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**Abstracts** 

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This volume comprises abstracts of papers to the XI General Meeting of International Mineralogical Association (IMA) presented at the sessions: rock-forming minerals; typomorphism of minerals; sulphosalts and platinum minerals; mineralogic criteria for the relationship between acid magmatism and ore mineralization.

The volume is intended for the broad section of specialists in mineralogy, petrology, geochemistry and processes of ore-formation.

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**ROCK-FORMING MINERALS** 

CHEMICAL CHARACTERISTICS OF THE ROCK-FORMING MINERALS AS CRITERIA FOR EVALUATION OF FLUID REGIME OF MIGMATITE FORMATION

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Some new evidence have been obtained for the association:quartz + plagioclase + K-felspar + Al<sub>2</sub>SiO<sub>5</sub> + garnet + biotite + cordierite, which may serve as a complex mineralogic thermobarometer. They, however, are poorly correlated with the modern interpre tations requiring special consideration. To the above evidence we assign: a) essential variations in the mineral compositions (Fe/Fe + Mg ratio of garnet and biotite varying by 20 at.%) within the small sites having the dimensions at most 10 x 15 km which belong to homogeneous geologic structure having undergone one-stage regional metamorphism, b) deviations from the univariant relationship unrelated with the change in the minor component activity (regression in MnO, TiO2, CaO, etc. concentrations with deviation from the univariance to differ from the functional dependence); c) in the samples of the given paragenesis including  ${\rm Al}_2{\rm SiO}_5$  -sillimanite (in some cases) as polymorph or andalusite (in some other cases) there has been observed an existence of a very high overlap region for the Fe/Mg + Fe ra tio of the garnet (for sillimanite-bearing rocks the Fe/Mg + Fe ratio of the garnet varies from 56 to 92 at.%, while for andalusite-bearing rocks it varies from 68 to 92 at.%).

The above given evidence permits one to suggest that the final metamorphic crystallization of migmatites even in the near-by sites is associated with the same epoch of metamorphism, though it fixes here some unsynchronous moments of mineral formation, and different P,T and water activity. This fact is provoked by the inhomogeneity in the degree of saturation of the rock series with anatectic melts. This may be responsible for the large spread in the partition coefficient values for Fe and Mg between garnets and bictites for one and the same values of Fe/Mg + Fe ratio of the garnets as well as some great variations in the H<sub>2</sub>O content in bictites, which, for example, for the sillimanite-bearing samples vary between 2.2 and 4.5 wt.%

The indicated differentiation in geologically homogeneous migmatite rock series with respect to P,T and especially water activity at the time of final metamorphic crystallization is a serious actual argument against the existence of the frontal fluid fluxes ascending from the Mantle, which would inevitably align conditions of metamorphism.

PECULIARITIES IN ROCK-FORMING MINERALS IN SUCCESSIVE GENERATIONS OF POLYCHRONOUS METAMORPHIC ROCK COMPLEXES

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In recent time still more data are being available for a polychronous (multi-staged) formation of metamorphic rock complexes of various types: from gneissic-pegmatitic to eclogite-glaucophanic ones. This phenomenon is strikingly observed in gneissic-pegma titic complexes of mobile belts. In the structure of these rock complexes two main structural elements are recognized: 1)a gneissic core which is a mobilized block of crystalline basement and 2) shaly framing of geosynclinal rock series which have undergone thermal and dynamic effects of diapiroidal transformation of the gneissic core. The complex and a long-time tectonic-metamorphic formation of gneissic-pegmatitic rock complexes may be subdivided into two main stages, with the two stages of metamorphic transformations manifested in the older rocks of gmeissic core , while only later stage is manifested in the shaly framing. The paper treats the peculiarities in the rock-forming minerals comprising the paragenesis of different stages of metamorphism in the main structural elements of metamorphic complexes.

The relict mineral paragenesis of the earlier stage of metamor phism is found mainly in the basic rocks; it is the following orthopyroxene (bronzite) + clinopyroxene (diopside-hedenbergite) + plagioclase  $(An_{42-58})$   $\pm$  garnet ( f = 81-90)  $\pm$  biotite (f = 35-38)  $\pm$  edenite (?). Crystallochemical formula of garnet from the paragenesis:

$$(Fe_{1,43}^{+2} \quad Fe_{0,03}^{+3} \quad Mg_{0,24} \quad Ca_{1,18} \quad Mn_{0,06})_{2,94} \quad (Al_{1,92} \quad Fe_{0,08}^{+3})_{2,00}$$
 $Si_{2,99} \quad O_{12}$ 

Paragenetic associations of later stage of metamorphism are:

- 1) in the rocks of gneissic core in metabasites: hornblende (f = 60) + plagioclase (An<sub>25-35</sub>)±
   garnet (f = 81) ± biotite (f = 36-39) ± gedrite;
   in metapelites: plagioclase (An<sub>18-25</sub>)+ quartz + biotite (f =
  35-37) + garnet (f = 79) + kyanite + K-felspar;
- 2) in the rocks of the inner zone of shaly framing in metabasites: hornblende (f=49) + plagioclase (An<sub>20-24</sub>)
   + garnet (f=82) + gedrite + biotite (f=39-40);
   in metapelites: quartz + biotite (f=38) + muscovite + garnet
   (f=90) + kyanite (+ staurolite, plagioclase) (An<sub>12-20</sub>);
- 3) in the rocks of outer zone of shaly framing in metabasites: actinolite (f=30) + clinozoisite + epidote + garnet + plagioclase (An<sub>6-11</sub>), in metapelites: quartz + muscovite + garnet (f=85) + biotite (f=40-42) + epidote + chlorite + kyanite + plagioclase (An<sub>3-8</sub>).

The crystallochemical formulas of the garnets from the above mentioned associations are:

1) 
$$(Fe^{+2}_{1,83}Fe^{+3}_{0,13}Mg_{0,62}Ca_{0,15}Mn_{0,02}^{2}_{2,75}(Al_{1,96}Fe_{0,042,00})$$

2) 
$$(Fe^{+2}_{1,91} Mg_{0,51} Ca_{0,43} Mn_{0,13})_{2,98} (Al_{1,80} Fe^{+3}_{0,04})_{1,84}$$

3) 
$$(Fe^{+2}_{2,14} Mg_{0,31} Ca_{0,31} Mn_{0,07})_{2,83} (Al_{1,81} Fe_{0,08})_{1,89}$$

Thus the successive changes in the generations of the rock-forming minerals in the course of time depended on decreasing level of regional metamorphism from Pre-Cambrian to Upper Paleozoic. ZONING NATURE OF THE ROCK-FORMING MINERALS AND THEIR GENESIS

### I.T. Rass, Moscow, USSR

The leading methodological trend of modern petrology is parage - netic analysis of mineral associations; its origin was developed by D.S. Korjinsky. Paragenetic analysis is based on the differential mobility of components and local equilibrium concepts. Until recent time it was based on the data for the gross chemical composition of minerals. Plagioclases alone, whose chemical compositions have a simple relation with optical parameters were an exception. A microprobe application to petrology offered an opportunity of quantitative determination of zoning (or heterogeneity) of all other minerals of variable composition, reflecting thus the changes in physico-chemical conditions of crystal genesis.

Zoning in the rock-forming minerals fixes the changes in the successive equilibria between the surficial layers of the solid phase and the liquid phase; this results from different rates of crystallization and diffusion in solids (the former being greater than the latter).

Investigations of the zoning nature in minerals permit one to use a new genetic approach (proposed by Kravchenko S.M., Boronikhin V.A. and the present authors) to distinguish the metasomatic and magmatic rocks of similar composition: in case of fractional crystallization the mineral zoning is described by a diagram of melting, whereas zoning of the rock-forming minerals of metaso-matic genesis cannot be determined from melting correlations. The latter was not experimentally investigated.

The data obtained for the mineral zoning in metasomatic rocks provides a new evidence. It permits one to know: 1) type of metasomatic process, 2) to use an additional criterion for the determination of the degree of approximation of the mineral parageneses to equilibrium conditions, 3) to elucidate the correlation between the mineral composition and the level of chemical potentials of the perfectly mobile components, 4) to provide a quantitative estimation of the displacement in the local equili-

bria as a function of intensive parameters changes.

The data on the component distribution in the minerals of magmatic rocks provides the following opportunities: 1) to guess about the initial temperature by means of the two-mineral geother - mometers, 2) to classify the differential rock types (when fractionation for micro-and macro-trends coinside), 3) to draw up a genetic picture (when microfractionation trend of the ore component fits the definite genetic model).

The investigations of zoning in metamorphic rock-forming minerals permit one to solve the problem of the process duration and the direction (progressive or regressive), as well as the pressures in definite temperature facies.

BEHAVIOUR OF THE TRACE ELEMENTS IN THE ROCK-FORMING MINERALS OF IGNEOUS ROCKS

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Numerous chemical data on the rock-forming minerals of magmatic rocks allows one to understand (with some approximation) a certain trend in the behaviour of some chemical elements of mine -rals successively discharged from the magmatic melt.

Among the peculiarities in the trace element distributions in minerals of basic rocks we would mention some contradictions (a kind of antagonism) in the behaviour of certain chem\*cal components.

A typical example of the behaviour is nickel (Ni) and cobalt(Co) on the one hand, and vanadium (Va) and scandium (Sc), on the other. The former are mainly concentrated in minerals that had been discharged from the magmatic melts (i.e. in olivine and pyroxene), while vanadium and scandium behave quite differently.

From the distribution manner of the trace elements in the rockforming minerals of the acid rocks, one can find a peculiar behaviour of a number of volatile and ore components. The main mass of the latter is available in minerals which are relatively rich in volatiles (F, OH, etc.).

The behaviour of the trace elements of minerals of alkaline rocks has its specific features, especially in some elements (Sr, etc.).

One of the problems is the behaviour and the form of the existence (presence) of platinoids in minerals of ultrabasic rocks.

In certain rock-forming minerals the conjugation of some main components with the trace elements is observed.

Some rock-forming minerals which appeared under various thermodynamic conditions are characterized by different amounts of certain chemical elements. The probable reasons for this phenomenon are considered.

ROCK-FORMING MINERALS IN ABYSSAL SECTION OF PRE-CAMBRIAN EARTH'S CRUST

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Pre-Cambrian Earth's Crust forms the greater part of continents. On the surface of recent erosional section on shields in the limits of various blocks there crop out rocks formed on various depth. Complex investigation of these formations - geological, petrological, petrophysical with the data of abyssal geophysical investigations (seismometry, gravimetry, magnetometry) allow one to draw abyssal sections of the Pre-Cambrian Earth's Crust.

For the Pre-Cambrian Crust of the Ukrain and Baltic shields on the basis of circumstantial data it was possible to obtain abyssal sections up to 30 km. They are of three types; the first characterizes the regions of wide display of the Archean and Early Proterozoic granitoids with the most widely represented "granite" layer, the second - the regions of display of the Archean and Early Proterozoic basic rocks with the most widely re presented "basaltic" layer; the third - regions of development of the Middle Proterozoic basic rocks in tectonic structures superposed on the Archean formations.

In general form the vertical abyssal section of the Pre-Cambrian Earth's Crust may be the following: from 0 to 7-10 km there predominate the basic magmatic rocks of the Middle Proterozoic (or the Early Proterozoic) metamorphosed in the conditions from prehnite-pumpellyite to epidote-amphibolite facies.

"Granite" layer: from 7-10 to 12 km there predominate granitoid in epidote-amphibolite and amphibolite facies of metamorphism; from 12-15 to 20 km there predominate granitoids in granulite facies of metamorphism (Charnockite series).

"Basaltic" layer: from 20 to 25-30 km there predominate the basic magmatic rocks in granulite facies of metamorphism.

We studied a series of rock-forming minerals: plagioclases, felspars, quartz, hornblendes, garnets, biotites, pyroxenes which characterize this vertical abyssal section of the Pre-Cambrian Earth's crust up to 80 km in depth. For all femic minerals there are established the increase of magnesium content in their composition with depth and the decrease of parameters of elementary cells and the increase of density. For plagioclases there is established the increase of degree of structural irregularity. In quartz optical anisotropy and density increase.

IRON CONTENT OF SILLIMANITE AS A FUNCTION OF TEMPERATURE AND METAMORPHIC GRADE

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Sillimanite in regionally metamorphosed rocks is a binary solution  $(Al_{1-x} Fe_x^{3+})_2 SiO_5$ , where x ranges from 0.002 to 0.018. The iron substitutes for aluminum in both octahedral and tetrahedral sites in the sillimanite structure.

The increase in molar entropy of sillimanite,  $\delta\,\bar{s}$  , associated with the substitution of iron for aluminium is approximately:

$$\delta \bar{S} = x(\bar{S}_{hem} - \bar{S}_{cor}) + \bar{S}_{conf}$$

where  $\bar{S}_{hem}$  and  $\bar{S}_{cor}$  are the molar entropies of hematite and corundum and  $\bar{S}_{conf}$  is the configurational entropy associated with the distribution of aluminum and iron on the two sites in sillimanite. Because of this added configurational entropy, the iron content of sillimanite coexisting with quartz and hematite should increase with temperature. The limited data availa ble from natural systems are consistent with this prediction. Sillimenite associated with titaniferous hematite in granulitefacies rocks from Wilson Lake, Labrador ( x = 0.017 to 0.018 ) and Labwor, Uganda (x = 0.013 to 0.015) is richer in iron than that found with titaniferous hematite in amphibolite-facies rocks from Taos, New Mexico (x = 0.007) and Glen Clova, Scotland (x ≤ 0.011: Chinner, Smith and Knowles, 1969, Am.J.Sci., v. 267A, p. 69). The Wilson Lake hematite contains 19 to 20 mole percent FeTiO, in solid solution, whereas the Labwor and Taos hematites appear to contain more than 20 percent FeTio3 (no data available on Glen Clova). These differences in hematite composition are probably not sufficient to account for the diffe rences in sillimanite composition.

In some cases, however, the iron content of a given rock may decrease with metamorphic grade, particularly, in ilmenite-bearing rocks. This decrease would be associated with a general "reduction" of the host rock that accompanies increasing metamorphic grade, such as, for example, the reduction of hematite

to magnetite commonly observed in low-grade rocks. The decrease in iron content of sillimanite is suggested by analogy with andalusite, in which ferric iron also substitutes for aluminum in two sites. Evidence for a decrease in iron content in andalusite with increasing temperature is that cores of zoned and alusite in some contact aureoles contain considerably more iron than the rims: this zoning is reported by Okrusch and Evans (1970. Lithos, v. 3, p. 261). A decrease in iron content with temperature may also explain why andalusite associated with sillimanite in the aureoles described by Okrusch and Evans contains up to twice as much iron as sillimanite in the same rock. This difference has previously been attributed to unequal partitioning of iron between coexisting andalusite and sillimanite. The decrease in iron content with temperature in the AloSiOs minerals may be related to dehydration reactions among the silicate mi nerals, by analogy with Thompson's (Proceedings, Inter. Geol. Congress Montreal, 1972) proposed explanation for the reduction of hematite to magnetite.

HIGH-MAGNESIAN GARNETS OF DIAPHTHORITES OF THE HIGH-PRESSURE POLYMETAMORPHIC COMPLEXES

### A.I. Belkovsky, Miass, USSR

Garnets from the Ufalei metabasitic association as an example show that grossular-almandine of eclogitized hornblendites-eclogite-like rocks-eclogites are replaced with time by high-magnesian grossular-almandines of apoeclogitic amphibolites , which in turn are transformed into the high-magnesian Ca-alman dines and almandines of metasomatites of the quartz-paragonite and quartz-ferrimuscovite facies. Garnets of the eclogitized hornblendites and eclogite-like rocks contain up to 40% calcic and 5-10% pyropic components (ao= 11,707 Å) and garnets of paragonite-quartz and ferrimuscovite-quartz metasomatites contain 18-6% calcic and up to 20% pyropic components (ao= 11,529 Å). A size of an edge of the elementary cell of the later generations reduces by 0.178Å. The P-T conditions of the formation of poly-and bimineral metasomatites with the high-magnesian garnet are discussed in the report.

FACTORS DETERMINING THE COMPOSITIONS OF THE ROCK-FORMING MINERALS OF SCHISTS IN METAMORPHIC ZONING OF MODERATE PRESSURES

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The chemical composition of rocks and coexisting minerals in metapelites, meta-aulerolites and metagraywackes were studied in the crossing metamorphic zoning of Central Khamar-Daban area. The grade of metamorphism changes from biotite-chlorite zone (greenschist facies) to sillimenite-orthoclase zone (amphibolite facies). The migmatization front and pegmatite-bearing bands coincide with the boundaries of metamorphic zoning. The chemical compositions of rocks are constant for a majority of petrogenetic and rare elements up to the zones of granitization. The rocks lost only water and carbonaceous matter. The SiO<sub>2</sub>, Na<sub>2</sub>O and partly FeO concentrations increase in the zone of migmatization.

The comparisons of petrogenetic and rare elements contents in biotites, amphibolites and garnets of the rocks of all varieties from successive metamorphic zones has shown that the initial chemical composition of the rocks, their parageneses and PT-conditions of metamorphism produce varying effect on the compositions of the studied minerals.

Some of the minerals such as biotite and chlorite are the controlling conditions as buffering phases. Their compositions depend largely on the varied initial rock composition, their paragenesis, and in a lesser degree on the change in the PT-conditions.

The type of garnet reflects the initial rock composition. The change in the garnet composition in a succession of metamorphic zones is based on the pressure and temperature in that the garnet Fe content (iron index = Fe/(Fe+Mg)) reflects the type of facial series by pressure, while the Ca and Mn contents reflect the temperature zoning. The applicability of the garnet-biotite geothermometry is discussed for a series with high Mn-garnet.

Most of the complications are connected with the classification of factors affecting the amphibole composition. Interbedding of cummingtonites and hornblend parageneses with calcic plagicclases

is but well manifested. There is observed an influence of the low  $P_{\rm CO_2}$  (during earlier stage of metamorphism) on the genesis of tremolite and hornblende-bearing parageneses including a basic plagicclase. The change in the iron index of amphiboles in successive metamorphic zones depends greatly on the mineral parageneses (on initial chemical composition of the rocks).

As for the PT-conditions of metamorphism, the trace elements such as Ba, Rb, Be may provide a greater information, while am - phiboles provide a smaller one.

THE PRINCIPAL ISOMORPHOUS SERIES AND MICA NOMENCLATURE

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The recent data on the chemical composition, structure and physical characteristics of natural and synthetic micas permit one to consider them as a complex solid solution of many di-and trioctahedral members (minals).

Structurally the micas are subdivided into three types: diocta - hedral (octahedral occupancy, Y = 2.0 - 2.45), trioctahedral (Y = 3.00 - 2.65), mixed and intermediate (Y = 2.45 - 2.65). The de termination of a considerable isomorphous miscibility of dioctahedral and trioctahedral mica components and, firstly, in the composition field of lithium muscovites, lithium phengite-muscovites, zinnwaldites and protolithionites is important. The range of the miscibility gap between the di- and trioctahedral micas depend on their composition, temperature and fluorine activity.

The following main series are distinguished in the multidimensional compositions field of natural potassium micas: biotites series; muscovite-seladonite series; muscovite-biotite; biotite-lepidolite and a new series of phengite-muscovite-protolithionite-zinnwaldite and protolithionite-lithium annite. The compositional variations in the series are approximated by rather simple schemes of replacing or correlating the minals. The mineral species and subspecies of dioctahedral, trioctahedral and inter-

mediate micas are distinguished in the series. The composition field boundaries of subspecies in the series are considered as to physical characteristics variations of the micas.

In stable conditions there is an obvious trend in the mineral species and subspecies of micas to crystallize to form definite mostly simple forms of polytypes. The polytypism of micas depends firstly on their composition and growth conditions. Temperature, pressure and composition of the system affect the polytypism as much as they do the mica composition, crystallization mechanism or the level of structural control.

The chemical composition, the structure and ability of micas to mutual solid solutions are assumed as a basis for the suggested nomenclature of potassium micas of the biotite-muscovite-lepido-lite system. A number of diagrams as: "composition-2V,Ng'", Ng-2V-composition, polytypism", "composition-polytypism", "composition-unit cell parameter", "composition-thermic characteristics" illustrate the correlation between the chemical composition and the physical characteristics of micas. The diagrams may be used to determine micas.

The evolution of chemical composition and the distribution of the trace elements in natural micas series of different paragenetic groups are investigated as to their genesis conditions fixed for granitoids, ongonites and pegmatites (over 500 original analyses). BEHAVIOUR OF LITHIUM IN TRIOCTAHEDRAL MICAS: A KEY FOR THE GENERALIZATION OF A CRYSTAL CHEMICAL THEORY GOVERNING ION EXCHANGE REACTIONS INVOLVING ALKALINE CATIONS

### J.L. Robert and M. Volfinger, Orlean, France

Among alkaline cations, lithium is known to have peculiar properties due to its smaller size. The coordination number of Li<sup>+</sup> is usually 6, whereas it is 8 to 12 for Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>. Then, what will be the behaviour of lithium during the reaction of a trioctahedral mica (phlogopite) with solutions of LiCl under hydrothermal conditions (600°C, 1 kbars)?

Two cases may happen during such a reaction:

- Li<sup>+</sup> replaces Mg<sup>2+</sup> in the octahedral sheet; this replacement is accompanied by complementary substitution(s) involving Si,Al,Mg to compensate the charge imbalance. These substitutions may lead to three trioctahedral lepidolites:

taeniolite	K <sub>2</sub> (Mg <sub>4</sub> Li <sub>2</sub> )Si <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub>
trilithionite	K <sub>2</sub> (Al <sub>3</sub> Li <sub>3</sub> )(Si <sub>6</sub> Al <sub>2</sub> )0 <sub>20</sub> (OH) <sub>4</sub>
polylithionite	K <sub>2</sub> (Li <sub>4</sub> Al <sub>2</sub> )Si <sub>8</sub> O <sub>2O</sub> (OH) <sub>4</sub>

-or, Li<sup>+</sup> replaces K<sup>+</sup> in the interlayer sheet, as the other alkaline cations do. This reaction would lead to a lithium phlogopite.

Experiments have been performed at 2 kbars from 400°to 900°C to know the extent of solid solutions between phlogopite and each of the previous lepidolitic end-members and the properties of the obtained micas. The main results of this study are: the (OH) lepidolitic end-members are not stable; the solubility limit of these lepidolites in phlogopite increases when temperature decreases (up to 70 moles percent of taeniolite in phlogopite at 400°C); in the three series of micas,  $d_{005}$  and  $d_{060}$  decrease as linear functions of the lithium content:  $d_{005}(\text{Å}) = 2.033 - 0.4135.10^{-6}\text{X}$ ;  $d_{060}(\text{Å}) = 1.535 - 1.235.10^{-6}$  X (X ppm of Li). These relations are valid for the three series.

The exchange reactions between phlogopite and solutions of LiCl lead to mices whose  $d_{060}$  is quiet constant, and whose  $d_{005}$ 

obeys the relation  $d_{0.05}(\mathring{A}) = 2.0333 - 4.583.10^{-6}X$  ( x ppm of Li) A simple comparison of these reticular distances with that of the previous case shows that Li + enter the interlayer sheet under these conditions. One can prove that Li + does not occupy the position of K+ in that sheet but another cavity rounded by 6 oxy gens, whose localization is discussed. This observation permits to understand the abnormal behaviour of lithium during ion exchange reactions. It was recently proved that the partitioning coefficient of an alkaline cation X (Na+, Rb+, Cs+) between a hydro thermal solution and a potassic mineral is a function of a structural parameter  $\partial = \zeta + \zeta_0 - d_{\kappa-0}$ , where  $\zeta$  and  $\zeta_0$  are the ionic radius of the alkaline cation X and oxygen. The relation of the partitioning coefficient of Li with that parameter is abnormal. But, considering the real cavity occupied by Li+, one can generalise the above relation, defining a  $\partial' = \Gamma_X + \Gamma_O$  d<sub>C-O</sub> where C is the center of the occupied cavity. This relation is valid for all the alkaline cations.

SUBSOLIDUS RELATION STUDY OF THE SKAERGAARD PYROXENES BY ANALYTICAL ELECTRON MICROSCOPY

### N. Morimoto, K. Nobugai and M. Tokonami, Osaka, Japan

Within augite and pigeonite grains of the Skaergaard ferro-gabbro 4430, the Ca-poor phases contain only three mol percent of CaSiO<sub>3</sub>, and the Mg-Fe partition coefficients between the Ca-poor and Ca-rich phases are extremely small with 0.46 for augite and 0.50 for pigeonite grains. These values indicate existence of diffusion within each grain (intra-granular diffusion) at considerably low temperatures.

The compositions of the Ca-rich phases in augite and pigeonite grains are different from those of the Ca-poor phases in augite and pigeonite grains. This indicates that the diffusion among the grains (inter-granular diffusion) has not taken place under the subsolidus condition of the Skaergaard intrusion.

THE CALCIC AND ALKALI PYROXENES OF THE OSLO PERMIAN IGNEOUS COMPLEX: CHEMISTRY AND OPTICAL PROPERTIES

### R.A. Howie and Z. Ali, London, England

The variation in the chemical composition among pyroxenes from the Oslo alkaline complex (kjelasites, larvikites, lardalites, ekerites, nepheline syenites, essexites and pyroxenites) has been studied in detail. Chemical analyses, optical properties and specific gravities have been determined for a total of 39 pyroxenes from this complex, including 16 salites, 13 augites, 4 aegirine-augites and 6 aegirines (taking the boundaries for the last three species as 0-15, 15-70 and > 70 mol% aegirine end-member composition). In the calcic pyroxenes virtually straight-line relationships are observed between specific gravity and the Mg/Fe<sup>2+</sup> ratio, and between tetrahedral Al and total Al; the limits of calcic pyroxene composition are close to Fe<sub>14</sub> - Fe<sub>25</sub> mol.%. In the alkali pyroxenes, (Mg+Fe<sup>2+</sup> + Mm) varies directly with Ca, (Na+K) varies directly with (Fe<sup>3+</sup> + Ti + Al<sup>IV</sup>), and (Na+K) varies inversely with Ca; there is also a general increase in specific gravity with increase in the aegirine content.

### TRANSFORMATION OF PIGEONITE AND HYPERSTHENE

### K. Nobugai and N. Morimoto, Osaka, Japan

Natural pigeonite has been transformed to hypersthene by heating the crystals embedded in plastic at 200°C. The produced hypersthene always shows augite lamella parallel to (100). This indicates that pigeonite does not invert but decomposes to hypersthene and augite. The mechanisms of the decomposition of pigeonite has been studied by examining the synthetic hypersthene by high resolution and analytical electron microscopy.

MICAS FROM PHLOGOPITE-BEARING PROVINCES OF THE EAST SIBERIA

### Z.I. Petrova, V.I. Levitsky, Irkutsk, USSR

Micas from metasomatites to occur in Aldan and Near-Baikalia phlogopite-bearing provinces are studied. The mica-bearing rocks are in all ancient series of basic composition, metamorphosed in granulitic facies and afterwards exposed to a high-temperature diaphthoresis in conditions between granulitic and amphibolitic facies and those of amphibolite facies metamorphism.

Micas were formed during some stages of metamorphic processes. They take part in the composition of some metasomatic bodies developed during ultrametamorphic and postmagmatic stages. Phlogopites from the ore shows and deposits were formed during the post magmatic stage of recrystallization of the earlier phlogopite-bearing rocks. In spite of a broad variation in the chemical composition, all the studied micas belong to the phlogopite-annite series with a significant quantity of eastonite (siderophyllite) component. The chemical composition of micas depends almost likely (1) on the composition of the initial and enclosing rocks to show very distinctly in the general Fe-content (iron index =Fe/Fe + Mg) (0.5 - 16.0) and Al index (micas of metasomatites from carbonaceous beds and near them are distinguished by a lower Fe content and higher Al-content) (2) on the general chemical trend in the metamorphic process and consequently on the period of the genesis and position in some definite parts of the zoning metasomatic bodies ( micas of the external zone and of the earlier stage differ regularly from the compositions of micas from the inner zones and later stages). Micas of the deposits contain al ways more F and less Fe than the micas of more widespread phlogopite-bearing rocks. In the studied micas the levels of Ba.Sr. Rb, Li, Co, Ni, Cr, V, Sn, Ce, Nd, La, Y and Yb contents depend in a lesser degree on the initial rock composition and in a higher degree on the general chemical trend of metasomatic processes (higher Ba, Rb, F and other elements are contained in micas of later stages and inner zones of metasomatic bodies). Ba-phlogopites containing up to 8.5% BaO were found to occur in the Near-Baikalia. Their geologic position, as well as chemical

and rare-metal composition have been studied. The detailed investigations established an isomorphous Ba entering the mica structure by the following scheme: (Ba+Al<sup>IV</sup>) — (K+Si).A discovery of the high Ba-phlogopites in nature confirms the idea about a wide compositional variations in trioctahedral micas making possible the existence of Ba-variety in the group of brittle micas.

The existence of regional average fluorine content anomalies has been discovered along with the regular (normal) fluorine content variation in phlogopites depending on their origin time and the position of metasomatic body zoning: phlogopites from the Aldan region are characterized by higher F contents than similar phlogopites from Near-Baikalia, especially, Slyudy-anka region.

STRUCTURAL VARIATIONS IN LITHIUM MICAS IN THE LIGHT OF ELECTRON DIFFRACTION DATA, NOMENCLATURE AND CLASSIFICATION PROBLEMS

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Lithium micas are distinguished by wide isomorphic substitutions both in octahedral and tetrahedral positions, by replacements of OH for F and by the existence of species which are intermediate between the di- and trioctahedral micas.

The existing classifications of the lithium micas based on the peculiarities in the chemical composition (occupation of the octahedrons by lithium and divalent cations) ignores the structural variations and has some contradictions as to the data obtained by different authors. Besides the position of (Li,Fe)-micas recently found in rare-metal granites has not been established.

The detailed mineral-structural study of the systematic collec tions of lithium micas permitted one to obtain some new data and to refine in some respects the existing classification of lithium micas.

By the nature of replacement in the octahedral positions in the

group of lithium micas, the trioctahedral micas can be distinguished, in which the replacement of Si-Al is practically absent (polylithionite, tainiolite) and the di-trioctahedral micas, in which the Al<sup>IV</sup>content varies from 0,5 to 1,5 (units by the formula) (protolithionite, zinnwaldite, lepidolite, Li-muscovite, Li-phengite).

ISOMORPHISM AND ORDER-DISORDER IN MICAS BASED ON IR-SPECTROSCOPY

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The IR-spectra investigations of the monocrystal species of both di-and trioctahedral micas shows the local symmetry peculiarities in polyhedrons, proton group positions and structural order - ing.

Ordering as an invariant state of structuré is considered with reference to cation and anion positions in all symmetry operations.

The cation distribution in the non-equivalent cis-and transoctahedra is elucidated for the absorption band frequency positions. A discontinuity in the biotite-phlogopite series (the lack of the miscibility gap is 30% of the Fe content) and the order of Fe in the phlogopite lattice was observed. It is expected that there exist some partially ordered vacancies in the octahedral layer and a statistical distribution of Al in biotite.

The Si-Al order in tetrahedrons depends on the crystallization conditions: process duration, temperature, pressure and alkalinity of environment. The position of OH-stretching vibrations occur as a function of Si-Al order and local symmetry of tetrahedral layer as well as nature of the interlayer cations.

It is shown (for muscovite from rare-metal pegmatites) that the spectrum configuration in the OH-stretching vibration region depends on the formational conditions and distinct for the micas of various genesis. It is supposed that Si-Al order in Rb muscovite (polytype 2M<sub>1</sub>) is a consequence of large interlayer cation of Rb entering.

The IR spectra characteristics (OH-structural position, the band width, the position and the degree of splitting of the absorption band) may be considered as a typomorphic sign of specific di-and trioctahedral micas.

SPURRITE, TILLEYITE AND GEHLENITE IN THE ROUMANIAN CARPATHIANS

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In the southern part of the Apuseni Mountains (western Roumanian Carpathians) there have been identified spurrite, tilleyite, and gehlenite, rarely occuring minerals, formed in the contact aureoles at high temperature and low pressure. They make up the monomineral rocks or are found in association with spinel, wollastonite, garnet, vesuvianite and calcite to give rise to calc skarns at the contact of shallow Laramian quartz-monzodicritic intrusion with neo-Jurassic limestones.

When considering the field data, one may distinguish the following zones developed outwards from the contact:

- 1) the gehlenite zone + garnet, wollastonite, vesuvianite;
- 2) the spurrite zone + andradite;
- 3) the tillegite zone;
- 4) calcite marble.

There are presented physico-chemical, X-ray, DTA and infrared data for spurrite, tilleyite and gehlenite, abyssophobe minerals typical of the spurrite-merwinite facies and as possible genetic conditions we assume the temperature exceeding 750°C and up to 250-300 bar total pressure.

DIOCTAHEDRAL AND TRIOCTAHEDRAL POTASSIUM MICAS: COMPOSITIONAL LIMITS

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Over 600 analyses of potassium micas published in the literature were recalculated to crystallochemical formulas and sequestered in groups according to their crystallochemical acceptability. The attention was concentrated on analyses including determination of lithium and on pairs of coexisting micas or micas from phase associations requiring limiting mica compositions. A tetrahedral graphical grid used for plotting was tested for response to possible impurities, analytical deficiencies and simplifications involved in data processing.

The distribution of octahedral compositions in trioctahedral micas confirms the Mg-Fe<sup>2</sup>+ and Fe<sup>2+</sup>-(Li.Al) substitution series as dominant. The data do not suffice to prove or disprove the possible miscibility gap between Mg and (Li,Al) trioctahedral micas. Octahedral substitutions in muscovite avoid the direction towards Fe<sup>2+</sup> and prefer Mg and (Li.Al) with (Li.Al): Fe<sup>2</sup>= 1:1. The data available yield a new insight into the miscibility gap between dioctahedral and trioctahedral micas. The miscibility limits are defined reasonably well over most of the dioctahedral side, less so on the trioctanedral side. The reasons for the lower order among the limiting trioctahedral compositions may be due to a number of factors, with evidence pointing to lack of thermodynamic equilibrium as a chief cause. Idealized diagrams showing the phase chemistry in potassium micas were constructed that will hopefully provoke a search for the new data, both natural and experimental.

RELATIONSHIP BETWEEN CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF METAMORPHIC ORTHOPYROXENES

Michael Raith, Kiel, FRG

The relationship between the physical properties and chemical composition of the orthopyroxene series has been studied repeatedly during the last three decades (c.f. Hess 1952, Kuno 1954, Howie 1963, Winchell and Leake 1965, Smith and Stevenson 1969).

The published correlation diagrams exhibit, however, only a poor correspondence and a rather large scatter of the data. This is caused by (1) low number of samples, (2) the presence of exsolved phases and impurities in the samples analyzed by wet chemical techniques, and (3) the different origin of the orthopyroxenes (volcanic-magmatic, metamorphic).

In the present investigation a thorough reexamination of the relationship between physical properties and chemical composition of metamorphic orthopyroxenes has been carried out. For this purpose, cell parameters, optical properties and magnetic susceptibility have been measured for 60 orthopyroxenes from granulite facies rocks. Mineral compositions have been determined by microprobe and the Fe<sup>3+</sup> content and the Fe<sup>2+</sup>-Mg partition by Mossbauer spectroscopy.

On the basis of these new data and selected data from recent literature, refined diagrams were derived relating (1) cell dimensions to Mg, Al, and Ca (2) ny to  $\sum$  Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn, Ti,(3)  $2V_{\rm X}$  to Mg and Al, and (4) magnetic susceptibility to total Fe content. These diagrams enable the determination of the Mg, Al and  $\sum$  Fe, (Mn,Ti) contents with an accuracy of 0.03 atoms per formula unit (based on 6 oxygens).

