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A reappraisal of the Decrepitation - Inductively Coupled Plasma Spectroscopy (D-ICP) for bulk analysis of fluid inclusions in minerals

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Abstract

The complexity of the fluid inclusions in minerals as an analytical object causes development of several methods for the purpose. To specify the field of application of D-ICP technique among the other contemporary methods of fluid inclusion analysis, is the aim of this study.

In this work the analytical train included a “decrepitator” on line between the nebulizer and the plasma torch. The heating element was a fast operating (~ 400 grad/ min) “nude” oven ensuring well reproducible heating program.

Time-resolved evolution curves of Na, K, Li, Ca, Mg, Al, Cu, Zn, Fe, Mn and Pb featured a single, well-shaped maximum at ca. 300 ˚C, which fitted also the maximum of decrepigrams. S and As appeared at higher temperatures (T > 500 ˚C), probably due to the thermal decomposition of sulphide microimpurities in the quartz sample.

The elemental ratios X/Na were found to be independent from the sample mass (0.1-3.0 g) or the size of the mineral grains (0.10-1.60 mm), which is a good prove of the relation between decrepitation and formation of the analytical signal. Both the quotations did not differ significantly and actually can be pooled in a single body of evidence.

Data from analyses of fluid inclusions in the standard quartz obtained by three independent methods – bulk (D-ICP-AES and D- (C-) leach-AAS), and local (LA-ICP-MS) – were compared.

It is concluded that D-ICP-AES is capable of supplying reliable information on chemical composition of fluid inclusions.

Introduction

The aim of the fluid inclusions study is the reconstruction of the PTX – environment of the mineral formation, being “actual samples – the only samples we have – of former fluid existing at some time in the history of the earth. As such they are important clues in understanding the geological *modus operandi*”.[1] The chemical analysis, as a part of this study, is expected to supply reliable information for the chemical composition (X) of the mineral-forming solution(s).

The fluid inclusions are a very complicated object from analytical point of view, as they may be hosted in various minerals, may differ also in dimensions, habit, composition, location, which needs a complex approach to chemical analysis. As a result many methods of different abilities were developed.[2] The features of importance of the fluid inclusion analysis for the most effective contemporary destructive techniques are given in Table 1. It is evident that LA-ICP-MS answers most of the requirements of the chemical analysis. The other techniques, however, have also their fields of application. Here we may mention Roedder's sentence[1]: “There is no panacea for the problems of determining the composition of fluid inclusions … no known method or combination of methods will give an accurate, unambiguous analysis of any given inclusion in any given mineral.” Hence, the fluid inclusion study needs a set of analytical methods at our disposal, which could be applied according to their capabilities.

Table 1 Some features of analytical methods used with respect to the fluid inclusions analysis.

	Leach (AAS, ICP-AES/ MS)		D-ICP	LA-ICP MS
	Crush (C)	Decrepitation (D)		
Analyte transport to the analyzer	leachate	leachate	gas flow	gas flow
Sample form	grains	grains	grains	transparent slides only
Inclusion size needed	> 1μm	> 1μm	> 1μm	> 20μm
The amount of inclusions that participate in the analyte formation	bulk	bulk	bulk	single
Ability to analyze				
• ion species in the water phase	yes	yes	yes	yes
• daughter minerals	yes	no	no	yes
• trapped minerals	if soluble	no	no	yes
Capability for determination of the chemical composition of inclusions from different FI assemblages	no	no	no	yes
Productivity (analyses per day)	2 - 3	2 - 3	15 - 20	5 - 10
Relative cost	low	low	low	high

One of these methods is decrepitation-linked ICP-AES.[3 ,4] This technique was developed more than three decades ago by a scientific group at Imperial College, London. The procedures, values and limitations of this technique are reviewed by Rankin *et al*.[5] The principle advantages of Decrepitation ICP-AES (D-ICP-AES) analysis, mentioned in this publication are: 1) Small sample sized required (0.2 to 0.5 g typically); 2) No dilution (when compared with the classical leach-ICP method) and, hence, much higher sensitivities; 3) Simple sample preparation and introduction into analytical tract; 4) Rapid "turn-around" time for samples.

The D-ICP-method is a typical bulk technique.[2] The limitations of the method could be recognized easily on the base of the Table 1-content. The other constraint of the decrepitation, as a tool for opening of inclusions, is the relatively narrow field of application: it can be used successfully only for electrolyte determination in inclusions of low to moderate salinity.[6] The impossibility for obtaining selective information for different inclusion generations is considered also as principle limitation of the bulk methods This obstacle is the reason for the great interest in the analytical techniques, applicable to single inclusions. Thus, in 1992, the same scientific group[7] successfully combined a laser-ablation (LA) technique for opening of individual inclusions with an ICP-spectrometer. Hence, this method (LA-ICP) is used in emission spectroscopy (AES); in the last two decades the more sensitive MS-detection (LA-ICP-MS) was preferred over the AES technique.[8] As a result to the best of our knowledge only two studies on the D-ICP-AES were published after year 2000. [9, 10]

As a bulk method, D-ICP may be used in some extreme cases, when the direct microscopic observation, just in the course of the chemical analysis, is unnecessary (as it is in the case of LA):

1. Specimens populated by a large number of very small (µm-sized) inclusions. In this case D-ICP may gain even over crush-leach technique, which will need crushing to very small particles (powder, a<10 µm);
2. Entirely opaque specimens can also be examined successfully;
3. Inclusion-poor specimens or trapped solutions of low salinity (≤ 5 wt.% NaCl-eqv.) can also be analyzed, since decrepitation can open thousands of inclusions and consequently can supply enough substance for analysis;
4. A simple laboratory-made attachment to a conventional ICP-spectrometer is needed only, which reduces the price of analysis in comparison to the LA-methods.

On that account we believe in any case D-ICP needs a re-assessment being a method that can supply geochemically significant results relatively quickly and cheaply.

The philosophy of the chemical analysis demands that all capable analytical methods, bulk or individual, applied correctly to one and the same object of analysis (e.g. ion species in the inclusion fluid), should yield identical results. This identity is used to be proven simply by comparison, which is the aim of this study.

Another intention is a contribution to the validation of a specimen of natural quartz (see below) as an intra-laboratory standard in respect to fluid inclusions.

Sample material

The investigated material came from a cavern in the barren quartz zone of the main ore vein of Kroushev Dol deposit of Madan ore district, Bulgaria.

A very detailed study, on the tectonometamorphic evolution, geochronology, and epithermal ore deposition in Rhodopian metamorphic complex was published by Kaiser Rohrmeier *et al.*[11] Although the deposits are spread over a significant area of about 300 km^2, they are very similar either as mineral assemblages or in respect to the mineral-forming conditions, probably due to a common heat source and identical parent rocks. A lot of published T_h (temperature of homogenization) and salinity data derived from microthermometric measurements were reviewed by Piperov;[12] more modern results were reported by Kostova *et al.*[13] and Kotzeva *et al.*[14] Ore stages in all Madan deposits display T_h = 200-350^{o}C and a total salinity of 3-9 wt.%; in some cases (sphalerite, unpublished data) up to 12 %. This similarity between the ore-forming conditions offers a good opportunity to use the data from different deposits as a reliable base for comparison.

The gneissic walls of the cavity (up to 1 m wide), where the quartz specimen is found, are coated by a crust of long prismatic columnar quartz. The crystals are up to 8-10 cm long and 0.5-1.5 cm wide. The tip part (1/3 to 1/2) of the quartz crystals is (semi-)transparent, while the base part ("the root") is nearly opaque.

All free surfaces, and especially the terminal rhombohedral faces, are overgrown by small needle-form quartz crystals (< 0.5 mm) and, as it was found later, single small pyrite crystals (< 0.3 mm). These obviously later minerals are covered by a thin crust (up to 5 mm thick) of latest calcite, which deposition is accompanied by partial limonitization of the previously crystallized pyrite.

