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# ABSTRACTS VOLUME

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> FIFTYFIRST ICCP MEETING 12 – 18 September 1999 Bucharest

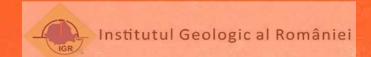
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Institutul Geologic al Romaniei Bucuresti 1999



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The editor has changed the name as follows: Institutul Geologic al României (1906–1952), Comitetul Geologic (1953–1966), Comitetul de Stat al Geologiei (1967–1969), Institutul Geologie (1970–1974), Institutul de Geologie şi Geofizică (1975–1993), Institutul Geologic al României (since 1994).

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Rom. J. Mineralogy is also the Bulletin of the Mineralogical Society of Romania, a member of the EMU and IMA. Thus, this journal follows the rules of the Commission on New Minerals and Mineral Names of the IMA in all the matters concerning mineral names and nomenclature.

The manuscripts should be sent to the scientific editor and/or executive secretary. Correspondence concerning advertisments, announcements and subscriptions should be sent to the Managing Editor.

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### Introductory talk to the 5th Symposium of the Mineralogical Society of Romania

Born seven years ago, both the mineralogical society and its symposia were paid increasing attention by Romanian and foreign mineralogists and petrologists. As a member of IMA and EMU, the M.S.R decided to regularly held the symposia (every two years) in such a way that overlapping should be avoided. In spite of careful planning there were several cases when avoidance was impossible.

However, the symposion attendance was quite good and the quality of papers greatly increased. This years the MSR Symposium hosts also two supplementary meetings, i.e. a HP / HT Metamorphism Conference and the 51<sup>st</sup> ICCP Meeting (International Committee for Coal and Organic Petrology). The Abstracts Volume will therefore include mixed papers of all the meetings.

Lack of participants resulted in cancellation of the main field trip intended to be organized in Dobrogea. In such a case the Supplement No. 2 of the Rom. J. Mineralogy Vol.80 (excursion guide) will no more published. We hope to have the possibility to re-plan this field trip, which should have covered an important area with mineral occurrences and petrologic topics of utmost importance in Romania. On the enclosed map locations of the past MSR symposia and field trip areas are shown as well as the missed Dobrogea.

The topics of the 5<sup>th</sup> Symposium are very different including petrographical and petrological data, some general metallogenetic aspects, geochemistry, but the majority of papers deals with mineralogy: both rock-forming and ore-related. Not only rare minerals are presented e.g. dypingite, nambulite, natronambulite, the first occurrences in Romania; cymrite, some Bi sulfosalt and skarn minerals but also new methods for data refinement (deconvolution, Mössbauer spectroscopy, stable isotopes of salt melt inclusions) as well as some ideas about minerals of gem value.

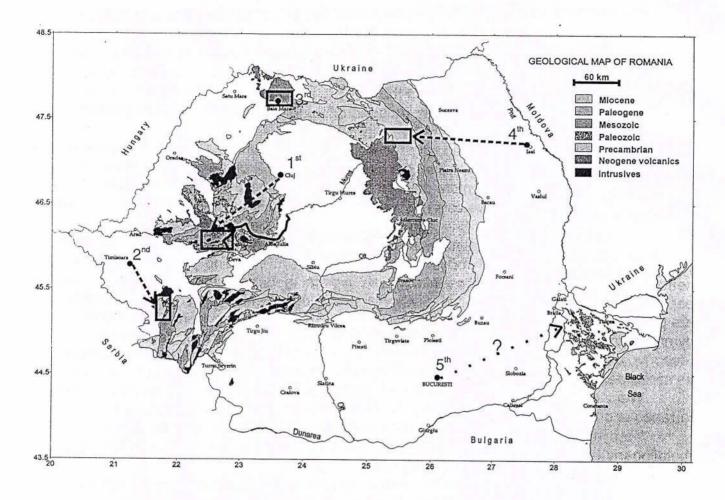
Welcome are also some few papers on general topics concerning the HP and UHP terranes and the serpentinisation of UB rocks (Medaris, Ghent, Maksimovic).

I am happy to see that the interest in mineralogy, petrology, geochemistry and metallogeny is still alive in spite of a general recession related to reducing the areas of mining activity. The question "Quo vadis geologia? / and mineralogia?" can be answered by "into the next millenium", provided we will be able to address topics which are and will be worth of influencing the appropriate financing...

August 1999

G. Udubasa President of the MSR

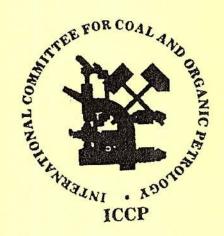




Sites of the Symposia on Mineralogy, and the corresponding excursions







The 51<sup>st</sup>

Meeting

of the

# International Committee for Coal and Organic Patrology

12<sup>th</sup> - 18<sup>th</sup> September 1999, Bucharest

Organised by:
The Mineralogical Society of Romania
Bucharest University



# INVESTIGATION ON THE ORGANIC/MINERAL MATTER ASSOCIATION AND DISTRIBUTION IN COAL USING COLOUR IMAGE ANALYSIS

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The formation of ash deposits on the heat transfer surfaces in a p.f. boiler is one of the major problems that power stations have to deal with. Uncontrolled deposits can interfere with operation and cause unplanned shutdowns or reduced output and efficiency. The high costs involved in the removal of mineral matter from the feedstocks demand that the search for solutions to the prediction and control of the growth of these deposits should be addressed, rather than the elimination of the mineral matter. The aim of a joined project of INCAR, ICSTM and TNO is to make an assessment of the changes undergone by the mineral matter when submitted to the environmental conditions typical of pulverised coal combustion. The propensity of minerals to form deposits in the boiler is studied on the basis of their different chemical compositions and association with the organic matrix.

In order to investigate the organic/mineral matter association and distribution in coal a procedure has been developed to combine information of different microscopical techniques by colour image analysis. Organic matter composition and distribution can very well be identified using incident light microscopy, whereas SEM-EDX can be used to identify of mineral matter composition and distribution. A combined analysis of incident light microscopy and SEM-EDX has been performed, analysing the composition of the coal along the same trace with both techniques. The different information can be used to identify the mineral matter and to describe different kinds of mineral and organic matter associations in coal.

25 reflected light and 25 fluorescent light images have been recorded for each coal sample at equally distanced points along a trace covering the whole sample. Thresholds for all macerals are set. Particles containing more than one maceral group have been assigned as special regions of interest (ROI). The areas of these bimaceral and trimaceral particles have been calculated, as well as the fractions of vitrinite, inertinite and liptinite within the ROI. For the identification of liptinite macerals the fluorescent images have been used in order to ensure a larger accuracy. The total amount of a maceral group within an image is calculated by addition of all the areas of the analysed particles.

The 25 images, which have been recorded by incident light microscopy, have also been analysed using SEM-EDX. Backscattred electron images have been acquired as well as EDX-pixel maps of the elements  $\mathrm{SiO_2}$ ,  $\mathrm{Al_2O_3}$ ,  $\mathrm{K_2O}$ ,  $\mathrm{CaO}$ , MgO, FeO, and S. The backscattered electron image which clearly indicates the location of the mineral particles within the coal particles has been converted to a binary image to produce photographical mask. The map of a certain element is combined with the binary image. The pixels of  $\mathrm{K_2O}$ ,  $\mathrm{Al_2O_3}$  and  $\mathrm{SiO_2}$  are used to estimate the amount of illitic clay in each particle. The residue of the pixels  $\mathrm{Al_2O_3}$  of  $\mathrm{SiO_2}$  and are combined to estimate the amount of kaolinitic clay. The residue of  $\mathrm{SiO_2}$  is used to estimate the amount of quartz for in each particle.

Ca, Fe, Mg and C are combined for the estimation of the amount of calcite, ankerite and dolomite. The amount of pyrite in each particle is estimated by combining the pixels of S with the pixels of Fe.

By combining the images of incident light microscopy and SEM EDX using colour image analysis it is possible to quantify several classes of mineral/organic matter associations within coal particles.



### STRUCTURAL CHANGES IN A THERMALLY STABILISED COAL

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A modified heat treatment procedure in a flow of air has produced a "thermally stabilised" coal for which the Equilibrium Moisture Content (EMC) has been irreversibly lowered. A lower EMC in an export coal will have commercial advantages. The structural changes, which have been induced in three sub-bituminous coals, have been studied by a variety of techniques such as FTIR, Solid State C13 NMR, elemental and petrographic analyses. The data suggest that although bituminous coals when subjected to oxidative heat treatments follow chemical pathways similar to those observed in thermally stabilised coals, a bias can be developed for the latter which leads to a denser, less oxidised product that is also less hydrophilic and hence has a lower EMC. Our chemical analyses have now allowed us to present evidence for crosslinking reactions in coals that have previously lacked a firm experimental basis. These chemical structural changes can also be closely correlated with petrographic analyse. FTIR analyses show that oxidation occurs to form carbonyl functional groups, however this technique is overly sensitive to these reactions but which are confirmed by the Solid State C13 NMR spectra. The NMR spectra, however, clearly illustrates that a range of oxygen substitution reactions occurs in the initial stages of a heat treatment. One major effect is to significantly lower the surface area of the coal despite the development of hydrophilic centres. Petrographic analyses show oxidative heat changes as alteration rims on the coal grains that exhibit a high Ro value. The inner rims have a reflectance slightly lower than the core of the grains suggesting that bitumen-like material may have been pushed ahead of the alteration zone into the less altered coal. The thermally stabilised coal shows a number of particles that have been completely altered, suggesting that the bitumen is reacting with the coal macromolecule and oxidised rim. The altered particles have a higher Ro value. These observations are reflected in the Pyrolysis / GC analyses at 340°C and 600°C where no volatile (mobile) material is released at 340°C. However, at 600°C where carbon-carbon bonds are broken, there is a large release of lower molecular weight hydrocarbons from the coals after heat treatment. The chemical and petrographic analyses are convergent and how these structural changes influence the EMC of the coal will be discussed in the presentation

## THE NATURE OF 'PSEUDOVITRINITE' IN GUNNEDAH BASIN COALS, NSW, AUSTRALIA

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Material resembling that described by Benedict et al. (1968) as 'pseudovitrinite' has been identified in Permian high-volatile bituminous coals of the Gunnedah Basin, NSW, Australia. In order to obtain more information about the nature and significance of this material, a study was undertaken to investigate the variation in reflectance and other properties for the different vitrinite components in vertical sections through the Gunnedah Basin sequence. Apart from routine reflectance measurement (maximum and minimum reflectance of different macerals present) microscopic observations were intended to evaluate the optical properties of pseudovitrinite, particularly the development of its slit pattern and other microfractures, the presence of remnant cellular structures, fluorescence properties and mineralisation. Chemical characterisation was based on the application of electron probe microanalysis. This technique provided direct quantitative data on the percentages of carbon, oxygen, and sulphur in the individual macerals, on spots approximately 5  $\mu m$  wide. Additional studies on samples containing 'pseudovitrinite' included polished thin sections from selected samples and etching tests.

'Pseudovitrinite' in the Gunnedah Basin coals commonly occurs in vitrain bands, as relatively thick lenses usually well above 30  $\mu m$  (in polished blocks), not associated with other macerals. The property that most generally identifies 'pseudovitrinite' in Gunnedah Basin coals is its relatively brighter appearance in polished section compared with 'normal' telocollinite or desmocollinite. The mean maximum reflectance of 'pseudovitrinite' is up to 0.15% higher than that of the telocollinite in the same samples. The histogram for 'pseudovitrinite' in all samples studied is represented by a sharper peak than that of the other types of vitrinite in the respective coal samples. This indicates a relatively narrow total reflectance range for 'pseudovitrinite' relative to other vitrinite types. The reflectance data for the pseudovitrinite in each coal also have a much smaller standard deviation than those of the other vitrinite types. No fluorescence has been observed from 'pseudovitrinite' in any of the Gunnedah Basin samples studied. However, resinite bodies within 'pseudovitrinite' bands sometimes give strong fluorescence under mercury-lamp illumination.

Maceral analyses of selected samples containing 'pseudovitrinite' were carried out on specimens representing whole seam composites or individual plies within coal seams. Many of the coal samples studied for this project were, however, based on hand-picked vitrain; some of these contain up to 100% vitrinite in the form of 'pseudovitrinite.' Maceral analyses show that 'pseudovitrinite' often makes up over 5% of the total macerals present. Many samples contain up to 10% and a few coals approach or surpass 20% 'pseudovitrinite' content. Because of the relatively low overall proportions of vitrinite in most of these coals, 'pseudovitrinite' may make up in some cases almost half the total vitrinite present

Electron microprobe analyses indicate that 'pseudovitrinite' has an organic sulphur content close to that of the desmocollinite and telocollinite in the same coal samples,



and is consistently higher than that of the associated semifusinite or fusinite. Carbon and oxygen contents are also similar to those of the other vitrinite macerals in iso-rank coals.

"Pseudovitrinite" in the Gunnedah Basin coals quite commonly exhibits slits characterised by s-comma shapes, usually from a few to 10 microns long. On polished blocks cut perpendicular to bedding the slits usually are at right angles to bedding or are slightly inclined. The density of slits has been found in the Gunnedah Basin coals to be highest in boreholes close to the Hunter-Mooki Thrust Fault. This may imply that some tectonic force is responsible for slit formation as well. Preferential fracturing only in the more highly-reflecting vitrinite bands suggests that, at the time of stress emplacement 'pseudovitrinite' was more brittle than other vitrinite macerals. 'Pseudovitrinite' in coals from the Gunnedah Basin commonly contains small pyrite crystals in the individual slit fractures. This indicates that slit development took place at a relatively early stage, and was not an artefact of sample preparation or exposure of the coal to the atmosphere.

While traditional etching with acidified potassium permanganate revealed only a number of scratches on vitrinite layers, particularly interesting information was obtained by extended exposure of coal samples containing 'pseudovitrinite' to immersion oil over several weeks. The particular type of immersion oil used was found to act, long term, as a selective etching agent. The etch effects in the first stage were apparent only in pseudovitrinite layers, while other vitrinites were unaffected. 'Pseudovitrinite' which appeared homogeneous in normally polished sections displayed botanical structure after "etching' by immersion oil. Another form of etching applied to Gunnedah Basin coals, revealing a cryptotelinitic structure of 'pseudovitrinite,' was the use of an electronically excited oxygen plasma in a low-temperature asher. Examination of thin sections of Gunnedah Basin coals also shows a cell structure in the 'pseudovitrinite' material. Further study using these techniques will be directed to determine the botanical origin of the cellular structure revealed in 'pseudovitrinite' and other vitrinite types.

# COMPARATIVE ASSESSMENT OF GLOBAL COAL FACIES MODELS TEMPORARY REPORT OF THE INTERNATIONAL COMMITTEE FOR COAL AND ORGANIC PETROLOGY

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The Coal Facies Working Group (WG) began to make an overview on recent and older coal facies studies three years ago. "The objectives of this working group are concerned with the re-evaluation of concepts used in coal petrography for facies analysis and interpretation of paleo-depositional environments including new approaches. The concepts considered at the International Committee for Coal and Organic Petrology (ICCP) meeting range from lithotype and microlithotype analysis, maceral analysis and derived Tissue Preservation and Gelification Indices to etching procedures including paleobotanical studies, sequence stratigraphy and palynology, etc....." (Minutes of Commission 2, 48th Meeting of the ICCP held in Heerlen, The Netherlands, ICCP News, 1996)

To make easier the review on different facies analysis methods we ask the members of the WG to comply different facies analysis models from relevant publications according to geographical areas. By the end of 1998 from 16 different geographical area, 18 compilations were completed by 20 authors. Extended abstracts and tables were published last year in the special publication of the ICCP in 100 pages.

References have been cited in this work since 1922. Compiled coal facies works in most cases based on organic pertography and palynology, however extended stratigraphic works and coal geology preceded organic matter studies. Some paper focused on recent peat forming environments to reveal main processes during peat accumulation and preservation. Others dealt with palynofacies-coal facies interpretations to make evidence in terms of moor types. Many cases organic petrology was extended by organic geochemistry as well. For coal facies works authors used mainly microlithotype and maceral analysis, interpreted their results in triangle diagrams.

Beside of analytical methods characterization of depositional environments was very heterogeneous. Some author used more extended facies terms like paralic or limnic, topogenous or ombrogenous. Others distinguished peat-forming environment after the characteristics of deposition like ground water level and dissolved ion concentration. From this point of view we established that the studied economical coal measures formed in paralic, topogenous, telmatic conditions.

Most studied coal formations carried out from Carboniferous, Perm and Tertiary coal bearing measures. Rank of the investigated peat-forming environments ranged from peat-lignite to anthracite. The most published formations were sub-bituminous coals, although reconstruction is the easier the less altered is the organic matter by biochemical and geochemical processes.

In summary the WG could make a good overview on reported and published studies in America (Brasilia, Canada, Peru, Eastern USA), Australia, Europe (United Kingdom, Spain, Germany, Hungary, Poland, Bulgaria, Denmark and Greenland, Ukraine) and in some references China, Africa, and Indonesia. In the near future we would like to extend these compilations to the whole USA and to get more information on Asian, Indonesian and African works as well.



### SAPROPELIC COALS FROM THE UPPER SILESIAN COAL BASIN (POLAND)

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The presence of sapropelites and saprohumolites has recently been discovered during mining works in Gómósl'Hskie Zaglębie Węglowe (Upper Silesian Coal Basin). They were taken out from coal beds (Namurian A,B,C) and subjected to examination. Petrographic, chemical, fluorescent and pyrolitic examinations carried out. The obtained results allowed to prove the genetic petrographic differences.

Diversified petrographic composition of sapropelites allows to distinguish the following: spore-cannel, tissue-cannel, sporous-tissue cannel, boghead-cannel and boghead.

Spore cannel is characterised with a considerable fraction of liptinite, represented mainly by lipodetrinite and sporinite, and to a certain extend by inertinite. It was named cannel shale due to significant fraction of mineral matter.

Tissue cannels, represented in great number, have fraction of components originated from plant tissue, i. e. semifusinite, fusinite and also occasionaly of vitrinite (streeaks of colinite). The content of inertinite is higher than liptinite.

The sporous tissue cannels are characterisde by similar or a little higher fraction of tissue components than liptinite.

Boghead-cannel has high fraction (14.406) of lipodetrinite and contains alginite (1.5%); whereas in samples of cannels the alginite is not present.

In cannels and in boghead-cannels the mass which joins minerals of liptiniteand inertinite is dark vitrinite, which has desmocollinite features, containing variable quantities of micrinite and mineral substance. Only in one case, the mineral matter turned out to be the basic mass.

Boghead contains 43.0% of relatively well maintained alginite and 36% of groundmass, which shows distinct fluorescence. Reflectance of sapropelites value range from 0.84% to 1.12%.

Sapropelites have variable bituminuos feature because II/C = 0.73: 11.21 and tar flow-off also is different Tk $\S = 3.27 + 43.16\%$ . Tissot's genetic diagram cannels are located in the area of type III kerogen (humic one). Only boghead is located within the area of type II kerogen (sapropelic one). Also, on the diagram of hydrogen index (HI) versus organic coal (TOC), cannels are located in neighbourhood of humic coal.

Results of research had shown that cannel coals and humic coal were formed of humic organic substance but in different facial conditions, which is expressed by variable petrographic features but in lesser extention of chemical-technological properties.



