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# XI GENERAL MEETING OF INTERNATIONAL MINERALOGICAL ASSOCIATION

## Abstracts

## Volume II

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This volume comprises the Abstracts of the papers presented at the XI General Meeting of International Mineralogical Association (IMA) on high-pressure minerals, experimental mineralogy and the problem of the Upper Mantle, inhomogeneities in minerals, gem minerals and gemology, electron probe microanalysis in mineralogy and a number of problems dealing with mineralogy, petrology and concepts of minerals and ore deposits.

# HIGH–PRESSURE MINERALS

# CHEMISTRY OF ILMENITE NODULES AND CLINOPYROXENE-ILMENITE INTERGROWTHS IN KIMBERLITES FROM NORTHERN COLORADO AND SOUTHERN WYOMING

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Discrete nodules of ilmenite are abundant in most of the kimberlites of the Colorado-Wyoming State Line and Iron Mountain, Wyoming, districts, and clinopyroxene-ilmenite intergrowths have been recovered from several kimberlite pipes. The ilmenite nodules average about 1-3 cm in **diameter**(with some as much as 13 cm), whereas the intergrowths rarely exceed 1 cm. The largest intergrowth recovered is 4.5 cm in maximum dimension.

The ilmenites typically are magnesian but show a pronounced variation in composition within and between pipes. $MgTiO_3$ contents range from 10 to 50 mole percent, and $Fe_2O_3$ from 3.5 to 40 mole percent. Ilmenites from the Iron Mountain district to the north are strongly enriched in iron relative to State Line district nodules. Furthermore, ilmenites from the more northerly pipes in the State Line district have increased iron contents, but they do not show the degree of enrichment or extreme variation of iron present in Iron Mountain ilmenites. Similar chemical trends with respect to Mg-Fe occur also in discrete nodules of garnet and clinopyroxene. $Cr_2O_3$ contents of ilmenites also show a regional change; the more magnesian-rich nodules from the southern pipes of the State Line district are noticeably enriched in $Cr_2O_3$ as compared to ilmenites from Iron Mountain pipes ($\sim$ 2.5 - 10.6 versus 0.25 - 1.5 percent $Cr_2O_3$).

Northernmost State Line pipe ilmenites contain intermediate amounts of $Cr_2O_3$. A MgO versus $Cr_2O_3$ plot has a parabolic shape similar to that reported for African ilmenites by S.E. Haggarty, in a 1975 study. Most of the Iron Mountain samples plot on the left limb or low MgO side of the parabola, which reflects a small increase in $Cr_2O_3$ levels as the $Fe_2O_3$ content **of the ilmenite increases.**

Clinopyroxene-ilmenite intergrowths, which are found primarily at Iron Mountain, contain *the most magnesian ilmenite* (43 mole percent $MgTiO_3$) and Fe-rich clinopyroxene ($FeO + Fe_2O_3 \geq 5.4$ percent) in that district. $Cr_2O_3$ contents in the intergrowth ilmenites are uniformly low, averaging 0.38 percent. $Cr_2O_3$ - NiO plots reflect a sympathetic relationship between Ni and $Fe^{2+}$ *in ilmenite* nodules, and roughly show a separation of source areas.

General compositional trends are interpreted to reflect liquid fractionation. The *"parabolic relationship" between* $Cr_2O_3$ and MgO may reflect crystallization of ilmenite under different pressures in the Iron Mountain as opposed to the State Line district. The high-Fe clinopyroxene-high-Mg ilmenite intergrowths at Iron Mountain suggest that most silicate discrete nodule phases crystallized before ilmenite and that the intergrowths represent a transition from silicate to oxide crystallization. The more *Mg-rich ilmenites of the State Line district* may represent either earlier members of the fractionation sequence, or phases that crystallized in a higher pressure regime.
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## *DIAMONDS: GENESIS AND MINERAL INCLUSIONS*

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Since the mid-1960's a large amount of information pertaining to the mineral inclusions in natural diamond has been obtained. This information, mostly of mineral chemistry, is from worldwide localities where diamonds occur and includes South Africa, South and North America, USSR and Australia. Furthemore, the geological ages when the diamonds reached the earth's surface are also diverse, ranging from Pre-Cambrian to late Mesozoic. During the same period (mid 1960's to present) a large amount of mineralogical and petrological research has been undertaken on kimberlite and associated xenoliths. For the most part there are still several unresolved problems concerned with the petrogenesis of these rocks. As a result complications occur regarding the interpretation of the mineral chemistry of the inclusions in diamond relative to minerals in kimberlite and associated xenoliths.

The mineral types occurring as inclusions are generally similar throughout the world (e.g. olivine, pyroxene, garnet, spinel). In detail, however, significant variations in mineral chemistry do occur notably with regard to the compositions of clinopyroxenes and garnets. These differences presumably reflect very local variations in mantle compositions in the region wherein diamond was forming. Nevertheless at this time it is possible to indicate two geochemical environments in which diamond has grown, are eclogitic and are ultramafic. Furthermore, these two environments in terms of diamond genesis are mutually exclusive. However, in terms of pressure-temperature regime it is likely these two geochemical environments are not too dissimilar, and are broadly within the same regime defined by the chemistry of xenoliths in kimberlite.

Diamonds containing eclogitic suite inclusions are not genetically related primarily to kimberlite. The question of diamonds with ultramafic inclusions is not so clear to answer but in all probability the diamonds are xenocrysts and not phenocrysts in kimberlite. The solution of this problem is important with regard to defining accurately provenance of diamonds and upper mantle structure in general.

# INCLUSIONS IN DIAMONDS FROM THE PREMIER MINE

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More than 350.000 diamonds from the Premier Mine have been studied to determine the relative proportions of mineral inclusions present.The chemical compositions of approximately 100 mineral grains recovered by physical cracking of the diamonds have been determined.

Olivine, orthopyroxene, garnet, clinopyroxene, kyanite, chromite and one amphibole have been identified. Visual identification of inclusions inside diamonds supported by the subsequent analysis of selected grains indicates that apart from abundant sulphide, the commonest mineral is olivine. Orthopyroxene, and eclogitic clinopyroxene and garnet are also common. Purle garnet is rare and only one garnet with less than 3.5 wt% CaO has been analysed.

Notable features of the mineral compositions, consistent with other studies on diamonds, are the trace element concentrations of sodium, potassium and chromium in the eclogitic garnets, the eclogitic clinopyroxene and in the olivines respectively.

Inspection of the published data on mineral compositions in the peridotite xenoliths from Premier Mine does not confirm a close association between these common xenoliths and the inclusions in the diamonds.

The $K_D$ ratios for the Fe/Mg distribution between co-existing garnet and clinopyroxene are consistent with a higher temperature origin for the Premier eclogitic inclusions, when compared to Koffiefontein or Finsch Mines.

Premier Mine inclusions are similar to those of the Finsch Mine in respect of the abundance of sulphides, and olivine, the presence of both eclogite and peridotitic minerals, the rare occurrence of kyanite and the scarcity and possible absence of chrome diopside of the peridotite paragenesis. They differ markedly in the enhanced proportion of eclogitic inclusions, the rarity of high chromium, low calcium garnet and the higher orthopyroxene/olivine ratio at Premier.

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# WHITE MICAS, SODIUM AMPHIBOLES AND PYROXENES THERMOBAROMETRY

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White micas (phengites) and Ca-Na amphiboles are most informative minerals in low-grade metamorphics. Maximal Na-content of phengites in each zone may be used for estimation of temperature. Maximal content of celadonite component, $KR^{+2}\ AlSi_4O_{10}\ (OH)_2$ in association white micas-K-feldspar and additional Fe-Mg mineral decrease with temperature increasing and pressure decreasing. This may be used for estimation pressure if we estimate temperature. Maximal Na content of amphiboles ($Na(\ U_1) = 2.0-Ca$) in association with albite, chlorite and magnetite and maximal jadeite content of pyroxenes in association with albite and quartz have been used for the same aims.

Correlated estimations on white micas, sodium amphibolites and pyroxenes give us the possibility to construct the phengite-pyroxene and crossite-pyroxene thermobarometers and to have objective P-T estimations of low-grade metamorphism. This estimations in the glaucophaneschist belt of the USSR correspond to 400-500°C and 10-11 kbar in Renjina belt (Koryakia), 500-550°C and 13kbar in Maksyutov complex (S.Urals), 450-500°C and 7-10kbar in the belts of South Tjen-Shan. They have been based on the original microprobe analysis of more than 60 micas, 40 amphiboles and 30 jadeitic pyroxenes.

## PECULIARITIES IN THE DIAMONDS FROM SOME KIMBERLITE BODIES OF MASERU, LESOTHO

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Crystallomorphology of the diamonds from the kimberlite bodies of Kolo and Lighobong-Lemfane has been studied. Pipe Kolo is situated in the low-lying western part of Lesotho and breaks through sedimentary rocks of Befort strata and dolerites of Karru system. Kimberlite bodies of Lighobong-Lemphane are situated in the Alpine northern part of the country, where it breaks through thick covers of the basaltic drifts of the Stromborg series.

Basic morphological types of the diamond crystals are represented by the rhombic dodecahedra with curved faces, polyhedra of the transitional type (from octahedron to rhombic dodecahedron) and octahedras, Diamonds with curved faces (rounded) in all bodies prevail. The diamonds have distorted appearance. The development of cavities and faces is characteristic. The cavities have irregular outlines, persisting from face to face "corroding" the faces seams and edges. The bottom and the walls of cavities are triated. Light pictures from the cavities are analogous with reflexograms from 3-, 4-, 5-, and 6-angled hollows and correspond to the phase of different trigon- and tetragontrioctahedra. Many crystals are ornamented by the strips of plastic deformation,

In contrast to the diamonds from the kimberlite bodies of Lighobong-Lemphane among the diamonds from Kolo pipe there are more octahedra, transitional types; twins and crystals with numerous graphite inclusions. There are many yellow diamonds in the bodies of Lighobong-Lemphane. The parameters of curvature of yellow rounded diamonds are: AB - 48-54°, CD - 13-15°, DD - 8-12°, CC - 35-40°.

Angular magnitudes of curvature of the rounded diamonds from Lesotho correspond to the same of the rounded diamonds from different deposits of the World.

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## ARE THE GARNET LAMELLAE IN ARIÈGITES EXSOLUTIONS?

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Ariègite isolations in weathered bodies of serpentinized peridotites have been found in Kozlany and Horní Kounice localities in the area of Moldanubicum (Czechoslovak Socialist Republic, west of Brno, capital of Moravia). They contain spinel (ceylonite), pyrope and diopside. Enstatite is also present in Kozlany locality.

Spinel forms black grains about 2 mm which are rimmed with the light-red pyrope. Pyrope also occurs as narrow lamellae in clinopyroxene and orthopyroxene. These lamellae show a thickness of the order of thousandths to tenths of mm and a length of 1-2 cm. Green clinopyroxene is most common as cm-large grains. Orthopyroxene from the Kozlany forms grains about 1 cm, grey-white in colour. Microscopic study has revealed that the lamellae and both large and small anhedral grains of pyrope crystallized later than clinopyroxene and orthopyroxene grains cleaved by them.

The pyrope of anhedral grains and of lamellae (both in diopside and in enstatite) is very similar by its chemical composition. In the Kozlany anhedral garnet grains the content of pyrope component was found to be 71-73%, in the garnet lamellae in diopside - 68%, and pyrope lamellae in enstatite - 72%. The Horní Kounice anhedral garnet grains and garnet lamellae in diopside revealed nearly the same content of the pyrope component (69,5%). The Moldanubian griquaites, whose genesis is analogous with that of the described ariègites, do not contain garnet lamellae. Their amount of pyrope component in garnets is on the average 70%.

The clinopyroxenes from the Kozlany and Horni Kounice ariègite contain on the average 2.5% of $Al_2O_3$, the clinopyroxenes from the Moldanubian griquaites contain 3.5% of $Al_2O_3$. The $Al_2O_3$ content in the Kozlany orthopyroxene is less than 2%, that of the orthopyroxenes from the Moldanubian griquaites is on the average, 3%.

Small differences in the chemismus of the two pyroxenes in the Moldanubian ariègites and griquaites of identical provenance do not offer sufficient support for the interpretation of the origin of the garnet lamellae as exsolutions from individual pyroxene grains. There is also difficult to explain that the garnet lamellae of a very similar chemical composition should originate by exsolution from the surrounding grains of orthopyroxene or, otherwise, of clinopyroxene.

Moreover, partly occupying the position of the lamellae, occur the isolated pyrope crystals with sharp edges. Their habit reminds that of metacrysts.

The results presented throw some doubts as to the generally accepted opinion that garnet lamellae in ariègites, eclogites griquaites and pyroxenites originate as exsolutions from individual host pyroxene grains.

## GROWTH MECHANISM OF NATURAL OCTAHEDRAL DIAMONDS

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Surface microtopography and X-ray topography of natural diamond octahedrons from Siberia which suffered very little dissolution were studied. One to one correlation between the summits of growth pyramids on the octahedral faces and the outcrops of screw type dislocations was established, from which it is concluded that the diamond crystals grew by the spiral growth mechanism from high temperature solution phase of very low supersaturation by the addition of atomic entities. Synthetic diamond crystals exhibit very different surface microtopographs, about which discussion will also be made.

## POLYCRYSTALLINE AGGREGATES OF DIAMONDS IN THE USSR

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Specific types of diamonds, balas and carbonado, are characterized by microcrystalline texture with component grains of 1 to 50 mkm. Balases have radial structure which may be detected visually in fractures, as well as by X-ray analyses. The latter show considerable angle of dispersion (up to 30°) accompanied by twinning of crystallites.

Two varieties are distinguished among carbonados found in the USSR in the last few years. The first one is identical to the Brazilian carbonados and differs from them only in somewhat larger average size of crystallites. The second one has been found for the first time. It is characterized by the presence of traces of lonsdailite which is oriented to the cubic diamond lattice. The size of the diamond grains is rather uniform and small (less than 1mkm).

In comparison with the diamond monocrystals balases and carbonados are enriched in the elements such as Si, Al, Fe, Ca, K , and oth. Carbon isotopic composition of balases and carbonados also differs from that of monocrystals from kimberlites. It is 29.0% for carbonado and 14.2% $\delta C^{13}$ PDB for balas.

Carbonado and balas are not known from kimberlitic pipes. They are found only in placers in the Urals, the Sayans, North Yakutia and the Far East, where they are associated with almandine, zircon, corundum and other minerals, which are not typical of kimberlites.

Judging by the distribution and specific features of the composition of balases and carbonados it is supposed that the primary rocks of diamond polycrystalline aggregates are not kimberlites but some other deep-seated rocks.

# HIGH-PRESSURE MINERALS AS EVIDENCE OF DEEP-SEATED (UPPER MANTLE) CRYSTAL FRACTIONATION OF THE ALKALINE BASALTIC MAGMAS

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The Cenozoic alkaline basaltic rocks from Mongolia contain inclusions of large (2.-10cm in size) megacrysts of high-alumina augites ($Al_2O_3$ = 7-8%, CaO=15-17%, jadeite component = 15-22%) with f = 20-30% (f $\frac{\Sigma Fe}{\Sigma Fe+Mg}$ at.%); pyrope (CaO = 4-5%, $TiO_2$ = 0.5-0.6%, $Cr_2O_3$ = 0.03 - 0.06%, f≈36-40%); titanphlogopite ($TiO_2$ = 9-12%, $K_2O$ = 9-10%, f = 33-36%); titanbiotites (as inclusion in sanidine megacryst, f = 56%); olivine with f = 8%; K-Na feldspars (high potassic and sodium sanidine, anorthoclase) with low concentration of Rb (15-95 ppp) which is close to the Rb amount in the host basalts.

Megacrysts are characterized by high homogeneity in contrast to zonal phenocrysts and inherited geochemical peculiarities in the host basalts. The megacrysts origin is proved to be related (consanguineous) to host basalts and have characteristics peculiar to high-pressure minerals and definitely different both from the composition of similar minerals in phenocrysts and deep-seated xenoliths.

Mineralogical and geochemical features of the megacrysts and comparison with experimental results allow to consider the majority of megacrysts as near-liquidus phase crystallised from alkaline basalt melts at high-pressure and temperature ($T > 1300$, $P > 20-30$ kbar). Megacrysts represent the evidence of deep-seated (upper mantle) crystallization of corresponding magmas.

The presence of near-liquidus phases of augite, pyrope, titan - phlogopite in potassic basaltoids and of the same phases of augite, olivine in sodium basaltoids indicate that the upper mantle fractionation of the potassic alkaline basalt magmas takes place at the higher pressure and temperature than the fractionation of sodium basalt magma. This process is regarded as one of the possible mechanisms which defined tholeitic trend of the sodium basaltic magmas of Mongolia and particularly deep evolution in the potassic basaltic magmas increase of "f" in the remaining melts with low saturation in $SiO_2$ and constant or decreasing alkalinity.

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# INCLUSIONS IN SOUTHERN AFRICAN DIAMONDS

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A study of inclusions in Southern African diamonds from known sources has shown major differences between the inclusions and minerals in the mantle rocks represented as xenoliths within those kimberlites. Although both suites are present at all localities, Roberts Victor and Finsch are characterised by peridotititc diamond inclusions and Orapa is predominantly eclogitic. Others are intermediate.

The peridotitic inclusions as a group are always very refractory in composition and have lower Fe,Ca, Al and Na and higher Mg and Cr than the corresponding minerals in the xenoliths.The eclogitic inclusions are characterised by sodium in the garnets potassium in the clinopyroxenes and by high Ca,Fe, Al and Na and low Mg and Cr. They are therefore amongst the geochemically most evolved eclogitic minerals found in the kimberlites.

The association of the extremely refractory peridotitic inclusions with diamond can be possibly explained by consideration of the effects of a small degree of $CO_2/H_2O$ induced low temperature melting of mantle peridotite, whilst the eclogitic diamond inclusions may be formed in a small volume late stage differentiated liquid which has evolved from a larger partial melt towards water and $CO_2$ saturated compositions by eclogite accumulation.