The inclusions trapped

As it was mentioned above, more than a half of the crystal body is opaque, being split by many oblique cracks, probably following invisible rhombohedral faces. Their topography reveals an episodic appearance in the early stages of the crystal growth. These later healed cracks are populated by a large number of pseudosecondary fluid inclusions, typically 10-100 µm in size. On that account the base opaque part of the crystals is about an order of magnitude inclusions abundant than the transparent tip part.[14] Excluding the near-to-surface vacuoles, all other inclusions are three-phase: V+W+S, i.e. they contain a very small (µm sized), not identified, most probably trapped solid phase. No daughter minerals are observed.

The fluid inclusions in the opaque parts of the crystals represent more than 90 % of the inclusion bulk. In a recent publication[14] it was shown that, even of different types, these inclusions (n = 51) contain a relatively homogeneous solution with trapping temperature between 329 and 348 ^{o}C with a mode at 338 ^{o}C. Some inclusions in the transparent zones (late) display lower T_h: 320-312 ^{o}C. The microcryometry revealed a total salinity in the range 5.7-9.1 wt.%, with a mode of 8.5 wt.% NaCl eqv.

Sample preparation

A lump of aggregated quartz was broken into pieces, 0.5-3 cm sized fragments were hand-picked free of visible impurities. These fresh bits were crushed in a steel mortar and later separated into grain fractions (12) by sieving. In our first experiments the quartz grains had been cleaned by boiling in distilled water; later a more “deep cleaning” was applied: overnight treatment with 10 M HNO_3 and heating to boil finally. Subsequently, the quartz grains were rinsed repeatedly with doubly distilled water (DDW) and dried at T = 80 ^oC.

Analytical technique and procedures

The method utilizes decrepitation of fluid inclusions for obtaining an aerosol, which is transported by carrier gas to the plasma of a multichannel ICP-spectrometer. The time-resolved version of D-ICP analysis[5] is obviously a progressive mode for establishing the temperature interval over which bulk decrepitation take place. The revealing of the dependence of bulk decrepitation on the time (i.e. temperature) scale presumes a short-time analytical response. Three premises must be realized for the purpose: 1) A short path from decrepitator to the plasma torch; 2) Multichannel ICP-spectrometer and 3) Short signal integrating time. The assembling of the main parts of the analytical line is shown on Fig. 1. The differences from well-known original study[15] are:

1) Online compounding of the nebulizing chamber, the decrepitator, and plasma torch.

2) A very short path (silicone tubing 12 cm long, 4 mm i.d.) from decrepitator to the torch. It ensures a wider, but higher signal peak, i.e. it should lead to lower limits of detection.

3) Well reproducible heating program. The oven heater (770 W at 220 V) is of bare-type: a resistance wire (63 Ω), wound over a silica-glass test-tube with 16 mm i.d., forms a 9 cm heating zone. The end of another silica-glass test-tube (“decrepitator”), containing the mineral sample, is placed in the middle of this zone. The decrepitator is covered by a dismountable PTFE stopper. A test was performed aiming definition of the heating rate. A naked Pt/Pt90Rh10 thermocouple was buried in 3 g 1.25-1.60 mm quartz grains, poured in the test-tube, and connected with a X-t recorder. A gas stream of 1.25 l/min through the decrepitator was supplied. Three temperature vs. time records (Fig.2) showed that in the temperature interval from 100 to 450 ^oC temperature increases nearly linear with a rate of 7±1 grad/s (i.e. about 420 grad/min). The reproducibility of this heating test is surprisingly good: ±8 grad at 500 ^oC, i.e. < 2 %. A higher rate of heating is not appropriate, because of serious problems with heat transport and homogeneity of the thermal field in the sample depth.

A sequential 32-channel SPECTROFLAME-ICP M apparatus was utilized. The grate is holographic with 2400 gratings/ mm ensuring a spectral range from 175 to 790 nm at linear dispersion 0.55 nm/ mm and experimental resolving power of 0.02 nm. The torch is Fassel type; standard Meinhard nebulizer with Scott type coaxial spray chamber was used. The integration time was 5 s, followed by a 2 s pause for checking back ground (“dark signal”). Hence, the heating time (82 s) was divided into 12 intervals, analytical data being obtained in the end of every integrating time. For example, first integration step took 5 s and corresponded to temperature 36 ^oC, when the starting room temperature was 21 ^oC. The next time interval lasted new 7 s (2 + 5) and ended at the 12th second, corresponding to a temperature of 56 ^oC; the third integration (19 s from the start) fits 90 ^oC etc. At the end of heating after 82 s sample temperature was 512 ^oC.

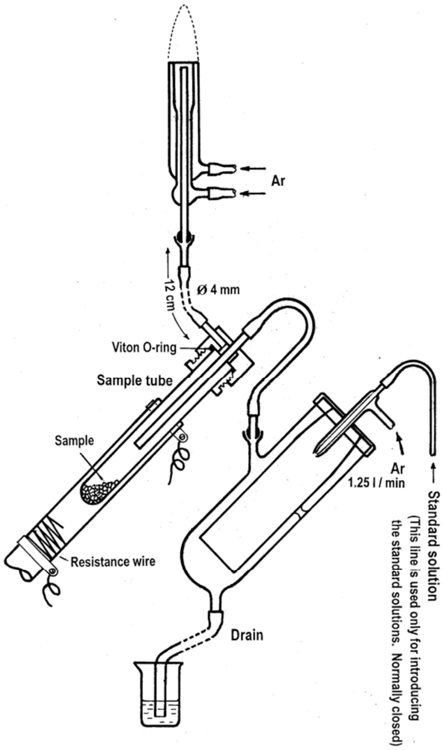

Fig.1. The analytical line, including a simple device (“decrepitator”) between nebulizer and plasma torch.

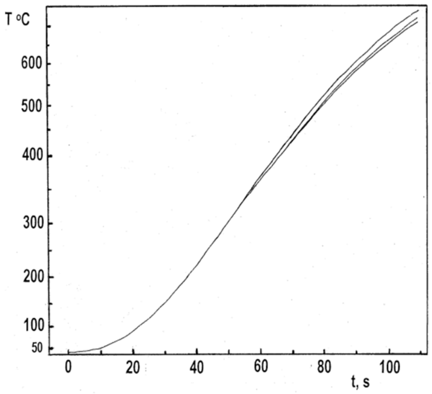

Fig.2. Three temperature vs. time records. Time–temperature scale shown is constructed on the base of the median curve.

As the spectrometer sensitivity (*S*) to the different elements is very uneven (e.g. S_K = 0.0404; S_{Ca} = 879), calibration was needed for quantitative measurements. The lining up of the nebulizer, decrepitator and torch offers a new possibility for introducing standard solutions without demounting of decrepitator. The original program covered 16 elements; finally the menu was reduced to 11. Chlorides of the elements traced were used for preparing 2 M or 1 M (here and below M = mol/l) solutions (for Pb – 0.1 M nitrate). The initial mixture contained ~1 wt.% Na; the concentrations of the other elements were one to two orders of magnitude lower. A standard 1B (“Base”) solution was obtained by 50-fold dilution of those initial mixture and later two working “cocktails” 0.4B and 0.16B were prepared. The accurate element concentrations finally obtained were checked by ICP-AES and AAS measurements, using “Titrisol”-standards (Merck, Darmstadt) as references. So, 0.16B standard contains (wt. ppm): Na 36.8, K 12.0, Li 1.2, Cu 1.9, Mg 3.1, Fe 1.8, Zn 2.0, Al 1.7, Pb 0.7, Mn 2.6 and Ca 5.8.