# THE EFFECT OF VOLCANIC TEPHRA DEPOSITION ON PEAT FORMATION IN PTOLEMAIS BASIN (HELLAS)

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The intermontane Neogene basin of Ptolemais is a tectonic graben located in western Macedonia, Hellas. The sediments filling the basin include the following members: a) the Lower member, which consist of a basal conglomerate, as well as of sandy marls and clays (Upper Miocene-Pliocene); b) the coal-bearing sequence (up to 130 m thick), which consists of lignite seams intercalating with marly and clay layers; c) the Upper member, which includes limnic and terrestrial sediments (Upper Pliocene); and finally d) the Quaternary sediments. The lignite is mined in open pit and used for power production covering around 70% of the domestic energy supply.

A distinct layer of volcanic ash occurs in the lower part of the lignite-bearing sequence. The tephra layer is up to 30 cm thick and extends over the whole deposit.

Twenty-seven lignite samples were collected for maceral analysis from seven different locations, in order to study the possible influence of the volcanic ash deposition on peat-forming conditions. In every location, two lignite samples were obtained just above and bellow the tephra layer; moreover, one or two more samples were also taken in a distance of 2 m above and/or bellow the same layer.

Micropetrographic studies of the lignite samples suggest that huminite is the dominant maceral group, while liptinite shows low to moderate values and inertinite rarely occurs in significant amounts. Maceral analysis reveals a low Tissue Preservation Index (TPI) and a low to moderate Gelification Index (GI), without indicating any significant difference among the samples. Coal-facies diagrammes suggest that the peat was derived mainly from herbaceous vegetation and probably accumulated in a fen under wet conditions and rather intense bacterial activity. Factor analysis on the values of maceral and minerals states a relative enrichment on inertinite and attrinite for some samples which are in direct contact with the tephra layer.

Consequently, the deposition of the volcanic tephra did not significantly affect the peat-forming palaeoenvironment.



# SOURCE ROCK MATURITY IN THE CENTRAL AND VIKING GRABEN, NORTH SEA – EVALUATION OF OPTICAL AND GEOCHEMICAL MATURITY PARAMETERS

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Generally source rock maturity is best determined by vitrinite reflectance measurements (Ro%). However, most oil prone source rocks are lacking proper vitrinic macerals. Even if vitrinite is abundant, reflectance values are often substantially suppressed by associated liptinitic hydrogen-rich macerals. In the present study 46 samples of organic-rich source rock intervals (Kimmeridge Clay, Heather Shale, Pentland and Brent coals) from the Central and Viking graben areas, North Sea, were analised for maturity. While the Upper Jurassic Kimmeridge Clay is the proeminent type Il sourcerock of most oils in the North Sea, the underlying Heather Shale is regarded as a poor type II/IV source rock. In some parts of the basin Middle Jurassic Pentland and Brent coals are underlying the oil source rock sequences. Samples were obtained from cores and sidewall samples covering a depth range from 1863 to 5064 m and were prepared for a variety of optical and chemical analyses according to standardized procedures. The methods applied included optical analysis (vitrinite reflectance, spectral fluorescence, spore colouration index (SCI), photometric colour measurements of structureless organic matter (SOM) and sporomorphs in translucent light, Rock Eval on whole rock and isolated kerogens and infrared spectroscopy.

<u>Vitrinite Reflectance.</u> The reflectances range from 0.33% Ro\_(immature) at relatively shallow depth (1879 m) to 1.16% Ro (highly mature) at 5064 m. Most of the samples yielded two clearly defined vitrinite populations, showing essentially the same trend, namely a slow increase in the depth interval from 1800-3000 m, followed by a rapid increase of maturity at greater depth. The sample set comprised also 5 coal samples (0.52 – 0.63% Ro), while the reminder of the saples consisted of dispersed organic matter (DOM).

<u>Spectral Fluorescence</u>. Fluorescence spectra were obtained from telalginite, which was found to be abundant in many samples. From the spectral curves lambda max and the red/green quotient were determined, both showing significant changes to longer wavelenghs as a function of increasing maturity. Correlation with vitrinite reflectance showed that the fluorescence spectra at Ro < 0.5% showed a wide variation, while vitrinite values changed only slightly.

Spore Colouration Index (SCI). Spore colour indices were determined using a scale from 1 to 10 and corresponding vitrinite reflectances were estimated. The SCI values range from 2.0 to 9.0, with corresponding estimated vitrinite reflectaces ranging from 0.32 to 1.20 %. The correlation of SCI and vitrinite reflectance is almost linear, except at higher maturity, where for the same SCI values quite a spread of vitrinite values is apparent.



Photometric spore colour analysis. In this method kerogen concentrates were used to carry out absorption measurements on mainly structureless organic matter (SOM) and some isolated spores/gymnnosperms using band pass filters of 497 (green) and 659 (red) nm for defining translucency (T) values by the Absorbance ratio (A656/A497). The spread/variation in maesured Absorbance ratios is relatively large (e. g. A SOM 0.48-0.67, A sporomorphs 0.35-0.45) at the same maturity level (0.60-0.70 Ro%). Values are also generally too low at higher maturities (Ro% >0.80%) and the method is limited to Ro% levels < 1.20% because of the opacity of palynomorphs at higher maturity.

Rock Eval Analysis. Standard Rock Eval analysis was performed on whole rock and isolated kerogen samples. Tmax values of both sample sets ranged between 415-451 Tmax (°C). However, highest correlation coefficients with true vertical depthwere obtained for the measurements on the isolated kerogen.

Infrared Spectroscopy. Although infrared analysis for maturity measurements was originally developed on quantitatively isolated kerogen, in this study a split of the same kerogen concentrate which was prepared for the photometric spore colour analysis was used for infrared spectroscopy. However, no final oxidation of samples by HNO<sub>3</sub> was allowed. Maturity was estimated based on the distribution of aliphatic and carboxyl/carbonyl bonds relative to aromatic bonds (A-Factor/C-Factor). The C-Factor from IR analysis shows relatively poor correlation with true maturity. The main reasons for this are mineralogical impurities in the kerogen concentrates and the presence of dead organic carbon in most Kimmeridge Clay samples of the Viking Graben area.

Since the burial history in the study area is relatively simple and present day burial is equivalent to maximum temperature, vitrinite reflectance measurements of the Pentland and Brent coal samples show a very good correlation with true vertical depth. Therefor-true vertical depth data could effectively be used to evaluate the reliability of the different maturity tools on the samples of the oil prone Kimmeridge Clay source rock. From Table 1 it is apparent that Tmax (°C) from Rock Eval analysis and vitrinite reflectance yield the highest overall correlation coefficients for the sample interval studied.

Ro%	Lamda	Q		Tmax	Tmax	A-ratio	C-Fact.	
high pop.	max	ratio SCI		kerogen	rock	(SOM)	IR	
0.87	0.84	0.80	0.88	0.93	0.86	0.60	0.81	

Table 1: Correlation coefficients between true vertical depth and the various maturity parameters

### SCATTER OF VITRINITE REFLECTANCE VALUES OF COALS - REMARKS ON THE COMPARABILITY OF ARITHMETIC MEAN REFLECTANCE DATA WITH INCREASING RANK

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Searching for a measure of the potential range of reflectance values of rank-typical particulate vitrinite contained in mineral sediments, the scatter of vitrinite reflectance readings of coals was investigated using range, standard deviation and the variation coefficient as statistical parameters for the scatter of random (Rr %) and maximum (Rmax %) reflectance. Altogether data from 175 coal samples with Rr ranging between 0.17 % and 5.17 % were available. The evaluations for Rmax are based on 63 samples. Range and standard deviation of Rr do not increase linearly with increasing coalification. For both the parameters best fitting trendlines are third-degree polynomial functions with the constraint (0,0). Up to about 2 % to 2.5 % Rr the relationship is approximately linear.

A parameter of special interest concerning the scatter of measurements is the variation coefficient which allows a comparison to be made of different arithmetic means with regard to the scatter even if the means have different orders of magnitude (like coals of increasing rank), so that the standard deviation inevitably varies. Unfortunately it turned out that the variation coefficient is not independent of the level of the random reflectance. It is constant up to 2.5 % Rr with an average of about 7.5 %. A variation coefficient of maximum reflectance (Rmax) 10 % can be a useful value for the assessment and comparison of random reflectance measurements on coal samples up to 2.5 % Rr. Above 2.5 % Rr it is not a suitable parameter for comparing the scatter of determinations of different orders of magnitude.

For maximum reflectance (Rmax) a linear relationship exists between the range or the standard deviation with increasing Rmax. However, the scatter of the data is very broad. The variation coefficient increases slightly with Rmax - if at all. For this measuring method it is well suited as a parameter of the scatter of measuring data throughout the total range of coal ranks. On average the variation coefficient amounts to 4 %. A variation coefficient of = 7 % could be used for the evaluation of the quality of measurements on coal samples.

Concerning the Rr-determinations, for most of the coal technological applications and for oil exploration the field up to a maximum of 2.5 % Rr, which is well comparable using the variation coefficient as a measure of the scatter, would be sufficient. But measurements for gas exploration, for geological and tectonic questions as well as for research on ore deposits reach much higher degrees of coalification and Rmax measurements are advisable.

Altogether according to the results presented measuring only Rmax for rank determinations would be useful. In this way conversions could also be avoided for which the equations are not yet robust enough. Problem: Time needed is substantial especially for measurements on dispersed vitrinite and the method is nearly impracticable on very tiny particles.



# THE COAL BALLS FROM THE CHIMU FORMATION (LOWER VALANGINIAN) IN THE ALTO CHICAMA BASIN (PERU): HYPOTHESIS ON ITS ORIGIN AND FORMATION

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In the Alto Chicama Basin, one of the most important coal basins in Peru which is located in the western range of the Andes in the Northern part of the country, there are frequent occurrences of coal balls. These coal balls seem to be associated with the number 5 coal bed in the productive coal series of the middle-upper part of the Chimu Formation (Lower Valanginian) in some of the coalfields e.g.: Los Andes, Victoria and

Callacuyan from the southeastern sector of the basin.

The coal balls have typical tabular, elongated and rounded morphologies showing a sequence of formation from the initial tabular coal beds. They are all a part of the same coal bed. One important difference with respect to the other coal balls described in the literature (see Stach et al., 1982; Taylor et al., 1993) is that related to composition. The coal balls from the Chimu Formation are almost totally organic as shown from petrographic analysis and chemical determinations, with a high vitrinite content and a chemical composition similar to that of the coal beds in which they were found. Moreover, their mineral matter is made up of clays, quartz and feldspars, a composition, which is also very similar to that of the associated coal beds. The mean random vitrinite reflectance of these coal balls varies between 4,2% and 5,2% and they show an optical biaxial negative character. Therefore, their rank is equivalent to the anthracite stage as in the case of the other coals in the upper part of the Chimu Formation.

Taking into account the new data obtained from the study of these coal balls it seems that they were formed "in situ" from the same coal beds in which they were found and at the initial stages of coal evolution (lignite coal rank). The tectonic movements of the Sub-Hercynian phase (105 m.y. approximately), which affected the western edge of the Alto Chicama Basin, caused the coal beds to tip over and then the subsequent gravitional instability originated fracturation and fragmentation of the coal into blocks of different sizes. Next, these blocks underwent a relative deplacement acquiring different and variable morphologies as a function of the relative distance covered. Later, the coal balls thermally evolved at the same time as the coal beds from which they derived because both were affected by the successive tectonic phases of the Andean Orogeny and the intrusive stocks of Tertiary age. The hypothesis proposed in this work for the origin of the coal balls from Alto Chicama basin is different to that previously given by Lipiarski and Szymoniak, (1977) and to that given for the coal balls of inorganic composition, mainly of Carboniferous age.

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## LITHOTYPES OF THE LIGNITES AND BROWN COALS FROM ROMANIA (preliminary notions)

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The subject of lithotypes is old, but very actual and unclear yet. There were very many attempts to make a classification and a nomenclature. We kept them our respects. In this paper, we want to put a problem: the quality of the coal as rock. What is coal? An energetic substance or a rock? As a petrologist, I'm naming it in petrological way. In General Petrology we can describe some types of andesites, of metamorphites, sands, sandstones, clays,.....); why not of coal: lithotypes. How does is characterised an andesite? We make a petrographic description: colour, composition, structure, texture, consolidation....

Can we apply a natural petrographical description in the study of coal? Our answer is yes. The coal is a rock, firstly. In a coal bed we can describe many lithotypes, often. For exemple, in bituminous coals we can see vitrain, clarain, durain, fusain. It's easy to make a nomenclature or a classification of lithotypes from bituminous coals. Rarely, in bituminous coal, we can describe the components, the origin of the vegetable materials. But in lignites we can observe the structure and the origin of hard vegetable materials in good condition. In lignites and brown coals we can notice: composition (the major vegetable structure components), colour, texture, gelification, minerals components, bedding/stratification. Our proposal for classification and nomenclature of lithotypes from lignites, in bed or in industrial deposit, starts from the character of coal as a rock.

In many coal beds from lignites of Romania, we remarked the next lithotypes: yellow xylitical coal; yellow-brown xylitical coal with a little gelification: mat brown xylitical coal with gelification; bright black xylitical coal with gelification; brown detrital bedded (or unbedded) coal with a little gelification; mat brown-black detrital (bedded or unbedded) coal with gelification; bright black detrital (bedded or unbedded) coal with total gelification; bright black detrital gelificated coal with pyrite/clay....

It would be necessary an international classification and nomenclature of lithotypes from lignites? If we want to obtain a good industrial using, it is need to do it. In our paper, we shall demonstrate the existence of theese lithotypes from the lignites of Romania (Sinersig ore, included in sedimentary deposits of Portaferrian; Livezile deposit, included in Neogen sedimentary deposits of Carpathian Foredeep mollasse filling; Rovinari deposit, included in Miocen-Pliocen; Supur-Babţa deposit from Pontian; Ojasca deposit / Miocen-Pliocen; Balta Sărată /Badenian; Bozovici deposit / Badenian; Borozel deposit / Sarmatian; Comăneşti deposit / Sarmatian).

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# PRELIMINARY RESULTS FROM THE STUDY OF A NEOGENE LIGNITE DEPOSIT OF W. PELOPONNESE, HELLAS

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A number of coastal lignite deposits in Hellas are located in the SW part of the country, in the region of Western Peloponnese. They include thin, non-extensive matrix-coal layers alternating with fluviolacustrine Neogene sediments. Their quality appears to vary from site to site, implying different depositional environments. In a first attempt to interpretate the genesis and the characteristics of these lignite deposits several different analyses were carried out on a number of samples from the Magoula deposit.

Maceral analysis resulted in low Gelification Indexes (G.I.) and low to moderate Tissue Preservation Indexes (T.P.I.) revealing probably a back barrier depositional environment. High ash contents indicate a large influx of inorganic material during the initial peat-forming stage. Reflectivity measurements on ulminites quote a very low rank

for these samples.

Factor analysis on the values of element content such as Si, Al, Fe, Ca, Mg, S, Cr, Ti, Pb, Ni, Zn, Mn, and Cu states that Al, Si, Fe, Cr, Pb, and Ti are antagonistic to Ca while Cu and Ni are antagonistic to Mn. Also some samples appear with high positive

loading factors in S or Mg.

Using a microprobe, the distribution of elements such as Si, Ca, Al, Fe, Cl, K, Mg, P, and S was X-ray mapped into huminites from two different lignite samples. It appears that, in these macerals, S and Ca are in affiliation with the organic matter since their distribution is uniform. Si and Fe are restricted in small areas indicating an inorganic affiliation. On the other hand, mineral matter is dominated by Si, Al and K revealing a possible occurence of feldspars.

The study of two more deposits in the same region is now in progress.



### FURTHER RESULTS ON THE INFLUENCE OF MOISTURE IN COAL ADSORPTION ISOTHERMS

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The influence of moisture in coal adsorption isotherms is an important issue to study the coal ability to retain gas.

Experimental data was obtained in one sample (Moisture-Holding Capacity = 4.3%) under the following conditions:

- a) Sample particle size  $\leq$  212  $\mu$ m; temperature of the bath 35 $^{\circ}$ C; pressure up to 5.5 MPa;
- b) Total moisture between 3% and 11.5%; sample mass between 88.30 g and 93.44 g.

The general conclusions reached confirm the overall previous conclusions published by Joubert (1973) concerning the influence of moisture in coal adsorption isotherms i.e. the Moisture-Holding Capacity (MHC) is a critical value that influences the adsorption of gases by coal: at total moisture contents equal to or greater than the MHC value we always obtain the same isotherm; with total moisture contents below the MHC value the isotherms obtained denote that they are dependent of the total moisture value.

Finally, the authors emphasise the importance of "volume calibration" measurements (on the basis of pressure and temperature) in the experiments, especially the so-called "void volume" measurement, which also dramatically depends on the relation between the mass of the sample and its moisture content.



# THE EFFECT OF NONMACERAL MICROSTRUCTURES ON COAL PYROLYSIS IN A FLUIDISED BED LAB SCALE REACTOR

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Work in coal petrography at U.S. Steel, Bethlehem Steel, W.F. Berry Associates, and elsewhere has shown that coals may contain numerous nonmaceral microstructures that are not necessarily comprehended by maceral analysis but may significantly affect the coal's performance in a variety of processes.

A system for the classification of the nonmaceral microstructures has been developed and is employed at U.S. Steel, in which the individual categories include: normal coal, fine coal, pseudovitrinoids, microbrecciated coal, oxidised coal (weathered and thermal), coarse mineral matter, cenospheres, and miscellaneous materials such as contamination.

In the present poster we show examples of effects of nonmaceralic microstructures on coal pyrolysis performed in a fluidised bed lab scale reactor. The examples presented follow the U.S. Steel classification: unburned after pyrolysis trials, confirming some failure during the trials; fine coal surrounding coal particles and their implications on char development and shape; oxidised and thermal affected particles before and after the trials; the way coarse mineral matter affects char development; and finally anthracite contamination.

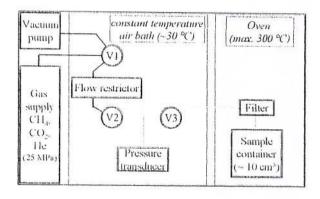




## ADSORPTIVE GAS STORAGE CAPACITY OF CARBONIFEROUS COALS

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An automatised experimental set-up has been constructed for gas adsorption measurements on coals at temperatures of up to >200 °C and pressures of up to 25 MPa (250 bar). This equipment has been used extensively in several studies to assess the methane sorption capacity of coals of different rank and maceral composition. Experiments have been performed mainly on dry samples but individual measurements were also carried out on samples with a defined moisture content. For a high-volatile A (0.82% VR<sub>r</sub>) coal with 4.4 wt% water content the methane sorption capacity decreased by 25-30 % as compared to the dry sample



<u>Figure 1:</u> Flow scheme of experimental set-up for gas adsorption measurements. V1, V2 and V3 are valves operated by a PC-based control system.

Adsorption measurements have recently been extended to carbon dioxide (at 55°C and pressures up to 4.8 MPa). First results from this ongoing study support earlier findings that sorption capacity (expressed in molar units) for CO<sub>2</sub> is approximately twice as high as the sorption capacity for methane under the same conditions.

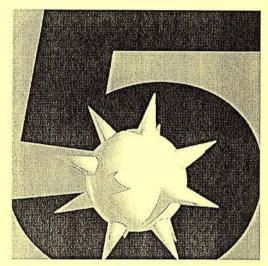
Measurements on selected coals using pure gases and methane/CO<sub>2</sub> mixtures are under way to assess the sorption behaviour under geologically relevant temperature, pressure and moisture conditions.