Mössbauer spectroscopic studies and preliminary heating experiments on the investigated samples demonstrate that the degree of  ${\rm Fe^{2+}}$  - Mg order decreases not only with rising temperature but also with increasing Al content (Seifert, pers.comm.). Thus, the observed strong positive correlation between the optical angle  $2{\rm V}_{\rm X}$  and the Al content may partly be attributed to the different degree of  ${\rm Fe^{2+}}$ -Mg order.

### ON THE COMPOSITION OF CLINOPYROXENES FROM IGNEOUS ROCKS

### I.Ya. Tsenter. Leningrad. USSR

In the course of investigation of clinopyroxenes from lavas of basalt-andesitic association with normal alkalinity and hyperal-kalinity (Cenozoic and Mesozoic volcanogenous formations of the Minor Caucasus) it is established that the variability of clinopyroxene composition is characteristic of all the studied associations.

Examples of such variability on various scales are considered:

- a) within one flow from the chilled zone to its central part:
- b) in one rock from phenocrysts to microlites of the groundmass;
- c) in some flows around quartz xenocrysts crystallizes pyroxene the composition of which differs greatly both from that of phenocrysts and of microlites:
- d) within one zoned crystal the range of composition variation can be not less than in the above-mentioned cases. A difference though a slight one, is established in the composition of sectors in crystals having the structure of a "hour-glass" type.

In each case typical examples of the trend character are given based on the results of chemical or electron microprobe analyses and X-ray powder diffraction data.

Pyroxene composition is jointly influenced by crystallization temperature, cooling rate and melt composition (including the strong influence of its alkalinity) which are as a rule dependent variables.

Volcanic associations having different composition, differentiation degree and tectonic position differ from each other namely in the character of variability of pyroxene composition, peculiarities of isomorphous replacements connected with each trend type.

### CRYSTALLOCHEMISTRY OF Ti IN NATIVE CLINOPYROXENES

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### Leningrad, USSR

The presence and relative content of Ti in tetrahedral position (Tiz) of clinopyroxenes (Kn) from diopside-augite series established from the volcanogene and intrusive rocks of the Urals and Altai-Sayan folded region were determined by IR spectroscopy. From the earlier established characteristic areas of absorption for variations of the Ti-0 bond in octahedrons of Ti06 (400-600 cm<sup>-1</sup>) and tetrahedrons of Ti04 (700-800 cm<sup>-1</sup>) the band of absorption 765 cm<sup>-1</sup> of the IR spectra investigated by Kn refers to the valence variations of Si-0-Ti type. The optic density values of the band of absorption (D) were used for estimating the relative content of TiZ. The sensitivity of the method does not exceed 0.01 of the atomic units or 0.2 - 0.4wt%.

The analysis of the distribution of Ti in Kn structure witness the possibility of its entering into the tetrahedron irrespective the quantity of Al which suffices for the filling of deficiency of silica. The crystallochemical formula of Kn, containing Ti in tetrahedron is represented by the following formula:

$$(R^{2+}R)_{M_2} (R^{2+}R^{3+}Ti_{1-x})_{M_1} (Si^{4+}R^{3+}Ti_x)_Z$$

The favourable factors for Ti to enter in tetrahedral position of Kn are the following:

- a) the increase in the degree of undersaturation of rocks in SiO2;
- b) irregularity in crystallization of Kn either from the hightemperature dry fusions in chilling conditions (effusive rocks) or in conditions of strong hypercooling of the fusion and high pressure for volatiles (intrusive rocks);
- c) the definite order of separation of minerals: plagioclase iron-magnesial silicates iron-titanium oxides.

CLINOPYROXENES FROM ALKALINE ROCKS OF THE TURIJ PENINSULA

### E.P. Sokolova, T.L. Kochurova, Leningrad, USSR

Investigations of clinopyroxenes from alkaline-ultrabasic rcck complex (Turij Peninsula), such as pyroxenites, nepheline pyroxenites melteigites, ijolites and urtites have shown that their compositions correspond to the general course of evolution of the magmatic process.

Clinopyroxenes of complex and variable compositions, stipulated by simultaneous manifestation of both isovalent isomorphism between magnesium and iron in  $\rm M_1$  octahedron, between calcium and iron in a large structural polyhedron  $\rm M_{II}$  and Mg in  $\rm M_{II}$ , between Si and Al in tetrahedron, but also of the two types of heterovalent isomorphism with simultaneous substitution of cations in two structural positions according to the following schemes:

$$(Mg,Fe)_{VI}$$
 +  $Si_{IV} \rightleftharpoons (Al,Fe^{3+})_{VI}$  +  $(Al,Fe^{3+})_{IV}$ ;

$$Ca_{VIII} + (Mg, Fe)_{VI} \rightleftharpoons Na_{VIII} + (Fe^{3+}, Al)_{VI}$$

Difficulties in using the nomenclature for diagnosis of clinopy-roxenes of the above composition, to represent it in form of minals (components) is quite obvious. The analytical approach to recalculations of the results obtained from chemical analyses for the minal compositions with crystallochemical formulas and the unitary cell parameters taken into account.

It has been crystallochemically proved (parameters, IR spectro - scopy) the tetrahedral coordination of Ti in the clinopyroxenes under study with the lack of deficiency in the threevalent iron and sometimes even aluminium.

### CRYSTAL-CHEMICAL STUDIES ON SODIC CLINOPYROXENES

### G. Rossi, V. Tazzoli, L. Ungaretti, Pavia, Italy

Seventeen sodium-bearing clinopyroxenes from different metamorphic facies have been investigated by means of crystallographic analysis. The X-ray diffraction data were collected using an automatic single crystal diffractometer. The same procedures were followed both in the X-ray data collection and in the refinement in order to ensure the maximum possible homogeneity in the experimental data and in the crystal-chemical results. The final discrepancy factors (R) range from 0.02 to 0.04 for the reflections with intensities greater than three standard deviations. The site occupancy refinements were carried out without any chemical constraint and the results are compared with the data of the conventional chemical analyses.

Nine of the examined pyroxenes are ordered omphacites with P2/n space group. In four of them ordering of the divalent and trivalent cations into M1 and M1(1) sites of Na and Ca into the M2 and M2(1) sites approaches the maximum. In these samples the reflections with h+k=2n+1 (class  $\underline{b}$ ), examined with the single crystal diffractometer and with precession photographs, appear sharp. In the remaining P2/n omphacites incomplete ordering occurs-even for chemical compositions which are typical of fully ordered omphacites - and the class  $\underline{b}$  reflections are diffuse. As for pigeonites, the phenomenon could be related to the domain structure and to the thermal history.

The examined eight disordered C2/c pyroxenes comprise omphacites, aegirine-augites and impure jadeites (some of them have unusual compositions) which were never studied from a crystallo - graphic point of view. The variations of the structural parameters with chemical composition and some peculiar features of the electron density will be discussed.

CLINOPYROXENES OF THE ROCKS OF DIFFERENT VOLCANIC ASSOCIATIONS

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Leningrad, USSR

Comparisons of the composition, crystallochemical peculiarities and trends in the clinopyroxenes from the rocks of various basicity from volcanic associations of different types and ages were carried out (using the data from 200 analyses of clinopyroxenes and corresponding rocks).

The most significant differences were established in the clinopyroxenes in the course of comparisons of associations of essentially porphyric (where clinopyroxenes form phenocrysts) and aphyric rocks. In the former ( unlike the latter ones) clinopy roxene is characterized by higher Ca- and Si-content as well as lower Fe2+ and Ti content crystallochemically expressed by a lower value of the parameter "b" and the sudden increase in "a.sin B". The main trend in clinopyroxene from aphyric associations coincident with rock differentiation of Fenner type) results in Fe<sup>2+</sup>, Fe<sup>3+</sup> and Ti increase at the expense of Si, Mg and Ca, whereas in porphyry associations ( due to a differentiation of Bowen type) - it results in Si and Fe increase at the expense of Al. and more rarely Ti. The former trend reflects the increase in "A" and "c" values, while the latter reflects the decrease in the "c" parameters of elementary cell. The above mentioned differences in clinopyroxenes may be explained by crystallization conditions (shallow or intratelluric) also by the position of pyroxene in crystallizing mineral series, crystallization temperature, which, in turn, depend on water saturation of melts.

The increase of alkalinity in the rocks (both in aphyric and porphyric varieties) results in the increase of Al, Ti, Fe<sup>3+</sup>, also Na and Ca content in clinopyroxenes at the expense of Si, Fe<sup>2+</sup> and Mg. The degree of alkalinity plays a leading role in heterovalent replacement in clinopyroxenes compared with isovalent ones.

Variations in the clinopyroxene composition associated with the

rock occurrence in the magmatic bodies are seen in the  $Fe^{3+}$ , Al, Ti content increase at the expense of Mg and Si(in the flow top rocks) and in Ca, Mg increase at the expense of  $Fe^{2+}$  (in central parts of sills and dykes). They are determined mostly by the volatile behaviour in open or closed systems.

CLASSIFICATION AND RATIONAL NOMENCLATURE FOR THE CALC-SODIC AMPHIBOLES BASED ON DISTINGUISHING SEVERAL TYPES OF HETEROVALENT SUBSTITUTIONS

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The Ca-and Na amphiboles represent a multicomponent solid solution based on tremolite. The need to classify these minerals according to the nature of heterovalent substitutions is generally accepted. A series of finite members is distinguished, such as edenite, tschermakite, glaucophane, etc. However, it is sometimes difficult to define the degree of proximity of a given compound, analysed for a particular finite member.

Leak's classification according to which the mineral composition boundaries are outlined by certain numerical intervals of individual element contents is not invariably and completely consistent with the actual relationship between heterovalent substitutions.

To provide a full description for heterovalent isomorphism in amphiboles, separation of the five types of cations and two types of anion-cation heterovalent substitutions is considered as necessary and sufficient. A volume of each of the substitutions would be expressed by a set of structural positions, in which the given substitutions occur, i.e. the quantity of atoms per formula unit participating in this particular substitution.

We propose to subdivide all the Ca- and Na amphiboles into tschermakite, edenite-tschermakite, glaucophane, glaucophane-tschermakite, glaucophane-edenite-tschermakite and others by their relative role played in different types of heterovalent substitutions in their composition. Either oxidation or hydration may be

added to each of these combinations. When classifying amphiboles the total volume of heterovalent substitutions should be taken into consideration.

THE CORRELATION BETWEEN THE SYMMETRY OF Ca-RICH PYROXENES AND THE CONDITIONS OF THEIR ORIGIN

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The structure of three clinopyroxenes with the crystal-chemical formulae (Ca $_{0.90}$  Na $_{0.06}$  Mg $_{0.72}$  Fe $_{0.25}^{2+}$  Fe $_{0.05}^{3+}$  0.05 Al $_{0.05}$ )(Si 1.90 Al $_{0.09}$  Ti  $_{0.01}$ )06-semple /1/; (Ca $_{0.77}$  Na $_{0.01}$  Mg $_{0.67}$  Fe $_{0.48}^{2+}$  Fe $_{0.06}^{3+}$  Al $_{0.01}$ ) (Si  $_{1.94}$  Al $_{0.06}$ )06 - sample /2/; (Ca $_{1.00}$  Fe $_{0.81}^{2+}$  Mn $_{0.13}$  Mg $_{0.05}$  Al $_{0.01}$ ) (Si  $_{1.99}$  Al $_{0.01}$ )06 -sample /3/ is refined using the single-crystal X-ray method. The samples are, selected from the rocks of hornblende-granulite subfacies (~700°C) of middle pressures.

The unit-cell parameters are a=9.737(4), b=8.898(4), c=5.270(3)  $\mathring{A}$ ,  $\mathring{\beta}$  =106.11(3) for the sample /1/; a=9.766(2), b=8.958(3), c= 5.246(2)  $\mathring{A}$ ,  $\mathring{\beta}$  =105.70(2) for the sample (2); a=9.852(4), b=9.031 (3), c=5.242(3)  $\mathring{A}$ ,  $\mathring{\beta}$  =104.84(4) for the sample /3/. The average distances T-0 for the samples /1/, /2/, /3/ are 1.640; 1.638; 1.636 $\mathring{A}$ , respectively  $\mathring{\delta}$  M1-0 are 2.068; 2.093; 2.134 $\mathring{A}$ , M2-0 are 2.496; 2.501; 2.514  $\mathring{A}$ .

The increase of  ${\rm Fe}^{2+}$  in M1 position leads to deformation of all polyhedrons, their coordination being preserved to change the bond lengths and distortion of tetrahedral chain.

The samples /1/ and /2/ have some weak reflections (10-15% of the whole number) of hkl type with h+k=2n+1 violating C2/c symmetry, showing that the symmetry of these samples is lower than C2/c.

The structure refinement of the sample /1/ heated in vacuum  $(1000^{\circ}\text{C}, 1000 \text{ hrs}, \text{pO}_2 = 10^{-5}\text{mm} \text{ Hg})$  indicates the rotation of tetrahedra around the edge 03-03 and alteration of all bond

length. The intensity of reflections with h+k=2n+1 essentially diminishes representing the increase of symmetry of initial sample with heating.

Two polymorph modifications of Ca-rich pyroxenes are proposed: high-temperature (C2/c) and low-temperature ones with the symmetry lower than C2/c.

PARTICULAR FEATURES OF KAOLINISATION OF ROCK-FORMING MINERALS IN CRUSTS OF WEATHERING

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The clay minerals formed at the early stages of weathering of alumosilicates have been studied with an electron microscope vacuum decoration method.

The particularities of kaolinisation of the rock-forming minerals are determined primarily by their composition differences (they define the type of a newlyformed mineral) as well as by their physical properties (they define the particular conditions of clay mineral crystallization). Kaolinite is formed as a result of weathering of potassic minerals only (microcline, muscovite, biotite) whereas halloysite is formed from the Ca-Na minerals and montmorillonite is formed from the Ca-Mg ones.

Three consecutive stages of kaolinite crystal growth have been found: a) growth of one-layer rhombic or pseudo-hexagonal nuclei reaching the first hundredths of micron; b) dendritic growth of the two-dimensional nuclei and formation of flattened one-layer and multilayer dendrites of several dozens of microns; c) three-dimensional crystal growth by layer and layer-spiral mechanisms; d) pseudomorphic growth as a result of simultaneous dissolving of the host mineral and overall kaolinite crystal growth.

When kaolinite is formed on microcline there is no dendritic growth stage. The two-dimensional nuclei grow to form the three dimensional kaolinite crystals by layer and layer-spiral mechanisms. As a microcline has several cleavage systems, the kaolinite pseudomorphs on this mineral have a lower degree of orientation than on micas. Depending on the composition plagioclases change differently in the crust of weathering: the acid plagioclases give rise substantially to halloysite, the basic onesto montmorillonite.

MINERALOGICAL INVESTIGATION OF MONCHIQUE NEPHELINES (ALGARVE, PORTUGAL)

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The use of nepheline for the extraction of its aluminium is of great interest. This fact would bring us to study this mineral on samples from nepheline syenites from the Monchique massif, where the nepheline content is variable over a large range ( 30 to 0 per cent by weight).

Fourteen samples have been examined by X-ray diffraction; these studies, in addition to the usual petrographic work, allowed us to conclude that the nephelines are partially replaced by different secondary minerals like analcite and cancrinite. The results of this investigation have shown that the Al content, in the nephelines, is lower than in the pure mineral.

We are studying the field variation of the ferrous iron by the Mossbauer spectrometry method.

Simultaneously the nephelines are being analysed with the electron microprobe.

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The non-alkaline pyroxenes rich in both titanium (above 2.5 wt % of TiO<sub>2</sub>) and alumina are as a rule referred as titanaugites. Similar pyroxenes can be found in different parageneses, therefore they are rather differentiated depending on the contents of the three main cations(Ca,Mg and Fe). The most calcic pyroxenes(Ca content exceeding 50% vs the sum of the indicated cations) are regarded as titanfassaites. They are characteristic of hornfelses and scarns as well as of some types of base-nites, etc.

As a particular example of a wide development of titanfassaites from different associations we take the Tazheran alkaline mas - sif (West Near-Baikalia); the detailed characteristics of the main peculiarities in the developed titanfassites are given.

Titanfassites developed in hornfelses of gabbroic type at the contact of the latter with marbles. They are the black anchimonomineral rocks in the form of reactionary metasomatic border within hundreds of meters. Titanfassites contain 2.5-3.0% of  $TiO_2$ , 7-9% of  $Al_2O_3$ , 6-11% of  $FeO+Fe_2O_3$  (wt.%).

Titanfassaites being the principal mineral in some spinel-pyroxene scarns formed due to the interaction of nepheline syenites with dolomites. Owing to titanfassaite these scarns are characterized by the violet colour. The titanfassite contains 3-4% of titanium oxide, 6-10% of Al<sub>2</sub>O<sub>3</sub> and 2-3% of FeO+Fe<sub>2</sub>O<sub>3</sub>(wt.%). From the chemical analyses of special sort it was found that most of the titanium in this pyroxene is in trivalent state. It was shown that scarns involve up to 5% of pyrrhotite. Titanfassites from hornfelses are associated with magnetite, and the trivalent titanium is not available.

Titanfassites being present in the composition of garnet-melilite-wollastonite rocks. The latter sporadically contain calcite, kirsteinite, cuspidine, kalicilite, nepheline, perovskite, troillite and jerfisherite. This paragenesis is rather similar to the association of the Allende meteorite with rather titanic fassai-

tes.

These three variations of titanfassaites from Tazheran were metasomatically formed during the magmatic stage of intrusive formation under the conditions of high temperatures (up to  $1000^{\circ}$ C) and small pressures (less than 1 kb) and under varying reduction-oxidation conditions.

GENESIS OF PAMBAK PSEUDOLEUCITES (ARMENIA),

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The characteristic feature of the Oligocene Pambak volcano-plutonic alkaline complex is a wide development of pseudomorphs after leucite in all types of the alkaline rocks: volcanic (leucite trachytes, phonolites, leucitophyres, italites), subvolcanic(leucite phonolite-porphyries, trachy-phonolite-porphyries, intrusive (different types of pseudoleucite syenites, syenite-porphyries , tephrites and leucitite) rocks.

Among the rocks containing pseudomorphs after leucite the epileucites and proper pseudoleucites are distinguished. On the basis of crystallomorphological, mineralogical, phase-chemical and X-ray investigations the typification of epileucites (6 types) and pseudoleucites (5 types) was done, which enables to determine conditions of their genesis.

Among the epileucite rock groups the mineral parageneses consisting of 2-3 as well as 4-5 phases are distinguished and that is connected with the direct transformation of the primary leucite into the analcite, orthoclase, muscovite, on the one hand, and with the alteration of the pseudoleucite into the epileucite, on the other hand (where pseudomorph filling minerals are muscovite, paragonite, natrolite, thomscnite albite, sodalite and cancrinite). In the chemical composition of the epileucites the constancy of the inert components and constant deficiency in the alkaline group (5-20%) are found.

In the intrusive endomorphic nepheline syenites proper pseudoleucites (besides the widespread cvoid-polygonal aggregates) often

form the well-shaped triakisoctahedron crystals, which are filled with the micrographic aggregates of the intergrowths of orthoclase and nepheline in the 3:1 ratio. As compared with leucite whose hypothetic composition was recalculated after a crystallochemical formula, a constant substitution of 30-35% of potassium atoms by sodium in the pseudoleucites, and an increased content of Fe<sup>3+</sup>, as well as rather unusual high concentrations of Rb, Cs, Ba, Be (3-5 times) are observed.

It is established that in comparison with nepheline syenites , the nepheline-orthoclase paragenesis of the pseudoleucites is a lower temperature (700-800°C and 500-550°C respectively). In the main mass of pseudoleucite syenites the orthoclase (the  $0{\rm r}_{65}{}^{\rm Ab}{}_{35}$  content) associates with nepheline (Ne $_{80}{}^{\rm Ks}{}_{20}$ ) and in the pseudoleucites which were poor in sodium, the orthoclase (0r $_{90}{}^{\rm Ab}{}_{10}$ ) coexists with rich potassium nepheline Ne $_{70}{}^{\rm Ks}{}_{30}{}^{\star}$ 

The analysis of petrogenetic peculiarities of the Pambak volcano-plutonic complex helps to determine the following temperature conditions of leucite crystallization in the alkaline rocks i.e. T=1150-900 in the volcanic stage (P\_s=2000 bar) and the intrusive stage (P\_H\_0 =1000 bar, T=800-700). The possibility of existence (in conditions of increased sodium content in the melt and of unquilibrated crystallization) is proved for the high-temperature solid solution of leucites (28-40 NaAlSi\_20\_6) which transforms (T inversion = 600°C) into the pseudoleucite without the participation of fluid phase: KNa-leucite  $\rightarrow$  KNa -orthoclase  $\rightarrow$  KNa -nepheline.

### SODIUM IN LEUCITE AND ITS PETROGENETIC SIGNIFICANCE

### J.Roux & W.S. Mackenzie\*. Orlean, France

Part of the join KA1Si<sub>2</sub>O<sub>6</sub>-NaAlSi<sub>2</sub>O<sub>6</sub>-H<sub>2</sub>O has been re-investigated at P<sub>H<sub>2</sub>O</sub> =1 kb and 750<sup>O</sup>C in order to resolve the conflict between experimental data which indicates on the one hand fairly extensive solid solution of sodium in leucite at 760<sup>O</sup>C (FUDALI, 1963) and on the other hand very limited solid solution in natural leucite and experiments at lower temperatures.

The results of this study indicate that the solution of sodium in leucite is metastable under the conditions of formation; an even more extensive metastable solid solution than has been previously demonstrated is possible. These solid solutions, which may persist for long periods, are responsible for the existence of pseudo-leucites. From the experiments the range of composition of pseudo-doleucites can be explained.

Discussions of the significance of potassium-rich rocks should not exclude the pseudoleucite rocks since these are in many cases as rich in potassium as many leucite bearing rocks.

PSEUDOLEUCITE FROM TEZHSARSK, USSR, AND ITS GENESIS

Kenzo Yagi and Alok K. Gupta, Sapporo, Japan

The pseudoleucite from Tezhsarsk alkalic complex, Armenia, USSR, forms beautiful icositetrahedral crystals, 3-5 cm in diameter, in the porphyritic tinguaite. The host rock consists of potash feldspar, nepheline, plagioclase, biotite, aegirine-augite and hastingsite and has high contents of  $\rm K_2O$  and BaO and low contents of MgO and Na<sub>2</sub>O (Table 1). The pseudoleucite is composed mainly of potash feldspar ( $\rm Or_{92}Ab_8$ ) and nepheline ( $\rm Ne_{87.9}~Ks_{3.0}~Qz_{9.1}$ ) with small amounts of sericite, biotite, analcite, kaolinite.ti-

tanite and epidote. Chemically it is very high in  $\rm K_2O$  and very low in  $\rm Na_2O$  and the ratio of  $\rm K_2O/Na_2O$  is the highest among the pseudoleucites from the world (Table 2). It is worthy of noting that the crystal has well-preserved original crystal form of leucite and that the whole crystal consists of fairly homogeneous aggregates of potash feldspar and nepheline.

From these features it is concluded that the leucite which crystallized out from the tinguaitic magma reacted at subsolidus temperature with the Na-rich fluids in the later stage of crystallization, and changed into aggregates of potash feldspar and nepheline by solid reaction, accompanied by K=Na substitution.

Table 1 PSEUDOLEUCITE TINGUAITE, TEZHSARSK, USSR

SiO <sub>2</sub>	51.57	Or	53.93	
TiO <sub>2</sub>	0.76	An	15.57	
Al <sub>2</sub> 0 <sub>3</sub>	20.90	Le	3.92	
Fe <sub>2</sub> 0 <sub>3</sub>	1.98	Ne	12.78	
FeO	1.79	Wo	1.74	
MnO	0.21	En	1.00	
MgO	0.68	Fs	0 <b>.6</b> 6	
CaO	3.97	Fo	0.49	
$Na_2^0$	2.78	Fa	0.31	
K <sub>2</sub> 0	10.23	Mt	2.66	
H <sub>2</sub> 0+	3.73	Il	1.22	
H <sub>2</sub> 0	0.12			
BaO	0.56			
P <sub>2</sub> O <sub>5</sub>	0.12			
Total	99.40		Analyst: S.	Kanisawa

<sup>\*</sup> On leave of absence from Manchester University.

Table 2. ANALYSES OF PSEUDOLEUSITES FROM VARIOUS LOCALITIES.

	1	2 2	2 3 3	3 4	5	6	7	8	9	
$5i0_2$	60.06	55•55	55.06	58.15	58.30	<b>56.</b> 9	56.26	57.42	57.46	
TiO2	0.28	0.11	-	-	-	0.1	-	0.24	0.07	
A1203	21.39	22.27	25.26	23.66	23.80	22.6	21.93	21.85	21.94	
Fe <sub>2</sub> 0 <sub>3</sub>	0.29	1.66	-	1.59	-	0.6	0.67	1.70	0.66	
FeO	N.D.	0.33	-	-	-	-	0.00	0.00	0.13	
MnO	0.03	tr.	-	-	-	-	-	0.03	0.04	
MgO	0.08	0.09	0.28	0.21	0.17	-	0.00	0.07	0.00	
CaO	0.39	2.16	0.06	0.43	0.96	1.3	1.46	0.19	0.20	
Na <sub>2</sub> 0	2.85	2.80	7.60	7.08	5.80	3.9	4.95	4.78	4.78	
к20	12.33	10.37	10.34	8.49	10.94	10.8	10.63	13.40	13.76	
H <sub>2</sub> 0+	2.28	4.09	1.78	1.35	-	3.5	4.16	0.27	0.36	
н <sub>2</sub> о-	0.07	0.99			-	-	4.10	0.03	0.00	
Rest	-	-	-	-	_	-	-	0.28	0.50	

Total 100.05 100.42 100.92 100.96 99.97 99.7 100.06 100.26 99.90

- 1. Tezhsarsk, Armenia (Yagi and Gupta, This paper)
- 2. Tzu Chin Shan, China (Yagi, 1954)
- 3. Magnet Cove, Arkansas (Williams, 1890; cited by Knight, 1906)
- 4. Spotted Fawn Creck, Yukon Territory (Knight, 1906)
- 5. Vesuvius, Italy (Knight, 1906)
- 6. Highwood Mountains, Montana (Larsen and Buie, 1938)
- 7, Loch Borolan Laccolith, Scotland (Shand, 1939)
- 8. Bearpaw Mountains, Montana (Zies and Chayes, 1960)
- 9. Bearpaw Mountains, Montana (Fudali, 1963)

### CRYSTAL-CHEMICAL CHARACTERIZATION OF BLUE AMPHIBOLES

L. Ungaretti, F. Mazzi, G. Rossi and A. Dal Negro, Pavia, Italy

Twenty-six crystallographic refinements of blue amphiboles have been carried out in the glaucophane-ferroglaucophane-riebeckite triangle. No magnesioriebeckite has yet been found among the numerous samples (about 100) analyzed with single crystal diffractometry.

Experimental data have been collected by means of a four-circle automatic diffractometer following, as much as possible, a similar strategy for all the samples; also the refinement procedures have been performed following the same scheme, in order to obtain homogeneous results. The chemical composition of the sites involved in isomorphous replacements has been deduced on the basis of crystallographic parameters.

Among the samples which have been refined 11 are, according to a generally accepted nomenclature, glaucophanes, 4 are ferroglaucophanes, 8 are crossites and 3 are riebeckites. In these refined blue amphiboles Fe<sup>3+</sup>, Fe<sup>2+</sup> and Ca<sup>2+</sup> range respectively bet ween 0.0 and 1.9, 0.55 and 2.74, 0.0 and 0.16 atoms per formula unit. No significant Al-Si replacement has been observed and the occupancy of the A site is quite negligible.

The results of the refinements allow to say that Fe<sup>3+</sup> is always ordered in the M2 site, independently from the Fe<sup>2+</sup> content; Fe<sup>2+</sup> occupy the M1 and M3 sites following an hyperbolic distribution which favours the M3 site; M-O distances are in good agreement with the chemical composition of the sites deduced from the refinements. Cell parameters have been plotted against the iron content of the octahedral sites, finding, however, poor correlations, due to the complex pattern of the isomorphous replacement; the best correlation occurs between the a parameter and Fe<sup>3+</sup>content. The de-hydrogenation of one riebeckite has been studied with single crystal diffractometry heating the sample at 500°C for 3 days; the same crystal has been used for X-ray data collection before and after the heating treatment. The de-hydrogenation, consequent to the oxydation of Fe<sup>2+</sup>, is accompanied by a complete rearrangement of the M cations.

AMPHIBOLES IN SULPHIDE COPPER-NICKEL ORES (EXEMPLIFIED BY THE NORTH-WESTERN KOLA PENINSULA)

### A.K. Yakovleva, Yu.N. Yakovlev, Apatity, USSR

Amphiboles are the most wide-spread secondary minerals of metamorphosed basic rocks and ultrabasites with which the copper-nickel ores are dimensionally and genetically related being the constituent of disseminated epigenetic ores. In ores and contact aureoles they are represented by two groups:Ca-amphiboles as isomorphous series of tremolite-actinolite and hornblendes (actinolitic magnesio-tchermakite) and Fe-Mg-Mn-amphiboles as a series of anthophyllite-gedrite (anthophyllite, gedrite) and cummingto-nite-grünerite (P- and C-cummingtonite, grünerite, Mn-grünerite).

Amphiboles are united in two different groups by their age: early, considerably predominating, widespread, formed in conditions of different facies of regional metamorphism: greenstone slates (Pechenga region), amphibolitic (Allarechenski region) and granulitic (Lovozerski region) and late ones developed locally, formed in the process of contact metamorphism in conditions of the greenstone slate facies. Early amphiboles are represented by hornblendes and partially by Mg-cummingtonites (Allarecheski region) and late amphiboles are represented by actinolites, cummingtonites and anthophyllites. Hornblendes of granulite facies are mainly tschermakitic with a high Al and Ti content and of amphibolite one: magnesio-hornblendes with a high Mg content and alkali-deficiency.

Epigenetic disseminated ores are closely connected in time with mass amphibolization (early amphibole formation) of basic and ultrabasic rocks. Hornblendes form close intergrowths with sulphides. Late amphiboles are mainly post-ore: at this period local ore transformation and insignificant new formation of sulphides, mostly of chalcopyrite composition take place.

Amphibole composition depends on the total chemical composition of the original rocks, metamorphism conditions and the following transformation (repeated metamorphism, intensity of sulphide mineralization, crushing, mylonitization and etc.). P-T metamorph-

ic conditions dominate among these phenomena. In the case of sulphide mineralization, associated with the change in the PT metamorphic conditions, some new amphiboles can appear or the present ones can essentially change (for example, dynamic metamorphism in the rich ores of Allarechenski region causes magnesiocummingtonite to form with  $P_{2_{\perp}}/m$  cell).

ZONAL ARRANGEMENT AND THERMAL METAMORPHISM OF CARBONATE MINERALS TN THE UBÉ SERPENTINITE MASSES, YAMAGUCHI PREFECTURE, W.JAPAN

Goro Shibuya, Yamaguchi, Japan

Serpentinite masses in Ubé City, Yamaguchi Prefecture, West Japan develop in three regions; seashore (southern), middle and northern regions. Along 10 km of the seashore, there have been found three essential kinds of carbonate minerals, i.e. calcite, dolomite and magnesite, associated intimately with the serpentinite masses which intrude the Sangun metamorphic rocks. The carbonate minerals arrange regularly in the order of calcite, dolomite and magnesite from the central part of mineralization to the both outer sides in the masses, intercalating the transitional zones of calcite-dolomite paragenesis and dolomite-magnesite paragenesis. And to the further outsides, inversive repetition of this order is also recognised. At the northern region about 5 km apart from the seashore, the serpentinite masses contact directly with spacious granite mass of Cretaceous age, and are suffered by thermal metamorphism, resulting in the secondary generation of great va riety of minerals. In the northern region, carbonate minerals decrease in their quantity, compared with the seashore region, and the aragonite species of carbonate occurs predominantly with a small amount of calcite, dolomite and magnesite. And the restricted find is known of calcite-dolomite, dolomite-magnesite, calcite-magnesite. calcite-aragonite, dolomite-aragonite and magnesi te-aragonite parageneses, in which the latter four ones have never been found in the seashore region. This fact is supposed to be due to the metamorphism by thermal effect of the granite int rusion.

The minerals other than the carbonates having been found in the Ubé serpentinite masses are as follows: antigorite, clinochryso -

tile. orthochrysotile, six-layer orthoserpentine, lizerdite, olivine, hypersthene, augite, diopside, grossular, vesuvianite, tremolite, actinolite, talc, clinozoisite, epidote, biotite, muscovite, fuchsite, vermiculite, chlorite, albite, orthoclase, microcline, natrolite, prehnite, sphene, quartz, cristobalite, chalcodony, saponite, montmorillonite, halloysite, allophane, deweylite, chromite, picotite, magnetite, hematite, goethite, pentlandite, millerite, vioralite, heazlewoodite, bravoite, chalcopyrite, cubanite, bornite, chalcocite, digenite, covellite, pyrrhotite, pyrite, marcasite, mackinawite, maucherite and niccolite.

THE ENIGMATIC ROLE OF C1 IN THE ALTERATION OF ULTRAMAFIC ROCKS

J.C. Rucklidge, Toronto, Canada

Several lines of evidence suggest that a compound with the likely composition of (Fe,Mg)<sub>2</sub> (OH)<sub>3</sub>Cl acts as an intermediate phase in the serpentinisation of olivine. This phase, which is stable only with pH > 7 is created when olivine is exposed to acid brines and forms in submicroscopic particles in the resulting alkaline environment. As alteration proceeds the fresh acid brines dissolve and remove the hydroxy-chloride phase, taking Fe and other metals into solution. Increases in fO<sub>2</sub> or fS<sub>2</sub> may cause precipitation of Fe in the form of magnetite or sulphides in alteration veins away from the reaction front, as commonly observed in serpentinites. A Cl halo can be seen, on a microscale, surrounding the actively altering areas of olivine but this is a temporary feature, which vanishes when alteration is complete and there is no further buffering of the acid brines.

THE COMPOSITION OF OLIVINES FROM ULTRAMAFIC ROCKS OF SIBERIAN PLATFORM

Yu.R. Vasiljev, A.V. Sobolev, O.S. Chmel'nikova, Novosibirsk, Moscow, USSR

Application of MS-46 ("Cameca") electron microprobe permitted one to determine the major and minor element compositions (Ti, Al, Mn, Ni, Ca, Cr) in 150 olivines from various ultramafic type rocks of the Siberian Platform (dunites, meymechites, picrites and picrite porphyrites). The statistical treatment of the obtained data made it possible to fix the following results.

- 1. Ti and Al are absent or available in the amounts detectable by the apparatus in majority of olivines irrespective of the rock type.
- 2. The amounts of some other minor elements in olivines vary in a wide range: Mn 0.05-0.49,  $\bar{x}$ =0.20,  $\delta$ =0.06; CaO -0.01-0.79,  $\bar{x}$ =0.36,  $\delta$ =0.15; NiO 0.0-0.46,  $\bar{x}$ =0.22,  $\delta$ =0.05;  $\text{Cr}_2\text{O}_3$  0.0-0.18,  $\bar{x}$ =0.04,  $\delta$ =0.03 (wt.%).
- 3. According to the type of distribution of major and minor elements and correlations between them, the olivines were subdivided into, at least, 2 separate groups.
- a) Olivines from the dunites, meymechites, picrites and picrite porphirites are characterized by certain set of minor elements and correlations between them and FeO content. Olivines from komatiites and picrites, the diamond inclusions, peridotite xenolites in kimberlites are very similar to olivines from this group. However, this group is not uniform relative to Cr and Ca contents and their relations, allowing further subdivisions.
- b) olivines from olivinite massives of alkaline-ultramafic rock complexes are characterized by wide chemical compositions to differ from the group "a" in the distribution of minor elements, especially Ni and Cr. All the correlations between the minor elements and FeO content are not significant, except FeO-MnO.

The distribution of the minor elements in olivine is an important indicator of their origin.