It was found that empty decrepitator at room temperature as well as on standard heating did not provide analytical signal for any trailed element. This is also the case of loaded decrepitator at room temperature. On repeated heating of a quartz sample only evolution of sulphur was observed (see below).

D-ICP technique does not consider the water content of inclusions and, hence, the determination of concentrations is not possible. Therefore, results for any element “X” are expressed as X/Na ratios, involving the term “pseudo-concentration”:[5] $C_X = I_X - I_{base}$, where I_X is the net integral intensity of analytical signal for a given element “X”, which signal is automatically (computer) sensitivity corrected on the base of 2-3 standard solutions (Titrisol, Merck) and the standard mixture.

A simple vacuum device was designed for registration of decrepitation in advance. The mineral grains were heated in vacuum ($P \leq 10^{-5}$ Torr) with a heating rate of ~10 degr/min and pumping out continuously. The explosions of the (large?) single inclusions caused short-term increase in pressure (pulses) on account of the (water) vapour only, which pulses were detected by a fast response vacuum gauge, e.g. ionization or Penning type. The inevitable slow, but large increase in the pressure (more than one order of magnitude) was easily eliminated from the record by an electrical "high-pass" filter at the recorder input. So, a raw of lines (traces, strokes) was recorded: "decrepigrams" (Fig. 3 and 4).

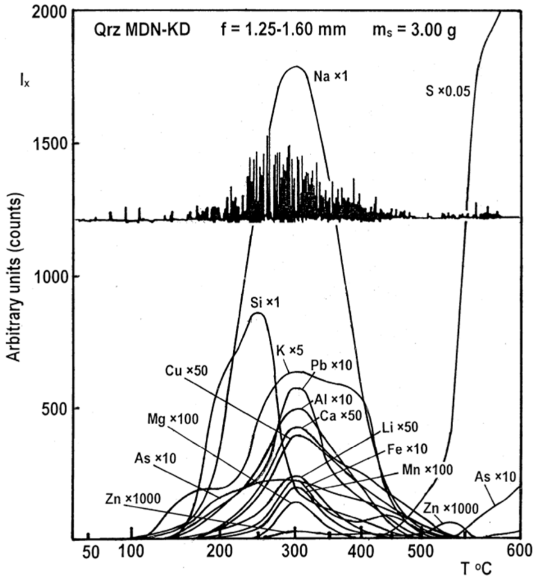

Fig.3. Decrepigrams of six 0.100 g grain fractions (mm) of Qrz MDN (KD)

Crush (C)-leach and Decrepitation (D)-leach

Aiming a comparison of D-ICP with other methods for fluid inclusion analysis, the same material (Qrz MDN (KD)) was treated by leach techniques after crushing or decrepitation. The respective stages of the analytical track are shown in Table 2. The difference from our recent study[16] is the final stage of analysis: ICP-AES and ICP-MS instead of AAS.

Many preliminary experiments concerning optimization of the work, may be found in Kotzeva et al.[16] and Kotzeva[17].

The utilization of an adsorption suppressor (La^{3+})[18] did not show detectable differences, out of the error limits.

Table 2 The steps of the analytical track for preparing leachates after decrepitation or crushing

Decrepitation	**Crushing**
Precleaned material - quartz grains 1.25 - 1.6 mm	
↓	↓
3 Samples 1, 2 and 3 g	5 Samples 2 g each
1. The sample is placed in a beaker 25 ml, 7-8 ml 0.1 M HNO_3 is added and then heated up to 80 - 90^0 C for 1 - 2 min	
↓	

2. The acid is poured out and the sample is washed by DDW

↓

3. The wash water is poured out. A new portion of 8 ml 0.1 M HNO_3 is added and the sample is U-sound cleaned for 10 min

↓

4. Washing with DDW repeatedly

↓

5. The sample in the beaker is dried at 80 - 90^0 C after pouring out the water

↓	↓
6. Transfer into the decrepitator	**6.** Transfer into the mortar
↓	↓
7. Simulation of heating and cooling (ca. 15 min total)	**7.** Simulation of crushing with (or without) 4-5 ml eluent (0.1 M HNO_3)
↓	↓
8. Transfer back into the beaker (25 ml)	**8.** Transfer into another beaker (50 ml), washing the mortar by 2-4 ml eluent and stirring
↓	↓
9. 8 ml eluent 0.1 M HNO_3 is added and the beaker content is stirred	**9.** The leachate is decanted in a cone tube and centrifugated
↓	↓

10. After sedimentation the leachate is devided in 2 aliquots of ~ 3 ml each: **blanks**

↓	↓	↓
To "Jobin Yvon - Optima 02" ICP-AES	↓	To "THERMO Scientific X Series 2" ICP-MS
	↓	

11. The material in the beaker is washed and dried as in **step 5**

↓	↓
12. Transfer into the decrepitator	**12.** Transfer into the mortar
↓	↓
13. Real heating to 550^0 C for 60 sec.	**13.** Real crushing
↓	↓

The next steps repeat the points **8 - 10**, but the samples are decrepitated or crushed

The last steps of both the tracks yield decrepitation and crush leachate respectively. Hence, every sample provides 2 pairs of analytes: a leachate, devided in two aliquots - for ICP-AES and ICP-MS and a blank, devided also in two aliquots, respectively.

Results

Time-resolved D-ICP analysis[5]

As a pilot test 3 g 1.25-1.60 mm grains were heated under the appropriate conditions (see above) but for a longer time: 119 s or 17 integrations up to temperature above 600 ^oC. The following 16 elements were traced: Al, As, Ca, Cu, Fe, K, Li, Mg, Mn, Na, P, Pb, S, Si, Te, and Zn. The analytical signal for P and Te was sporadic and, hence, not usable; the results for these elements were not checked later.

The processing of the raw data is documented on the results of D-ICP analysis of 3.00 g quartz sample, 1.25 - 1.60 mm (ā = 1.42 mm) grain fraction, as example. The baseline corrected and sensitivity normalized values are presented in Table 3 and used for construction of the time- (temperature-) resolved curves (Fig. ~~3~~4). So, the total area confined between the baseline and the respective curve for every element is a measure of its amount. Although the analytical signal appearance corresponds to the decrepitation activity very well, some overlapped interferences cannot be excluded however.[5]

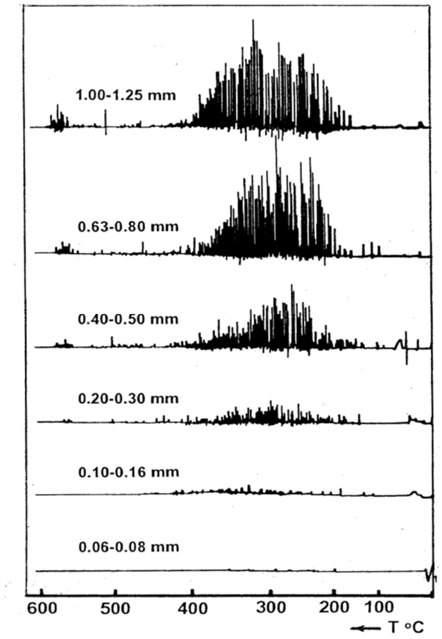

Fig.4. Idealized curves of analyzed elements (arbitrary units = counts) as a function of the temperature.

The bulk methods for fluid inclusion analysis are based on the hypothesis that all inclusions analyzed are equal in their chemical composition; hence the element ratios in every sub-integration (profile) must be equal to the same ratios in the other temperature profiles, as well as in the general quotation. Table 4 was made to verify this hypothesis. Some profiles, and especially high-temperature ones, display differing (high) X/Na ratios probably due to some complications[3] which did not fit the Q-criterion[19] and were rejected. On that account the final results (Table 4, last right columns) are obtained by averaging the data of the four central columns 7 -10, i.e. for the temperature interval 244 - 430˚C. Inclusion poor samples (m < 0.3 g or ā < 0.35 mm) yielded an analytical signal only in the same temperature interval.