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### CYMRITE, BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>H<sub>2</sub>O, AN UNUSUAL SILICATE MINERAL: RENEWED IDEA OF SCHWANTKE MOLECULE?

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Cymrite is a quite rare mineral. However, it was found in the last years in a wide variety of occurrences such as Mn ores, Pb-Zn and Au ores, bedded barite sequences, metasedimentary rocks, as well as the Franciscan formation. In spite of its simple composition, cymrite shows still many problems, i.e. of crystallography (hexagonal or monoclinic), of chemistry (water amount, related to the so-called intermediate cymrites, Viswanathan et al., 1992), of genesis and/or mode of formation etc.

In some occurrences cymrite was found to contain ultrafine exsolution lamellae of quartz, sanbornite and barite, e.g. at Nezilovo in Macedonia and Blazna Valley, Rodna, Romania (Bermanec et al., 1996).

Optically homogeneous grains of natural cymrite from both Macedonia and Romania show hexagonal symmetry. Cymrite samples have quite a constant unit cells: a=5.340(1), c=7.695(1) Å Nezilovo samples and a=5.338(1), c=7.688(1)Å, for Rodna samples. After heating up to 600 °C cymrite looses the water and become hexacelsian with a=5.260(5), c=7.740(8) Å (for samples from Nezilovo). This proces is followed by decreasing the unit cell volume (190.02 for cymrite and 185.46 ų for hexacelsian).

But single crystal photographs of cymrite show many satellite reflections all around the hexagonal pattern. These satellites have been always interpreted in terms of possible lowering of symmetry due to order-disorder. The sanbornite exclution webs together with quartz found in the cymrite host gives a new possible interpretation. It is easy to imagine a hypothetical reaction of decomposition of a high pressure (or high temperature?) phase during an overall decrease in pressure and temperature. If sanbornite and quartz lamellae are assumed to be a product of the proposed reaction, than this reaction could be described by the next equation:

Ba[AlSi<sub>3</sub>O<sub>8</sub>]2+H<sub>2</sub>O \_ BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>.H<sub>2</sub>O + BaSi<sub>2</sub>O<sub>5</sub> + 2SiO<sub>2</sub> Ba-equivalent cymrite sanbornite quartz of Schwantke molecule

#### Literature:

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Viswanathan, K., Harneit, O., Epple, M. (1992) Hydrated barium aluminosilicates, Ba Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>. nH<sub>2</sub>O, and their relations to cymrite and hexacelsian. Eur. J. Mineralogy, 4, 271-278.



# DECONVOLUTION, AN USEFUL MEANS FOR THE DETERMINATION OF THE ILLITE 'CRYSTALLINITY' IN SCHELA FORMATION (ROMANIA)

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The illite "crystallinity" (IC) method has been used successfully worldwide in the last decades in order to quantify the low-grade metamorphism. IC is influenced by several factors, the most important ones being temperature, time, lithology and the diffractometer settings. The presence of other phases than illite that give peak in 10Å region (paragonite, pyrophyllite, biotite, etc) can be an impediment in IC determination. In such cases, deconvolution is applied in order to determine the contribution of each phase to the diffraction maximum in the 10Å region.

The problem of overlapping peaks in the 10Å region had to be solved in the great

majority of the samples from Schela Formation (Lower Jurassic, Gresten facies).

Schela Formation has a complex mineralogy of the clay fraction: illite, paragonite, pyrophyllite, chloritoid, mica/paragonite interstratification and quartz. Chlorite is present only in 40% of the samples; taking into consideration the reaction pyrophyllite + chlorite  $\rightarrow$  chloritoide + quartz + H<sub>2</sub>O it means that the chlorite has been entirely consumed by this reaction. Kaolinite is also present in some of the samples analyzed. The microprobe investigations show that kaolinite is a secondary mineral, formed by the alteration of pyrophyllite, chlorite and chloritoid; consequently, its presence is not related to the reaction kaolinite + quartz  $\rightarrow$  pyrophyllite + H<sub>2</sub>O as has been stated in previous papers. The mineral association identified in Schela Formation points to upper anchizone - lower epizone.

From chemical analyses of chlorite and mica/phengite, temperatures of 340-400 degree C and minimum pressure of about 3kbar have been deduced. Higher minimum

pressure conditions (~5kbar) are inferred for an early mica/phengite generation.

Due to the presence of paragonite and pyrophyllite the first peak of illite is frequently broadened; therefore, the deconvolution programs have been applied to calculate IC. In order to verify the reliability of the results obtained by deconvolution, IC was also calculated using the 2Å peak, which is not influenced by the presence of paragonite and pyrophyllite. The equation of the regression line describing the 10Å-2Å peaks correlation was calculated from samples with only illite peaks in the 10 and 2Å regions. The obtained equation has been applied to convert IC2Å into IC10Å for samples with two or three phases in the 10Å region and compared the results with those obtained by deconvolution method (see table below).

sample	207	212	218	210b	206	210a	201	203	210	202	208a	216	217
IC calc	0.19	0.20	0.21	0.19	0.18	0.20	0.20	0.21	0.23	0.24	0.20	0.24	0.20
IC dec	0.16	0.17	0.18	0.18	0.19	0.20	0.20	0.20	0.20	0.21	0.21	0.21	0.22
difference	0.03	0.03	0.03	0.01	-0.01	0.00	0.00	0.01	0.03	0.03	-0.01	0.03	-0.02

Table. IC values obtained by deconvolution method and calculated from IC2Å

As can be seen, the values obtained with both methods are similar, but usually the deconvolution method gives lower values than the calculated ones.

The IC values obtained both ways indicate upper anchizone-epizone. These results are in good agreement with the indications given by the mineral association and microprobe chemical analyses.



### STRUCTURAL CONTROL OF THE ORE DEPOSITS FROM MARAMURES AREA. ROMANIA

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Base-metal deposits are known in the Maramures area since the Roman Empire time. The mineralogy and petrography of these deposits have been intensively studied in the last decades and are quite well known.

Unfortunately, only a few studies concerning structural control of the gold-bearing and base-metal deposits have been undertaken.

To highlite the structural features of the Maramures area, we use in this paper (1) seismic lines, (2) remote sensing data, (3) aerial photographs, and (4) surface and subsurface structural data. These data are integrated in the already known geological structure. A structural map where kinematic data are drawn is also presented. All data indicate a late Miocene to Pliocene strike-slip tectonic regime, which controlled the development of mineralized veins. The mineralized veins are either related to the west-striking, sinistral strike-slip faults or to the secondary structures related to the movement along the previously mentioned faults.



### INVESTIGATION OF MANGANOAN FAYALITE BY MÖSSBAUER EFFECT

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The Mössbauer spectroscopy is a very sensitive experimental method to investigate the surrounding of the probe sites by the occupancies, the intracrystalline exchange ordering, the co-ordination symmetry, the oxidation states, the local electric and magnetic fields.

The five samples of manganoan-fayalite  $\{\text{Fe, Mn, Mg, Ca}\}_2[\text{SiO}_4]$  have been obtained from two olivine assemblages corresponding to rhodocrosite (208, 138, 155) and mangangrunerite (088, 101) matrices of the regionally metamorphosed Fe-Mn deposit at Răzoare.

The spectra have been carried out at room temperature (RT) and liquid helium temperatures (HeLT), in a transission geometry, with  $^{57}$ Co in Rd sources and Cu matrices, in the velocity range of  $-10\div$ mm/s. The spectral parameters have been extracted with a  $\div$  <sup>2</sup> - procedure using the fitting program MOS-90 [1]. The RT spectra show broad line-resonances corresponding to large quadruple doublets of high spin ferrous ions in M1 and M2 sites and also to small magnetic phases' contributions. The HeLT spectra showed the existence of sublattices corresponding to both the important contribution of iron in the magnetic phases and the main one of ferrous ions in coupled magnetic and electric gradient fields.

The following items were discussed and correlated with the PT conditions of the Răzoare deposit:

- the presence of superparamagentic relaxation particle of magnetic and Mn-related phases,
- the possibility of the coexistence of the orthorhombic and cubic crystal structures,
- the preferred Fe2+ and Mn2+ occupancy of the M1, M2 sites,
- the effect of the Mn increasing amount on the spectral parameters of the investigated samples, taking into account the experimental [2] and computing results obtained by using specialised program QSCOMP [3] for synthetic samples.

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## BI-SULPHOSALTS FROM THE CUPRIFEROUS MINERALISATIONS FROM NISTRU, BAIA MARE AREA

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Bi-sulphosalts have been identified in the hydrothermal vein mineralisation associated with the intrusion of quartz-monzodioritic character in the Nistru zone. This is the first occurrence chemically documented for the Bi-minerals in the NW Baia Mare area.

The Bi sulphosalts contain most often members of the lillianite homologous series that correspond to phases of the lillianite-gustavite solid solution series. N values have been calculated after Makovicky and Karup-Møller (1977). N is ideally 4 for phases along the lillianite-gustavite join. The members of the lillianite-gustavite series show a deviation from the ideal N value. This could be explained by phenomena of disorder caused by rapid crystallisation The homogeneity in composition is remarked in the chemical formula that has been calculated based on the microprobe analyses:

 $(\mathsf{Pb}_{1,65\text{-}1,97}\mathsf{Ag}_{0,46\text{-}0,62}\mathsf{Fe}_{0,03\text{-}0,20}\mathsf{Cu}_{0,07\text{-}0,32}\mathsf{Bi}_{2,40\text{-}2,53}\mathsf{Se}_{0,01\text{-}0,02}\mathsf{Te}_{0,01}\mathsf{S}_{5,48\text{-}6,05}).$ 

The elongate grain with fibrous aspect are included in anhedral pyrite crystals or they are situated in the marginal zones of the massive chalcopyrite. They also frequently appear in quartz associated with native gold grains in the central part of the vein.

The members of the bismuthinite-aikinite group whose composition varies between pekoite and krupkaite with the very subordinated participation of the gladite have also been emphasised:

 $- Pekoite- Cu_{0,55\text{-}0,70} Fe_{0,06\text{-}0,33} Pb_{0,28\text{-}0,90} Bi_{7,14\text{-}7,48} Se_{0,04\text{-}0,35} S_{11,50\text{-}12,2;} \\$ 

-Gladite-Cu<sub>1,30</sub>Fe<sub>0,13</sub>Pb<sub>1,21</sub>Bi<sub>6,66</sub>S<sub>11,58</sub>

-Krupkaite -  $Cu_{1,88-2,17}$  $Fe_{0,08-0,27}$  $Pb_{1,85-2,07}$  $Bi_{5,78-6,04}$  $S_{11,98-12,19}$ 

They appear as inclusions in chalcopyrite. The matildite has been encountered with a subordinated participation ( $Ag_{0,87-0,94}Cu_{0,08}Bi_{0,94-1}S_{1,87}$ ) being associated with the minerals of the aikinite-bismuthinite series. A small number of analysed grains gave the composition of the cosalite:

 $(Pb_{1,53-1,57}Ag_{0,013-0,014}Fe_{0,07-0,1}Cu_{0,26-0,33}Bi_{1,85-1,93}S_{4,58-4,76})$ , which appears as anhedral grains within quartz, among the pyrite crystals.

The association of the bismuth minerals with gold suggests their simultaneous precipitation; their relation with pyrite and chalcopyrite suggests their crystallisation after the sulphides.

The temperature of homogenisation of the fluid inclusions in quartz ranges between 240-280TC. It can thus be considered that the Bi-minerals were deposited at about 300TC. This interpretation is confirmed by the relation of the cupriferous sequence with the monzodioritic intrusion.

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## NEW DATA ABOUT THE BISMUTH SUPHOSALTS FROM THE HIDROTHERMAL MINERALISATIONS FROM VĂRATEC-BĂIUŢ, BAIA MARE DISTRICT

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The hydrothermal ore deposits in the Baia Mare metallogenetical district are very well known due to the presence of a great number of sulphosalts having the type localities here the fülöppite (Dealul Crucii), fizelyite (Herja), semseyite (Baia Sprie), andorite (Baia Sprie). The presence of the bismuth sulphosalts in the Baia Mare area is of recent date (Cook 1997, Cook, Damian 1997). The Vãratec Băiuţ mineralisations are of vein type, being located in a volcanic stratotype, pierced from place to place by intrusive bodies of porphyry microdiorites of Pannonian age. The mineralisations are predominant copper dominated with base-metal and considerable contents of gold.

The bismuth sulphosalts have been identified in the copper mineralisations from the NW part of the ore deposit, within a mineralogical association somewhat uncommon for the Baia Mare area; quartz + chalcopyrite + hematite + native gold + bismuth sulphosalts ± wolframite. The bismuth sulphosalts are represented by members of the lillianite-gustavite series and partially by vikingite and heyrovskyite, and are associated only with chalcopyrite and native gold. They appear as needles and anhedral grains included in chalcopyrite or in quartz associated with iron oxides. The native gold appears as rounded grains included in chalcopyrite and especially in lillianite-gustavite. The fineness of the gold is quite high; i.e. of 820 to 830. The investigations by an electron microprobe (BRGM, CAMECA SX 50) made on the grains from this association allowed to obtain a number of 8 analyses. The empirical formula calculated on the base N=5, is between the following limits:

 $\mathsf{Pb}_{1,29\text{-}1,56} \mathsf{Ag}_{0,67\text{-}0,94} \mathsf{Bi}_{2,32\text{-}2,61} \mathsf{Cu}_{0\text{-}0,06} \mathsf{Fe}_{0\text{-}0,42} \mathsf{Sb}_{0\text{-}0,01} \mathsf{Se}_{0,23\text{-}0,31} \mathsf{Te}_{0\text{-}0,01} \mathsf{S}_{5,08\text{-}5,82}$ 

The number of octahedra in the elementary cell is N=4.20-5.08. They are similar with those described by Cook and Damian (1997) for the mineralisations from the central area of Văratec. The selenium is also present in considerable quantities. In the diagram  $Ag_2S-Bi_2S_3-Pb_2S_2$  most of the analyses are distributed along the line lillianite-gustavite at approximately  $Gu_{35-50\%}$ , i.e. in the field of miscibility of the series lillianite-gustavite except one sample which is getting close to the composition of the vikingite, which has N=5.08. Another analysis  $(Pb_{1.9}Ag_{0.84}Bi_{2.1}Cu_{0.04}Fe_{0.02}S_{5.06}Se_{0.28})$  has and would correspond to the heyrovskyite for which the value close to the ideal value is N=7. The deviation from the theoretical line of N=4 of the members from the lillianite-gustavite series could be due for the rapid cooling of the solutions and which would unbalance the structure in the moment of rapid crystallisation. The vikingite and heyrovskyite appear as micronic grains intimately intergrown with lillianite-gustavite and which can not be microscopically recorded.

The homogenisation temperature of the biphasic inclusions in quartz grains associated with chalcopyrite, bismuth minerals and native gold is between 279°-320°C, and the temperature of homogenisation for the biphasic inclusions from the centre of the vein is 235°C. The high temperature is also correlated with the high fineness of the native gold (820-830), which correspond to a mesothermal mineralisation. The bismuth sulphosalts have formed by instant cooling of some residual solutions rich in silver after the crystallisation of the principal quantity of pyrite and chalcopyrite at relatively high temperatures, >300°C.

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### THE GARNETS FROM ȚICĂU CRYSTALLINE MASSIF (NW TRANSYLVANIA BASIN, ROMANIA)

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*Țicău Massif* appears like a crystaline island, in the north-west of Transylvania Basin, surrounded by Terttiary sedimentary formations. From the petrographical point of view it is formed of metamorphic rocks belonging to the amphibolite facies (plagioclase-bearing gneisses, micaschists, K-feldspar-bearing gneisses, quartzites, amphibolites).

The presence of the garnet in the constituient rocks of Ţicău has been notified even in the first papers which deal with the geology of this massive (Szadeckzy, 1930, Szadeckzy-Kardoss, 1930, Kräutner, 1938). Dimitrescu (1963) notices their abundance in some zones, especially in micaschists, where the garnets may reach dimensions up to 3 cm. According to the refraction index, the density and the elementary cell parameter, Kalmar (1972) considers the garnet as being of almandine type and an isomorphic mixture between almandin (80%) and spessartin (20%).

As a result of the microscopical study, Denuţ (1998) describes four mineral associations in Ţicău Massif: (1) qtz + pl + ms + bt  $\pm$  grt, chl, kfs, ep; (2) qtz + ms + bt  $\pm$  grt  $\pm$  chl, cld, pl; (3) qtz + pl + kfs + ms + bt  $\pm$  chl, grt; (4) qtz + pl + amph + bt  $\pm$  chl, grt.

The garnet is present in all the mineral associations indetified - in subordinate quantities, except for the association corresponding to the micaschists - under the following aspects:

- belts, more or less homogeneous and generally irregular, parallel to the foliation; the garnet presents inclusions and fissures;
- porphyroblasts, with xeno- or hypidioblastic contours; it is sometimes presents inclusions, fissures, zonings and can be associated with shades of pressure;
- small crystals, practically not constrasting dimensionally with the rest of the associations, with hypidio- or idioblastic contours.

The chloritization and the deferization are aspects observed, with different intenssites, in all there presentation forms.

The following analyses were made on the porphyroblastic granules:

- 1. Spectroscopic IR absorbtion the spectrum obtained has been compared to the standards for almandin and pyrop and it has been found the resemblance with that of the almandin.
- **2.** X-ray diffraction the value calculated for the elementary cell parameter is closer to that of the almandin.
- 3. Microprobe analyses confirms the assigning of the garnet to the almandin species, with the following composition: almandin 63-82%, pyrop 6-18%, spessartin 0-4%, grossular 4-21% and andradit 2-5%. The optic zonality is emphasized by the profiles executed through two crystals and consists of: (a) the reduction of the spessartin and grossular components (so a reduction of the Mn and the Ca) from cores to rims; (b) the increase, in the same direction, of the almandin and pyrop (so an increase of the Fe and the Mg); (c) one of the samples shows, in the extreme marginal rim, a sudden increase of the grossular and the spessartin and the reduction of the almandin and the pyrop.

These modifications of the chemical composition, from core to rim, reflect different physical conditions manifested during the growth of garnet and they have been correlated to different metamorphic events.



# THE SIGNIFICANCE OF THE IGNEOUS MINERALS FOR THE GENESIS OF THE GRANITOIDIC DIKES AND SILLS FROM NORTH SEBEŞ-CIBIN MTS - SOUTH CARPATHIANS

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Phenocrysts assemblage of the granitoidic sills and dikes from north Sebeş-Cibin Mts. consists of plagioclase ( $An_{29}$ -  $An_{9.5}$ ), biotite [Fe<sup>3+</sup>/Fe<sup>tot</sup>= 0.52 – 0.62; Mg/(Mg+Fe<sup>2+</sup>) = 0.67 – 0.68], quartz, rare amphibole (tschermakite), scarce epidote, and other accessory minerals like magnetite, ilmenite, zircon, apatite, sphene. Fine-grained crystalline groundmass of quartz, plagioclase, alkali-feldspars, comprises 60-70% of the sills and dikes rock. Petrographic and microprobe data on the typical metaluminous assemblage are used to distinguish genetic significance for the hypabyssal bodies.

Two geobarometers and a geothermometer have been applied to estimate the PT conditions of crystallization. Using the average Al content of hornblende as an empirical geobarometer, it shows pressures ranging between (6.22 - 8.10 kb)± 1 kbar (Hollister et al., 1987; Schmidt, 1992). The empirical hornblende-plagioclase geothermometer of Blundy and Holland (1990) yields temperature of 740°-810°C.