MINERALOGICAL AND PETROLOGICAL ASPECTS OF OLIVINE-CHROMSPINEL PARAGENESES IN HYPERBASITES

### E.P. Tzaritsin, Sverdlovsk, USSR

Paragenetic analysis of olivine and chromspinel in rocks from the dunite-clinopyroxenite and dunite-harzburgite associations showed that chromspinels belonging to the dunite-clinopyroxenite association are represented by high-oxidised variaties rich in titenium. Their composition varies greatly both within separate samples and massives, over different massives and regions, that is related to the different level of high-temperature metamorphic effects and tectonic rocks movements. On dunites from this association the present olivine-chromspinel paragenesis corresponds to the granulite metamorphic facies with a temperature range from 600 up to 800°C.

Rocks of the dunite-harzburgite association are characterized with chromspinelide possessing a "universal" make up not only within separate massives (taking rock composition into account), but also within hyperbasite belts, geological regions and the planet in the whole. A great deal of feature (low oxidation degree, low titanium and high magnesium contents, isomorphism regularities and so on) make accessory chromspinelides similar or analogous to those from allied inclusions in oceanic and continental basalt rocks and kimberlites. Calculation of the KD (partition coefficient) values between olivine and chrome-Mg-Fe spinel makes it possible to speak of formation's temperature close to those of ultrabasic melt existence. Formation's temperatures of the ore-forming chrome-spinels are 150-250° higher than estimated values, established for the formation of their enclosing rocks (1300-1500°C against 1150-1300°C).

Both associations are characterized by widely displayed diffusion processes of solid matter at contact of two mineral phases (olivine and chromspinel) both at the grain boundary (duniteclinopyroxenite association) and at that of geological bodies (the dunite-harzburgite association).

Emil Jagoutz, Bernhard Spettel and Heinrich Wanke, Mainz, FRG

Olivine and pyroxene mineral separates were made by hand-picking under a binocular microscope from ultramafic nodules and archean ultramafics (komatiites). The separates were chemically and mechanically cleaned from surface contamination and minor phases.

<u>olivine</u>: Sr isotope systematics suggest that olivine is an open system for some incompatible elements in this type of samples. Ni, Cr and Sc show systematic variations. These elements are generally enriched in olivine from archean ultramafics, but Zn, Co and Mn are nearly constant in olivines from all samples investigated. Trace element contents can be used to identify cumulative olivine.

<u>Pyroxene</u>: On coexisting clinopyroxenes (in supposed cumulates) the concentrations of incompatible elements in clinopyroxene were studied. From the REE and partition coefficients from the literature possible coexisting liquids were calculated.

These calculated liquids show systematic chemical variations (in trace elements and Mg-values) and possible parent magma can be deduced by extrapolation. These liquids are compared with accepted primitive basalts.

NEW DATA ON THE MINERAL COMPOSITION OF THE PRODUCTS OF EARLY DUNITES SERPENTINIZATION

D.S. Shteinberg, I.S. Tchastchukin, M.V. Lagutina, Sverdlovsk, USSR

The separation of minerals forming the products of early dunite serpentinization by standard physical methods is impossible owing to their submicroscopical structure. We used therefore a group of specific methods: thermomagnetic one for qualitative determination of cohenite (Fe<sub>3</sub>C) with the Curie point at 210-215°C, a thermic for the estimation of iron content in brucite

according to its dissociation temperature, the dissolution of brucite in acetic acid for the determination of its chemical composition, a coulometric performed by the combustion of samples purified of brucite at 400°C (for carbide carbon) and 600°C (for free carbon) a chemical-analytical method for the determination of chemical composition of a thinly dispersed cohemiteserpentine mixture obtained by olivine and chromite separation in heavy liquids, while brucite - through dissolution in acetic acid.

The study of II samples of dunites from the Nizhny Tagil and the Kitlim massifs (Central Urals) with a different serpentinization degree established the following:

- a) serpentine consists of two minals  $H_4Mg_3Si_2O_9$  and  $H_4Mg_2Fe_2^{+3}SiO_9$ ; at serpentinization degree varying from 20'to 90%, the amount of  $H_4Mg_2Fe_2^{+3}SiO_9$  ranges from 16% (molecular) to 7,5%;
- b) at serpentinization degree varying from 0 to 100% the amount of cohenite ranges from 0 to 2%;
- c) Fe:(Fe+Mg)ratio in brucite decreases from 25 to 10%, while carbon dioxide contained in it drops from 10 to 2.5%, the amount of chlorine reaching 1 3%.

The above study confirms the earlier conclusion that serpentinization degree is defined by the conditions under which the process takes place, that is, the partial pressure of water coming from enclosing sequences and the temperature specified by it; i.e. serpentinization degree characterized definite meta morphic facies.

EVOLUTION OF CHROME-SPINELIDE COMPOSITION AT THE LOW TEMPERATURE METASOMATISM OF ULTRABASITES

V.N. Sazonov, Sverdlovsk, USSR

The change in the composition of chrome-spinelides at listvenitization of serpentinites and replacement of serpentinites by talc-carbonate rocks and quartzites is studied. In the apoharz-burgite lizardite serpentinites the grains of chrome-spinelides are usually homogeneous, and in the chrisotile-antigorite and antigorite the grains are heterogeneous with two peripheral zones developed: magnetitic (external) and Cr-and Al-magnetitic (internal).

At the chrysotilization and antigoritization of harzburgites Cr. Al. Mg are carried away from the marginal parts of the chrome spinelide grains, while Fe is introduced there. In the grain cores with a rise in serpentinization degree of ultrabasites the Cr.Fe3+content initially decreases, Al increases (replacement of lizarditization by chrysotilization), and vice versa the Cr. Fe3+ content increases, while Al diminishes (antigoritization). In replacing serpentinites by talc-carbonate rock, zones of magnetiza tion of chrome-spinelide grains are destroyed. Mg.Al are derived from grain cores, the Fe and Cr content increases. In aposerpen tinite listvenites relics of magnetisation zones of the mineral grains are destroyed and their cores become destroyed too. The trend in the compositional change of the latter is the same as that in the talc-carbonate metasomatites. During quarzitization of serpentinites the chrome-spinelide grains "are destroyed" and Mg, Fe, Al are extracted from them, and the Al content somewhat increases.

The evolution of the chrome-spinelide composition during the processes involved is determined by variations in P, T and particularly, pH,  $\mu$ CO<sub>2</sub>. It is quite natural, when it is considered that serpentinization of ultrabasites takes place in the alkaline environment of mineralization and the rest processes in acid one.

COMPOSITIONAL EVOLUTION IN CHROMESPINELLIDES FROM THE URALIAN ZONED ULTRAMAFIC COMPLEX

### O.K. Ivanov, Sverdlovsk, USSR

The dunite massifs intrude the Upper Silurian volcanic rocks of Tagil synclinorium. They provoke appearance of the hornfels and metasomatic pyroxenites with shaping of concentric haloes of hornfelsic rocks, tilaites and clinopyroxenites. The dunite nucleuses compose from four rock types. The first being fine-grained "protodunites" with equally distributed anhedral chromespinellides. Second, the "pseudodunites" with partially recrystallized grains of olivine and chromespinellide (inside and at the boundaries of olivine grains). The third, recrystallized dunites ("dunitoids") with variable grain sizes irregularly spaced chromespinellides. At last, the coarse-grained dunite-pegmatites with unequally spaced chromespinellides.

During recrystallization the dimensions of chromespinellides grains increase from 0.05 to 30 mm, the parameter value ao decreases from 8.367Å to 8.306Å, the magnetization decreases as well, the composition changes from chrome-magnetite to sub-ferrochromite. The oxide contents in wt% (Tagil'sk massif) are as follows: TiO<sub>2</sub> 0.6-0.3; Al<sub>2</sub>O<sub>3</sub> 7-9; Cr<sub>2</sub>O<sub>3</sub> 41.3-54.5; Fe<sub>2</sub>O<sub>3</sub> 19-10.4; FeO 21-13; MnO 0.5-0.2; CoO 0.05-0.02; MgO 5.4-13. The recrystallization of chromespinellides results in the in-crease of Cr, Mg and Ni contents, while Ti, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mn, V and Al contents and the degree of iron oxidation decreases. The amount of elements with relatively large ionic radius decreases too. The compositional evolution is caused by the take-off process of large cations during the postmagmatic recrystallization of orthomagmatic dunites.

### Z. Johan and L. Le Bel, Orlean, France

Several hypothesis of origin for chromite layers and podiform chromite have been proposed: contamination of basic magma with melted acid roof rocks (IRVINE, 1975), magmatic cumulation along the accreting plate boundaries (DICKEY, 1975), mixing of two mafic liquids of different compositions (IRVINE, 1977).

The study of chromitite layers in dunites occuring near the bottom of the ophiolitic complex of Al Ays (Saudi Arabia), composed mainly of olivine and clinopyroxene cumulates and emplaced in the Precambrian of the Arabic shield, showed the following features:

Chemical composition of massif chromite is distinctly different from disseminated chrome-spinel in dunites and other rocks.

Chromite layers contain always inclusions of olivine (subhedral crystals), amphibole and occasionally of clinopyroxene, never observed in disseminated chromite.

Fluid inclusions have been found only in massif chromite; they are lacking in other minerals, including disseminated chromite.

It should be noted that olivines occurring as inclusions in chromite are extremely magnesium-rich (Fo: 94.0 - 97.7 mol %), showing high chromium (up to 0.6 wt %  $\mathrm{Cr}_2\mathrm{O}_3$ ) and nickel (up to 1.0 wt % NiO) contents, but they are manganese-poor (0.0 - 0.2 wt % MnO). In contrast, olivines in dunites surrounding chromitite layers have Fo: 83.9 -90.7 mol %, are enriched in MnO (0.3 - 1.6  $\rm wt$ %) but poor in NiO (0.0 - 0.3 wt %) and very low in  $\operatorname{Cr}_2\mathsf{O}_3$  (0.0 -0.2 wt %). The included amphibole is a chromium-rich pargasite (up to 3.4 wt % Cr203). Rare clinopyroxene inclusions have a composition of chrome diopside En<sub>46</sub>,7-50.2 Fs<sub>2.1-2.3</sub> Wo<sub>51.2-47.6</sub> with 1.0 - 1.2 wt % Cr<sub>2</sub>0<sub>3</sub>. Equilibrium temperatures calculated for coexisting olivine-massif chromite range from 970° to 1050°C: the projection of the clinopyroxene composition on the pyroxene solvus gave 900°- 1000°C. These temperatures are significantly lower than those obtained for olivine-chromite pair in dunites: 1250 - 1350°C. Most fluid inclusions fill negative crystal ca vities. The fluid is anaqueous solution with 5 equiv. wt % NaCl,

containing minor CO<sub>2</sub>, CH<sub>4</sub> and heavier hydrocarbons, and having a density of 0.68 g/cm<sup>3</sup>. Homogeneization temperatures range from 337.5° to 357.5°C. Taking into account the equilibrium temperatures for the mineral assemblage in the chromitite layers and the isochore of the fluids, one obtains a pressure of 6-7 kbars. It is concluded that the origin of the chromitite layers could be explained by incongruent melting of highly chromium-rich pargasite, following the reaction: Pa — Chr + Ol + Liq + Fl.

THE COMPOSITION OF TRAPP MINERALS AS INDICATOR OF THE MAIN PETROLOGICAL PROCESSES

V.V. Ryabov, V.V. Zolotukhin, Novosibirsk, USSR

There are two viewpoints on the origin and composition of the trapp (tholeite basalt) magma: 1) the magma comes in its final form due to melting from the mantle rocks as much as from eclogites, quartz eclogites or pyroxenites with its composition corresponding to "average trapp"; 2) the initial melt has more basic composition, all the trapp varieties result from magmatic differentiation.

The composition of the main rock-forming minerals of trapps practically covers the whole range of isomorfic olivine series (from Fo to Fa), plagicclases (from An to Ab) and pyroxenes (from 8 to 100% ferriferous composition). The extreme compositions are fairly rare developing: high magnesial in the minerals of Norilsk-type intrusions, high-ferriferous in the the intrusions with Scaergaard scheme of differentiation. Most common are minerals enriched in ferriferous component, developed in rocks having chemical composition similar to "average trapp".

The variations in the mineral composition are correlated with those in the rock composition following a universal trend established in different trapp intrusions for the rocks of varying composition. Let us stress a close association between the upper differentiates, analogues of the "average trapp" and the

picrite gabbro-dolerites of Noril'sk intrusions as well as the constant cycle of Noril'sk region with picritic basalts to occur in effusives. This indicates to a more basic composition of the initial melt than that of the "average trapp".

The composition of clinopyroxenes varies regularly with the chemical composition of rocks, permitting one to separate very distincly the trapps from some different basaltoid formations. The universal trend in the chemical composition variations in the trapp minerals indicate to a consanguinity of the melts giving rise to their varieties as a whole.

Taking into account the presence of magnesial trapps, the initial magma is rather the product of melting of undereclogite material corresponding both to pyrolite and chondrite models of the upper mantle composition. The possibility of formation of the "average trapp" analogues as a result of melting of eclogites and pyroxenites is not excluded, though this model fails to explain the crystallization of the magnesial trapps.

The appearance of magnesial trapps as well as mineral deposits connected with them may be expected to occur, with the same probability on the whole area of the Siberian Platform under some definite structural and tectonic conditions.

TYPOMORPHISM OF MINERAL ASSOCIATIONS OF ULTRAMAFITES, ALKALINE MAPITES. ALKALINE AND NEPHELINE SYENITES OF ALDAN SHIELD

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During the Post-Archean magmatism there were formed some of the alkaline complexes of various age and formation appurtenance on the area of Aldan shield.

The rocks of various petrographic series: 1) ultramafites,2) alkaline-mafites, 3) nepheline-syenites, 4) alkaline-earth (alkaline granitoids) and 5) carbonatites take part in the composition of confocal massifs. Complex investigations of the rock-forming minerals has allowed one to establish their peculiarities.

Olivines of the ultramafite series are represented by several generations of various compositions. Pyroxenes are represented by augite-salites and titanous augite-salites. Spinellides are represented by magnoferrichromite and ferrichromite, magnetites by chromous magnetite and titanomagnetite. The composition of all the minerals depends on the position in the massifs and facial rock peculiarities.

The pyroxenes of alkaline-mafite series are represented by diopside-hedenbergite with varying contents of the acmite components and by disordered omphacite and acmite-diopside. Nephelines and pseudo-leucites are characterized by unconstant phase compositions and different degree of ordering. The K-Na feldspar is high orthoclase with various degrees of ordering. There also occur magnetite and ilmenite.

The pyroxenes of alkaline (nepheline-syenite) series are represented by acmite-salite-augite, jadeite-acmite and acmite with high Ti content. Amphiboles are represented by richterite and magno-arfvedsonites, micas are represented by biotite and lepidomelane. Feldspathoids are represented by epileucite and high potassic nepheline.

The pyroxenes of alkaline-earth series are hypersthene, diopside hedenbergite and acmite-diopside (with hornblende, plagioclase,

microcline, etc.).

The assumptions are made on the depth of magmatic body formation and specialization of subcrustal magma origin on the basis of mineral compositions, their structure and parageneses.

ISOTOPIC STUDIES ON WHOLE-ROCK AND MINERAL SAMPLES FROM ALKALINE COMPLEXES FROM THE USSR AND SCANDINAVIA

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The recent isotopic (Rb-Sr and K-Ar) data from alkaline complexes within the USSR and Scandinavia provide new insights into the origin and chronological development of these alkaline magmas. Rb-Sr data from the Kola and southern Urals alkaline provinces indicate that intrusion of some of these complexes may have taken place in Caledonian times, considerably earlier than previously suspected from K-Ar data. Examination of the Rb-Sr systematics of minerals from the Ilmen nepheline syenite, however, confirms that this complex was substantially isotopically reset during a later, Hercynian event. Very low initial 87 Sr/86 Sr ratios (~0.7035) from both Kola and Urals complexes indicate that, in common with other major alkaline complexes ( for example the Precambrian Gardar province of South Greenland and the Mesozoic province of central Nigeria), a substantial juvenile (? mantle) component is present in the magmas. Previous isoto pic studies of some highly reactive phases (particularly those rich in fluorine) produced in the final stages in alkaline magma development have shown that these may be highly enriched in radiogenic 87 Sr; this observation is being further investiga ted in the Urals alkaline complexes.

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Monticellite alneites constitute a rare group of igneous rocks associated with the alkalic ultrabasic magmatism including kimberlite.

In the north of the Siberian Platform many occurences of olivine-monticellite rocks have been discovered both within the alkalic-ultrabasic assemblages containing carbonatites of the Mymecha-Kotui province and in a close vicinity to kimberlite rocks.

Monticellite alneites from different localities are characterized by common porphyritic texture, clivine composition of phenocrysts and fine-grained monticellite matrix with the mineral impurities of perovskite, ore mineral, phlogopite, carbonate and occasionally melilite and clinopyroxene.

The table given here shows the microprobe analysis data on the composition of minerals coexisting in Tamakh intrusion rocks intruding archean metamorphic rocks. Two rock varieties have been found here: olivine-monticellite rocks and phlogopite-pyroxene carbonate rocks.

Their geological relations are not determined yet. The data ob - tained show that olivine of monticellite alneites is more ferruginous than that of kimberlite breccias and xenoliths of ultra - basic rocks.

Monticellites of alneites and Indian kimberlite rocks as ferruginous are as those of the metaigneous paragenesis. Phlogopite and diopside are highly magnesian. Ore mineral is magnesium-chromealumina titanomagnetite (?). The structural features of monticellite alneites and mineral composition data indicate the igneous nature of monticellite and other minerals.

Olivine	-	Monticel- lite, aver. of 5	Diopside, average of 3	Phlogopi- te *)	Ore mine- rals, aver. of 2
si0 <sub>2</sub>	40.18	36.63	54.40	41.1	0.08
TiO2	0.00	0.00	0.49	0.79	14.71
A1203	0.08	0.07	0.18	16.4	7.64
<sup>Cr</sup> 2 <sup>O</sup> 3	0.05	0.02	0.25	0.13	14.27
FeO	12.15	8.59	3.11	4.42	46.92
Mm0	0.18	0.44	0.16	0.04	0.56
MgO	45.56	19.69	16.92	24.9	13.48
CaO	0.23	34.17	24.16	0.02	0.05
$Na_2^0$	0.00	0.00	0.15	0.54	0.00
K <sub>2</sub> 0	0.00	0.00	0.00	9.34	0.00
NiO	0.16	0,00		0.00	0.00
	98.59	99.61	99.82	101.69	97.71

<sup>\*)</sup> The total includes 4,5% H<sub>2</sub>0

The analyses were carried out in the microanalyser IXA.50-A, Geological Institute of the Yakutian Branch of the Siberian Department of the USSR Academy of Sciences.

APPLICATION OF RECIPROCAL EQUILIBRIA TO THE STUDY OF DISTRIBUTION OF ELEMENTS BETWEEN MINERALS AND MAGMAS

- F. Delbove, J.T. Iiyama\*, Z. Johan, J.L. Robert, J. Roux.
- G. Sabatier, M. Volfinger, Orleans, France

The study of elements distribution can be approached in two different ways: (1) Direct methods, i.e. analysis after phase separation or punctual analysis of coexisting phases. (2) Indirect methods, i.e. successive studies of reciprocal equilibria between a suitable reference solution (hydrothermal solution, molten salt) and each phase of interest.

The pros and cons of these two methods are discussed and several applications of the second method extensively used in our laboratory are presented:

- \* Distribution of alkali and alkali-earth elements between albite and albitic melt, using a hydrothermal NaCl solution as a refererence solution. Influence of cationic radii and charge on distribution coefficients, related to  $\Delta G^{\circ}$  (Henry's law) is discussed.
- \* Distribution of transition elements between clivine, clinopyroxenes and simple magma, using molten salts (CsI, BaC12...).

RARE-EARTH ELEMENT DISTRIBUTIONS AMONG COEXISTING GRANULITE-FACIES MINERALS

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Little data is currently available on the distribution of the rare-earth elements (REE) among mineral phases in metamorphic rocks. For this study 31 separates of the major rock-forming minerals from granulite-facies gneisses of the Lewisian complex, Scotland, have been analyzed for La, Ce, Sm, Eu, Tb, Yb and Lu by instrumental neutron activation analysis. Clinopyroxene, orthopyroxene, hornblende, garnet, plagioclase and quartz were investigated in gneisses ranging in composition from felsic to ultramafic.

Clinopyroxene generally shows the highest REE concentrations, except in assemblages where hornblende is present. Although abso - lute concentrations vary by a factor of five, all samples have a consistent pattern with preferential incorporation of the intermediate REE. Orthopyroxene has the lowest concentrations, except for quartz, and shows a preference for both the light (LREE) and heavy (HREE) members. Garnet exhibits a strong linear enrichment in HREE, whereas plagioclase shows a linear depletion in the HREE and a ubiquitous, large positive Eu anomaly. All the other major rock-forming minerals show negative Eu anomalies.

Mass balance calculations demonstrate that the bulk (generally >80%) of the REE are located in the major rock-forming minerals. The consistent distribution patterns from gneisses of widely different composition strongly suggest that the REE occupy regular lattice sites in granulite-facies minerals. Crystal-chemical considerations and interelement correlations lead to suggestions of possible sites in the structures of the investigated minerals. The REE distribution coefficients between coexisting phases show consistent patterns indicative of equilibrium distributions, and are similar to distribution coefficients from other rock types, most notably dacites.

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TRANSFORMATION OF THE ALBITE CRYSTAL STRUCTURE WITH TEMPERATURE

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The X-ray crystal structure investigation was undertaken to study the phase transformations dynamics in the sodium feldspars. The three-dimensional intensity data (about 2000 reflections for each sample) were obtained with the "Syntex P2<sub>1</sub>" four-circle automatic diffractometer for a native low albite (Or<1%, An 1%;  $\Delta^{2\theta}_{131-131} = 1.05$ ) from pegmatites of the North-Baikal muscovite province (Siberia) and two high albites which was received by heating of the native sample at  $1030^{\circ}\mathrm{C}$ : (1) - for 11 days ( $\Delta^{2\theta}_{131-131} = 1.86$ ) and (2) - for 27 days ( $\Delta^{2\theta}_{131-131} = 1.91$ ).

The cell parameters determining by least-squares refinement of the single crystal data in sp. g. C1 are:

High Ab(2) 8.176(2) 12.891(3) 7.123(2) 93.40(2) 116.59(2) 87.69(3) High Ab(2) 8.176(2) 12.891(3) 7.125(1) 93.50(2) 116.41(1) 90.19(4) High Ab(2) 8.176(2) 12.891(3) 7.123(2) 93.40(2) 116.50(2) 90.27(2)

The atomic coordinates and anisotropic thermal parameters were calculated by means of the full-matrix least-square refinement with the XTL-programmes. The mean T-O bond lengths are:

	Low Ab	High Ab(1)	High Ab(2)		
P <sub>1</sub> (0)	1.739	1.651	1.646		
T. (m)	1.609	1.646	1.644		
T <sub>2</sub> (0)	1.616	1.645	1.642		
T <sub>2</sub> (m)	1.622	1.642	1.644		

This results have proved the existence of high albites row with different interatomic distances and Al-Si distribution for its components and defined more precisely the sodium feldspar nomenclature.

### THE SANIDINE-ORTHOCLASE TRANSITION TEMPERATURE

### V.N. Zyrianov, Chernogolovka, USSR

The knowledge of critical phase transition temperatures in alkali feldspars is important for establishing the conditions at which the host rocks were formed. Extremely low rates of the Si-Al ordering preclude virtually a direct study of polymorphous transition. Under the experimental conditions the sanidine-orthoclase transformation is too sluggish to assess it kinetically. The temperature for the sanidine-orthoclase transition was established in the exchange equilibria experiments involving solid solutions of the alkali felspar sanidine and orthoclase series, and alkali chloride and carbonate aqueous solutions at 500, 600. 700°C.100kg/cm<sup>2</sup>. The phase diagram for the assemblage sanidinehigh albite-orthoclase-intermediate albite based on these expe riments, shows both stable and metastable equilibria of the mi nerals. The sanidine-orthoclase transition temperature of 680+ 15°C, 1000 kg/cm<sup>2</sup>, has been established from the points for the coexisting sanidine and orthoclase from natural specimens, plotted on the diagram. The sanidine compositions are more potassic than the orthoclase compositions in this assemblage. The disordered polymorphs equilibrate during Na and K partitioning among sanidine, orthoclase and the fluid. The regime of the cooling of the sanidine-orthoclase-bearing rocks is responsible for the limited occurrence of the assemblage in nature. The fluid leaves sanidine lavas and pyroclast material above the transition tem peratures. The fact that orthoclase alone occurs in phenocrysts and bulk effusives suggests that they cooled at lower rates, and the loss of the volatiles had taken place below 680°C. Two phases found in the transition crest and differing in composition make the transition an inversion of the first order.

GEOCHEMISTRY OF TRANSFORMATION OF CHLORITE INTO BIOTITE FROM PHYLLITE BY GRANITE CONTACT METAMORPHISM

### Ana M.R. Neiva, Coimbra, Portugal

In central northern Portugal the granite magmas intruded chlorite phyllites with intercalations of metagraywackes. A progressive sequence of mineral paragenesis during the process of contact metamorphism by the granite magmas intrusions can be expressed by the following assemblages: 1) quartz-sericite-muscovite-chlorite-biotite-albite; 2) quartz-sericite-muscovite-chlorite-biotite-(oligoclase-andesine)-potash feldspar-andalusite schorlite and 3) quartz-muscovite-biotite-andesine-potash feldspar-andalusite-sillimanite-schorlite. The second and third mineral assemblages (inner zone) occur in direct contact with granites, while the first one (outer zone) is away from the contact.

The chlorite of the inner zone has more Si, Ti, K, Cl, F, Nb, Sn, Li, Ba, Rb, Tl, Cs and less Al, Mg, Cr, V, Zn, Ni, Co, Sc, Er than the chlorite of the outer zone.

The biotite of the inner zone has more Si, Ti,  $Fe^{2+}$ , K, Cl, F,  $H_2O^+$  ( $H_2O^+$  + Cl + F), W, Nb, Zn, Sn, Li, Er, Y, Gd, Nd, Pb, Rb, Tl, Cs and less Al,Mg, Cr, V, Ni, Co, Ce than the biotite of the outer zone.

Most of the elements and the ratios Li10<sup>3</sup>/Mg, K/Rb, Ni10<sup>3</sup>/Al, Co10<sup>3</sup>/Mg show the same behaviour in chlorite and biotite from the outer to the inner zone. However, Zn, Sc and Er behave in an opposite way in chlorite and biotite. Chlorite suffers recrystallization, while biotite is of neoformation at the expense at least of chlorite and also probably muscovite.

The empoverishment of chlorite and biotite of the inner zone in some elements compared with chlorite and biotite respectively of the outer zone is due to increase in temperature, while the enrichment in other elements may be due to diffusion and infiltration metasomatism but also to increase in temperature for a few elements.

There is general increase in Si, Ti, Mn, K, F, W, Nb, Sn, Li, Ba Rb, Cs, Li10<sup>3</sup>/Mg and a decrease in Al, Fe"+, (Fe<sup>3+</sup> + Fe<sup>2+</sup>), Mg,  $\rm H_20^+$ , ( $\rm H_20^+$  + Cl + F), Cr, V, Zn, Ni, Co, Sc, Er, Ni10<sup>3</sup>/Al, Co10<sup>3</sup>/Mg in chlorite  $\longrightarrow$  biotitised chlorite  $\longrightarrow$  biotite of the outer or inner zone.

There is desiquilibrium between chlorite and bictite of the outer and inner zones. Chlorite and bictite compositions do not depend on the composition of their host rocks.

The temperature of the fluid-biotite exchange is  $440-460^{\circ}\mathrm{C}$  in the outer zone and about  $500^{\circ}\mathrm{C}$  in the inner zone. The pressure of the outer zone is about 400 bars, while in the inner zone it can be 428 bars and in hornfelses about 1300 bars.  $f_{\mathrm{H_2O}}/f_{\mathrm{HF}}$  in the fluid with which the biotite is equilibrated is smaller in the inner zone than in the outer zone.  $f_{\mathrm{O_2}}$  is higher in the magmas than in the inner zone.

### Peter W. Mirwald, Bochum, FRG

Evidence of a high-temperature transition of calcite at 985°C has been reported by Boeke (1912), Cohen & Klement (1973) and Mirwald (1976). The latter high-pressure study revealed, in addition, the occurence of a further high-temperature transition at 800°C. Extending Bridgman's nomenclature (1939) the transition at 800°C was referred to as calcite'I - calcite IV and that at 985°C as calcite IV - calcite V (Mirwald, 1976).

The calcite I - IV transition has been confirmed at one atmosphere using differential thermal analysis and electrical conductivity. A transition interval of 780 - 820°C was established. Further structural evidence was obtained from high-temperature X-ray diffraction: while the co -parameter of the unit cell ex hibits only a slight increase in its expansion rate, the  $\acute{a}_o$  pa rameter reverses from contraction to expansion within that tem perature interval. The intensity of the (113)-reflection to 900°C shows a marked decrease in intensity within this temperature interval. Because this reflection is determined by the CO3-group position in the calcite lattice, the intensity loss may be related to rotational disorder in the CO2 sublattice which is characterized by a parallel-antiparallel order at ambient conditions. Furthermore, a reevaluation of available CO2 partial pressure data revealed an inflection in the Gibbs energy vs temperature at 800°C which corresponds to a peak in heat capacity. The data are consistent with the idea that the calcite I - IV transition is not of first order, but of diffuse kind, probably related to rotational anion disorder.

The calcite IV-V transition, first established by Boeke (1912), was confirmed by electrical conductivity data, X-ray intensity data extrapolated above 900°C indicate that the (113)-reflection vanishes at the transition boundary. This suggests that the CO3-sublattice has entirely lost its parallel-antiparallel order which implied an increase in crystal symmetry from R3c to probably R3m. Available CO2 partial pressure data indicate that the calcite IV-V transition might be a left type transition.

### Witold Zabinski, Krakow, Poland

The widespread occurence of Zn dolomite is one of the most characteristic mineralogical features of the Silesian-Cracovian ore deposits. In its crystal lattice Mg<sup>2+</sup> ions are partly replaced by Zn<sup>2+</sup>. The influence of Zn on lattice parameters of dolomite as well as on its infrared absorption spectrum is but insignificant. On the other hand, it reflects in a considerable shifting of the first endothermal peak of this carbonate towards lower temperatures on DTA curve. An univoqual test for the presence of Zn in dolomite crystal may be obtained by using of electron microprobe. The origin of zincian dolomites in the Silesian-Cracovian deposits is an open question. They may be partly due to supergene alteration of zinc sulphides in the environment of carbonate rocks, but may also be the primary product of ore mineralization.

### MESOZOIC CARBONATES OF THE WEST SIBERIA

### A.I. Sidorenkov, Tyumen, USSR

In the Mesozoic-Cenozoic sedimentary cover the most widely distributed minerals are carbonates which occur in a disseminated form and as concretions. Their investigations were held with the use of chemical, spectrographic determinations, X-ray diffraction and petrographic methods.

Concretion carbonates contain calcite, mangano-magnesium-ferricalcite, siderite, sideroplesite, mangano-calcio-siderite, dolomite, brown spar, ankerite. Concretion carbonates represent paragenetic series. Basic calcite-siderite (the western slope of the Urals), intermediate siderite-dolomite-calcite (Shaim, Surgut, Nizhnevartovsk regions), basal incomplete dolomite-calcite and siderite-mangesite series (Chulym-Yenisei region) are most wide-spread. Classification of carbonate concretions formed of calcite-dolomite-siderite-magnesite series is proposed in accordance with their chemical-mineral composition and the ratio of

concretion-forming elements to the terrigenous component. It has been established that in lithologically screened hydrocarbon deposits concretion coefficient sharply increases in the direction of their wedging out. This allows to use it for explorational corrections. Carbonate contents in pay zones control carbon dioxide concentration in pore fluids: its amount in oils and gascondensates of lithologically screened deposits is usually higher, than that of arched sheet deposits; this effect aids in defining "the degree of trap screening".

### RADIOACTIVE PLACERS

### M. Andac, Ankara, Turkey

Radioactive minerals: uranothorianite and thorite distributed as accessory minerals in the margins of Esine syenitic massif south of Troy (West Anatolia) were analyzed for their mechanical and chemical resistance to weathering (at some distance from the host rocks up to the coastal placers). Gradual destruction of their crystalline structure becomes quite evident though it is manifested differently in the direct vicinity from the aplitic veins of syenitic massif as well as in the coastal placer concentrations. They were studied both morphologically and crystallo - chemically.

Applying electron microscopic observations combined with elect - ron microprobe analyses (EDAX) we succeeded in rolating the intensity of changes in the minerals having corresponding degree of weathering to thorium/uranium ratio.

The results obtained provide wide possibilities for predicting the occurence of uranium and thorium in the fine-grained marine sediments from the shelf zone of Eagean Sea between Dardanelles and the area under study; it permits understanding some general peculiarities in the concentration of uranium minerals among the sea floor sediments.

### CHEMICAL VARIATION IN HYDRATED ZIRCONS

Olaf Medenbach, Ahmed ElGoresy, Bochum, Heidelberg, FRG

In 1973 Krogh and Davis described botryoidal alteration features in zircons that interfered with the determination of uranium-lead-ages. Our microscopic study of similar zircons from world-wide localities shows that this late stage alteration starts along grain boundaries and cracks, affects only metamict areas, and plays an important role in most zircons. An intensive investigation with a fully automated microprobe measuring 30 elements including the REE was undertaken to reveal the chemical variations in these areas with low reflectivity.

During the botryoidal alteration a significant change in the chemistry takes place Evidently the cracks work as two way streets for elements coming in and out of the metamict parts of the crystals. The most obvious change is a drastic leaching of Si and Zr. Hydration probably accompanies this change since the analyses of these areas never total 100%. Furthermore, the hydrated parts can be highly enriched in other elements, e.g. Fe, Ca, Al, Y, REE, and P. The amount of iron is in good agreement with the more magnetic behaviour of the highly altered zircons.(Y+REE)203

can reach maximum values of more than 25 wt% in some analyses. The charge balance in such analyses is open to question since usually  $P^{5+}$  is only present in minor amounts and other 5-valent cations are absent. Therefore, no stoichiometric xenotime molecule can be formed. Most probably  $H_2^0$  plays an important role for the charge balance. The use of hydrated zircons in geochronology is called in question by the fact that U and also The enrichment up to several wt% of oxides have been observed as a result of late stage alteration.

### EUROPIUM-RICH DARK MONAZITE

### S. Rosenblum, Denver, USA

Eu-rich dark monazite was identified in 64 panned alluvial con centrates from Alaska in a wide zone between the Canadian border and the western tip of the Seward Peninsula. This variety of momazite is characterized by a dark gray to black pelletlike form. and high Eu-and low-Th contents. Density ranges from 4.27 to 4.72, because of many inclusions of silty detrital minerals. Otherwise, the physical, chemical, and X-ray properties are similar to those of yellow monazite. Eleven dark monazites average (in percent): La<sub>2</sub>0<sub>3</sub> 13.54, Ce<sub>2</sub>0<sub>3</sub> 29.00, Pr<sub>2</sub>0<sub>3</sub> 3.34, Nd<sub>2</sub>0<sub>3</sub> 14.00, Sm<sub>2</sub>0<sub>3</sub> 1.92, Eu<sub>2</sub>0<sub>3</sub> 0.31, Gd<sub>2</sub>0<sub>3</sub> 0.98, Y<sub>2</sub>0<sub>3</sub> 0.47, P<sub>2</sub>0<sub>5</sub> 22.36, ThO<sub>2</sub> 0.88, SiO<sub>2</sub> 8.35, TiO<sub>2</sub> 0.66, Al<sub>2</sub>O<sub>3</sub> 1.98, Fe<sub>2</sub>O<sub>3</sub> 1.77, CaO 0.28, MgO 0.23, H<sub>2</sub>O 0.94 = 101.01. Chondrite-normalized ratios and shale-normalized ratios of rare-earth elements (REE) in dark monazite from Alaska are remarkably similar to these ratios in dark monazite from France, Taiwan, Zaire and USSR. These patterns differ greatly from the ones for yellow monazites from igneous and high-grade metamorphic rocks, but are similar to the patterns for REE in sedimentary rocks, especially shales.