## FRAGMENTS OF VARIABLE ECLOGITES FROM KIMBERLITES OF LESOTHO

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Eclogitic xenoliths in kimberlites are seldom characterized by *varying parageneses within one boy or body group. In this connection* fragments of eclogites reaching 1 cm in the longitudinal dimensions belonging to bimineral (1), kyanite (2) and corundum (3) -bearing parageneses seem to be of special interest. These represent the two samples of each type to occur in the concentrate of kimberlite dyke 157A in South-Western Lesotho with 12 km strike of varied thickness from 4 cm to 3 m.

The kimberlitic concentrate of this dyke predominantly contains minerals of ultrabasic type of paragenesis among which the leading role belongs to garnet. Only 3-5% of the creme-pink garnets may be preliminary assigned to eclogitic type.

The common peculiarity of eclogitic garnets studied by electron probe as well as pyroxenes is very low iron index (f):18.1-23.2 % along with varied Ca-content making up eclogitic garnets of the 1-st type: 11.7 and 25.0% and 29.9,and 38.2% for the 2-nd type, being 31.0 and 47.5%,respectively for the 3-rd type. Clinopyroxenes of the four samples of 1 and 2 types are specified by *higher jadeite content in the average* (21-42%). However, pyroxenes from eclogite of the 3-rd type have sharply varying composition, mainly in jadeite (7-47%) and Tchermak molecule contents (32 and 11%,respectively). Judging by the peculiarities in the minerals, the 1 and 2 type eclogites are distinguished by their chemical composition and temperature of their equilibration fixed by the iron-magnesium partition in garnet and pyroxene varies between 1000 and 1200°C at 30-40 kbar pressure. *For corundum eclogites, the T-range is wider* (1000-1400°C).The highly aluminous eclogite with low sodium content is most high temperature one from all the known corundum eclogites. The obtained data are indicative of a complex composition of eclogitic part of the Upper Mantle for South-Western Lesotho.

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## Ia AND IIa TYPES AMONG THE ECLOGYTIC SPECIMENS,MICROCRYSTALS AND IN THE GROWTH ZONES OF NATURAL DIAMONDS

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A hypothesis was suggested about the earlier crystallization of the IIa type vs Ia type in natural diamonds. The type IIa diamonds occur more frequently among the microcrystals (Tolansky et al.) which may be explained by the fact that natural diamonds first begin to grow as type IIa and later change to type Ia. The idea was discussed by Rugichka, who believed that nitrogen-free crystals could have grown on great depth in nitrogen-poor magma,while type Ia could have grown in higher zones. We measured the nitrogen content ( by IR and UV-absorption) in a) 50 diamonds from the eclogitic xenolith; b) 200 microcrystals (less than 0.5 mm) from several pipes; c) in growth zones of 50 specimens of Ia and intermediate types. The method of distribution curves was applied. Investigation of eclogitic specimens revealed different nitrogen content, varying from $10^{19}$ to $3.10^{20}/cm^3$, the maximum on distribution curve was near $1.5.10^{20}/cm^3$ exactly as a main maximum for the kymberlitic crystals from that pipe. The comparisons of microcrystals and large specimens shows that their distribution curves are practically equal, but the pipe dependence does occur; the results of Tolansky et al. were shown to be connected with the qualitative nature of their methods. Investigation of the history of growth zones did not reveal the initial zones of IIa type, but zones of this type were detected in the central and (more often) in the marginal parts of several specimens. Thus the experimental data contradict the hypothesis about the earlier crystallization of type IIa diamonds - they can grow near the type Ia specimens in the time-intervals under definite conditions. We think that the medium and chemistry of the processes of crystal growth(or zone growth) of Ia and IIa types were compositionally similar,while variations in the nitrogen contents are due to the impurity-capturing ability.

## *THERMAL EFFECT OF KIMBERLITIC MELT ON DIAMONDS*

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After V.S.Sobolev, the diamond content in kimberlites is a function of physico-chemical conditions of crystallization in the Upper Mantle as well as velocity of melt ascent being diamond transporter. In a majority of cases one does not observe the thermal effect of kimberlite melt on xenoliths of the host rocks, which may be indicative of rather low temperature conditions of kimberlite formation in diatremes. The exception are kimberlite bodies of the Upper Muna and some other northern areas in which high-temperature metamorphic rocks were found to occur as composed of montichellite, andradite-grossular, clinopyroxene, cuspydine, apatite and some other minerals. These rocks were formed from xenoliths of sedimentary rocks under the effect of kimberlitic melt. Xenoliths of crystalline schists at the contact with kimberlites are frequently melted. In this case the temperature of kimberlitic melt seems to be not lower than 900-1000°C,while pressure did not exceed several hundreds atm with increased oxygen fugacity. Such conditions were naturally unfavourable for preserving diamonds and one may expect that some of the diamonds from these pipes were destroyed and the preserved crystals bear the traces of dissolution. Indeed, the detailed study of kimberlites from the Upper Muna region permits one to establish some specific corrosional cavities of irregular shape with wavy contours and regular geometry of sculptures (striating, polygonal cavities) on the flancs and bottom. The morphology of the cavities varies as a function of their position relative to symmetry elements of the crystals. They are confined generally to rounded surfaces. We have experimentally produced these sculptures in specific conditions by etching the diamonds with water vapors at 900°C with the nonuniform supply of corrosional agent.

Thus to study the peculiarities in the diamond content in kimberlites it is necessary to take into account the possibility of partial dissolving of diamonds when kimberlites were formed in diatreme conditions.

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## CHEMISTRY OF DISCRETE NODULES OF GARNET IN KIMBERLITES FROM NORTHERN COLORADO AND SOUTHERN WYOMING

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Abundant discrete nodules (megacrysts) of pyrope garnet occur in association with megacrysts of clinopyroxene, orthopyroxene ilmenite, rare clinopyroxene-ilmenite intergrowths and rare olivine in kimberlite pipes in the State Line and Iron Mountain districts of the Colorado-Wyoming Front Range. Garnet megacrysts average 1-3 cm in maximum dimension, although larger specimens up to 20 cm in maximum dimension have been collected.

Two megacryst assemblages (Cr-poor and Cr-rich) are physically and chemically distinct. Garnets of the Cr-poor assemblage are red to orange, contain 0 - 4.5 percent $Cr_2O_3$, are subcalcic (CaO = 3.0 - 7.9 percent) and magnesian (MgO = 17.3 - 21.9 percent), and are variable in FeO (6.9 to 17.1 percent, total Fe as FeO; Mg/Mg+Fe = 0.521-0.848). Cr-rich garnets are deep reddish-purple to black or greenish black, have more restricted Mg/Mg+Fe (0.818-0.845, with MgO = 17.5-20.3 percent and FeO = 6.5-7.5 percent), and are higher in CaO (5.7-8.6 percent). Cr-poor and Cr-rich garnets have similar $TiO_2$ contents (0.14-1.3 and 0.54-0.94 percent $TiO_2$, respectively), although the Cr-poor assemblage has slightly wider ranges. Cr-poor garnets are chemically and physically similar to discrete nodules of garnet in Lesotho kimberlites except that the Colorado-Wyoming samples range to slightly higher CaO, $Cr_2O_3$, and FeO contents. Cr-rich garnets are chemically equivalent to garnet in depleted garnet peridotite nodules from Colorado-Wyoming kimberlite, but they are likely not derived from disaggregated xenoliths , because no xenoliths with comparable grain sizes have been collected.

Inclusions of other minerals of the megacryst assemblages (orthopyroxene, clinopyroxene, and ilmenite) occur in both Cr-poor and Cr-rich garnets but are more abundant in the Cr-poor suite. Cr-poor garnet commonly occurs as inclusions in ilmenite. Host/inclusion relationships between Cr-poor and Cr-rich phases have not been observed.

Chemical trends of garnets of the Cr-poor megacryst assemblage are suggestive of high pressure crystallization from a liquid fractionating from high-Cr and Mg, low-Fe to low-Cr and Mg, high-Fe compositions. Fractionation trends are especially pronounced in garnet from the Iron Mountain district to the North, where associated clinopyroxene and ilmenite megacrysts also show Fe, Ca and Ti enrichment with progressive differentiation. Cr-poor garnets began crystallizing before initiation of ilmenite or clinopyroxene-ilmenite intergrowth crystallization. Cr-rich garnet megacrysts have more restricted compositional limits and do not display evident fractionation trends, but they are also thought to have crystallized from a liquid because of their coarse grain size. Subtle differences in the chemistry and abundances of garnet and other megacryst phases between different kimberlite pipes or clusters of pipes imply: (1) that the megacryst assemblages are cognate to parental kimberlite melts, (2) that discrete conduits existed from the source area to the surface, and (3) that differences may exist in the source area magmatic environments of different kimberlites.

## $Fe^{3+}/Fe^{2+} + Fe^{3+}$ -RATIO IN GARNETS ORIGINATED FROM THE UPPER MANTLE

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In Mössbauer spectra of Fe-Mg garnets, $Fe^{3+}$ is displayed as a quadrupole doublet which differs from $Fe^{2+}$ doublet by its parameters in 8-th coordination. The relation between the squares in these doublets calculated on EC in view of the difference between the resonant absorption $Fe^{2+}$ and $Fe^{3+}$ provides a quantitative expression of the degree of iron oxidation in the mineral. The table given below lists the $Fe^{3+}/Fe_{total}$ ratio for the garnets from the Mantle xenoliths in kimberlite pipes of Yakutia.

Table 1

| Pipe | Number of samples | Rock represented by xenoliths in kimberlites | $Fe^{3+}/Fe_{total}$ in garnets |
|---|---|---|---|
| Obnazhennaya | 1 | Pyroxenite with garnet replaced by chromespinelide | 7.5 |
| | 1 | garnet peridotite | 6.9 |
| | 1 | garnet peridotite with ilmenite | 13.3 |
| | 5 | eclogite | 6.8 |
| | 1 | eclogite with corundum | 5 |
| Udachnaya | 3 | Sheared chloric garnet peridotite | 17.5 |
| | 1 | diamond-bearing eclogite | 6.8 |
| | 2 | kyanite diamond-bearing eclogite | 5 |
| | 1 | diamond-bearing eclogite | 7.2 |

The obtained results do not permit one to discuss the Upper Mantle as a region of absolutely prevailing highly reductive conditions. Small but significant amounts of ferrous iron (mean $Fe^{3+}/Fe^{2+} + Fe^{3+}$ 7%) have been established for garnets from the Mantle facies rocks of various depth up to diamondiferous eclogite facies.

The alumina-rich rocks practically possess the total iron reductivity up to ferrous iron form. Higher $Fe^{3+}$ content in ilmenite-garnet peridotite agrees with the presence of ferrous oxide in ilmenites from kimberlites. Rather high $Fe^{3+}$ content in garnets of the so-called sheared peridotites attracts one's attention, the latter by their P and T values both from Africa and Yakutia belong to most deep-seated ones. It may be concluded that the peculiarity established for these garnets is associated with shearing processes reflecting oxidative-reductive conditions of asthenosphere.

## RECONSTRUCTION OF CONDITIONS OF DEEP-SEATED CRYSTALLIZATION OF MEIMECHITES FROM THE NORTH OF THE SIBERIAN PLATFORM USING COMPOSITIONS OF CHROMITE-OLIVINE PHENOCRYSTAL ASSEMBLAGE

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Electron microprobe analysis was applied to detailed study of olivine and chromespinelide compositions from meimechites of different phases of Gulin intrusion. It is shown that irrespective of the similarity in the overall chemical composition of meimechites of different age, the chromite-olivine assemblage composition varies distinctly by their iron content: the mean iron content (f): 10.8; $f_{chr}$: 48% for meimechites of the 1-st phase of intrusion and $f_{ol}$ : 7.9; $f_{chr}$: 34.5 for meimechites of the second phase of intrusion. Moreover, a significant positive correlation has been found between the iron content of olivine and chromites included in it (the coefficient of the paired correlation $\rho = 0.94$, overall number of analyses =30). Based on the above evidence and continuous change in the composition of the studied minerals it is assumed that the heterogeneous meimechites correspond to different stages of recrystallization of the common ultramafic melt. The variations in the composition of the phenocryst assemblage are caused by the T-differences in the later deep-seated equilibrium of the system: olivine-chromite-melt, evaluated experimentally in the average as $\triangle T = 100\text{-}150^{\circ}C$.

Based on the equilibrium: olivine-melt is the estimate of the fluid phase composition and the degree of crystallization of heterogeneous meimechites and the composition of theprimary melt whose MgO content was likely to exceed 30 wt.%.

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## COESITE OF ECLOGITES FROM THE UDACHNAYA KIMBERLITE PIPE, YAKUTIA,

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Aluminous suite of the upper mantle in the region of the Udachnaya Pipe is formed by bimineral and kyanite eclogites, grospydites and alkremites.

A wide spread of coesite is identified in xenoliths of grospydites, biminerala and kyanite eclogites. Coesite is identified with certainty in fifteen specimens and also in two eclogites which contain diamonds. The results of petrographic examination, determination of optical properties, X-ray diffraction and X-ray spectral analysis show complete analogy with synthetic coesite. Four genetic groups are distinguished according to the conditions of coesite spreading in the above mentioned rocks.

Coesite inclusions in basic rock-forming minerals of eclogites: in garnet, clinopyroxene and kyanite.

Equilibrium parageneses of coesite with eclogite minerals wherein coesite is rock-forming according to grain size, euhedrality, and content (up to 8 percent).

Subgraphic (regular) intergrowths of garnet and coesite.

Association of coesite with fusion products of eclogites, wherein coesite is in association with spinel, plagioclase, clinopyroxene and other minerals, i.e. it is more late than the primary eclogite minerals.

In a majority of cases coesite is partly or entirely replaced by polycrystalline quartz aggregates. Sanidine or adular may be occasionally found in close association with coesite.

Experimental results for coesite parageneses with eclogite minerals and parageneses with diamond show a wide range of P-T parameters for coesite existance from 30 kbar to 50-60 kbar.

## HIGH-PRESSURE CLINOPYROXENES

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The phase relations in the system $CaMgSi_2O_6$ - $NaAlSi_2O_6$ - $CaAl_2SiO_6$ - $SiO_2$ have been established at 35kb and 1200°C. A volume containing no free silica was detected within the system and its boundaries fixed. The boundary with free $SiO_2$ along which a monomineral clinopyroxene is crystallized sets up along the joins $CaMgSi_2O_6$ - $Ca_{0.5}AlSi_2O_6$ and $NaAlSi_2O_6$ - $Ca_{0.5}AlSi_2O_6$ in the end-member system and in the plane $CaMgSi_2O_6$ - $NaAlSi_2O_6$ - $Ca_{0.5}AlSi_2O_6$ in the tetrahedron Di-Jd-CaTsch-$SiO_2$. The excess silica was first experimentally shown as dissolved in high-pressure clinopyroxenes as a pyroxene minal $Ca_{0.5}AlSi_2O_6$ (Ca-Eskola's molecule). The maximum $SiO_2$ in the excess in clinopyroxenes in this system is of the order of 19 eq.cat.mol.%, i.e.21 wt.% or 48 mol.%. The solubility limits of the Eskola's minal in pyroxenes of the series: diopside-jadeite are found to be 47 wt.% in the diopsidic and 12 wt.% in jadeitic component.

Clinopyroxenes with excess silica were analysed crystallochemically using X-ray and optical data for the formation of clinopyroxene solid solutions. Excess of $SiO_2$ dissolves as $Ca_{0.5}AlSi_2O_6$ by Si substituting isomorphically $Al^{IV}$ which is present in the clinopyroxenes in notable amounts as a Tschermak's molecule, with simultaneous isomorphism in M1 ($Mg^{2+}$-$Al^{3+}$) and M2($Ca^{2+}$ - $Na^{+}$) sites (for the compositions within the tetrahedron Di-Jd-CaTsch-$SiO_2$). The M2 site of the pyroxene becomes cation-deficient.

The excess silica in high-pressure parageneses with pyroxenite and eclogite is essential for understanding the origin of the quartz-bearing magmatic series of the Mantle matter.

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## ON STABILITY OF PYROPE-GROSSULAR SOLID SOLUTION

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The peculiarities in the pyrope-grossular solid solutions are discussed in the light of measurements of their physical properties. The importance of the approach lies in a new method of investigation compared with the previous ones based on the experimental study of mineral equilibria. According to Newton et al., the dependence of mixing enthalpy on solid solution composition is asymmetrical, so the pyrope-grossular solid solution deviates significantly from the previously proposed model of regular type. The enthropy and excess thermal capacity values are calculated from the measured enthropy and thermal capacity values for grossular and pyrope as well as by the calculation of thermal capacity and enthropy of intermediate compositions by Leibfrid formula, based on the lattice theory of solids. The literature and original data on the garnet elasticity constants and spectroscopic frequencies were used in our calculations. The function of excess thermal capacity and enthropy from the solid solution composition is asymmetrical as well as that for the mixing enthalpy. The composition of garnets from the equilibrium with anorthite sillimanite and quartz, calculated with the help of the proposed method of excess thermodynamic functions shows fair agreement with the Henson's experimental data.

The change in chemical potential of grossular as dependent on the function of solid solution composition shows that pyrope and grossular form stable solid solution at temperature above 400°C, and at any admissible pressure. The high content of Ca in garnets from the same mantle rocks is conditioned probably by the peculiarity in the Ca distribution between the equilibrated phase and the gross composition of rocks.