Magmatic epidote exhibiting two kinds of textural characteristics (euhedral homogenous and zoned inclusions) can be found in the hypabyssal granitoids from Sebeş-Cibin Mts. Low  $TiO_2$  (0.8 – 0.11wt%) and pistacite contents ( $Ps=[Fe^{3+}/(Fe^{3+}+Al)]$ ) of  $Ps_{21.8}$  –  $Ps_{26.4}$  are chemical diagnostics for magmatic epidote (Dawes & Evans, 1991). It seems not to be associated with hornblende in the same bodies. Magmatic epidote formed at more than 6 kbar (maybe at ¬8 kbar, as it is usually stable in granitoidic magmas), the bodies seeming to have been emplaced at 4-5 kbar. The occurrence of magmatic epidote phenocrysts in these relative shallow-level bodies suggests that they were preserved by rapid magma transport from the source region, along approximately 7-11 km of ascend. A combined compositional and optical study on biotite crystals reveals good correlation between the Mg-rich, high  $Fe^{3+}/(Fe^{2+}+Fe^{3+})$  and the green – brown colour of biotites from the granitoidic bodies of north Sebes-Cibin Mts, typical for arc-related graitoidic magmas. This assumption is confirmed by the distinct composition plotting of the analysed biotites in the calk-alkaline field of orogenic suites (Abdel-Rahman, 1994).

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### ECLOGITIC RESIDUAL ASSEMBLAGES BENEATH CORDILLERAN BATHOLITHS; CORROBORATION OF EXPERIMENTAL DATA AND OBSERVATIONS

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The depth and bulk compositions of source zones of continental margin batholiths, as well as the processes that trigger large-scale granitic magmatism in arc environments are unresolved. Experimental results suggest that dehydration melting of non-peridotitic assemblages is the only mechanism capable of producing liquids similar to the ones found in batholiths. Dehydration melting experiments have been carried out in the past two decades using a variety of starting compositions from basaltic, to andesitic, and higher silica metamorphic rocks at pressures ranging from 3 to 32 kbar. All experiments that produced calc-alkaline, batholith-like major element compositional trends, are reviewed in this study to investigate relationships between physical parameters (e.g. T, P, water content) and the compositions of the residues. Important results: (1) the main liquidus minerals are: garnet, clinopyroxene, amphibole, plagioclase, and orthopyroxene, (2) garnet and clinopyroxene are the main melting reaction products at pressures higher than ~15 kbar regardless of the bulk starting composition, (3) more than 15-25% partial melting and generation of calc-alkaline granitoids at >15 kbar should always result in an "eclogitic" (garnet pyroxenite) residue, even if garnet and clinopyroxene were not present in the starting assemblages, (4) the ratio of garnet/clinopyroxene is a sensitive indicator of the percentage of partial melt in experiments, the higher the degree of melting, the more clinopyroxene in the residue, and (5) the modal proportions of garnet in high pressure residues reflect the bulk starting compositions, the more silicic the source, the less garnet in the residue.

Large Cordilleran batholiths (>1 x10<sup>6</sup> km<sup>3</sup>) have trace element concentrations signaling garnet-rich, plagioclase-poor residues, which together with the great thickness of their "melt" column indicate depths of magma generation exceeding 35-40 km. Unless these batholiths can be proven to have been derived entirely from high-silica, evolved continental crustal assemblages, they must represent partial melts complemented at depth primarily by garnet pyroxenites, i.e. an eclogite facies assemblage. Such residual assemblages, unambiguously related to continental arcs have so far only been documented as xenoliths from beneath the Sierra Nevada batholith (e.g., Ducea and Saleeby, 1998), and as an exposed deep lithospheric terrane in the Kohistan arc of Pakistan (Ringuette et al., 1999). The bulk compositions of these arcs can be constrained to be basaltic or basaltic andesite from the chemistry of the batholith and residual assemblages, and from the relative proportions of residue/granitoids. The Sierra Nevada xenoliths have mineral proportions and chemistries similar to those of solid residues determined experimentally during highpressure partial melting of wet basaltic materials. Eclogitic keels complementing at depth large Cordilleran batholiths are significantly denser than typical mantle peridotites (0.2 g/cm³ or more), hence making them prone to recycling in the mantle by foundering. Refs: Ducea, M. and Saleeby, J., 1998, Contrib. Mineral. Petrol., 133, 169-185; Ringuette L, Martignole J, Windley BF, 1999, Geology, 27: (2) 139-142.

## GENETIC CONSIDERATIONS ON JASPER IN THE BRAD AREA (APUSENI MTS., ROMANIA)

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Polycolored jaspers occur in the Neogene andesitic pyroclastites near Brad, Apuseni Mountains. The mineralogy of the jasper reveals (acc. the nomenclature of Flörke *et al.*, 1991 and Graetsch, 1994) the presence of cristobalite/tridymitic, quartz-cristobalite/tridymitic, and quartzitic jasper varieties (table 1).

Table 1. The mineralogy of the jasper varieties

Jasper color- varieties	Jasper mineralogy						
Black	Fibrous and granular microquartz + cristobalite/tridymite opal						
Brown	Cristobalite/tridymite opal + quartz						
Red and red-brownish	Cristobalite/tridymite opal ± quartz						
Orange	Cristobalite/tridymite opal + fibrous disordered quartz (chalcedony)						
Yellow and white- yellowish	Cristobalite/tridymite opal ± quartz						
Grey	Cristobalite/tridymite opal + granular microquartz						
Ochre	Granular microquartz + fibrous disordered quartz (chalcedony) + cristobalite/tridymite opal						
White-cream	Granular microquartz + fibrous disordered quartz (chalcedony)						
White	Granular microquartz						

A fossil flora (algae, diatoms, leaves, silicifiated woods) and fauna (gasteropods, lamellibranchiats) are present in the geyseritic mass, as well as silicifiated fungi hiphae, bacteria and nannoplancton (*Pontosphaera multipora* / Badenian).

The genesis of the jasper deposits begins with the accumulation of various detrital fragments in sea-side basins formed nearby a Neogene volcano. The volcanic-related subaquatic hot springs supplied silica gels which precipitated as cristobalite/tridymite. The fragments (biomicritic limestones, andesites, andesitic and rhyolitic volcanic tuffs) deposited inside the basins were included in the precipitated silica, then got cemented and substituted for cristobalite/tridimite. Afterwards, the microcrystalline quartz and fibrous disordered quartz (chalcedony) partly replaced the cristobalite. The variable  $SiO_2$ ,  $Fe_2O_3$  and MnO contents accounted for the various colors of the jaspers.

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# THE SUBSTITUTION RELATIONS - REAL OR FALSE - IN THE CALC SILICATE ROCKS FROM THE WESTERN PART OF THE SOUTHERN CARPATHIANS (SEBESLOTRU GROUP)

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In the calc silicate rocks belonging to the metamorphics of Semenic, Godeanu and Mehedinti Mts. From western part of South Carpathians, intermineral relations can frequently be observed. They can suggest the substitutions which are involved in the crystalisation order, the blastesis stages, different genetical types inclusions, a.s.o.

If these relations express a certain succession of formation, for example the pyroxen systematically substitutes the amphibole which preserves itself as a relict, the rock develops in a determinated manner, in this case, to its "pyroxenisation".

When the formely-invoked relations are equivocal (a large granulated pyroxen is presented, which includes the seeming relict of amphibole and is bordered by the same amphibole, both having an relationship, between the two minerals. Contrary to expectation, the amphibole is late by comparison with the pyroxene; it is in constant crystalographic and optic relations compared with the last one.

The amphibole's indicatrix is turned by compare with that of the pyroxene by 41° around an axis oriented with azimuth inclination 130/45 in relation with reference system (the pyroxene's indicatrix-the pole of the (111) face in the crystal, respectively).

The substitution textures-false or real can indicate the physical factors, which cause the formation conditions of a sequence of the calc silicate rocks. Returning to the question of the succession of formation, these can supply indications of the nature of a possible unconventional protholite, which the calc silicate mineral bearing rock generated.



# THE NAMBULITE AND NATRONAMBULITE IN Mn-ORE FROM BISTRITA MOUNTAINS, FIRST OCCURRENCE IN ROMANIA AND THE FOURTH OCCURRENCE IN THE WORLD

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Nambulite and natronambulite have been found in the metamorphosed carbonate-silicate Mn ore from Tolovanu, Dadu, Caprarie, Sarisor, Mandrileni, Todireni deposits, Bistrita Mountains.

The metamorphic manganese ore belongs to upper Proterozoic-lower Cambrian Tulghes Series, mainly made up of quartz-sericite-graphite-albite-chlorite-calcite schists with some relics of biotite, almandine, hornblende, ilmenite, etc. It is a polymetamorphic retrograde series. The primary ore consists of a silicate-carbonate type with few oxides and sulphides: 70% carbonates (mainly rhodochrosite and less kutnohorite, siderite, dolomite), 25% silicates (tephroite, spessartine, pyroxmangite, rhodonite etc.) and 5% oxides (hausmannite, jacobsite, magnetite, braunite, bixbyite, hematite, galaxite) and sulphides (alabandine, Ni-Co-As sulphides). The ore is bedded. The nambulite and natronambulite occurr both in veins and beds up to 20-30 cm thick, which run approximately parallel with the rhodonite and the braunite-bixbyite-hausmannite beds. The veins of natronambulite and nambulite are cca. 20 cm thick and cross the old metamorphic ore. The nambulite and natronambulite grains are up to 10x10x5 mm in size and have an orange-red color. Under the microscope they are biaxial positive, with 2V=30° for nambulite and 2V=45° for natronambulite. Chemical analyses give: SiO<sub>2</sub>=49.23, TiO<sub>2</sub>=0.11, Al<sub>2</sub>O<sub>3</sub>=0.40, Fe<sub>2</sub>O<sub>3</sub>=0.63, FeO=0.00, MnO=40.90, MgO=2.18, CaO=1.36, Na<sub>2</sub>O=0.83, K<sub>2</sub>O=0.27, Li<sub>2</sub>O=1.34,  $P_2O_5=0.10$ ,  $H_2O(+)=1.23$ ,  $H_2O(-)=0.30$  for nambulite and  $SiO_2=49.69$ ,  $TiO_2=0.20$ , (Al<sub>2</sub>O<sub>3</sub>=0.52, FeO=0.00, MnO=38.84, MgO=3.21, CaO=2.95, K<sub>2</sub>O=0.07, Na<sub>2</sub>O=3.11,  $P_2O_5=0.20$ ,  $H_2O(+)=0.91$ ,  $H_2O(-)=0.30$ ,  $Li_2O=1.10$  for natronambulite. Natronambulite has Na>Li and it is rich in Ca, but Ca is less than Mn. The main powder lines (in A) with relative intensities are for nambulite: 7.09(33), 6.70(25), 3.33(33), 3.17(69), 2.954(100), 2.92(30), 2.6006(35), 2.19(25) and 7.09(45), 6.66(44), 3.55(100), 3.34(40), 3.17(20), 2.96(70), 2.50(40), 2.18(30) for natronambulite, respectively.

The results of IR analyses on nambulite and natronambulite are very similar.

Nambulite and natronambulite represent a type of ore very important in its evolution.

The parageneses with nambulite are:

- Nambulite-rhodonite-quartz-rhodochrosite-microcline;
- Nambulite-braunite-bixbyite-kutnahorite-albite-aegirine-quartz;
- Nambulite-winchite-spessartine-aegirine-quartz;
- Nambulite-kozulite-braunite-bixbyite-hausmanite;

And the parageneses with natronambulite are:

- Natronambulite-rhodonite-hematite-quartz;
- Natronambulite-aegirine-rhodonite-spessartine-quartz;
- Natronambulite-kutnahorite-kozulite-braunite-hausmannite;
- Natronambulite-eckermanite-rhodonite-albite-quartz-microcline.

All the parageneses of nambulite and natronambulite are oxidized parageneses enclosing many minerals with Fe<sup>3+</sup> and Mn<sup>3+</sup>, too, as it can be seen above. It is very interesting the presence of norrishite (a manganoan phlogopite with Mn<sup>3+</sup> and some nichel in its composition).

Nambulite and natronambulite seems to have appeared through a lithium metasomatosis, and a sodium metasomatosis on rhodonite, respectively.



## THE OPTICAL STUDY OF THE FLUID INCLUSIONS OF SOME PURE QUARTZ FROM ROMANIA

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The mineralogical study point out that quartz from metamorphic acumulations is ultra-pure quartz (commonly more than 99,9% quartz). The associated mineral phases in the quartz bodies are mainly related to the grain boundaries. Muscovite, phlogopite, lepidocrocite, beryl, pyrite and rutile are frequently found. We have investigated 17 quartz accumulations that correspond to three distinct genetic types: metamorphic, pegmatitic and sedimentary.

The quartz from pegmatites is less tectonized than the metamorphic one. Its mineralogical composition is characterized by the frequent association with feldspar – a mineral that in the metamorphic quartz is almost lacking. Graphic intergrowths of quartz with feldspar, visible only under a microscope with high magnitude, are observed in places: apparently quartz seems to be limpid, but under the microscope micron sized veinlets of feldspar can be noticed.

The microscopic study of metamorphic quartz revealed the existence of at least two quartz generations belonging to two different metamorphic moments. The first quartz generation occurs as irregular, large grains. Optically, it displays a slight biaxiality, having an optic angle (+2V) of 5-10° and an undulatory extinction. The surface of the grains shows inclusions more frequently than the quartz of the second generation. The second generation, that is the recrystallized quartz, is almost euhedrally developed and shows polygonal shapes resulting in mosaic-like structures. The grain surface is limpid, without inclusions. It is uniaxial positive. The undulatory extinction occurs in the quartz grains, which grew concomitantly with the deformation. The undulatory extinction of the quartz grain is generally subparallel to (0001) and it is the result of the heterogeneous shearing along this plane during the deformation. The increasing degree of deformation leads to the development of some discreet kink bands, more accurately defined than the undulatory extinction zones.

Under the microscope the inclusions in quartz as parallel trails and include very small quartz inclusions, with a parallel optical orientation. The abundance of fluid inclusions suggests a fluid-rich regime during crystal growth at the peak of the metamorphism. They are represented by the earliest unoriented inclusions. The secondary inclusions display an almost parallel arrangement, related to the post-crystallization process. These planes with inclusions occurr in the thin section as linear trails, intersecting each other at angles of 90°, 60° or 45°. The primary and secondary fluid inclusions can be used for the assessment of the metamorphic rock evolution.

The fluid inclusions from the pegmatitic and metamorphic quartz present similar features. Two major types of fluid inclusions, belonging to two different genetic types, can be identified: a) primary inclusions resulting from the initial solution from which the pegmatite quartz from crystallized; b) secondary inclusions formed after crystallization, oriented as parallel trails, which intersect at angles of 90° and 60°. The primary fluid inclusions usually have smaller sizes (5-10 $\mu$ m) and are generally hard to be studied under the microscope as compared to the secondary inclusions, with larger sizes (15-40 $\mu$ m).

The secondary fluid inclusions can be mono or bi phase with prevalence of the fluid and gaseous phase, easily removed by crushing and grinding. The solid phase from the primary fluid inclusions consists, besides quartz (negative crystals), of fine (sub-micron) inclusions of mica, feldspar, beryl etc., which can be regarded as captive minerals. They may influence the degree of purity of the quartz.



### NON-CUBIC SPESSARTINE GARNETS IN Mn METAMORPHOSED DEPOSITS FROM ROMANIA

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Optically anisotropic garnets have been known since the last century (Brewster, 1840). Although there are noumerous occurrences of optically non-cubic garnets, no ultimate explanation exists as to the origin of anisotropy. It was attributed either to residual strain in the structure or to Fe<sup>3+</sup> and Al ordering. Sectorial twinning was also involved in explaining the aenigma of optically anisotropic garnets but with cubic outlines and *Ia3d* space group.

Romanian anisotropic spessartine is described here for the first time. It was found in the regionally metamorphosed Mn deposits in the Bistrita and Sebes Mts., as a second generation, contrasting thus the first generation of isotropic spessartine of the gonditic ore type. It is also present in the Razoare Mn deposit. The associated minerals of non-cubic spessartine are: Mn-Mg-Fe amphibole alkali amphibole and Mn-carbonates. Sometimes it occurs together with pyroxmangite and magnetite-quartz. In Sebes Mts. the spessartine is associated with Mn tremolite. Some specimens of spessartine are optically biaxial (positive or negative) and may be triclinic, judging from the relations between optical and crystallographic orientations. Other may be monoclinic or orthohombic; the 2V values vary between 65-80° and birefringence is 0.003. In the Bistrita Mts. in the Mn deposits, some specimens of the spessartine are optically uniaxial positive or negative. It can be observed that the optical symmetry is lower than usually shown by X-ray analyses and morphology of crystals which always exhibit cubic outlines. The textures of the abnormal spessartine show complicated appearances under the microscope - (a) some spessartines present radial sectorial birefringence and (b) others show alternative isotropic and birefringent lamellae parallel to the (110) – which are probable, the growth planes. The hourglass texture is also very characteristic of such sperssartines. The twining is another special texture that can be seen. The sector twin components of these garnets are optically nonhomogeneous although the optical orientations of the sectors are roughly symmetrical with respect to the (001) axes. These sector twins are not twins in a strict crystallographic sense but denote a relation between two sectors whose growth directions and optical orientations are roughly symmetrical with each other (Akizuki, 1984). The trace of sector twin planes of the spessartine a from Bistrita Mts. is parallel of normal to (001) or the (110) faces. The sector twins plane may be parallel to (001) or normal to it. These differences are a result of differences in the crystal growth features. The spessartine shows also fine lamellae normal to the growth surface and which were produced during growth. The optical orientations of the fine lamellae are roughly symmetrical with respect to the sector twin boundaries. The non-cubic garnets are not homogeneous, like cubic garnets, showing a heterogeneous texture characteristic of metastable minerals. The symmetry of the metastable garnets is not merely the results of the chemical composition but result from Fe<sup>3</sup>/Al ordering in the octahedral sites (Akizuki, 1984). The crystal symmetry is not controlled by the macroscopic form of the crystal but by the microscopic form of growth hillocks, that is, the order-disorder structure determined by the directions of growth steps (Akizuki, 1984). The chemical compositions of the anisotropic spessartine from Romania shows higher contents of Fe<sub>2</sub>O<sub>3</sub> (cca. 3-5%) with respect to FeO (0.5-1.08%), the lack or very low content of MgO and relatively high content of CaO (cca. 2-4%). The birefringent spessartine-garnets are typically of oxidised paragenesses; they grow statically and unoriented. Sometimes they contain some Ti, which would suggest a low formation temperature. The crystal faces are clear, denoting a slow growth. They grew anizotropically from the beginning. The formation and growth of birefringent spessartine from Bistrita Mts. is linked to strong transformation minerals from Mn-deposits caused by Li-Na-K-F-Cl-B metasomatosis and it is a secondary result of this strong transformation of Mn minerals in the second stage (M<sub>2</sub>) of the Variscan retrograde metamorphism.