A contact-metamorphic origin was successfully tested in Montana, USA. If this origin is generally true, then the presence of dark monazite indicates an area that should be prospected for metall-iferous ores and phosphatic layers as well as REE.

ON THE CORRELATION OF URANIUM CONTENT WITH ELEMENTARY CELL PARAMETERS OF QUARTZ FROM GRANITOIDS OF ALDAN SHIELD

### L.D. Kholodova, V.B. Vasilenko, Novosibirsk, USSR

The 78 quartz samples were studied from: a) granite-gneiss Early Aldan rock complex (Archean, upper stream of r. Aldan), formed in thermodynamic conditions of granulite rock facies of metamorphism, b) massive granites, granite-like and pegmatoid rocks of the Late Aldan rock complex (Archean, from the same region) formed as a result of remelting of granite-gneiss rock in conditions of amphibolite facies of metamorphism and c) weakly gneissic and massive granites of Ungrin rock complex of hypothetically Proterozoic age (amphibolite facies). The parameters of elementary cell and the U-contents were determined by luminescent-sintering technique from the same carefully mixed quartz sample.

The mean concentration values of uranium contained in quartz of the analysed varieties of the above mentioned rock complexes have no significant difference between each other. The mean U-content  $(\overline{U})$  in the quartz of granitoids under study (Aldan rock complex), as observed, seems to be much lower than the mean U-content in quartz of granitoid rocks from E. Transbaikalia it is in agreement with the granites from the same region, which also have the lowest U-content in quartz. The U-contents in quartz and those in rocks (from the same samples) are in fair agreement with the peculiarity established for E. Transbaikalian granitoids.

The elementary cell parameters were determined by focussing inverse photographing in the RKE camera (Cu-anticathode). The reference silicon and germanium of semiconducting purity were used for determinations of the  $\Theta$  angles. A significant difference between the mean parameters values "a", "c" and "v" for quartz of the above mentioned granitic complexes have not been found. The mean parameter values of the elementary cells of quartz for all the studied granitoids of Aldan shield are: a - 4.91320  $\pm$  0.00006Å, c - 5.40455  $\pm$  0.00007Å; V - 112.984  $\pm$  0.003Å.

The correlation coefficients were calculated for the samples under investigation between the parameters "a", "c", "v" and the uranium content in quartz. The significant correlation (95%)was determined only for the pair "a"- $U_k$ . The correlation coefficient are  $\mathcal{L}_{\alpha.u_k}$  = 0.304. Thus about 10% of varied U-content in the quartz under study relates to the dispersion of the parameter"a" of the lattice.

Owing to the fact that the isomorphous admixtures entering the lattice to form a mixed crystal changing the lattice parameters (Vegard's law), the relationship between the metrics of the quartz lattice and the U-content may enter the quartz lattice as microstructural admixture.

URANIUM CONTAINED IN THE QUARTZ OF GRANITOID ROCKS FROM EAST TRANSBAIKALIA

### V.B. Vasilenko, Novosibirsk, USSR

a) about 88% of the overall U-content in quartz statistically calculated is a function of a varied U-content of rock:

b) the uranium contained in quartz is mainly in dispersed form, as its amount in quartz does not depend on the crystall-

ine lattice and associates with the U-content in the melt. From this correlation it is possible to calculate the  $\overline{U}_r$  by  $\overline{U}_q$  and vice versa (in the units n.10<sup>-4</sup>%) by the following equations:

$$\overline{\overline{U}}_{q} = 0.09 + 0.042 \overline{\overline{U}}_{r}$$
 (1)

$$\overline{U}_{\mathbf{r}} = -0.97 + 20.895 \overline{U}_{\mathbf{q}}$$
 (2)

Eqs. (1) and (2) are valid provided 0.1  $<\overline{U}_{q}<$  1.0 and 2.0  $<\overline{U}_{r}<$  21.0

Comparison of the mean values of uranium contents in quartz as a function of petrochemical, formation, and age peculiarities of granitoid rocks, their regional positions and multiphase nature has shown that the only correlation between  $\overline{U}_q$  and the mean  $\mathrm{SiO}_2$  content in the rock has been found to be extant. The correlation is linear and positive. The correlation coefficient is  $\overline{U}_q = 0.725$ . The testing of the particular correlations permits one to conclude that this relationship appears to exist owing to the presence of the correlation between  $\overline{U}_r$  and  $\overline{\mathrm{SiO}}_2$ . Eqs. 3 and 4 are given below for the calculated mean values from the experimental data:

$$\overline{U}_{q} = -3.41 + 0.055 \overline{SiO}_{2}$$
 (3)

$$\overline{\text{SiO}}_2 = 66.39 + 9.701 \overline{\text{U}}_q$$
 (4)

When calculating the correlation for  $\overline{U}_q$  and  $\overline{U}_r$  we have not taken into account the data for the 4 sampled collections of the Undin granitoid rocks whose formation is responsible for the processes of hybridization and magmatic substitution as well as the sampled collection for one of the Carboniferous stocks whose rocks display the signs of hydrothermal alterations. The Undin dioritic and granodioritic rocks and the 1-st stage granites (94 analyses as a whole) are characterized by low (above the clark for dioritic rocks, but below the clark in case of granites) and by similar uranium content in rocks and some higher uranium content in quartz. Anomalously high  $\overline{U}_q/\overline{U}_r$  ratio refect the genetic peculiarities in these granitic rocks. As shown by careful mineralogic-petrographic studies the process of alteration of the enclosing rocks and xenoliths begins with and is accompanied by the intense replacement of all the rock-forming

minerals by quartz. It implies that quartz may crystallize in a wide range of conditions equilibrated with uncontaminated melt to trap uranium in the amounts proportional to its content in the melt. The mean uranium content in the quartz of hybridic rocks reflects the mean(with respect to uranium and  $\mathrm{SiO}_2$ ) initial composition of contaminated melt. The hypothesis on the hybridic nature of the rocks may be regarded as a probable one if  $\overline{\mathrm{U}}_{\mathbf{r}}$  and  $\overline{\mathrm{SiO}}_2$  values calculated by Eqs. 2 and 4 are much higher than the experimental ones.

If  $\overline{U}_r$  and  $\overline{SiO}_2$  calculated by Eqs, 2 and 4 will be essentially lower than the experimentally found mean values, then the hypothesis on participation of the postmagmatic processes in forming the observed uranium concentrations is most probable.

NIGERITE - A RARE ROCK-FORMING MINERAL IN GRANITE FROM PRIBYSLAVICE, CZECHOSLOVAKIA

# F. Novák & F. Čech, Kutna Hora, Prague, Czechoslovakia

Nigerite was found as rock-forming mineral at Pribyslavice, central Bohemia, Czechoslovakia. Its host rock is a tin-bearing facies of a muscovite granite.

Nigerite forms euhedral crystals up to 3 mm large. The colour of nigerite is brown. Some crystals have the zonal arrangement. The density measured D =  $4.39 \text{ g/cm}^3/\text{D}_{\text{calc}}$ : =  $4.37 \text{ g/cm}^3$ . Its rhombohedral crystals are tabular along (00.1) of pseudohexagonal or trigonal habitus with forms {00.1}, {10.4}, {10.1}, {10.7} and {10.5}. The X-ray data correspond to the 12 R polytype with a = 5.7150/6/, c = 55.464/7/ Å / =  $12 \times 4.622 \text{ Å}$  /, c/ e= 9.705 /2/, V =  $1568.83/34/\text{ Å}^3$ . Z = 6.

Chemical composition /0.12 CaO, 0.80 MnO, 11.55 ZnO, 53.32  $\rm Al._2 e_3$ , 10.90 Fe<sub>2</sub>O<sub>3</sub>, 18.16 SnO<sub>2</sub>, 1.07 TiO<sub>2</sub>, 0.51 SiO<sub>2</sub>, 0.37 Ta<sub>2</sub>O<sub>5</sub>, 0.96 H<sub>2</sub>O, 98.26 wt.% sum/ corresponds with the following crystallochemical formula:

Besides quartz, orthoclase, albite and muscovite the nigerite-bearing facies of granite contains small amounts of almandine, tourmaline and apatite. The other rare minerals present are: stauro - lite, dumortierite, cassiterite, sillimanite, gahnite and kyanite. Oriented intergrowths of nigerite with gahnite and staurolite were not observed.

Nigerite, gahnite, staurolite and some other accessory minerals are supposed to be assimilation products of aluminium-rich rocks by granite. This opinion is supported also by the presence of graphite, abundant apatite, small lens-like accumulations of different Li-Fe-Mn-Ca phosphates and xenoliths of metamorphic rocks in the neighbouring parts of granite intrusion.

MINERALOGY AND PARAGENESIS OF NEW MINERALS, OHMILITE AND NUNAKAWAITE, IN THE RIEBECKITE-ALBITITE ASSOCIATED WITH SERPENTINITE FROM THE OHMI AREA, CENTRAL JAPAN

## K. Chihara, M. Komatsu and T. Mizota, Niigata, Japan

In 1971 two new minerals (ohmilite and nunakawaite) associated with benitoite, leucosphenite and other minerals were found in an magnesicriebeckite-quartz-phlogopite-albitite dike cutting serpentinite in the Ohmi area, Niigata Prefecture, Central Japan.

Chemical analysis of nunkawaite gave, in weight %,  $\sin_2$  35.12,  $\sin_2$ 05 1.42,  $\sin_2$ 12.48,  $\sin_2$ 3 0.27,  $\sin_2$ 3 1.12,  $\sin_2$ 4.75,  $\sin_2$ 5 1.42,  $\sin_2$ 6 1.248,  $\sin_2$ 7 0.27,  $\sin_2$ 7 1.12,  $\sin_2$ 7 0.19,  $\sin_2$ 7 0.19,  $\sin_2$ 8 0.274,  $\sin_2$ 9 0.94,  $\sin_2$ 9 1.274,  $\sin_2$ 9 0.94,  $\sin_2$ 9 1.274,  $\sin_2$ 9 1.275,  $\sin_2$ 9 1.276,  $\sin_2$ 9 1.2776,  $\sin_2$ 9 1.2776

\* RE wt. = 100 \*\* Ta<sub>2</sub>0<sub>5</sub>=0

The precession photographs show this mineral to be orthorhombic with a 9.777  $\pm$  0.005 Å, b 10.517  $\pm$  0.006 Å, c 22.392  $\pm$  0.12 Å,and possible space group  $P_{\text{cam}}, P_{\text{ca2}}$ . Optically biaxial with (+) 2V = 42-48°,  $\alpha$  =1.707  $\pm$  0.003,  $\beta$  = 1.778  $\pm$  0.003, and weakly pleochroic with axial colours X = Y = colourless and Z = light yellow. The hardness is 5.5 (Mohs); cleavage (001) perfect; density = 3.62 (measured), 3.87 g cm<sup>-3</sup>(calculated).

The nunakawaite (joaquinite-like mineral) is yellow in naked eyes and occurs as a spotted aggregat. (up to 1 cm in diameter) or lens (up to 3 cm in length) consisting of anhedral angular crystals less than 2 mm in length.

Although its X-ray powder data are very close to those for joaquinite, it is compositionally different from those of Californian and Ilimaussaq materials re-examined and studied by Seme nov et al. (1967), respectively, due to its very low rare earth and higher barium and strontium contents. A new Sr-Ti hydrous silicate mineral (ohmilite) occurs as aggregate of fibrous crystals of light pink in colour. The mineral is monoclinic with a = 10.958 Å; b = 7.778 Å; c = 7.799 Å,  $\beta$  = 100°54′, space group P2<sub>1</sub>/m. Crystals are elongated along b-axis, density 3.38; hardness 3.5, weak pleochroism,  $\alpha$  =1.849,  $\beta$  = 1.715. Chemical analysis of ohmilite gave SiO<sub>2</sub> 34.79, Ti<sub>2</sub>O<sub>3</sub> 10.27, Fe<sub>2</sub>O<sub>3</sub> 0.20, SrO 47.37, H<sub>2</sub>O 6.68, total 99.31. The chemical formula of the mineral is Sr<sub>3</sub>TiSi<sub>4</sub>O<sub>12</sub>(OH)·2H<sub>2</sub>O.

#### THE TWIN FORMATION OF EMELEUSITE

Ole V. Petersen, Copenhagen, Denmark

Emeleusite (Li<sub>2</sub>Na<sub>4</sub>Fe<sub>2</sub><sup>III</sup>Si<sub>12</sub>O<sub>30</sub>) is an orthorhombic (pseudohexagonal) mineral occurring as euhedra within a facies of a peralkaline trachyte dyke on the island of Igdlutalik, Julianehab Distr., South Greenland.

Emeleusite forms pseudohexagonal, interpenetrations, normal triplets, with {110} as the twin plane. The single individuals are tabulated parallel to {011} and strongly elongated after [100] The c-axis forms the pseudo six-fold axis of these triplets. In many of the triplets each of the three orientations is represented by several parallel individuals.

MINERAL FORMATION UNDER THE CONDITIONS OF MODERN WEATHERING PROCESS (AS EXEMPLIFIED BY KHIBIN AND LOVOZERSKY ALKALINE MASSIFS, KOLA PENINSULA)

#### M.D. Dorfman, Moscow, USSR

Sr.Ti.Ba-concentration).

The investigation of modern mineral formation processes is of vital importance in that it allows to determine the main factors responsible for mineral formation accessible to experimental verification. In this respect of particular interest are the unique intrusive massifs of alkaline magmatic rocks in the Kola Peninsula (Lovozersky and Khibin) which are characterized by a wide variety of secondary minerals. A specific feature of these massifs is the formation of aqueous solutions of the surficial origin, which are rich in alkalies and fluorine. The interaction of such solutions with the rocks sharply increases the rate of hypergene process.

Most illustrative are the processes to occur during weathering of such hypomorphic minerals of alkaline rocks as nepheline, eudialite, lomonosovite, etc. The reaction products were studied with use of modern methods such as electron microscopy, microdiffraction, electron diffraction analysis, etc. A common feature of these processes is the transformation of minerals of complex composition (Ti-Zr silicates) in the exchange chemical reactions with nepheline and aqueous sodium fluorine and carbon dioxide solutions:

 $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 + 12NaF + 8CO_2 = 2(3NaF \cdot AlF_3) + 8NaHCO_3 + 2SiO_2$  eudialite  $\longrightarrow$  zirfesite (subtraction of alkalies, Zr,Fe,Si-concentration); lamprophyllite  $\longrightarrow$  anatase + barite (subtraction of alkalies, Si,

These and some other reactions were reproduced to a considerable degree under laboratory conditions, which allowed determination of the main physico-chemical parameters of hypergenesis ( pH, time, concentration, solubility, etc.).

TYPOMORPHISM OF MINERALS

THEORETICAL FOUNDATIONS OF TEACHING ON MINERAL TYPOMORPHISM

E.K. Lazarenko, V.I. Pavlishin, V.S. Mel'nikov, Kiev, USSR

Typomorphism of minerals as a scientific trend (teaching) embracing a wide range of scientific and applied aspects, has been treated as one of the fundamental problems of modern mineralogy.

This determines the actuality of theoretical elaboration of the teaching on mineral typomorphism.

From the wide comprehension of the term "typomorphism" of mine - rals we give the following formulation for the principal concepts of the doctrine on mineral typomorphism.

Typomorphism of minerals is the mineral ability to determine the conditions of the mineral-forming environment reflecting them in the process of formation of specific minerals, associations and (or) in the individual features of minerals.

Typomorphic minerals are the minerals formed only under specific chemical-physical conditions and make it possible to judge about these conditions.

Typomorphic features and associations of minerals appearing in the peculiar conditions of their formation or transformation and making it possible to judge about these conditions.

Typoomorpho us analysis is the method of determining the conditions of mineral complex formation on the basis of mineral typomorphism. The classification of typomorphic peculiarities of minerals is based on the principle of correlation of the mineral features with the mineral-forming environment. According to this point of view, four groups of features are distinguished: 1) Constitutional typomorphic features; 2)Inclusions as typomorphic features; 3) Morphologic typomorphic features; 4) Physical properties as typomorphic features.

#### THE STRUCTURE TYPOMORPHISM OF MINERALS

# V.A. Frank-Kamenetskii, Leningrad, USSR

The classical conception of typomorphism connected the morphological differences of mineral crystals with the conditions of their origin in nature. Later on this conception broadened due to some other macrocharacteristics used (physical properties, composition, etc.).

The more profound application of structural crystallochemical ideas is the characteristic feature of modern mineralogy. The fine differences and certain defective forms of the structure of minerals become available for investigation on the basis of modern methods of structure investigation and their automatization. The investigation of structural and crystallochemical characteristics of rock-forming minerals of different genesis and their synthetic analogues allows to determine the variations of interatomic distances and angles temperature constants and in dividual forms of positions distribution.

The morphological aspect of typomorphism preserved its significance provided the structural control of morphological differences occurred. The speculative character of attempts to substantiate morphological differences in minerals by conditions of their crystallization is linked with insufficient elaboration of crystal growth theory. In general, the morphological and physical differences in minerals depend on their structural differences.

The clear relationship between nature of structural defects and conditions of genesis is shown by the investigation of natural and synthetic structural varieties in pyroxenes, amphiboles, layer silicates, quartz, feldspars, berylls, etc. The best results in solving this problem are achieved when the data on natural minerogenesis are compared with experimental data. The experimental investigation of layer silicates behaviour in hydrothermal mineralized media shows that the structural transformations are seldom accompanied by clear morphological changes.

Structural typomorphism is the complex of data on structural differences in minerals of different genesis. It makes possible to reveal the relations between the form of structural defects in a mineral and conditions of its genesis.

The effective criteria of structural typomorphism are the nature of atoms and their complexes (chains, layers, etc.) distribution among the different structural positions, certain forms of its defects (the variations in interatomic distances, the nature of ordering for different positions, formation of derivative structures, nonstoichiometry, morphotropy, etc.).

METASOMATIC AND CONCRETIONARY PROCESSES AND THEIR ROLE IN THE FORMATION OF HYDROTHERMAL VEINS

## V.F. Barabanov, Leningrad, USSR

The postmagmatic mineral formation is the process of interaction between hydrothermal solutions (juvenile, residual, interstitial, metamorphic, vadose or others) and the host rocks. This process combines a primary metasomathosis and secondary concretionary redeposition of its products. Metasomatic-concretionary mechanism of formation mineral associations has universal character.

The origin of mineral bodies of this kind of genesis results in the process of the system development: wall rock - mineral-forming solution. In this case a vein fissure-forming, wall rock alteration and hydrothermal filling are different sides of a single process.

The typomorphic properties of minerals make it possible to reconstruct the real conditions of natural mineral formation. PECULIARITIES IN TYPOMORPHISM OF CRYSTALLINE STRUCTURES (EXAMPLIFIED BY DIOCTAHEDRAL PHYLLOSILICATES)

B.B. Zvyagin, A.P. Zhukhlistov, O.V. Sidorenko, S.V. Soboleva, Moscow, USSR

On the basis of high voltage electron diffraction studies new data have been obtained on structural peculiarities in diocta - hedral phyllosilicates consisting of 1:1 or 2:1-layers with Al or Fe<sup>3+</sup> in octahedra, K or Na in interlayers. They have permitted to refine the concept of typomorphism and to specify the field of its application.

The most important feature of the typomorphism of crystal structures enables one to use the structural peculiarities in minerals in order to explain the existing typomorphic relations and to differ natural, law-governed relations from those which are occasional.

This problem includes: 1) Consideration of energetic advantages of crystal structures regarding their abundance in nature, 2) Revealing fine structural particularities of single mineral samples which are influenced by concrete formation conditions. 3) Finding the real processes that induce the formation of unfavourable in general and unstable structures. 4) Finding of such detailed particularities in the structures that compensate for the general instability factors, and indication of processes that cause these particularities.

In case of dioctahedral phyllositicates the following structural features have manifested their typomorphic significance: a) the nature of octahedral and tetrahedral cations; b) the average Si-O bond length; c) energetically favourable and unfavourable layer stackings; d) order-disorder of the isomorphic distributions; e) degree of perfection of the layers and strictness of order of their alteration.

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The structural state of potash feldspars (Kfs) from palinogenic granitoids of different depth, hypabyssal and near-surface intrusions of rare-metal granites and from pegmatites was studied. It was found that structural properties of Kfs are typomorphic signs of formation conditions and ore specialization for granitoids and pegmatites.

Studying the Kfs structural state was carried out by an X-ray method using powder patterns according to the authors techniques (Afonina et al., 1976). Two coefficients of Kfs structural state  $\Delta_Z$  and  $\Delta_p$  corresponding to coefficients 2 and Y of J. Thompson (1969) were determined:

$$\triangle_{Z} = Z = (Al_{T_{1}} + Al_{T_{1}^{m}}) - (Al_{T_{2}^{0}} + Al_{T_{2}^{m}}),$$

$$\triangle_{p} = Y = Al_{T_{1}^{0}} - Al_{T_{1}^{m}},$$

where  $\Delta_Z$  is a degree of monoclinic ordering and  $\Delta_p$  is a degree of triclinicity calculated by powder patterns. These coefficients reflect a relative character of ordering and an absolute distribution of Al and Si in tetrahedral positions of Kfs lattice. The diagram of Kfs structural state with coordinates  $\Delta_Z$  and  $\Delta_p$  is proposed.

Series of Kfs samples from different granitoids and pegmatites form specific "ordering rows" in the diagram of structural state. "Ordering rows" of Kfs are established for the following granitoid and pegmatoid types: a) granitoids of calcic-al-kaline series originated from abyssal granitoid magma, 2) palingenic autochtonous and negligibly displaced granitoids and pegmatites, 3) rare-metal intensively differentiated granites, 4) rare-metal pegmatites. Several rows are observed among the latter in accordance with different conditions of their formation.

The influence of Kfs composition on their structural state is studied. There are some properties of ordering processes in Kfs containing different large cations (Ba, Rb, Cs). It is found that the presence of Ba disturbs the far order of Al and Si distribution in Kfs. Ions of Rb and Cs hinder the ordering process.

#### NON-STOICHIOMETRY: BASE OF MINERAL TYPOMORPHISM

#### I.A. Chairetdinov, Ufa, USSR

The mineral composition reflects the activity of ions in the mother solution, and therefore their non-stoichiometry serves as a biographic sign. Pyrite as a kind of mineral is characterized by variations in the ratio of Fe/S from Fe<sub>1,11</sub> S<sub>2</sub> to Fe<sub>0,89</sub> S<sub>2</sub> (or: from FeS<sub>1,78</sub> to FeS<sub>2,2</sub>) with the singular point around the composition FeS<sub>2</sub>.

Non-stoichiometric minerals actively and selectively concentrate in themselves the admixtures: in the case of deficiency of cations they are essentially cations; in the case of redundancy of cations they are anions.

Metamorphism can disturb the initial ratios of Fe/S. In such a case the admixtural elements make it possible to restore the initial value of the Fe/S ratio by calculation.

The pyrite non-stochiometry correlates with many of its physical and physico-chemical properties and connected to that are the future use for concrete definition of the conclusions on the conditions of mineral formation which are obtained on the basis of non-stoichiometry. Of particular importance is the fact that the non-stoichiometry enables one to interpret the space regularities in the development of geochemical processes.

#### STRUCTURAL TYPOMORPHISM OF CHLORITES IN EPITHERMAL DEPOSITS

#### O.V. Rusinova, V.L. Rusinov, Moscow, USSR

Chlorites and mix-layerd silicates, containing chlorite component, have been found among the chloritic minerals in veins and in the host rocks of the epithermal deposits. The chlorites are aboundant in the propylitized rocks and in the vein-bordering zones represented by quartz-chlorite-hydromicaceous and by quartz-chlorite-sericitic composition. The mix-layered silicates are common in argillized host rocks. X-ray structural studies have permitted to reveal several structural types of chlorites: monoclinic with IIb packets (aboundant in propylites, mostly) and with Ia packing; orthorhombic (Ib); and those conventionally called chamosite-like chlorites. The latter (three of them) usually occur in wall rocks and differ from the propylitic ones by a higher birefringence and by a higher Fe-content.

Swelling chlorites, to soudites, weakly swelling and non-swelling chlorites whose packets slightly reduce when annealed have been individualised among mix-layered silicates. To soudites are usually represented by ordered varieties characterized by structures of alternating di-trioctahedral cookeitic and dioctahedral montmorillonitic packets. In a number of deposits to soudites possess Li, positioned probably in the single-store layers of the mineral. The other layered silicates associated with Li-containing to soudites (kaolinite, hydromicas, etc.) have insignificant quantities of this element or have not any. The close association is found between to soudites and the kaolinite group of minerals, sometimes with diaspor and pyrophyllite.

The geological position analysis allows to suppose the development of chlorites and mix-layered minerals being defined mainly by the temperature and the acidity of the solution as well as by the composition and the degree of alteration of the enclosing rocks.

METAMORPHISM OF ROCK-FORMING MINERALS ON THE BASIS OF TYPO-MORPHIC FEATURES

#### S.A. Rudenko, M.A. Ivanov, Leningrad, USSR

Metamorphism of minerals includes the type of their transformation in a solid state which take place from the moment of nucleation to the period of mineral individuals disintegration without any essential changes of crystal forms. Metamorphosed individuals keep belonging to one or another mineral species. At the same time during metamorphism there occur the changes in many typomorphic indications concerning crystal structure (rate of regularity, etc.), internal crystal morphology (twinning,unmixing structures, block forming, granulation), physical properties (extinction angles, angles of optical axes, irisation, colour, thermoluminescense, etc.) as well as the content of chemical elements - admixtures. All rock-forming minerals and mineral deposits of endogenous origin undergo metamorphism, during which process considerable volumes undergo alterations.

The principal factors of mineral metamorphism are P-T environ - mental condition changes, influence of tectonic regime and of solutuons of endogeneous origin. As a rule, several stages of metamorphism are distinguished, the presence of which reflects the pulsating manifestation of tectonic movements.

One must take into account mineral metamorphism phenomena when solving the problems of thermo-barometry; evaluation of the absolute age of rocks and minerals; the laws of chemical elements admixtures migration; correlation of intrusive complexes, etc. Particular data testify to the possibility of grave errors in solving these problems if mineral metamorphism phenomena are ignored. The retamorphism of minerals is, to a great extent, connected with the processes of ore-formation affecting metamorphosed and igneous rocks.

Mineralogical mapping of metamorphosed areas in granite and pegmatite bodies shows that this method can be used for large-crystalline metasomatic micaceous zone prospecting.

#### R.M. Konstantinov, Moscow, USSR

An application of some mathematical methods to look for genetic information concealed in minerals and mineral associations is especially advantageous in typomorphic studies. A mathematical approach consists of two stages. Primarily, it is a statistical analysis - a scientist looks for typomorphic manifestations in the behaviour of various parameters (dispersion analysis), then he checks the results obtained with statistical criteria. After that the typomorphic signs must be organized following their relations to changes in geological environment (main components method).

Secondly, logical-informational methods must be employed in order to study the complicated geological systems. These methods permit to compare quite a number of different minerals and mi neral associations whose properties would be variably ranged according to the gradually changing mineral-forming media. Sta bility of the typomorphic parameter and its consistence in the changing environment have to be disclosed. The stability is understood in the form of changes that occur constantly, irrespective of the geological conditions. A typomorphic feature is assumed stable if it is present in all the studied (standard)combinations, regarded in certain conditions. In contrast, it is variable if it demonstrates no changes in a changing environ ment and if it is present but in a part of the studied combinations. The relative effectiveness of the relations existing between the typomorphic parameters and the changing geological conditions are characterized by a dividing weight which may be determined in special mathematical logical and combinational operations.

A number of examples are drawn in order to illustrate the mathematical approach in typomorphic studies in stanniferous, polymetallic and gold deposits. TYPOMORPHISM IN THE MINERALS AS A BASIS FOR THE PROSPECTING MINERALOGY

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Any of the minerals being in relation to environment possess "imprints" of the conditions, in which it had been formed. The main purpose of the typomorphic studies is to decipher this imprinted information.

The typomorphic studies are based theoretically on a series of crystallochemical, chemical, physical and physico-chemical laws.

The information supplied by the mineral can be used in order to determine the mineral-forming environment and to solve certain geological theoretical and practical problems related to the prospecting and estimation criteria.

Typomorphism of minerals is the basis for prospecting mineralogy, i.e. for the mineralogical studies in complex whose purpose is to obtain the information that would be necessary to elabo rate the criteria for prospecting and estimating the mineral deposits and to create mineralogical methods of prospecting. The prospecting mineralogy is to solve the following major problems: defining both the genetic and formational type of deposits from the schlich and mortared bedrock grains; finding indicative minerals that would be used as new prospecting indications; delinesting anomalous areas among the eruptive or metamorphic, metasomatically changed homogenous rocks by their typomorphic fea tures; estimating ore potentials of the intrusive complexes by making use of the rock-forming or accessory minerals; classifying the newly found ore shows to individualize the promising ones during prospecting by minerals or their associations; de termining erosion level of deposits by making use of the mapp data for typomorphic minerals or their properties. ing

It seems useful to create a classification system based on the typomorphic features of the minerals. It is urgent for the prospecting mineralogy to start using geological, geochemical, mi-

neralogical and nucleo-physical methods in rational complexes to make the prospecting and evaluational surveys more effective.

GEOCHEMICAL AND STATISTICAL ESTIMATION OF TYPOMORPHISM OF THE MAJOR ORE MINERALS

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Statistical estimation of the average content of Cd, In, Tl, Se, Te, Re and other impurities contained in the major ore minerals (sphalerite, galenite, pyrite, molybdenite, cassiterite, etc.) has been made. A comparative analysis of each estimations made in a great number of similar deposits in various regions has shown an absence of any significant differences in a majority of cases.

The estimation of the average content of such trace element im purities in the minerals to study is a good piece of information to determine their formational group. The character of distribution and the concentration level of the trace elements in mine rals, when compared to the general estimationa published in " "Sredniye soderjania elementov-primesei v mineralakh" (Nedra, Moscow, 1973) makes it possible to guess more certainly not only at the mineralization type and at the form of the trace elements in question but also at the conditions of mineralization, including its duration, depth and scale (sometimes). The geochemical and statistical estimation in complex permits one to propose a specific group of deposits for a certain type of mineralization (in the enlarged scale of geological and geochemical classifi cation) and to guess at the geotectonic conditions of ore for mation and, to a certain degree, at the primary sources of the ore-forming components.

The trace elements distribution data may be used in order to clarify the topomorphic peculiarities in the minerals, though it would be possible in case of statistical generalization of the geochemical data in question.

CHEMICAL COMPOSITION OF NATIVE GOLD-SILVER MINERALS AND ITS DEPENDENCE ON PHYSICO-CHEMICAL CONDITIONS OF FORMATION (Experimental)

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To elucidate native gold-silver minerals' typomorphism there has been experimentally studied the most important physico-chemical parameters' effect on the process of electrochemical co-precipitation of gold and silver in the system HAuCl<sub>4</sub>+AgNO<sub>3</sub> + NH<sub>4</sub>OH. Crystalline gold-silver solid solutions of different composition have been obtained being analogous to native minerals.

There has been revealed artificial mineral composition depen - dence on the Au:Ag correlation in the solution and two areas of solid solutions being present: based on gold of extensive sil - ver solubility as well as based on silver of gold limited solubility. There has been noted an area of break along the curve, showing the dependence of sediment composition on solution composition related with crystallization mechanism changes.

The effect of solution anion composition on probity of native minerals is revealed with silveriness of sediments in the presence of halogenides (Cl,F); increase of gold content in them and carbonate-ion presence (CO<sub>3</sub><sup>-2</sup>, HCO<sub>3</sub>) and indeference PO<sub>4</sub><sup>-3</sup> - ion. It has been shown that mineral composition dependence on a system potential, when rising results in solid phase silverness increase. A complex dependence of the sediment composition on pH of solutions in different systems has been revealed. There has been established a tendency to increase in intensity of metal sedimentations and probity increase of solid phases in 150-250°C temperature range.

The mineral-precipitants effect is due to reasons of variation of chemical composition of studied phases. Differential behavior of gold and silver is revealed in their being precipitated on various sulphides as well as silver being intensively precipitated on manganese minerals (Rohdonite-rhodochrosite) ores.

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More than 5400 touchstone tests checked by some 900 atomic absorption and microscopic analyses produced in auri-argentiferous and gold-bearing deposits have demonstrated the average standard to be <750, the selected dispersion being > 5000. The standard distribution has its maxima in the range of 850, 730, 650, 590 and of some smaller values. The modal values for the Au-telluride type of deposits (of low depth as well) have been registered in the range of 850 and 750, whereas for individual deposits in the range of 700 - 930. The impurity range in the randomly selected deposits is larger than that in the deep ones. Compa ratively more important contents of Sb, Pb, Te (0.0n - 0.n%)have been stated. The typical endogenic changes consist of modi fication and obliteration of zonalities, of development of a secondary zonation and of intergranular streaks depleted in Ag. Relict structures also witness for the endogenic transformations. The regular changes in gold properties in vertical and lateral sections follow the mineralogical zonation. The  $\mathrm{H}_2\mathrm{O}$  and  $\mathrm{CO}_2$  contents in quartz are taken as parameters of the physico-chemical crystallization conditions and of the metamorphic transformations. These contents are considered in units of relative optic densities  $D_1$  and  $D_{II}$  of the absorption bands for  $H_2O(3460 \text{cm}^{-1})$  and for  $CO_2(2350 \text{ cm}^{-1})$  as related to the inner standard (2200 cm<sup>-1</sup>). The maximum D<sub>T</sub> values are registered for auri-telluric deposits, and the less important ones - for the mezo-cenozoic auri-argentiferous and gold-bearing deposits (3,8-28; 1-31; 1, 1-10 respectively). The mean arithmetic values are 12 - 15; 6; 5 5 - 7; 4 - 5,2). The water content is more important in quartz of the late mineral associations than in that of the earlier ones, though it drops in the vicinity of post-mineralisational intrusions. CO2 content in quartz of the most part of deposits is not high ( $D_{TT} = 0.02 - 0.5$ ; the mean arithmetic being 0.15-0.20), though it grows in metamorphic ore bodies.

THE FUNDAMENTALS OF PROSPECTING CRYSTALLOMORPHOLOGY

#### N.Z. Yevsikova, Leningrad, USSR

The fundamentals of prospecting in crystallomorphology are the three laws of natural crystallogenesis: 1. The zoned ore deposition; 2. The directed evolution of crystal habit; 3. The existence of the same physical and chemical peculiarities of mineral type crystallization in physical and chemical features of individual structures (typomorphism).

Recently the interconnection of these laws has been observed on hydrothermal cassiterite samples, the closest cassiterite satellite-anatase and auric pyrite.

The distribution of crystals with different morphologies in a mineralized space is autonomous for each individual ore body and is cubjected to the rule of the primary downward changes, i. e. at a larger distance from the ore-bearing solution source (or parental rocks) the faces of later origin begin to dominate in crystal habit. When carrying out the crystallomorphological mapping, the degree of "rejuvenation" of crystal shape is determined according to:

$$X = (2.V + IV) - (II + 2.I),$$

where I-V is the percentage of the corresponding morphologi cal crystal type, provided that type I is the earliest, II, III, IV are intermediate, and V is the latest.

