc- conglomerate halite mixed salt, sc- whole salt conglomerate, T_n - renucleation temperature, scale bar in microns.

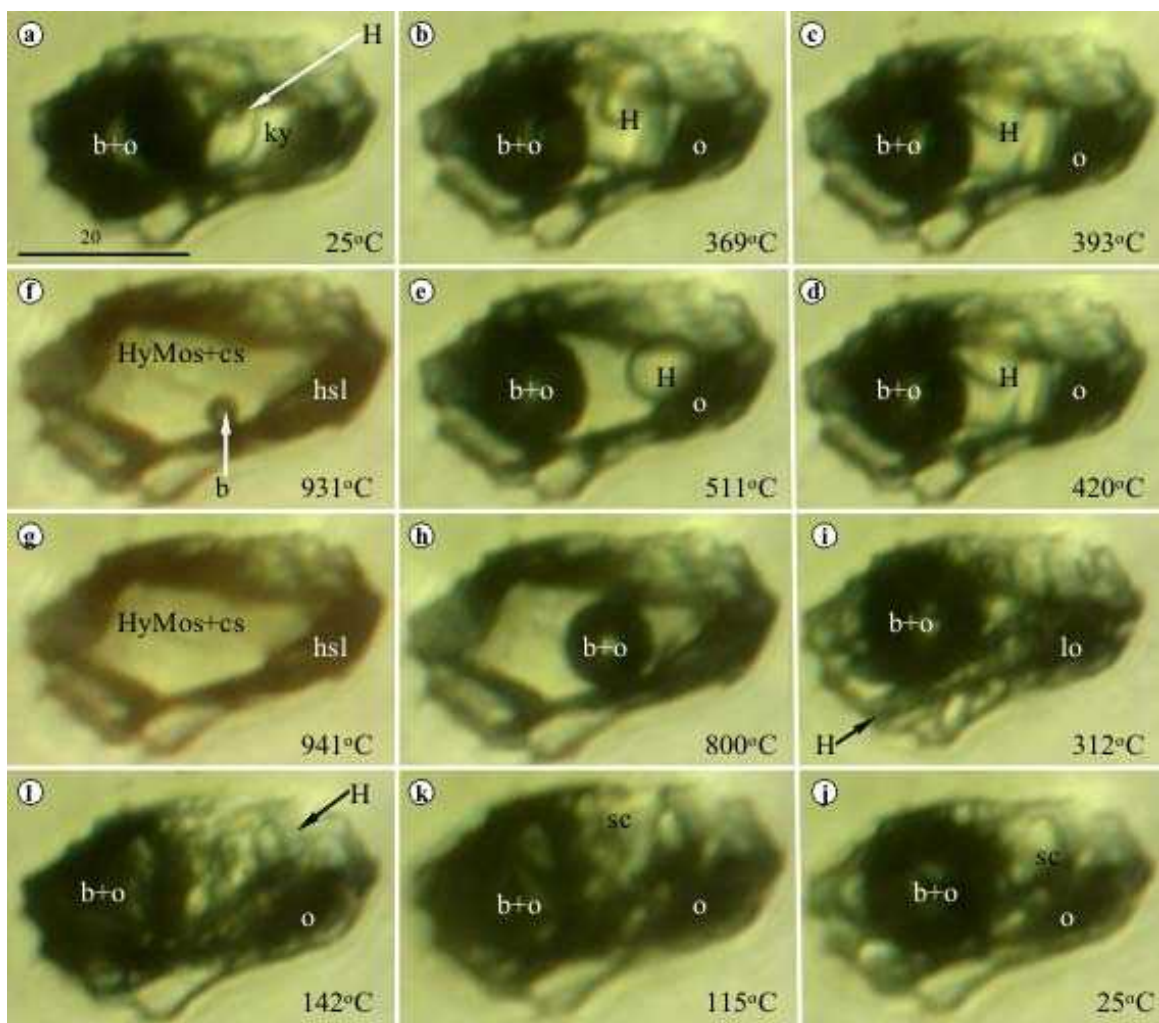


Fig. 183. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo. (Ro-H10). Pintea et al., 2021. Halite retrograde solubility in **b-c**. Microthermometric data: $T_mH=522^{\circ}C$, $T_h(V)=936^{\circ}C$, $P=1596.84$ bar, $W_s=63,0048$, $d=0.995068$ g/ccm, $x_{NaCl}=0.34$, V+L phase state. Notations: H-halite, b-bubble, o-opaque, HyMos-hydrothermal molten salt, hsl-Fe-rich hydrosilicate liquid, cs-clathrasil, cs-conglomerate salt. Scale bar in microns.

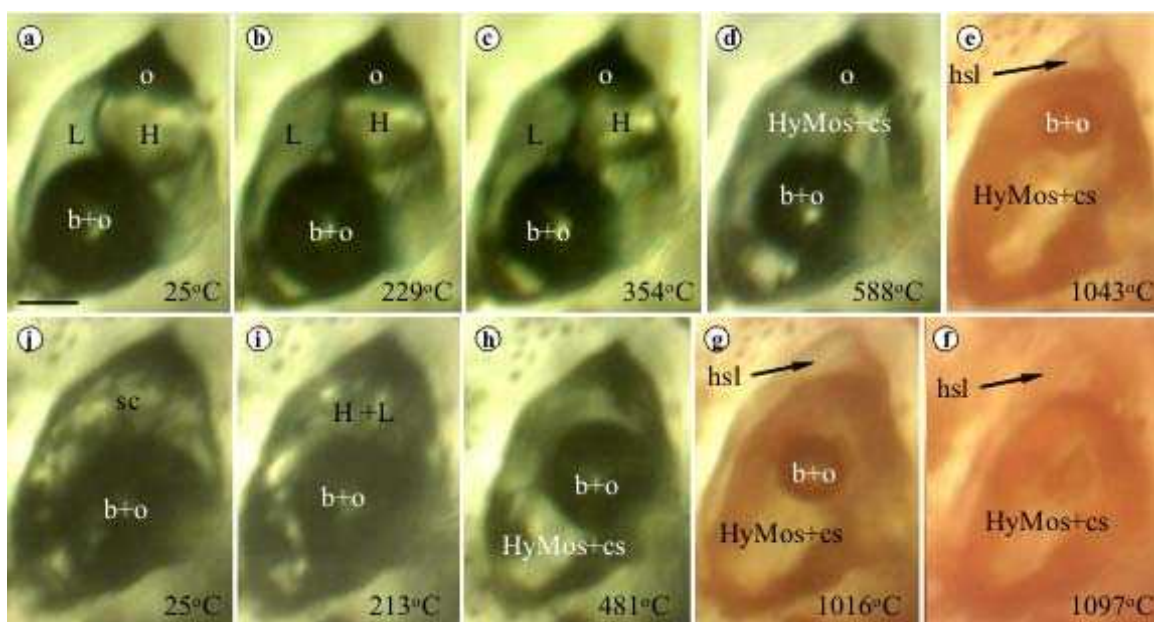


Fig. 184. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposit. (Ro-H12-1). Pintea et al., 2021. Microthermometric data: $T_mH = 509^\circ\text{C}$, $T_h(V) \geq 1096^\circ\text{C}$, $P = 2298.22$ bar, $W_s = 61.165$ wt% NaCl eq., $X_{\text{NaCl}} = 0.33$, $d = 0.954659$ g/ccm. Notations: L-aqueous liquid, H-halite conglomerate, b-bubble, o- opaque, hsl- hydrosilicate liquid, HyMos-hydrothermal molten salt, sc- conglomerate salt. Scale bar: 10 μm.

Note: Immiscible fluxing fluids penetrates already crystallized quartz microfissures at $\geq 1097^\circ\text{C}$ generating heterogeneous pseudosecondary trail of hydrosaline melt inclusions; ones are single phase others V+L or L+H even V+H suggesting large range of temperatures but they trapped various quantity of the fluid phases; Decreasing P and T are very fast and the differences of trapping condition are very large, apparently. In such cases Roedder, 1992, suggested to take the minimum P-T-X values from such assemblages, for further interpretations.