# ALABANDITE FROM METAMORPHOSED MN DEPOSITS FROM BISTRITA MOUNTAINS (ROMANIA)

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Alabandite occurs in the Argestru, Caprarie, Sarisor, Dealul Rusului, Oita, Tolovanu deposits from Bistrita Mts. The Mn-ore is enclosed in the Tulghes Series – a retrograde polymetamorphic one. Alabandite occurs macroscopically in tephroite type ore as grains (up to 1cm) in mosaic aggregates with rhodochrosite, tephroite, jacobsite. The primary metamorphic ore comprises seven main types, from old to new: tephroite, gondite, pyroxmangite, rhodonite, aegirine, nambulite and pyrosmalite type. All the parageneses shown above were cross cut by vein minerals of hydrotermal type. Alabandite belongs to the tephroite type ore; it is generally associated with tephroite, Mn-humite, jacobsite, pyrophanite, Co-Ni-Bi-As sulphides. Alabandite was found exclusively in the tephroite type ore and seems to be incompatible with pyroxmangite, mangangrunerite and hausmannite. It was found only in the silica undersaturated ore.

In the Argestru Mn-deposit the chemical composition of alabandite is: Mn=50,921% and S=49,079%. Here the pure alabandite is associated with pure tephroite (with very small content of MgO) without FeO. Jacobsite contains also some AI, probably representing a galaxite solid solution. Another paragenesis from Argestru Mn-deposits is the following: ribbeite-jacobsite-galaxite-alabandite-kellyite-rhodochrosite. In these two parageneses of alabandite there occur some accessory minerals like Co-Ni-Bi-As sulfides, pyrophanite, fluor-apatite.

In the Sarisor Mn-deposit, alabandite (with 4-5% Fe in its composition) is associated with Mn-humites which contain small amounts of Ti, Fe and Mg.

In the Caprarie Mn-deposit the pure alabandite is associated with jacobsite, galaxite, tephroite, rhodochrosite. In the same deposit, another paragenesis of alabandite is: pure alabandite-riebbite-jacobsite (with some Al), tephroite (some Mg). Finally the third parageneses of alabandite in Caprarie deposit is: ribbeite FeO-Fe) with Ti, tephroite (cca. 1-3% FeO and cca. 1% MgO), jacobsite (with some Ti), pyrophanite and of course, the alabandite that have in its composition little Fe (cca. 3-4% Fe). The sulfides are at least locally abundant and are represented by Co-Ni-Bi-As (cattierite, cobaltite, rammelsbergite, gerssdorfite, etc.).

The protolith of these parageneses with alabandite was a sulfide and carbonate rich body poor in Mn-oxides, particularly Mn³+ oxides. The jacobsite has the same wide oxidation and reduction stability as magnetite but shifted to some parageneses what more oxidizing conditions. The conditions to form the alabandite were probably buffered throughout metamorphism by reaction, within a sulfur rich, oxygen-poor protolith.

The  $fO_2$  and  $fS_2$  conditions of the Mn ore are quite different than those in adjacent rocks and must have been maintained as distinctly different throughout metamorphism. The  $fO_2$  and  $fS_2$  have been locally buffered at different levels within the manganese ore.

We can say that the alabandite parageneses have formed probable at (relatively) low oxygen fugacity (near QFM) and high sulfur fugacity (near pyrrhotite-pyrite).



### NORMAL VERSUS INVERTED TECTONO-METAMORPHIC ZONATION IN PRE-ALPINE METAMORPHIC TERRANES OF THE SOUTH CARPATHIANS.

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### Pre-Mesozoic basement of the South Carpathians includes:

- Upper Carboniferous-Permian sedimentary deposits, related to Variscan colaps;

- Pre-Upper Carboniferous, Variscan granitoids: 450-350 Ma (in Danubian) and 350-328 Ma to 310 Ma (in getic basement); small bodies of anatectic granitoids crop out in Getic.

- Pre-orogenic, Lower Paleozoic mafic-ultramafic magmatic rocks, cropping out in Upper Danubian, as Tisovita-Iuti ofiolitic type complex and marking a Paleozoic plate boundary, later involved in a magmatic arc environment;

- Sedimentary and volcano-sedimentary Paleozoic rock sequences; they are paleontologically dated as: Cambrian-Ordovician-Silurian and Devonian-Lower Carboniferous interval ages and

are affected by prograde (low grade) Variscan metamorphism;

- Medium-high grade metamorphic rock assemblages, of pre-Upper Carboniferous protolith age (Proterozoic and Paleozoic), with a complex and diversified polymetamorphic (poly-stage or poly-orogenic) history, resulted in Pan-African and/or Variscan orogenic events.

Two main types of protholiths can be distinguished: Proterozoic: Cadomian, represented by Lainici-Paius (older than 591-567 Ma) and Dragsan (817-777 Ma) of the Danubian basement, (involved in the pan-African orogeny, cf. Liegeois et al., 1996); Proterozoic and/or Paleozoic, represented by internal, "gneiss units", in the Getic-Supragetic basement (Sebes, Lotru, Cumpana, Fagaras, Ursu), strongly affected by Variscan events.

- Tectono-metamorphic zonation.

The apparent metamorphic zonation is, in most areas, an effect of tectonical relationships, as was demonstrated in the French Massif Central; a downgrade or an upgrade change in the physical conditions of the peak metamorphism of different litho-tectonic units, generally separated by mylonitic rocks (simple shear zones), gives a false metamorphic zonality. Some isolated areas in the gneiss units of the Getic basement preserve coeval, prograde metamorphic zonation (Hartopanu, 1986), especially at the level of late metamorphic history (M2).

"Tectono-metamorphic zonation" is a composite effect (result) of the contrasting metamorphic history of some prograde versus prograde-retrograde rock assemblages, whose tectonic relationships are responsible for an apparent "normal", downward increase in metamorphic degree or an "inverted" (upward) increase of the metamorphic degree. Metamorphic and structural discontinuities are sometimes connected with syn-metamorphic and post-metamorphic Paleozoic (Variscan) shear zone related metamorphism, the syn-tectonic neoblastic mineral

paragenesis marking significant breaks in the normal facies series zonation.

Some key areas are selected to demonstrate this, as: Almaj-Tarcu area (Upper Danubian basement), marking an important Paleozoic plate boundary (a part from an ofiolitic-type paleosuture); Sichevita-Bozovici-Poniasca zone (Getic), with a preserved Variscan nappe complex, responsible for a tectono-metamorphic inversion; Locva-Dognecea-Bocsa zone (Supragetic), in which a marker bimodal magmatic complex metamorphosed in epidote-amphibolite facies conditions overlay different pre-Alpine units; Leaota-Iezer mountains (Getic), where complex, polystage tectonic history is related to both types of relationships mentioned: apparent downward increase in the metamorphic degree (inclusions of exhumed HP rocks are embedded in a tectonic melange) and an apparent inverted metamorphic zonality, resulted in the tectonic superposition of the highest degree metamorphic units over lower-grade sequences.

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# THE MICROSTRUCTURE OF AGATES FROM TECHEREU AREA (APUSENI MOUNTAINS, ROMANIA)

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The agates from Techereu are found in cavities of strongly decomposed volcanic rocks (Mesozoic ophiolites or Neogene volcanics) as andesites, basalts, trachyandesites, vitrophiric rhyolitic spherulites (Băiţa rhyolites), rhyolitic lentils or in Neogene sedimentary rocks (Faţa Băii conglomerates) but they may be found loose as pebbles in some streams as Bodii Brook, Techereu Brook, Almaş Brook or Dumbrăvii Brook. The main types of agates in the area may be summarised as follows: wall-layered type agates, agates with collomorphic structure ("coral agates"), sagenitic agates, moss-agates and carnelian agates. Techereu agates are often large, up to 20-30 cm in diameter. They are characteristically coloured in startling shades of red, yellow-brown or bluish-grey as those of Cheviot Hills, Great Britain (Macpherson, 1989). Usually their associated minerals are represented by chalcedony, jasper, opal, quartz, amethyst, zeolites, celadonite, calcite, siderite, pyrite, marcasite, goethite and hematite.

The bulk chemical analyses of agates show high values of  $SiO_2$  (92.60 to 98.20%) and minor amounts of  $TiO_2$  (0.00-0.15%), Al2O3 (0.20-1.50%),  $Fe_2O_3$  (0.19-0.45%), CaO (0.25-0.59%), MgO (0.00-0.26%), Na<sub>2</sub>O (0.03-0.28), K<sub>2</sub>O (0.00-0.14%) and S (0.00-0.08%).

The typical structure of agates observed under the polarising microscope is the petrographic fibrosity, usually formed after crystallisation has started from a small spherulite. Based upon the spherulite, the main structural types observed in the Techereu agates are the *long fibres* from the textures based upon the long fibrous type, *rosette* from those based upon the spherulitic growth and *block system* from band textures (Moxon, 1996). In wall-layered bands, the length-fast chalcedony fibers radiate towards the center of the geode from many nucleation points on the wall surface, forming parabolic fiber bundles. Interference of neighboring bundles results in a parallel-texture of the fibers. Between crossed polars, wall-lining chalcedony exhibits a rhytmic extinction banding normal to the direction of fiber elongation (Graetsch, 1994).

The samples were also studied with a combined JEOL 6400 scanning electron microscope (SEM)-cathodoluminescence (CL) analytical system at the University of Manchester, England, which was operated at an accelerating voltage of 15 kV, a 5.5 nA probe current and 15 mm working distance. The phenomenon of cathodoluminescence (CL), whereby a mineral emits visible light in response to electron bombardment, is well known (Lloyd, 1994) and is due to molecular distortions in the crystal lattice (e.g. impurity atoms, lattice defects, non-stoichiometry etc.). Such distortions may act as CL activators or suppressors, leading to variations in luminescence characteristics between/within minerals which often reveal important detail invisible via other techniques (e.g. optical and/or SEI/BSEI electron microscopy). The CL images of agates from Techereu show concentric bands with different luminescence. The chemical analyses obtained by SEM with EDS reveal higher contents of Al<sub>2</sub>O<sub>3</sub> for the bands with higher luminescence.

Due to its compact microstructure, agate is exceptionally hard. The Brazilian test of an agate from Techereu done with a simple motor-driven press (supply voltage 12,302 V), revealed a high value of 23.85 MPa for the tensile strength at failure which was caused by a force of 16.79 kN.

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### CHEMICAL CHARACTERIZATION AND PARAGENESIS OF NUFFIELDITE FROM VALEA SEACĂ, BIHOR MTS., ROMANIA

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At Valea Seacă, nuffieldite was found in the mining adit "IV" which investigated a thin mineralized contact aureole located between Upper Cretaceous – Paleogene igneous rocks (quartz monzodiorites, diorites, syenites) and Lower Cretaceous sedimentary formations of mostly carbonate nature (limestones, marls), with subordinate shales, sandstones and bauxite.

Nuffieldite occurs in association with aikinite, wittichenite, two generations of galena, chalcopyrite and pyrite. Galena I is replaced by aikinite and wittichenite, forming a complex aggregate with micrographic aspect. Included in this aggregate are irregular grains of nuffieldite, tightly intergrown with galena II. The second generation of galena takes the form of a fine network of anastomosing veins, locally coalescing in thicker, elongated patches. Galena II is strictly confined to the nuffieldite grains, suggesting that the two minerals resulted from the decomposition of a Pb-rich phase. A number of seven large-beam microprobe analyses carried out on nuffieldite-galena II grains led to the following average composition of this hypothetical phase: Cu<sub>1.14</sub>Pb<sub>2.69</sub>Ag<sub>0.06</sub>Bi<sub>2.47</sub>Sb<sub>0.02</sub>S<sub>6.97</sub>. This composition does not correspond to any known phase in the chemical system of nuffieldite.

In terms of major elements, the chemical analyses of nuffieldite from Valea Seacă compare well with the data published in the literature (e.g., Moëlo, 1989; Efimov et al., 1990; Mozgova et al., 1994; Marcoux et al., 1996). However, our analyses indicate significantly lower contents of Sb and slightly higher contents of Ag. Average contents of Sb range between 0.17 and 0.22 wt. %, but with standard deviations of the same order, thus precluding the use of these data in crystal-chemical interpretations. The presence of silver, with an average participation of 0.39 - 0.42 wt. % is difficult to interpret given the steric features of nuffieldite. The variation of this element does not correlate with any other major chemical component, thus suggesting its rather accidental character.

The chemical data converge to a substitution mechanism of the type  $Cu^+ + Pb^{2+} \rightarrow \Box + Bi^{3+}$  also known in the bismuthinite – aikinite series. The mechanism is well illustrated both by the clustering of values in the ternary diagram  $Cu_2S - Pb_2S_2 - Bi_2S_3$  and by the binary diagrams of correlation Cu - Pb, Cu - Bi and Pb - Bi. The values of substitution coefficient x in the general formula of nuffieldite:  $Pb_2Cu_{1+x}(Pb_xSb_yBi_{1-x-y})Bi_2S_7$ , ranges between 0.26 – 0.40, close to those determined by Moëlo (1989) for the nuffieldite occurrence at Houches. The differences between the maximum and minimum x values calculated independently on the basis of atomic proportions of Cu, Pb and Bi, are very small: 0.056 – 0.071, thus confirming once more the assumed substitution mechanism.

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# DYPINGITE - PRODUCT OF THE BRUCITE ALTERATION IN THE BUDUREASA - PIETROASA AREA (BIHOR MTS., ROMANIA)

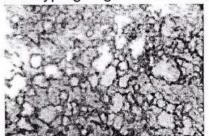
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In exogenous environment, the brucite lamellae are covered with thin white layers which occur, microscopically, as "alteration rims" (Fig. 1). The X-ray diffraction analyses performed on thin alteration crust of brucite-rich dolostones (in Budureasa and Pietroasa area) show the presence of dypingite  $Mg_5[(OH)_2 \mid (CO_3)_4]$ .  $5H_2O$  (table 1).

SEM investigations (Fig. 2) show the presence of short-fibrous crystals, covering brucite lamellae.

The dypingite genesis is related with the action of the meteoric waters rich in CO<sub>2</sub>.



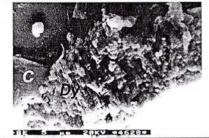


Fig. 1. Dypingite rims around brucite nests. Gallery 6, Budureasa-Valea Mare. 1N, 85X.

Fig. 2. SEM image of dypingite (Dy) + dolomite and calcite (C) mineral association.

Budureasa.

Table 1. X-ray diffraction data for Budureasa brucite + dypingite mineral association (without dolomite and calcite lines)

Brucite + Dypingite (Budureasa)		Brucite- File JPDG 7-239			Dypingite (Raade, 1970)-File JPDG 23-1218	
dÅ	I	dÅ	I	hkl	dÅ	I
15.3	4				15.2	30
10.8	6			7.00	10.6	100
6.34	6				6.34	60
					5.86	90
4.781	100	4.770	90	001		
2.718	5	2.720	6	100	2.78	20
2.541	5				2.53	50
2.362		2.365	100	101	2.36	5
					2.17	50
1.791	40	1.794	55	102		
1.570	20	1.573	35	110		
1.492	12	1.494	18	111		
1.370	12	1.373	16	103		
		1.363	20	200		
1.306	8	1.310	12	201		
1.188	5	1.192	2	004		
1.183	5	1.183	10	202		
Budureasa brucite: $a_o = 3.14(0) \text{ Å}$ $c_o = 4.76(6) \text{ Å}$ $\lambda_{Cu} = 1.54056$		Standard file of brucite: $a_o = 3.147 \text{ Å}$ $c_o = 4.769 \text{ Å}$ $\lambda_{Cu} = 1.54056$				

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### TRITIUM AS A GEOCHEMICAL AND ECOLOGICAL TRACER

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Tritium (3H, half-life of 12.43 years) is an isotope commonly used in hydrology to distinguish between recent water and old water (recharge after of before 1952) or to date groundwater up to about 70 years old. The concentrations of tritium in water from different locations show the influence of bomb-produced 3H. The "bomb tritium" peak occurred about in 1963 and reached monthly mean concentrations of nearly 5000 T.U. for rainfall. The geochemistry of tritium is perforce linked to the geochemistry of water. Groundwater that had a natural tritium input of 5,5 T.U. would need to be isolated from environment. The environmental tritium may trace directly those regionally and locally distributed contaminants. Based on the tritium data, the regional and local pattern of the water vulnerability may be used in predicting the possible ground water quality changes due to technologic impact. However, the hydrogen isotopes (protium, deuterium, tritium) provide a natural tracer for water, and their variations have been useful in elucidating problems in hydrology, meteorology, and, in general, the origins of geologically important aqueous fluids such as ore-forming solutions. It may be worth considering that the subsurface production of tritium via the reaction  $^6Li(n,a) \rightarrow ^3H$  might be significant in cases of high U and Th, and common Li concentration in the host rock. In situ neutron irradiation of 6Li in the rock matrix produces tritium atoms which can readily diffuse until they form molecular 3H2 by mutual collision, 3HH by exchange with H<sub>2</sub>, or much more likely, until they exchange for OH, H on hydroxyl sites in clay minerals (montmorillonite). Tritium within the fracture porosity of the rock and fluid inclusions may be produced. The clay minerals with higher Li content may be used in natural barriers for radioactive waste repositories. In area with high U and/or Th concentrations and, if the Li contents are not too low, same production of tritium should be expected. Natural clay minerals contain amounts of alpha emitting elements (U and Th concentrations are in the range 1 - 30 ppm) which are too small to allow any interference of long-term radiation effect in such materials. The possible role of alpha-radiolysis has also been advocated. The high concentrations of tritium also allow the investigation of radiation effect. Radiation effects can affect various properties of waste-forms; for instance, radiation induced dissolution and diffusion, solid and/or liquid radiolysis can be used for the study of performance assessment of geological disposal of wastes. The IRspectroscopy method has proved that gamma-irradiation accelerates the exchange of hydrogen isotopes in internal and intrasurface structural hydroxyls in clay minerals. In conclusion, tritium can be used: (a) as the retardation factor for migration of radionuclides, (b) as isotope tracer, (c) in geochemical surveying, (d) for nuclear well logging. All these demonstrate that tritium can be successfully used as a geochemical and ecological tracer.

## PRESENT DAY WEATHERING AND SERPENTINIZATION OF ULTRAMAFIC ROCKS IN SERBIA

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Two processes are active in the ultramafic rocks of Serbia: weathering and serpentinization.

Weathering of harzburgites, Iherzolites, dunites and serpentinites occurs under the present moderate climate, usually in the southern parts of the ultramafic massifs. As a result a yellowish to redish crust on the surface of the rocks is formed, usually 1–2 cm thick, but in places up to 5–6 cm. The process consists of leaching of MgO, oxidation of  $Fe^{2+}$  and relative enrichment of  $Fe_2O_3$ ,  $Al_2O_3$ , Ti, V, Pb, Ba and Rb, especially in the resulting reddish soil. The process is very similar to the formation of thick weathering crusts (up to 60 m) in the geological past, but in a very restricted extent. The mineralogy of the weathering products was studied. The running of this process is also evident by presence of  $Mg^{2+}-HCO_3^-$  – type waters in all ultramafic massifs.

The present day serpentinization was described by Barnes et al. (1978), with low temperature formation of lizardite-chrysotile assemblage. Fluids resulting from this process have been found in the form of Ca2+-OH- - type waters in a few places in the world. This type of waters issuing only from fresh or partly serpentinized peridotites, mostly lherzolites, was found along three parallel faults in the Zlatibor ultramafic area, in the Western Serbia. Although they are generally found in the bottom of deep gorges, they may be issuing from hillsides also. The water composition is similar, with Ca2+ as dominant cation and OH as dominant anion, and pH ranging from 11.3 to 11.9. In spite of issuance from highly magnesian rocks, the waters are extremely poor in Mg2+, Fe2+ and SiO2. For this type of water springs from Zlatibor area it is characteristic the presence of gases released in all localities. Hydrogen is the dominant gas, with methane, nitrogen and a little of oxygen. The isotopic study showed that these waters are of meteoric origin. In addition to the geochemical evidence for modern lowtemperature serpentinization, given by Barnes et al., based on hydrogen isotope data, the release of hydrogen and methane in these springs could be connected with the present day serpentinization process, as a result of partial oxidation of Fe2+ from olivines, ortho- and clinopyroxenes, according to the reaction 3Fe(OH)<sub>2</sub> = Fe<sub>2</sub>O<sub>3</sub> + 2H<sub>2</sub>O + H2.