Some observations can be made at once:

(1) The evolution maxima of more of the elements appear at T ~ 300 °C, which temperature coincides with the most active decrepitation as it is revealed by a decrepigram (Fig. 4) and also by decrepigrams on Fig 3. This fact suggests a good fit of fluid inclusions decrepitation and appearance of the elements monitored in the decrepitate.

(2) The evolution pattern of some elements differs substantially from the releasing of the most constituents:

Silicon. Its maximum signal appears at lower temperature: about 250°C and in fact it reveals only the beginning of decrepitation. We believe that very small quartz particles, obtained at explosions of near-to-surface inclusions, are carried away by argon flow and introduced into the plasma.[2, 3]

Sulphur (and probably *arsenic* – second maximum) appeared at T > 400°C, but displayed a very strong signal. It is evident that its evolution is not connected to decrepitation of fluid inclusions.

Table 3 The baseline corrected and sensitivity (*S*) normalized intensities (I, counts) are plotted on the Fig 4 to built the time-resolved (evolution) curves for the elements trailed. The integrated values of the central profiles 7-10 (bold tipped) were used to calculate the X/Na mol ratios (‚pseudo-concentration').

Elements (X):			S	As	Na	K	Li	Cu	Mg	Fe	Zn	Al	Pb	Mn	Ca	(Si)
Channel			55	53	44	42	43	27	29	31	20	28	19	15	2/5	
λ,nm			180.731	193.759	589.592	766.490	670.780	324.754	279.553	240.400	213.856	308.215	220.351	257.610	317.933	
Sensitivity (*S**)			1.91	1.58	**1.000**	0.040	10.9	16.6	27.8	0.480	463	1.07	0.740	12.7	879	
No[&]	t[#], s	T˚C[§]														
1	5	36	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	12	56	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	19	90	4.7	-	-	-	-	-	-	-	-	-	-	-	-	-
4	26	126	27	1.9	-	-	-	-	-	-	-	-	-	-	-	-
5	33	171	97	3.8	24	49	0.5	-	-	2.1	-	-	-	-	0.1	-
6	40	224	189	12.6	315	25	0.6	-	-	2.1	-	14	16	0.1	0.6	590
7	47	275	304	20.2	**1380**	**124**	**2.0**	**-**	**0.1**	**6.2**	**-**	**29**	**22**	**0.5**	**3.5**	806
8	54	326	490	23.4	**1790**	**124**	**4.8**	**(14.5)**	**1.4**	**23**	**0.03**	**50**	**58**	**2.0**	**8.5**	179
9	61	377	655	17.1	**1290**	**99**	**2.1**	**(8.4)**	**0.3**	**4.1**	**0.01**	**34**	**24**	**0.7**	**5.6**	107
10	68	430	2.09k	14.6	**481**	**124**	**0.7**	**(3.0)**	**0.2**	**4.1**	**0.02**	**19**	**15**	**0.7**	**5.4**	72
11	75	472	9.23k	6.3	130	25	0.6	-	0.1	2.1	0.01	3.7	11	1.2	2.9	17

12	82	512	30.8k	-	32	-	-	-	0.1	2.1	0.02	-	-	-	1.9	8
13	89	552	79.6k	-	24	-	-	-	-	-	0.06	-	-	-	0.1	-
14	96	591	350k	7.2	-	-	-	-	-	-	-	-	-	-	-	-
15	103	628	390k	11.0	-	-	-	-	-	-	0.02	-	-	-	-	-
16	110	663	460k	17.6	-	-	-	-	-	-	0.02	-	-	-	-	-
17	117	695	495k	21.0	-	-	-	-	-	-	0.03	-	-	-	-	-
		$\sum_{7-10}$			4941	471	9.6	(25.9)	2.0	37.4	(0.06)	132	119	3.9	23	
X/Na mmol/mol						95	1.9	(5.2)	0.4	7.6	(0.01)	27	24	0.8	4.6	

Notes: Results in brackets were considered uncertain.
[*] Relative sensitivities at $S_{Na} = 1.000$
[&] Consecutive number of profiles (sub-integrations)
[#] Time from the start of the heating to the end of the respective sub-integration
[§] The temperature in the end of every sub-integration

Table 4. X/Na (mmol/mol) ratios evaluated within 8 sub-integrations (profiles), when sample Qrz MDN (KD) was analyzed.(Table 3). Three last right columns contain the ratios (medians and means), obtained by statistics of the 4 central profiles (from No7 to No10), as compared with the mean values, calculated by another processing (in columns, i.e. for elements) for the same 4 profiles (Table 3, bold tipped). The values in brackets do not answer the Q-test for identity[19] and were excluded from calculation.

Consecutive No of sub-integration (profile)	5	6	7	8	9	10	11	12	$\sum_{7-10}$	Median	Mean	Table 3
I_{Na} (from Table 3):	24	315	1380	1790	1290	481	130	32				
Element (X)	X/Na mmol/mol											
Li	(20)	2.0	1.1	2.6	1.6	1.4	(4.6)	-	6.7	1.5	1.7	1.9
K	(2040)	79	90	69	76	(258)	(192)	-	235	76	78	95
Ca	4.0	2.0	3.0	5.0	4.0	11	22	(59)	22.5	4.5	5.6	4.6
Mg	-	-	0.1	0.8	0.2	0.4	0.8	(3.1)	1.5	0.3	0.4	0.4
Al	-	44	21	28	26	40	28	-	115	28	29	27
Fe	(88)	7	4.5	13	3	8	16	(66)	28	6.2	7.0	7.6
Mn	-	0.3	0.4	1.1	0.5	1.4	9	-	3.4	0.8	0.8	0.8
Cu	-	-	-	(8)	(6.5)	(6)	-	-	-	6.5	(7)	5.2
Zn	-	-	-	0.02	0.01	0.04	(0.7)	(0.6)	0.07	0.02	0.02	(0.01)
Pb	-	51	1.4	32	19	31	85	-	83.4	25	21	23

When different grain fractions were examined, it was found that finer fractions (a < 0.4 mm) released more S, than coarser ones. The assumption that S is a product of pyrolysis of accessory sulphides was proved by:

(i) Optical microscopy. Single cubic pyrite crystals of respective grain size were observed in some fractions. Very rare fragments of some other sulphides (chalcopyrite, sphalerite) were also detected.

(ii) Quantitative determination of sulphide sulphur in 12 grain fractions from 0.06 up to 1.60 mm. The acidimetric method as a semi-micro version was used. Quartz grain samples of 5 g were heated in an oxygen flow at 800 ^{o}C. Sulphur dioxide (and also SO_3) obtained were absorbed in 4 ml 3 % H_2O_2, producing H_2SO_4, which was titrated by 0.01 M $Na_2B_4O_7$.

The results obtained (μg S / g Qrz-sample) are plotted in Fig. 5, overlapping the ICP-data. It is evident that S amounts released from different fraction samples correspond very well with the sulphides content of these fractions.

It may be concluded also that those (pyro-) ICP-technique could be used as a sensitive tool for detection of traces of accessory or trapped sulphides. On the base of these observations we decided to “clean” material for analysis more carefully by acid treatment as described above.

Potassium. The determination of this element is overburden by methodological limitations, due to the spectral interferences of the argon plasma with the strongest potassium lines. This is the reason for significant fluctuations, low specific sensitivity, “bad” form of the evolution peak and, as a result, for a relatively large uncertainty in K-determination.