The representativity of crystallomorphological investigations is provided by a great number of samplings (hundreds) and observed crystals (thousands). The combination of prospecting crystallomorphology with heavy concentrate and pounded furrow probe mineral in situ analysis is of great importance for practical use. The isolines X give the possibility to single out the less eroded ore deposit blocks and separate ore bodies. The presence of two and more crystallomorphological characteristics for horizontal sections in one profile gives the possibility to determine the gradient of crystallomorphological variability and thus delineate the ore body at a certain depth outstripping the data of boring. The horizon of richer ores is

characterized by statistical domination of type III crystals (more seldom II or IV), where the most reticular dense faces in habitus formation are involved.

TYPOMORPHIC PROPERTIES OF TI AND Zr SILICATES FROM THE AGPAITIC ALKALINE ROCKS

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The authors have found a rich occurence of raremetal mineralization in the Han-Bogd massif of alkaline granites, the greatest in the world and relique one placed in the South Gobi, Mongolia. In this massif a new Zr-silicate (armstrongite), some minerals of the elpidite-armstrongite series and some Ti-, Nb-Tr minerals with decomposed structure were discovered.

The typochemical properties of Ti-, Zr-silicates were considered using diagrams of Ti-Si-(Na,K,Ca) and of Zr-Si-(Na,K,Ca). In these diagrams the stability fields of Ti- and Zr-silicates for alkaline granites, nepheline syenites, ultramafic alkaline rocks and carbonatites are plotted. Investigation of the diagrams allow one to estimate the isomorphic series of minerals varying in SiO<sub>2</sub> content and to clear out gaps of miscibility in these series.

It is shown that the changing of Si-O radical between isomorphous series is discrete and regular and that the radical is complicating (i.e. tetrahedra are condensing) in the range of ultramatic rocks-alkaline granites. In the last Si-O radicals become so complicate that corresponding minerals appear to be unstable on the Earth surface and its structure is destroyed. The studying of the composition of the destroyed minerals allow one to localize the boundary between the stable and unstable minerals. Peculiarities in the chemical composition of minerals from Han-Bogd granite massif are discussed in detail.

ON THE TYPOMORPHISM OF NATIVE GOLD FROM PRECAMBRIAN OF THE MIDDLE DWIEPER AREA

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In this paper are considered the typomorphic features of native gold from different types of mineralization in Precambrian formations of the Middle Dnieper area.

The gold-antimony-arsenic-nickel type of deposits is characterized by the simple face and more complex forms of gold. The simple face forms have small size and high-standard. The gold is in the accretion with pentlandite. This fact permits to confirm the abyssal nature of gold mineralization connected with the processes modification of the ultrabasitic rocks. The complex forms of gold are low-grade ones and having sizes under 1.5 mm. This gold connected with the late processes of polymetallic mineralization is not abyssal formation.

The gold-pyrite type of deposits belongs to the formation of middle-depth. The admixtures of silver and copper in the gold characterized geochemical peculiarities of the area. The sizes of gold are under 0.4 mm here. This type of mineralization is connected with the sedimentary-volcanogenic complex of rocks.

In the gold-quartz type of deposits with arsenic, gold is characterized as crusted in the cracks. The size of gold is under 0.01 mm. These formations are not abyssal.

The later processes of polymetal mineralization with gold from all types of deposits are connected with the processes activation on the Ukrainian Shield. The further study of typomorph ism of native gold from Precambrian formations permits one to solve the problem of prediction in full length.

MICRO-CONTENTS OF MERCURY AS A TIPOMORPHIC CHARACTERISTIC OF GOLD DEPOSITS

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Investigation of contents of mercury in minerals of hydrother - mal deposits is significant from two aspects: for understanding the genetic characteristics of ore deposits, and for improving the mercurymetric methods of prospecting. Gold deposits are very interesting for such an investigation, because they occur in different metallogenetic provinces, are formed in wide temperature intervals and interrelate differently to mercury deposits. We have investigated the contents of mercury in different gold deposits of the USSR, Yugoslavia and others.

The distribution of contents of mercury, in gold and in the sulphides that follow it, should be pointed out. Gold appears as a particularly good collector of mercury. Mercury ingredient is noticeably bigger in low-temperature deposits, compared to midand high-temperature deposits, especially in those that are located in the belts of mercury metallogenetic profiles. This tendency of mercury has been observed in gold, pyrite, galena and stibnite. It has also been noticed that the later generators of minerals contain more mercury compared to the earlier phases. The micro-distribution of mercury in the frame of separate grains, has been investigated only in gold, where it is highly concentrated and can be determined by microprobe. Different types of distribution of mercury are observed and reverse correlation determined between mercury and silver in gold.

At present, mercury is used in geochemical prospecting for gold deposits. Positive results are known to have been obtained in the USSR, USA, Japan and some other countries. Better knowledge of typomorphyc characteristics of hydrothermal minerals will enable us to establish a more reliable prospecting significance of mercury anomalies in the surrounding rocks of gold-pearing provinces.

TYPOMORPHISM OF MINERALS AND MINERAL FORMING MEDIUM OF UKRAINIAN MERCURY PARAGENESIS

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Volcanogenetic-opalite types of mercury paragenesis of the Transcarpathians were formed by low concentrated solutions containing negligible quantity of carbon dioxide with the temperature 250-60°C and pressure 300-200 atm. Stages of mineralization were fixed with crystallization of different morphological types of quartz, cinnabar, markasites, calcites and oth., these stages were fixed with antyskeletal, skeletal and normal deposition of substance and changing of normal solutions by colloids. Two generations of cinnabar have been distinguished in the composition of ore. The first generation is the simple form of rhombohedron (1013) or (1012) and it is often of antyskeletal development. Crystals of cinnabar of the second generation are more flattened forms of rhombohedron (1015) and (1014). The changes of habit are noted across the vertical line and on the flancs of the deposits.

Mercury paragenesis of the Donbass and its neighbouring territory are represented by different mineral associations. Evolution of hydrothermal solutions connected with tectono-magmatic activizations led to the ore formation which were comparatively simple mineral composition (ore field Nikitovka). Mercury formations connected with alkaline magmatism are characterised with the presence of highly and middle-temperature mineralization of fluorite and other minerals (saline dome structures, the zone of Donbass and the Periazovial district joint). The difference in the conditions of the ore formation and ore discovery were reflected in the typomorphism of habit types of cinnabar crystallization: prismatic - Dokuchayevsk; rhombohedral - Nikitovka; microcrystalline dipyramidal and pinacoidal - Slavyansk.

Typomorphic formations of the Transcarpathians and the Donbass are organic carbonaceous minerals and methane which are detected in the gas phase of the quartz inclusions, calcite and oth. Infrared spectra and isotopic composition of carbon show the oil nature of carbonaceous matter.

TYPOMORPHISM OF SULPHATE-SULPHIDE MINERAL PARAGENESIS (Exemplified by Karamazar deposit, TadjSSR)

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The sulphate and sulphide sulphur spring of region deposits. The sulphate metasomathosis is presented by anhydritization, alunitization and barytization of the enclosing rocks.

The regular combination of sulphate and sulphide minerals in the single paragenesis, due to similar sulphur concentration. The occurence of synchronous pair of minerals: anhydrite-pyrite barite-galenite, arising from sulphate ore-forming systems.

The typomorphic features of sulphate-sulphide paragenesis. In the pyrite-anhydrite pair: a) for pyrite- the finest oktahedral crystals scattered in anhydrite. The content of selenium, gold, nickel, cobalt and arsenic in pyrite is inversely proportional to its quantity in anhydrite mass. The lessened isotop sulphur composition (by 3-5%) due to the sulphate sulphur reduction; b) for anhydrite-metasomatic and veined character; from light to violet colour. Luminescence at the cost of manganese. EPR shows more than 40 faulty structures in the crystals, connected, in part, with ore-forming elements present. The isotopy of anhydrite sulphur shows its primary sediment origin. The anhydrite-molybdanite pair is characterisite of preferential development of the polytype 2H in the true anhydrite veins (deep levels), and 3R arises in more higher levels of anhydrite-quartz veins.

In the synchronous barite-galenite pair: a) for galenite - the occurrence of silver, bismuth, antimony, arsenic and mercury. The isotopy of sulphur is of a lighter content than that of barite; b) for barite-white colour (rose in ore-free parts); thermoluminescence at the cost of iron and manganese. The presence of high strontium content. The isotopy of sulphur is similar or close to that of anhydrite sulphur.

The synchronous sulphate-sulphide paragenesis and their typo - morphic features are consequences of the development of single physico-chemical systems with an active participation of underlying enclosing rocks.

TYPOMORPHISM OF QUARTZ THERMOLUMINESCENCE OF BULGARIAN DEPOSITS

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Directed thermoluminescence (TL) of quartz samples from seven different deposits of Bulgaria and connected with certain stages of development of different deposits was observed. Among the stages the following are distinguished: changes in vertical section, succession of quartz formation; its type (vein-type, crystal:opaque, transparent, smoky, amethyst) and different mineral associations. The received experimental results testify TL intensity dependence on the temperature of crystal formation. The determination of the changes in the TL intensity in vertical section has not brought satisfactory results.

The aspect of TL curves is determined to depend upon the chemical composition of mineral formation, that is the type of deposits and the composition of surrounding rocks.

The experiments on thermodiscolouring of artificial colour of quartz were conducted (this colour appeared after irradiation of the Y-rays Co<sup>60</sup>, dose 1,6.10<sup>6</sup>r). The experiments gave the opportunity to attribute certain TL glow peaks to certain size centers.

The division of TL curves into separate peaks was carried out, intensity of which being proportional to the temperature of crystallization and mineral formation of mineral-forming solutions or melt.

Theoretical ground for this division of quartz curves with the help of the analysis of peak intensity dependence upon the size centre concentration and other parameters are given.

TYPOMORPHISM OF MINERAL ASSEMBLAGES IN GOLD DEPOSITS OF SHALLOW DEPTHS

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The deposits born in the shallow depths always possess mineral assemblages called "pre-productive" that consits chiefly of quartz with minor quantities of chlorite, micas and carbonates; early productive assemblages containing pyrite and finely dispersed gold; and late productive ones with broad variety of sulphides and sulphosalts and a late generation of gold. This genetic line is terminated with assemblages having late generations of quartz, carbonates, pyrite and, frequently, antimonite.

The textural and structural particularities of the mineral aggregates of shallow depth deposits are manifested in well-known finely banded (metacolloidal and crustificational) and lamellar structures. These aggregates possess also some "ovoide"(spheroid) structures where sulphides, quartz and native gold take part. We consider them to be the products of a local segregation of the ore substances which has suffered a redistribution during the diffusion processes in the layers of the non-solidified silica gels.

Another typical feature is represented by structures of multi ple inter-and intra-layered crossing of one mineral aggregate
by other ones as well as by spots of some recrystallized mine ral aggregates indicative of a prolonged metastable state of
the early products and of a revivification of gels (thyxotropy).
In certain ore regions the redistribution of mineral substances
has been active in zones of gas eruption.

The typomorphism of compositions of mineral assemblages of shallow depths is manifested in the appearance of minerals that are not typical of deeper deposits: marcasite, adular and, sometimes, fahlores and tellurides in early assemblages; Ag sulphides and sulphosalts (argentite, polybasite, pyrargirite) in the late assemblages. High telluride content in productive assemblages may be explained by specific geochemistry of the regions

(Middle Asia, Carpathian Mts, the American Rocky Mountains, etc)
This tendency may be demonstrated by the distribution of Terich fahlors too.

The temporal change of mineral assemblages depends on the cyclic variation of activities of sulphur and oxygen during the polystaged development of ore-forming process. The redox potential of the solutions has been governed by the opening regime of fissures which controlled the intensity of mixing between the superficial waters and juvenile fluids and their saturation with gases. There are signs of significant role of leaching and rearrangement of mineral substances during the ore-forming processes.

# TYPOMORPHISM AND TOPOMINERALOGY OF SPHALERITE OF PAICHOI-NOVOZEMEISKAJA MINERALOGICAL PROVINCE

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The sphalerite with its wide range of variations of the constitution and properties, stipulated by genetical reasons, is one of the most informative objects of topomineralogical investigations. The methodical peculiarities and results of a middlescale mineralogical mapping are discussed on the example of Paichoi-Novozemelskaja mineralogical province.

As an element of mineralogical mapping, the distribution of the sphalerite, its content in mineralogical system, typomorphic associations, chemical composition and more important typomor - phic properties have been used. The contraction of information for generalized comparisons was carried out by statistical me - thods and by the calculation of entropy and anentropy in the composition and factor weights.

The diversity of sphalerites of the province is determined by three independent tendencies in their composition change, realized in three isomorphic series:

series of sphalerite-Fe with ranges 100% ZnS 90% ZnS + 10%FeS; series of sphalerite-Mn with ranges 100% ZnS 85% ZnS + 15%MnS; series of sphalerite-Cd with ranges 100% ZnS 93% ZnS + 7%CdS.

The last two series in the pure state are established in nature for the first time and in any other mineralogical provinces of the world are not known.

The correlation between the composition and properties of the sphalerite is described by the system of equations of multiple regression:

 $a_0$ =5,4083 + 0,000456 FeS + 0,00210 MnS + 0,00424 CdS (Å); d =4,0812 - 0,00498 FeS - 0,00817 MnS + 0,00741 CdS (gr/cm<sup>3</sup>); =-0,30 + 0,619 FeS + 0,945 MnS (  $10^{-6}$ cm<sup>3</sup>/gr) and so forth.

With the help of the analysis of the sphalerite typomorphism, the mineralogical zoning of the province is found out and a number of regions with specific peculiarities in the mineral formation are distinguished.

The factor analysis permits to establish the main reasons of the sphalerite typomorphism. Observed variations of typomorphic peculiarities are almost completely determined by three factors:  $F_1(20\%) = +(a_0, Mn, Cd, Sb, H, Cu, V, Sn, Ga)-(Zn, Fe, Co, S,Ge)$  interpreted as the chemical composition of the mineralogenetic environment;  $F_2(14\%) = +(Fe, S, Co, colour, Pb, Ti, Mn)-(Zn, Cd, Ht, <math>\sum$  Tl, Ga), identified as the medium temperature;  $F_3(6,2\%) = +(Cd, Tl, Fe, Co, Ti, Pb)-(S, Sb, Mn, Zn, Ht)$  showing the medium pH.

The conditions and regime of the formation of sphalerite-bearing associations were established and general evolution of the mineral formation in the province was stated.

A PARTICULAR CASE OF FORMATION OF THE RARE MINERAL SOMOLNOCKITE

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The somolnockites, described up to now, have been observed mainly in two genetic types. The findings in altered pyritite ores refer to the first type. Those ones, formed along coal shales as "efflorescence" refer to the second type.

The somolnockite, described in the present paper, belongs to the second genetic type. It was found in a peculiar deposit — in a semicarbonificated fire-cone (probably of genus Pinus) included in kieselgur of Plinocene age. It is white in colour and occurs as fine stalactite-like aggregates. The X-ray analyses show that this is a somolnockite mixed with kieserite. The quantitative chemical analysis showed the following results: 84,10% FeSO<sub>4</sub> .  $\rm H_2O$ ; 14,40% MgSO<sub>4</sub> .  $\rm H_2O$  and 1,67% of hygroscopic water.

The somolnockite has been formed during diagenesis of the kieselgur, when the circulating solutions have deposited it along the lower side of the semi-carbonificated flakes of the fire-cone. Bearing in mind the deposit in Belgium described by R. Van Tassel of similar type and a number of other water sulphates as "efflorescence" along coal shales, it must be emphasized that the formation of the observed somolnockite just on the coalificated substrate of the fire-cone takes place. The fact should be accepted as an important typogenetic sign.

#### TYPOMORPHISM OF MINERALS IN ALKALINE MASSIFS

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The alkaline rock is assumed to contain other alkaline minerals than the main rock-forming feldspars and micas. Such minerals have more than 5 a.p.c. of alkalies (Na and K) - normally more than that in micas. This definition entrain in the alkaline rock group leucite, natrolite, riebeckite, omphacite NaCaMgAlSi206, leaving away hastingsite NaCa2Mg4Al3Si6022F (3%Na), thompsonite, apophyllite and some other hyperalkaline silicates. In contrast, the group of ultralkaline minerals would contain minerals with more than 15 p.c. of alkalies: kasakovite, khibinskite etc. The main alkalies ratios make all these hyperalkaline and alkaline associations divided in sodic, potassic and intermediate groups (natisite, khibinskite, tinaite). Considering possible combinations of the rock-forming minerals (feldspars and quartz) with the alkaline ones (feldspathoids, aegirine) six types of alkaline associations are to be named:

1) feldspathoid: nephelinites, leucitites, etc.; 2) plagicclase-feldspathoid; 3) feldspar-feldspathoid; 4) feldspar-aegirinic; feldspar-quartz-aegirinic; 6) carbonate-aegirinic.

The alkaline association evolution has for its indicators volatile and alkaline components as well as hetero-valent ones that occupy extreme positions in the Periodic system (groups VII and I).

It would be more reasonable to compare the massifs and the deposits while considering the corresponding abundances of Li, Na K, Rb, Mn, Fe<sup>3</sup>, F. Cl, H in similar minerals - micas and amphiboles. They would contain the most of useful data.

Four evolution stages are to be specified. The first one brings high temperature minerals, poor in volatile and alkaline components (hastingsite), whereas the second one gives rise to Na-, Cl-, Fe- and sometimes F-rich minerals (arfvedsonite); the minerals rich in Na,K,Li,F,Mn (LiFMn-riebeckite) are born during the III-d stage of evolution, and the water-rich ones (hydro-

richterite, etc.) - in the final stage.

COMPOSITION AND SOME PHYSICAL PROPERTIES OF TOURMALINE FORMING CONDITIONS

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Tourmaline is a widespread mineral that usually accompanies a number of commercial commodities. This fact may be used as a good mineral-indicator.

As it has been shown in detailed studies, the main typomorphic feature of tourmaline is the correlation of tis minor constituents. The average contents of Sn,Mn,Sc,Ni,Pb,Cr and V have been found. A high Sn content in the mineral taken from cassiterite-silicate fomations is made known. It is an order higher than in tourmalines of other ore deposits and two orders higher than in the minerals born elsewhere. A probable statistical method based on the spectral analysis data is proposed to define the genetic affiliation of unknown tourmaline samples.

The real Fe<sup>3+</sup>/Fe<sup>2+</sup> ratic that seems to be a strong typomorphic sign has been found with Mossbauer, IR-spectrographic and mag - netometric techniques. The same studies have made it possible to establish cases of ordered and disordered crystalline structures in natural tourmalines. The degree of structural order is also an important typomorphic sign, which is defined by composition and by the growth temperature of this mineral. The structural variations constitute a factor that produces its effect on tourmaline behaviour in oxydizing annealing and in thermographic analysis. The ordered modifications are characterized by low-temperature effects, the Fe<sup>2+</sup> oxydation being more easily permitted there.

TYPOMORPHISM OF ROCK-FORMING MINERALS IN RELATION TO THE PROBLEM OF THE GENESIS OF THE KHIBINA APATITE DEPOSITS

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Anchieutectic character of the apatite-bearing intrusion and the co-incidence of the crystallization order of apatite ores with the regularities in the crystallization of the experimentally investigated phosphate-silicate systems show that the principal process in the formation of apatite deposits was the crystallization differentiation. In order to elucidate the mechanism of the apatite ore formation , the typomorphic characteristics (grain size and composition) of the rock-forming minerals (apatite, nepheline and pyroxene) were considered. The detailed granulometric analysis established the variations in the grain size of the rock-forming minerals in vertical crosssection of apatite deposits. The shape of grains and the varying sizes of minerals were controlled by the conditions of their separation from parent ijolite-urtite magma. The strik ing uniformity in the grain sizes of crystals building out different zones of apatite deposits is observed.

The distinct sorting of minerals in the vertical cross-section of intrusion is noted: the smaller grains (of pyroxene and apatite) are in the upper parts of the deposits. The observed sorting of the mineral grains together with the calculated hydraulic equivalent and the consistency of the regularities in the distribution of rock-forming minerals with the position of hydraulic curves permit one to propose a hypothesis that the main mechanism of the genesis of apatite ores was gravitational differentiation. Other typomorphic features of the minerals of apatite-bearing intrusion are the shapes of nepheline, pyroxene and apatite, belonging to various generations and phase composition of microinclusions are also consistent with the proposed model of the genesis of apatite ores.

TYPOMORPHISM OF THE MINERALS OF THE KHIBINA MASSIF AND
POSTMAGMATIC PROCESSES IN THE ORIGIN OF ITS MINERALIZATION

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Each of the rocks and pegmatite type in the Khibina massif possesses proper compositional and structural features pertaining to the rock-forming minerals as well as certain accessory mineral associations corresponding to the temperatures and chemical conditions of crystallization of the alkaline melt. As a whole, all these associations are of miaskitic character that is indicative of a comparatively low alkalinity of the primary magma. The associations formed during the contact interactions of the melt and the enclosing rocks are determined by the chemical composition and by their situation in the massif (contacts, xenoliths).

Typical agpaitic minerals (aegirine, eudialyte, aenigmatite, rinkite, lamprophillite etc.) were formed in all the containing rocks and pegmatites a bit later, during the autometasomatic stage, which is indicative of a rise of alkalinity in postmagmatic solutions.

The most profound effect of the post-magmatic processes is observed in the central arch of the massif. Because of tectonic and magmatic activities and of and intensive and prolonged heating of the rock the highly alkaline and highly hot solutions induced a recrystallization of a certain part of melteigite-urtites and of the bordering nepheline-syenite to form some adular-bearing poikilitic nepheline-syenites (juvites and rischorrites). The local mineralisation characterized by an intense development of K, Ba, Sr minerals of K-, Zr- and Ti-silicates and of K-bearing sulphides is specified as an ultraagpaitic one.

Far away from the central active zone and on lowering temperature and alkalinity the surrounding rocks suffered a nephelinization, an aegirinization, an albitization and a zeolitization. The apatite rock is partly recrystallized and the new apatite is enriched in Sr.

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One of a great achievement in the mineralogy of the latest de - cade is the discovery of K-bearing sulphides: djerfisherite, rasvumite and bartonite, the former being the most frequent in nature. The study of djerfisherite from some deposits made it possible to specify its typomorphic features related to different genesis.

The typomorphism of djerfisherite is manifested first of all in changes of its chemical composition. More than 50 analyses enable one to establish three mineral varieties: 1) Fe-rich (Tajeran skarns), this composition approaches that of djerfisherite from the stone meteorites; 2) Ni-rich (up to 20 w.p.c.) - Yakutian kimberlites; 3) Cu-rich (up to 22,4 w.p.c.) from Talnakh and Khibina deposits. Fe-rich djerfisherite has been found recently in the latter deposit. This djerfisherite has Na content (up to 0,65 w.p.c.).

A statistical treatment of 27 analyses of djerfisherite from kimberlite defined the reliable correlations Fe-Cu (-0,603),Cu-Ni (-0,845) and no correlations between Fe-Ni (+0,189). The variations in the composition influence djerfisherite's physical properties: reflectance, hardness and unit cell parameters.

Crystal structure determinations have made it possible to obtain more precise crystallochemical formulae of the mineral, to give the crystallochemical interpretation of the wide compositional variations and to find the isomorphic substitutions of tetrahedral Fe, Cu and Ni cations which are controlled by a constant number of d-electrons in cluster.

The typomorphic peculiarities in djerfisherite are indicative of the compositional changes in the host rocks and in sulphide assemblages and, sometimes, the degree of development of the alkaline metasomatism.

#### TYPOMORPHISM OF ZIRCONS IN ZONES OF ALKALINE METASOMATHOSIS

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It has been established that in highly alkaline environment zircons are subjected to corrosion, hydration, regeneration and recrystallization. The degree of face corrosion is inversely proportional to reticular density of their flat nets. As a result of corrosion rounded, "egg-shaped", "melt" zircon grains appear (Vakhrushev, 1956, Starkov, 1961, Starkov, Flass, 1966, Ichimura, 1955 and oth.).

In Baikal-Caledonian type of granites, sienites (derived from anatexis, according to V.A. Rudnik, and in alkaline metasomatites in Timan Province, the typomorphic varieties of zircons are distinguished: a) zenogenic zircon in rounded-columnar grains (D<0,2 mlm) remaining during solution treatment or melting of sedimentary-metamorphic rocks, b) authigenic zircon in euhedral grains (d>0,2 mlm). A gradual transformation of xenogenic zircon is observed on the periphery of the masses and veined bodies from the rims to their centre: 1) rounded-columnar grains without indications of solution and regeneration, 2) the same grains with irregularly corroded faces, partially malaconized, 3) the same ones regenerated and malaconized grains with dipy-ramidal-prismatic polyzonal malacons (in granites) or dipyramidal-nonzonal zircons and malacons (in sienites and alcaline metasomatites) recrystallization.

Index of refraction in zenogenic and recrystallized zircons is similar. Close relationship between typomorphic zircon trans - formations is described for granites from Scotland (Uaitt, 1954, Preobrazhensky, 1955, Transbaikalia). Thus the above typomorphic zircons are considered as mineragenic indicators of alkaline metasomathosis, derivation of rare metals from the country rocks and geochemical inheritance. They also give evidence to deny the relationship between the rounded forms and similar zircon grains and the processes of their solution.

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Minerals of glauconite group (MGG) are low-temperature micas of IM polytype with high content of silicium (4,0-3,4). They differ from high-temperature micas by peculiar isomorphism, special structural features and proton behaviour (I.Nikolaeva, 1977).

Statistic investigation of more than 600 analyses permitted to establish the main tendency in cation ratio SiK - R3+R2+ and isomorphism by the scheme  $3R^{2+} \rightarrow 2R^{3+}$  that is characterized by all micas in general. The MGG shows perfect isomorphism  $\mathrm{Fe}^{3+}$ -- Al never displayed by high-temperature micas of the muscovite group. Bivalent cations behave differently: they form a minal (Mg<sub>0.7</sub> Fe<sub>0.3</sub>)<sub>1.0</sub> in sedimentary minerals and easily replace each other Mg-+Fe<sup>2+</sup> in hydrothermal minerals. The predomi nating octahedral cation distinguishes five various minerals: Fe<sup>3+</sup> - glauconite, Al - scolite, (MgFe<sup>2+</sup>) - bulajinite, Mg-ce ladonite and Fe2+ (unnamed vet). Theoretical sum of octahedral cations for the  $\mathbb{R}^{3+}$  series minerals is 1.7 - 2.0 and for the  $\mathbb{R}^{2+}$ series minerals it is 2.5. The MGG infrared spectra range gradually from those typical of dioctahedral micas up to the spectra typical of trioctahedral micas. EPR spectra show the four positions of a three-valent iron, the intensity of their bands depending on the MGG chemical composition. Parameters of the unit cell vary as determined by the mineral chemical composition. The amount of hydroxyl anions exceeds 2.00, some of them reveal instability under normal pressure and in vacuum.

There has been established a relationship between the MGG mineral composition and the age of enclosing formations. It enables one to conclude on geochemical specification of the authigenous silicate formation in various geological epochs and the element differentiation in coeval deposits. In view of this fact the MGG may serve as a reliable index of the ocean salinity evolution and the epochs of sedimentary mineral formation.

DEVELOPMENT OF PYRITE COMPOSITION AND PROPERTIES AND ITS ROLE IN METALLOGENY OF THE YENISEI MOUNTAIN RIDGE

W.G. Prokhorov, Krasnovsk, USSR

The studying pyrite of sedimentary rocks and the deposits from Yenisei mountain ridege has shown that during the advancement up the section of Proterozoic accumulations from Petchenga to Kyrgitey Suite, the peculiarities in decrepitation, stoichio - metry, thermoelectric potential of pyrite change. The distinct dependence of the composition of the trace-elements of pyrite on stratigraphic position or level of rock metamorphism is established.

The thermoelectric properties of pyrite correlate with the intensity of regional metamorphism. In the lower parts of section in metamorphosed rocks at epidote-amphibole facies level pyrites with electronic conductivity prevail. As metamorphic grade lowers, part of pyrite with positive thermoelectric conductivity grows. The formula for the composition of pyrite changes. The calculation of the sulphur balance, sublimated under the metamorphism of sedimentary rocks shows that the pyrite contained in them is the source of sulphur in sulphide deposits in higher parts of the section. The change in pyrite properties as a geochemical barrier is the reason for the origin of zoned mineralization.

The main part of elements, which have similarity with sulphur, deposited on this level, where the temperature of regional metamorphism was not higher than 200-250°C and pyrite kept positive thermoelectric conductivity.

The deposits of gold, antimony, arsenic cannot be discovered above this level. Up to the section there is more possibilities of discovery of elements with lover similarity with sulphur, such as copper, lead and zinc. The existence of correlative connections between typomorphic properties of a real pyrite and metallogenic peculiarities in deposits enabled one to work out the methods of definition of pyrite belongment to standard types of ore mineralization.

PLATY QUARTZ VARIETIES IN GOLD-SILVER DEPOSITS

A.A. Sidorov and V.I. Naiborodin, Magadan, USSR

Platy quartz is a typomorphic mineral of volcanic gold-silver deposits. Most investigators are inclined to envisage it as a pseudomorphic formation after carbonates. The authors have found the platy aggregates to have different structural features and conditions of formation. On the basis of ontogenic analysis at least three types of platy aggregates can be recognized:

- 1. Metasomatic (or pseudomorphic after calcite) ones that are of insignificant distribution since carbonates are formed during the concluding stage of the ore-generating process everywhere.
- 2. Common infillings of vein cavities of agate-forming type are of wide distribution. However, at the initial period there appear thin plates of intermediate X-modification of silica which is subsequently covered by agate-like strips. Plate frameworks then remain empty or otherwise are filled with different silica varieties, including coarse-prismatic crystals of quartz of water-transparent or amethyst colours.

Deformational platy aggregates are formed in the result of cracking gels, chalcedony or colloform aggregates of quartz. They are related to breccia aggregates and comprise fragments of host rocks and vein minerals.

Platy quartz varieties are usually of grey-white or milky-white colours since they are impregnated by single-phase inclusions that make the mineral succumb to selective replacement by carbonates, adular, rhodonite, pyrite and other minerals.

GALENA TYPOMORPHISM OF POLYMETALLIC ORE OCCURENCES IN THE POLAR URALS

V.S. Mityusheva, T.I. Zolotarev, Tjumen, USSR

To distinguish typomorphic features, the galena properties of the three genetic types from the Polar Urals' ores were studied: stratiformic, regenerated and hydrothermal. Stratiformic mineralization, found in two ore-controlling stratigraphic levels of the Ordovician section is associated with epigenetic galena mineralization, located in veins of "Alpine" type. Widespread redeposition processes in the ores of the upper ore-bearing stratigraphic level resulted in formation of independent ore bodies (regenerated type).

High concentration of Ag and Bi are characteristic of galena from hydrothermal ore occurences. The absence of Pb vividly indicates galena from stratiformous ores of theupper ore-bearing level. Galena with variable thermo-e.m.f. is characterized by an increase of the grid parameters.

Isotopic relations of S in stratiformic ore galena vary greatly. Galena sulphur in the ores of the lower ore-bearing level is much heavier  $68^{34}$  from -1.6 to +26.6%, the average value +11.7%) and of the upper level - sufficiently lighter  $68^{34}$  from +5.4 to -20.9%, the average value - 7.3%). Galena from veins of "Alpine" type inherits sulphur from "source" ores with slight homogenization of its isotopic composition. Homogenization of sulphur isotopic relations is most evident in galena of regenerated ores  $68^{34} + 5.0$ %). Galena sulphur of hydrothermal occurences is slightly heavier  $88^{34} + 8.6$ %).

In most samples galena has electron conductivity. Galena samples of the upper ore-bearing level and some samples of the lower level with "washed-out" histogram of thermo-e.m.f. (-30 -34mV), right to "np" appearance - atype of conductivity. For galena with the "compact" histogram of thermo-e.m.f. of the lower le - vel and for galena from hydrothermal ores, model values are markedly higher (-50 mV). Galena of regenerated ores has medium

values (-42mV).

The preliminary analysis of the results allowed to establish some peculiar features of galena from different morphogenetic types of mineralization. Sulphur isotopic composition and thermoelectric properties are the most characteristic features.

TYPOMORPHISM OF ALKALINE PLUTON MINERALS IN RELATION TO THE CONTENT OF PHOSPHATES

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In alkaline intrusive massifs apatite deposits are spatially connected with the products of the most saturated with phosphorus differentiates of abyssal melts: early carbonatites, melteigite-urvites, fergusites. The composition of apatite alkaline massifs reflects the bulk chemistry of the primary magmas: in alkaline-ultrabasic rock complexes, rich in calcium and carbonates, apatite is poor in isomorphic with calcium impurities and contains  $\rm CO_2$ ; in agpaitic nepheline - syenite complexes rare-earth-strontium or strontium hydroxyl-fluorine-apatite is significantly spread; in pseudo-leucite syenite complexes rare-earth strontium apatite occur, and in fergusite it has carbonate-ion impurity.

Within each manifestation of apatite mineralization of an industrial type a trend toward decrease of cation impurities content in apatite with an increase of this mineral content in rock is observed.

Apatite of the most large deposits was formed in several stages under different physical and chemical conditions, as evidenced by heterogeneity in chemical composition and physical properties of apatite.

Most apatite concentrations in alkaline massif rocks is accom - panied by relatively high magnetite (titanomagnetite) content and with accumulation of phosphorus in rocks titanium and chromium behaviour regularly changes in this mineral.

Along the contacts between apatite-nepheline rocks and apatite-bearing melteigite-urtites of nepheline-syenite massifs development of specific apatite-sphene formations with characteristic prismatic linear oriented sphene grains is ragular.

In contact zones of apatite-nepheline Khibiny deposits certain types of late endogenic mineralization are displayed: natrolite pectolite, sulphide, villiaumite. In these manifestations near apatite bodies rare minerals including those first discovered in the Khibiny are found.

Thus, in large alkaline intrusive massifs the most significant manifestations of apatite mineralization (Khibiny, Kovdor, Synnyr) are accompanied by changes in chemistry and physical properties of apatite and minerals from magnetite group by appearance of specific high-temperature apatite-sphene associations on phosphate-bearing rock contacts, by development of certain late mineralization processes in contact zones of apatite-nepheline deposits.

Gas-liquid inclusions in apatite, the composition of gas occluded by its crystals, late mineral associations, accompanying apatite rocks - all these facts indicate that phosphate deposits in alkaline plutons developed in the process of separation and evolution of complex by composition alkaline-carbonate fluids, typical of abyssal supplies.

TELLURIDES IN MINING FORMATIONS OF THE ARMENIAN SSR AND THEIR TYPOMORPHIC PECULIARITIES

G.O. Pidjian, Sh.O. Amirian, A.I. Karapetian, A.S. Faramazian, Erevan, USSR

On the territory of the Armenian SSR, representing a small section of Mediterranean metallogenic belt, wide-developed layers of copper-molybdenum, copper-pyrite, polymetallic, gold-mining and iron-mining formations are found.

It has been established that numerous tellurides of bismuth, gold silver, lead, mercury, copper and nickel, which form various associations depend on formational types of layers, mineral composition of ores and on the conditions of their formation.

The typomorphism of tellurides is shown in their quantitative and qualitative contents, successions of deposits in the process of mining formation, structural peculiarities, crystal-optical and physico-chemical properties.

The typomorphic peculiarities of tellurides served as supplementary signs of mining typifications, exploitation of effective schemes of their treatment and complex utilization.

The tellurides and their associations are most characteristic of meso-Cenozoic metallogeny. As a rule, the telluride containing ores are formed in middle-low-temperature conditions on moderate and little depths. The higher concentration of tellur is usually combined with the late stages of mineralization of hydrothermal mining formations.

The characteristic peculiarities in tellur and tellurides are in close affinity with gold, which frequently results in origination of gold-tellur formation of ores. The affinity of tellur with gold, silver, bismuth, lead, mercury, copper and nickel represents one of the most important typomorphic features of hypogenic ores.