## SPINEL GROUP MINERALS IN ULTRAMAFIC INCLUSIONS FROM SAN CARLOS, ARIZONA

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Ultramafic inclusions from San Carlos, Arizona have been classified into two major groups (Frey and Prinz, 1978). Group I inclusions are magnesian and chromiferous olivine-rich peridotites (mainly lherzolites), and spinel is rich in the chromite and spinel end members. Group II inclusions are dominated by clinopyroxene-rich peridotites with aluminous augite, and spinel is enriched in the hercynite molecule. Group I inclusions are partial melt residues (Component A) containing an additional minor amount of melt which is the result of a small degree (< 5%) of garnet peridotite melting, probably within the low velocity zone. Group II inclusions are more iron-rich and appear to be cumulates derived at moderate pressures from a $SiO_2$-undersaturated magma, possibly related to the host basanite. In addition, there are some inclusions which are transitional between Groups I and II. There are also inclusions which contain plagioclase in addition to spinel and are transitional toward the host basanite. Some of these inclusions contain plagioclase-spinel-pyroxene coronas (symplectites) surrounding pyroxene crystals. Spinels record some of the history in all of these environments, including the host basanite. Spinels and all coexisting minerals in a suite of about 50 inclusions of all types have been analyzed with an electron microprobe, and other mineralogic techniques. *The Fe/Mg ratio of spinels in Group I* inclusions vary inversely with Fe/Mg ratio of coexisting ferro magnesian silicates, whereas Fe/Mg ratio of spinels in Group II inclusions varies sympathetically. The crystallochemical reasons for these relationships will be discussed. Spinels are homogeneous in composition within each sample, except for those that are transitional between Groups I and II. This differs from some equilibrated ultramafic inclusion localities, where silicates are homogeneous within a single sample, but spinel *is heterogeneous (e.g. Itinomegata, Japan; Bandera, New Mexico)*. The implications of equilibrated vs unequilibrated spinels will also be discussed. Minor and trace element correlations differ for some elemental pairs when present in Group I as compared to Group II inclusions. Spinel in Group II inclusions is usually a major phase, and is sometimes the dominant phase indicative of a cumulate origin. The presence of hercynite-rich rocks and cumulates, and the entire Group II inclusion suite in general, represent a poorly known but major component of the lower crust.

## INFLUENCE OF PRESSURE ON ENERGETIC MIXING PARAMETERS AND SOLVUS IN MINERAL SYSTEMS

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Pressure dependence of isomorphous miscibility gaps is usually analyzed with account of deviations from the molar volume additivity (from Retger's rule). If the deviation is negative, the pressure gives rise to miscibility, if the deviation is positive, pressure decreases the mutual substitution resulting in the decomposition of the solid solution.

The quantitative theory of isomorphous miscibility allows to find out more fundamental factor of pressure effect, which is the pressure dependence of interaction parameters, i.e. the increase of mixing energy during pressure rise because of the decrease of compressibility in the solid crystal solution. It results in the increase of critical temperature of miscibility gap (up to polymorphous transitions) and the limitations in the mutual substitution of mixture components. This rule is offered to call the "isomorphous depression rule".

The above theoretical conclusion is confirmed by a number of experimental data obtained in the course of the past years for the systems halite-sylvinite, enstatite-diopside, forsterite - montichellite, albite-microcline, etc.

# NITROGEN CENTERS IN NATURAL DIAMONDS

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More than 10 different centers of different structure with participation of doped nitrogen were separated, their structural models worked out. Five of these centers are fixed for a majority of crystals: N(ESR, IR,UV), $N_2$(IR,UV-system A), $N_3$V (ESR, UV-system 415 nm), $N_s$ (III) (IR-$B_1$, UV-N9, lum.,etching,electr. microprobe), $N_s$(100) (IR,UV-system $B_2$, lum.,etching, electron microprobe, X-ray, spikes). The maximum nitrogen content in the form of $N_2$ may reach $5.10^{20}/cm^3$, in the form of $N_s$(III) - $4.10^{20}/cm^3$. The crystals from various deposits reveal statistical difference in the content of different centers. The topographic study of the five main centers of distribution by specimens show no traces of their mutual transformation after formation of crystal,which contradict the widely accepted hypothesis that associations were formed from solitary nitrogen atoms in the process of postgrowth diffusion. The growth nature of the main nitrogen centers is suggested; the scheme has been developed , according to which the $N_2$ centers are associated with the original form of nitrogen supply from the mineral-forming medium (possibly $CN_2$), N-centers are regarded as a result of dissociation of the pair at ordering,while seggregation by cube and octahedra are regarded as evolution of polumerization. The scheme describes numerous established peculiarities in the interrelation of the centers, for example, constancy of the relationship between the N and $N_2$ centers for colourless samples, the relation between seggregations by cube and octahedron,etc. A group of centers has been separated being derivative from the principal ones: NV(ESR, lum., system SI), $NV_2$(ESR, lum.-system 440.3nm) - from N; $N_2$V (ESR), $N_2$D (ESR).$VN_2V_{trans.}$ (system H3) from $N_3$; $VN_2V_{gauch}$ (system H4) - from $N_s$(III). Some of these can be induced artificially by irradiating with fast particles and annealing or plastic deformation of crystals. The topographic registration of the five main nitrogen centers with resolution to 1mcm reveals a complicated history of crystal growth providing the possibility of tracing the dynamics of crystallization in the crystallization medium.

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# GARNETS OF VARIABLE COMPOSITIONS IN THE SHEARED LEHRZOLITE XENOLITH FROM "UDACHNAYA" KIMBERLITE PIPE, YAKUTIA

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The electron microprobe method was applied to mineral composition studies of xenoliths of sheared garnet lehrzolite containing homogeneous mineral grains of variable composition in various xenolith sites. Highly distinct variations in the composition of garnet grains were found of the following dimensions: 1.4 cm of brown-orange colour; 1-2 mm of dark lilac colour.

Based on the studies of the compositions of 14 individual garnet grains are the variations in the oxide contents: $TiO_2$:1.12-1.61% $Cr_2O_3$ : 1.67-8.99%; FeO: 8.47-10.6%; CaO: 4.89-7.05%. Higher $Cr_2O_3$ contents in garnets are associated with higher Ca content and low iron content, which seems to be rather uncommon thing, and higher $TiO_2$. Stable sodium content has been established for all the garnet grains from 0.05 to 0.10 wt% of $Na_2O$.

Clinopyroxenes belong to subcalcic chromediopsides with Ca/Ca + Mg ratio for them varying from 38.7 to 39.4% which is indicative of rather high temperature nature of the equilibrium for the studied association. Some differences have been established for them(within 4-6 relative %) in the MgO, CaO,FeO, $Cr_2O_3$, $Al_2O_3$, $Na_2O$ contents. The $K_2O$ admixture (about 0.05 wt.%) indicates existence of pressures exceeding 30 kbar at the time of equilibration. $Cr_2O_3$ admixture was found for olivines (about 0.04wt.%).

Analysis of the obtained data permits one to assume that the studied rock is the product of intermixing of the deep-seated ultrabasic rocks in the process of dynamic evolution of the deep-seated substrate.

Essential variations in the Cr-admixture contents in garnet reflects the compositional differences in the alumina content of primary rocks subjected later to intermixing.

# PROBLEMS OF CLINOPYROXENE CLASSIFICATION FROM PLUTONIC INCLUSIONS IN BASALTS

M.I. Rozinov,

Pyroxene-containing inclusions are subdivided into two types ("metamorphic" and "magmatic") according to their textures and ten classes as for their mineral paragenesis. The composition of clinopyroxenes varies from one class to another.

Diagrams (Al+Ti+$Fe^{3+}$) - Mg/$Fe^{2+}$-Cr and $Al^{IV}$-Ca/(Mg+$Fe^{2+}$)-$Fe^{3+}$ are used for graphic presentation of pyroxene composition. There are established 15 groups of clinopyroxenes, each having the definite place on the diagrams: 1. omphacites, 2. magnesian omphacites, 3. juriite-diopsides, 4. jadeite-diopsides, 5. jadeite-containing chrome diopsides, 6. jadeite-containing chrome diopsides, 7. magnesian chrome diopsides, 8. magnesian alumina-containing chrome diopdies, 9. chrome diopsides, 10. alumina-containing chrome diopsides, 11. alumina-containing chrome endiopsides, 12. diopside-augites, 13. chrome diopside-augites, 14. chrome endiopside-augites, 15. fassaites.

Pyroxenes of the 1-8 groups are characteristic of paragenesis of "metamorphic" type, reflecting facies stratification of the upper mantle. These mineral associations correspond to residuum of mantle differentiation. According to isotopic data granites and kimberlites may come forward as complementary material formally belonging to the same initial geochemical system.

Pyroxenes of 9-15 groups occur in mineral associations of both "metamorphic" and "magmatic" types which are spread in the uppermost mantle, probably within 40-60 km. Isotopic data witness to the appurtenance of these inclusions to a geochemical system represented by basalts. It allows to suppose the existence of a zone of buried magmas at this depth. The position of such a zone may depend on $CO_2$ behaviour in basaltic melts.

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# GARNETS AND PYROXENES OF ECLOGITES AND GLAUCOPHANE SCHISTS FROM THE POLAR AND SOUTHERN URALS

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To study the chemical composition of garnets and pyroxenes of eclogites and glaucophane schists 110 chemical and microprobe analyses of garnets (50 of them new ones) and 57 analyses of pyroxenes (16 of them new ones) have been made. A great dispersal in the chemical composition has been found. The ferrugineity of garnets ranges from 37 to 98%, the pyrope content 4-52 %, almandine 26-66%, spessartine 0.6-14%, Ca-component 16-33%, the ferrugineity of pyroxenes ranges from 8 to 33%, jadeite content 26-80% (with break of miscibility).

The composition of garnets and pyroxenes strongly depends on the composition of rocks and varies conspicuously under diaphtoresis (amphibolization, glaucophanization, acid leaching, greenschist alteration) and depends in less degree on the conditions of metamorphism (for Uralian rocks). The microprobe investigations have revealed new types of garnet zoning in eclogites.

Several stages of eclogitization and spatial coincidence of eclogite-gneissic and eclogite-glaucophane-schist types of metamorphism have been discovered in the Polar Urals. The composition fields of garnets and pyroxenes from both types of eclogites overlap.

The origin of eclogites and glaucophane schists, especially in the Polar Urals is connected with comparatively narrow zones of plastic flow and blastomylonitization under various P-T conditions, the "eclogitization" and "glaucophanization" being superimposed not only in the basic rocks, but also in granitoids.

It is probable that these zones are characterized by high fluid pressure resulting in the transition between gabbro,ultramafics, porphyrites, amphibolites, to eclogites within one sample and in the origin of metasomatic veins of eclogites in amphibolitic blastomylonites.

## CRYSTALLOPHYSICAL PRINCIPLES OF CALCULATION OF THERMODYNAMIC CONDITIONS AND TIME OF DIAMOND GENESIS

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A number of important parameters of physico-chemical conditions and time of diamond genesis was obtained through application of crystallophysical principles based on diamond-solid inclusion system.

The residual strains amounting to 0.9 - 22.7 kbar at the room temperature were determined in minerals included in diamond. We may assume that sometimes residual strains should reach the true pressure of diamond crystallization.

As it is known the diamond and its syngenetic mineral inclusions form epitaxial growths. These growths may be formed at 70-90 kbar (220-280 km) that was shown by crystallophysical calculations. The temperatures of diamond crystallization are likely to amount to 1700-2000°C at these presssures because the maternal melt was ultrabasic in composition.

Solid mineral inclusions of uncommon forms, the so-called negative crystals, are known in diamonds. These inclusions belong to ultrabasic or basic (eclogitic) mineral associations. These negative crystals were being formed for billion years in solid mantle's matter as it was proved by crystallophysical calculations.

These crystallophysical investigations testify that the diamond is an upper mantle mineral but not kimberlitic one. The kimberlitic magma transfers the diamonds and other mantle minerals to the earth's surface.

## CLINOPYROXENES FROM JADEITIC ROCKS IN THE ULTRAMAFITES OF WEST SAYAN REGION

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Clinopyroxenes and some ore minerals of jadeitic rocks of Boruss ultramafic massif were studied by electron probe, X-ray and chemical analyses using the optical spectroscopy method.

The two series of clinopyroxenes are distinguished: soda-chrome series of cosmochlore-jadeite range with enstatite component admixture (to 25%) and soda-aluminium with the predominance of jadeite component (70-90%).

The emerald-green cosmochlore-jadeite pyroxenes in the paragenesis with millerite and pentlandite together with zinc-bearing chrome-spinelide form breccia-spheroidal aggregates, the external zone of which is composed by the layers of jadeite-albite - phengite composition with the admixture of strontium-bearing calcite.

The significant $Al^{IV}$ presence, large Na and Fe content and elevated ferriferous index differ them from the chrome-bearing clinopyroxenes in abyssal kimberlite xenoliths of the Yakutian region.

Dark-green and green-grey clinopyroxenes of jadeite and diopside-jadeite composition in the paragenesis with rutile and sphene have low Cr-concentration and high $Al^{VI}$ content being typical rock-forming pyroxene representative of monomineral jadeitic rocks in ultramaphites (Ural, Kazakhstan, Burma).

The optical absorption spectrum of these pyroxene varieties are characterized by absorption bands of Fe-ions, which is the main chromophore component.

The pyroxenes of cosmochlor-jadeite series with enstatite have been formed later than jadeite-diopside pyroxenes. Their origin can be explained as igneous.

High-content of chrome in pyroxenes is considered as a result of hybrid alkali-ultrabasic melt resulting from the monomineral jade bodies raising into the upper structure floors.

## MINERALOGY OF PYROPE FROM THE UKRAINIAN TERRIGENE DEPOSITS

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Pyrope is one of the most characteristic accessory minerals of kimberlites, widely used in research for country and field sources of diamonds. In the Ukraine garnets of pyropic composition are established in the whole Fanerozoic time and also in some more ancient deposits. Differences of orange, pink, lilac, colours distinctly differing in their chemical and component composition and physical properties are distinguished.

The main compositional parts of orange garnets are pyrope (68-70%) and almandine (20-22%), spessartine, grossular and andradite being present as admixtures.

In pink differences the amount of pyrope varies from 64 to 76%, the content of almandine being nearly twice lower than that of orange garnets, though they usually contain from 5 to 10% of uvarovite and from 3 to 7% of coharite. In lilac garnets the contents of pyropic component varies from 54 to 65%, of almandine - from 15 to 18%, of uvarovite - from 10 to 13%. The characteristic feature of lilac pyropes is 2.5 to 12% of knorringite content.

The variations in the composition and properties of pyropes from the Ukrainian terrigene deposits is evidently caused by their different origin. At the same time beyond any doubt is the presence of chromium-enriched varieties close to pyropes from kimberlitic pipes.

## HIGH-PRESSURE CARBON POLYMORPHS IN THE DEPOSITS OF FAR ABLATION

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Dence high-pressure carbon polymorphs differ from the majority of minerals by their highest chemical passivity, hardness and stability to the abrasion. Fine-grained deposits of far ablation are natural traps of stable minerals and represent the unique possibility to study statistic totalities of varieties of dense carbon modifications connected with different mother sources.

Grains of dense carbon modifications in the deposits are divided into two groups: 1) monophase (cubic diamond) mono- and polycrystalline grains which are the products of equilibrium crystallization from silicon melts oversaturated with carbon of upper mantle diamond facies ($P_{min} = 40-50$ kbar, $T \geqslant 1400^{\circ}C$). These are diamonds of different types, particulary, well-known varieties from endogenic sources (Orlov , 1973); 2) polyphase (cubic diamond +hexagonal diamond±graphite±chaoite) polycrystalline grains which are the products of direct polymorphous transformation of crystalline graphite ($P_{min} = 250$ kbar, $T \geqslant 1000^{\circ}C$) under the influence of impulses. Carbon polymorphs of the second group are analogues to some varieties of meteoritic and synthetic diamonds (Frondel, Marvin, 1967; Bakul, Andreev, 1975).

Carbon polymorphs of the first group are predominant practically in all regions. The study of their morphology, colouring, statistic distribution of the luminescence centers shows the existence of considerable differences between totalities of grains from different regions and allows to distinguish specific provinces. There are, for example, distinct differences between fine-grained diamonds from Dnestr, Dnepr-Don and Kazakhstan-West Siberia provinces (Yurk et al, 1973). These differences reflect, apparently, the large-scale heterogenity of the upper mantle and, accordingly, conditions of diamond crystallization.

**The grains of the second group have variable phase composition which does not correspond to equilibrium conditions. The main peculiarities of this group are: polyphases, polycritallinity, little size mosaic blocks, high dencity of dislocations, absence of paramagnetic nitrogen admixture (Sokhor and al., 1973). The complex of accessory minerals is specific.**

## *KARINTIN AND SMARAGDITE-MAGNESIUM HORNBLENDS OF HIGH-PRESSURE FACIES*

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Specific magnesium hornblendes with high alumina content have *been studied from eclogites, garnets, perydotites* and amphibole-garnet rocks (the garnets containing from 40 to 70% of pyrope component) from the schisto-gneissic metamorphic complexes.

The study has been related to their paragenetic associations , *their chemistry* crystallochemical particularities and structures.

It is revealed that karintin has the most ordered *structure* with the highest packing index of all the hornblendes known in the nature.

The thermodynamic conditions of the formation of minerals are being *discussed. The parageneses of Cr-containing smaragdites* and kyanites ($Cr_2O_3$ 0.5 - 3 and 0.1 - 9 w.p.c. correspondingly) are found for the first time.

The studies permit to advance an idea of the existence of some *karintin* and *smaragdite* type hornblends in the lower horizons of the Earth's Crust.

## ON "ESCOLA'S SILICATES" AMONG THE COMPOSITIONS OF ARTIFICIAL AND NATURAL PYROXENES

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Pyroxenes of omphacite type with 5-8% mol. of Ca-jadeite component - $Ca_{0.5}AlSi_2O_6$ were for the first time detected (Escola, 1921) in lens-like eclogite bodies concordantly lying among metasedimentary rocks of West Norway. Later on, diopside-augite pyroxenes with 20-24% mol. of Ca-aegirine component - $Ca_{0.5}Fe^{3+}Si_2O_6$ were found in archean granulite facies rock series from Cis-Baikalia (Korzhinsky, 1946) and from the Aldan shield (Serdyuchenko, 1960). Our calculations of the "minal composition" showed that in highly aluminous schists of high pressure (10-12 kbar) pyroxenes ( in paragenesis with garnet, cordierite, sillimanite, sapphirine, corundum a. oth.) contain $(Ca,Mg)_{0.5}AlSi_2O_6$ from 3 to 11% mol. in Anabar complex (Lutz, Kopaneva, 1968) and Sutam-complex (Kadensky, 1960; Kastrykina, 1976) in Siberia, also in Limpopo valley, South Rodesia (Chinner, Sweatman, 1968) - about 2.5%mol.