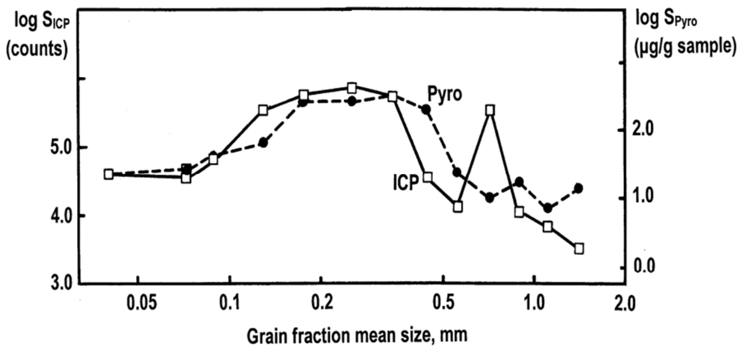

Fig.5. Sulphur release on heating as a function of the sample grain size. Two evolving techniques were utilized: D-ICP and pyrolysis (Pyro).

The bulk analysis is based in principle on the hypothesis that fluid inclusions have trapped a single sufficiently homogeneous fluid. In the object examinated (Qrz MDN (KD)) most of the inclusions (at least 90 %) answer this premise.[14]

The destruction of the inclusions cannot be controlled visually when bulk methods are applied, in contrast to the single inclusion microprobes. On that account the relation of the analytical signal to the decrepitation must be convincingly proved. It can be achieved by examination of samples, which contain decreasing number of inclusions – fine grain samples, for example. It is evident that grains, smaller than a critical size (e.g. $a<10$ µm)[20, 21, 22], would not contain sufficiently large inclusions and, hence, would not supply enough material to reach the detection limits of the analytical method.

Nine samples of 1.25-1.60 mm grain size and masses from 0.10 to 3.00 g (±0.001 g) were analyzed aiming a proof of the foreseen linear correlation. The results obtained are shown in Fig. 6. They display however a notably complicated relation: small samples (0.1-0.5 g) present a significant analytical signal, commensurable with that of 5-10 times greater samples. The coarser grains ($\bar{a} = 1.42 \pm 0.2$ mm) usually produce a larger dispersion of the results, probably due to the uneven distribution of the “enormously” large inclusions. On that account, another set of samples, but of finer grains ($\bar{a} = 0.72 \pm 0.1$) was studied. The dependence of the analytical signal on the sample mass, however, shows in general a very similar to the coarse fraction non-linear trend.

The “burial effect” may give a plausible explanation of this finding. Only a surface layer of relatively constant thickness (i.e. constant mass) provides the greater amount of decrepitate and, hence, forms the analytical signal. The decrepitate released from the underlying “buried” material remains on the grains and does not run into carrier gas. Hence, the affirmation, that great samples supply inadequately small amount of decrepitate, seems more correct.

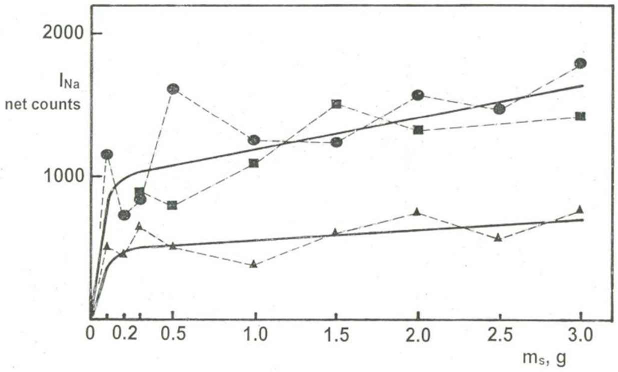

Fig.6. A check on of linearity of the analytical signal (I_{Na}, counts) as a function of the sample mass. Two grain fractions were employed: 1.25-1.60 ($\bar{a} = 1.42$ mm, 2 series: circles and squares) and 0.63-0.80 ($\bar{a} = 0.72$, triangles).

The presence of such an active layer of constant thickness (and mass respectively) stipulates nearly equal analytical signal for all sample masses. The maximum Na-signal for 3 g sample is only 40-60 % higher than this maximum for 0.1 g sample, as may be seen on Fig 6. This observation is in good agreement with Rankin *et al*.[5] finding that samples of 0.3-0.5 g are enough for D-ICP analysis.

As it was mentioned above a nearly linear correlation between the bulk mass of inclusions and the analytical response is evident.[23] The elemental ratios (X/Na), however, *must* be constant, independently from the sample mass or the size of the mineral grains, which will be a good proof of the common source of the elements trailed. Hence, in coordinates X/Na vs. sample grain size (sample mass, respectively) straight lines parallel to the abscissa are expected (Fig. 7).

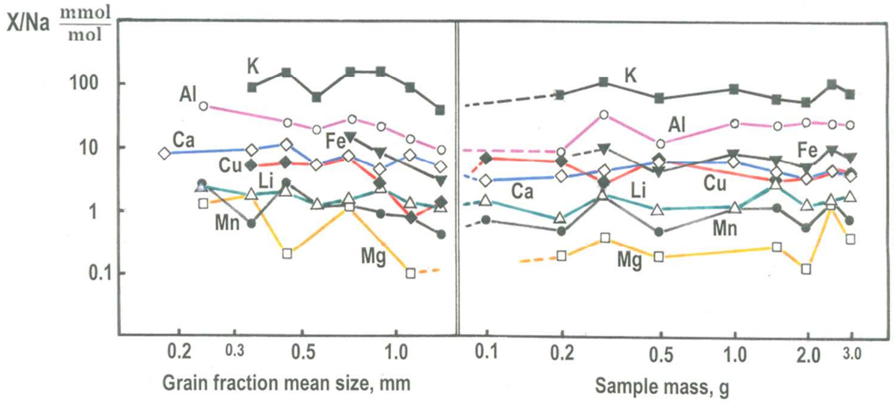

Fig.7. The processed analytical results, presented as X/Na (mmol/mol) vs. grain fraction mean size/ sample mass, respectively.

The fluid inclusion content, at least in the object under investigation, is assumed to represent a homogeneous fluid. On that account the single runs of the two series of analyses, mentioned above, can be considered as replicate analyses and, hence, can be processed statistically to evaluate the precision of the method. The results for X/1000 Na atomic ratios (i.e. mmol/mol) are presented in Table 5, as well as the standard deviations (SD). Finally, using identity criterion, it was found that both the quotations do not differ significantly and actually can be pooled in a single body of evidence.

Discussion

Data from analyses of fluid inclusions in quartz Qrz MDN (KD) obtained by three independent methods – D-ICP-AES, D (C)-leach (three kinds of detection: AAS, ICP-AES and ICPMS) and LA-ICP-MS, are presented in Table 6 and Fig. 8.

The juxtaposition of the X/Na ratios obtained by 3 (4) different methods (Fig. 8) reveals a significant discrepancy between the results. An acceptable correlation was found for the major element (K) only[29].

In general, the ratios Mg/Na determined are similar and agree also with experimental (model) values found by Ryzhenko and Krainov[30] at water / rock interaction. Traces of intimately incorporated accessory carbonates may contribute to the relatively higher variations of the results obtained by leach techniques. The Mn/Na ratious show acceptable coincidence. The high Al/Na values found may be ascribed to micro-impurities of some accessory silicates: micas, feldspars.[4, 15, 31] They cannot be removed by acid pretreatment of the quartz samples and their (sub-)microscopic particles (crystals) are blown by the carrier gas to enter the plasma.

A review on the Fe/Na ratios reveals a good coincidence between D-ICP-AES data for Madan quartz and the results obtained by spectrophotometry of the inclusion fluid from macro-inclusions in Madan galenas[32] (cf. Table 6). The data of chemical geothermometers as well as the comparison with other methods reveal low Li/Na (and Ca/Na) ratios obtained by D-ICP-AES. This technique, applied to 7 sphalerite samples from a neighbouring location yields “normal” data for these ratios (Table 6).