TYPOMORPHISM OF MUSCOVITE AND GEOCHEMICAL FEATURES OF THE QUARTZ-WOLFRAMITE ORE FORMATION

#### S.A. Korenbaum, Vladivostok, USSR

Muscovites (Mu) of the ore-bearing bodies of quartz-wolframite deposits are discussed. Differences in fluorine content of Mu allow one to divide these deposits into low-fluorine and moderate-fluorine types. Mu of the 1-st type have constant number of cations in the octahedral site:

$$K_2(Al_{4-n} R_n^{2+})_4$$
  $\left[Si_{6+n} Al_{2-n} Q_{20}\right]$   $(OH, F_{0,25})_4$ ;  $n < 0.3$ 

The octahedral occupancy in Mu of the second type is more than 2. Isomorphous substitution in this type of Mu are described by the following formula:

$$K_2(Al_{4-m} R_{1,5m}^{2+})_{4+0,5m} Si_6Al_2O_{20} (OH,F_{0,25-0,5})_4;n<0,3$$

The most enriched by the bivalent cations Mu associates with ferromagnesian minerals. The variation in the  $R^{2+}/Al$  ratio in Mu from different mineral assemblages is not considerable in any ore body's cross section. Manganese content in Mu does not correlate with manganese in wolframite (Wt), but the partition coefficient (K=  $\frac{(Mn/Fe+Mn)\ Mu}{(Mn/Fe+Mn)\ Wt}$ ) calculated for all types of deposits is constant and equal to  $\sim 0.09$ .

The compositional dependence on Mu from types of mineral assemblages and mutual correlation in manganese content in coexist - ing Mu and Wt suggest that Mu would be in chemical equilibrium with other minerals of ore bodies. Based on this are the methods of thermodynamic analysis of multicomponent systems with the variable number of phases used.

It has been established that the substitution in muscovite-phengite group takes place at low activity of volatile components and moderate acidity. Trioctahedral member content in Mu increases with activity of volatiles (mainly fluorine) and acidity increasing.

#### A.P. Khomyakov, Moscow, USSR

The studies relate to pegmatoid derivaties designated as ultraagnaitic pegmatites and hydrothermalites being of certain interest in the last years because of a necessity to understand the nature of some alkaline rocks and of the related deposits. These derivatives are composed of minerals with extremely high concentrations of Na, K and volatile and rare elements, these mine rals including changable alkaline Ti-Zr silicates (kasakovite. zirsinalite), water-soluble Na silicates and phosphates (natrosilite, natrophosphate). Accompanied by natrosilite and natro phosphate, the normally alkaline Ti-, Nb- and Zr silicates stable in paragenesis with villiaumite and frequent in more aboundant agpaitic associations, become unstable and decompose to give highly alkaline formations of the same elements (zirsinalite pseudomorphs after audialyte). The latter, when in epythermal and hypergenic conditions and in contact with the atmosphere, are easily substituted by hydrate minerals, which inherit the main constitutional features of the protophase (homoaxial pseudomorphs of lovoserit after zirsinalite, that of epistolite after vuonnemite and of murmanite after lomonosovite). The ultraagpaitic pegmatites accompany the world's greatest deposits of rare metals and phosphate raw materials and form independent stocks and sheet bodies, containing Ta, Nb, Tr, Zr ores. Relations existing between the pegmatites and the ores in question indicate to special conditions where these deposits were formed with the participation of the silicate-salt liquids supersatu rated with alkalies as well as with volatile and rare elements.

#### TYPOMORPHIC FEATURES OF POTASSIUM FELDSPARS

Z.G. Karaeva, V.S. Gaidukova, V.T. Dubinchuk, G.K. Krivokoneva. L.S. Solntseva. Moscow. USSR

Potassium feldspars of some magmatic complexes, pegmatites and subalkaline metasomatites have been examined. An X-ray powder method was applied to determine their structural state using cell parameters for defining Al/Si distribution and the X-ray line broadening to estimate the degree of structural perfection. It was found that there exists a relationship between the IR-spectra constants  $\Delta V$ , A, C and X-ray characteristics of potassic feldspars structural state. Transmission electron microscopy permitted us to make evident the block-like textures of the potassic feldspars and the submicroscopic exsolution of them (perthites) with  $\lambda = 1000-2000$  A as well as to determine the density of dislocations. Potassic feldspars of various origin was found out to be characterised by different solubilities in acid and alkali.

The low-temperature metasomatic potassic feldspars differ from high-temperature magmatic-autometasomatic ones by less perfect structure and more ordered Al/Si classification. They have block like microtextures and most solubility in acid and alkali. The features of microtextures and structural state data give information of the degree of feldspars'recrystallisation. IR-Spectra characteristics of potassic feldspars and data of trace element distribution in them give possibility to determine distinct relations between the potassic feldspars and their genetic types and ore-bearing complexes. This investigation allowed us to find features of the potassic feldspars from various geological provinces.

#### DISSYMMETRIZATION OF CORDIERITE CRYSTALS

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Crystallochemical nonequivalence of cordierite growing faces may cause crystal dissymetrization up to formation of two types of crystallochemical matrices within one crystal. Depending on isomorphic impurity the dissymetrization is either intensified or decreased (examples are given). First of all it is reflected in the anatomy of synthesized cordierite-tripling takes place not over the whole crystal, but selectively over the growth sectors. Physical properties of growth pyramids also greatly differ so that hexagonal (disordered) cordierite variety develops mainly in one growth sector whereas rhombic (ordered) one occurs in another.

Some morphological types of sectorial twinning can be expected depending on character of isomorphic impurity doping to growth sectors of matrices and heterometry display, their number depend on quantity of developed faces in crystal. There is no strain in crystal and it does not twin under regular impurity distribution. This is characteristic of extreme members of isomorphoys series (illustrated by plot).

Milarite and jeremijevite can also be striking instances of crystal dissymmetrization displayed in morphological plan. Simultaneous sectorial twinning of neither of the prims and pinacoid observed in synthetic cordierite.

Sectorial twinning and other morphological features (character of cracking, zoning and optical extinction of crystal, etc.) are dissymetrization indications.

TYPOMORPHISM OF THE MINERALS IN LAYERED INTRUSIONS

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The fundamental characteristic feature of the layered intrusion is a "latent" stratification, caused by the processes of a fractional crystallization and expressed in a gradual enrichment of the minerals with the easily fusible components from the back to the hanging side of this intrusion. The minerals of the layered intrusions represent special highly determined association whose properties change gradually in the section of the intrusion. Practically, all mineral properties are determined by the position of the mineral in the section.

The first detailed study of these properties has been made in relation with the layered ijolite-urtite apatite-bearing intrusion in the Khibin massif. Apatite, nepheline, sphene, aegirine diopside and titanomagnetite have been analysed.

The position effect for the chemical composition (and for some other properties) is most indicative in the case of apatite:

$$LgSr0_{g} = 0,185 LgX + 0,732$$

where X is the distance between the sample and the top side of the section taken as a whole. The density ( $\rho$ ) correlation factor and the correlation coefficients for the parameters  $a_0$  and  $c_0$  in Sr0-bearing apatite are 0,849; 0,970; 0,898, respectively.  $\rho$  = 0,0126 $^{\rm Sr0}$  + 3,212;  $a_0$  = 0,0074 $^{\rm Sr0}$  + 9,369;  $c_0$ =0,0054 $^{\rm Sr0}$  + 6,885.

The results obtained enable us to draw certain conclusions on the character of changes in the properties of the mineral association of the layered ijolite-urtite intrusion depending on physico-chemical forming conditions. They make it possible also to specify the most informative qualities of the association and to graduate the intrusion section. CRYSTALLOCHEMICAL ADMIXTURE OF Fe IN BASIC PLAGIOCLASES AND QUESTIONS OF THEIR TYPOMORPHISM

F.P. Lesnov, M.Ya. Shcherbakova, V.S. Lysakov, V.N. Korolyuk, Movosibirsk, USSR

The peculiarities in heterogenic plagicclases are examined on the basis of data about containing common and three-valent iron. The data were obtained from electron microprobe analyses, EPR and X-ray luminescence methods.

Concentrations of Fe in plagicclases increase from 0,0 % wt in very deep rocks to nearly 1% wt in basalts. The quantity of admixture defects, which are caused by Fe-ions penetration into the structure of plagicclases is inversely proportional to the magmatic body formation and growth velocity of crystals.

Considerable part of iron in earth plagioclases is in Fe<sup>3+</sup>form. According to EPR data, Fe<sup>3+</sup> ions make three different types of complexes in the structure of plagioclases. The complexes are fixed by 3 line systems with g-factors near 4 on the spectra. Five types of EPR Fe<sup>3+</sup> spectra had been established for basic plagioclases. Local structure well regulation degree near Fe<sup>3+</sup> ions decreases from the 1-st to the 5-th type. The EPR Fe<sup>3+</sup> spectrum forms of the same igneous body of plagioclases are often similar.

Four lines for plagioclases were determined on the X-ray luminescence spectrum in 350, 430-480, 564-570 and 737-770 nm ranges. The direct qualitative dependence of the last line intensity upon the common Fe-admixture concentration was discovered. The line was ascribed to Fe<sup>3+</sup> hole center. The intensity of this line did not change after specimen annealing at 450°C (Temperature of filming - 77 and 300°K). According to the data a conclusion was made that Fe<sup>3+</sup> admixture centres are in the specimens of plagioclases from the moment of their formation.

Complex examination of crystallochemical admixture of Fe distribution in basic plagioclases have important meaning for in vestigation of this rock-forming mineral's typomorphism.

# ISOMORPHIC PECULIARITIES IN FLUORITES FROM MONGOLIA

# J. Lhamsuren, B. Tumenbayar, Sh. Batzbargal, Ulan-Bator, MNR

Fluorites from Mongolian deposits of different genetic types differ in origin and mechanism of individual growth, occurences of aggregates, crystal morphology, colour, type of zoning and the character of gas-liquid inclusions.

Colourless, azonal large high-grade monocrystals are characteristic only of chambered pegmatites, while hydrothermal deposits contain bright-coloured zonal (becoming fine-zonal during the last stages of growth) crystals with growth discontinuities.

Fluorite bodies are formed multistagely and this results in various structural-textural types of fluorite ores.

Vividly and comprehensively it revealed the evolution of fluorite crystallo-morphology both for interrelated endogenic formations and separate deposits. General evolutionary series begins with octehedral, which further through combinations of simple forms changes to cube completing the series complex combinations including epatrial volumetric-positive peaks, not infrequently turning to framework-edged forms, spheric crystals, antiskeleton forms and phantom-crystals.

The evolution of forms takes place on the background of decreasing temperature and concentration of fluorite-forming medium. The medium inclusions permit one to determine some typomorphic peculiarities of fluorite. The presence of impurities is an important typomorphic feature of fluorites. Comparatively high contents of rubidium, Na and Ca are characteristic of fluorites from the rare-metal deposits, it can serve as additional search sign. Fluorites associated with granites of the lithium fluorine geochemical type are considerably enriched in lithium. The correlation coefficient of impurities in fluorites from the rare-metal deposits is always very high in comparison with that of the rest types of deposits.

Occurence of fluorites almost in all endogenic formations, their characteristic typomorphic features and their spatio-temporal distribution allow one to consider fluorite as important typomorphic mineral.

# ON TYPOMORPHIC PECULIARITIES IN VEIN-TYPE ALUMOFLUORITE, FLUORITE AND HALOGENIDOSILICATE ASSOCIATION

#### A.D. Nozhkin and I.T. Bakumenko, Novosibirsk, USSR

Alumofluorites are very uncommon, presumably sodium minerals. They are nearly all of common occurence in cryolite deposits of Ivigtut, Greenland, their later occurences were found from alkaline granites, pegmatites and greisens.

The Ca-Ba-alumofluorite-usovite, Ca-jarlite, prosopite and hypergene gearksutite association has been found to occur firstly in E. Siberia in fluorite veins. The veins consist by 80-85% of fluorite of various colour with higher Th contents (to 0.15%) and Tr (to 1.18%). The green-coloured muscovite associates with violet fluorite and thorite, while usovite, Ca-jarlite and prosopite replacing them associate with both green-coloured and colourless fluorite. The fine-grained mass and mineral microspherolites of similar composition and structure with topaz in association with diaspore are of common occurence in fluorite as nodules and veinlets, the suncite admixed with thorite, pyrite, sphalerite, quartz and other minerals are also common.

It has been found that in the mineral-forming process there have been a successive alteration of fluorites, alumofluorites followed by halogenidesilicates of aluminium and finally silicates which was the result of gradual reduction in acidity of rluorine-bearing liquids. The typomorphic peculiarities in the minerals are a function of the high-acid fluorine mineral-forming medium properties with higher Ca,Ba,Th,Tr and Al activities in addition to mineral crystallization in conditions of high-middle temperatures. Geologically and geochemically it was

found that there is a genetic correltion between the mineralization and alkaline-syenite post-Proterozoic complex activity of the region under discussion.

SULPHOSALTS AND PLATINUM MINERALS

#### CRYSTAL CHEMISTRY AND SYSTEMATICS OF THE SULPHOSALT MINERALS

#### I. Kostov, Sofia, Bulgaria

The compositions of the "true" sulphosalts are represented by wholesome ratios of metallic ( $M^2$ -S resp.  $M_2$ -S) and semi-metallic ( $X_2S_3$ ) constituents, each ratio obtained by addition of adjacent ratios (e.g. 2:1, 3:2, 4:3, 1:1, 2:3, 1:2 etc.). Their structural schemes are based on accordingly polymerised, discrete or infinite groups of  $XS_3$  pyramids or derivative coordination polyhedra, attached to which are the metals (chiefly Cu, Ag, and Pb) in coordination ranging from threefold to nine-fold. The bismuthian sulphosalts are with predominant chain-like (axial or A-type) development, the antimonian with pseudoisometric or (I)-type development, and the arsenian with layered (planar or P-type) development. There is a tendency the bismuthian sulphosalts to be enriched in Se and the arsenian in Tl.

Taking into account crystal chemistry and natural assemblages the following scheme is proposed as more rational for the classification of the sulphosalt minerals:

# a) Fe-Cu-Pb(Tl) Assemblages

# Bismuthian(sulphobismuthites) Axial Types

Planar Types Pseudoisometric Types

# Antimonian (Sulphantimonites)

Axial Types Planar Types

Pseudoisometric Types

# <u>Arsenian</u>(Sulpharsenites)

Axial Types Planar Types

Pseudoisometric Types

### b) Ag(Pb)-Hg-Tl Assemblages

<u>Bismuthian</u>(Sulphobismuthites)
Axial Types
Planar Types

Pseudoisometric Types

# Antimonian (Sulphantimonites)

Axial Types Planar Types

Pseudoisometric Types

Arsenian(Sulpharsenites)

Axial Types
Planar Types

Pseudoisometric Types

Sulphosalts with mixed semi-metallic constituents are classed according to predominant semi-metal. When the ratio of the semi-metals is 1:1 the species should enter both subdivisions but its

significance should follow the trend Bi-Sb-As. Tetrahedrite, tennantite, enargite and alike minerals with extra sulphur are referred to the sulphide and kindred minerals with sphalerite and wurtzite derivative types of structures.

NON-STOICHIOMETRY AND HOMOLOGICAL SERIES OF SULPHOSALTS

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The researches of sulphosalts with the aid of the modern methods of analyses show that sulphosalts are non-stoichiometric compounds (those of variable compositions) with every particular feature of this class. The major particularity of these compounds is the capacity to exsolve into separate structurally related ordered phases (characterised by a less wide range of homogeneity) under the change of physic-chemical conditions. This quality is found out in sulphosalts of various compositions (systems Pb-Sb-S; Pb-Ag-Sb-S; Pb-Cu-Bi-S; Pb-Ag-Cu-Bi-S; Cu-Sb-As-S etc.) and it must determine the nature of their homological series. Such series must form a base for a classification of these minerals. The collection of experimental data on the exsolving of sulphosalts into compounds with less wide range of homogeneity can be used later on as geothermometers.

The specification of the sulphosalts as non-stoichiometric compounds, with all the consequences thus conditioned, helps one to explain some particular mysterious features of these minerals. In particular, it explains the indefinite character of many formula of sulphosalts that have been considered as mineral spaces of constant compositions. The same explanation can be given to the ambiguous x-ray pictures. These particularities, when considered from non-stoichiometric position, acquire and informative value.

SULPHIDES - THE PECULIARITIES OF COMPOSITION, CRYSTALLOCHEMISRY SYSTEMATICS

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Common natural sulphides are the compounds with covalent bond, developed by the donor-acceptor mechanism.

They consist of the elements with high enough electronegativity, the atoms of which can play the role of electron couples acceptors in formation of covalent bond by the donor-acceptor mechanism, - "cations", and the elements with low enough electronegativity, the atoms of which can play the role of electron donors - "anions".

The peculiarities of bonding in sulphides determine the occurence in natural sulphides of Va-and Vla-elements with high enough Z as "anions" and of atoms of p-elements with the  $\,{\rm p}^{1-3}-{\rm electrons}\,$  and d-elements with 5 or more d-electrons as "cations". The occurence of "cations" with lower electronegativity leads to ionic and well hydrolysing sulphides, appearing in nature rarely and in small quantities. The growth of "cation" electronegativity leads to the formation of molecular crystals, such as realgar, orpiment, stibnite, etc.

The showed peculiarities of properties and constitution of atoms determine the role of VIIIb-elements (especially Fe) and those usually referred to as chalcofile elements as of typical cations in natural sulphides.

The genesis of sulphide structures is determined by the regularities of combinations of "cations" with definite types of hybridization, in the dependence of which is the number of valent orbitals used as acceptors, with "anions" of definite construction, defining the number of donor electron couples, by the organization of definite electron assemblages around "cations", following the N.V. Belov's rules.

The structures of natural sulphides depending on genesis may be:

1) homocoordinational (they are usually called coordinational by analogy with ionic compounds), 2) quasihomocoordinational, 3) he-

terocoordinational and 4) molecular. The structures of monosulphides (troilite, sphalerite, galena, bornite etc.) are the examples of the first type, those of persulphides (pyrite, arsenopyrite, etc.) - of the second type, thyosalts - of the third one, molecular crystals, such as realgar, orpiment, molybdenite tellurobismuthite, etc. - of the fourth.

It is shown that the systematics of natural sulphides, based on the above mentioned data, allows one to understand deeper the peculiarities and genesis conditions of large taxons as well as of individual sulphides, and the regularities of their relations.

POLYMORPHISM AND HOMOLOGY IN SULPHIDE MINERALS (Structural aspect)

N.L. Smirnova, N.V. Belov, Moscow, USSR

Mutual relationships between compounds are considered as a category of the general theory of systems meaning that all the objects including systems, may be obtained one from another as a result of constructuve transitions: ordered combination of n-dimensional structural fragments (including formation of homo-logous series both polytypic and heteropolytypic), insertion of atoms (including replacement of atoms by groups), subtractions, deformation(including n-gonalization). Transformation of substances on polymorphic transitions, disproportionations occur in accordance with the constructive laws. There are considered the formation of homologous series in a close packed layer of open structural elements and their realization in the structures of sulphosalts and other sulphides. It is shown that the structure formation obeys the law of three columns.

E.A. Pobedimskaya, L.N. Kaplunnik, I.V. Petrova, N.V. Belov Moscow, USSR

The crystal structures of some Hg sulphosalts (aktashite, galkhaite, tvalchrelidzeite) and of some Pb ones (krupkaite, boulangerite) as well as the structure of the synthetic Pb, Sn sulphosalt(phase XA) have been determined. X-ray structural studies of these phases have been carried out using a single-crystal P1 autodiffractometer "Sintex" (2 0 method). The structures are found in  $\mathbf{F}^2$  and  $\mathbf{F}$ -syntheses. The structures have been refined by a least square method isotropically. The table (below) gives the lattice parameters, Fedorov groups and a brief structure description.

Table

8

pa3

Sulphosalt and its composition	Unit cell parameter			Space group	Atomic coordinations	
	a, b, c	8,8,0		-	Рb	Hg
1	2	3	4	5	6	7
1.Aktashite	a=13,73			R3		4
Hg3Cu6As4S12	c = 9,33	γ =120°	3			
2. Galkaite	a=10,42	·	12	-		4
Hg <sub>0,74</sub> Cu, Zn <sub>0,26</sub>				J43m		
AsS <sub>2</sub>						
3. Tvalchrelid- zeite						
Hg5Sb2As2S8	a=4,39	→ =88,17				
	b=11,57	p =90,01	2	P1		4 and
	c=15,67	γ =89,98				
4.Krupkaite	a=4,02					
CuPbBi 3S6	b=11,21		2	Pmc2 <sub>1</sub>	8	
	c=11,56					
5.Boulangerite	a=21,30		4	Pbnm	6 and	7
Pb5Sb4S11	b=23,47					
	c=4,04					

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6. Phase XA

(Pb,Sb)6SnSq

a=11,55

#### STABILITY AND CRYSTAL STRUCTURES OF POLYMORPHS OF BORNITE

#### N. Morimoto, Y. Kanazawa and K. Koto, Osaka, Japan

The intermediate form of bornite (Cu<sub>5</sub>FeS<sub>4</sub>) has been determined to be stable in the range from 167°C to 230°C by the DSC and high-temperature x-ray method. The change of the cell dimersions indicates appearance of the transitional form, different from the intermediate form, by quenching of the high form.

The crystal structure of the intermediate form has been determined at 185°C. The space group is Fm3m, and  $a_0$  = 10.981(1)Å. Sulfur atoms form the ideal cubic closest packing and metal atoms are distributed statistically in the tetrahedral interstices of sulfur atoms. The structure consists of two different kinds of cubes with the antifluorite type structure; one has a half metal atom in each tetrahedron and represents disorder of Cu atoms and vacancies and the other has one metal atom in each tetrahedron and represents disorder of Cu and Featoms. The intermediate form represents an intermediate stage between the low and high forms from the structural viewpoint.

#### STRUCTURES OF CYLINDRITES OF DIFFERENT COMPOSITIONS

# N.I. Organova, A.I. Gorshkov Moscow, USSR

The necessity to make the cylindrite structural model by Makovitsky more accurate appeared when high Pb content samples were found in our country.

A comparative study of cylindrites of Poopo (Bolivia) and of the deposit "Smirnovskoye" (USSR) was made by X-ray and electron diffraction methods (with selected area electron diffraction in the latter instance).

Theoretic and experimental intensity data for two projections with (okl) and (hko) reflections made the crystallochemical formula of the mineral more precise.

#### CHEMICAL REACTIONS IN SULPHOSALT MINERAL FORMATIONS

#### V.V. Shcherbina, Moscow, USSR

The various sulphosalt-forming reactions may be groupped in several types as follows:

- 1) Reactions of sulphobases and sulphoacids combination:  $Ag_2S + SnS_2 = Ag_8SnS_6$  (argentite + berndtite = canfieldite);  $Tl_2S + As_2S_3 = 2TlAsS_2$  (carlinite + auripigment=lorandite).
- 2) Reactions of sulphosalts and sulphobases combinations that give birth to more basic salts: amplectite  $\text{CuBiS}_2 + \text{Cu}_2\text{S} = \text{Cu}_3$   $\text{BiS}_3$  wittichenite; miargyrite  $\text{AgSbS}_2 + \text{Ag}_2\text{S} = \text{Ag}_3\text{SbS}_3$ -pyrargyrite; or reaction of sulphosalt with sulphoacids that end to form more acid salts; boulangerite  $3\text{Pb}_5\text{Sb}_4\text{S}_{11} + 14\text{Sb}_2\text{S}_3 = 5\text{Pb}_3$   $\text{Sb}_8\text{S}_{15}$  fülöppite.
- 3) Reactions where sulphosalts and a third component take part: cuprostibite CuSbS<sub>2</sub> + RbS = CuPbSbS<sub>3</sub>-bournomite.
- 4) Reactions where intermediate compositions are born: jordanite + sartorite = rahtite:  $Pb_5As_2S_8 + 7PbAs_2S_4 = 4Pb_3As_4S_9$ .
- 5) Substitution of some hard soluble compositions for the easily soluble ones (pyrargyrite for proustite): Ag<sub>3</sub>AsS<sub>3</sub> + SbS<sub>3</sub><sup>3</sup>-• Ag<sub>3</sub>SbS<sub>3</sub> + AsS<sub>3</sub>.
- 6) Double change reactions:  $Ag_2FeSnS_4 + CuBiS_2 = Cu_2FeSnS_4 + AgBiS_2$  okartite + emplektite = stannin + matildite.
- All these reactions that end at more stable parageneses form the great variety of sulphosalt associations. It is to note also the formation of isomorphous mixtures and intermediate compositions.

PHASE RELATIONS IN TERNARY SECTIONS OF THE SYSTEM Fe-Pb-Ag-Sb-As-S AND THEIR SIGNIFICANCE FOR MINERALOGY OF SULPHOSALTS Moscow, USSR

N.S. Bortnikov, U.Ya. Nekrasov, N.N. Mozgova, Moscow, USSR

Phase relations in the sections of the system Fe-Pb-Ag-Sb-As-S were studied by means of evacuated silica-glass tubes, isothermal synthesis under hydrothermal conditions, X-ray powder diffraction and electron microprobe analysis. The stable phases in an equilibrium with a vapor in the system  $FeS-FeS_2-PbS-Sb_2S_3$  at the temperature between 300-500  $^{\circ}$ C are boulangerite, phase 1 (Pb2Sb2S5), phase II (Pb5Sb6S14), robinsonite, zinckenite, berthierite, jamesonite. The limited solid solutions have formed all phases except phase II and berthierite. The stable phases in an equilibrium with solution of 10%  $\mathrm{NH_{4}Cl}$  at the temperature between 175-400°C and the pressure 500 atm in the system PbS-AgoS-SboS3 are lead sulphantimonides (Nekrasov, Bortnikov, 1975) pyrargyte, and -miargyrite, brogniardite, diaphorite, andorite, ramdohrite. A complete solid solution exists between -miargyrite. The limited solid solutions has been determined for andorite and ramdohrite. The chemical compositions of the lead sulfantimonides of the plagionite group have a stoichiometric ratios of PbS and Sb2S3. Madokite, veenite, sorbyte, playfairite, antimony baumhauerite, twinnite, quettardite have been synthesized in the system PbS-As<sub>2</sub>S<sub>3</sub> -3b<sub>2</sub>S<sub>3</sub> at the temperature 300-400°C and the pressure 500 atm under hydrothermal conditions.

The experimental results were used to explain physico-chemical conditions of formation of sulfosalts Pb, Ag, Fe in different types of ore deposits and peculiarities in the chemical composition of these minerals.

TETRAHEDRITE-TENNANTIE SERIES IN THE SULFIDE ORE DEPOSITS OF WESTERN STARA PLANINA MOUNTAINS, BULGARIA

V.A. Atanasov, Sofia, Bulgaria

The investigation of minerals and varieties of the polymetallic sulphide deposits Sedmochislenitsi, Plakalnitsa, Izdremetz, Vattya, Chiprovtsi etc. showed considerable differences in composition. The differences are along the traditional line tetrahedrite-tenmantite, as well as in the directions:  ${\rm As}^{3+}{\rm -Bi}^{3+}$ ,  ${\rm Cu}^{1+}{\rm -Ag}^{1+}{\rm Cu}^{2+}{\rm -(Zn}^{2+}$ ,  ${\rm Fe}^{2+}$ ,  ${\rm Hg}^{2+}$ ). The data obtained show that the antiparallelism between  ${\rm Zn}^{2+}$  and  ${\rm Fe}^{2+}$  should be extended according to to the expression  ${\rm Cu}^{2+}{\rm -(Zn}^{2+}$ ,  ${\rm Fe}^{2+}$ ,  ${\rm Hg}^{2+}$ ). There is no antiparallelism between Ag and Hg.

There are differences in the physical properties of the varieties: reflectivity, hardness, cell dimension. Ag and Hg as structural impurities decrease hardness, increase (Ag) or reduce (Hg) reflectivity and bring about the increase of  $a_{\rm o}$ . The largest  $a_{\rm o}$  (10,64Å) and the lowest absolute hardness (223 kg/mm²) were measured for argentian mercurian tetrahedrite from the Chiprovtsi ore deposit.

Considerable variations in composition are proved not only in the different types of ore deposits, but also within the boundaries of a separate deposit. In Sedmochislenitsi ore deposit the variations are along the directions tennantite-tetrahedrite, tetrahedrite-freibergite-tennantite-Bi-tennantite, and in the Chiprovtsi one: tetrahedrite-tennantite, tetrahedrite-freibergite, tetrahedrite-argentian mercurian tetrahedrite.

The composition of the minerals and the varieties of the tetra - hedrite-tennantite series depends on the paragenetic conditions within an individual ore deposit or ore region.

CHLORINE-CONTAINING SULPHOSALTS FROM THE MADJAROVO POLYMETALLIC DEPOSIT IN BULGARIA

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Appreciable amounts of chlorine-element unusual for sulphosalts have been determined for these minerals by means of electron microprobe analysis for the first time in lead sulphantimonides presented in small segregation in galena from the upper levels of the Madjarovo polymetallic deposit (Eastern Rhodopos, Bulgaria) as follows:

Elements	J		Conc	Concentration (wt.%)				
Pb	55,89	57,70	56,95	55,93	54,07	45,19		
Sb	22,75	21,52	22,31	23,79	28,14	38,11		
S	15,58	14,93	15,62	16,78	20,75	22,73		
Cl	4,03	3,83	3,56	3,02	0,02	0,03		
Total	98,24	97,98	98,44	99,53	102,98	103,07		

No chlorine was discovered in the enclosing galena, Pb-Sb-oxi - chloride-nadorite was found in association with the Cl-contai - ning Pb-sulphantimonides.

The constitutional nature of the presence of Cl in the sulphantimonides of Pb is proved by the presence of this element (0,1-4,62 wt%) in boulangerite, jamesonite and another sulphantimonides, synthetezed in aqueous solutions of chlorides at 300-400°C and in liquids of chlorides at 300°C, no other Cl-containing compounds being found in the products of the synthesis.

The selective incorporation of Cl in the Pb sulphosalts is obviously related with the peculiarities of their structure. From crystal chemistry point of view the incorporation of Cl in Pb-Sb sulphosalts is quite natural, because of the existence of chemical compounds of the SbSBr type and thelkind, in which semi-oc tahedras of Sb constituting the stibnite-like (sulphosalt-like) ribbons contain haloid elements. It is quite possible that Cl oc-

cupies independent positions in their structures as it was determined for jerfisherite.

The rare paragenesis of the Cl-containing sulphantimonides, of Pb with nadorite and anglesite indicates that the minerals were deposited at high chemical potential of oxygen and chlorine.

BISMUTH SULPHOSALTS INTERGROWTHS AND ITS GENETIC INTERPRETATION

### E.F. Minzer, Moscow, USSR

Microintergrowths are typical of sulphosalts in general and of bismuth sulphosalts especially. As it is revealed by study of many Bi deposits proper and complex Bi-bearing deposits in the Soviet Union this feature appears to be the result of intermineralizational metamorphism of protogene Bi-Minerals (Bismuthinite, native bismuth, tellurides) under conditions of thermodynamically inert behaviour of Bi during a considerable period of ore deposition (alkalinity of ore-forming solution being increasing).

A detailed study of Bi-minerals intergrowths gives evidence to several stages of hypogene transformation of these minerals.

Formation of intergrowths with signs of reaction replacement in situ (e.g. replacement of bismuthinite by galenobismuthite, co-salite, krupkaite, kobellite; replacement of native bismuth by wittichenite).

Formation of intergrowths with signs of breakdown (formation of ordering phases). The texture of mineral intergrowths depends on degree of crystallochemical likeness of breakdown products.

Recrystallization of breakdown products (in situ or with slight displacement).

The report presents examples of intergrowths illustrating the stages described.

MINOR CONSTITUENTS OF ACCICULAR LEAD SULPHANTIMONIDES; THEIR PART IN CONDITIONS OF FORMATION OF THESE SULPHOSALTS

#### Y. Moelo. Orleans, France

Recently, numerous studies on sulphosalts indicate great influence of minor chemical constituents on stability relations of these minerals. In the boulangerite group (acicular lead sulphantimonides), some examples, show that these minor constituents act through three ways:

1) A minor constituent in solid solution does not influence the stability conditions of the sulphosalt.

Substitution of Sb by As is the most characteristic example, as showed by experimental study of the PbS-Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> system(WALIA and CHANG - 1973). Other substitutions are possible: Sb--Bi, 2Pb--1Sb + 1Ag, 2Pb--1Sb + 1T1(exceptional), but apparently those are less important (only some tenths of a percent in natural zinkenite).

2) A minor constituent in solid solutions stabilizes structure of the sulphosalt.

Studies of HODA and CHANG (1975), and WANG (1973, 1977) have proven that the meneghinite structure is stable at low temperature only with copper present. We have also detected by microprobe analysis minor amounts of copper (0.9%) in numerous samples of zinkenite. There is a positive correlation between the amount of copper and the Pb:Sb ratio. Structural considerations (LEBAS and LE BIHAN -1976) indicate, as in meneghinite, the following sub-stitution: 1Sb + 1 -- 1Pb + 1Cu, where copper occupies usually vacant tetrahedral sites. It is possible that copper contributes to the stabilization of the zinkenite structure at low temperature.

3) A minor constituent is necessary for the formation of sulphosalt, e.g. iron in jamesonite (2.7% Fe).

It has been possible to attribute the same function of chlorine for dadsonite, cwing to the hydrothermal synthesis of two leadantimony chlorosulfides. Analogies between these phases and dadsonite (X-ray powder diagrams; synthesis conditions) have resulted in finding chlorine in dadsonite 0.3% by microprobe analysis in samples from Wolfsberg (Germany) and St.Pons (France).

Dadsonite is the first known example of a natural chlorosulphosalt.

Cristallochemical studies of natural lead sulphantimonides can be used to refine some structures. It also brings precious information on the geochemistry of their formation; this may help in understanding the genesis of Pb, Zn, Ag, Sb, Cu ores, where lead sulphantimonides are frequently minor components (more than a hundred occurences in France alone).

BI-SULPHOSALTS RELATED TO LARAMIAN SKARNS OF THE BIHOR MOUNTAINS (NORTHERN APUSENI, ROMANIA)

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Pipe-like, banded, tabular or vein-like bodies of calcic and magnesian skarns associated with Baita-Dedes Laramian intrusive contain pyrometasomatic-hydrothermal mineralization. The ores display various structural features from impregnations up to massive occurences.

The pyrometasomatic association (molybdenite+bismuthinite +scheelite) is followed by several hydrothermal paragenesis of comp lex character, which include Bi-sulphosalts (aikinite, bursaite, galenobismutite, cosalite, wittichenite, emplectite) and Bi-tellurides. Detailed investigations of the Bi mineralogy in such setting point out to the existence of various terms which define the series bismuthinite-aikinite, bismuthinite-cosalite, bismuthinite-tellurobismutite. ON THE CONDITION OF FORMATION OF COPPER BISMUTH SULPHOSALTS

#### A.B. Ptytsin, G.R. Kolonin, Novosibirsk, USSR

The direct relationship is shown between sulphosalt composition and the equilibrium solution parameters (the concentration of sulphur, sulphosalt-forming metals, complex-forming ligands, pH, etc.) by thermodynamic method.

The results of experimental determination of copper, bismuth and sulphur concentrations in solutions, which was coexisting with wittichenite  ${\rm Cu_3BiS_3}$  or cuprobismutite  ${\rm Cu_6Bi_8S_{15}}$  and quenched from 300° to 20°C are reported. It is established, that these concentrations reach the value of  $10^{-2}$  -  $10^{-3}{\rm M}$  in strongly acidic (pH < 3) and strongly alkaline (pH > 11) solutions, going as low as  $10^{-5}{\rm M}$  in the range of moderate pH.

The activity products of the formed sulphosalts are calculated from the results of chemical analyses of solutions for some experiments using stoichiometric individual ion activity coefficients of copper, bismuth and sulphur. The resulting values are close to those of activity products of sulphosalts at 300°C calculated from thermodynamic data providing the additivity of free energy of formation of sulphosalt from simple sulphides.