The presence of diopside - $Ca_{0.5}AlSi_2O_6$ solid solutions was established in experimental studies (35 kbar and 1200°C) of pyroxene melts with alumina and silica surplus (Khanukhova, Zharikov et al., 1976); the authors call this minal "Escola's silicate" similar to those of "Tschermak's silicate".

Pyroxenes with Escola's silicate (10-15% sometimes to 20% mol.) are also typical of many grossular-omphacite-kyanite rocks (grosspydites) from kimberlite pipes in Yakutia (Bobrievich et al., 1960; V.Sobolev, A.Sobolev, 1977) and Africa (Smith, 1977). The "Escola's silicate" forms part of pyroxenes containing sesquioxides with deficient of $Na_2O$ for a wide or not ordinary jadeite- or aegirine-formation.

In case of abundance of $SiO_2$ silicon almost completely fills the structural tetrahedrons in pyroxenes and limiting formation of Tschermak's molecules ensures Escola's molecules, the two minerals are almost always found together.

But there are lacking the data for the evaluation of the physico-chemical conditions and isomorphic mixture limits in the limestone-magnesial and alumo-ferrous series $(Ca,Mg)_{0.5}$ (Al , $Fe^{3+}$) $Si_2O_6$.

## TWO MEW TITANATE MINERALS FROM INCLUSIONS IN SOUTH AFRICAN KIMBERLITES

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The crichtonite group of minerals consists of a series of isostructural Fe, Mg, Cr titanate minerals each of which contains one large-radius cation site per 38 oxygens in the unit cell. The described members of this series: crichtonite, senaite, davidite, landauite and loveringite are named on the basis of the principal large-radius cation: Sr, Pb, U/RE, Na, Ca, respectively. Two new end-members of the series have been identified in peridotite inclusions from South African kimberlite pipes; one containing Ba and the other K as the large-radius cation. The minerals are associated with rutile, Cr-diopside, phlogopite, and K-richterite and may be a result of metasomatic alteration of peridotites within the upper mantle. The larger ionic radii of Ba and K relative to the other members of the series is consistent with the higher pressure of origin (2.5 - 4.0 GPa) postulated for peridotite inclusions in kimberlite. The barium end-member has the approximate formula $Ba(Fe^{2+},Mg)(Mg,Fe^{3+},Cr)_6(Ti,Zr,Nb)_2Ti_{12}O_{38}$ and the potassium end-member $K(Fe^{2+},Mg)(MgFe^{3+},Cr)_6(Ti,Zr,Nb)_2Ti_{12}O_{38}$. The minerals appear to be isostructural and allow complete crystalline solution between the end members. Up to 25% of the large-radius cation sites of specimens analyzed appear to be occupied by Sr, Ca and Na. These minerals may provide a significant site for large-radius cations within the upper mantle.

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## GEOCHEMISTRY OF ULTRAMAFIC XENOLITHS FROM KAPFENSTEIN, AUSTRIA

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The alkali-basaltic tuff of Kapfenstein, Austria, contains abundantly ultramafic xenoliths of upper mantle origin. The population is highly dominated by spinel lherzolites. Only a few samples document local inhomogeneities within the upper mantle underneath that locality: Two hornblende spinel lherzolites (Ol + Opx + Cpx + Sp ± Phlog.) and one garnet spinel websterite (Opx + Cpx + Sp + Ga).

Major, minor, and trace elements have been determined for some selected xenolith samples, the host basalt and mineral separates.

The <u>lherzolites</u> typically represent an ultrabasic depletion sequence with respect to incompatible element contents which allows a chemical characterization of "undepleted" upper mantle material by small scale extrapolation.

The websterite according to its major and trace element content must have had a two-stage genesis: It is probably a residuum of a partially melted eclogite of tholeiitic composition.

For the two <u>hornblende-lherzolites</u> investigated two different modes of origin were found:

a) One of the hbl lherzolites contains a K-poor hornblende. Its major and trace element contents fit the main lherzolite sequence. The formation of hornblende therefore is simply the result of $H_2O$ -metasomatism.

b) The second hornblende lherzolite contains a K-rich "Primary" hornblende and additionally phlogopite. That rock has experienced addition of a wet basaltic component and was subsequently metamorphozed.

Some samples show contaminations which in our case are of two different types:

a) A strong U anomaly was found in the websterite. The U was localized within oxidized sulfide particles and therefore is obviously a surface contamination introduced during weathering.

b) Some lherzolite samples show in spite of their general depletion in incompatible elements some enrichments of Ba and K and of LREE over the HREE. The contaminating component is easily leachable by dilute HCl and shows a strongly fractionated REE pattern with the LREE strongly enriched over the HREE. This component very likely is located at grain surfaces and probably represents deposits from fluids or gases which migrated through the upper mantle.

## ARE GROSPYDITES METARODINGITES? IMPLICATIONS FOR UPPER MANTLE MODELS BASED ON XENOLITHS FROM SOME DIAMONDIFEROUS KIMBERLITES

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Grospydites are composed of grossular-rich garnet, clinopyroxene, and kyanite and occur as xenoliths in diamondiferous kimberlites from Yakutia, South Africa, and Botswana. Rodingites are dense calc-silicate rocks of metasomatic origin found on the *ocean floor and in ophiolites at contacts between basic and serpentinized* ultrabasic rocks.

*We postulate that grospydites are deeply subducted rodingites* or rodingite-like rocks because: 1) Grospydites and rodingites have similar whole rock compositions (high CaO, low $SiO_2$) which are unlike those of primary igneous rocks; 2) The association basite-rodingite-serpentinite survives into the eclogite facies (Lepontine Alps) as eclogite-metarodingite-garnet peridotite and may correspond to the xenolith association eclogite (±kyanite)-grospydite-garnet peridotite; 3) Eclogite-facies metarodingites and grospydites show a continuous gradation in chemical composition (especially in CaO content) into their accompanying eclogites. In metarodingites such gradation can be explained by varying degrees of rodingitization prior to metamorphism; 4) Corresponding to the gradation in bulk composition the garnets show a continuous range from grossular-poor (eclogite) to grossular-rich (metarodingite and grospydite); 5) A possible intermediate stage between rodingite-like rocks and grospydites is represented by lawsonite-garnet-clinopyroxene rocks found as xenoliths in the non-diamondiferous kimberlites from the Colorado plateau. These rocks occur together with jadeite rocks, sodic eclogites, and hydrated ultrabasic rocks and are thought to correspond to rodingite-like calc-silicate zones around jadeite pods such as those in the New Idria serpentinite of California. The xenolith suite has been interpreted as fragments of subducted oceanic lithosphere. The lawsonite rocks have grospydite compositions and the mineral assemblages of both rock types can be related by the reaction,

$$\begin{array}{l}\text{lawsonite + garnet(gross.-poor) + clinopyroxene(sodic)}\\ \rightleftharpoons\ \text{garnet(gross.-rich) + kyanite + clinopyroxene}\\ \text{(more sodic) + } H_2O.\end{array}$$

If grospydites are metarodingites, associated garnet-peridotites may be metaserpentinites, not samples of pristine upper mantle material.

Diamondiferous grospydites in Yakutian kimberlite pipes may indicate that at the time of eruption the upper mantle beneath this part of the Siberian shield contained remnants of oceanic lithosphere subducted to depths of at least 120 km.

# EXPERIMENTAL MINERALOGY AND THE PROBLEM OF THE UPPER MANTLE

## GARNET-PYROXENE EQUILIBRIUM AND DEEP-SEATED XENOLITHS

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The equilibrium was first studied at 45 to 70, 1000-1400°C. According to the data obtained for the kinetics of the shifted reactions, high-temperature equilibrium can be achieved within 24 hours. The PT-$Al_2O_3$ concentration in the orthopyroxene from the paragenesis orthopyroxene+clinopyroxene+garnet+olivine has been established.

Unusual solid solutions of the coexisting pyroxenes are detected in the 1200-1300°C region, complicate PT-$Al_2O_3$ concentration relationship. The experimental data were treated thermodynamically to derive the PTX-diagrams for evaluating thermodynamic conditions of garnet-bipyroxene equilibria in the mantle. The equilibrium PT-conditions for some dozens of xenoliths from the kimberlite pipes in South Africa and Yakutia were estimated. The temperature was read from a bipyroxene thermometer (Perchuk,1977).
The 250 to 300 km geotherms differing from those of Boyd were derived from these data.

## SPECIFIC PROPERTIES OF PHASE TRANSITIONS IN ENSTATITE UNDER PRESSURES UP TO 20 KBARS.

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A method of electroconductivity measurement was used for investigation polymorfic transitions in synthetic enstatite. It was found that at low pressures in the temperature range up to 700°C clinoenstatite is a stable form. Complete transition from clino- to orthorombic enstatite takes place at 900°C.There are two phases, ortho- and protorombic, which exist in the temperature range up to 1080-1300°C. A small jump in conductivity at 1380°C may be considered as the evidence for existence of high clino phase. At high pressures only reversible transformation from clyno- to orthorombic enstatite was fixed.

## STABILITY OF GARNETS AND CLINOPYROXENES IN THE SYSTEM $MgSiO_3$ - $CaSiO_3$ - $Al_2O_3$ AT 30 KBAR

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Phase relations in the system $CaSiO_3$ - $MgSiO_3$-$Al_2O_3$ define those in more complex system $MgO$-$CaO$-$Al_2O_3$-$SiO_2$, which is of paramount interest for the upper mantle petrology. The data about the stability of the main phases are however lacking. Therefore the joins diopside - Ca - tschermakite and pyrope-grossularite have been studied within the temperature range 1000-1600°C at the pressure of 30 kbar.

Clinopyroxene solid solutions between diopside and Ca-tschermakite is continuous in a narrow range between 1500 and 1550°C. At lower temperatures diopside solid solution is stable, the solubility limit toward Ca-tschermakite decreases rapidly to 35-40 mol.% at 1000°C.

The major feature of the pyrope-grossularite join is the sharp decrease of the field, where the garnet solid solution is unstable, with temperature decrease from 60-65 mol.% at 1450°C to 10-15 mol.% at 1000°C. The garnet solid solution between pyrope and grossularite becomes continuous at 900-950°C according to the reaction $Cpx_{ss} + Cor = Gr_{ss}$, which have a positive dT/dP slope. In the region where the garnet solid solution is unstable, the clinopyroxene field contains 50 mol.% of Ca-tschermakite. This field is decreasing with the fall of temperature. Thus the phase relations in the system $MgSiO_3$-$CaSiO_3$-$Al_2O_3$ are defined, generally, by that with increase of temperature the clinopyroxene field cuts the garnet join.

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## THE P2/n→C2/c TRANSFORMATION IN OMPHACITE

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Heating experiments on natural omphacite specimens at 15 to 18 kbar, using a piston-cylinder solid media apparatus, have established the critical temperature for the order-disorder P2/n ⇌ C2/c transition at 725± 20°C. The disordering reaction P2/n → C2/c is quite abrupt and observed transformation temperature is independent of run duration for one day and one week experiments. Reaction rate data give an activation energy for disordering of about 12kcal.mol$^{-1}$, which suggested that cation disorder in omphacite is a cooperative process involving both M1-type (Al, $Fe^{2+}$, Mg) and M2-type (Ca, Na) cations. It appears that the antiphase domain structure in blueschist facies omphacite does not form through inversion, on cooling, of earlier C2/c omphacite and, in general, the geothermometric applications of the omphacite phase relations are somewhat limited.

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## SYNTHESIS AND STRUCTURE ANALYSIS OF THE ILMENITE-TYPE HIGH-PRESSURE PHASE OF $MgGeO_3$

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In the course of the study of the phase transformation of pyroxenes as a function of pressure and temperature we have also investigated the homologuous compound $MgGeO_3$ up to 65 kbar and 1350°C:

$$\begin{array}{ccccc} MgGeO_3 & \xrightarrow[900^\circ C]{5\ kbar} & MgGeO_3 & \xrightarrow[900^\circ C]{47\ kbar} & MgGeO_3 \\ \text{orthopyroxene} & & \text{clinopyroxene} & & \text{ilmenite type} \end{array}$$

Compared with $MgSiO_3$ (transformation at ~175 kbar) we have with $MgGeO_3$ much lower pressure. We were able to grow a few single crystals of the $MgGeO_3$ high pressure ilmenite type phase and we have studied them further by X-ray diffraction.

The specimen selected for single crystal X-ray diffraction analysis was twinned with respect to a mirror plane (001). The extraction of two undisturbed F-sets and their independent refinements clearly established the structure of $MgGeO_3$ to be isotypic with ordered $FeTiO_3$. The structural results were correlated with available data of ilmenite and corundum type compounds and used to calculate predicted fractional coordinates for the high pressure ilmenite type phase of $MgGeO_3$.

## EXPERIMENTAL STUDY OF THE SOLID SOLUTION OF PYROPE-GROSSULAR AND PYROPE-UVAROVITE SERIES, AND STABILITY FIELD OF Ca-RICH CHROME PYROPE UNDER UPPER MANTLE CONDITION

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Garnets in most ultramafic nodules have higher $Cr_2O_3$ and CaO contents than the garnets in the common lherzolite nodules in many other kimberlites. Stability field of the garnet solid solution series of pyrope-grossular and pyrope-uvarovite were studied from oxide mixtures at 15-40 kbar and 1000°C using piston-cylinder apparatus.

At pressures less than 20 kbar of part of the pyrope-grossular join exists as spinel-bearing assemblage such as $enstatite_{ss}$ + $diopside_{ss}$ + forsterite + spinel. One phase garnet field increasing grossular content increases the pressure of reaction. Complete solid solution of part of the pyrope-uvarovite series exists more high pressure region than those of the pyrope-grossular solid solution. Phase assemblage at pressures less than 20 kbar of this series are $enstatite_{ss}$, $diopside_{ss}$ forsterite and $spinel_{ss}$.

The experimental data indicate the existence of continuous solid solutions between both the pyrope-grossular and pyrope-uvarovite at high pressure, and stability field of Ca-rich chrome pyrope shows more low pressure than those of Ca-poor chrome pyrope.

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## VIRIDINE, $(Al_{1-x}Mn^{3+}_x)_2(O/SiO_4)$: ITS STABILITY RELATIONS IN DEPENDENCE OF P, T AND $f_{O_2}$

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The mineral viridine (vir), a $Mn^{3+}$-substituted andalusite, occurs in nature in a wide variety of rock types. In the presence of the $MnO_2/Mn_2O_3$-buffer stable viridines with $0.05 \leq x \leq 0.22$ were synthesized in the wide range of 500° to 1000°C and 1 to 14 kbar. At 1050°C, 10 kbar in presence of water, vir (x=0.2) begins to melt incongruently to $braunite_{ss}$(brn) + $corundum_{ss}$(cor) + liquid. Because $brn_{ss}$ diminishes with higher temperatures (up to 1400°C), it is concluded that the liquidus will be located in the corundum-field. The dependence of viridine stability on the oxygen-fugacity is as follows: at 10 kbar, 900°C, vir (x=0.2) breaks down on $Mn_2O_3/Mn_3O_4$-buffer, to → vir ($x \simeq 0.16$) + spessartite (spess) + $brn_{ss}$ and, on $Fe_2O_3/Fe_3O_4$-buffer, to → sillimanite (sill) + spess + cor.

Seeded runs in the pseudobinary join $Al_2SiO_5$ - "$Mn_2SiO_5$" at 900°C, $MnO_2/Mn_2O_3$-buffer, show that vir has a wide pressure range of stability with respect to both, kyanite and sillimanite (Holdaway, Am.J.Sci. 271, 97, 1971; Richardson, Gilbert and Bell Am.Miner. 44, 1261, 1969).

In detail the results are: single phase viridine is stable up to 12 ($x \simeq 0.08$) and 14 kbar($x \simeq 0.22$). This field is limited at $P \leq 12$ kbar by the fields vir + $sill_{ss}$ respectively vir + $brn_{ss}$ + qu + pyrolusite (pyr). At higher pressures vir + $ky_{ss}$ coexist and above 14 kbar follows the field $ky_{ss}$ + $brn_{ss}$ + qu + pyr.

The striking stability of $Mn^{3+}$-substituted andalusite may be understood by crystalchemical considerations. From the refinement of the structure and the measurements of the absorption spectra of viridines (Abs-Wurmbach, Langer and Tillmanns, Natw. 64, 527, 1977) it may be concluded that the andalusite structure is stabilized by $Mn^{3+}$, with its $3d^4$-electronic configuration, due to the Jahn-Teller stabilization in the tetragonally distorted M1-position.

## EXPERIMENTAL STUDY OF THE $SiO_2$-$GeO_2$ SYSTEM AT HIGH PRESSURES *UP TO 100 KBAR AND THE PROBLEM* OF OCTAHEDRALLY CO-ORDINATED SILICON IN MANTLE MINERALS

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Phase equilibria *in the* $SiO_2$-$GeO_2$ *system* have been studied at temperature 1200 °K and pressures up to 100 kbar.On the basis of the experimental data and thermodynamic calculations the P-X diagram of the system was constructed.The solid solutions $(Si,Ge)O_2$ of the $\alpha$- and $\beta$-quartz structures are in equilibrium with practically pure tetrogonal *germanium dioxide* at pressures below 33 kbar.Boundary concentration of $GeO_2$ in the solid solution decreases rapidly while pressure increases (from 82% at 1 bar to less than 3-4% at 30 kbar).Above 33 kbar practically pure coesite coexists with tetragonal solid solutions $(Ge,Si)O_2$, their $SiO_2$-contents beeing *increased from* 2-3% at 60 kbar to 17% at 90 kbar There are two tetragonal solid solutions with 6% and 84% of $GeO_2$ respectevly within the stability field of stishovite.The experimental results are described thermodynamically in terms of the subregular solution model,enthalpy of mixing beeing estimated from crystal-chemical *considerations.*

The presence of octahedrally coordinated silicon in depth minerals such as garnets is connected with heterovalent isomorphous substitution: $({}^{6}Al^{3+}\ {}^{6}Al^{3+}) \rightleftarrows ({}^{8}Mg^{2+}\ {}^{6}Si^{4+})$.In this paper the boundary solubility of pyroxenes *in pyrope-garnet* and pyrope in corundum at high pressures and temperatures has been calculated assuming different disordering-models.For the enstatite-pyrope system the results are compared with the experimental data (Akaogi,Akimoto,1977).The microquantities of silicon are shown to be enter in six-coordinated *positions of pyrope*-structure even at pressures of the lower stability limit of pyrope-garnet, and portion of six-coordinated silicon increases exponentially while pressure increases.