The X/Na ratios of lead and the other ore elements determined by D-ICP-AES are more than one order of magnitude higher than results obtained by other methods, at least for Cu and Pb. The presence of some Pb-compounds, and most probably accessory galena, even in trace amounts, may be a source of Pb (and of S, also)[29]. In any case the Pb/Na and Cu/Na ratios are suspiciously high. The concentrations of ore elements, evaluated on the base of LA-ICP-MS data[14] seems more realistic.

The reliability of the analytical results is estimated by the error limits of the method applied. So, the validation of a method needs certified standards and (or) comparison with the results obtained by another (certified) method. The certification of synthetic multicomponent fluid inclusions, however, requires without fail an additional check on the element concentration, because the preparation of those inclusions is accompanied also by significant uncertainty. Hence, at the present, the validation of analytical technique by comparison with other methods comes up as the most realistic. Many authors[7, 24-27] consider the juxtaposition of the results obtained by point analyses and by leach technique as an evidence for high confidence in the methods utilized.

The bulk methods supply averaged results *a priori*; they cannot be used to establish possible distinctions between chemical composition of different inclusion generations. The best way to prove the application of such a bulk method like D-ICP-AES is a comparison with the results obtained by the most powerful local technique: LA-ICP-MS. The laser ablation is a destructive method; it does not supply duplicate results, the error limits cannot be estimated by conventional statistics. Furthermore, significant dispersion, far beyond the limits of the instrumental error, is observed for results of chemical analysis, as well as for homogenization temperatures (T_h) and the last ice crystal melting temperatures (T_m), even when two neighbouring, syngenetic inclusions were examined. So, the dispersion of the results may be explained either as error of the method or as real natural variations in the inclusion content.

Single fluid inclusions are considered as individual fluid samples. However, if petrographic evidence exists, that fluid inclusions that can unambiguously be assigned to individual fluid inclusions trails (or FIA) they should all represent one fluid. Hence, analyses of syngenetic “next-door” inclusions, belonging to a certain fluid inclusion association (FIA), could be considered as duplicates and processed statistically as a body of evidence. Finally, categories as "mean" (value) and standard deviation (SD) can be inferred (*cf.* [28]).

Unfortunately, the dispersion of the results obtained is significant. In a recent review[33] we summarized to compare 45 representative studies (years 1980-2000), concerning fluid inclusion analysis by both destructive and non-destructive methods. The RSD of the results published reached 30-40 % for major elements and even 150-200 % for minor and trace elements. The LA-ICPMS technique had been preferred in the first decade after years 2000. The method uncertainty, however remains in the same limits: from 10-20 % for major components up to 50-100 % for the traces.[34]

We must admit that chemical analysis of fluid inclusions is a very complicated process, being dependent on many uncontrollable and irreproducible details such as the features of the host crystal (cleavage, chemical composition in macro- and micro-scales, history) and also the inclusion characteristics (form, size, salinity etc.). They contribute substantially in the relatively large uncertainty of the chemical analysis of the fluid inclusions, as mentioned above. This fact greatly obstructs the demonstration of variations of the chemical composition of the single inclusions or the separate FIA. For example, the impressive study of Audétat *et al.*[35] deals with examination and LA-ICP analysis of single fluid inclusions in a quartz crystal. The microthermometry (T_h and T_m) reveals many (29!) FIA; the chemical analysis, however, did not recognize them: "the concentrations of most major and minor elements follow the same trend, *maintaining constant concentration ratios* throughout the fluid history of the vein" (*loc. cit.*).

Table 5. Summarized data from two series of D-ICP analysis of the water phase of fluid inclusions in the intralaboratory standard Qrz MDN (KD). The results are presented as X/1000 Na atomic ratios (= mmol X/mol Na)

	X:	K	Li	Ca	Mg	Al	Fe	Mn	Cu	Zn	Pb
Grain fraction mean size, ā, mm	0.13	-	-	(18)	-	-	-	-	-	-	-
	0.18	-	-	7.6	(4.6)	-	-	-	-	-	-
	0.25	(720)	2.2	(14)	1.3	44	-	2.7	(12)	-	-
	0.35	90	1.7	8.1	1.6	(71)	-	0.6	4.9	-	-
	0.45	150	1.9	11	0.2	26	-	2.8	5.6	-	(27)
	0.56	64	1.3	5.4	-	21	-	1.2	5.4	-	(19)
	0.72	160	1.4	7.4	1.1	29	15	1.3	6.7	-	(19)
	0.90	160	2.2	4.6	-	22	9.0	0.9	2.8	-	-
	1.12	90	1.2	8.0	0.1	14	-	0.8	0.7	-	3.6
	1.42	40	1.1	4.9	0.0	9.4	3.0	0.4	1.3	-	9.1
	mean	108	1.6	7.1	0.7	23.6	9.0	1.3	3.9	-	6.4
Quartz sample mass, g	0.1	(18)	1.5	3.2	(0.1)	(3.4)	(3.7)	0.7	6.9	-	-
	0.2	70	0.8	3.5	0.19	9.1	-	0.5	6.4	0.02	8.6
	0.3	117	1.9	4.6	0.38	40	11	2.0	2.9	-	6.4
	0.5	65	1.0	6.5	0.20	13	4.8	0.5	7.4	-	2.6
	1.0	97	1.2	6.4	(2.6)	30	8.8	1.2	(13)	-	(18)
	1.5	65	2.8	4.5	0.30	26	7.8	1.3	3.4	-	7.1
	2.0	55	1.2	3.6	0.12	28	5.8	0.6	-	-	(12)
	2.5	114	1.6	4.7	1.5	28	11	1.4	-	-	9.0
	3.0	95	1.9	4.6	0.40	27	7.6	0.8	5.2	0.01	(23)
	mean	85	1.5	4.6	0.44	25	8.1	1.0	5.4		6.7
Total	$\sum$	1417	26.9	98.6	7.39	366	84	19.7	59.9		46.4
	n	15	17	17	13	15	10	17	13		7
	mean	**94**	**1.6**	**5.8**	**0.57**	**24**	**8.4**	**1.2**	**4.6**	**(0.01)**	**(6.6)**
	w	120	2.0	7.8	1.6	35	12	2.4	6.7		6.5
	SD	**31**	**0.5**	**1.9**	**0.4**	**9**	**3.8**	**0.6**	**1.9**		**2.0**

Notes: Results in brackets were considered uncertain and were rejected before processing.
SD = $w/n^{0.5}$ (*cf.*[19]), where *w* is the range, *n* – number of measurements.

Mironova *et al.*[36] made similar conclusion, when compared the ability of a bulk method (Decrepitation Gas Chromatography (D-GC)) with a local technique (Laser Excited Raman Spectroscopy (LERS)) for analysis of volatiles in fluid inclusions.

The destructive methods discussed here proceed in two stages: (1) extraction from the host and transportation of the inclusion content to the analytical device either as a leachate or by a carrier gas and (2) the measuring itself, which is the more precise stage – the instrumental error being usually below 5 %. The uncertainty accumulated during the first stage is greater and, hence, definitive; it is ascribed to the changes in the inclusion content before formation of the analytical signal. This discrepancy is specified in general as fractionation. An incomplete leaching after decrepitation, but even after crushing, may cause a distortion of the element ratios. D- and LA-techniques produce the analyte as a cloud of submicroscopic (nm) particles and many events in the carrier-gas flow are till now unknown. These particles – salt crystals (halite, sylvine etc.) in the case of decrepitation, and drops of glasses, in the case of laser ablation – may have very different masses (up to 2-3 orders of magnitude), which would be a reason for their gravimetric separation before entering the plasma torch. A selective electroprecipitation or thermoprecipitation on the tubing walls seems even more effective.