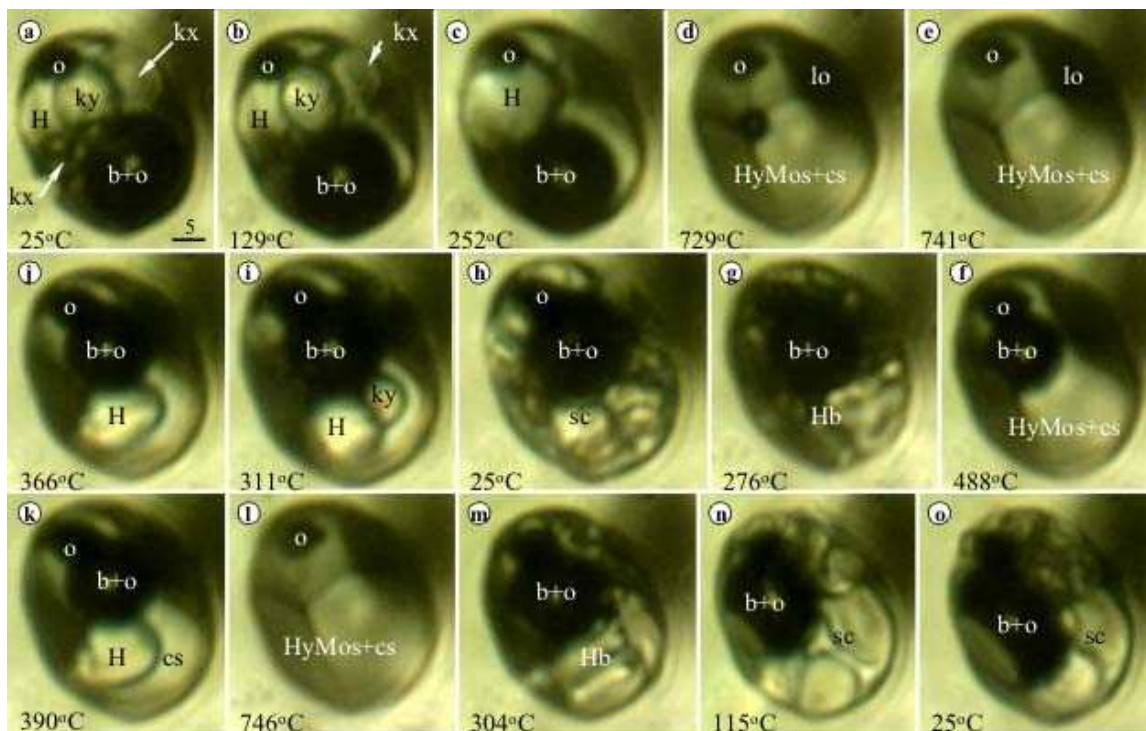


Fig. 185. Hydrosaline melt inclusion microthermometry. Double cycled. Rovina porphyry Cu-Au-Mo deposit. (Ro-H12-3). Pintea et al., 2021. Microthermometric data: **cycle 1**: Tm1= 69°C, 87°C; Th= 572°C (overestimated?), Th(L)= 740°C, TnV= 672°C, TnH= 278°C, TnKx= 70°C, P= 729.457bar, Ws= 70.1965 wt%, d= 1.13032 g/ccm, xNaCl= 0.4 V+L phase state; **cycle 2**: Tmky= 106°C, Tm bursted halite= 313°C, 348°C, 358°C, 450°C; Th(L)= 741°C, TnV= 673°C, TnH= 314°C, TnKx= 81°C, T= 741°C, P= 1091.64 bar, Ws= 53.177 wt% NaCl eq., xNaCl= 0.23; V+L phase state.. Notations: (**a-h** cycle 1; **h-o** cycle 2), H-halite, Hb-bursting halite conglomerate, b-bubble, o-opaque, lo-liquid opaque, kx-sylvite + unknown, ky-unknown, HyMos-hydrothermal molten salt, cs-clathrasil, sc- salt conglomerate; scale bar in microns.

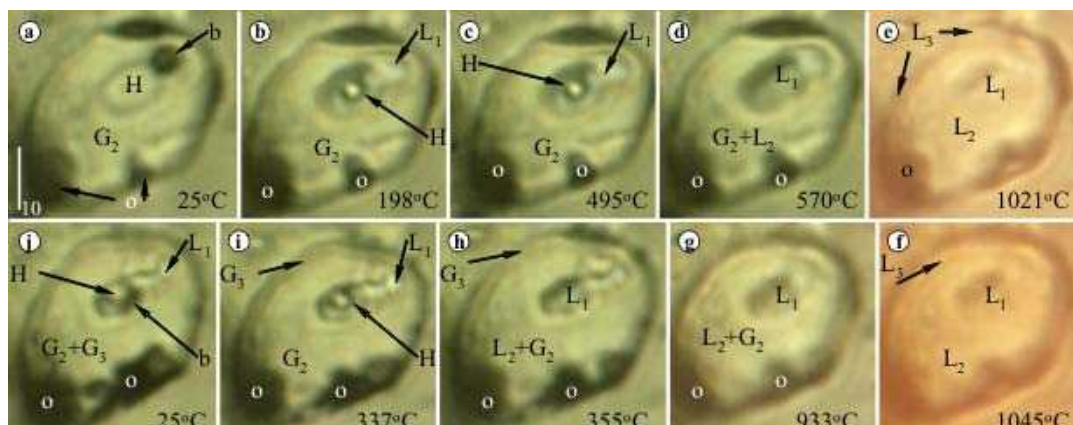


Fig. 186. Complex hydrosilicate (carbonate-sulphate-phosphate) - hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposit. Ro-H17-1. Secondary magmatic fluids. Notations: H- halite, G2- sulphate – silicate glass, L1- hydrous salt melt, L2-sulphate- silicate liquid, L3- hydrosilicate liquid, G3- silicate glass, o- opaque (oxide, sulphide)

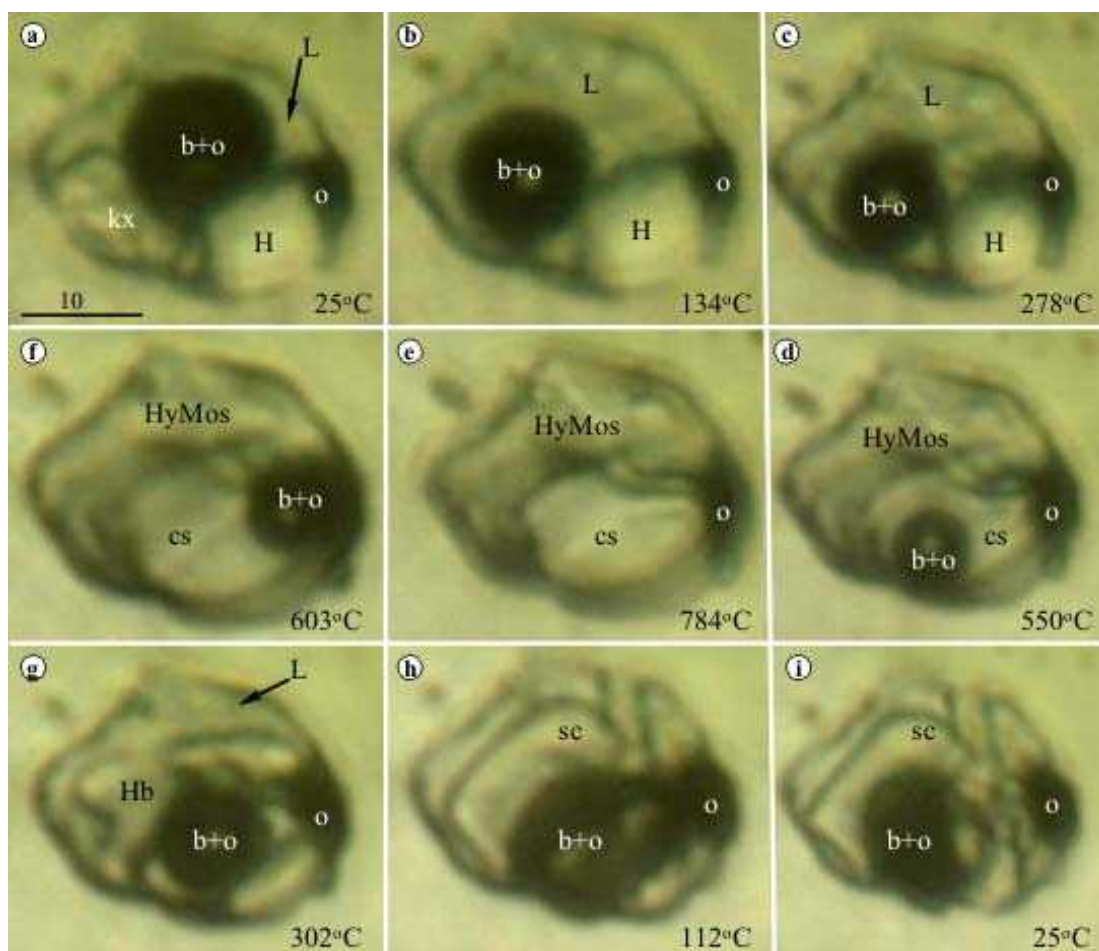


Fig. 187. Hydrosaline melt inclusion microthermometry. Rovina porphyry Cu-Au-Mo deposit. Ro-H18. Microthermometric data: $T_mH = 511^\circ\text{C}$, $T_h(L) = 713^\circ\text{C}$, $P = 834.754 \text{ bar}$, $W_s = 61.4467 \text{ wt\% NaCl eq.}$, $d = 1.03153 \text{ g/ccm}$, $x_{\text{NaCl}} = 0.33$, single phase state, $T_{nV} = 632^\circ\text{C}$, $T_nH = 315^\circ\text{C}$. Notations: Kx-unknown, H, halite, b-bubble, o-opaque (Fe oxide, sulfide), L-brine, HyMos-transparent hydrothermal molten salt, cs-clathrasil, Hb-burst halite, sc-conglomerate salt, scale bar in μm .