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## PHASE STABILITY OF GERMANATE FORSTERITE

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Solid phase transformation between olivine-type ($\alpha$) and spinel type ($\gamma$) $Mg_2GeO_4$ was investigated under high temperature-pressure conditions up to 2200 °C and 8 GPa. Pressure dependency on melting temperature of the same substance was also examined.

On experiments, starting material was prepared by hydrothermal treatment of powder of MgO and $GeO_2$ mixed in the molar ratio of $Mg_2GeO_4$. The material was confirmed as $\gamma$-$Mg_2GeO_4$ by X-ray powder diffraction and was subjected to high pressure experiments .

After maintaining at a given condition of temperature and pressure for several minutes, the sample was quenched to room temperature and ordinary pressure. The structures and the textures of products were examined by an X-ray diffractometer and a microscope. The obtained data were used to draw the boundaries between liquid and solid phases and also between $\alpha$ - and $\gamma$ -phases.

The results are summarized as follows; 1) The melting temperature of $\alpha$-$Mg_2GeO_4$ increases with the increase of pressure, the rate being 30 °C/GPa. It is relatively low compared with that of forsterite determined in the range up to 5 GPa. The present result is obtained at conditions close to the triple point of coexistence of $\alpha$-, $\gamma$-, and liquid phases which is at 1900 °C and 4 GPa. Since the melting temperature of forsterite obeys the Simon's relation, dT/dP is expected to decrease and approaches to that of $\alpha$-$Mg_2GeO_4$ near the triple point of forsterite. 2) Boundary between $\alpha$- and $\gamma$-phases of $Mg_2GeO_4$ is represented not by a straight line but by a curve concave upwards. The deviation of the boundary from the Clapeyron's law is explained by interchange of $Ge^{4+}$ ions in octahedral sites with $Mg^{2+}$ ions in tetrahedral sites, the amount of the interchange being estimated to reach 2.5% of total numbers.

# CALDERITE, $Mn_3^{2+}$ $Fe^{3+}_2$ $Si_3O_{12}$ , A HIGH PRESSURE GARNET

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In a howieite-bearing metachert from the high-pressure contact aureole around peridotite near Brezovica, Yugoslavia, a garnet was discovered which contains 36 mole percent of the calderite end member which is otherwise extremely rare in natural rocks. For a better evaluation of this occurence high-pressure experiments were carried out on a mixture representing the ideal end member composition using a piston-cylinder apparatus with the magnetite/hematite buffer. Nearly complete reaction to a garnet phase was achieved at a pressure of 30 kb between 750 and 1000° C. Seeded runs at lower pressures using the garnets synthesized at 30 kbar indicated that the lower pressure stability limit for this garnet lies near 26 kb at 800°C but increases with temperature. At temperatures below 800°C the assemblage pyrox - mangite + hematite formed as low-pressure breakdown product of the garnet, whereas at higher temperatures hematite gave way to a spinel phase of unknown composition, in addition to a $MnSiO_3$ polymorph. The garnets synthesized have $a_o = 11.8134 \pm 0.0052$ and a refractive index near 1.972. Microprobe analyses of the brownish garnet crystals synthesized indicate, however, that they are not of ideal calderite composition but give structural formulae such as $(Mn_{2.6}\ Fe^{2+}_{0.4})_{3.0}\ Fe^{3+}_2\ Si_3O_{12}$. In detail they contain between 9 and 18 mole % of the skiagite component, $Fe^{2+}_3\ Fe^{3+}_2\ Si_3O_{12}$. Synthesis of pure calderite seems to require higher oxygen fugacities than those provided by the hema - tite/magnetite buffer. Nevertheless, it is clear that the stability of pure calderite must be confined to very high pressures obtaining only in the Earth's mantle.

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# HIGH-PRESSURE CRYSTAL STRUCTURES

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The miniature,opposed-anvil diamond cell described by Merrill and Bassett has been used on a four-circle,single-crystal diffractometer.The lattice constants and crystal structures of the following minerals and mineral analogues have been studied:nickel and iron silicate spinel,grossular and pyrope garnet,zircon, pyroxene,ilmenite,corundum (ruby),phlogopite,chlorite,analcite, berndtite,soda niter,and manganese difluoride.Through the use of a gasketed cell with a methanol-ethanol mixture for the pressure transmitting fluid,hydrostatic pressures up to 80 kbar have been attained.The operating procedures for the single-crystal diffractometer have been modified to improve the quality of the lattice constants and single-crystal intensities that are measured at high-pressure.Most structures have refined to residuals of 2-4%.

The general results of isothermal compression may be characterized as follows: 1) Large coordination polyhedra are more compressible than small ones, 2) Coordination polyhedra tend to become more regular with increasing pressure,and 3) To a first approximation,the compressibility of a given polyhedron does not depend upon the remainder of structure.The latter result has been used to infer the pressure range for the transformation from tetrahedrally coordinated to octahedrally coordinated silicon in various minerals.The inferred pressures and depths are in agreement with the depths at which large density gradients occur in the mantle of the earth.Below 900 km all silicon is predicted to be in octahedral or greater coordination.

## *INFLUENCE OF VOLATILE COMPONENTS ON UPPER MANTLE PROCESSES*

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There is good evidence that minerals and magmas derived from the upper mantle contain $H_2O$ and $CO_2$. It is not clear to what extent these components are derived from primordial material deep in the mantle, or through recycling of the hydrosphere via subduction. The existence of diamonds and graphite in mantle nodules demonstrates that the oxygen fugacity is not high enough to oxidize all carbon at depth, but the depth range within which carbonate coexists with carbon has not been established. The system peridotite-$CO_2$-$H_2O$ provides a first step for interpretation of processes occurring in the mantle system peridotite-C-H-O. Peridotite reacts with $CO_2$ and $H_2O$ under pressure. Considering depths of 300 km or less, and temperatures above 800°C, mantle peridotite can be completely hydrated by less than 0.5% $H_2O$ producing amphibole or phlogopite. The mantle is a better potential store-house for $CO_2$, because it requires about 30% $CO_2$ to carbonate peridotite completely. At depths of more than 300 km, $H_2O$ if present can be stored in DHMS (dense hydrated magnesian silicates). Divariant subsolidus reaction surfaces for decarbonation, dehydration, and hydration-carbonation reactions buffer mantle vapor phase compositions, if there is a vapor present. The major effects of $H_2O$ and $CO_2$ in the upper mantle are to lower the solidus temperature, and to cause large changes in composition of near-solidus liquids as a function of pressure, temperature and $CO_2/H_2O$. This has applications to kimberlites and other continental volcanism. If there is any $CO_2$ or $H_2O$ in the upper mantle, then incipient melting must be at least partly responsible for the seismic low-velocity layer. The subcontinental upper mantle is probably heterogeneous with respect to incompatible elements, because local melting due to sparsely distributed $CO_2$ and $H_2O$ is followed by magmatic flushes, as the melt migrates into or through the lithosphere.

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## KINETICS OF THE OLIVINE, PYROXENES AND PYROPE DISSOLUTION IN BASALTIC MELT AND WEBSTERITE MODEL OF THE UPPER MANTLE

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Kinetics of the olivine, orthopyroxene, clinopyroxene and pyrope dissolution in the alkaline basalt melt has been investigated. Olivine was found to dissolve 1.5-37 times slower than all other minerals and pyroxenite and eclogite nodules disintegrate in basaltic magma 5-20 times quicker than peridotite nodules. On the basis of the data of chemical composition and relative content of the ultrabasic nodules in basalts and kimberlites, *the average composition of the upper mantle was calculated.* In this case, the relative content of the peridotites among the nodules was decreased 10 times to compensate the slower disintegration of peridotites in basaltic and kimberlitic melts in comparison with eclogites and pyroxenites when lifting to the surface. The upper mantle composition (Table) is close to that of olivine garnet websterites from the nodules in basalts and kimberlites. Hence it may be assumed that garnet websterites and not Ringwood's pyrolite is the primitive undifferentiated substance of the Upper Mantle.

| N | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2C_3$ | FeO | MnO | MgO | CaO | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 47.6 | 0.25 | 5.35 | 2.2 | 5.8 | 0.15 | 31.7 | 6.4 | 0.4 | 0.15 |
| 2 | 47.4 | 0.5 | 7.85 | 2.3 | 6.8 | 0.15 | 24.5 | 9.2 | 0.95 | 0.05 |
| 3 | 47.87 | 0.40 | 10.10 | 1.2 | 3.61 | 0.14 | 25.31 | 7.95 | 0.81 | 0.08 |
| 4 | 47.99 | 0.22 | 5.20 | 1.99 | 5.28 | 0.15 | 30.65 | 6.85 | 0.48 | 0.05 |

1 - continental upper mantle,

2 - oceanic upper mantle under the Is. Oahu,

3 - websterite from the nodules in the kimberlitic pipe "Obnazhennaja" after N.V. Sobolev,

4 - websterite from the nodule in the basalts of Itinome-gata after K. Aoki.

## THE INFLUENCE OF ALKALINE AND FLUID COMPONENTS ON THE GENESIS OF MANTLE MAGMAS

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Experimental melting of basalts and related rocks was carried out dry and in the presence of fluids of differing compositions ($H_2O+CO_2+H_2$) at high pressure (25-45 kb). The effect of alkalis on melting temperature, composition and phase relations was of particular concern. The authors' earlier hypothesis on the nonisochemical evolution of the primary mantle matter has been supported by the experimental *evidences and the analysis of the* available experimental and natural data from different sources. Fluid regime and fluid interaction with the mantle matter is primarly responsible for the two major trends in mantle magmatism: loss in alkalis gives rise to a calc-alkaline series, while their gane (or any other means of enhancing alkaline activity) resuts in ultrabasic alkaline series. The mode of melt transportation within the upper mantle is of considerable importance.

## POTASSIUM IN EDENITES, PARGASITES AND HASTINGSITES

*Th.J.Hinrichsen*, K.U.*Schurmann*, *Marburg*, FRG

Experimental investigation for Na/K-substitutions in edenites, pargasites and hastingsites have been made at temperatures between 700°C and 1100°C and at pressures between 0.5 and 20 kbars. These investigations indicate complete solid solution series for Na/K-edenites and for Na/K-hastingsites. No amphiboles could be synthesized in the higher pressure range above 15 kbars; stable phases above the amphibole stability fields are (nephiline)+phlogopite+diopside+forsterite+melt+fluid phase for the Na/K--edenites and (nepheline) +phlogopite+diopside+spinel+melt+fluid phase for the Na/K-pargasites.

# INHOMOGENEITIES IN MINERALS

# DISSYMETRIZATION AND MICROINHOMOGENEITY OF CRYSTALS OF MINERALS

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For crystals of natural mineral series and of their synthetic analogues there has been established the reduction of symmetry of some physical properties with respect to the point symmetry of their crystal structure-disymmetrization of real crystals. It is shown by the method of electronic paramagnetic resonance (EPR), that dissymmetrization is caused by the different concentration of structure-equal point defects in the systems of the translationally-equal positions formed from the same regular system of points.

It is shown that the layer-by-layer tangential growth of crystal is the main reason in a sectorial selection capture of point defects in the same pyramid of growth. The symmetry of the arrangement of point defects in the different parts of the pyramid of growth is not the same as the symmetry of plane of simple form and cannot be higher than $C_1$ or $C_s$ .

The theory-group method is used for describing the dissymmetrization, which permits to find the multiple of regular systems of points, arising from the original system at the reduction of the point symmetry of structure.

The question of the methods of the crystal-optic, the radio - spectroscopy (EPR) and X-ray investigations of the mineral disymmetrization is considered. A correlation of the intensity of a dissymmetrization, found from EPR with the characteristics of the microinhomogeneity (microblocks, microeffort) determined by X-ray methods is carried out. It is shown that the distortions in the layer-by-layer tangential growth, caused by the formation of blocks and dislocations decrease the degree of dissymmetrization.

The ways of the practical use of dissymmetrization for the solution of a number of mineralogical problems - study of the mineral typomorphism, localization and diffusion of point defects, isomorphic and nonisomorphic admixtures, the theory of the crystal growth, problems of homogeneity-unhomogeneity of the minerals,etc. are discussed.

The results of the experimental investigation of the dissymmetrization in the quartz crystals, corundum, phenaksite, baryte, astrakhanite, skorodite, krohnkite and in some of their synthetic analogues are given.

## STUDY OF SULPHIDE MINERALS FROM THE WEST CARPATHIANS BY MEANS OF X-RAY ELECTRON PROBE MICROANALYSIS

J.Jarkovský, B.Cambel, J.Krištín, Bratislava, ČSSR

The paper deals with complex results of pyrite, pyrrhotite,chalcopyrite and antimonite investigations of different genetic and deposit ore types from the West Carpathians by X-ray electron probe microanalysis. It is the aim of this work to give a mineralogic-geochemical characteristics of these sulphides. The results of planar line and point X-ray electron probe microanalysis showed the difference in genetically important microelement contents in sulphides from various genetic deposit types. In combination with other methods, especially electron microscopy, the authors studied also the problem of homogeneity and heterogeneity of these sulphides. They utilized X-ray electron probe microanalysis also for distinction of pyrrhotite structure modifications on pyrite-pyrrhotite deposits. By means of X-ray electron-probe microanalysis some rare minerals (horobetsuite, Fe-alabandine, Sb-gersdorfite,etc.) have been established at the deposits.

## CAUSES OF INHOMOGENEITY IN NATIVE GOLD

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Gold usually occurs in nature alloyed with various proportions of silver. Apparent inhomogeneity in native gold and frequency of occurrences of gold of a certain fineness are mainly caused by the following factors: 1) physico-chemical conditions of deposition of minerals ($T^{\circ}$, P, Eh, pH); 2) short-range order in Au-Ag system; 3) metamorphism of gold.

The temperature of ordering ($T_c$ - 100°C) calculated from experimental parameters of short-range order in Au-Ag model alloys shows that the formation of fully ordered combinations in native gold is impossible. Ordering energy in Au-Ag system depends on concentration of components and is maximum at 50 at.% Au, thus causing different stability of both separate grains and crystals and blocks composing these grains.

During low-temperature metamorphism (up to 400°C) silver is not practically removed from the system and redistribution of components results in the formation of electrum-energetically more stable mineral typical of young near-surface deposits.The curve of frequency of occurrences of gold fineness in such deposits is similar to the curve of dependence between ordering energy and composition

In higher temperature metamorphism when silver is partly removed, the finenness of gold particles increases. In this case maximum of the curve of frequency of occurences of finenness of native gold from ancient deposits shifts to the area of 70-80 atm.% Au, characterised by minimum lattice parameters

## ELECTRIC HETEROGENEITY OF MINERALS AND ITS IMPORTANCE FOR ONTOGENY

**M.N. Maleev,** Sofia, Bulgaria

Decoration patterns of natural, radiated and thermal treated minerals (quartz, halite, sphalerite, galena) make possible to visualize at electromicroscopical and optical levels localities of electric activity with different order of magnitude (separate point defects, geometrically regular or irregular groups of 3, 4 and 6 active centres, concentrations up to 1 μm of round and and fringed shape, surface micro-regions of up to 50 μm diameter with opposite electric charge.

Localities of electric activity are the points of prevalent nucleation on the smooth surface of the crystal. The identity of the successive stages of decoration material growth (individual particles and their groups, bridges between particles, net-structure, hollowed film and continuous film) for the smooth and stepped localities of the surface prove the electric nature of active centres attached to the surface steps and breaks. The morphology of crystals formed by coalescence of regular groups of decorating particles depends on the geometry of that group which can be carious for the same mineral.

The major part of decoration experiments has been carried out under extreme conditions (high and superhigh vacuum) which do not exist in nature. The geological interpretation of the decoration results raises the question of effectivity of active centres in natural processes.

Autodecoration which is noted in crystallization of solutions from liquid inclusions released by splitting minerals is performed by the actual mineral forming substance. Its results prove that charge point defects ever present in minerals determine many aspects of their individual history (ontogeny).

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## COMPLEX OXIDE FERROMAGNETIC MINERALS INHOMOGENEITIES AND SOME PHYSICAL METHODS OF STUDING THEM

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New techniques of using electron-probe instruments including the building up of two-dimensional X-ray contour maps and content profiles, heating device from X-ray microanalyzer JXA-50A with computer controlled system; studing minerals and their aggregates small angle scattering effect under qualitatively new application of a Primary X-ray macroanalyzer JPX-3 as a diffractometer of wide X-ray emission range; a large complex of primary (Curie points and specific magnetization), secondary (magnetic viscosity factor, magnetic saturation field, saturation field, build up of coercive spectra) and tertiary (various types of remanent magnetization) magnetic characteristics; thermomagnetic analysis at the temperature range of (-196°C) - 800°C permit to obtain important information on composition, crystal and magnetic structures, micromorphology under the conditions of mineral formation belonging to class complex oxides,classes of spinel and corundum-ilmenite structural types.

Field of application, advantages and disadvantages of these methods in studing of natural ferrimagnetic minerals have been considered. The optimal techniques of directional study of these minerals is being considered.

There are given new data on complex oxide minerals possessing spinel and corundum-ilmenite structures (micro-discontinuity dementions and microporosity relation with magnetic viscosity factor; order-disorder transformations in maghemites and their relation with conditions of maghemitization; cation distribution in isomorphous series magnetite-magnesioferrite, chromospinelides and their dependence on rock-formative conditions;data on a phase composition of Cr-bearing ilmenites and spinels of exotic compositions from Jakutia kimberlites and present-day Kamchatka volcanoes) obtained by means of a complex use of classical and modern physical methods of investigation.

# BRAZIL TWIN IN MILKY QUARTZ CRYSTAL

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Fibrous optical texture radiating outward from the center is seen between crossed nicols in euhedral milky quartz crystal with lineage structure that have grown in open spaces. A well illustrated account has been given of these features in Alps and Urals quartz crystal, and they also have been observed in quartz from Dauphiné, France and Brazil and other localities. Soviet mineralogists have studied the optical texture and the morphology in details. Some examples are seen in magnificent textbooks, Onto - geny of minerals (first and second editions) by Professor Grigoriev.