From the geomedical point of view there is a marked relationship between Mg-rich drinking waters and the lowest cardiovascular mortality rates in the Zlatibor area, compared with other regions in Serbia. This is supported by pathophysiological and clinical importance of magnesium in cardiovascular risk (Durlach et al., 1989).

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# NEW MINERALS IN THE EPITHERMAL PARAGENESES FROM THE METALLOGENETIC DISTRICT BAIA MARE: STIBARSEN AND CHALCOSTIBITE

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The metallogenetic district Baia Mare is situated in the NW of Romania and includes more vein deposits of gold-silver and non-ferrous deposits [Pb, Zn, Cu], all of hydro-thermal genesis [ex: Ilba, Nistru, Săsar, Dealul Crucii, Herja, Baia Sprie, Cavnic, Băiuţ, Jereapăn]. These are disposed near a transcrustal fault [Bogdan Vodă] oriented E-W in the zone of the southern flank of the Gutâi Mountains. The new encountered minerals, belong to the Cavnic deposit, and consist in identifying the stibarsen [AsSb] and chalcostibite [CuSbS2] [Marias, 1996]. The metallogenetic processes occurred only in one stage, but with seven moments of tectonic and metallogenetic evolution of the fluids M1 - M7 (Marias, 1996a). As far as the aspect of the structural level is concerned, the fluids that generated the mineralization M4 where, besides stibarsen and chalcostibite also appear Au, Ag, tetrahedrite, bournonite, freieslebenit, bertierite, jamesonite, ring-shaped jamesonite, realgar, goldpigment, etc., are exactly under the andesite plate, in the interface zone between the heavier saline [magmatic], heavier fluids, "used" during the boiling process, with higher temperatures, and the colder, meteoric, covering fluids. This aspect also results from the smaller  $\delta^{18}\text{O}$  values of M4, as compared to the ensemble of the preceding moments [Marias, 1996a, b]. Due to the cooling that occurred at the base part of the interface and due to the heating appeared in the superior part by transfer of heat, the conduction cells that were formed increased the heat transfer towards the surface of the hydrothermal system, favouring the settlement of the above-mentioned minerals. The composition and thermal oscillations of the system, with the development of some pararhythmical textures in millimeter bands, given by the alteration: sulphosalts - kaolinit-illite minerals with important gold content, plead for such an understanding of the phenomena. The stibarsen identified in the mine Boldut [losif vein], is a natural intermetallic alloy of As and Sb, given by the difference between the atoms of the two metals of 13.8%: As = 2.5 Å; Sb = 2.9 Å, which almost represents the limit dimensional difference for an intermetallic solution. The identified stibarsen is of type I [Quensel et al.,1937 and Wretblad, 1941], being a mixture between stibarsen and Sb eutectoid granules, as they were seen at the microscope [immersion in oil]. Megascopically, it appears as large-size globular-mamelonar aggregates [>1m], in the distensional zones the vein, between the levels + 280 m and 530 m, and on the direction, on a length of 50 - 80 m. Within the occurrence the intermetallic precipitate [stibarsen] contains fibrous grains of Sb and is associated with Au, Ag, As, all native. According to published data, the As concentration in different geothermal waters, are between 1-10mg/kg, and they may adequately contain residual H2S. Seward [1974] suggested that the As colloidal sulphide washes the Au from the solutions, the recrystallization of As taking place in realgar and goldpigment, and Brown et al., [1983], suggests that the As amorphous sulphides can also be precipitated by acidulation. The morphologic aspect of the section with stibarsen suggests the existence of a paleochannel within the vein fracture, representing a conduction cell for some late fluids that are withdrawing downwards. The chalcostibite was identified in the mine Roata, as tabular blackish micro-grains aggregates [0.06 - 0.08 mm], situated at the end of the kaolinitic microbands; it is slightly anisotropic in the reflected light. The identification was carried out in the laboratories of the Karlsruhe University (Germany). Brown, K.L., Mc.Dowell, G.D., Lichti, K,A. and Bijnen, H.J.C. [1983] pH control of silica scaling: Proceedings 5th New Zeeland Geothermal Workshop, p.157 - 162 Mariaş, Z.Fr., [1996a] Unpublished Doctor's Degree Thesis - University "Babeş-Bolyai" Cluj Napoca Mariaş, Z.Fr., [ 1996b] Ann.Inst.Geol.Rom. vol..69, suppl. no.1, Bucureşti Quesnel, P., Ahbong, K. and Westgren, A. [1937] Geol. Foren Farhandl 59, p.135 - 144



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# PARAGENESES OF ALTERATION IN HIGH-TEMPERATURE CALCIC SKARNS FROM CORNET HILL (APUSENI MOUNTAINS, ROMANIA)

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The occurrence of high-temperature skarns at Cornet Hill (Metaliferi Massif, Apuseni Mountains, Romania) has been known for over two decades. Spurrite, tilleyite, gehlenite, Tiandradite, wollastonite and vesuvianite were noticed in these very spectacular skarns by the discoverers (Istrate *et al.* 1978). Due to hydrothermalism and weathering, secondary assemblages, overlooked until now because the very small dimensions of their composing minerals, locally overprinted the primary ones. In fact, only scawtite was identified by Piret *et al.* (1997). This study gives preliminary data on plombierite, tobermorite, xonotlite, gismondine, aragonite and portlandite found in the secondary parageneses.

Plombierite frequently lines fractures in the tilleyite mass with crusts of acicular crystals grouped in sheaf-like aggregates. Sometimes this mineral forms coatings and encrustations on scawtite, which occurs as seams on tilleyite. The mean structural formula, derived from a composition based on 18 point analyses, is:  $(Ca_{4.897}Mg_{0.002}Mn_{0.003}Fe^{2^+}_{0.012}Na_{0.004}K_{0.012})$  (Al<sub>0.084</sub>Si<sub>5.976</sub>)(OH<sub>2</sub>)O<sub>16</sub>·6H<sub>2</sub>O. The cell parameters, taken as mean of least-squares refinements on 5 different sets of X-ray powder reflections are a = 6.621(8) Å, b = 3.677(7) Å and c = 27.998(34) Å.

Tobermorite (the 11 Å polytype) most commonly occurs as sheaf-like aggregates of radiating acicular or fibrous crystals up to 10 μm long and 1 μm wide, associated with plombierite. The cell parameters are a=11.255(2) Å, b=7.365(8) Å and c=22.732(16) Å, and the mineral is, in this case, Al-poor [(Ca<sub>9.010</sub>Mg<sub>0.005</sub>Mn<sub>0.001</sub>Fe<sup>2+</sup><sub>0.007</sub>Na<sub>0.026</sub>K<sub>0.003</sub>)(Si<sub>11.973</sub>Al<sub>0.011</sub>) O<sub>30</sub>(OH)<sub>6</sub>·4H<sub>2</sub>O]. A fluorine-bearing Al-rich variety [(Ca<sub>8.765</sub>Mg<sub>0.091</sub>Mn<sub>0.005</sub>Fe<sup>2+</sup><sub>0.004</sub>K<sub>0.052</sub>) (Si<sub>10.835</sub>Al<sub>1.626</sub>)O<sub>30</sub>(OH<sub>5.778</sub>F<sub>0.222</sub>)·4H<sub>2</sub>O] occurs as filings of fractures in the gehlenite-bearing skarns, together with gismondine and hydrogrossular.

Xonotlite occurs as bundles of acicular crystals which grows onto wollastonite. Crystals are usually less than 50  $\mu$ m long, and rarely as long as 300  $\mu$ m. The cell parameters, refined on the basis of 51 X-ray powder reflections of a high-purity separate, are a=17.058(7) Å, b=7.390(4) Å and c=7.015(4) Å. The structural formula, derived from a composition taken as mean of 17 point analyses, is:  $(Ca_{5.992}Mg_{0.020}Mn_{0.005}Fe^{2+}_{0.010}Na_{0.004})(Si_{5.975}Al_{0.014})O_{17}(OH)_2$ .

Gismondine occurs as fan-shaped aggregates of lath-like crystals up to 1 mm long, in the gehlenite-bearing skarns. The cell parameters (least-squares on 23 unambiguously indexed reflections in the X-ray powder pattern) are a=10.013(5) Å, b=10.609(3) Å, c=9.846(3) Å and  $\beta=92.33(2)^{\circ}$ . The mean structural formula, calculated for a composition taken as average of 11 point analyses, is:  $(Ca_{1.566}Na_{0.732}Mg_{0.059}Mn^{2+}_{0.001}Fe^{2+}_{0.015})Al_{3.894}Si_{4.076}O_{16}\cdot 8H_2O$ .

Portlandite [(Ca<sub>1.993</sub>Mn<sup>2+</sup><sub>0.005</sub>Fe<sup>2+</sup><sub>0.002</sub>)(OH<sub>1.994</sub>F<sub>0.006</sub>)] occurs as tabular crystals which, together with aragonite and calcite, line the walls of the very thin cracks in the spurrite mass. The cell dimensions (least squares on 15 unambiguously attributable X-ray powder reflections) are a = 3.593(1) Å and c = 5.694(10) Å.

Aragonite (a = 4.974 (5) Å, b = 7.917 (8) Å, c = 5.694 (10) Å) was identified on fissures traversing the spurrite - tilleyite mass. The mineral occurs as radiating bundles of prismatic crystals, reaching up to 0.5 mm in length. It is intimately associated with calcite and sometimes with portlandite. A mean structural formula, calculated on the basis of 6 point analyses, is  $Ca_{1.998}Mg_{0.001}Fe^{2+}_{0.001}(CO_3)_2$ .

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## GEMOLOGICAL VALUE OF THE AREA BETWEEN THE AMPOI AND GEOAGIU VALLEY (APUSENI MOUNTAINS)

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#### Geological units containing minerals of gemological value

The ophiolitic complex (magmatic are type) is developed in the Capalnaş - Techereu Nappe. It appears at Balşa (S) and Techereu (N) and is represented by lava flows and basic pyroclasites insertions (Dumbrava, the Popii brook, Marului Hill etc). The ophiolitic complex contains silicolitic structures; i.e:

some mm or cm thick veinlets with polychrome chalcedonies (white, grey, reddish and sometimes greenish):

agate - shaped layers of chalcedony, either inside the veinlets or inside the rock itself displayed in a concretions manner; due to the high degree of craking and disintegration, samples of gemological value are seldom visible;

massive red monocoloured jasp; massive red polychrome jaspis (red and pink, grey, white) with a lacy fissue, beautiful and good - looking after having been processed (polished), massive yellowish jaspis (ochre yellowish waxen).

Laramian rhyolites (Ştefan et. al., 1988) - contain three main types of silicolites: vein-like, star-shaped, concretionar.

The Almaşu Mare Gravels (Badenian) are an important source of gemological minerals: jasp is fragments (red, yellowish), agate-shaped concretions (polychrome chalcedony), agates with marcasite (the Popii brook), Mesozoic limestone fragments (sometimes containing fossils) and metasomatically siliciphied andezite fragments.

Quaternary deposits are highly important in the concentration of silicolite-gems in all the deposits mentioned. Among these, most frequent alluvial soil, except terraces (slightly developed) dejection cones and eluvia; a distinct element are deluvia in the Pârâul Grohotelor, formed by the disntegration of the banatitic rhiolites (fragments of with vein-like nodular, agate-shaped chalcedony).

*Mineralogy of silicolites*. The varieties of silica in the epithermal and diagenetic silicolites in question, with some exceptions are similar. More fragment are theof jasp is the fibrous chalcedony, sometimes associated with quartz (in both genetic types) - and the opal in the diagenetic facies. The microtextural aspects of the silicolites are extremely various, due to the mineral components.



# RECONNAISSANCE INVESTIGATION OF PEAK METAMORPHIC CONDITIONS IN HIGH-PRESSURE METAMORPHIC ROCKS, GETIC-SUPRAGETIC BASEMENT, SOUTH CARPATHIANS

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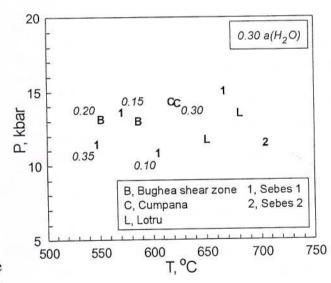
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Eclogites, high-pressure granulites, and garnet peridotites are widespread in three gneissic tectonostratigraphic units (Sebes, Lotru, and Cumpana) of the Getic-Supragetic basement (Median Dacides) in the South Carpathians. These high-pressure rocks yield information on the pre-Alpine (Variscan) tectonothermal evolution of the South Carpathians and provide a comparison between this, the easternmost occurrence of the European Variscan belt, with those in western and central Europe. This abstract is an initial report from a Wisconsin-Calgary-IGR cooperative investigation on the petrology of high-pressure rocks in the South Carpathians.

Thirteen samples of relatively fresh garnet peridotite, granulite, eclogite, phengite eclogite, zoisite eclogite, and kyanite eclogite were analysed by EMP. Special attention was paid to chemical zoning in minerals, to select appropriate compositional domains for determination of peak metamorphic conditions. In particular, garnet in some samples has strong prograde zoning, and in a few others, has an unusual pattern that mimics sector zoning. Temperatures, pressures, and H<sub>2</sub>O activities were determined from combinations of pertinent equilibria, depending on specific mineral assemblages, utilizing the GEOCALC program (Berman, 1988; Brown et al., 1989), appropriate activity models, and Fe<sup>3+</sup> contents estimated from charge balance calculations.

Two samples of garnet peridotite (Sebes 3) yield 1160 °C, 26.0 kb and 1295 °C, 32.2 kb,

similar to T-P values for garnet peridotites in the Gföhl Nappe of the central European Variscides. Among the metabasic rocks, garnet-clinopyroxene granulite (Sebes 2) gives the highest temperature, 705 °C, at 11.7 kb (see inset). The eclogites span a T-P range from 545 to 680 °C and 11.0 to 15.2 kb. Although many of the eclogite T-P values are minima, phengite barometry in three samples yields the same pressure as does the X<sub>Jd</sub> barometer. Temperatures are lowest in eclogites from the Bughea shear zone (in an external terrane boundary) and the Sebes 1 unit (except for one outlier), higher in the Cumpana unit, and highest in the Lotru unit. Consideration of zoisite equilibria



indicates that H<sub>2</sub>O activities were significantly less than 1.0.

Investigation of additional samples is being carried out to verify the apparent differences in peak metamorphic conditions among the different tectonostratigraphic units, to evaluate fluid compositions more precisely, and to construct the complete prograde and retrograde T-P paths in the various units. Age determinations of peak metamorphic mineral assemblages are clearly required to establish whether Variscan high-pressure metamorphism was contemporaneous or diachronous in the different units of the Getic-Supragetic basement in the South Carpathians.

### GARNET PERIDOTITES IN EURASIAN HP AND UHP TERRANES: A DIVERSITY OF ORIGINS AND THERMAL HISTORIES

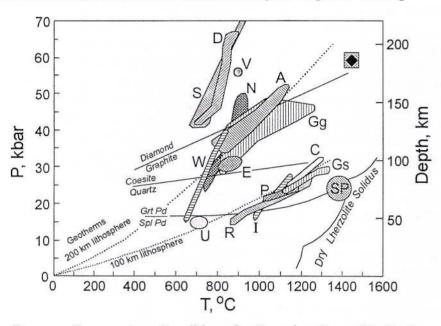
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Garnet peridotites and pyroxenites have been reported from eleven of the fifteen or so HP/UHP terranes in Eurasia. Most of these ultramafic rocks are Mg-Cr types, derived from depleted upper mantle, but some are more Fe-rich and originated by crystallization in ultramafic-mafic igneous complexes. The peridotites are polymetamorphic, with HP/UHP garnet-bearing assemblages being followed by a succession of retrograde assemblages related to exhumation and cooling, and some also contain evidence for a pre-HP/UHP stage, such as spinel inclusions in garnet or the presence of Ti-clinohumite.

Equilibration conditions have been calculated from all available analyses of garnet-bearing

assemblages by application of the olivine-garnet Fe-Mg exchange thermometer (O'Neill and Wood, 1979, 1980) and the Al-in-orthopyroxene barometer (Brey and Köhler, 1990), resulting in two distinct P-T regimes for garnet peridotites, one at high P/T in the coesite and diamond stability fields, and another at low P/T in the vicinity of the spinel to garnet transition.



Pressure-Temperature Conditions for Eurasian Garnet Peridotites Labeled fields: A, Lepontine Alps, Switzerland; C, Southern Carpathians; D, Dabie, China; E, Erzgebirge, Bohemian Massif; Gf (grt pd) and Gs (spl to grt pd), Gföhl Nappe, Bohemian Massif; I, Sulawesi, Indonesia; N, Western Gneiss Region, Norway; P, Gory Sowie, Poland; R, Ronda, Betic Cordillera, Spain; S, Sulu, China; SP, spinel peridotite protoliths for Ronda and Ultental garnet peridotites; U, Ultental (Nonsberg), Austridic Alps; V, Vosges, France; W, Schwarzwald, Germany; •, derivation from the diamond field of Ronda and Beni Bousera pyroxenites, which contain graphite pseudomorphs after diamond.

Garnet peridotites are thought to have evolved in at least four different tectonothermal settings, including: 1) emplacement of peridotites into oceanic or continental crust, as serpentinized bodies or crystal cumulates from basaltic magmas, followed by transport of peridotites and associated crust to UHP conditions by a subducting plate, 2) transfer of peridotites from a mantle wedge to the crust of an underlying, subducting plate, 3) derivation from upwelling asthenosphere that passed through a high-temperature spinel peridotite stage, followed by cooling into the garnet peridotite field, and 4) extraction of garnet peridotites from ancient subcontinental lithosphere, perhaps by deep-seated faulting within a continental plate.



#### THE GEOCHEMISTRY OF BERYLLIUM IN ROMANIAN PEGMATITES

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The rare metal beryllium is a typical litofile element of granitic pegmatites. The unusual crystal-chemical properties of beryllium result from its exceedingly small ionic radius coupled with its +2 ionic charge. During the geochemical evolution of pegmatitic processes, Be is isomorphically scattered in the crystal lattice of the minerals, or it may form proper minerals, among all, beryl being the must important one. Geochemical research established that up to 90% of the pegmatite beryllium is found in beryl.

The most important Be contents from pegmatites, occur in the rare-metal pegmatites: 0,01-0,08% (Solodov, 1971; Borisenko, 1980), but the highest contents occur in the beryl type pegmatites and in the complex type pegmatites (Eerny, 1992). Comparatively, in the sterile pegmatites the Be contents are much lower: 0,0002-0,001% (Beus, 1960).

The pegmatites from the Carpathians pegmatites province are considered to be granitic pegmatites which have been generated by metamorphic differentiation. Based on the mineralogical and geochemical features, these pegmatites belong to the following groups: (1) feldspar pegmatites, (2) mica-bearing pegmatites, (3) rare elements pegmatites, which include two types of pegmatites: beryl type (beryl + columbite + triphylite) and albite-spodumene type (spodumene + montebrasite + tantalite + cassiterite). The beryl type pegmatites occur in both Apuseni Mts. (Gilau - Muntele Mare subprovince) and, mainly, Southern Carpathians (Getic subprovince).