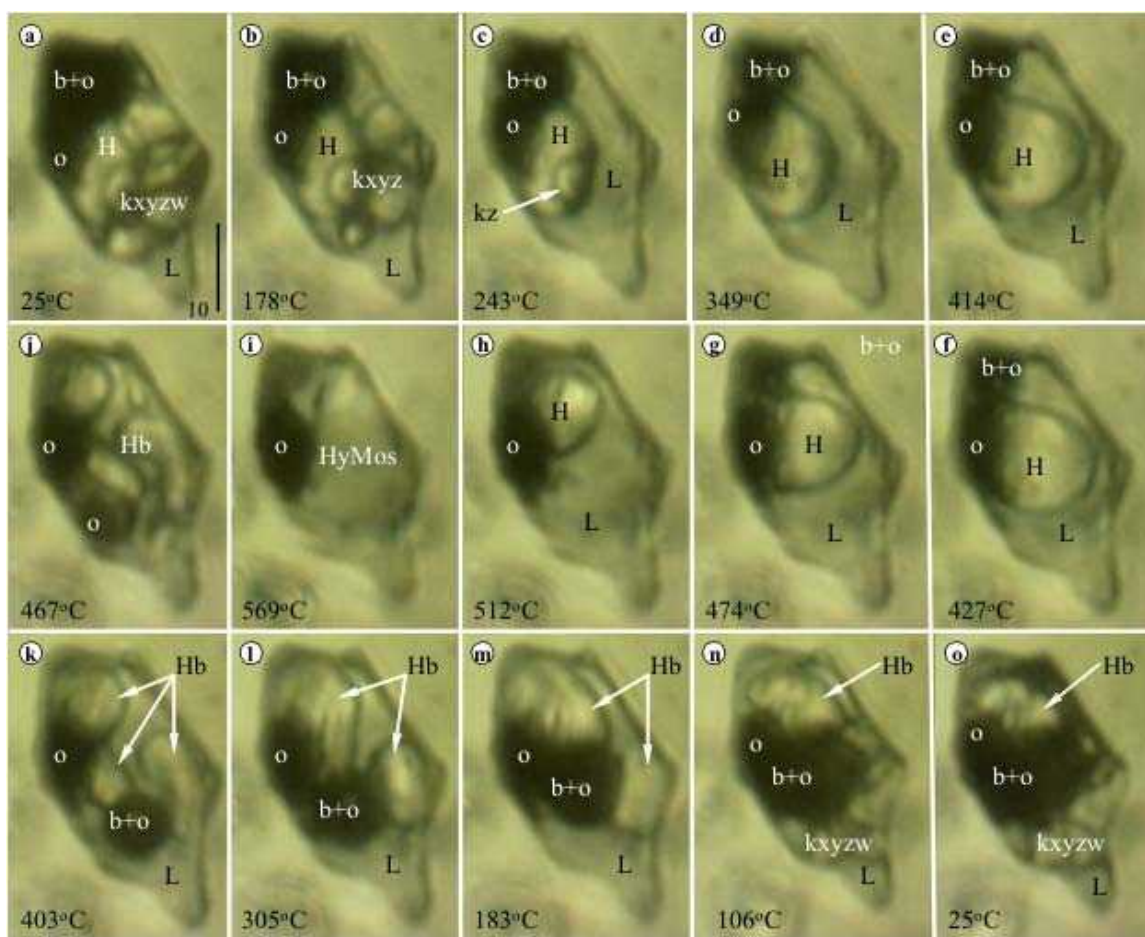


Fig. 188. Hydrosaline melt inclusion microthermometry by halite homogenization. Rovina porphyry Cu-Au-Mo. (Ro-H19-1). Pintea et al., 2021. Microthermometric data: T_{m1} = 98°C, 112°C; $T_h(L+H)$ = 508°C, $T_h(L)$ = 566°C, T_{nH} = 452°C, T_{n2} = 263°C, 108°C; T = 566°C, P = 947,428 bar, W_s = 68.7552 wt% NaCl eq., X_{NaCl} = 0.41, d = 1.28198 g/ccm, fluid is in the (L+H) state. Notations: H-halite, o-opaque (Fe oxide, sulfide), Kxyzw- sylvite + unknown, L-brine (aqueous molten salt or a hydrosilicate brine liquid or solidified metastable crust), HyMos-hydrothermal molten salt, Hb- bursted halite, scale bar in μm .

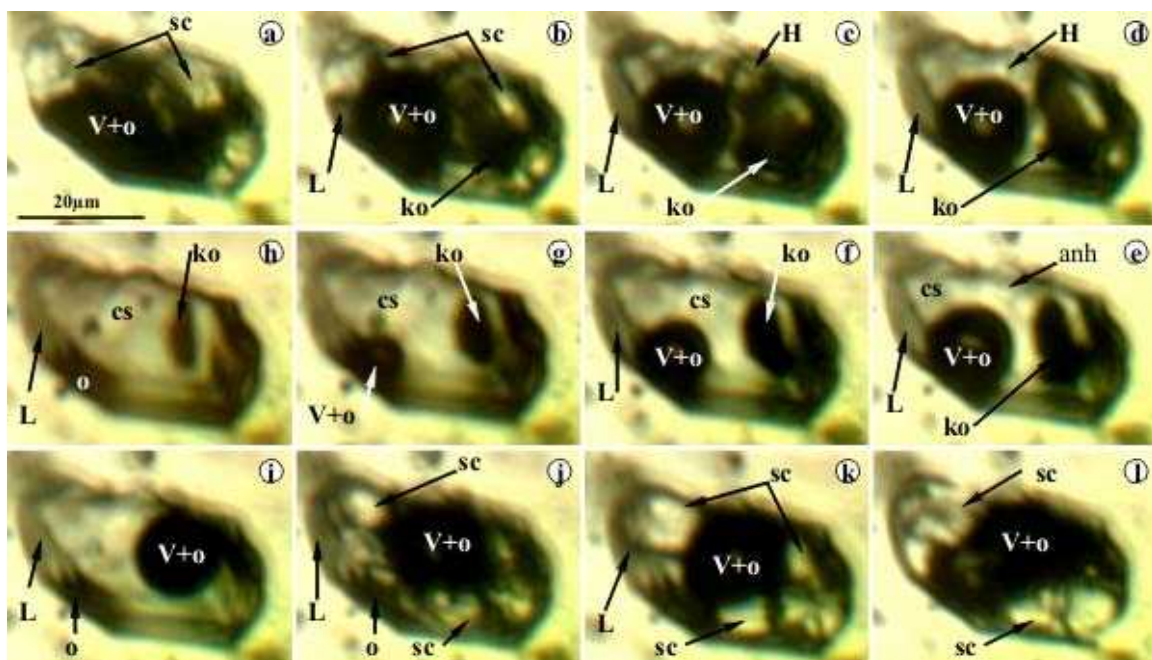


Fig. 189. Replicated (after one year) hydrosaline melt inclusion microthermometry from Rosia Poieni porphyry Cu-Au-Mo deposit.(RP18-rep). **a.** 25°C, **b.** 420°C, **c.** 560°C, **d.** 755°C, **e.** 932°C, **f.** 969°C, **g.** 861°C, **h.** 567°C, **i.** 567°C, **j.** 218°C, **k.** 118°C, **l.** 25°C; Microthermometric data: Tm (sc)= 126°C, 312°C, 370°C, 446°C, Tm last H= 580°C, Tm anh?= 836°C, Th(L)= 965°C, TnV= 926°C, TnH= 369°C, Tn (sc)= 234°C, 161°C, 83°C; T= 965°C, P= 1339.56 bar, Ws= 71.3519 wt% NaCl eq., xNaCl=0.42, (V+L) state. Notations: v-vapor-o-opaque (oxide, sulfide), bH- bursted halite, L-hydrosaline melt, H- last halite grain, sc- salt conglomerate, cs- clathrasil, lo- liquid opaque.