Present writer studied the milky quartz crystals from Japan by means of various microscopies (polarized and phase contrast optical microscopies, Transmission electron and scanning electron microscopies) to find the origin of the texture. The specimens have high dense Brazil twins with many kinks, whose composition plane is parallel to pyramidal plane. The optical fibrous texture was interpreted by Brazil twin.

The following genesis is suggested for the Brazil twin. Amorphous silica particles were formed by alteration of silicate minerals in a mother rock under hydrothermal condition. The amorphous particles crystallized into small quartz particles at higher temperature than 100-150°C. The quartz particles sticked on the large quartz crystal growing in the solution. If the crystal orientation (left or right hand) of both quartz crystals are the same, they will become single crystal, because free energy of single crystal is lower than Dauphiné twinning. If the both orientations are different from each other, the Brazil twin will be made at the boundary. The Brazil twins were made on the side plane of small rectangular hills found on the prism and pyramidal faces by scanning electron microscope. Brazil twins in amethyst, which co-exist frequently with chalcedony, may be formed by the similar mechanism.

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# HETEROGENEITY OF MINERALS AND THE NATURE OF LIMITED ISOMORPHISM OF THE SCHEELITE-POWELLITE SERIES

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A limited character of isomorphism in the series scheelite-powellite is stressed by a natural predominance of the extreme members of the series, especially of molybdoscheelite with $CaMoO_4$ content from 10 to 12 and sometimes from 20 to 25 mol.%. The molybdoscheelite crystals have a zoned sectoral structure which reflects variations of Mo contents in the course of growth. They are often substituted by scheelite or (and) molybdenite.

The minerals of the scheelite-powellite series demonstrate a non-additive character of their physical properties dependence on their composition. The proofs of discontinuity and instability of the isomorphic range are the signs of an order in structures and the decay of the solid solution that have been made evident in photo- and cathodic luminescence and in electron microscopy procedures.

It has been also shown in thermodynamic calculations that the decay curve is distinctly asymmetric.

The high-temperature calorimetry technique by Calvet has supplied us with new thermodynamic constants for the extreme members and for the intermediate phases of the isomorphic range.

It has been stated also that Mo-W interactions in the crystal structure (charge, change and redistribution of degrees and possibilities of electron and hole occupancies of levels of different states in 4(d') Mo shells and in 5(d') W shells) is accompanied by the Jan-Teller dynamic effect that is the cause of the isomorphism polarity and of some other signs of imperfection of the solid solution scheelite-powellite.

The analysis of the paragenetic mineral associations and a number of other experimental and theoretical data witness for the dependences of molybdoscheelite composition on the mineral-forming temperatures and chemical conditions as well as on Eh and pH parameters.

## DEFECTOLOGY OF MINERALS BY FLUID INCLUSIONS OF MOTHER SOLUTIONS

N.P. Ermakov, Moscow, USSR

The defectology of crystal commodities in the USSR is based on analysis of inclusions of small quantities of mineral-forming fluids. The inclusions are to be distinguished as syngenetic (primary) that are naturally distributed in the zones or in the segments of growth and as pseudo-secondary ones accumulated in micro-fractures and healed in the process of growth. Epigenetic inclusions that were formed later are by convenience called secondary inclusions. Establishing types of these inclusions of melts and solutions, and a study of their aggregate states and compositions has constituted a base for ecologic investigations and determined later on the contents of a new geologo-mineralogical science - the thermobarogeochemistry.

The faster is the growth of an individual mineral, the greater is the number of inclusions deteriorating crystal structures. In certain conditions (e.g. during the changes of temperature ) the inclusions of the crystal-forming media caused epigenetic defects in minerals. Freezing of solutions included in Iceland spars of permafrost zones produces inner jointing aureoles (cryodecrepitation effect). A post-genetic heating of fluid inclusions above the conservation (homogenisation) temperatures produces the same effect. So, the syngenetic defects in a crystal are accompanied by epigenetic discontinuites.

A multi-form influence of the geochemical inclusion system on properties of natural crystals and on some physical properties of minerals will be treated in this report.

## ZONING IN MELILITE GRAINS AS AN INDICATOR OF REGRESSIVE EVOLUTION OF CONTACT METAMORPHIC PROCESS IN CARBONATE-BEARING ROCKS

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We have continued further investigations of mineral assemblages generated during thermal metamorphism of siliceous dolomitic limestones and marlstones in the exocontact zone of Anakit dolerite (trapp) massif (Lower Tunguska river,USSR). The contact metamorphism manifested at this locality was first described by Prof.V.S.Sobolev in 1935. The higher-temperature calc-silicate mineral associations at the immediate contact with dolerite intrusion are characterized by the following compositions: wollastonite+rankinite, rankinite+spurrite (+melilite?), spurrite+melilite+merwinite+calcite and merwinite+monticellite+melilite + calcite. The melilite of this associations is usually unzoned; its composition being essentially gehlenitic; akermanite component making up about 25 mol.%

At decreasing temperature during the regressive stage of contact metamorphism the equilibrium between merwinite and essentially gehlenitic melilite is violated. New akermanite-rich melilite and calcite were formed by the replacement of merwinite and earlier gehlenitic melilite with participation of $CO_2$.The newly forming melilite grains may be distinguished for their sharp compositional zoning: from 25 mol.% akermanite component in the centres (relict mineral sections of progressive stage of metamorphism) to practically pure akermanite in the periphery (rims). A regressive alteration of metamorphic rocks at the contact resulted also in the replacement of spurrite by tilleyite and rankinite by cuspidine.All these processes were mainly manifested at the areas in which carbonaceous rocks were readily permeable for magmatogenetic fluid to penetrate into the zones of pronounced microfissuring.

It is supposed that the maximum temperatures of progressive metamorphism have reached in intrusive contacts approximately 950-970°C at a lithostatic pressure (= $P_{total}$ ) 300-350 bars. The composition of intrapore fluid equilibrious with metamorphic minerals cannot be exactly determined; the $P_{CO_2}$ -values were from 0,2-0,3 to 0,8-0,9 $P_{total}$ according to different estimations. During regressive stage of contact metamorphism the temperature decreased to 750-800°C with simultaneous drop of $P_{CO_2}$ up to 0,1 $P_{total}$ and less. The later skarn and hydrothermal postmagmatic processes proceeded at the exocontact zone of Anakit dolerite intrusion at temperatures below 700°C followed by drop of $P_{CO_2}$ .

## CHEMICAL AND STRUCTURAL HETEROGENEITY OF THE POTASSIC WHITE MICAS IN THE SCHISTS AND GNEISSES OF THE VANZONE AREA (PENNINE ALPS, ITALY)

D.Laduron, J.Thoreau , Belgium

The chemical and polymorphic characteristics of the potassic white micas of Vanzone area (Italian Pennine Alps) have been studied by electron microprobe and X-Ray diffraction.

In the same specimen, the white micas varies between two poles: one more celadonitic (richer in Si,Fe and Mg) and the other closer to pure muscovite (richer in Al and Na).

The known relationship between the polymorphic types 3T and 2M with the 2V values=0° and 40° is confirmed by diffractometric analysis of white micas of both types coexisting in the same sample.

Microprobe analysis of coexisting plates with 2V=40° (therefore 2M) and with 2V=0° (therefore 3T) shows that the 3T polymorphs are generally more celadonitic than the 2M polymorphs.

The authors discusses then different petrologic interpretations.

## MICRO-HETEROGENEITY AND ISOMORPHISM OF MICAS

L.N.Ovchinnikov, T.A.Kapitonova, N.F.Chelishchev, Moscow,USSR

Detailed investigations of micas have made evident the importance of mineral micro-heterogeneity studies and the necessity to revise our concepts of the role of isomorphic substitutions in minerals. The mica group minerals, apart from the purely isomorphic substitutions, are characterised by finely layered micas of aggregates of various modifications, by crystal zoning layered vermiculitization and by an invariable presence of micro-inclusions of other minerals.

The micro-inclusions are made visible in micas by methods of acid decationisation resulting in colourless foliated Si and O structures where any mineral inclusion is to be detected optically or by X-ray spectral technique. The decationisation possibilities permit to revise the problem of utilisation of mica's waist. One can extract rare alkali metals, obtaining superlight layered material of high Si content demonstrating a number of unique properties.

The evaluation of the chemical composition of some monomineral fractions of micas in crystallochemical formulae gives a constant shift in the calculated coefficients obtained from the theoretical values. The shifts follow certain laws and are related to the nature of the material, in particular, to its heterogeneities, inclusions, layered aggregates of various micas, as well as to the alteration in all the mentioned particularities, induced by a hydration or dehydration of micaceous matter. It has been shown also that the presence of the important part of the trace-elements in micas is to be explained otherwise than by the isomorphism phenomenon. They are related rather to the micro-inclusions of different minerals.

## EXSOLUTIONAL MICROINCLUSIONS OF SULPHATES AND SULPHIDES IN ENDOGENIC CALCITES

L.Z.Reznitskii, E.I.Vorobyov, Irkutsk, USSR

While studying the phlogopite and lazurite deposits in south - western Pribaikalye, the regularly oriented microinclusions in barite, pyrite and markasite absent in coexisting calcite minerals have been found in calcite of several generations. The amount of inclusions of some definite content in calcite from each generation is constant. The inclusions are represented by spicular, capillary, banded andplane-tabular microcrystals, often unusual for the minerals of habit type as a result of the influence of elements of calcite symmetry. Long axes of micro - crystals are oriented parallel to edges $[r_1:e_2]$, $[r_1:e_3]$, $[e_1:r_2]$ of the host calcite.

Having considered possible ways of microinclusion formation,the authors arrived at the conclusion on their exsolutional nature. High temperatures for formation of calcite isolations studied (from 550 to 665°C) exclude their co-crystallization with barium and markasite. Peculiarities in the distribution of microinclusions (not forming accumulations in cracks) contradict the suggestion on the superimposed barite and sulphide mineralization. These peculiarities may be explained by their relationship with decomposition of solid solutions.

Isomorphic calcite capacity in relation to barium, iron and series of other elements is significant and many calcite variations (in particular, with high barium content) remain stable under low temperature conditions. Isolation of barium or iron into an independent phase in the form of sulphates or sulphides is due to the presence of sulphur primarile isomor - phically involved into the calcite structure.

The data obtained suggest that under certain conditions the carbonate rocks may serve as a potential source of the sulphate and sulphide mineralization owing to sulphur mobilization from these rocks by ore-forming solutions.

In sulphur-bearing variations of calcite one may find the presence of exsolutional isolations: sulphides of lead,zinc,manganese and sulphates of strontium,calcium,etc. (in calcites under consideration, the proto-,syngenetic microinclusions of anhydrite have been discovered).

## HETEROGENEITY OF GOLD-BEARING PYRITE COMPOSITION

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The presence of arsenic is a distinctive feature of gold-bearing pyrite composition forming disseminations in black shale rocks. Its content in pyrites varies sharply and averages 2%. Using X-ray microanalysis the heterogenous mainly zoned distribution of arsenic in pyrite grains was established with variation of its content from 0.04 to 6 percent. The position of zones enriched in arsenic , their shape, thickness, border nature is variable.

Shortage of sulphur was determined from chemical analyses of the arsenic pyrite composition. The compensation of sulphur deficiency by arsenic is distinctly observed in the concentration curves. Iron content remains constant. The increase of pyrite crystal lattice parameters with arsenic content increase indicates that its entry is isomorphous. With arsenic content of 3 percent the lattice parameter distinguihes highly from that of arsenic -free pyrite ($a_o = 5.415$ Å) reaching $a_o = 5.4323 \pm 0.0002$ Å.

It was found that the gold content is associated with arsenic content in pyrite. Some gold is assumed to enter the pyrite crystal lattice in isomorphous form.

## MICRO-HETEROGENEITY OF TANTALO-NIOBATES

S.I.Lebedeva, I.D.Beljaeva, Moscow, USSR

New data pertaining to micro-heterogeneities in compositions and structures have been obtained in studies of minerals of pyrochlore, columbite-tantalite and perovskite groups.

Zr-hatchettolites, Zr-pyrochlors, and Si-pyrochlore assumed formerly to be independent species are found now to be fine heterogenous mixtures of common pyrochlore with micro-inclusions of Zr-bearing (baddeleyite and zirconolite) and Si-bearing minerals. Metaloparite of Lovosero massif is turned to be a poly-phase micro-aggregate which composition corresponds to that of aeschynite, ilmenorutile, monazite and apatite.

Block-like micro-heterogeneities have been found in Ba pyrochlore (pandaite) and in Pb-betafite; BaO content varying from 0,n to 36,6 % and that of PbO - from 12 to 43 %. Micro-block structures have been found also in Nb-perovskite (latrapite) of Canadian and in Khibinian Nb-loparite, the blocks contain different portions of Nb, Ca and Ti. Ixiolites and wodginites taken from Altaian pegmatites and from Siberian metasomatites are often represented by a fine mixture whose components are suggested to be a disordered ixiolite phase and an orderly one of wodginite. Two phases have similar contents of Ta and Nb and different Mn, Fe and Sn compositions.

In a number of natural Ta-Nb minerals signs of certain radiation and of inter-block defects, as well as different dislocations have been discovered. The micro-inclusions and micro-segregations of trace elements are related often to these defects. When heating the metamict tantalo-niobates (samarskite and Zr-pyrochlore) their matter recrystallise and form compositionally different phases. The higher is the temperature of treatment the greater are the dimentions of the newly formed phases

## ANATOMY OF MINERAL INDIVIDUALS AND AGGREGATES - ONE OF THE PROBLEMS OF MINERALOGY

V.N.Sergeev, Tomsk, USSR

The structure of mineral individuals depends on various combinations of a relatively small number of morphogenetic elements both singenetic and epigenetic: zonal growth, edge growth pyramides, suture joints of such pyramides, fractures and plastic deformation structures, microporosity, leaching traces, recrystallization areas,etc.

The paper deals with the types of zonal growth, the crystal splitting structure, the evolution features of the zonal structure of mineral individuals in the process of their growth, the formation of pseudospherolitic and "collomorphous structures". Different combinations of the above elements determine the individual structure of minerals. Their "anatomy" is at times so characteristic that it allows to judge on the mineral structure formation as well as of the particular deposit the mineral sample was taken from.

The conditions of mineral aggregate formation also influenced their anatomic structure (oölites, spherolites, parallel shistosity, banded-rhythmic, drusy structure, different mono-and polygrained aggregates, etc.).

The structural peculiarities in the mineral individuals and aggregates are typomorphous. Their investigation allows to widen the set of reliable mineralogical criteria in order to correlate ores and rocks as well as to prospect and evaluate the mineral deposits. The anatomy of individuals and aggregates is to be a topological basis while examining the nonuniformity of their chemical composition and physical properties. When such a basis is not available research workers often restrict themselves to the definitions of "gross" mineral composition which leads to the simplified interpretation of the data and is fraught with erroneous opinion of the nature of relations among the composition properties and genesis of natural formations.

Deepening the knowledge of the anatomy of mineral individuals and aggregates will allow to obtain plenty of *information with* relatively small quantities of matter under investigation which is especially significant in studying the abyssal formations and cosmic bodies.

## HYDROCARBONS IN ENDOGENOUS MINERAL FORMATIONS

F.P. Mel'nikov, Moscow, USSR

Endogenous mineral, gas and oil formations were considered up to now to be separate, non-correlated natural phenomena. Though a certain content of organic substances has now been stated to be present in some auriferous, polymetallic, iron and mercuriferous deposits. A U-association containing bitumen matters has also *been reported*.

Primary inclusions of hydrocarbons of oil and of bitumens in the rock crystal (Aldan, Caucasus, Donetsk basin), in morion (Volyn') and in fluorite (Kazakhstan, Pakistan) have been made known and studied.

The bitumoides of inclusions contain complex mixtures that would present an almost continuous range of hydrocarbons from light to predominantly resino-asphaltic ones, the intermediate fraction being represented by pure oil with equal or smaller portions of resins and of asphalt.

A number of experiments has been conducted in order to observe the hydrocarbon phase transformations when heating and cooling the inclusions. The signs of successive changes have been filmed.

The paragenetic and the purely genetic relations among the hydrocarbons are of no doubt any more. These relations make it possible now to see into the new and untreated particular feature of endogenous mineral formation - the part of the hydrocarbons in these processes.

## IMPURITY DISTRIBUTION IN NATURAL GOLD BY SPARK SOURCE MASS SPECTROMETRY DATA

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A procedure for analyses of natural gold by spark source mass spectrometry has been developed that allows to determine simultaneously impurities from Li up to U with detectability to 0.01 ppma from 3-5 mg samples and study impurity distribution in the bulk of the nuggets analyzed. Spatial element combinations in relation to steihiometric ratio are discussed as indicators of corresponding mineral inclusions in natural gold. There *are observed inclusions of pyrites, arsenopyrite, tellurobismuthite*, galena, jamsonite and others in the analyzed nuggets taken from the North-Eastern USSR and Buryatian deposits. A set of inclusions corresponds to that of minerals found in ores. Mineral inclusions being typical of gold placer, root sources occur in gold placer nuggets. Throughout there can be found rock-forming minerals. Impurities that sometimes mineral inclusions contain have been determined: nickel and cobalt in pyrites; cadmium in sphalerite; selenium in galena; uranium, thorium and a complete set of rare earth elements in monazite, xenotime and zircon.

Somewhat homogeneously is distributed in nuggets only mercury. It is for the first time that iodine and bromine have been detected in natural gold.

Heterogeneity of impurities distribution in natural gold should be taken into account while discussing the type of deposit formation and its geochemical peculiarities, on the one hand , and the type of the root sources in gold placer, on the other.

## TYPOMORPHISM AND HETEROGENEITY OF HYPERGENE GOLD

S.V. Yablokova, Moscow, USSR

A sure identification of hypergene gold is to be taken as a basis for any idea on a redistribution of gold in hypergenetic zones, on a reenrichment of ores and on possible accumulation of the "new" metal in placers.