The assumed interferences are very probable, but their participation is not proved. The validation of the analytical procedures remains problematic, as even synthetic inclusions cannot copy adequately the natural objects, at least due to the difference in the life-time.

This observation is important, but it cannot show which of the methods is the "good" one. As none of these techniques is certified, we assume that putting the results into the geochemical practice may contribute at least partly to elucidate the problem of most realistic data. The results obtained could be cross-checked by a comparison between the T_h-measured (mode = 338°C) and some chemical geothermometers based on the Na/K, Na/Li (and Ca/Na) ratios[37, 38] (cf. Table 6).

The Na/K geothermometer yields lower temperatures, confirming systematically low K/Na-ratios, obtained by all the methods examined, excluding C-leach ICP-AES. The Na/Li geothermometer shows even lower temperature (167 ˚C) and points probably to a significantly low Li-concentration, determined by D-ICP-AES.

Table 6. Summarized results (X/ 1000 Na atomic ratios, ±SD[b]) from the chemical analyses of the water phase of fluid inclusions in the quartz specimen Qrz MDN (KD)[a]. A comparison between 3 methods: cruch-and decrepitation-leach (in 3 modes of detection: AAS (FES), ICP-AES and ICP-MS), D-ICP (AES), and LA-ICP-MS is proposed. Analytical data for single inclusions in galenas from Madan district are also included.

Method	X										Chemical geothermometers (T ˚C)		
	K	Li	Ca	Mg	Al	Fe	Mn	Cu	Zn	Pb	Na-K-Ca[38]	Na/K[37]	Na/Li[37]
D-ICP-AES (this study)	94±31	1.6±0.5	5.8±1.9	0.6±0.4	24±9	8.4±3.8	1.2±0.6	4.6±1.9	(0.01)	6.6±2.0	300 (-15; +25)	261±50	167±20
D Leach AAS (FES)[16]	70±32		19±7	4.2±1.7			1.4±0.6				265 (-15; +25)	235±50	
D Leach ICP-AES	< 260	13	12	(19)	–	5.1	2.0	< 8	–	< 120			370±30
D Leach ICP-MS	101±26	12±5	9.1±5	0.05±0.04	0.5±0.3	0.7±0.5	0.3±0.1	0.04±0.02	0.1±0.7	–	300 (-15; +25)	268±50	365±30
C Leach AAS (FES)[16]	90±37		20±9	6.1±2.0			1.4±0.6				275 (-15; +25)	257±50	
C Leach ICP-AES	151	16±10	60±50	14±10	25±15	7.9±3.3	4.0±2.0	< 100	< 43	< 156	330 (-15; +25)	311±60	404±50
C Leach ICP-MS	80±15	9±8	60±30	1.1±0.5	3.1±2	1.0±0.8	3.4±2.0	1±1	3.3±0.3	0.02	255 (-15; +25)	247±50	326±30
LA-ICP-MS[14]	110±20		60±10	0.5±0.2	(<1)	(<2.5)	7.0±1.6	0.25	0.8±0.2	0.14±0.05	280 (-15; +25)	277±53	
Fluid inclusions in galena[c] Gal MDN	190±60		85±25	~2	<0.2	10	~6	<0.4		<0.1	310 (-15; +25)	335±64	
D-ICP-AES Sph MDN[d]	104±40	18±10	64±20	10±5	18±10	7.6	1.5±1	(14)		(17)			

[a] This specimen is an intra-laboratory standard in respect to fluid inclusions. The total salinity of 8.5 wt % (mean) is evaluated; T_h = 329-348˚C with a mode of 338˚C. A detailed description of the inclusions and the host quartz was given by Kotzeva *et al*.[14]

[b] Standard deviation (SD) is calculated as SD = $w/ n^{0.5}$, where *w* is the range of the values obtained and *n* is the number of measurements.[19] The SD for single results cannot be evaluated.

D – decrepitation, C – crushing.

LA-ICP-MS. Mean values from 51 fluid inclusions, most likely primary or pseudosecondary, of sufficiently close chemical composition, T_h, and salinity from a single quartz crystal.

[c] Mean values from 18 macro-fluid inclusions in galenas from 5 locations in Madan ore district.[32]

– below detection limit

[d] Summarized data from 7 samples, Shumachevski dol location, Madan district.

Two destructive techniques for chemical analysis of fluid inclusions, using a carrier gas for analyte transportation, are compared here: D-ICP-AES as a representative of bulk methods and LA-ICP-MS as an example of single inclusion analysis. The last stage of analysis – registration of the analytical signal – although different in principle, may not be considered as a source of disagreement of the results, obtained by both the techniques.

The methods of opening of inclusions differ, however. The decrepitation is a "softer" method in contrast to the laser ablation. Our microscopic observations found that near a half of inclusions do not explode on heating but simply leak through the micro-cracks formed. The water phase, which is overheated under these conditions, boils spontaneously and the vapour pushes out the inclusion fluid through the crack. Here must be emphasized that solid phases, occurring in the inclusions as trapped or, especially, as relatively large daughter minerals, can hardly leave the vacuole through these narrow cracks. Hence, the analytical results are expected to represent in a higher degree the ion composition of the water phase of inclusions only.[4]

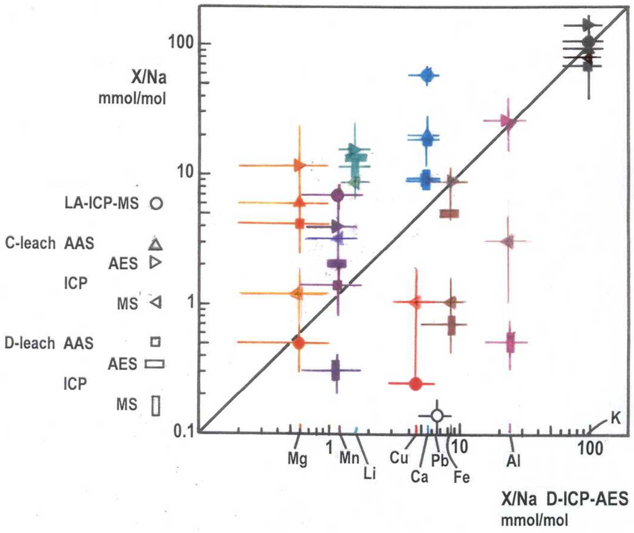

Fig.8. A juxtaposition of the ratios X/Na (mmol/mol, Table 6), obtained by LA-ICP-MS (circles), crush (C)-leach (triangles) and decrepitation (D)-leach (rectangles) vs. D-ICP-AES (abscissa), in a log-scale. The colours are: black for K, blue for Ca, green for Li, pink for Al, brown for Fe, violet for Mn, orange for Mg, red for Cu and white (empty symbols) for Pb, which is indicated on the abscissa.

The chipping off submicroscopic fragments of the host and entering them into the plasma is a specific disadvantage of D-ICP technique.[5] When fluid inclusions in sphalerite samples were analyzed (unpublished data), this process compromised entirely the results of Zn (and also of Fe, in the case of dark, Fe-containing sphalerites).

The laser beam is too powerful and always evaporates not only inclusion content (solute and solids – daughter and/or trapped phases), but also the matrix (host) in inclusion vicinity. The melting and evaporation of the host is necessary and even obliged, as this material is used successfully as a blank. The daughter minerals, being exsolved product of the inclusion fluid, may also provide useful information.