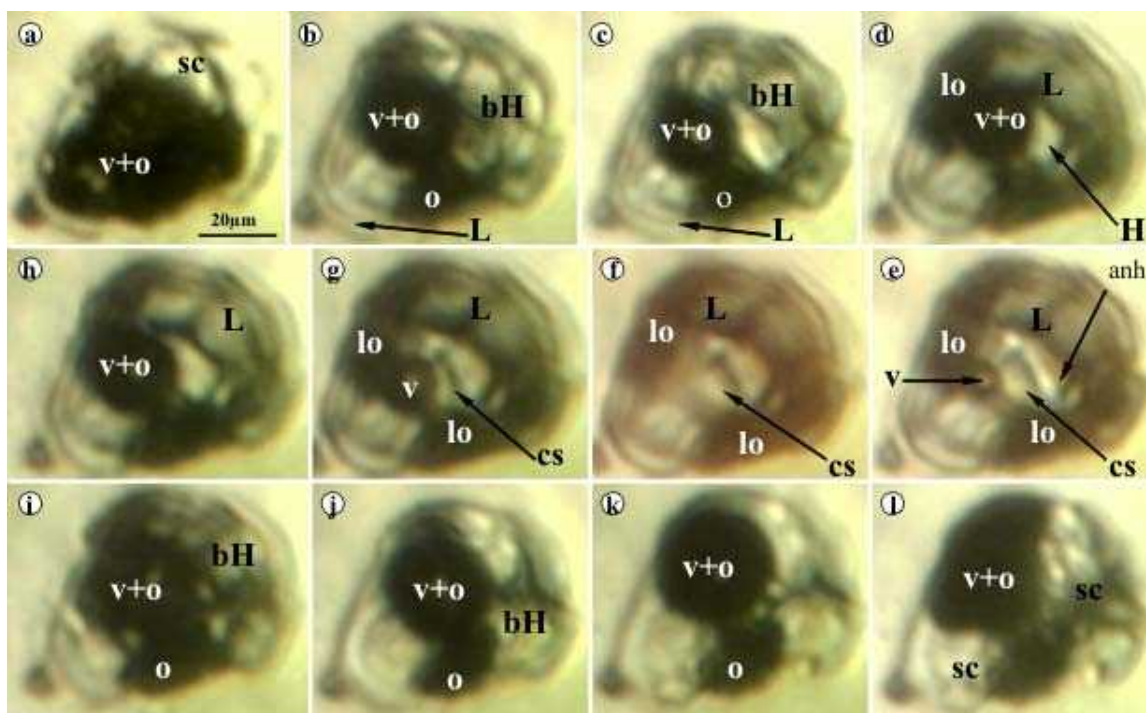


Fig. 190. Complex hydrosilicate – chloride – sulphate – phosphate – fluoride - bromide inclusion from Tarnita porphyry Cu-Au-Mo deposit. (T-Ta-T-8). Pintea et al., 2020. Microthermometric data: $T_{msalt}=313^{\circ}\text{C}$, 391°C , 443°C ; $T_{mH}=592^{\circ}\text{C}$, $T_{m\text{ anh}(?)}=711^{\circ}\text{C}$, $T_h(L)=1078^{\circ}\text{C}$, $T_{nbH}=379^{\circ}\text{C}$, $T_{nsalt(zeolite-?)}=138^{\circ}\text{C}$; $T=1078^{\circ}\text{C}$; $P=1639.51\text{ bar}$; $W_s=73.0815\text{ wt\%NaCl eq}$; $d=1.0726\text{ g/ccm}$, $x_{NaCl}=0.45$, (V+L) phase state inside hydrosaline melt. Notations: V- vapor, o- opaque, hsm- hydrosaline melt, hsl- hydrosilicate liquid, sc- conglomerate salt, G- silicate glass, CL- chloride melt.

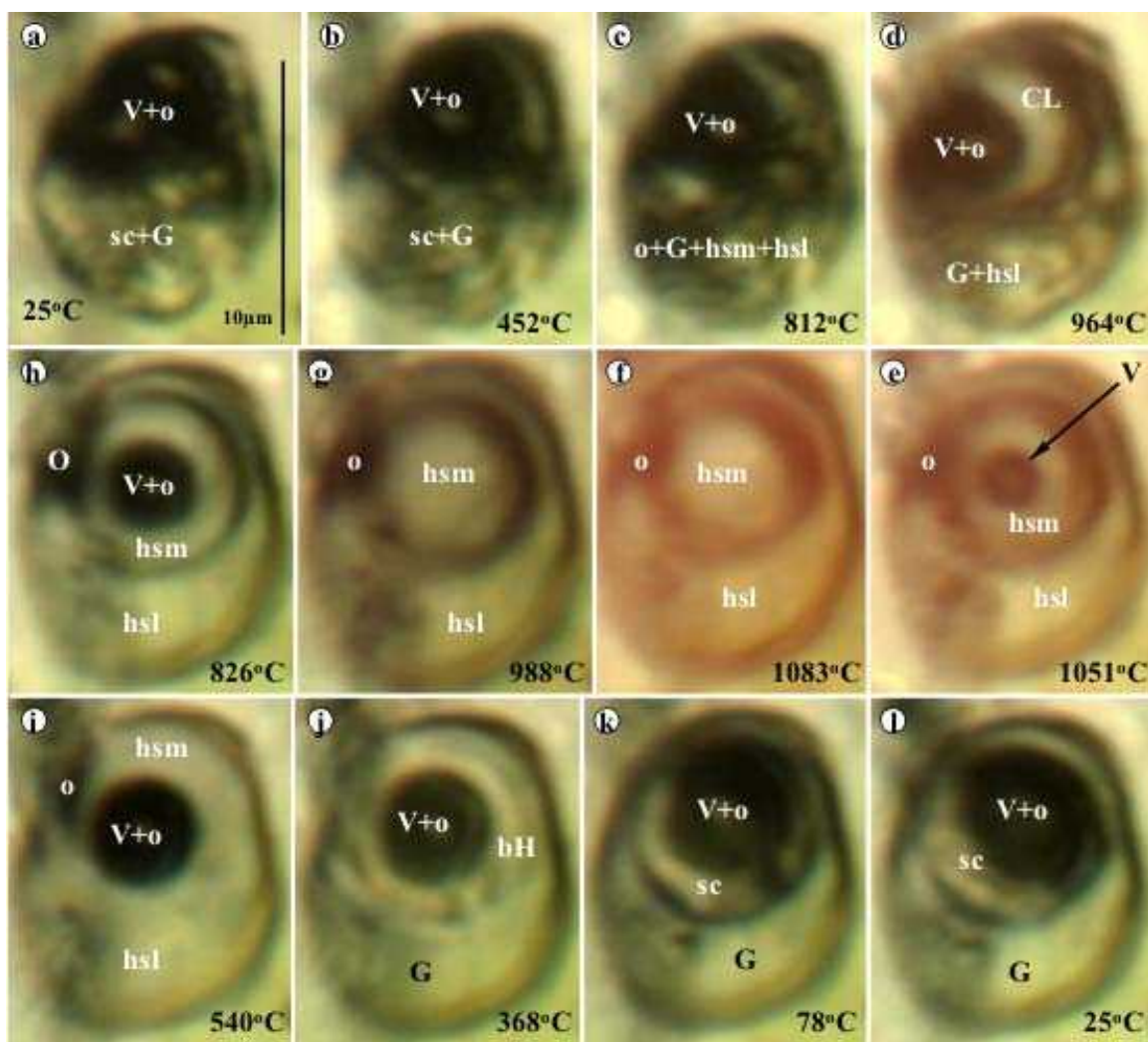


Fig. 191. Complex hydrosilicate – chloride – sulphate – phosphate – fluoride - bromide inclusion from Tarnita porphyry Cu-Au-Mo deposit. (T-Ta-T-8). Pintea et al., 2020. Microthermometric data: $T_{msalt}=313^{\circ}\text{C}$, 391°C , 443°C ; $T_{mH}=592^{\circ}\text{C}$, $T_{m\text{ anh}(?)=711^{\circ}\text{C}}$, $T_{h(L)}=1078^{\circ}\text{C}$, $T_{nbH}=379^{\circ}\text{C}$, $T_{nsalt(zeolite-?)=138^{\circ}\text{C}}$; $T=1078^{\circ}\text{C}$; $P=1639.51\text{ bar}$; $W_s=73.0815\text{ wt\%NaCl eq}$; $d=1.0726\text{ g/ccm}$, $x_{NaCl}=0.45$, (V+L) phase state inside hydrosaline melt. Notations: V- vapor, o- opaque, hsm- hydrosaline melt, hsl- hydrosilicate liquid, sc- conglomerate salt, G- silicate glass, CL- chloride melt.