The most important signs of the hypergenic nature of gold - the marks of coprecipitation of this metal with minerals formed in oxydation zone conditions have been studied. The coprecipitation products are represented by spongeous concretions of different density where small gold particles are cemented by secondary minerals ("Fragile" gold). Normally, the particles do not exceed 1 mm, though there are exceptions as great as 20 mm. The new formations are born during the decompositions of tellurides. The heterogeneity of this hypergene gold is stated to be its special feature: four Au-Ag phases have been found to form emulsion subgraphic aggregate structures. The standard of the native gold is subject to variations. It depends on Au/Ag ratios in the primary minerals and on the redeposition conditions (solution content and Eh, pH). The abundance of trace elements in gold is determined by the compositions of secondary minerals in the aggregates.

A limited development of secondary gold has been noted in oxydation zones of moderately sulphidic deposits of N-Western Asia. It is a rarity in less sulphidic and poorly sulphidic deposits, and when found, it is related generally to some decomposed Au tellurides and antimonides. Unique deposits localized in carbonate rock presenting favourable conditions for Au redeposition in karsts are considered to be an exception.

The "new" gold is being localized in placer deposits in the vicinity of original sources presenting finely dispersed metal and relating to areas of crusts of weathering.

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## ON APATITE HETEROGENEITY

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Epitaxial inclusions of a tetracalcium phosphate (hildenstockite) in apatite have been discovered. Formerly hildenstockite $Ca_4P_2O_9$ was considered to be an exclusively synthetic mineral. The presence of these inclusions in apatite is corroborated by the deviations from the chemical stoichiometry in the mineral, a low specific weight, by fragility and jointing of grains as well as by different hardness in different zones of a sample and by etch cavities after a hydrochloric acid treatment. The structures of apatite and hildenstockite are known to be very similar, hence there are not great differences in their X-ray powder patterns. Their IR-spectra are also similar. So the above methods are of no use to detect hildenstockite inclusions in the mineral. It has been established that hildenstockite is a wide-spread accessory mineral in apatite that was formed in rocks with high Ca-content (ultrabasic rocks carbonatites,etc.). A direct relation between the dimensions of the apatite separations and that of hildenstockite inclusions has been observed.

The phosphate matter of phosphorites is represented not only by aparites but by other Ca phosphates in form of finely dispersed aggregates.

It is a known fact that Ca phosphate precipitates obtained in laboratory conditions demonstrate different compositions depending on every growth condition: solution pH, temperature of ignititon, ammonia, surplus,etc.

The inhomogeneity of the natural apatite being a certainty, it is necessary to identify scrupulously the products of its synthesis.

# DISTRIBUTION OF POINT DEFECTS IN QUARTZ AND SPHALERITE

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Natural and synthetic quartz crystals differing in colouring, as well as luminescent and nonluminescent sphalerites have been examined by the method of electron-microscopic decoration. As a result of the investigation a significant irregularity in the distribution of electrically active point defects in a volume of crystals of coloured quartz and luminescent sphalerite is established.

Point defects have a greater density and give reticulate pictures of decoration in quartz crystals coloured by structural admixture. The spherical accumulations of point defects may be observed in crystals, coloured by non-structural colloidal ad - mixture.

Luminescing sphalerites, natural and synthetic as well as coloured quartz exhibit irregular distribution of some point defect in a volume of a crystal. Rounded segments, free from decorating parts, or the ones of the same kind, but covered by some particles of a greater density may be observed on the shear surface of sphalerite grains. This testifies to the presence of spherical accumulations of the point defects.

The accumulations of the point defects in quartz and sphalerite are unstable thermally and decompose while heated with disappearance of colouring and luminescence.

There is a direct connection between the structural unhomogeneity of quartz and sphalerite and their colouring and luminescence qualities.

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# HETEROGENEITY OF NATIVE GOLD AND SOME PROBLEMS RELATING TO STABILITY OF NATURAL SOLID SOLUTIONS OF METALS

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The concept of homogeneity of natural solid solutions of silver in gold have been revised in our studies made by electron microscopy, electron microprobing, LASER spectral analysis,etc. Heterogeneities differing by genesis and by the age of formation have been disclosed.

Relict accumulations of microscopic mineral particles in gold and microzones of petrogenetic element concentrations are stated to be protogenetic formations. It is the first experience to find such syngenetic heterogeneities of native gold as its finest mosaic and foliated substructures born in special crystallisation conditions. It appears now that the epigenetic hetero - geneities provoked by deformation and recrystallization of native gold are repeated formations and they may be employed as indicators of some dynamic and thermal factors of ore changes. For the first time now a phase inhomogeneity in gold (Ag-content = 30 to 50%) becomes surely proved.

The Ag-rich phases clearly visible with their phase boundaries are related to weak grain zones. The hypothesis is being proved - the solid Au-Ag solutions are metastable and they "age" slowly and become ordered to form more stable intermetallic compounds. A number of such aged structures (emulsion, linear and reticulated) have been made known. First reliable information on structure (microdiffraction) and phase composition of native gold has been obtained. These phases correspond to the compositions of AuAg and $AuAg_3$ types and to pure silver. The analyse groupings are similar in some instances to decay structures of cupreous gold whose phases are represented by AuCu and $AuCU_3$.

The metastable character (in geological concept of time) of the solid solutions of metals (even of homologous ones) is states to be a certainity, if their quantitative correlation greatly differs from the stoichiometric ones which are proper for more stable intermetallic compounds.

## T.E.M. STUDY OF A COMPLEX SULPHIDE ORE - FIRST RESULTS

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The aim of this work was to study lattice defects and chemical heterogeneities in a pyrite-chalcopyrite-sphalerite-galena ore (size of minerals $\sim$ 30 um) of volcanic sedimentary origin before and after crushing, using a transmission electron microscope with a goniometer stage and a solid detector X-ray analyser.

Transparent specimens for T.E.M. have been prepared by ion milling from double polished thin sections which were previously observed with an optical microscope. Special thinning conditions have been determined in order to avoid sulphide dissociation during the preparation. Furthermore, it has been checked that there are no electron irradiation damages in the sulphides during T.E.M. observations.

In the microscope, specimens have been analyzed (excited area $\sim$ 0.5 um), observed with a x 20 000 magnification and examined by electron diffraction (studied area $\sim$ a few um). Lattice defects, chemical heterogeneities and nanoinclusions have been observed. The more studied sulphides are pyrite and sphalerite.

In pyrite, $\{100\}$ planar defects have been observed. Their density (up to 5 $um^{-1}$) is similar in crushed and uncrushed samples There are few dislocations in pyrite meanwhile they are numerous in the surrounding quartz.

In uncrushed sphalerite, it has been observed area with high dislocations density ($\sim 10^9 cm^{-2}$) or subgrain boundaries, and twin lamellae parallel to $\{111\}$ with a density up to 50 $um^{-1}$. After crushing, there are only twins. These observations indicate that planar defects in pyrite and twins in sphalerite have not been produced by crushing.

The sulphides contain small inclusions which have been characterized by TEM and X-ray analysis: sphalerite (1 µm wide) or chalcopyrite (0.1 um) in pyrite, and galena (0.1 µm) in sphalerite.

The studied sphalerite contains iron with a ratio Fe/Zn $\sim$ 0.06. It is generally supposed that iron is substituted to zinc in the lattice. Part of this iron could be in clusters 0.01 to 0.02 µm wide which were observed by T.E.M.

Further work will be done to study these clusters and to check if such precipitates can be observed in different kinds of zinc sulphides (for instance in marmatite).

The first results of this work show that new data on microstructures of sulphides from complex ores, can be obtained by TEM studies.

# CHRYSOTILE-ASBESTOS STRUCTURAL AND MORPHOLOGICAL HETEROGENEITIES AND THEIR APPLICATION TO EVALUATING RAW QUALITY

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Electronoptical studies and microdiffractional analysis of chrysotile-asbestos from Baghenovskoye subtype deposit enabled to determine structural and morphological heterogeneities in identification of this mineral. There are four types of identification.

A) Monochrysotiles are tubular particles with homogeneous packet of layers which due to microdiffractional pictures belong to one of the three modifications; orthochrysotile, clinochrysotile and parachrysotile.

B) N-layer polytypes are fibres whose point electronograms are characterized by additional regular "Hol" reflexes on even layer series. Overstructural period C-values range from 14.6Å to 65.7Å. This pseudo-period occurs, with no exception, in regular displacements of the consequent series of layers.

C) Combined chrysotiles are complex tubular particles formed by layers of heterogeneous structure. Microdiffractional pictures indicate that the combination of two or three structural modifications have crystallographic axes which are parallel (ortho + clinochrysotile, ortho + parachrysotile, clino + parachrysotile, etc. ).

D) Chrysotiles of spiral lattice are fibres with screw axis dislocations (a or b) of separate series of layers or of the whole tube, the axes being turned into screw lines Point reflexes of their electronograms where $K \neq 0$ are splitted into descrete series. The amount of reflexes for each series give the degree of homogeneity and layer deformation character.

Electronomicroscopic observations (magn.25-30th) showed the inner parts of some compound tubes to be screwed curved lines with both left and right bend. Conchiformed and complex curved lathes have been identified. Chrysotile - asbestos peculiarities have been revealed in different ore types having different engineering properties. All these peculiarities allow to distinguish normal fibre, brittle modifications and those of poor engineering properties.

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# GENETIC CONSIDERATION ON THE ZONING OF FE-S-O MINERALS AT THE KAMAISHI CU-FE PYROMETASOMATIC DEPOSIT,JAPAN

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The Kamaishi copper-iron metasomatic deposit (39°16'N and 141°40'E) situated at the eastern margin of the Kiatakami mountainland of northeastern Japan was formed along the boundary between the limestone strata of Carboniferous age and diorite porphyrite by the intrusion of Cretaceous granodiorite. A traverse away from diorite porphyrite would encounter successively grandite skarn, oxide ore (magnetite), green skarn (clinopyroxene and ferroactinolite), sulfide ore (pyrrhotite and chalcopyrite), and finally white bleached limestone.Oxide ore zone develops within the grandite skarn close to porphyrite intrusives, whereas sulfide ore zone occurs along the outer fringe of the green skarn near the limestone host. The two ore zones differ markedly from each other both in predominant ore minerals and in preexisting host skarn minerals, but not much in paragenetic sequence of ore minerals. Metallization stage overlapped with reconstruction-hydration stage of skarn, at which preexisting skarn minerals of clinopyroxene and grandite were replaced by ferroactinolite, calcite, quartz, and chlorite.

Iron minerals belonging to the system Fe-S-O were formed sequentially in such a increasing order of sulfur as magnetite,hexagonal pyrrhotite (47.3 ∼ 47.7 atomic per cent Fe), monoclinic pyrrhotite, and finally pyrite. From data available for geothermometry and salinity in addition to the textural interrelations it is assumed that a transition from magnetite formation to pyrrhotite occurred nearly at 350°C and an ore-forming fluid was an acid aqueous solution with $m_{t.NaCl} \approx 2.0$. Equilibrium calculation shows that the solution at this temperature contained about $10^{-2.49} \sim 10^{-2.35}$ molality of sulfur, and was at the oxidation state of $\log(m_{t.SO_4^{=}}/m_{t.S^{=}}) - pH = -9.69 \sim -6.99$. The paragenetic sequence of iron minerals is a proof that the mineralizing system continued to cool from 390° to less than 315°C without radical changes in sulfur concentration and oxidation state of the solution flowing onto the area. Since the zoning and paragenesis will be cogenetic, it may be reasonable to conclude that the oxide zone had its golden age of metallization at an earlier and higher temperature stage than the sulfide zone. The reason why the golden ages of metallization were different between the two zones may be found not only in the time lag between them, but also in the temperature gradient that may be existed in the whole area concerned to the igneous emplacement.

The marked difference in preexisting mineral composition between the two zones was also responsible for development of ore zoning. The difference in oxidation state of iron between grandite and clinopyroxene resulted in the different directions of compositional change of the solution through the irreversible reaction with them. In the grandite zone the oxidation state of the solution became higher, while in the clinopyroxene zone lower. When isothermal transition from magnetite deposition to hexagonal pyrrhotite could take place by a slight change of the solution composition, it was promoted in the clinopyroxene zone, but not in the grandite zone.

# GEM MINERALS AND GEMOLOGY

# APPLICATION DE LA MICROSONDE RAMAN LASER A L'IDENTIFICATION D'INCLUSIONS DANS DIFFERENTES GEMMES

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La microsonde à effet Raman inventee au Laboratoire de Spectrochimie Infrarouge et Raman permet à partir des spectres de vibration moléculaire l'étude de micro-echantillons, sans préparation speciale, c'est a dire à l'air libre ou en inclusion dans des matrices non-opaques.

Parmi des diverses applications à la mineralogie (ètude d'objet archéologiques en pierre, determination des **minéraux** et de leurs inclusions solides et fluides ...) l'étude des inclusions des gemmes est particulièrement aisee avec cet appareil.

Les spectres Raman d'inclusions de quelques dizaines de microns ont ete enregistrés in-situs dans les gemmes à l'aide de la microsonde utilisant la raie à 514.5 nanomètres d'un laser à argon ionise. Les spectres témoins ont été réalisés à l'aide d'un spectrometre à triple monochromateur T 800 ainsi qu'a la microsonde Raman laser en utilisant la même longueur d onde excitatrice.

Les inclusions des premiers echantillons étudies mesuraient entre 10 et 400 microns, ce sont: Pargasite dans saphir(Cachemire) Sphalerite et calcite dans rubis (Birmanie), Feldspath dans aigue-marine (Brésil), Monazite et zircon dans saphir(Birmanie), Britholite dans saphir (Australie, Ceylan). Apatite dans grenat (Madagascar), $CO_2$ liquide et gazeux dans beryl (Brésil).

Les resultats de la presente étude ont permis de confirmer ceux obtenus, avec plus de difficultés, par d'autres méthodes (microreflectometrie, microsonde electronique...).

# *MINERALOGY OF CHRYSOPRASES FROM THE DEPOSITS OF LOWER SILESIA*

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Isolated finds of chrysoprase are known for almost all the serpentine massifs of Lower Silesia, but the classical and one of the largest deposits in the world is the one at Skliary where *chrysoprase is also mined as* a by-product. The deposit is confined to the serpentinites crust. Chrysoprase occurs in the form of whole veins up to 25 cm thick that are traced up to 5 m along the strike. Two generations of it are observed:finely cryst-talline druses (very rarely) and continuous cryptocrystalline formations. Varieties of chrysoprase are from opaque light-green to translucent dark-green. The latter is uniformly fine-grained (*the size of grain* is about 0.005 mm) and has practically no pores or cavities. The grains of light-coloured varieties are somewhat larger. Refractive index is on the average 1.447.

The results of X-ray diffraction analysis have showed that the *chrysoprase* from Skliary forms different stages of crystallization of silica - from opal to chalcedony. Its basis consists of $\alpha$-quartz with a minor amount of $\alpha$-tridimite and molecular water. Chrysoprase is characterized by non-uniform texture,this having been corroborated by microscopic and electron-microscopies studies. NiO in the amount of *0.03 to 1.30% serves as a* chlorofor.

The second economic accumulation of chrysoprase in Poland is in a magnesite mine in Vira, not far away from Vrozlav. Chrysoprase veins and veinlets, forming stockwork zones, were found at the depth of 50 m in the lower part of the weathering crust of serpentinites. The extent of chrysoprase veins in Vira does not exceed 5 m, while their thickness varies from fractions of a centimetre to 10 cm. *They often have* complicated internal texture due to their heterogeneous mineral composition and structural-textural peculiarities. An association of silica minerals - chalcedony, opal, opal-chalcedony, quartz, usually constitutes a part of vein structure.

Under a microscope all the varieties of chrysoprase are structurally non-uniform, there having been noted allotriomorphic , granoblastic and spherulitic structures. This chrysoprase is mostly of light colouring, with grains up to 0.1 mm. The result of X-ray diffraction analysis show that chrysoprase from Vira is chalcedony of greenish colour, containing up to 1% $N_\omega = 1.543 \pm 0.002$, $N_\varepsilon = 1.552 \pm 0.003$.

# QUANTITATIVE COLOR DETERMINATION IN AUSTRALIAN SAPPHIRES

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In this work we intend to establish a relation between the color of corundum crystals from Australia, and its chemical composition.

To do this, polished sections of a set of crystals with different colours have been obtained. These sections have been cut in the direction of optical axis, in order to obtain measurements of both mean directions of vibration.

We have measured the reflectance of these samples in the visible range of the optical spectrum (from 400 nm to 700 nm). And with these values we have carried out the colour coordinates of each sample by the CIE system.

The same samples have been analysed by a Scanning Electron Microscope with the Edax System incorporated, in order to obtain the chemical composition of each crystal.

As a conclusion, we establish a relation between the cations of sapphire lattice and the position of the colour in CIE coordinates.

# MINERALOGY OF LAZURITE DEPOSITS OF THE USSR

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The lazurite deposits of the USSR (near-Baikal region, Pamyrs) are composed of metamorphic, magmatic and postmagmatic rocks formed in the course of a single process of petrogenesis. Lazurite-bearing rocks are formed at one of the early periods of the post-magmatic stage under definite lithologic and tectonic conditions, mainly during the process of bimetasomatosis at the contact between magnesial marbles and alumosilicate rocks. The latter are represented by granitoids, syenites, nepheline-syenites, schists, plagioclasites, skarns.

The lazurite-bearing metasomatites are formed under the conditions of high alkalinity at 520-605°C.
The principal types of lazurite-bearing metasomatites are apocarbonate lazurite calciphyres and diopside-lazurite metasomatites developing over alumosilicate rocks. These lazurote-bearing metasomatites are characterized by a paragenesis lazurite+diopside+calcite (±apatite pyrite). Diopside-lazurite rocks have the greatest practical value. There occur locally lazurite-orthoclase (sanidine), lazurite-plagioclase, lazurite-forsterite, lazurite -wollastonite metasomatites.