An abrupt increase of sulphide solubilities in strongly acidic and strongly alkaline solutions accounts for a considerable inensification of formation processes of sulphosalts in them.

This is illustrated by the results of kinetic experiments, carried out at different pH of the solution.

The composition of the sulphosalt formed from a mixture of simple sulphides in the hydrothermal solution is defined by the ratio of metals in the charge, which was established at equilibrium. The occurrence of cuprobismutite  $\text{Cu}_6\text{Bi}_8\text{S}_{15}$  from charge with ratio  $\text{Cu}_2\text{S}:\text{Bi}_2\text{S}_3=1:1$  can be explained by the more intensive solubility of copper sulphide and by relative increase of bismuth in the solid phase.

THE PHASE EQUILIBRIUM OF THE SYSTEM Cu-Bi-S BELOW  $400^{\circ}\mathrm{C}$ , ESPECIALLY THE RELATION BETWEEN EMPLECTITE AND CUPROBLSMUTITE

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The phase relations of the system Cu-Bi-S, especially the relation between emplectite and cuprobismutite were determined by the evacuated silica tube method and the hydrothermal recrystallization method below  $400^{\circ}$ C.

Both of emplectite and cuprobismutite have been believed in polymorphic relations (Nuffield 1952) and Buhlman (1971) described the low temperature polymorph of emplectite ( $\beta$ -CuBiS<sub>2</sub>)inverts to the high form of cuprobismutite ( $\checkmark$ -CuBiS<sub>2</sub>) at 290 °C.

As the results of the detailed synthetic experiments in the present study, it seems most reasonable to conclude that both minerals are not in polymorphic relations but two independent minerals with different compositions. Emplectite was synthesized in the composition of stoichiometric  ${\tt CuBiS}_2(50{\tt Cu}_2{\tt S.50Bi}_2{\tt S}_3)$  at 250°C and 275° after long period heating runs, whereas it was surely determined cuprobismutite has a composition of  $45{\tt Cu}_2{\tt S.55Bi}_2{\tt S}_3$  ( ${\tt Cu}_3{\tt Bi}_{11}{\tt S}_2$ ). And both minerals have little solid solution field.

The thermal stabilities of emplectite and cuprobismutite have been determined by the annealing experiments in long periods at the temperatures between 250°C and 325°C. Emplectite becomes unstable at 319 $^{\circ}\pm$  2°C and decomposes into wittichenite and cuprobismutite, while cuprobismutite is never synthesized below the temperature.

In the hydrothermal syntheses, emplectite was synthesized as beautiful acicular crystal at the temperature below 350°C and cuprobismutite was synthesized above the temperature. As the temperatures were measured in the well on outside of the test tube type high pressure vessel, the results obtained from the hydrothermal experiments might be almost the same with those from the dry syntheses after the correction of the difference in temperatures between inside and outside of the vessel.

CHEMICAL COMPOSITION OF BISMUTH MINERALS FROM SOME DEPOSITS OF THE NORTHERN PART OF THE SPIŠSKO-GEMERSKE RUDOHORIE MOUNTAINS (EASTERN SLOVAKIA)

- J. Hurny, Spišska Nova Ves
- J. Krištin, Bratislava, ČSSR

During a mineralogical study of deposits of the siderite-quartz sulphide formation in the northern part of the Spišsko-gemerské rudohorie Mountains, bismuth minerals have been reported. They are present as accessory minerals in this type of this formation and occur in association with quartz, siderite, chalcopyrite.tetrahetrite, pyrite and other ones. Minerals occur'in form of minor inclusions (0,1 - 0,001 mm) of different morphological types veinlets, elongated and irregular grains, closely intergrowth structures and desintegration structures. By using dates of the ore microscopy only native bismuth and in some cases bismuthite have been determined. Because they occur in a minor amount and they are closely intergrown with the other minerals(tetrahedrite, chalcopyrite) their optical determination is difficult. Minerals were described only as bismuth sulphosalts or bismuth minerals. We studied chemical composition of these minerals using electron microprobe analyses (JXA - 5A, Jeol.).

Results of 38 analyses of these minerals show variable composition. Many of them contain antimony and have variable Bi: Sb ratios. According to the type of "radical" and cations ratio we discovered the presence of the following minerals: alkinite, rezbanyite, lindstromite, bismuthite, nuffildite, cuprocosalite (?), Bi-jamesonite, hypothetic mineral of Johansen -  $Pb_3Bi_4S_9$ , sacharowait (?) - (Pb, Cu, Fe)  $Bi_2S_3$  and mineral  $x - Cu_{12} Pb_4$  ( $Bi_6S_{17}$ )<sub>2</sub>.

The present results give new data in the study of chemical com - position of the bismuth minerals in the veins of the siderite-quartz-sulphide formation in Spišsko-gemerske rudohorie Mountains.

ON THE OCCURENCE OF STRATABOUND GALENA AND NI-SD SULPHOSALTS
IN THE EARLY PRECAMBRIAN ISUA SUPRACRUSTAL BELT, WEST GREENLAND

## P.W.U. Appel, Mainz, FRG

The Isua supracrustals form a ca 30 km long arcuate belt within the Amitsoq gneisses ca 150 km northeast of Godthab, West Greenland. The supracrustals as well as the Amitsoq gneisses give radiometric ages in the range 3.7 to 3.8 b.y. (Moorbath et al., 1975). Rb-Sr dating of gneiss veins found within the supracrustals (Moorbath et al., 1977). The Isua supracrustal belt consist of meta-sediments and metamorphosed volcanic extrusive and intrusive rocks. The sediments are mainly quartzites, carbonates and different facies of iron-formation. The volcanic rocks comprise mainly basaltic lavas and tuffs, together with rhyolites (Appel and Jagoutz, this volume). The supracrustals and the gneisses have suffered lower amphibolite facies metamorphism, and have been folded isoclinally, at least twice.

Within the banded iron-formation and in the basaltic tuffs stratabound sulphide mineralizations are found. There is a characteristic distribution of the different sulphides within the different facies of iron-formation. Pyrite is the characteristic and almost sole sulphide in oxide facies, whereas chalcopyrite and pyrrhotite are the dominating sulphides in the more reducing facies of iron-formation.

In the tuffaceous amphibolites sulphides are generally very fine-grained, and occur as thin layers parallel to the layering of the amphibolites. Most of the mineralised amphibolites show a rather simple sulphide paragenesis, the dominating sulphides being pyrrhotite, chalcopyrite and cubanite. The relative proportions of pyrrhotite and copper sulphides varies within wide limits. During the field season 1977, three tuffaceous amphibolites were found, that had a distinct different sulphide assemblage. The dominating sulphides in all three horizons are still pyrrhotite and chalcopyrite, but in addition they often carry an appreciable amount of galena and traces of sphalerite. Cubanite is absent.

The galena-bearing amphibolites can be classified into two groups according to their sulphide paragenesis. The first group is characterized by small amounts of ullmannite, bravoite and a number of complex Ni - Fe - Sb sulphosalts, some of which presumably are silver-bearing. Most of these sulphides occur as inclusions in galena. The second group is characterized by small but consistent amounts of linneite. The linneites analy - sed so far can be classified as siegenites with up to 10% Fe.

Based on field and textural evidence, as well as on their geochemistry it is shown that the sulphides are of submarine exhalative origin. Sulphur isotope ratios of the sulphides in the iron-formation and in the tuffaceous amphibolites show clearly that the sulphides were chemically precipitated, and that no sulphur bacterias existed in the Isua ocean 3.7 - 3.8 b.y. ago ( to be published).

The main implications of the discovery of galena-bearing sulphide mineralisations are two fold. First of all we have now been supplied with the least radiogenic terrestrial lead found so far. Second, we have an indication of a much more advanced differentiation in the earliest Precambrian than hitherto expected.

A NON-FERROUS METAL MINERALIZATION IN THE TRIASSIC GYPSUM DEPOSIT FROM MYRTHENGRABEN(LOWER AUSTRIA) IN THE MESOZOIC OF THE EASTERN ALPS - A NEW TYPE OF SULPHOSALT-OCCURRENCES

#### W. Tufar, Marburg/Lahn, FRG

The gypsum deposit from Myrthengraben (Lower Austria) located in dolomites of Carnian age of the Semmering Mesozoic is distinguished by a Fe-poor non-ferrous metal mineralization which is expected to be a worldwide rarity. The element assemblage is complex (Cu, As, Pb, Zn, S  $\pm$  Sb, Sn, Se, U, etc.) and shows a mine ral paragenesis of rare and in part unknown ore minerals and intergrowths.

The primary ore mineralization (sulphosalts and sulphides) con - sists mainly of enargite, tennantite, wurtzite/sphalerite, galena, pyrite and jordanite. Characteristic subordinate or minor ore minerals are luzonite, seligmanite and stibnite. In addition a Cu-Zn-Sn mineral (weak anisotropism, reflectance in the range 436 nm - 624 nm in air is 23.3 - 24.3 %, in oil immersion 10.1 - 10.5 %), which may be a kösterite and a mineral which shows the optical properties of getchelite are present. Preliminary electron microprobe investigations show evidence of a new As-S-phase in which As is only in small amounts substituted by Sb. For this mineral reflectance fluctuates at 548 nm in air from 18.6 -28.2% and in oil immersion from 7.0 - 12.8%.

Typical gangue minerals are dolomite, gypsum, anhydrite and magnesite. In part epsomite is relatively abundant. With the secondary ores an uranium mineral, andersonite, has been recognized.

The formation temperatures of the mineralization are supposed to be close to or lower than 100°C which is supported by primary gypsum inclusions in enargite, tennantite, and pyrite, and by the existence of primary bravoite.

In enargite, tennantite, luzonite, jordanite, and seligmanite As also is substituted in small amounts by Sb.

A worldwide novelty is the observation of myrmekitic intergrowth of enargite. In the Myrthengraben several different myrmekitic intergrowths of enargite were recognized: in association with jordanite, seligmanite, wurtzite, stibnite, the new As-S-phase, and also together with alteration products after jordanite, seligmanite and stibnite.

Further characteristics of this mineralization are small crys - tals of wurtzite after 0001 , idiomorphic luzonite and weakly anisotropic galena.

Concerning the ore paragenesis as well as the intergrowths the Fe-poor non-ferrous metal mineralization from Myrthengraben reflects a new type of sulphosalt-occurrences.

ON CHEMICAL COMPOSITION OF SULPHIDES FROM STARE RANSKO ORE DEPOSIT

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The Ni-Cu-Zn ore deposit Staré Ransko is situated in the complex of basic and ultrabasic rocks in the SE Bohemia. Among sulphidic minerals formed by liquation or partially, may be, even hydrothermal processes, pyrrhotite prevails; minor minerals are pentlandite, chalcopyrite, pyrite, sphalerite, cubanite; mackinawite marcasite, violarite, millerite and cobaltite rank among the accessory ones. Sulphides were analysed quantitatively by means of electron microprobe and spectrochemical analysis. There are many interesting conclusions following from the analyses.

Pyrite forms two types: the first one contains from 0.13 to 3.64 % Co, the second one less than O.X %. The Ni concentration is low in both the types (0.0X - 0.00X%), it re the the values of 0.X - 1.03 % only exceptionally. Pyrrhotite - the hexagonal type has Fe content from 60.5 to 61.5%, its content of the monoclinic one is lower than 60.5 %. The Ni and Co concentrations vary with in the range of values 0.X - 0.0X %. There is a relatively ele vated content of V (up to 0.1 %) in the monoclinic type in com parison with the hexagonal one. Troilite contains from 62.7 to 63.5 % Fe, 0.00 to 0.46 % Ni and 0.01 to 0.05 % Co. Pentlandite can be on the basis of Ni: Fe ratio devided into normal type (the ratio of 0.90 - 1.30) and Fe-pentlandite (the ratio is lower than 0.90). Both the types contain a few percent of Co (up to 5.8 %). Chalcopyrite and cubanite show no substantial difference in their chemical composition. Sphalerite can be characterized by the following admixture contents: Fe 7.7 - 9.5 %, Mn 0.03 -0.52 %, Cd 0.14 - 0.88 %. Mackinawite is rich in Ni content. Millerite shows the admixture of Fe(3.79%) and Co(0.02%). Violarite is poorer in Ni and richer in Fe. Cobaltite is highly nickeliferous (12.45%).

The results presented should be considered as partial and will be further made exact during the continuous geochemical studies.

DETERMINATION OF IDEAL FORMULAE FOR NEW MINERALS OF THE PLATINUM-GROUP

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The large number of newly reported species and varieties of platinum-group minerals, particularly, in the last decade, has created considerable confusion because of incorrect ideal formulae assignements. Some errors arise from difficult microanalyses of minerals with no known synthetic equivalent and where differences of less 1 wt% are critical to any proposed stoichiometry. These minerals may end up by being reported with erroneous stoichiometric or non-stoichiometric formulae. Other errors arise from insufficient knowledge of the crystal structure or from the non-recognition of the ideal end-member for variants. Correct assignment of stoichiometry may be made by careful consideration of crystallographic, synthesis, microanalysis and density data.

Specific examples are found among the palladium antimony arsenic minerals. Arsenopalladinite was first reported as hexagonal Pd<sub>3</sub>As, redefined as triclinic Pd<sub>5</sub>(As,Sb)<sub>2</sub> and recently shown to be triclinic Pd<sub>8</sub>(As,Sb)<sub>3</sub> with As:Sb 5:1. Mertieite was first reported as pseudohexagonal (Pd,Cu)<sub>5tx</sub> (Sb,As)<sub>2-x</sub>, later as rhombohedral Pd<sub>8</sub>(Sb,As)<sub>3</sub> with hexagonal axes and equivalent to synthetic and natural Pd<sub>8</sub>Sb<sub>3</sub>. Unnamed Pd<sub>5</sub>As<sub>2</sub> is either Pd<sub>22</sub>As<sub>9</sub> or Pd<sub>23</sub>As<sub>9</sub>, very close to stillwaterite, Pd<sub>24</sub>As<sub>9</sub>. Isomertieite was first reported as cubic (Pd,Cu)<sub>5</sub>(Sb,As)<sub>2</sub>, later as Pd<sub>8</sub>(Sb,As)<sub>3</sub> and now considered to be Pd<sub>11</sub>(As,Sb)<sub>4</sub>. Stibiopalladinite was originally reported as Pd<sub>3</sub>Sb, later as Pd<sub>5</sub>Sb<sub>2</sub>, and recently shown to be either Pd<sub>5+x</sub> Sb<sub>2-x</sub> or Pd<sub>8-x</sub> Sb<sub>3+x</sub>.

PLATINOID MINERALS IN Cu-Ni ORES. SOME GENETIC PECULIARITIES

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Pt mineralization in the major Cu-Ni deposits differs markedly by the composition of Pt metals minerals (PMM). In Sudbury(Canada) prevail Pt arsenides and tellurides as well as Pd bismutho - tellurides; in Merensky Reef (SAR) Pt-Pd and Pt-sulphides and Pt-Fe alloys are more frequent; whereas in Norilsk deposits(USSR) Pd, Sn, Pb and Bi compositions Pt-Fe alloys and Pt, Pd arseni - des and sulphides are predominant.

PMM of Norilsk ores have a broad variety of compositions with multiple isomorphic substitutions of Pt and other metals. It is possible to specify three groups of minerals: 1) Native metals and alloys (Pt-Fe compounds); 2) intermetallides (Pt metals + Sn Pb, Bi, As, Sb and Te compounds); 3) sulphides, sulphoarsenides and arsenides of the Pt group metals. The specific feature of the first group is broad substitution possibilities for Pt, Pd, Fe, Cu, Sn and a formation of solid solutions The minerals of the second group are distinguished for a variability of composition of Pt group and of the other components, the relation  $\Sigma$  Pt, Pd/ $\Sigma$  met being constant. The third group is characterized by a broad isomorphism of platinoides and by stoichiometric correlation  $\Sigma$  Pt/ S, As(or S + As).

PMM occurs in different Cu-Ni ores: from massive and dissemina ted ores in certain horizons of the stratified intrusions to stringer and disseminated sulphide zones in their exo-contacts.

The PMM compositional differences in ore types are due to crys - tallisation parameters and to the regularities in the initial sulphide melts. A correspondence in compositions of the inter - grown minerals is noted. This feature witness for a crystallisation from separate portions of the ore-bearing fluids.

The polymineral PMM aggregates in the massive Norilsk ores form a paragenetic association, though there appears a certain growth succession: Sn - Pb - As, Sb - Te minerals. Their relation to the major ore-forming sulphides and to galenite, sphalerite and

to galenite, sphalerite and djerfisherite  $K_6(\text{Fe,Cu})_{26}S_{26}\text{Cl}$  witness for a growth in the last stage of crystallisation from a residual fluid saturated with Sn, Pb, As, Sb, Bi, Te, Cl a. oth.

The synthesis of Pd intermetallides (Pd-Sn and Pd-Sn-Cu systems) in chloride solutions at 300-400 °C and  $P_{\rm H_2O}$  = 1 kbar has proved a possibility to obtain synthetic PMM analogues under these conditions.

NATURAL AND SYNTHETIC COMPOUNDS IN THE SYSTEM Pd-Sn-Cu

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Minerals containing Pd, Sn and Cu as the basic components, as well as analogues synthetic compounds have been studied. Using the compositional and structural data the limits of substitution Pd-Cu and Sn-Cu in these phases were determined.

The synthetic Pd, Sn and Cu minerals are obtained for the first time in hydrothermal chloride solutions at temperatures of 300-400 °C and pressures of 1 kbar. Athokite (Pd\_3Sn), paolovite (Pd\_2Sn), solid solutions of Sn in Pd and Phases Pd\_3Sn\_2(Pd Sn) and PdSn\_2 are obtained in the system Pd-Sn-HCl, and the solid solutions of Sn and Cu in Pd, as well as Pd\_SnCu and Pd\_5-6  $^{\rm Sn}_{2-3}$  Cu in the system Pd-Sn-Cu-HCl. The particular features of these compounds have been studied under various synthesis conditions.

The "fo<sub>2</sub>-T" stability fields of  $Pd_3$ Sn and  $Pd_2$ Sn have been defined, and "fo<sub>2</sub>-T" relations have been found for the reactions:  $Pd_3$ Sn (athokite) +  $O_2$  =  $Pd_3$ solid sol. +  $SnO_2$ (1) and  $Pd_2$ Sn(paolovite) +  $O_2$  =  $Pd_3$ Sn +  $SnO_2$ . It is shown that the existence of the high Pd content phases in the nature may be explained by a rise of  $f_{O_2}$  in the solutions when  $f_{O_2}$  goes down.

THE MINERAL ASSOCIATION OF PLATINIFEROUS DUNITE PIPES IN THE EASTERN BUSHVELD

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Considerable efforts have, in recent years, been directed at the investigation of platinum group minerals (PGM) in concentrates from pipes in the Eastern Bushveld. However, limited data only have become available on platinum minerals in their "natural habitat", and on textural relationships and compositional parame ters within the platiniferous rocks - data which are invaluable for our understanding of the petrogenetic evolution of the pipes and their mineralization

The present investigation attempts to assist in filling this gap. Platiniferous and barren olivine dunites, hortonolite dunites including hornblende- and phlogopite; bearing varieties), and chromitites from the Onverwacht, Mooihoek and Driekop pipes have been investigated in transmitted and reflected light, by X-ray diffraction, and by electron probe microanalysis. Oxides, sulphides and PGM occur as a primary and as a secondary association; the latter can be related to serpentinization of varying intensity.

Primary spinels differ in composition and reflectance. They may be zoned and generally carry higher amounts of Cr and Mg than their secondary counterparts. PGM recorded include members of the system RhAsS - IrAsS - PtAsS, as well as sperrylite and geversite. There is a tendency for sulphides and PGM to occur preferentially in phlogopite/hornblende-bearing and/or serpentini - zed portions of the pipes.

MINERALOGY OF PLATINUM ELEMENTS GENETICALLY RELATED TO ALPINE-TYPE ULTRABASITES BELONGING TO THE NORTH-WEST OF THE ASIATIC BRANCH OF THE PACIFIC MOBILE BELT

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This paper being supported to original data on studies of platinum-bearing occurences in the North-East USSR, for the first time summarizes the results of investigations into mineralogy of platinum group elements (PGE) whose parent endogenous rocks are Alpine-type ultrabasites. The investigations are based on the most recent geologic and mineralogic methods. The PGE minerals'compositions were determined with electron probing.

The platinum metal mineralization under investigation is represented by disordered solid solutions of platinum with iron and iridium (isoferroplatinum, ferriferous platinum, native platinum) as well as osmium with iridium and rhutenium (iridosmine, rhuteniridosmine, osmiride). A characteristic feature is an accompanying complex of rare sulphides of the PGE (osmium laurite new unnamed sulphides of rhodium plus copper and rhodium, copper and nickel, sulphides of rhutenium plus platinum and rhutenium, palladium and osmium, and oth.).

Parageneses of the PGE minerals in occurences related to dunite harzburgite formation of the Pacific mobile belt's inner and outer zones were found to have different compositions.

The described mineralization has Ru-Ir-Os-Pt geochemical specialization and it is peculiar to complex platinum-gold placers whose primary bedrock sources were massifs of dunite-harzburgite formation in eugeosynclinal zones of the Earth's folded areas from Pre-Cambrian through Cenozoic.

PLATINUM-GROUP MINERALS IN THE NEW RAMBLER COPPER-NICKEL DEPOSIT WYOMING

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Copper-nickel ores of the New Rambler Mine in the Medicine Bow Mountains of southeastern Wyoming contain appreciable concentrations of Pd and Pt (average 75 ppm and 4 ppm respectively) that occur principally as discrete platinoid minerals. Rh, Ru and Ir are present as minor constituents in the ores and appear to be related substitutionally to the Pt and Pd minerals.

Nine platinum-group minerals have been recognized during preliminary mineralographic and electron microprobe studies of ore samples. These are sperrylite (commonly rhodian), platiniferous merenskyite, moncheite, michenerite, kotulskite, temagamite, and three unknown Pd minerals referred to as Pd Phase B[-(Pd,Pt)<sub>5</sub> (Te,Bi,Sb)<sub>2</sub>], Pd Phase C (PdTe<sub>2</sub>), and Pd Phase D[-(Pd,Pt,Bi)<sub>2</sub> BiTeO<sub>4</sub>·2H<sub>2</sub>O]. Another Pd mineral that was provisionally termed Pd Phase A (McCallum et al., 1976) has the approximate formula Pd<sub>5</sub>(Bi,Sb)<sub>2</sub>Te<sub>4</sub> and is probably a variety of kotulskite [Pd(Te,BiSb)]. Palladian pyrite (up to 60 ppm Pd) is present in the carliest stage Cu-Ni ores of the deposit.

Chalcopyrite and its supergene covellite replacement are the principal hosts to Pd minerals, whereas the major platinum minerals generally are found in jasperoid and pyrite after pyrrhotite. Elemental correlation coefficients indicate that Pd associates most significantly with elements concentrated in secondary sulfides and thus demonstrates a pronounced chalcophile tendency. Pt shows a strong correlation with Rh and As which is consistent with the abundance of rhodian sperrylite. A very weak correlation between Pt and Pd suggests that the majority of the Pt in the deposit resides in sperrylite rather than in the Pd bismuthotellurides and tellurides.

The New Rambler deposit is considered to have evolved by lateral secretion processes in which base metals were derived by hydro-thermal leaching of nearby gabbroic rocks. The dominant abundance of merenskyite along with other bismuthotellurides provides strong evidence for such a hydrothermal origin.

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Studies of solid solutions of the Pt group elements (PGE) in the ore-forming sulphides is a new trend of approach to Pt mineralization, contributing to understanding of the general forming conditions and the genesis of the Pt metals group minerals. In the processes of formation of Cu-Ni deposits PGE may enter pyrrhotite, pentlandite and chalcopyrite.

The conditions for the platinoids solution in sulphides have been studied in natural assemblages and in experimental systems Fe-S-Me and Fe-Ni-S-Me (Me being a PGE). Pt metals fractionation among the sulphides depends on their distribution between mono - sulphide solid solution and residual melts. The former is enri - ched with Rh, Ru, Ir, Os, whereas the latter - with Pt and Pd. The limit of solubility is a function of Me/S in the monosulphide solid solution. The miscibility field growth is in a direct relation with S fugasity in the system. Some series of PGE solubility have been determined: Rh Ru Pd and Ir Os Pt. The platinoids concentration being higher than the condition-allowed solubility, the PGE sulphides or the platinoids + Fe and Ni alloys may crystallize from the melt.

The significant Rh, Ru, Ir and Os solubility in pyrrhotite and in pentlandite is the major cause of the absence of their proper minerals in Cu-Ni ores.

The ESCA method study of sulphides, with platinoids being in solid solutions, has shown that the platinum metal entry is followed by a simultaneous charge growth on the major element as well as on the entered metal. The energetic state of S line in the compositions of  $\text{Fe}_{1-x}$  S -  $\text{Rh}_{1-x}$  S type corresponds to the intermediate value for the extreme phases, but it is a bit closer to the values for  $\text{Fe}_{1-x}$  S. Such spectral particularities undoubtedly point out that Rh in pyrrhotite is chemically bonded with FeS groups and it is a component of a solid solution, but does not form any independent domain groups.

STUDY OF SULFIDES FLOTATION PROPERTIES

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Results of an experimental study of monomineral galena fractions from 52 deposits (60 samples), sphalerite from 26 deposits (32 samples), pyrite from 15 deposits and chalcopyrite from 7 deposits, conducted to investigate the relationship between physical superficial and flotational properties and chemical, mineralogical and structural analytical results are presented.

It was established that the collector quantity retained superficially by a mineral (in mg/cm²) makes up one of the most important parameters, which characterizes the flotation activity of a given mineral and its variation due to other reagents used in flotation. The actual value of this parameter allows to recognize genetic peculiarities of a mineral, influence of admixtures on the extraction (in particular, that of copper and different iron ore contents) and gives the opportunity to compare ore and mineral properties.

Some examples of polymetallic sulfide ores dressing are given in which the reagent flotation regimes are optimized in accordance with contents of homologous minerals having different technological properties. In the case of galena, for example, this can be achieved by use of a combination of collectors, in that of sphalerite, through improved control of both alkalinity and better adjustment of reagent consumption of such reagents as sulfuric copper and cyanide.

Classification of flotation properties of galena collection on the basis of the reaction with the main reagents enabled us to elaborate some easy analytical techniques of predicting techno - logical properties of samples without studying them.

These are: 1) mineralogical determination of the crystallisation pattern; 2) xanthogenate determination a) absorbed (in mg/cm²) during the passage of the solution through a mineral layer of constant weight and granulometry, b) in desorbed products after reaction with mineral; 3) control of pH changes during the mix -

ing of the mineral in the xanthagenate solution of a constant concentration. The authors recommend this original technique for rapid analysis in geological studies.

PARTICULAR MINERALOGICAL AND GEOCHEMICAL FEATURES OF SULPHOSALT ASSOCIATIONS FROM SOME YUGOSLAVIAN DEPOSITS

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Many different deposits and occurences characterized by an extensive development of sulphosalts of various compositions are known in Yugoslavia: 1 - schwazit-barite deposits (Dubrave, Zaiche, Yabuca-Focha, etc.); 2 - tetrahedrite deposits (Milieno, etc.); 3 - complex antimony-zinc deposits: a) with Pb sulphoantimonides and native arsenic (Ruevaz); b) with Pb and Pb-Ag sulphoantimonides (Chemerniza); 4 - polymetal deposits with Pb sulphoantimonides (Vitlovaz, etc.) and 5 - skarn-polymetal deposits with Pb sulphoantimonides and sulphobismuthides (Trepcha).

Detailed mineralogical studies by X-ray and electron microprobatechniques have been determined the widespread sulphosalts(boulangerite, jamesonite, zinckenite) and for the first time in Yugoslavia the rare ones - Pb sulphoantimonides of the plagionite group, Pb-Ag sulphoantimonide (andorite) and Sb-Pb sulphosalt (robinsonite). The later is surely described elsewhere only in two other deposits.

The sulphosalts appear in all deposits in various sequences, that proves the earlier established laws (Mozgova, Borodayev, 1972; 1973; Jankovic et al., 1977) and permits to see the peculiarities in the geochemical behaviour of the main ore-forming elements during the mineral-forming processes.

DEPENDENCES OF COMPOSITIONS AND PROPERTIES OF THE Pt METAL MINERALS

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The solid solutions are mostly distinguished in the Pt-Fe group minerals: polyxen (Fe up to 32-33% at.) and ferroplatinum (Fe-more 33% at.). Their reflection and hardness decrease as the Pt content decreases. In Os-Ir group (native Os, nevjanskite, native Ir) a decrease in Os content is followed by an increase in the reflection of the minerals, the hardness being about the same. In the minerals of Pd-Pt-Pb-Sn-Cu group the absolute value of ref lection increases and that of hardness decreases when Pt:Pd re lations go smaller (the values for some minerals are not stable). There are no relations established in the system Pd-Pt-Bi-Te. The Pd content increases in the phases Pt-Pd with lead and tin invokes a decrease in the lattice parameters in the corresponding compositions of (A B) and A3B types. The highest parameters are noted in purely Pt phases. Any lead substitution for tin provo kes a growth of the unit cell. The Pt phases of the  ${\rm AX}_2$  type(moncheite) are famous for bigger lattice parameters as compared to Pd phases (merenskite). The substitution of Bi for Te also causes an increase in the unit cell dimensions.

The highest values of hardness are noted in sulphides, the lowest ones in bismuthides, in the mineral phases rich in Bi or in Bi + Te, to be more particular. The intermediate values of hardness are related to the native platinum metals and to the intermetablic compounds, the decrease being registered from A- $\alpha_3$   $\rightarrow$  B<sub>2</sub>B (in structural formulae) or in the order Ir- $\alpha_3$  to fit the different electron d-level occurances.

MICROPROBE ANALYSES OF BISMUTH SULPHOTELLURIDES (Eastern Yakutia)

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About hundred microprobe analyses of bismuth sulphotellurides from eastern Yakutia carried out on the microanalyser JXA-50A provided new and improved data on this mineral group. The following mineral species are indicated: tetradymite, A-and B-joseite K, M and L-minerals as well as two more mineral conventionally named E and F.

A-joseite is the most widespread mineral that corresponds to the theoretical formula (Bi<sub>4,01</sub> Pb<sub>0,03</sub> Sb<sub>0,01</sub>)<sub>4,04</sub> (Te<sub>0,99</sub> S<sub>2,01</sub>)<sub>3</sub>. Tetradymite is also compositionally close to the theoretical formula - (Bi<sub>2,04</sub> (Te<sub>1,95</sub> S<sub>1,05</sub>)<sub>3</sub>. The results of 15 analyses of different grains showed the compositionally very stable F-mi-neral, following the formula - (Bi<sub>3,55</sub> Pb<sub>0.05</sub>)<sub>3.60</sub> (Te<sub>2.23</sub>S<sub>0.77</sub>)<sub>3</sub> Virtually, continuous series B-joseite (Bi<sub>3.96</sub> Pb<sub>0.01</sub> Sb<sub>0.01</sub>)<sub>3.98</sub> (Te<sub>1.99</sub> S<sub>0.99</sub> Se<sub>0.02</sub>)<sub>3</sub>, to K-mineral (Bi<sub>4.41</sub> Pb<sub>0.03</sub> Sb<sub>0.01</sub>)<sub>4.45</sub> (Te<sub>1.90</sub> S<sub>1.09</sub> Se<sub>0.01</sub>)<sub>3</sub> and L-mineral -Bi<sub>4.75</sub> (Te<sub>1.68</sub> S<sub>1.32</sub>)<sub>3</sub>, confirming the experimental data provided by Richter T.L.(1967) concerning solid solutions in the system Bi - Te - S. Above 40 analyses results plotted on the composition diagram Bi - Te - S and filled the field, extending between the minerals M-(Bi<sub>2.97</sub> Pb<sub>0.01</sub>)<sub>2.98</sub> (Te<sub>1.48</sub> S<sub>1.47</sub> Se<sub>0.05</sub>)<sub>3</sub>, E - (Bi<sub>3.11</sub> Pb<sub>0.02</sub> Sb<sub>0.01</sub>)<sub>3.14</sub> (Te<sub>1.93</sub> S<sub>1.03</sub> Se<sub>0.04</sub>)<sub>3</sub>, tetradymite and -tetradymite point also to this fact.

Observations of mineral interrelations show that the mineral pha ses separation takes place when their compositions lie on different sides from the line of divisible relations of components on Bi - Te - S diagram. Minerals, whose composition lie between the component divisible relations lines, do not form phases but are characterized by the compositional variability.

Reflection spectra, microhardness and X-ray diffraction data show that tetradymite, A- and B-joseite, close to K-mineral, can be recognized in the most certain way according to the parameter values.

Bismuth sulphotellurides composition according to microprobe analyses (Bast Yakutia)

Mineral	Number of enelyses		C o m p	Components (content intervals in per cents)	(content in	atervals in	per cent	<u>_</u>
Tetradymite	18	60 - 64	30 - 35	60 - 64 30 - 35 4,3 - 5,1	0,1 - 1,1		0	0,3
A-joseite	14	78 - 81	10 - 13	5,9 - 6,3	0,2 - 1,4	0,1	0,1 - 0,2	0,2
B-joseite	6	72 - 74	21 - 24	2,7 - 2,9	0,4 - 0,6		1	0,3
K-mineral	11	73 - 76	18 - 21	2,8 - 3,2	0,4 - 1,0	0		
L-mineral	٣	76 - 78	16 - 17	3,2 - 3,4				
M-mineral	47	63 - 68	24 - 30	4,6 - 6,1	0,1-7,1	0,1 - 0,3		1,5
E-mineral	10	67 - 72	25 - 28	3,1 - 3,9	0,1 - 1,4	0,1 - 0,2	0,1 - 0,5	0,5
F-mineral	-	02 - 69	27 - 29		0.5 - 0.9		0,1	0,4

30 KV Bi2S3, PbTe, the rest kV; for artificial 20 Sp galenite, antimonite, chalcopyrite, for tension conditions: working Analytical

SYMMETRY AND ISOMORPHIC SUBSTITUTIONS IN MINERALS OF THE SULVANITE GROUP

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A number of cubic pseudocubic minerals with a general formula  $\text{Cu}_3\text{RS}_4$  where Ge, Sl, V, As, Fe can take the position of R are referred to the sulvanite group.

Sulvanite, Cu<sub>3</sub>VSu, after which the group is named, is a most widespread mineral. Its structure can be considered as a derivation from the sphalerite structure of Zn<sub>4</sub>S<sub>4</sub>. Copper atom take the same positions as in zinc, and vanadium moves to the neighbouring vacant tetrahedron in sphalerite, thus violating Pouling's third rule, because all the edges of the vanadium tetrahedron become common with the copper edges, surrounding it.

Morphotropic transitions and isomorphic substitutions observed in the group are closely connected and are determined by the space symmetry and the construction of the main, parent structure, i. e. sulvanite. Substitution of vanadium by one or several of the above mentioned atoms not only changes interatomic distances and unit cell parameters but, which is more important, lowers the symmetry in such a way that the symmetry of the new crystalline space is a subgroup of the initial symmetry.

An isomorphic substitution of vanadium by arsenic is an example of such a phenomenon. The resultant variety is called arsenosulvanite and was first studied by A.G. Betekhtin and V.I. Mikheyev who considered it to be a new mineral formation. The substitution by arsenic does not change the symmetry of the crystal Td, but the symmorphic group of the structure symmetry T<sup>1</sup>d-P43m changes into the hemisymmorphic. Td<sup>4</sup>-P43m hemisymmerphic and asymmorphic groups can be considered as subgroups of the symorphic system with an n-multiple cell (Kopzik, 1966).

In full confirmity with the theory, a unit cell of arsenosulva nite is 8 times larger in volume than that of sulvanite. The symmetry limits the possibilities of the isomorphic substitution. It does not allow a statistical distribution and demands integer relations in atoms substituting each other.