In the Carpathian pegmatitic province, the Be contents are evidently increasing from the graphic pegmatites: 1-7 ppm, feldspar pegmatites: 1-10 ppm and mica - bearing pegmatites: 3,6-90 ppm, to rare - element pegmatites: beryl type (+Nb,Ta, Li): 360-380 ppm, and albite- spodumene type (+Be,Nb,Ta): 60-220 ppm . The geochemical distribution of Be in the minerals of the Carpathian province pegmatites revealed lower contents in quartz (0,52 - 0,72 ppm), potassium feldspars (1-2,6 ppm), garnets (1-4,5 ppm), biotite (1-5 ppm), spodumene (4,7 ppm), as distinct from higher values in aluminium rich minerals: muscovite (85 ppm) and tourmaline (17,5 ppm). All these contents are characteristic for the minerals occuring in the metamorphic pegmatites.

In Romanian pegmatites, muscovite is the main mineral to concentrate beryllium, which penetrates into muscovite, following the isomorphous substitutions:

$$2Al_{1V}^{3+} \leftarrow Be_{IV}^{2+} + Si_{IV}^{4+}; [SiO_4]^{4-} \leftarrow [BeO_2(F,OH)]^{4-}$$

The Be content increases with the muscovite alkalinity.

In the zoned pegmatites, the Be content increases from the minerals of the external zones, to those of the intermediate zones. The concentration coefficient k indicates the order of Be accumulation in the minerals of the Carpathian province pegmatites: muscovite > albite > tourmaline > spodumene > biotite > garnets > potassium feldspars > quartz.

In the beryl occuring in the Getic subprovince pegmatites, the BeO contents range between 10,5 - 14,8 %, as the literature data for this mineral suppose to . The  $SiO_2$  contents are rather constant, while the higher contents of  $Al_2O_3$  are due to the muscovite microinclusions. Often  $Fe^{3+}$  substitutes  $Al_{IV}$ . The alkali content indicates the beryl to be Na -beryl type, in wich  $R_2O > 1$ .

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# THE MAGMATIC-HYDROTHERMAL PROCESS EVOLUTION IN THE BAIA DE ARIEŞ BRECCIA PIPE SYSTEM, METALIFERI MOUNTAINS (ROMANIA)

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Integrate studies as: pyrite morphology, mineral phase relationships, mineral microinclusions, SEM-EDAX quantitative analyses, trace element and XRD analyses performed on ore minerals reveal a peculiar path of the metallogenetic process evolution in the Baia de Arieş breccia pipe system. This one is marked by a transitional process on the magmatic – hydrothermal interface and a mineralization hiatus between the base-metal and gold sequences deposition as well. This means that two main stage evolutions of the magmatic-hydrothermal processes at the Baia de Arieş structure could be drawn.

- I. The first stage mainly comprises the transitional *magmatic-hydrothermal processes* as follows:
- 1) The breccia pipe formation related to supercritical fluid evolution (Burnham, 1985)
- 2) The accumulation and ascension of some high temperature fluids of K, Fe-rich composition, requiring a 3 6 pH domain (Crerar, Barnes, 1976). This composition is also supported by the presence of K-Fe-Cl complexes in pyrite that reveal the role of chlorine as a transport agent of metals in the transitional processes (Nedelcu et al., 1998)
- 3) The H<sub>2</sub>S increase in solution and iron sulfides deposition
- 4) The Zn, Pb sulfides deposition at the same physico-chemical constraints (T =  $350 450^{\circ}$ C, pH = 3 6) favoring the formation of the pollymetallic replacement ore bodies at Valea Lacului zone.
- II. The second stage is characterized by the following processes:
- 1) The system opening, followed by a re-equilibration period of the physico-chemical constraints of the system resulted in a *depositional hiatus* (gap) and a gradual decrease of temperature;
- 2) An adiabatic détente accompanied by boiling, fissuring, filling and gold sequence deposition. In this stage, the conditions of the K-rich mineral (sericite, muscovite) stability are also maintained, requiring a pH in the near neutral region, a domain suggesting the gold transport as AsS<sub>2</sub> and As<sub>2</sub>S<sup>2</sup><sub>4</sub> type complexes (Seward, 1984). Therefore, arsenopyrite deposition appears as an effect of the fO<sub>2</sub> variation (Heinrich, Eadington, 1986);
- 3) The native gold and Au, Ag telluride deposition as a result of the As elimination from the system by arsenopyrite deposition, of some repeated adiabatic détente, of the solution cooling till about 100°C (TI-high content in pyrite), as well as of a variable fO<sub>2</sub>.

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# THE EVOLUTION OF PETROGENETIC PROCESSES RELATED TO THE INTERACTION BETWEEN MAGMA AND ENCLAVES (Subvolcanic zone of the East Carpathians, Romania)

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Neogene calc-alkaline subvolcanic bodies (andesites, microdiorites and dacites) from Bargau Mts. and Rodna Mts. contain igneous, metamorphic and sedimentary enclaves. Various interactions between the enclaves and the host rocks have been studied. These processes proceeded sequentially and tended to reduce the chemical and mineralogical contrasts between the coexisting magma and enclaves at different crustal levels, in magma chambers at depth, in the conducts or after emplacement. Hybridisation and assimilation processes (resulting in hybrid bands and reaction coronas) represent the cumulated effects of these interactions.

The mineralogical and chemical transformations of the enclaves, the effectiveness and spatial extent of thermal, mechanical and chemical exchanges are constrained by the initial temperature, composition, relative volumes, crystallinity and other physical and chemical parameters. In the metamorphic and sedimentary enclaves new mineral phases had formed biotite, garnet, andalusite, and sillimanite, K-feldspar, spinels, corundum. When the igneous enclaves contained the same minerals as the host rock the selective diffusion determined the migration of Fe and/or Mg from the magma to the enclaves, resulting either minerals of second generation (magnesio-hastingsite on ferroan pargasite, magnesian biotite on a more iron-rich one) or new mineral phases (spinels on hydrous silicates).

Around siliceous enclaves (usually pure quartz fragments), reaction coronas consisting of diopside, rhyolite glass, tridymite, apatite and hornblende occur. Around the feldspathic enclaves, sillimanite intergrowths, new feldspars or short amphibole prisms may occur.

There are instances when the host rock was modified by the interaction with the enclaves. Near the contact, in the host rock, poikilitic quartz, K-feldspar, biotite or sillimanite may occur. In the case of  $H_2O$ -rich enclaves, biotite or hornblende replaced the pyroxenes of the host rock. As effect of assimilation the host rock turned towards a more acidic composition and to more coarse texture.



### MERCURY IN ORES AT BAIA MARE REGION

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# CHLORIDE CONTENT AND CHLORINE STABLE ISOTOPE RATIOS OF THE SALT MELT INCLUSIONS FROM ROŞIA POIENI PORPHYRY COPPER ORE DEPOSIT (METALIFERI MOUNTAINS, WESTERN ROMANIA).

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Coarse quartz grains from a characteristic vein association in the potassic inner zone from Roşia Poieni porphyry copper ore deposit contain, based upon their room temperature assemblage, principally of three types of fluid inclusions. These types are: silicate melt, salt melt and vapor - rich inclusions. Biphase inclusions are also found but these are secondary generated mainly by the transformation of the older inclusions. A rough estimate of the salinity in the salt melt inclusions expressed as wt% (NaCl + KCl), for 206 determinations is between 60-90 wt%.

The fluid phase extracted from quartz grains by crush – leach procedure (Bottrel et al., 1988; Quan et al., 1987) was analyzed for chloride potentiometrically using a pair of ion - selective electrodes, i.e. EMIS - CI and a double junction reference one. For 35 determinations, a relative homogeneity of the chloride distribution in a vertical plain of the Roşia Poieni porphyry copper ore deposit was observed.

The calculated chemical composition of chlorides in the fluid phase released from the fluid inclusions are quite different from the salinity estimation of the melting points of halite and sylvite daughter minerals, i.e. NaCl (5 - 18%), KCl (13 - 40%), CaCl<sub>2</sub> (24 - 64%), MgCl<sub>2</sub> (0 - 13%), FeCl<sub>2</sub> (11 - 53%).

The coefficient  $\Sigma(\text{cations})/\Sigma$  (anions) is approximately 0.1.Larger values were also calculated, even larger than 0.3, which indicates that the fluid composition is very complex, which is caused by other cations and anions like  $SO_4^{2^-}$  etc. Although PIXE and SEM analyses (Daman et al., 1996; Pintea, 1996) showed complex chemical composition including S, CI, K, Na, Ca, Mn, Fe, Cu, Pb, Zn, Br, Rb, Sr, many of these elements are complexed in chloride species.

The chlorine stable isotope composition is determined on six samples, using the method described in Eggenkamp (1994). All of them are enriched in the light isotope  $^{35}$ CI.  $\delta^{37}$ CI values are between -0.6 and -0.3% relative to the standard SMOC (Standard Mean Ocean Chloride).

This study showed that the main fluid phase associated to the Roşia Poieni porphyry copper ore deposit is represented by a salt rich liquid evolved together with a silicate rich liquid and vapor during the retreating downward crystallization process.

The main metallic compounds are complexed as chlorides, and the calculated concentration is determined by the sum of these complexes.

The isotopic signature of chlorine fits very well in the range determined by other studies, e.g. at Bingham and Panguna porphyry copper ore deposit (Eastoe & Guilbert, 1992).

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### GLAUCONITES FROM TRANSYLVANIA: MINERALOGY, GEOCHEMISTRY AND CRYSTAL CHEMISTRY

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The last time glauconitic minerals appeared in Romanian literature was in the 1970's. Since then, important discoveries have been made concerning their mineralogy and crystal chemistry.

The results presented in this study are based on 22 occurrences in the Transylvanian Depression. For the detailed crystal chemical investigations eight representative samples were selected. They are hosted by three of the glauconitic formations of the Transylvanian Depression (Eocene, Oligocene and Miocene in age) and by the two Cretaceous occurrences in the adjacent areas.

New methods of investigation for glauconitic minerals (TEM - replica method) or recent procedures of processing and interpreting the analytical data (FTIR method, Mosswin software for Mössbauer spectra) were applied. The first Mössbauer analyses on Romanian glauconites were used for finalising a new method of interpretation, based on the study of the quadrupole splitting distribution. The morphology of the glauconites is very diverse; practically, all the types described in the literature are illustrated. The most frequent facies type is granular, but the impregnative (diffuse) type was also

identified in two occurrences.

By applying the classical XRD on powder mounts, all the mineral species in the series of glauconites were detected in our samples: ordered glauconite, disordered glauconite and, less well represented, interstratified glauconite/smectite. A relative small amount of expandable layers (<15 %) was identified, using XRD analyses on oriented (natural and glycolated) samples. The most evolved structures belong to the glauconites hosted by the Cäpuöu Formation (Eocene), which mainly consist of ordered glauconites. The interstratified glauconite/smectite is less common in the analysed samples and is mainly recorded in the Chechiö Formation (Miocene). The disordered glauconites showing a various degree of structural ordering - are the most frequent glauconitic species represented.

As far as the geochemical classification of glauconites is concerned, apart from the K-poor and high-charge glauconites all the chemical types described in the references were identified. Fe<sup>3+</sup>/Al ratio was used for defining three chemical types within the analysed glauconites: "Al-rich glauconites" - Fe<sup>3+</sup>/Al <2, " intermediate glauconites " - Fe<sup>3+</sup>/Al between 3-5 and "Al-poor glauconites " - Fe<sup>3+</sup>/Al >9. A new index of the maturity degree,  $CM_{Fe}$  was introduced for synthesising the geochemical and mineralogenetic information provided by the Fe<sup>2+</sup> and Fe<sup>3+</sup> contents in glauconites:  $CM_{Fe}$  = Fe total x Fe<sup>3+</sup>/Fe<sup>2+</sup> x Fe<sup>3+</sup>/Al.

The most important aspect of the REE pattern in Transylvanian glauconites is the presence of two different trends of fractionation; this feature was interpreted as being connected with regional geochemical factors, mainly inherited from the original terrigenous material.

From the structural point of view, Transylvanian glauconites prove to be more heterogeneous and disordered than those analysed by previous works. A relationship between the number of IR absorption bands and the ordering degree of the structure was observed. The more ordered the structure, the highest number of bands in the OH-stretching region. The number of Al-Al bands is also variable and we assumed a correlation between the number of bands and the crystal chemical ordering of Al cations in both octahedral and adjacent tetrahedral layers, without influencing the total Al content of the sample. By means of some high resolution structural methods, the position of octahedral cations and vacancies - in *trans* or *cis* types of octahedra - could be statistically deduced. The results of the XRD evaluation, based on the values of  $c\cos\beta/a$  ratio indicate that most of the Transylvanian glauconites are composed mainly of tv polytypes but also of subordinated cv polytypes, which influence the values of the cell parameters. These observations are supported by the Mössbauer spectroscopy interpretation: besides the effects of the *cis*-octahedral cation arrangements, also *trans*-occupied arrangements were taken into consideration. The Fe cations - both Fe<sup>2+</sup> and Fe<sup>3+</sup> - located in *trans* positions represent about 1/10 of the total Fe present in the octahedral layer.



# METAMORHISM IN EPIDOTE-AMPHIBOLITE FACIES FOR MINERAL ASSEMBLAGES FROM CODRU (BÂC) MASSIF, NW TRANSYLVANIA

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Among all the crystalline islands outcropping in NW Transylvania, the Codru Massif is characterised by an exceptional paucity of data concerning mineral assemblages present and interpretations of metamorphic evolution.

The majority of the metamorphic rocks in the Codru Massif are quartz-rich schists and quartz-rich gneisses, with lesser levels of mica schist and amphibolite. Syenite intrusions outcrop in the northern area and granitic intrusions in the southern area. Detailed petrographic study was carried out on samples of both mica schist and amphibolite, representative of the entire surface of the massif. Electron probe microanalyses were carried out on all the significant mineral phases.

Two distinct mineral assemblages are identified in the mica schists and amphibolites and correspond to geographic position. We choose to divide them into the northern and southern areas; the limit between them considered at south of Prihodiste Valley and Lespezi Peak.

In the northern area, the mineral assemblage for micaschists is quartz + muscovite ( $Ms_{58-69}Pa_{17-10}$ ) + biotite ( $PhlAnn_{30-48}$ ) + chlorite + garnet + plagioclase ( $Ab_{92-78}An_{8-22}$ ), with ilmenite ( $Ilm_{97-90}Hem_{07}$ ) + pyrite. In amphibolites the assemblage is amphibole ( $Al-Fe^{2+}$  pargasite - Mg-hornblende) + plagioclase ( $Ab_{99-73}An_{1-27}$ ) + garnet + biotite ( $PhlAnn_{50-60}$ ) + chlorite + epidote (Ps>Czo) + quartz  $\pm$  muscovite, with ilmenite ( $Ilm_{87-93}Hem_{10-5}$ ), pyrite,  $\pm$  sphene.

In the southern area, the mica schist contains quartz + muscovite ( $Ms_{63-78}Pa_{24-12}$ ) + biotite ( $PhlAnn_{21-45}$ ) + garnet + plagioclase ( $Ab_{82-68}An_{18-32}$ ) + chlorite ± kyanite ± staurolite, with ilmenite ( $Ilm_{92-99}Hem_0$ ), rutile, pyrrhotite, and chloritoid as inclusions in garnet porphyroblasts. In the case of the amphibolites, the assemblage is amphibole (Al-tschermakite) + plagioclase ( $Ab_{91-75}An_{9-25}$ ) + garnet + biotite ( $PhlAnn_{32-47}$ ) + chlorite ± epidote (Ps < Czo) + quartz ± muscovite, with ilmenite ( $Ilm_{92-99}Hem_{0-6}$ ), rutile, pyrrhotite, ± sphene.

In all assemblages, chlorite is present and considered as a stable mineral phase. Apatite and zircon were identified as accessory minerals in all studied samples.

The relationships between minerals suggests a sequence of three metamorphic events:  $M_1$  (prograde) and  $M_2$  (peak metamorphism) represented by syn-kinematic mineral growth, which is supported by compositional profiles across garnets, and  $M_3$  (retromorphic) with post-kinematic growth of muscovite, biotite, chlorite, and small resorption of garnet rims.

Using the program THERMOCALC v 2.4 (Powell, Holland, 1988), with Fe<sup>3+</sup> estimated for all mineral phases, the mineral compositions were processed and P-T conditions estimated for mineral assemblages from 12 mica schist and 8 amphibolite samples.

The data suggests that metamorphism in the Codru crystalline island followed a clockwise PT path, with a peak metamorphism around 9.5 - 10.0 kbar and 550 - 600°C. Samples close to syenite intrusions are reequilibrated at pressures of 4.8 - 6.4 kbar in the northern area (Teiusului and Furnicaru Valleys). In the southern area, a partial melting of the rocks (CD23, 8.6 kbars, 610°C,  $aH_2O = 0.15$ ) was recognised and small bodies of migmatite were identified in the field (Codru Peak zone). For the southern area, low  $fO_2$  and  $fS_2$  are assumed; higher  $fO_2$  and  $fS_2$  are suggested for Northern Area, due very probably to the influence of the syenite intrusions.

The authors are gratefully to S.C. Cuart S.A. for help in sampling, and to Mineralogical Institute, Würzburg, Germany for microprobe analysis.

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### DIFFERENTIATION OF ISLAND ARC BASALTIC MAGMA AND GENESIS OF HIGH-Mg AUGITE BASALT IN THE MURES ZONE

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The high-Mg augite basalts occur as thin (up to 5m thickness) intercalations of lavas and tuffs in the Upper Jurassic island arc volcanics of Mures Zone, formed mostly of normal porphyritic basalts. As lava flows they have been found on the Căstănescu Valley at Godinesti and on the Scoarta Valley north of Visca in the Metaliferi Mountains. The pyroclastic products (tuffs) of these rocks were described within the area north of Brad, at Balsa-Techereu and on the bottom of the Transylvanian Basin. The lava flows consist of a glassy groundmass in which augite and most rarely basic plagioclase (An 55-52) phenocrysts are present. According to their chemical composition, in which SiO<sub>2</sub> varies from 46.46% to 49.50% and MgO from 7.13% up to 16.54%, the high-Mg augite basalts are transitional rocks between the normal porphyritic basalts and ankaramites, and even between the last rocks and the Hawaiian olivine basalts. They resulted from an island arc calc-alkaline basic magma by fractional crystallization and a selective gravitational differentiation process in a magmatic chamber. It is probable that during a tectonic and magmatic quiet period, at a favorable temperature and gas-pressure, in the parental magma augite and basic plagioclase phenocrysts began crystallizing. The augite phenocrysts being heavier than the magma started sinking toward the lower part of the magmatic chamber. As the magma from this lower horizon of the magmatic chamber became more and more rich in Mg, Fe and related trace elements, especially Ni and Cr. it got a higher specific gravity. By consequence, the plagioclase phenocrysts that were more light commenced floating toward the upper part of the chamber. Therefore, there resulted a rather layered magmatic chamber, within which three superposed horizons were present:

1. A thin horizon in the lower part of the magmatic chamber, consisting of a mixture of high-Mg melt and augite phenocrysts;

2. A transitional horizon formed of a Mg-rich magma (around 7% MgO), in which both augite phenocrysts – still predominant – and plagioclase crystals were present;

3. An upper zone that occupied most parts of the magmatic chamber and consisted of normal basaltic magma including basic plagioclase.