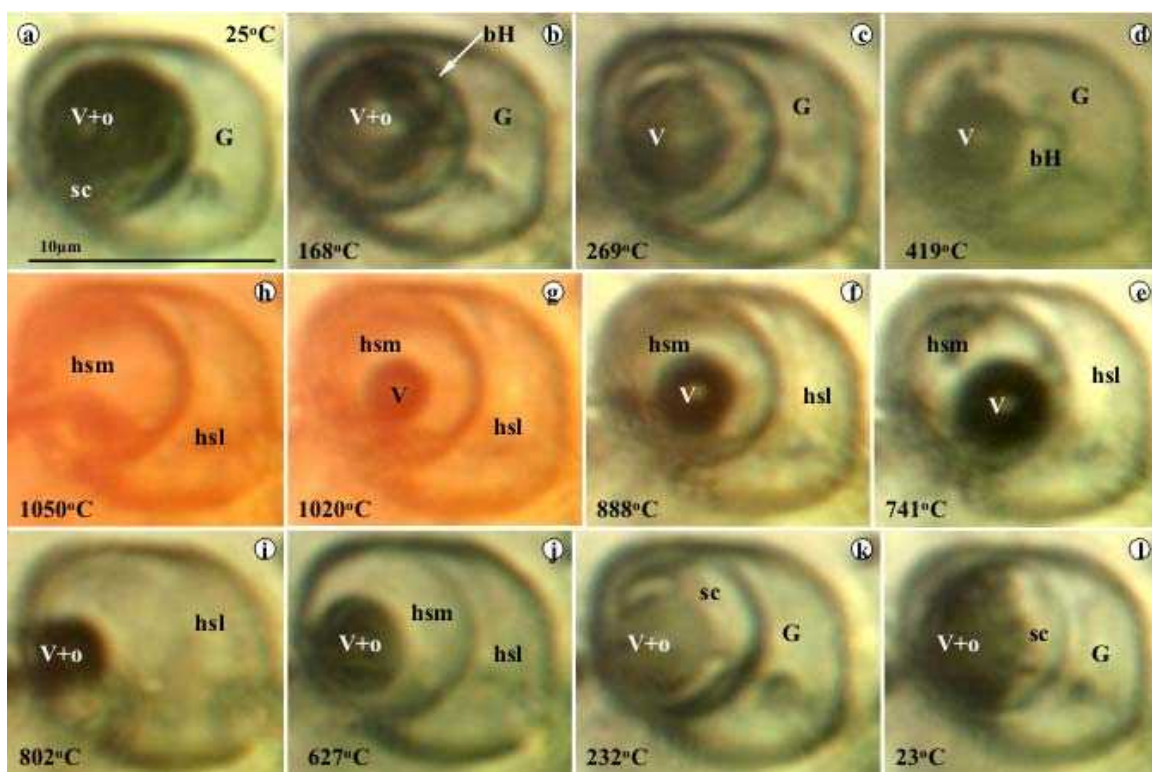


Fig. 192. The same complex hydrosilicate-salts inclusion from **Fig. 191**, replicated microthermometry after one year. (T-Ta-I-8, third cycle), Pintea et al., 2020. Microthermometric data: $T_{\text{msalt}} = 229^{\circ}\text{C}$; 348°C ; 478°C , $T_{\text{mbH}} = 558^{\circ}\text{C}$; $T_{\text{mglass}}(\text{start}) = 343^{\circ}\text{C}$, $T_{\text{mo}} = 829^{\circ}\text{C}$, $T_{\text{h(L)}} = 1045^{\circ}\text{C}$, $T_{\text{nmisc}} = 642^{\circ}\text{C}$, $T_{\text{nbH}} = 407^{\circ}\text{C}$, $T_{\text{nsalt}} = 330^{\circ}\text{C}$, 302°C ; $T = 1045^{\circ}\text{C}$, $P = 1819^{\circ}\text{C}$, $W_s = 68.1737 \text{ wt\% NaCl eq.}$, $d = 10339 \text{ g/ccm}$, $x_{\text{NaCl}} = 0.39$, (V+L) – phase state. Notations: V-vapor, o-opaque, bH- bursted halite, sc- salt conglomerate, G-glass, hsl- hydrosilicate liquid, hsm- hydrosaline melt.

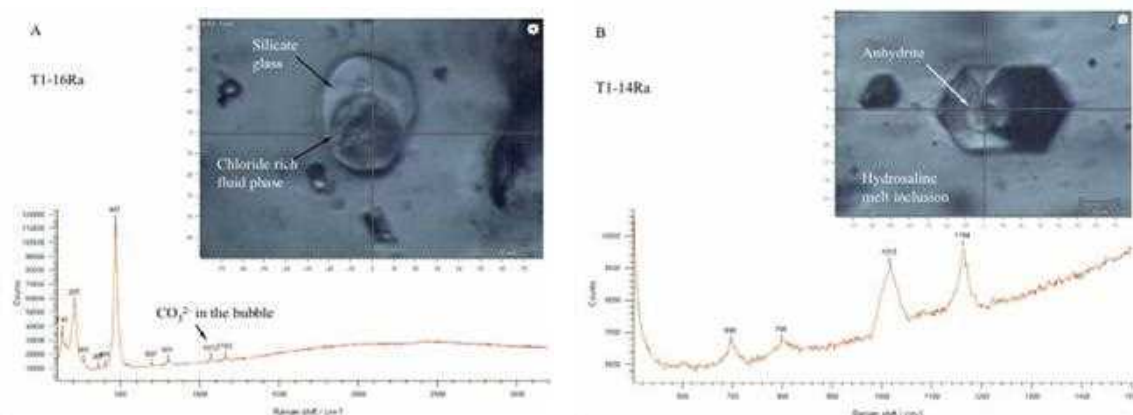


Fig. 193. Raman spectra of the same (left) complex silicate-hydrosaline melt inclusion pictured in **Fig. 191** and **Fig. 192** showing the presence of carbonate ion in the bubble of the salt melt phase surrounded by silicate glass (A) and anhydrite daughter phase (B) formed in hydrosaline melt inclusion (without liquid phase at room temperature) from the same quartz sample. Pinteá et al., 2020.