Isomorphic substitutions, as a rule, lead to a dissymetrization of the structure, which follows a generalized principle of the Neumann-Curie symmetry.

#### ON THE AU-BEARING FAHLORE

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Fahlore grains containing 0,7 to 2,3 w.p.c. Au have been found in the polymineral complex ore of an Au-sulphide-quartz formation (Eastern Uzbekistan).

X-ray (RKD-57, 3, Fe, no filters) and chemical composition studies of some optically homogeneous regions of the mineral grains (microprobe MS-46 "CAMECA") have shown that this mineral is an intermediate member in the goldfieldite-tetrahedrite series with variable from grain to grain compositions: (Cu<sub>11,01-11,61</sub> Fe<sub>0,14-0,76</sub> Zn<sub>0,1-02</sub> Au<sub>0,06-0,19</sub>)11,7-12,17 (Te<sub>1,82-2,04</sub> Sb<sub>1,38-1,64</sub> As<sub>0.51-1,02</sub>)4.05-4.32 S<sub>12,78-13,04</sub>.

The homogeneity of Au and other element distribution in the mineral has been studied by a plane and profile scanning method in various grain regions. The composition has been quantitati - vely tested in several dozens of points (electronic probe capacity is 1-2 mcm). The studies have shown that the distribution of all the elements is highly uniform. The indentation and reflection tests produced on the same regions of the goldfieldite grains have shown an insignificant variation in hardness and reflection properties. The results obtained make it possible to guess at the constitutional nature of the gold in the mineral.

The fahloreformation, as it appears, was a consequence of calaverite decomposition where the surplus Au separated and formed rounded concretions in goldfieldite.

# MINERALOGIC CRITERIA FOR THE RELATIONSHIP BETWEEN ACID MAGMATISM AND ORE MINERALIZATION

PHYSICO-CHEMICAL ANALYSIS OF THE ORE-BEARING CAPACITY OF GRANITIC ROCKS

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High temperature mobilization of the ore metals by magmatic fluids is principally controlled by the presence of halogene compounds. It is proved by thermodynamic calculations and experimen - tal data for Zn. Fe. Pb. Sn and Au.

The analysis of mineral assemblages of many rare-metallic granites testify to high fluoric and rather dry character of the parent magmas. The possible ways of the generation of such magma lie either in progressive melting of biotite-containing rocks of the sialic crust, or in the crystallization differentiation of more basic trachybasaltic (lattitic, monzonitic) melts. The equilibria with hydrous minerals (biotite, amphibole) result in the parallelism in the behaviour of fluorine and a number of the ore elements during these processes.

Chlorine behaviour at magmatic stage is primarily controlled by its transfer to the separating fluid and to a lesser extent by the crystallization of hydroxyl-bearing minerals.

The data on halogen distribution coefficients between the melt, fluid and solid phases of the acid magmatic systems show that in the case of the fractionation of the phases separating from the cooling magma the major part of chlorine compounds would be mo-bilized at relatively early stage of the process of magmatic distillation while the solutions with maximum fluorine content should be evolved by the end of the process. Probably it is one of the causes of the separation of lithophile (fluorophile) and chalcophile (chlorophile) elements in space and time.

MINERALOGICAL EVIDENCE ON THE RARE-METAL ORES CONNECTION WITH THE ACID MAGMATISM

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The problem of the connection of the rare-metal ores with acid magmas is considered on the base of: a - studying of the dist - ribution coefficients of the elements between phenocrysts and mattrix (glass) of acid effusives and ongonites; b - studying of melt and fluid inclusions; c - studying of the composition and structure of typomorphic minerals.

The distribution coefficients of Li, F, Sn, W, Ta, Nb are less than that in the ongonites. The increase of concentrations of these elements up to economic values in the residual acid melts is shown. Thus the formation of the rare-metal ores from the magmatic glasses and other rocks is possible. Be, Li, F, W can be extracted by the fluid and can be precipitated during the hydrothermal stage (greizens and quartz veins).

Inclusion studies of the minerals show that the temperatures of the rare-metal ores (rare-metal granites, pegmatites, graizens, quartz veins) varies from 1000 to 50°C; the character of mineralizing medium changes from the melts with the decreasing viscosity through concentrated solutions (80-50 wt% of salt) to less concentrated solutions (10-5 wt.% of salt) with decreasing temperature. The temperature interval of the coexistence of the melts and solutions is 750-550°C.

The mineralogical and geochemical aspects of the connection between the rare-metal ores and the geochemical types of the acid rocks are considered.

#### ACID MAGMATISM AND MINERAL FORMATION

I.T. Bakumenko, Y.A. Dolgov, O.N. Kosukhin, V.P Tchupin Novosibirsk, USSR

Conditions of crystallization and localization of both metal and nonmetallic minerals have been established from studying inclusions in minerals of acid igneous rocks, granitic pegmatites and postmagmatic rocks. The temperature and fluid regimes of crystallization of high- and low temperature granitoids and pegmatites from the facies of different depth of occurence have been fixed; temperature decrease (sometimes to 580°C) in the spical parts of some intrusives and their later phases is shown (owing to increase of water, fluorine and other volatiles in the crystallizing melts). Conditions of fluid separation are evaluated with their composition fixed.

The granitic pegmatites of low depth (chambered pegmatites) be -gin their crystallization from the melts (early zones, at 660 - 550°C), while the minerals from the inner zones and the crystals of their cavities are formed with participation of the melt so -lutions, melt-brines, gaseous and fluid solutions. Formation of the mean depth pegmatites (rare metallic) involves the magmatic stage usually followed directly by hydrothermal one. Pneumatho-litic (gaseous) states of solutions arise sporadically with a sudden increase in the volume of pegmatite chamber. High-depth pegmatites (ceramic and rare earth) are distinguished from the above mentioned in having higher temperatures of the magmatic stage of crystallization and in high density of the postmagmatic fluids.

The model of mobilization of solutions and localization of the ore matter owing to adiabatic process is discussed in the light of fracturing in the Earth Crust; increase in the volume occupied by solutions at fracturing results in the decrease of temperature, pressure, solution density in cavities and to separation of the interporous fluids as based on their volatility. Intrusion activate the porous solutions of the host rocks and intrusive crust, while fracturing mobilize the porous solutions leading to a deposition and localization of ores.

SOME MINERALOGICAL AND GEOLOGICAL ASPECTS OF BIOTITIC AND TWO MICA GRANITES OF CENTRAL EXTREMADURA (WESTERN SPAIN)

#### J. Saavedra, Salamanca, Spain

The considered plutons are non-oriented, Hercynian, hyperalumi - nous, subalkalic, shallowly emplaced granites. They are discor - dant to the main Hercynian folds and they are emplaced into epimetamorphic sediments; their ages range from 335 to 285 m.y. The typical mineralogy is: albite or oligoclase, iron-biotite, mus - covite, K-feldspar, quartz, apatite, zircon, cordierite, andalusite, almandine (sporadically), sillimanite and often tourmaline (schorl) and topaz. The main varieties are alkaline granodiori - tes, poor in Fe, Mg, Ti, Ca and rich in Na, K (Na<sub>2</sub>0+K<sub>2</sub>0 8,0%), Rb, Cs, Sn, W, Nb.

Geophysical and geological arguments are superposed and they allow coherently to characterize the area. Generally, the batho - liths expose features of doming (deformations in the wall rocks). Nevertheless, the following observations may be noted: a) Sharp and straight contacts (polygonal), b) A zonation of the batholith with sharp contacts of facies, and xenoliths within these, exist, c) By times, enclaves of wall rocks (tens of metres) appear into the last facies, far from the contact. This whole set of data suggests that the plutons began their emplacement during the last phases of the Hercynian compression in favour of deep-seated accidents, with some characteristic of doming mechanism. The younger facies were seated by large-scale stoping or cauldron subsidence.

It is proposed that the granites are of deep origin, generated by fusion of lower continental crust under the infracrustal influence and, perhaps, melange with a little of mantle material. The magma rises across older deep-seated fault. Their specific characteristics can be derived from the heterogeneous lower crust (as has been proposed by Soviet scientists), which, may be is distinct at neighbouring blocks.

BIOTITE COMPOSITION AND ORE-BEARING CAPACITY OF TRANSBAIKALIAN GRANITOIDS

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The compositions of about 250 biotites are considered of the main granitoid formations in the tin-tungsten Transbaikalian belt.

These granitoids are divided into four genetic series: granite batholith, gneiss-granite, monzonite-granodiorite, and leucogranite (rare-metal). The formation of the monzonite-granodiorite and leucogranite series are connected with the main phase of Mesozoic tectonic-magmatic activation of the Transbaikalia. The leucogranitic series is of a great metallogenic importance.

The comparative potential ore-bearing capacity of granitoids is reflected in the concentrations of granitophile rare elements in biotites. The most informative for estimating intrusions with tin-tungsten-rare metal mineralization are the concentration levels of lithium and tin in biotites (the latter is 60 ppm and more). Concentrations of beryllium and tungsten are less important; concentrations of fluorine are negligible.

There is no strong correlation between the chemical composition and rare-element content in biotites. This is directly connected with the genesis of initial melts of rare-metal intrusions melting in local parts of deep-seated fault zones under the influence of deep fluid flows. The chemical composition of biotites of the rare metal intrusions is largely determined by the biotite composition of the gneiss-granite substratum undergoing melting. The rare-element concentration of biotites of these intrusions reflects the concentration level of volatiles and trace elements in the residual melts and fluids directly taking part in the formation of the postmagmatic mineralization. This level has been reached during processes of intrusive emplacement into the upper part of the earth's crust and the following crystallization.

CHLORINE AND FLUORINE CONTENTS AND THEIR DISTRIBUTION IN SOME MINERALS FROM COPPER-MOLYBDENUM DEPOSITS WITH REFERENCE TO THE PECULIARITIES IN THE MINERAL-FORMING PROCESS

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Chlorine and fluorine are the important volatile elements of the mineral-forming solutions in copper-molybdenum deposits. They significantly influence the general development of endogene process, formation of some rock types and mineral associations. Biotite and apatite from a number of copper-molybdenum deposits in the USSR and Mongolia have been analyzed for chlorine and fluorine by electron microprobe methods. These minerals are practically the only concentrators of volatile elements. Chlorine and fluorine contents in gas-liquid inclusions have been also determined.

Apatites from all the examined rocks (granitoids of the ore-forming magmatic complexes, explosive breccia, metasomatic rocks) are fluorine rich. Chlorine concentrations in the weight percent range from 0.1 to 1.3. Maximum concentration of this element is fixed for apatite formed at an early high-temperature stage from gaseous fluid produced by volatilization of magmatic melt. Apatite with much lower Cl/F ratio is formed from later liquid solution though there is present significant amount of chlorine ion. Apatite is not usually homogeneous with respect to chlorine. Its amount decreases at the periphery of grains (according to decrease of mineral formation temperature).

The contants of chlorine and especially fluorine in biotite are lower compared with the coexisting apatite. The Cl/F ratio in biotite from potassic alteration decreases with regard to biotite from granitoids and explosive breccia. Halogen value decreases sharply in chloritic biotites.

Apatite and biotite from the formations temporally related to the ore deposition are characterized by minimum Cl/F ratio. Higher Cl/F ratios in biotite and apatite are one of the peculiarities in the copper-molybdenum-bearing granitoids.

#### A. Forster, Regensburg, FRG

Basing on a special petrological fieldmapping (1:5000 scale )in the well known Pegmatite-district of Hagendorf-Pleystein, a geophysical prospecting campaign should find large shaped felds -par-quartz-pegmatite deposits.

After having tested various geoelectrical prospecting methods inside of specifically selected areas covered by pegmatites, the strong contrast of electrical resistivities of the gneiss countryrocks, compared with those of pegmatites and similar rocks, indicated that geoelectrical resistivity surveys have to be considered the only efficient geophysical method of exploring these prospecting areas.

As a result of 82 geoelectrical traverses with a total length of 107,4 km by electrical trenching and 17 vertical electrical soundings, there were found many geophysical anomalies from 4000 to 15 000 0hm-m, descending from geological bodies up to 60 m and 120 m underground depth. Some anomalies, with extremely high electrical resistivities were leading to plots of feld-spar-and quartz-rich bodies with shapes similar to the known pegmatite stocks of Hagendorf and Pleystein. These bodies have been the targets for the following drilling program. The results of the petrological investigation of these rocks and core specimens, recovered by drillholes on the anomalies, finally showed the abundance of various localities with alkalizations and silifications on the country-rocks - showing shapes like domes - as a consequence due to the forming of pegmatite bodies.

Specifically, the alkalizations led to lenticular and stock-shaped feldspar-rich gneissbodies with coarse grains and 65-70% feldspar contents inside the country rock, which normally consists of biotite-gneisses, poor in feldspar-content.

These contact-metamorphozed and feldspatized gneisses, similar to orthogneisses and meta-aplites formed lenticular and stock - shaped special gneiss-bodies from 150 m to 300 m in diameter; concerning shape and volume, they look like pegmatite stocks of the Hagendorf-type. These bodies cause most of the detected geoelectrical anomalies without being real pegmatites. Neverthe - less, there were found big pegmatite bodies also where anomalies raised over 13 000 0hm-m.

USE OF MINERALOGICAL CRITERIA IN THE ASSESSMENT OF POTENTIAL RARE-METAL ORE CONTENT OF GRANITOID INTRUSIVES

Yu.B. Marin, Leningrad, USSR

Rare-metal-bearing granite formations are the following ones: leucogranite-alaskite, subalkaline-leucogranite (fluorine-lithium-granite) and alkaline granite. With each of them there are connected several, sometimes incompatible, types and subtypes of rare-metal deposits. Their recognition and the assessment of the potential ore-bearing content of concrete massifs should be conducted in the following stages, wherein there should be determined 1) what formation the massif belongs to; 2) subtype; 3) degree of erosional shearing; 4) intensity of the manifestation of petrogenetic ore-generation processes.

The use of mineralogical criteria is possible at all the four stages,

, but the combinations or criteria, the reliability and expediency of their application differ considerably. The possibility of using minerals as criteria are based on the study of the features of their composition, structure, properties, forms and details of internal structure, gas-liquid and solid inclusions, parageneses and individual minerals.

At the 1st stage sufficient information is supplied by type-mor-

phous (lithium micas and amazonite for the fluorine-lithium-grenite formation, alkaline pyroxenes and amphiboles for alkaline granite formation) rock-forming minerals (r.m.) and the modal composition of rocks; individual type-morphous accessory mine rals (a.m.) and the species composition of accessory associati ons; the composition of r.m.; composition and form of constantly occuring a.m.; at the 2nd stage - by composition and structure of r.m.; quantitative composition (or at least the frequency of occurence of individual minerals) of accessory associations: the composition of constantly occurring a.m.; at the 3rd stage - by composition, structure and properties of r.m.; quantitative correlations between a.m. of Fe group, rare-element ones and volatile components; composition and structure of constantly occurr ing a.m.; at the 4th stage - by the complex of postmagmatic mi nerals: dispersion of the contained a.m.; composition, structure, form, inclusions and properties of r.m. and constantly oc curing a.m.

A comparison of the mineralogical criteria used at different stages shows a general tendency of their constantly increasing complicatedness and the possibility of their recognition only with the aid of the most modern, accurate, but not always rapid methods. Therefore, the mineralogical criteria should be used consecutively; the most complicated ones should be resorted to only in case of such massifs, the formation and subtype of which have been recognized. Only in such a case and upon further development of simpler and more rapid criteria the mineralogical methods will be as widely used in exploration practice as the geophysical and geochemical ones.

GEOCHEMICAL TYPES OF TUNGSTEN DEPOSITS AND THEIR CONNECTION WITH GRANITOID MAGMATISM

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It is generally known that in tungsten deposits various stable ore element associations are present, stipulating the existence of a broad spectrum of complex tungsten-bearing deposits with various ore composition. This feature is not incidental and is determined both by diverse degrees of geochemical affinity of tungsten and various elements, and by association of tungsten deposits with various types of granitoid magmatism. Such a conclusion is based on the results of statistical processing of the data on ore composition peculiarities and ore-bearing granitoid intrusions at 200 tungsten deposits throughout the world (100 deposits in this country and 100 in the other countries).

Based on the frequency of occurence among the accompanying elements of tungsten deposits the frequent (Mo, Sn, Bi, Cu) usual (Be, Pb, Zn) rare (Au, Ag) and very rare elements are distinguished. According to the structure of correlation links they form a successive series: Sn-Nb-Be-Mo-Bi-Cu-Zn-Pb-Ag-Au-Sb-Hg.In this series the neighbour terms have strong positive correlation coefficients, to occur together and the extreme terms are characterised by strong negative correlative links being antagonists and are not found together in the ore bodies.

The given element series corresponds, on the whole, to the observed trend of change in the ore emplacement temperature conditions (from elements, found in the ores of high-temperature deposits to average - and low-temperature deposits) and types of cre-bearing metasomatic rock associations (greisen - Sn, Nb, Be, Mo, Bi skarn - Mo, Bi, Cu, Au; gumbeite - Mo, Zn, Pb; beresite-Cu, Zn, Pb, Ag; tourmaline - chlorite - Au,Sb; argilizite - Sb, Hg), which become apparent in connection with granitoid magma - tism of different types, varying in its composition from granite leucogranite to granodiorite - granite and the intrusions of a mixed composition.

The distinguished element series is also in a general way mani -

fested in specific tungsten-ore formations associated with certain intrusive formations. Ore formations can be clearly distinguished on the basis of frequently (+) and rarely (-) occurring elements: greisen quartz - wolframite formation (+Sn, Nb, Be;-Zn Pb, Ag, Au), skarn-scheelite formation (+Mo, Au; -Be, Nb, Sn, Pb Zn); hubnerite-sulphide formation (+Cu, Pb, Zn, Ag; -Be, Nb)etc.

The analysis which was carried out testifies to the existence of a certain dependence of geochemical type of tungsten deposits on the composition of granitoid intrusions with which they have a close spatial and, apparently, genetic association.

THE ROCK-FORMING AND ACCESSORY MINERALS OF THE GRANITOID ROCKS
AS INDICATORS OF THE RELATION OF ORE MINERALIZATION WITH THE
MAGMATISM

M.G. Rub, V.A. Pavlov, A.K. Rub, Moscow, USSR

The ore-forming capacity of granitoid melt is clearly reflected in the peculiarities of composition and other properties of the rock-forming and accessory minerals which formed during crystallization. The presence of the "through" accessory ore minerals in the magmatic rocks and associated ores is most general and known for a long time mineralogical indication of the relation of ore mineralization with the magmatism.

Recently it was established that some rock-forming (quartz,biotite, etc.) and accessory (apatite, fluorite, zircon,etc.) minerals of the ore-bearing (Sn, W, Ta, Nb) granitoids are enriched in the same ore and volatile components that are the main components of the ores, which accompany these granitoids. These ore and volatile components enter in a crystalline lattice of the rock-forming and accessory minerals or are as in the composition of a fluid inclusions.

It is shown that the ore-forming solutions began to isolate already at an early stage of the crystallization of magmatic melt. A later evolution of such solutions is reflected in direct changes of the composition and properties of such minerals as apatite, fluorite, topaz, tourmaline and others from the granitoids of the early phases to postmagmatic products.

A dependence of typomorphic features of the rock-forming (especially micas) and accessory (apatite, topaz, tourmaline, fluorite, ore) minerals of the granitoids from type an accompanied mineralization is also the mineralogical criterion of the relation of the ore mineralization with magmatism.

The future studies of the "through" minerals of the magmatic rocks and postmagmatic products with application of the newest methods of investigations (electron microprobe and microscope, IRS, track microradiography, etc.) will permit to enlarge the number of minerals-indicators of the ore-bearing granitoids and to extend the mineralogical criteria of the relation of the ore mineralization with the magmatism.

CATION EXCHANGE EQUILIBRIA BETWEEN AQUEOUS CHLORIDE SOLUTION AND TERNARY FELDSPARS (Ab, An, Or) FROM 400°C TO 700°C AND 1 TO 2 KBAR

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The "peristerite gap" in plagioclase series at relatively low temperatures is evident in petrographic samples, but few experimental studies are concerned with that problem.

The author, going on with the research performed by P.M. Orville (1972) in the system Ab-An, J. Wyart and G. Sabatier (1962) and J.T. Iiyama (1966) in the system Ab.An.Or, concludes that such a

composition gap raunot be revealed by experimental studies in hydrothermal conditions.

In nature the peristerite gap represents equilibrium between an ordered low albite and a disordered plagiculase. In experimental studies, albite is always close to high albite, even at the lower temperatures.

Ion exchange equilibria between synthetic plagioclase solid solution and aqueous chloride solution:

2 
$$\operatorname{NaAlSi}_3 0_8 + \operatorname{CaCl}_2 - \operatorname{CaAl}_2 \operatorname{Si}_2 0_8 + 2 \operatorname{NaCl} + 4 \operatorname{Si}_2 0_8$$

have been performed from 400° to 700°C and 1 to 2 kb over the peristerite composition range. The results indicate an ideal behaviour of the disordered sodic plagioclase at high temperatures. Even at lower temperatures, the behaviour is still close to ideality. No unmixing could be inferred from those results.

In the ternary system Or-Ab-An, ion exchange experiments don't reveal the existence of a three phases field as inferred by Iiyama. Very accurate measurements of the composition the hydro-thermal solution in equilibrium with a K.feldspar-plagioclase assemblage, show that the solution is never buffered by the presence of three solid phases.

The method of R.F. Martin (1969), who was able to synthesize ordered feldspars cannot be used here owing to the studied system.

As far as hydrothermal experiments are concerned, it will be impossible to synthesize low Albite with starting materials having the composition of the feldspar, and consequently to reproduce in the laboratory, the peristerite gap as it has been extensively done for the perthite gap.

MINERALOGICAL AND PHYSICO-CHEMICAL EVIDENCE FOR THE RELATION BETWEEN RARE-EARTH MINERALIZATION AND GRANITOIDS

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Studies of rare-metal granitoids and of Y and TR-bearing systems have established certain relationships between TR mineralization and these rocks.

TR and Y abundances in granitoids depend rather on the propor tions of rock-forming components in magmas rather than on TR and Y original concentrations in them. This factor predetermines both acid-base interaction in melt and fractionation in La-Lu series with respect to acid-base characteristics. That is why TR minerals, rich in cerium earths occur with granitoids of increased basicity, while granitoids of enhanced alkalinity are found with Y and yttrium TR minerals.

Type of TR mineralization depends on the composition of a fluid in equilibrium with magmas. Potassium-phosphate-fluoride-carbon dioxide fluids coexist with magmas of normal series and sodium-chloride or sodium-fluoride-borosilicate fluids should associate with magmas of enhanced alkalinity. Extent of mineralization depends on the degree of TR extraction from magma, assessed with  $K_D^{\rm TR}$  - a coefficient fo distribution of rare earth elements between fluid and melt. The highest  $K_D^{\rm TR}$  is in the melt-chloride fluid systems, and decreases in melt-CO2, melt-F, melt-B2O3 and  $\rm H_2O$ .

Experiments show that most of TR minerals (britholite, yttrialite, thalenite, Y-fluoride) may be deposited at 800-300°C, i.e. directly in granitoids and low-temperature metasomatites. This accounts for similar compositions of rare-earths in accessory minerals in granitoids and TR minerals in ore bodies. The stability of TR minerals in univariant equilibria may be said to depend only on concentration of well-soluble components of the system, such as  $B^{-3}$ ,  $C1^-$ ,  $P0_4^{3-}$ ,  $C0_2$  and others.

MINERAL ASSOCIATION OF CASSITERITE-BEARING PEGMATITES OF BASTAR DISTRICT, M.P. INDIA

S.K. Bose and M.L. Deshpande, India

The Paliam granite intrusive into Bengal metasediments with meta basic sills appears to have been emplaced during folding of these rocks during the Archean times. This anatectic granite dated at 1340 m.y. (K/Ar biotite age) appears to have different phases of mobilizations like Darbha granite with zones of migmarization greisenisation and have resulted into satellite pegmatites occupying axial plane fractures in the folded metabasic sills intrusive into sericite quartzites, andalusite schists and gneisses of the Bengal proterozoic group.

The pegmatites are both zoned and unzoned and occur in en echelon pattern in zones with strike length of 50 to 2500 m and width of 100 to 200 m. The zoned pegmatites are classified as rare metal type with quartz core and incipient zones of lepidolite -albite quartz, clevelandite-beryl, felspar green mica, etc. Cassiterite, columbite-tantalite mineralization appears to be of two different phases. The pegmatitic phase is represented by stunted pyramidal and twinned cassiterite crystals, prismatic crystals of columbite-tantalite, pseudomorphs of cassiterite after columbite-tantalite, stannite and rutile (?). This phase is pronoun ced in quartz core and lepidolite-albite and clevelandite zone. The autopegmatitic or hydrothermal phase is represented by solid cassiterite veins in fractures in quartz core and lepidolite-albite zone. Stringers of cassiterite, tantalite etc. are seen in certain fractures in a few pegmatites in greisen zones with lepidolite, zinnwaldite, fluorite, amazonstone, beryl and perhaps, corundum. Other associated minerals include smoky quartz, amblygonite, triplite, ilmenite, goethite, magnetite, varlamoffite, columbite-tantalite and garnet.

X ray diffraction studies on crystal samples have indicated crystals of cassiterite, tantalite and columbite as major constituents associated with pandaite (mica in traces). Presence of fersmanite and steretite in some samples is also confirmed. Native tin which is indicated in some samples may be formed due to re-

duction by acidic waters, which are responsible for sulphide quartz veins in the vicinity.

NATURALLY OCCURRING Sio<sub>2</sub>-GeO-Sno<sub>2</sub> SOLID SOLUTIONS AND THEIR EXSOLUTIONS

#### E.E. Horn and G.H. Moh, Heidelberg, RRG

Recent mineralogical and geochemical investigations have shown that the IV-A group elements, germanium, tin and lead can occur together in various types of ore deposits. For lead and tin, all simple oxides and sulfides are known as naturally occurring minerals, whereas for germanium neither the stable sulfides GeS and GeS, nor the dioxide GeO, are reported. In a recently performed spectrochemical research program on tin ores of known tin provinces of all continents, numerous mineral specimens were found to contain germanium concentrations up to several thousand ppm, some exceeding one percent. Of the analysed samples (cassiterites), some woodtin and varlamoffite specimens had the high est Ge-contents higher than 3000 ppm yielded to the discovery of naturally occuring GeO2 exsolved from cassiterite and varlamoffite, respectively. Gel-like or earth-textured variamoffites may exsolve their Ge-contents during recrystallization, these becoming visible via X-ray diffraction techniques. The characteristic GeO2 X-ray reflections were observed in tin ores of a few different localities, e.g. Homr Akaram/Egypt, Bangka/Indonesia, and a tin mine in Queensland/Australia, etc. Yet to be discove red is naturally occurring germanium sulfide. However, in some lead-zinc deposits, GeSo might be found as a secondary exsolution product of sphalerite, due to increased sulfur activity during the cooling stages after ore deposition.

# M. Štemprok, J. Voldan, Prague, ČSSR

Solubility of tin dioxide in natural and synthetic granite melts was studied under atmospheric pressure at 1600°C. Mixtures were prepared from tin-bearing granites of Prebuz and Krasno (Czechoslovakia) and from a synthetic melt of granite eutectic. Tin was added in the form of sodium disilicate glasses containing up to 20 weight percent of SnO<sub>2</sub>. The crystallization of the melts was followed between 800 and 1300°C by gradient method.

The results show that e.g. the melt containing 69.9 percent  $SiO_2$ , 11.7  $Al_2O_3$ , 6.0  $Na_2O$  and 3.9  $K_2O$  dissolves about 10 percent of  $SnO_2$ . With rising sodium content the solubility of  $SnO_2$  in creases to approximately 20 percent. The only phase crystallization above this solubility limit is cassiterite which precipitates also between 1000 and 1300°C from homogeneous glasses.

The field of cassiterite primary crystallization occupies the most part of the phase diagram expressed in terms of granite eutectic (E) -  $\mathrm{SnO}_2$  - sodium disilicate. The relatively high  $\mathrm{SnO}_2$  solubility at elevated temperatures shows that the entering of tin into silicate melts is not effected by the presence of aluminium or small amounts of FeO, Fe<sub>2</sub>O<sub>3</sub> or CaO as found by experiments with natural granites.

The heating of synthetic granite melts containing high amount of  $\mathrm{SnO}_2$  with water excess at 1 kb pressure between 600 and  $680^{\circ}\mathrm{C}$  showed the phase  $\mathrm{Na}_2\mathrm{O.3SnO}_2.9$   $\mathrm{SiO}_2$  among the products of crystallization whereas cassiterite was lacking.

These data indicate that some earlier assumptions about insignificant solubility of tin dioxide in silicate melts are incorrect as they are based on the observation of a low dissolution rate of tin dioxide. Increased sodium contents favourably affect the solubility.

Thus the existence of high tin sodium enriched silicate melts close to granite composition is possible at high temperatures.

Such melts could have been the product of a deep-seated differentiation of metallogenetically specialized granites and a possible source of constituents giving rise to tin deposits associated with plutonic acid magmatic rocks.

#### URANIUM MINERALIZATION AND GRANITE MAGMATISM IN BRITAIN

P.R. Simpson, G.C. Brown, J. Plant and D. Ostle, London, England

The uranium content of granites from the Caledonian, Hercynian and Tertiary provinces of Britain is reviewed in relation to their association with mineralization, age and structural setting. Uranium is positively correlated with intrusions characterized by high levels of incompatible elements, low K/Rb ratios, low total Sr, low initial 37Sr/86Sr ratios and emplacement in conditions of high geothermal gradients. Fission track studies indicate that the high "background" uranium content of the granites away from mineralization is caused by uranium occuring in resistate primary phases.

The regional trend of uranium and incompatible elements shown by late Caledonian (Devonian) and Hercynian granites in Britain is related to dehydration reactions during subduction of ocea - nic crust. The importance of phlogopite breakdown in accounting for the characteristics of uraniferous granites is discussed in relation to magma generation using closed and open system model with partial fusion of ocean crust of upper mantle. Uranium enrichment by scavenging of subcontinental lithosphere is considered important but late stage assimilation of uranium from higher levels in the crust is relatively insignificant.

EVALUATION OF THE ORE-FORMING CONDITIONS BY IRON CONTENT IN WOLFRAMITE

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The opinions concerning the parameters defining the wolframite composition from various deposits, veins or crystal parts are different. In our report we want to stress the intimate correlation between the Fe/Mn ratio in wolframite and the total composition between the Fe/Mn ratio in wolframite and the total composition of the ore-forming solutions. This is confirmed by: 1) the composition of natural wolframite assemblages; 2) the results of thermodynamic analyses and 3) experimental data.

The correlation between the Fe/Mn tatio in wolframite and the amount of sulphide minerals was first shown by D.O. Ontoev. This is demonstrated by numerous examples of some other deposits to confirm this peculiarity. It should be noted that both the increase in the total amount of sulphides in paragenesis and the presence of pyrite at the early pre-tungsten stages of formation of hubneritic deposits is of principal importance. For wolframite and, particularly, for ferberite deposits the later crystallization of sulphides is typical.

A thermodynamic equation has been derived to establish the quadratic dependence between the iron concentration in solution and sulphide and hydrogen ion activities in presence of pyrite; the iron concentration in less extent is also a function of the redox conditions in solution. The above parameters would determine the iron content in wolframite for paragenesis with pyrite. The Mn-content in wolframite in presence, for example, of rhodochrosite would similarly be a function of both the carbonic acid activity and pH of solution.

The recently obtained experimental data are reported for the effect of solution with different acidity and sulphide concentration on the stability and composition of natural wolframites at 300 and 350°C.

PARAGENESES OF Fe-Ti MINERALS IN GRANITIC ROCKS OF VARIOUS FERROPACIES

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The study of Fe and Ti distribution between biotites (Bi) and amphiboles (Am) on the one hand and oxide minerals, on the other, as well as the composition of rock-forming minerals made it possible to distinguish the following granitic rock types: magnetite-free, magnetite-bearing, magnetitic and titanomagnetitic corresponding to facies of the same name. On the first three types possessing the same bulk Fe content, its fraction held in silicates drops from 80-90% in the magnetite-free facies to 10-15% in the magnetitic one with the corresponding increase in the quantity of oxide minerals from 0.1-0.3 to 1.5-2%. The greater part of magnetite results here from decomposition of femic silicates. Paragenesis is represented by the low-titanium mag netite (TiO<sub>2</sub> < 3%) whose amount is correlated inversely to Fe/Fe+Mg ratio in silicates, fBi > fAm. Primary titanomagnetite is preserved as rare relics. The cooling of titanomagnetitic granitic rocks at low Poo values of the magnetite-free facies preserved the primary magmatic paragenesis: titanomagnetite (Ti  $0_2 > 4\%$ )8  $f_{Bi}$  and  $f_{Am} > 0.65$  and  $f_{Bi} < f_{Am}$ . The direct correlation of Ti and Mn concentrations in titanomagnetite shows that in granitic rocks this mineral is a solid solution of magnetite and manganous ilmenite rather than ulvospinel.

Ilmenites from granitic rocks are rich in Mn and they are in equilibrium with biotite and amphibole: Fe/Mn ratio as well as oxidation degree of the ilmenite phase correlates with the corresponding parameters of silicates. Mn content in ilmenite isolated as individual grains and lamellae in titanomagnetite is the same and thus points to its redistribution in the consolidated rock after the disintegration of titanomagnetite.

There is treated the matter of paragenesis evolution under various conditions and developed a system of granitic rocks ferrofacies in  $P_{0_0}$  - T coordinates.

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About a dozen known tungsten occurences in India including the two operative mines, one at Chhendapathar in West Bengal and the other at Degana in Rajasthan are found related to the three metallogenies - the oldest closing at about 2000 m.y., the second at about 850 m.y. and the third during the Mesozoic; indications of the latter having been found only lately in the Eastern Hymalaya.

At Chhendapathar, where the ore deposits, as mineralized quartz veins are solely confined within the garnetiferous quartz micaschist in close proximity to the adamellite bodies. The tungsten mineralization, represented by disseminated ferberite, is always associated with some degree of copper metallization and feeble but discernible effects of hydrothermal wallrock alteration, the zones of which are identified by physical, textural, mineralogical and chemical variations in an about 15-meter wide zone around the ore bodies. Tourmalinization and manganese metasomatism are important mineralogical and chemical ore-guides respectively in selection of quartz-veins for detailed exploration. In addition, the degree of copper metallization, having intimate spatial distribution with tungsten deposition, also serves as a very strong indicator of tungsten concentrations in the quartz veins. The Chhendapathar ferberite has MnO/FeO ratios varying from 0.06 to 0.09 and contains Nb, Ca, Ti, Sc and Bi as impurities. All the assembled data, including mineralogical, geochemical and geothermometric, converge to show that the tungsten mi neralization is temporally, spatially and genetically related to the adamellite intrusion, the ferberite having been deposited at about 290°C under mesothermal conditions.

Unlike Chhendapathar, the Degana tungsten field, where the Aravalli phyllites form the bedrock, presents a very striking example of highly differentiated acidic magmatism, whose crystallization-differentiation has yielded the granite. The first member

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of the differentiated suite is the porphyritic granite, and the greisen along with bodies of pegmatite, aplite and barren and mineralized quartz veins is related to its end member by systematic mineralogical variations. Chemical and geochemical studies on the two kinds of mica indicate that the mineralizers towards the pegmatitic stage had become relatively rich in Ca,Li, Sn, Te, P, Cu, Ni, etc., but much depleted in quantities of tungsten.

Suites of wallrock samples, both from the phyllite and the granite, show marked development of wallrock alteration zones - greisenization of the granite characterized by the introduction of excessive amounts of quartz, zinnwaldite, topaz and fluorite and silicification of the phyllite. The intensity of the two types impressed upon the wallrocks is being directly related to the ferberite enrichments in the veins. The main chemical changes that occurred during greisenization was the addition of the total iron, fluorine, lithium and alumina together with little Sn and W.

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