From this magmatic chamber were successively erupted pyroclastics of normal porphyritic basalts and lava flows and rarely tuffs of high-Mg augite basalts.



### CARBONATE NEOFORMATION RELATED TO POST-DEPOSITIONAL HISTORY OF LATE PROTEROZOIC TURBIDITES (HISTRIA FORMATION, CENTRAL DOBROGEA)

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Newly formed carbonates typically occur in both coarse and fine-grained lithologies of the Late Proterozoic (Vendian) basement of the Moesian Platform exposed in Central Dobrogea. The results obtained on these carbonates by optical microscopy, SEM, EDAX and XRD investigations are presented.

Compact, granular aggregates of large, milimetric crystals, completely replace isolated ripples or thin, discontinuous beds of ripple cross-laminated siltstones; the calcite crystals are poikiloblastic, including tiny albite and quartz grains from the recrystallized groundmass, and suggesting post-kinematic crystallisation; they are associated with post-kinematic chlorite porphyroblasts.



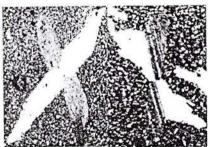


Fig. 1. SEM image (left) and microphotograph (right) of twinned calcite crystals in pelitic interbeds.

In some areas north of Casimcea village, sandstones contain milimetric nodules with elliptic or circular outline; the nodules are often dissolved, but when preserved, they consist of intergrown, poikiloblastic calcite crystals.

In pelitic interbeds, the calcite occurs as isolated, twinned crystals; they overgrow the bedding, and show a constant distribution of their long axis normal to bedding; the carbonate blades show a vertical lineation on the slaty cleavage planes.

It is still questionable if the carbonates are the result of diagenetic processes, if they replace a preexisting diagenetic mineral (gypsum), or represent metamorphic minerals related to the very low grade Cadomian metamorphism of the Vendian succession as suggested by the mineral association.

### CRYSTAL CHEMISTRY OF PYROXENE FROM UKRAINIAN CARPATHIANS

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Single pyroxene crystals from Miocene calc-alkaline volcanic rocks of Ukraine, have been studied by microprobe techniques to examine the relations between pyroxene crystal chemistry and the petrological features of the rocks. The examined rocks belong to two parallel arcs (here termed Outer Arc and Inner Arc) in the Ukrainian part of the Carpathians, which show petrological differences. In both arcs the clinopyroxene are chemically quite similar, represented by augite and pigeonite. Orthopyroxene are represented by ferroan enstatite. Geothermometry on clinopyroxene-orthopyroxene pairs were carried out to estimate the magmatic temperature at the time of crystallization. Calculated temperatures range between 1100-900°C for basaltic to andesitic magmas. Pyroxenes were major crystallizing phase involved in fractional crystallization processes of the magmas from the Ukrainian Carpathians.

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### CRYSTAL CHEMISTRY OF SCAPOLITE

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The crystal structures of fifteen members of the marialite (Ma) - meionite (Me) solid solution series with compositions ranging from Me<sub>0.2</sub> to Me<sub>100</sub> (9.02≥ Si ≥6.00) were examined using the Rietveld method. To fill the chemical composition gap, two synthetic end-members have been produced by high-pressure solid state synthesis. For thirteen scapolite samples from metamorphic rocks of Russia, Italy, Canada, USA, Tanzania, Madagascar and two synthetic endmembers X-ray powder-diffraction data was analyzed (autodiffractometer ADP-2 and STOE-STADIP,  $\lambda MoK_{\alpha}$ , Wyriet, version 3.3 program) using ionized X-ray scattering factors, and calculating isotropic/anisotropic temperature factors: Rwp 0.036÷0.072, RF 0.022÷0.076, s 1.00÷1.94, both in space groups I4/m and  $P4_2/n$ , to find the most adequate model of the scapolite structure.

Scapolite is a framework aluminosilicate with tetragonal symmetry and a general formula  $M_4T_{12}O_{24}A$ . Scapolite has three main forms of isomorphous substitution, Al<sup>3+</sup> for Si<sup>4+</sup> at the Tsites, Ca<sup>2+</sup> for Na<sup>+</sup> (±K) at the M-site, and CO<sub>3</sub><sup>2-</sup> or SO<sub>4</sub><sup>2-</sup> for Cl<sup>-</sup> at the A-site. Concentrations of Sr, Ba or Fe are minor (with negligible Mg, Mn, Ti, P, Br or F), but A-site substitution is complicated by significant H<sub>2</sub>O (as HCO<sub>3</sub>, HSO<sub>4</sub>, OH, or H<sub>2</sub>O). Relations between the variable composition of scapolite and changes in structure, i.e., phase transitions from space group I4/m to  $P4_2/n$  and again to I4/m is one of the major points of discussion of the crystal chemistry of the solid solution between marialite (Ma) Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl and meionite (Me) Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>CO<sub>3</sub>

For the first time crystal structures of both synthtic end-members Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl (Ma) and  $Ca_4Al_6Si_6O_{24}CO_3$  (Me) have been refined. Unit-cell parameters: (Ma) a = 12.0396(2), c =7.5427(2)Å,  $V = 1093.3(4)Å^3$ ; (Me) a = 12.2119(1), c = 7.5811(1)Å,  $V = 1130.57(1)Å^3$  could be regarded as references. Natural scapolites  $Me_{4.6}$  (PAM-1) (a=12.047(1)Å, c=7.5608(2)Å, V=107.3(2)Å<sup>3</sup>) and  $Me_{96.0}$  (MONT) (a = 12.1969(4)Å, c = 7.5763(2)Å, V = 1127.08(6)Å<sup>3</sup>) are closest to synthetic end-members in chemical composition. With variation in Si from 9.02 to 6.00 apfu, there is a linear increase in a from 12.04 to 12.21Å although the c unit-cell dimension remains almost constant. Total increase in a cell parameter is 0.1599Å, i.e. 1.3% of the smallest value, while in c parameter, 0.0384Å, i.e. 0.5%. The increase is closely related to the variation of T-O-T angles parallel to a due to a different stress of Si-O-Si bond along [100], [010] and [001].

Rietveld refinements from X-ray powder data of the scapolites revealed information about the population of the T(2,3) sites on the basis of the interatomic  $\langle T\text{-O}\rangle$  distances. Tetragonal symmetry described by space group I4/m is preferable for scapolites with  $9.00 \ge \text{Si} \ge 8.34$  and 7.09≥ Si ≥6.00 and space group  $P4_2/n$ , for scapolites with 8.34≥ Si ≥7.09. The number of weak reflections violating body-centered symmetry was constant for all the samples, characterized by space group  $P4_2/n$ . Structural differences between the space groups do not refer to the M and A sites as the choice of space group is determined only by ordering of Si and Al in the tetrahedral sites with sp. gr. P42/n corresponding to the ordered Si/Al distribution over Tsites of the scapolite framework. Thus three subseries within the solid solution series have been

To confirm a number of subseries in the solid solution series marialite-meionite, high established. temperature data for PAM-1 (Me<sub>4.6</sub>) and synthetic meionite (Me<sub>100</sub>) have been obtained in the range 28-600 and 28-900C correspondingly. The unit-cell volume and the a lattice parameter were observed to increase linearly, whereas the c lattice parameter was insignificantly varying. Rietveld refinement results established different thermal expansion coefficients for marialite and meionite confirming existence of three subseries within the scapolite solid solution series.



# METALLOGENIC POTENTIAL OF PEGMATITES FROM SOMEŞUL RECE-IARA VALLEY PEGMATITE DISTRICT, APUSENI MOUNTAINS (ROMANIA)

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In terms to establish the metallogenic potential of pegmatites from Someşul Rece – lara valley Pegmatite District potassium feldspar, muscovite, garnet, tourmaline and pegmatite samples have been analysed. In this purpose, classic chemical method and electron microprobe analyser (major elements), as well as an ICP analyser (minor elements) have been used.

Potassium feldspars as metallogenic indicator. The values of geochemical criterion (Rb/K)10³, as well as the Ba average participation in potassium feldspars show that pegmatite bodies from the investigated area belong to the so-called province of pegmatite with mica, that took place by mean of a metamorphic process; similar results have been obtained using Trueman and Eerny's (1982) diagnostic diagrams in which Li and Rb amounts have been projected.

Muscovite as metallogenic indicator. In terms to establish the metallogenic potential of pegmatites from Someşul Rece – lara valley pegmatite district by mean of muscovite, the values  $(Rb/K)10^3$ , the amounts of Li and Rb in muscovite as well as phengite:muscovite:annite (Foster, 1960), Rb:(K/Rb),  $Li:(Al_{VI}+Al_{IV})$ ,  $Al_{VI}:Al_{IV}$  (Eerny, 1982) and  $\Box VI:R_{VI}^{2+}$  (Eerny, 1982) diagrams have been used. All these geochemical criteria sustain the hypothesis that pegmatite bodies belong to the group of barren pegmatites (that's mean pegmatites with mica, respectively ceramic pegmatites), but they also have some of the geochemical features specific to mineralized pegmatites.

Garnets as metallogenic indicator. The projection of MgO, FeO and MnO amount values in the Salîie's (1975) diagram shows the disposing of garnet samples in the field of pegmatites with muscovite and rare elements. Using the almandine:spessartine:pyrope diagram (Sokolov et al., 1962) the tendency toward the features of pegmatites with rare and specific minerals group has been put in evidence; Li amount values in garnets have led us to similar conclusions.

Tourmaline as metallogenic indicator. The participation of Al, Fe<sub>tot</sub> and Mg in tourmaline (Henry and Guidotti's Al:Fe<sub>tot</sub>:Mg diagram, 1985) reveals the disposing of samples in the field of *Li-poor granitoids and their associated pegmatites and aplites*.

(Rb/K)10³ values in pegmatites as metallogenic indicator. This geochemical criterion has low values (4,3), specific to those put in evidence by foreign as well as Romanian geologists for the group of barren pegmatites (3,3 in pegmatites with feldspars from Preluca Mountains; 4,1 in pegmatites with muscovite from Rodna Mountains; 4,9 in barren pegmatites from Russia). On the other hand, one of our samples has showed a higher value (12,8) that match to those specific to mineralized pegmatites.

In conclusion, pegmatite bodies from Someşul Rece – lara valley district generally belong to the group of *barren pegmatites* but, in contrast with the other occurrences from the so-called Romanian Pegmatite Province, they also show some of the geochemical features specific to *mineralized pegmatites*.

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#### MAGMATIC MINERAL CHEMISTRY OF THE "DEJ TUFF"

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The Neogene volcanism started in Romania with large-volume explosive eruptions of acidic magma in Lower-Middle Badenian time (ca. 15 Ma ago) giving rise to the Dej Tuff Complex (DTC) widespread in the Transylvanian Basin, its surroundings as well as at the external part of the Carpathians. DTC consists of sequences, tens of meters thick, of reworked volcaniclastic sand, coarse to fine tuffs, tuffites and tuffaceous marls, collectively known as the "Dej Tuff". Its variable petrographic features are the result of grain-size and relative amount of volcanic and non-volcanic components. The volcanic component, of rhyolitic composition, includes vitroclasts (glass shards, pumice and obsidian), cristaloclasts and lithoclasts of volcanic origin. The non-volcanic component consists of non-volcanic lithoclasts and intraclasts, detritic minerals, authigenic minerals and bioclasts. The tuffs are pervasively zeolitized, especially their vitroclastic varieties in most occurrence areas.

This complex genesis is reflected in the complex mineralogical assemblages of the DTC. According to their origin, minerals of the Dej Tuff" are grouped in the following categories: (1) magmatic rock-forming minerals (quartz, plagioclase, biotite, K-feldspar, amphibole, piroxene); (2) magmatic accessory minerals (ilmenite, Ti-magnetite, rutile apatite, zircon, allanite, monazite, xenotime); (3) detritic minerals (muscovite, quartz, glauconite); (4) authigenic minerals (calcite); (5) diagenetic minerals (celadonite, clinoptilolite, opal-CT, mordenite, phillipsite).

Mineral chemistry of magmatic minerals has been studied by microprobe analysis.

An% content of plagioclase displays a wide range (9.6-70%) but most compositions fall in the range 15-40%. Two frequency maxima of the plagioclase population, at 20-25 and 30-40%An, respectively, have been pointed out. Individual zoned crystaloclasts display compositional spectrums as wide as 19.4 %An. An% content of plagioclase from different tuff horizons in the same outcrop shows discernible variations according to stratigraphic position.

The calculated structural formulae of biotites place them at intermediary positions between magnesian and ferriferous end members in the phlogopite – annite – siderophyllite – eastonite space. The  $Fe^{3+}/Fe^{2+}$  ratio and lack of correlation between  $Fe^{2+}$  and Mg indicate various, generally high oxidation states.  $TiO_2$  in biotites is generally high (5.3-12.9%).

K-feldspar is generally sanidine but orthoclase (in an igneous lithoclast) has also been identified in the tuffs.

The amphibole in the Dej Tuff belongs to the homblende (calcic amphibole) group. According to their calculated structural formulae, they are mostly magnesio-homblende and magnesio-hastingsite, but rare edenite and pargasite grains have also been identified. Accidental pyroxene grains are pigeonites.

Opaque minerals range in composition from almost pure magnetite to rutile, but most Fe-Ti oxide grains are ilmenite and titanomagnetite. MgO and MnO are subunitary in both the rhombohedric and spinel phases. MnO is higher than ilmenite. Ilmenite is more homogenous in composition than titanomagnetite. FeO/TiO<sub>2</sub> ratio in titanomagnetite shows two clusters, around 4 and 11. Accessory allanite is the main REE-bearing mineral, ubiquitous in the tuffs, and shows a relatively uniform composition. REE sums are in the 11.5-13.2% range. MnO is low (0.34-0.7%) whereas TiO<sub>2</sub> is higher and more scattered (0.73-2.36). Monazite and xenotime are REE minerals for the first time identified in the DTC.

Mineral chemistry of magmatic minerals provides important clues in understanding petrogenetic processes related to the "Dej Tuff" magma.



### IS THERE A CONTINUITY BETWEEN BAIA SPRIE AND SUIOR ORE DEPOSITS?

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Among the ore deposits of the Baia Mare mining district, the Zn-Pb-Cu deposit at Baia Sprie and the Au deposit at Suior occupy a special position and have both a particular significance. The Baia Sprie deposit is the largest one in the district (the longest vein systems, i.e. of about 5 km, known in Romania) and was nearly continuously exploited since the beginning of the last century. The Suior deposit, which is gold dominated (at least in the upper part) has been discovered in the last decades and became for a while the largest open pit for gold ores in the country.

In spite of some differences between the two ore deposits there are some reasons to consider that they belong to the same major structural element, that is a strong, double fracture running nearly E-W. The mineralized fractures are already known at Baia Sprie and their eastwards continuity was proved by the data obtained from several drillings. In addition, the whole graben-like structure hosting the Baia Sprie deposits is dipping eastwards and the fractures are seemingly connected to the Suior mineralized fractures. Several arguments supporting this idea are presented, as collected during many years of exploration works carried out by the author in the area.



#### BIOTITES AS INDICATORS OF EQUILIBRIUM IN ALKALINE MAGMATIC SERIES

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Biotite is an important constituent of the granitoids. As well as the amphiboles, the biotite represents a significant reservoir for water and halogens in the Earth's crust. The relationships between color, composition and phase stabilities of biotite depend on the P-T-X conditions of the magmatic system. Therefore, many petrologists consider the biotite as indicator or marker of evolution for alkaline magmatic series. Generally, these series are intruded or erupted in within plate tectonic environment and theirs differentiation trends are strongly controlled by fractionation of anhydrous or hydrous mineral phases. In the alkaline granitic system the ferromagnesiens are the late phases which crystallised from the liquid with or without oxides and some accessories rich in incompatibles. The crystallisation of biotite is indicated in alkaline system by drastically decrease in Ti, Zn, Mg, Sc, Co, Cr and a relative increase in Mn. In some situations this is in contradiction with the increase of Li and A/CNK in rocks. The compositional features emphasize the increase of Fe/(Fe+Mg) values at constant Al contents, which suggests a metaluminous origin, the strong octaedric substitution Al<sup>IV</sup>→Ti and the annite-siderophyllite tendencies. In alkaline system the biotite shows a large variation in tetrahedral aluminium (1.87 - 2.80) and is relatively iron-rich - Fe/(Fe+Mg) ranging from 0.52 to 0.86. The values of Fe/(Fe+Mg+Mn) and Mn/(Fe+Mg+Mn) ratios increase with decreasing temperatures during ferromagnesians crystallisation at equilibrium with fluids. Therefore, we consider that the onset of the biotites and amphiboles crystallisation is a very important step in metallogenic history of alkaline granitoidic system, because in this moment the fluids have a major role. If the oxygen buffers the crystallisation of biotite, for decreases with temperature. The incorporation of halogens in the biotite structure is controlled by Mg-Cl and Fe-F avoidance, by substitution in octaedral site and by variation in composition of fluids (f<sub>HE</sub>/f<sub>HCI</sub>). Another important aspect is the colour of the biotite that can be used to establish the trend of magmatic evolution. The red biotite enriched in Fe2+ and Ti is characteristic for the reduced peraluminousperalkaline granites. The green or greenish brown biotite enriched in Mg, Mn and Fe3+ is typical for the complex metaluminous-peraluminous-peralkaline trend.



### PETROGENETIC SIGNIFICANCE OF SODIC AND CALCIC AMPHIBOLES FROM A-TYPE GRANITOIDS, NORTH DOBROGEA, ROMANIA

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A-type granitoidic rocks crop out in Alpine Măcin Unit at Secarul, Piatra Roşie and lacobdeal hills. Petrotypes forming the A-type granitoidic association are:

Plutonites in the following succession (from E to W):

- sodic amphibole and/or pyroxen bearing subsolvus granites (SAPSG);

- quartiferous hypersolvus syenites (QSH);

- calcic amphibole bearing subsolvus granites (CASG);

- sodic pyroxen and/or amphibole bearing hypersolvus granites (SPAHG)
- Hypabisic or subvolcanic rhyolites.

Chemical composition of amphiboles is directly correlated with the chemistry of the A-type granitoidic rocks containing them.

The microprobe investigation reveals that the amphibole crystals are chemically homogeneous, excepting the frequent magnetite and ilmenite inclusions.

The classification presented by Leake *et al.* (1997) has been used for the characterization of the amphiboles. Sodic amphiboles from the North Dobrogea peralcaline rocks belong to riebeckite – arfverdsonite series and the calcic ones belong to the actinolite series. In the hypothesis that the two chemical different granitoides (hypersolvus and subsolvus) were cogenetic, in a reducing environment, the A site was occupied by the alkalis according to the following ion exchange:

- CaAl ⇔ NaSi and
- Fe<sup>3+</sup> ⇔ Na<sup>A</sup> Fe<sup>2+</sup>

The initial water content of the granitic magma determines its mobility and the crystallization processes. 4% H<sub>2</sub>O at 2 kbar (or 3% H<sub>2</sub>O at 8 kbar) are the conditions for the crystallization of hornblende from a granodioritic magma. The sodic amphibole crystallizes in the late stages, when the magma water content increases due to the crystallization of anhydrous minerals.

The characteristic temperature of the solidus line in F-rich magmas is below 600°C, while in magmas with a low F content it is 700°C. The rare fluorite crystals identified do not justify a low temperature for the beginning of the crystallization processes. Therefore, the low content of F suggests a temperature over 700°C for the solidus line.



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