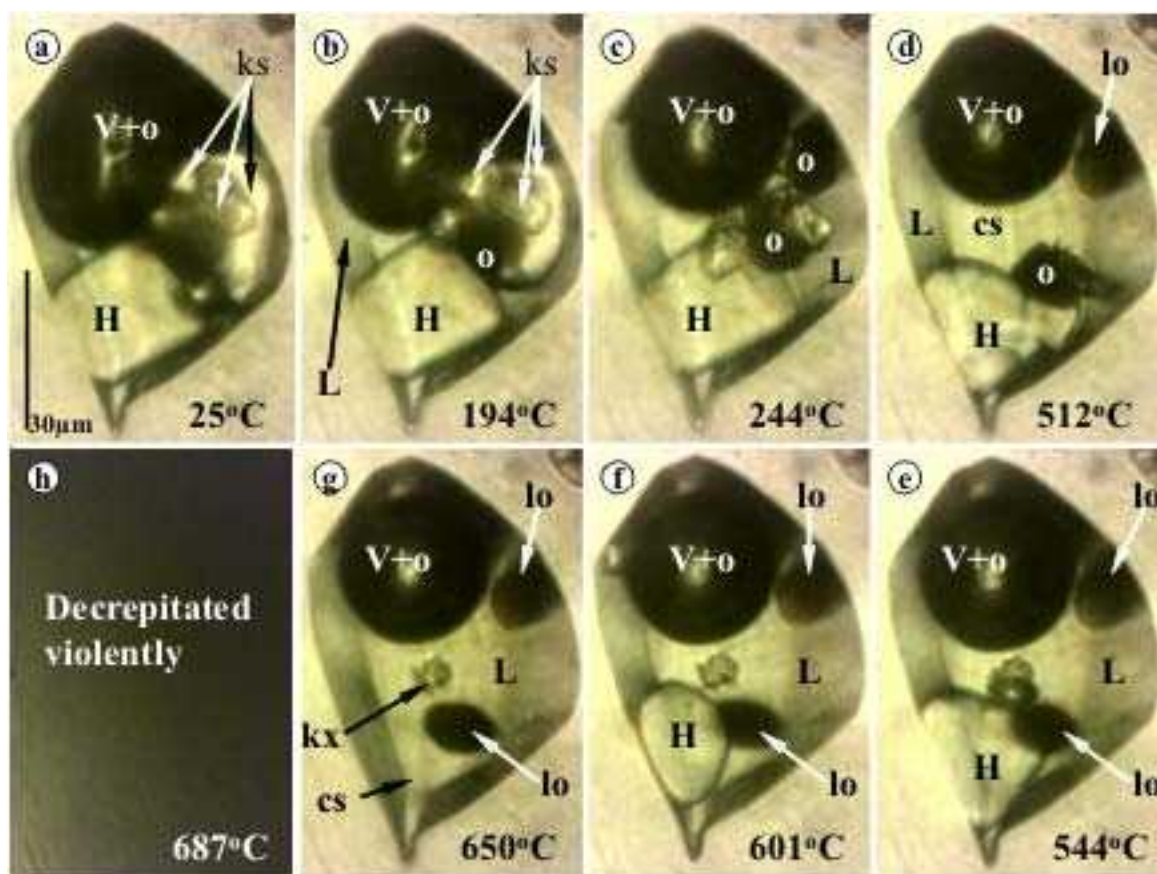


Fig.194. Hydrosaline melt inclusion microthermometry in quartz from Roşia Poieni porphyry Cu-Au-Mo deposit, decrepitated before final homogenization. (RPnew18-re3-4). Microthermometric data: TmKs=242°C, 253°C, 315°C; TmH= 638°C, Td=687°C, Th≥ 687°C, T≥ 687°C, P= 441.112 bar, Ws=79.6209 wt% NaCl eq., d= 1.30426 g/ccm; xNaCl= 0.56, Single phase state. Notations: V- vapor, o-opaque, H-halite, ks-other salts, L-hydrosaline melt, lo- liquid opaque , Kx-unknown, cs-clathrasil, Td-decrepitation temperature.

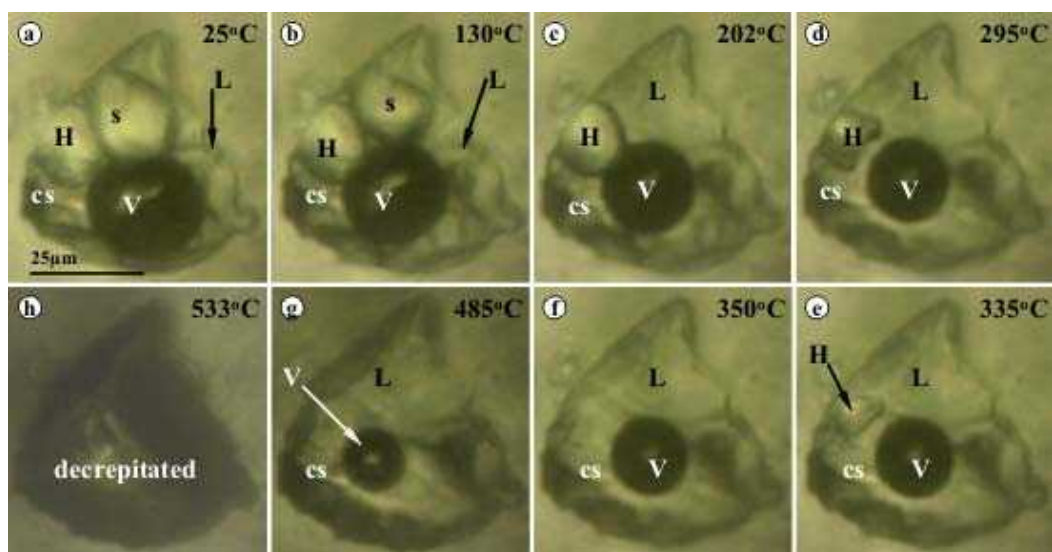


Fig.195. Hydrosaline melt inclusion microthermometry in quartz from Moldova Nouă porphyry Cu-Mo-(Au) deposit (Banat, Upper Cretaceous), decrepitated before final homogenization. (11W-1a-6a). Microthermometric data: $T_{ms}=198^{\circ}\text{C}$, $T_{mH}=349^{\circ}\text{C}$, $T_d=530^{\circ}\text{C}$, $T_h(L)\geq 530^{\circ}\text{C}$; $T\geq 530^{\circ}\text{C}$, $P=548.786\text{ bar}$, $W_s=41.8509\text{ wt\% NaCl eq.}$, $d=0.910066\text{ g/ccm}$, $x_{\text{NaCl}}=0.18$; Notations: H-halite, s- salt, L- hydrosaline melt, cs-clathrasil, Td- decrepitation temperature.

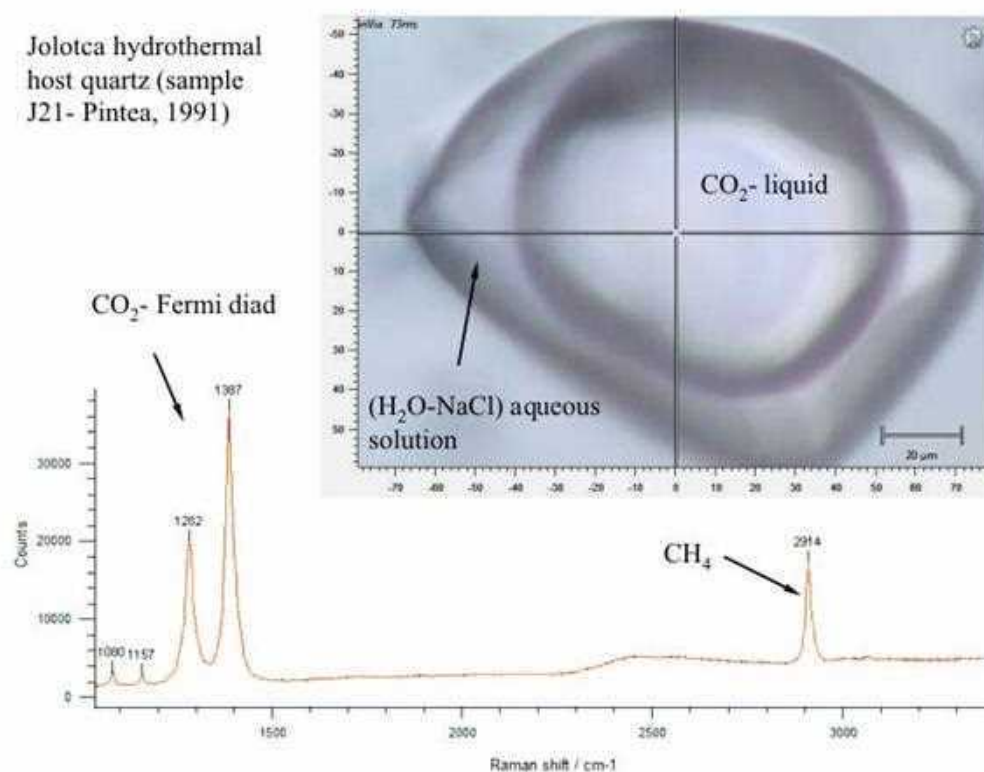


Fig. 196. Raman spectra of $\text{CO}_2\text{-H}_2\text{O-NaCl}$ fluid inclusion in hydrothermal quartz from the complex hydrothermal REE-sulfide mineralization from Jolotca, Ditrău Massif (Eastern Carpathian). The presence of CH_4 in the carbonic part of the inclusion was inferred firstly by freezing microthermometry showing lower solid melting temperature of the CO_2 -rich phase down to -57.7°C (e.g. **Fig. 118**). In Via Renishaw Raman spectrometer at IGR Bucharest (E. Ghinescu, operator- incident line 523 nm, lense x50, 1200l/mm, exposure 10s, accumulation 20).