The trapped minerals, however, are problematic. They are not a component of the inclusion fluid and consequently their evaporation and involving into analytical tract may cause significant misinterpretation of the analytical results. Unfortunately some solid phases (Au, chalcopyrite) often are microscopically hardly observable. (“invisible gold”, for example). They may happen to precipitate even before inclusion trapping. Then, being hydrophobic, these metallized micro-domains may cause formation of gas (vapour) rich inclusions,[32] and LA-ICP-MS may found in them unexpectedly high concentrations of Au or Cu.[31]

The grate capabilities of LA-ICPMS are undisputable; they could not be overestimated, however. In the frames of this study it may be concluded that LA-ICPMS could not be used for validation, because its precision was found to be relatively low, commeasurable with the uncertainty of the methods compared, which is a constraint on the accuracy discussion. The analysis of synthetic inclusions as standards, do not solve the accuracy problem, due to the significant errors during the preparation of such inclusions.

The most important differences between LA-ICPMS and D-ICP-AES are mentioned in Table 1. Here we emphasize especially the requirements of the sample preparation, which, in the case of LA- are too high; they are the principle difficult of its application. Well-transparent crystal plates (“wafers”) are needed, containing inclusions of appropriate location, form and size (over 30 µm typically); most of the inclusions are simply unsuitable for the purpose.

On the contrary, the bulk methods are more undemanding in respect to the sample properties. There are geological objects of interest which do not supply materials suitable for microscopic observations, e.g. fine-grained quartz, containing small, µm-sized inclusions. In such a case the bulk methods, and especially D-ICP, may yield geochemically significant information, at least for the major components (Na, K, Ca) in the water phase of inclusions (excluding brines) and thus may help in the gross estimation of the trapping temperature via Na/K and Na-K-Ca chemical geothermometers.[37, 38]

Conclusions

- The D-ICP-AES, when applied to analysis of the water phase of fluid inclusions of low to moderate salinity, may yield useful results, well comparable with other destructive methods, as bulk (D- and C-leach), as well as individual (LA-ICPMS).

• The method is able to supply relatively fast and cheap preliminary information; the D-ICP-technique can be applied to a wide spectrum of sample materials and especially to those, which cannot be formed as thin transparent plates. These properties are an advantage of the method which on that account is worth attention and reappraisal.

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In memoriam

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References

1. E. Roedder, *Data of Geochemistry*, 6th, Composition of Fluid Inclusions, Geol. Surv. Prof. Paper 440-JJ, 1972, Washington, 164pp.
2. P. Lattanzi, *European Journal of Mineralogy*, 1991, **3**, 689-701.
3. M. Thompson, A. M. Rankin, S. J. Walton, C. Halls and B. N. Foo, *Chemical Geology*, 1980, **30**, 121-133.
4. D. H. M. Alderton, M. Thompson, A. M. Rankin and S. L. Chryssoulis, *Chemical Geology*, 1982, **37**, 203-213.
5. A. H. Rankin, R. J. Herrington, M. R. Ramsey, B. Coles, M. Christoula and E. Jones, in: *Proc. 8th IAGOD Symposium, Carleton University*, Ottawa, 1990 (Publ. 1993), E.Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 183-198.
6. S.A.Gleeson, in: *Fluid Inclusions: Analysis and Interpretation,* Vancouver, 2003, **32**, 233-246.
7. A. H. Rankin, M. H. Ramsey, B. Coles, F. Van Langevelde and C. R. Thomas, *Geochimica et Cosmochimica Acta*, 1992, **56**, 67-79.
8. T. J. Shepherd and S. R. Chenery, *Geochimica et Cosmochimica Acta*, 1995, **59**, 3997-4007.
9. J. J. Wilkinson, C. E. Everett, E. J. Boyce, S. A. Gleeson and D. M. Rye, *Geology*, 2005, **33**, 805-808.
10. A. H. Rankin, *Acta Petrologica Sinica*, 2007, **23,** 3-14.
11. M. Kaiser Rohrmeier, A. von Quadt, T. Driesner, C. A. Heinrich, R. Handler, M. Ovtcharova, Z. Ivanov, P. Petrov, St. Sarov and I. Peytcheva, *Economic Geology*, 2013, **108**, 691-718.
12. N. B. Piperov, *Review of the Bulgarian Geological Society*, 2002, **63**, 121-129 (in Bulgarian).
13. B. Kostova, Th. Pettke, Th. Driesner, P. Petrov and Ch. A. Heinrich, *Schweizerische Mineralogische und Petrographische Mitteilungen*, 2004, **84**, 25-36.
14. B. G. Kotzeva, M. Guillong, E. Stefanova and N. B. Piperov, *Journal of Geochemical Exploration*, 2011, **108**, 163-175.
15. T. J. Shepherd, A. H. Rankin and D. H. M. Alderton, *A Practical Guide to Fluid Inclusion Studies*, Blackie & Sons, London, 1985, 239 pp.
16. B. G. Kotzeva, I. D. Gocheva, N. B. Piperov, I. P. Havesov and A. K. Detcheva, *Microchimica Acta*, 2004, **147**, 231-236.
17. B. G. Kotzeva, *Chemical analysis of fluid inclusions in some Bulgarian minerals*. PhD Thesis, Inst. of General and Inorganic Chemistry, Bulg. Acad. Sci., Sofia, 2010.
18. M. P. Smith, D. A. Banks, B. W. D. Yardley and E. J. Boyce, *European Journal of Mineralogy,* 1996, **8,** 961-974.
19. 31. D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, 3rdEdition, New York, 1976.
20. N. B. Piperov and N. P. Penchev, *Geochimica et Cosmochimica Acta*, 1973, **37**, 2075-2097.
21. N. B. Piperov, N. P. Penchev and B. P. Zidarova, *Chemical Geology*, 1979, **27**, 215-231.
22. G. Hladky and R. W. T. Wilkins, *Chemical Geology*, 1987, **61**, 37-45.
23. S. Lindblom, A. H. Rankin and M. Thompson, *Applied Geochemistry*, 1989, **4**, 473-481.
24. L. W. Diamond, J. A. Jackman and B.Charoy, *Chemical Geology*, 1991, **90**, 71-78.
25. N. Guillemette and A. E. Williams-Jones, *Mineralium Deposita*, 1993, **28**, 167-180.
26. I. M. Samson, A. E. Williams-Jones and Weining Liu, *Geochimica et Cosmochimica Acta*, 1995, **59**, 1979-1989.
27. D. Marshall, N. Meisser and R. P. Taylor, *Mineralogy and Petrology*, 1998, **62**, 147-165.
28. C. Fabre, M-C. Boiron, J. Dubessy, M. Cathelineau and D. A. Banks, *Chemical Geology*, 2002, **182**, 249-

264.

29. A. H. Rankin, M. F. Miller and S. J. Carter, *Mineralogical Magazine*, 1987, **51**, 517-525.
30. B. N. Ryzhenko and S. R. Krainov, *Geokhimya*, 2000, **38**, 803-815 (in Russian).
31. Ch. A. Heinrich, D. Günther, A. Audétat, Th. Ulrich and R. Frischknecht, *Geology*, 1999, **27**, 755-758.
32. N. B. Piperov, N. P. Penchev, I. K. Bonev, *Mineralium Deposita*, 1977, **12**, 77-89.
33. B. G. Kotzeva and N. B. Piperov, *Geochemistry, Mineralogy and Petrology*, *Bulg. Acad. Sci.*, 2000, **37**, 93-105 (in Bulgarian).
34. M. P. Smith, S. A. Gleeson and B. W. D. Yardley, *Geochimica et Cosmochimica Acta,* 2013, **102**, 89-112.
35. A. Audétat, D. Günther and Ch. A. Heinrich, *Science*, 1998, **279**, 2091-2094.
36. O. F. Mironova, A. N. Salazkin and V. B. Naumov, *Geokhimiya*, 1995, 974-984 (in Russian).
37. S. P. Verma and E. Santoyo, *Journal of Volcanology and Geothermal Research*, 1997, **79**, 9-23.
38. R. O. Fournier and A. H. Truesdell, *Geochimica et Cosmochimica Acta*,1973, **37**, 1255-1275.