Table 1. Characteristic microthermometry and related data obtained for a lot of brine inclusions from recrystallized quartz veins and pods from Țibleș Massif (Magura Neagră – Suplai mining district and Mestecanului Valley zone). V- Vapor, L-liquid, D- density, Wt % NaCl eq. brine salinity based upon Tm NaCl daughter phase. Red numbers represent salinity values for homogenization measured values. The sowat calculation at that Th had shown the coexistence of liquid and vapor phase as boiling pairs. The differences indicated some disequilibrium condition because water loss at high temperature, partial decrepitation and stretching. But liquid composition is very close to the initial fluid and that inclusion must have a counterpart vapor - rich inclusion nearby (e.g., Fig 23l above). Data were calculated with SoWat PC program version 0.1/2007 (Driesner and Heinrich, 2007). Supplementary unpublished data on Figs 23, 24 and 25

Nr	T,°C	P, bar	wt% NaCl eq	d, g/ccm	Fluid phase state
1	838	778.586	77.51	1.1835	single phase state
2	758	604.722	77.51	1.2224	single phase state
3	973	1069.98	77.51	1.1331	single phase state
			70.341		
4	705	647.34	0.49756 V	0.1749 V	V+L
			70.3571 L	1.15281 L	
5	872	1709.01	47.8048	0.84265	single phase state
				1.17291 L	
6	431	1037.16	51.6237	2.0576 H	L+H
			58.1057		
7	886	1556.36	8.0111 V	0.36964 V	V+L
			58.106 L	0.95206 L	
			56.7434		
8	886	1594.22	9.0325 V	0.38539 V	V+L
			56.744 L	0.93787 L	
			58.1057		
9	831	1336.53	9.0325 V	0.33107 V	V+L
			56.744 L	0.96116 L	
			74.8042		
10	902	1015.76	2.0775 V	0.21136 V	V+L
			74.804 L	0.96116 L	
			65.5795		
11	682	681.946	0.62135 V	0.19625 V	V+L
			65.58 L	1.1021 L	

Atlas of fluid and melt inclusions from Romania

82.8023						
12	910	725.044	0.85425	V	0.14371	V
			82.802	L	1.2187	L
						V+L
75.2334						
13	882	951.505	1.7286	V	0.20171	V
			75.233	L	1.1373	L
						V+L
60.8838						
14	552	439.361	0.18995	V	0.16303	V
			60.884	L	1.1345	L
						V+L
73.3692						
15	1035	1461.5	5.1088	V	0.27226	V
			73.369	L	1.0796	L
						V+L
16	1070	1587.35	73.3692		1.0755	single phase state
69.185						
17	830	1011.07	2.0221	V	0.23399	V
			69.185	L	1.0796	L
						V+L
31.3097						
18	458	376.642	0.49891	V	0.22456	V
			31.31	L	0.84732	L
						V+L
73.3692						
19	932	1151.23	2.89	V	0.23428	V
			73.369	L	1.1008	L
						V+L
73.3692						
20	985	1302.94	3.9306	V	0.25273	V
			73.369	L	1.0883	L
						V+L
66.2987						
21	993	1691.61	7.7234	V	0.34293	V
			66.299	L	1.0208	L
						V+L
66.2987						
22	1006	1746.85	8.3167	V	0.3512	V
			66.299	L	1.0196	L
						V+L
23	1050	1941.49	66.2987		1.0161	single phase state

Table 2. Leachate analyses (modified from Pintea et al., 1999) shown a different composition vs. microthermometry.

$\Sigma^+ / \Sigma^- = + 0.26$ which means that other ions could be present in solution, e.g. metallic cations and SO_4^{2-} etc.

As general observation the fluid was very rich in CaCl_2 and possible anhydrite phase was formed as daughter solid inside the brine inclusions. This is the same at Rosia Poieni porphyry Cu (Au-Mo) system from Metaliferi Mountains, which could be related to a special magma-fluid evolution regime during exhumation process in the postcollisional stage.

Sample/Cl $\mu\text{g/ml}$	Element	Cation concentration ($\mu\text{g/ml}$)	Total cations (wt%)	Cl needed to balance cations($\mu\text{g/ml}$)	Total chlorides (wt%)
Quartz	Na	1.206	5.40	1.86	5.69
26.2	K	7.272	32.51	6.62	20.25
	Ca	11.1	49.62	19.70	60.26
	Mg	0.578	2.59	1.71	5.23
	Fe	2.21	9.88	2.80	8.57
Total		22.37	100.00	32.69	100.00

Table 3. Microthermometry of the silicate melt inclusions trapped in zircons from Fagetel gneiss, Petreanu and Tismana granitoids from South Carpathians. (Pintea in Berza et al., 2006, unpublished). Z- zoned zircon, NZ- unzoned zircon, R- inherited zircon relict, St-glass, K- crystallized silicate phases (micas, feldspar, quartz, glass remnant etc), V-vapor, Ts- silicate melt, Tfo- final observation temperature in the stage, Tm- melting temperature. Reference works in silicate melt inclusions from zircons worldwide were published by Li Zhaolin, 1994, Thomas, 2003, Thomas et al., 2003 among others. Size in μm .

Crt. no.	Sample no.	Locality/ petrotype	Zircon type/size	Silicate melt inclusions content /size	Phases at Th ($^{\circ}\text{C}$)	Th ($^{\circ}\text{C}$)	Observations
				St +V(10)	Ts	835	U-PB
1	R126	Fagetel gneiss	*NZ,250/120	St +V(10)	Ts	904	777 Ma
				St +V(10)	Ts	678	secondary?
2	R16	Tismana granite	*Z,250/90	St+V(10)	Ts	826	U-Pb
							567Ma
			*Z,250/120	St+V(30)	Ts	959	
			*NZ,25/40	St+V(50)	Ts	923	
			*NZ,150/100	St+V(20)	Ts	637	secondary?

3	308	Petreanu granite	NZ,240/50	St+V(40)	Ts	959	U-PB
			*NZ,250/60	St+V(10)	Ts	906	320 Ma
			NZ,220/90	St+V(20)	Ts	977	
4	T ₁	Tismana	*NZ,150/50, R	St+V(10)	Ts	642	
		granite					
5	T ₂	Tismana	*NZ,230/100	St+V(40)	Ts	951	
		granite					
6	T ₈	Tismana		St+V(20)	Ts		
		granite	NZ,260/50			701	
			NZ,240/110	St+V(20)	Ts	835	Complete opaque at Th
				St+V(20)	Ts	881	
			NZ,250/80				
7	3287I	Petreanu					
		granitoide	NZ,250/70	St+V+K(30)	Ts+V(941)	?	Tm = 905°C
			NZ,130/50				
8	3302III	Furcatura		St+V(20)	Ts	923	
		syeno-	Z,230/		Ts+K+V?		Tm=607°C
		granite	80	St?+V?+K (40)	(1004)	?	

Table 4. Microthermometry of silicate melt inclusions from zircon prismatic crystals from some Neogene volcanic rocks from Eastern Carpathians and Metaliferi Mountains (extracted from unpublished IGR report – Pinte in Berza et al., 2007, unpublished). NZ- unzoned prismatic zircons with length-wide ratio; G- glass, V-vapor; Kx- unidentified solid phases, Th-total homogenization temperature. Size in μm . Detailed data set of Fig 123.

Crt. no.	Locality/ petrotype	Zircon type/size	Silicate melt inclusions content/size	Phases at Th (°C)	Th (°C)	Observations
1	Dej tuff	NZ/1:3 to 1:5	Silicate glass (G + V) /5-20	Silicate melt	552°C(?);	
					636°C;	Total
					720°C;	homogenization
2	Dej tuff	NZ/1:3 to 1:5	silicate glass (G+V)/10-30	Silicate melt + vapors	830°C	
					850-900°C and > 1000°C	Partial homogenization

3	Dej tuff	NZ rarely Z, 1;3 to 1:5	Silicate melt (G+V +Kx)/20- 30	Silicate melt + vapor + unmelted solid(s)	>750-1000°C	Partial homogenization
4	Danesti- Piatra Rosie dacite	NZ/1:3	Silicate glass (G+V)/20	Silicate melt	730°C; 783°C; 978°C;	Total homogenization
5	Danesti – Piatra Rosie dacite	NZ/1:3	Silicate glass (G+V)/10-60	Silicate melt + vapor	780-1041°C	Partial homogenization
6	Laleaua Alba dacite	NZ/1:3	Silicate glass (G+V)/5-10	Silicate melt	789°C 975°C 923°C(zircon embedded in quartz)	Total homogenization
7	Rosia Montana	NZ/1:3	Silicate glass (G+V)5	Silicate melt	894°C	Total homogenization
8	Sacaramb	NZ/1:3	Silicate glass (G+V)/5	Silicate melt	916-990°C	Total homogenization

ADDENDA

A. Up - to - date development of practical methodology and analytical protocols on fluid and melt inclusions in Romania.

No	Analytical method	Apparatus/Methodo logy	Analytical device and range	Applications	Authors
1	Microthermo- metry	Microthermo- metric stages ("custom-made") Analytical protocols	+20°C to +270°C; +20°C to +600°C	Homoge- nization temperature	Pomârleanu, 1958,1971
2	Microthermo- metry	Analytical protocol	"Boetius" Melting-point apparatus	Homoge- nization temperature	Borcoş, 1965; Manilici et al., 1965

					Pomârleanu, Filip,1966 ;
		Decrepitometer			Filip,1972 ;
3	Decrepitometry	“custom-made” Analytical protocols	+1100°C	Decrepitation temperature	Pomârleanu, 1975 ; Pomârleanu, Filip,1976
			Leitz 1350°C		
4	Micro- thermometry	Analytical protocols	Heating stage +20° to + 1350°C gCO ₂ /	Homoge- nization temperature	Borcoş,1970
			100g H ₂ O; molCO ₂ /		
5	Gas- Cromatography	Analytical protocol	1000 gH ₂ O “Porapaq” column and “custom- made” heating device	Gas content liberated by heating	Pomârleanu, Neagu,1981
6	Microthermo- metry	Analytical protocol	“Heiz- Kammer-400”	Homoge- nization temperature	A.Götz, (personal communi- cation, 1985)
7	Decrepitometry	Decrepitometer “home made”	1400°C	Decrepitation temperature	Pintea, 1982 ; Pintea,1983 (arh IPEG Harghita)
8	Microthermo- metry	“Termoinc-01” Microthermo-metric stage “custom-made”	-190° to +750°C	Heating – cooling microthermo- metry	Pintea, 1988; Pintea in Udubaşa et al,1989 (arch IGR) ; Pintea et al., 1992 ; Pintea, 1995b

9	Microthermo-metry	Analytical protocols	“Termoinc-01“;	Heating – freezing analyses	Pintea et al., 1992 ;
			(IMTG-1);		Sava and
			-190° to		Constanti-nescu (1992-unpublished);
			+ 750°C		Panaiotu C, 2001;
			Linkam THMSG600		Fall, 2002;
10	SEM-EDAX	Analytical protocols	-190° to +600°C	Daughter phase identification and semiquantitative analyses	Cioacă, 2007; Iatan, 2008;
			Scanning Electronic microscopy with X-ray analyzer		Pintea et al., 1992, arh IGR Nedelcu et al., 1998 ; 2001
11	Coupled Gas Chromatography-Mass Spectrometry	Analytical protocols	“Custom-made”- in vacuum crushing device coupled to mass spectro-metry;	Gas analyses CO ₂ , SO ₂ ,	Palibroda et al., (1990, unpublished) ;
				CH ₄ , H ₂ S, N ₂ ; µg/g; 10 ⁻⁹ g	Cuna et al 1991; 1992, unpublished) ; Cuna et al., 2001
12	« Crush leach »	Analytical protocols	Atomic absorption spectro-metry, X-ray spectro-metry	Chemical micro-analyses of Na, K, Li, Rb, Cs, La, Mg, Fe, Mn, Zn, Cl, SO ₄	Morar et al., (1990;1998, unpublished)
13	« Crush-leach »	Original Membrane-Selective ion « EMIS-Cl »	Selective ion electrode	Chloride determination and chlorine isotopes analysis by Mass Spectrometry	Hopârtean et al., 1998 ;
		Analytical protocols	10 ⁰ to 10 ⁻⁴		Pintea, 1998 ; Pintea et al., 1999b
14	« Crush-leach »	Analytical protocols	Capillary Electrophoresis “Mili Q”	Micro-chemical analyses of SO ₃ ²⁻ , S ₂ O ₃ ²⁻ ,	Halbauer, 1997;
				HS, Cl ⁻ , SO ₃ ²⁻ , HAsO ₄ ²⁻ , SeO ₄ ²⁻ , MoO ₄ ²⁻ , NO ₃ ⁻	Forray, Halbauer, 2000

				,WO ₄ ²⁻ ,F ⁻ , HCO ₃ ⁻ , acetate, propionate; NH ⁺ ,K ⁺ ,Na ⁺ , Ca ₂ ⁺ ,Sr ²⁺ ,Mg ²⁺ , Mn ²⁺ ,Li ⁺ , Zn ²⁺ , Cu ²⁺ ,Co,Ni Cu,Ba,Be	
15	Micro-thermometry	Analytical protocols	USGS Heating-cooling stage; -190 la +750°C	Heating-cooling micro-thermometry	Pintea, 1996b
16	Micro-thermometry	“Home-made” heating device	+20° la +1100°C	High temperature micro-thermometry	Pintea,1998, Arh IGR
17	Coupled Raman spectroscopy-High temperature micro-thermometry	Analytical protocol for Renishaw inVia-Linkam TS1500 system	+20 to + 1500°C	Raman Heating-quenching micro-thermometry	Pintea et al., 2018 (unpublished protocol)

B. The up- to - date analytical methods used in Romania - still in “the embryonic state” (Pintea, 2019).

Deposit/ Formation	Host mineral	Fluid/Melt inclusion association	Methods	Autor(s)
			HF-M, HT-M, NIR-M,	
	Quartz		CL-OM, Raman,	Alderton and Fallick, 2000; Bailly, et al., 2002; Gál, 2014; Grancea, 2002; 2003, Halbauer, 1997; Naumov et al., 2013; 2014; Nedelcu et al., 1995; Marias, 1996; Papp et al., 2003; Pintea, 1995a; Pintea et al., 2018; Pintea and Iatan, 2017; Wallier et al., 2006;
Epithermal Dacites	Calcite	Aqueous	LA-ICP MS, LA-OES, SEM-EDS,	
	Sphalerite	Brine	EPMA, SIMS,	
	wolframite	Silicate melt	CE (capillary electrophoresis)	
			MS	

Porphyry Cu- (Au-Mo)	Quartz	Aqueous	HF-M, HT-M, NIR-M,	André-Mayer et al., 2001; Bailly, com pers, 2002; Cioaca, 2007; 2011; Grancea, 2001; Heinrich et al., 2003; Iatan, 2008; Ivascanu et al., 2003; Kouzmanov et al., 2010; Nedelcu et al., 2003; Pintea, 1996b ; 2014a,
	Enargite	Brine	SEM-CL	
	anhydrite	Hydrosaline melt	LA-ICP-MS, PIXE,	
	pyrite	Silicate melt	SEM-EDS,	
			ISE, AAS, EPMA, MS, CG-MS	
Ditrau alkaline massif	Quartz,	Aqueous	HF-M, Raman, GC-MS	Pintea and Diamond, 1994; Fall et al., 2007;
	nepheline	Brine		
		Carbonic		
Pegmatite		Aqueous	HF-M	Pintea, 1993; 1996; 2014; Pintea et al., 2018; Pomârleanu & Filip, 1976; Pomârleanu & Pomârleanu, 1981
	Quartz	Brine	HT-M	
	Muscovite	Carbonic	GC, Decrepitometry	
	Garnets	Hydrosaline melt	Raman	
		Silicate melt		
Low- and amphibolitic grade	Quartz	Aqueous	HFM	Pintea, 1991, unpubl.;
		Brine	GC-MS	Udubaşa et al., 2003;
		Carbonic		
Sedimentary	Halite, calcite, gypsum	Aqueous	HF-M	Banerjee & Ghiurca, 1997; Nutu- Dragomir M.L., 2012; Panaiotu, 2001; Pintea, 1989 unpubl.; 1995; 2008; 2016; Pomârleanu & Mârza, 2003;
		Gaseous	GC-MS	
	baryte		FTIR-spectrometry	
Peridotite	Olivine	Carbonic	HF-M	Pintea & Mârza, 1989;
	Xenolits	Calcicarbonate in silicate matrix veinlets	SEM-CL	Chalot-Prat & Arnold, 1999;
			EPMA	

Notations: HF-M - heating-freezing microthermometry, HT-M- high temperature microthermometry, NIR-M- near infrared microthermometry, CL-OM – cathodoluminescence-optical microscopy, LA-ICP-MS- laser ablation- Inductively Coupled plasma – Mass Spectrometry, LA-OES- Laser ablation-optical emission spectroscopy, SEM-EDS- Scanning Electron Microscopy with Energy Dispersive Spectroscopy, EPMA- Electron Probe Micro

Analyses, **SIMS**- Ion Mass Spectrometry, **SEM-CL**-Cathodoluminescence Scanning Electron Microscopy, **PIXE**- Proton induced X-ray emission, **ISE**- Ion Selective Electrodes, **AAS**- Atomic Absorbtion Spectroscopy, **CG-MS**- Gz Cromatography-Mass Spectrometry, **FTIR**- Fourier – transform Infrared Spectroscopy

Note added in proof: Recent Raman spectra suggested that liquid hydrocarbons and pyrobitumen supposed to be present in the fluid inclusions from **Figs 38, 108, 112, 125 and 137** seem to be a complex hydrosilicate $\pm$ chloride $\pm$ carbonate $\pm$ phosphate $\pm$ CO₂ $\pm$ CH₄ vapor-rich “melt” inclusions or a clathrasil like component (Pintea et al., 2018; 2019).

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