Study of the mineralogy of lazurite-bearing rocks of the USSR has permitted, on the one hand, to know more accurately the composition and properties of the known feldspathoids and, on the other hand, resulted in the discovery of new mineral species: triclinic lazurite, sulphide cancrinite, as well as aphganite and hackmanote with inverse fluorescent properties. There has been recognized the existence of a continouos series of lazurites of different degree of regularity,with systems changing from the triclinic to the cubic one. The minerals of this series have been combined into a separate subgroup of the sodalite group. The cancrinite group has been divided into two groups:

a) group of cancrinite-wishnewite with a common formula $A_{6-8}B_{12}O_{24}X_{1-2}\cdot nH_2O$; b) group of aphgganite with a common formula $A_{6-8}B_{12}O_{24}X_3\cdot nH_2O$. Crystallochemically the aphganite group should be regarded as an intermediate one between the feldspathoids of the sodalite and cancrinite groups. A tendency for the formation of polytype modifications has been noted for the first time in feldspathoids.

A new classification of feldspathoids with additional anions, taking account of their crystallochemical features, has been suggested.

# GEMMOLOGY AS A MASTER ACADEMIC SCIENCE, NOT A BRANCH OF MINERALOGY. GENERAL PRINCIPLES AND CONCEPTS

**M. Superchi, Milano, Italy**

In a similar way to petrology and ore deposits, born in the sphere of mineralogy and then separated from it, also for gemmology it is time to be a science apart.

Knowledge of chemistry, physics, mineralogy, petrology, geology and ore deposits must be expected, but our science has its own principles. In this work it's considered the general index of a Gemmological Compendium, divided into three parts: general principles, descriptive theoric part, practical part.

Moreover, the author proposes the concept "colour of the stones" as arrangement criteria in gemmological collections. This feature seems ancient, simple and quick to define; on the contrary it's an argument of great interest in science and not so easy to adopt, but suitable to our range.

# SOME PROBLEMS OF GROWING AND IDENTIFICATION OF SYNTHETIC ANALOGUES OF NATURAL GEMS

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Last years are characterized by spread adoption of new synthetic gems into jeweller's industry. The production of synthetic emerald, spinel and rutile is greatly increased, though ruby and other varieties of coloured corundum are in the first place among them. Yttrium aluminum garnets and fianites, colourless diamond imitation, became popular as well as their coloured varieties. Large successes are achieved in growing precious opal, turquoise and vast family of coloured quartz, especially citrine and amethyst.

There are various methods of growing synthetic natural gems analogues, they don't practically differ from crystal growing methods for technical uses and they are rather far from the natural mineral forming conditions. This is the reason of typical pecularities in synthetic gems ( composition, inclusions, zoning, optical properties, density etc. ),which allow to identify them from natural minerals.

Achievements in crystal growing techniques and exhaustion of natural deposits will undoubtedly be favour in the development of synthetic gems production. The general problem is to develop such methods of crystallization, which allow to grow synthetic gems as natural ones. It is important to overcome the psychological barrier: as early as now prices of synthetic gems are well below those of natural, and though the best synthetic gems do not yield natural ones in beauty their aesthetical influence still depends on their relatively low price.

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# MINERALOGY OF PEGMATITE PRODUCTIVE MINERAL COMPLEXES WITH PRECIOUS STONES IN NURISTAN (REPUBLIC OF AFGHANISTAN)

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Probability of appearance and composition of mineral complexes with various precious stones is being considered on the basis of the known vertical and horizontal zoning of the pegmatite fields and stocks that was quite definitely recognized for Nuristan (Drumgal, Kanakan, Yarigal, Kulam and others; Alkhazov, Rossovski and others, 1977; Azimi and others, 1978). Vertical zoning (from bottom to top) is as follows: oligoclase-microcline- with biotite; quartz-microcline with muscovite, schorl, beryl; quartz-microcline-albite with spodumene and others; quartz microcline-spodumene-albite with columbite-tantalite and oth.; cleavelandite with spodumene (or without it), beryl, tourmaline, columbite-tantalite, microlite, lithium phosphates and oth.

Grass-green emeralds are restricted to biotite margins of desiliconized microcline-oligiclase-schorl pegmatite that occurs in actinolite rocks and glimmerite.

Greenish-blue and blueish-green short-columnar aquamarines are in schorl-muscovite-microcline aggregates of apographic texture and are observed together with quartz and muscovite. Sky-blue and blueish-green columnar crystals of aquamarine are connected with superpositioned white cleavelandite, muscovite and smoke-coloured quartz in microcline-spodumene-albite pegmatites with tantalite-columbite.

Cream-coloured thick-tabular or short-prismatic vorobyevite, blue, yellow-green, darkblue-lilac and violet precious varieties of spodumene, indicolite, dark blue-green and grass-green tourmaline, its achroite and polychromatic varieties and, to a lesser extent, pale-pink rubellite are in paragenesis with blue cleavelandite, sceptre-like rhombohedral quartz flattened by a , lilac lepidolite, montebrasite, pollucite, microlite, magnotantalite, manganous apatite with intergrowths of cassiterite and tantalite. They are localized in the segments of strongly albitized quartz-microcline zones.

## SYNTHETIC EMERALD

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The physical and chemical properties of synthetic emeralds are discussed in comparison with those of natural emeralds.

Synthetic emeralds $Al_2Be_3Si_6O_{18}$ are obtained under a wide range of physico-chemical conditions; using easily melting fluxes at the range 900-1250°C, hydrothermal acidic solutions of complex composition at temperatures 150-600°C and 600-1200 atm. pressure and by gas transport reactions at 800-1000°C.

In spite of great variety of crystallization reactions similarity is seen between the synthetically grown crystals and those from the Urals.

The best quality crystals with color hues in the range 510-519 nm are obtained at certain ratios of chromophores $Cr^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Sc^{3+}$.

Values of fringence and bifringence, lattice parameters of artificial and natural emeralds are given and these data are discussed in connection with mixture content.

The distinguishing features of the artificial samples are more rough structures of faces, some typical inclusions, intensive red fluorescence, considerable dichroism 10-11 nm, larger density and hardness.

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## NEW DATA ON THE COMPOSITION OF PEARL FOUND IN THE NORTH-WEST OF THE USSR

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So far no studies have been conducted of the composition of microimpurities in pearl and of their distribution in it. Such studies would be important, however, for understanding the processes of the formation of pearl. We have conducted such studies on fresh-water pearl taken from inland waters of the North-West of the USSR.

Quantitative spectral analisis of bulk samples of pearls has shown that they contain the following microimpurities: Mg (0.01-0.12%), Mn (0.004-0.400%), Sr( 0.1-0.3%), Ag(0.0003-0.0030%) Ba ( 0.03-0.08%), Si (0.03-0.10%) Al (0.01-0.03%) and some other elements.
It is known (Korago, 1976) that perl consists of a nucleus, which serves as a centre of pearl growth, whose prismatic layers are "columns" of prisms of calcium carbonate in an organic shell, and platy layers formed by plates of calcium carbonate also cemented by an organic substance.

The appearance of a number of microimpurities (Si,Al,Ti and some others) should be associated with the peculiarities of the composition of nuclei which are often, according to the data obtained from studies with the aid of optical and electron microscopes, rounded and half-rounded grains and plates of plagioclases, quarts, kaolinite, hydromica and other minerals. These elements have not been recognized in the prismatic and platy layers.

Studies of the distribution of such microimpurities as Mg, Mn, Sr and K were conducted by a method of laser microanalysis with the aid of IMA-1 instrument. The contents of elements were evaluated semiquantitatively. The studies of numerous samples of pearls and shells of native nacreous mollusks permitted finding that the microimpurities are localized mainly in the organic cement. The difference between the contents of *Mg and K microimpurities in the organic base and mineral component* attains a half-order and even a whole order. The way of the inclusion of microimpurities into the organic substance is obscure.

The absence of luminiscence in aragonite, which is a mineral component of pearl, and the noted confinement of microimpurities to organic substance witness to the high degree of chemical purity of the aragonite of biogenic origin.

## NEW DEVELOPMENTS IN AMBER AND OTHER FOSSIL RESINS MINERALOGICAL STUDIES

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Fossil resin mineral species designation (19-th centure) and classification (first half of20-th centure) took place without suff*iciently comprehensive and uniform representation of the objects* under study, in the similarity of such parameters as density, refraction index, colour, lustre, composition, etc. . It has resulted in certain confusion in terminology.

The application to amber and similar substances of IR, UV and mass-spectrometry, NMR, EPR, derivatography, and other methods has given completely new information on their composition and structure as well as new apportunites for diagnosis. We have been studying museum specimens alongside the newest amber-like finds in the USSR. It has been established that the fossil re*sins of the North Siberia, described by A. Middendorf as am*ber, are not succinite. Among the visually undistinguishable amber-like resins of the area 4 species are distinguished by IK spectres; 2 being quite close to the gedanite and walkhovite in their characteristics, whereas the third is analagous to fossil resins from the Alaskan low Cretaceous deposits and the fourth has no known analogues. They are of no gemmological value. This also refers to the fossil resins from Archangelsk area. Succinite has not yet been found among the fossil resins of the Middle Urals either.

Though thousands of samples from the Far East (Primorsky Region, the Isle of Sakhalin) and the Transcaucasus have been analysed, amber (succinite) has not been discovered there. Nevertheles there exist in the above areas samples presenting certain gemmological value. There are analogous to rumanite in their IK spectres and in a number of other properties.

The Carpation area is distinguished by strict succinite adherence to level platformical conditions of the containing rocks. In folding zones rumanite and schraufite are to be found. Rumanite has been discovered to originate from the intermediate row succinite-gedanite as a result of catagenic transformation of the row. Whereas schraufite is a product of hypergenious oxidation of rumanite.

Since resin fossilisation processes, determining to a large extent their structure, composition and properties (Savkevich,1966) may not be finalized (fully completed), the appearence of continuity in their parameters, which has been observed, is quite understandable. Hence the fossil resin species previously designated represent extreme or intermediate members of the rows, which can be identified with the mineral species possessing variability limits different for each specific case.

## TURQUOISE COLOUR AND SUPERGENE ENVIRONMENT, SAR CHESHMEH, IRAN

S.J.Haynes, St. Catharines, Canada

Turquoise, although rare in the Sar Cheshmeh porphyry copper deposit, is associated with a 20 cm wide quartz pebble dike at the boundary between the supergene oxide and enrichment zones present in the andesitic host rocks. However, it was found only locally, where the supergene oxide zone extends downwards into the supergene enrichemtn zone along the pebble dike.

In the pebble dike, turquoise forms as veinlets and cavity fillings. Its colour is green in the more oxidized parts of the pebble dike, where iron oxides and hydroxides are abundant, but blue-green in the less oxidized parts close to the contact of the dike with the supergene enriched andesites. In the andesites turquoise is sporadically distributed and restricted to thin stockwork veins of molybdenite-pyrite-chalcocite near the contact of the pebble dike.

Chemical analysis of the different coloured turquoise reveals an increase of iron and aluminum, with a sympathetic decrease in copper, from the blue, through the blue-green, to the green variety.

Because the pebble dike cuts hydrothermal stockwork veins, and therefore postdates hypogene mineralization, the formation of the different turquoise colour varieties must be attributed to the differential mobility of copper and iron in the supergene environment. Blue turquoise probably precipitated directly from the early, copper-rich, solutions that flowed down the pebble dike and permeated the immediately adjacent andesites along the stockwork veins. As the water table fell, on erosion of the surface, the green and blue-green varieties were probably formed by either: 1. direct precipitation from the later oxidized iron-rich , copper-depleted, solutions as these were reduced below the water table; or 2. replacement of copper in the blue variety by iron from the later iron-rich solutions. This may have taken place while these solutions were still oxidizing.

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## MOLDAVITES AS THE PRECIOUS STONES

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The composition of moldavites which fell in Southern Bohemia and Southwestern Moravia in the uppermost Tortonian (Middle Miocene) were not uniform. Major differences in composition are preserved between the moldavite localities in spite of some partial redeposition during the Pleistocene and Quarternary. The moldavite occurrences can be divided into three groups according to colour, maximum projection sphericity, lechatelierite content, frequency of bubbles and chemical composition: a) those in the area surrounding Radomilce (Southern Bohemia), b) the other occurrences in Southern Bohemia, c) the Moravian occurrences.

The study of a large number of moldavites shows that their colour ranges from green to brown is essentially of five shades: pale green, light green, bottle green, olive green and brown. One additional colour does not chromatically fit into this sequence - a relatively rare special intensive green shade.

In the 1891 the moldavites mounted in gold were displayed and sold as gemstones on General national exhibition in Prague. The material has been cut producing bottle-green stones which may have some resemblance to peridot, but are nearer in hue to green diopside. Cut moldavites have been sold under a variety of fancy and completely misleading names, such as "Bouteillenstein", "Obsidian", "Water chrysolite" and "Pseudo-chrysolite".

# GEM QUALITY RHODONITE, SALT SPRING ISLAND, BRITISH COLUMBIA, CANADA

W.R. Danner, Vancouver, Canada

The pink manganese silicate rhodonite has been known in outcrops on Salt Spring Island and to the northwest on Vancouver Island for many years. About 1950 a new deposit of exceptional gem quality was discovered by Fred Hollings and developed by him about 1960. It sold originally at the quarry for 25 cents per pound and production was worth about $4000 per year. In recent years good quality material from this deposit has been sold by retail dealers for as much as $ 25 per pound. The rhodonite occurs as lenses in a sequence of metachert, phyllite and schist. The exact geologic age of the deposit is unknown but the sequence containing the rhodonite is included within the Sicker Group of Devonian to Permian age. Rhodonite-bearing lenses are up to 15 feet thick and pinch out along the strike. They are underlain by metachert and overlain by metachert, phyllite and schist. A thin layer of hematite schist underlies at least one of the bodies. The rhodonite occurs as irregular bands within the lenses. Rocks overlying the rhodonite are sheared and faulted and contain cataclastic zones and gouge.

The rhodonite is believed to have originated as hot spring deposits on the sea floor forming lenticular mounds of manganese minerals, perhaps largely composed of manganese carbonates and manganese opal. The bodies were later metamorphosed into rhodonite. Still later, intrusions of small plutons and sills have caused some of the rhodonite to become more coarsely crystalline. The rhodonite in most of the deposits is fine-grained pink to bright red in colour and takes a good polish. Associated with it are brown manganese silicates, massive garnet (spessartite), quartz, black manganese oxides veins of neotocite.

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# ON NEW FINDS OF RUBBY AND SAPPHIRE IN THE KARELIAN-KOLA REGION

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Within the Baltic shield, in the North of Finland, there are known commercial alluvial deposits of ruby and sapphire, formed from metamorphogenous sources. In a similar geological environment there were the first finds of ruby in the west of Kola Peninsula. Further study of the distribution of precious corundum in the territory of the Karelian-Kola region allowed to distinquish two more types of corundum mineralization: ruby in the gneisses of the White-sea complex of Karelia and sapphire in the syenite-pegmatites of the Khibiny alkaline massif.

The main features of the first type are the following: 1)rubies are localized in the areas of migmatization of highly aluminiferous gneisses and amphibolites, occuring in paragenesis with kyanite, staurolite, garnet of a pyrope-almandine composition (rhodolite), phlogopite and hornblende. The constant presence of staurolite, rhodolite, kyanite and the cases of their replacement by corundum is a characteristic feature of this paragenesis. 2) Rubies are represented by well-formed prismatic crystals 1-5 cm long and 0.5 - 3 cm in diameter, pink and violet in colour, opaque and translucent, suitable for cutting by cabochon. By its external features and paragenetic association the ruby of this type is close to American amethyst coloured ruby from Cowee Creek deposit (North Carolina). 3)The formation of ruby is associated with the interaction between the injections of pegmatite melt and highly aluminiferous metamorphic rocks in the zones of the activization of karelids of the Baltic shield.

The following features have been recognized for the second type of corundum mineralization: 1) sapphire is confined to syenite-pegmatites occurring in aluminiferous hornfelses of the endomorphic parts of the Khibiny alkaline massif. Among the corundumbearing pegmatites there are distinguished those containing nepheline in their mineral composition and those without nepheline. The former are characterized by the association of sapphire, nepheline, sodolite, lepidomelane, orthoclase with nepheline replaced by corundum. The latter variety has sapphire associated with herzinite, lepidomelane, cordierite, muscovite and orthoclase. 2) In the nepheline varietes of syenite-pegmatites sapphire occurs as crystals of platy and curvi-faced habit, 2-7 mm across, of cornflower blue color, semitransparent, without inclusions. In pegmatites that contain no nepheline, sapphire forms prismatic and tabular crystals up to 2 cm in size, of indigo-blue, light blue or green color, non-transparent or translucent, with inclusions of orthoclase, herzinite, lepidomelane, pyrrohotite and other minerals. By its genetic features and paragenesis this type is most close to sapphire-bearing pegmatites of the Vishnevo-Ilmenogorsk alkaline complex of the Urals. 3) The formation of sapphire is believed to be associated with the action of pneumatolites of alkaline magma on the aluminiferous varieties of the hornfelses in the roof of the Khibiny massif.

## MORPHOGENETIC OCTAHEDRON - CUBE SERIES OF DIAMOND CRYSTALS

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Studies were made of diamonds from various deposits and regions using X-ray diffraction topography, luminescence, UV- and IR-spectroscopy.

The observed external form of diamond crystals usually reflect their last stage of formation, while the internal morphology shows the stages of their growth.

Complex studies of the physical properties and the internal morphology of diamond crystals and their correlation with crystal-morphological and other external readily diagnosed properties made it possible to distinguish the main internal morphological groups of diamonds: table octahedrons, pseudorhombic dodecahedrons, cubooctahedrons, and table cubes.

The picked out groups form a continuous morphological series from octahedron to cube according to the mechanism and growth conditions.

Rounded diamonds observed within this series are forms of growth. The formation of curvifaceted diamonds, according to data on their internal structure, differs from that of the table crystals.

# ON THE MINERALOGY AND GENESIS OF NEPHRITES IN THE USSR

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Nephrites are cryptocrystalline modifications of fibred monoclinic amphiboles having a specific fibro-blasted microstructure. Their hues are from snow-white to grass-green and black. The tone changes (the colour's dominant wave length),respectively from ≈ 574 nm for yellow-tobacco and to ≈ 484 nm for black (dark-blue) nephrites. East Sayan nephrites are most spectra-pure (pure: 32%, bright: 13%). Methods of optics, IK- and EPR-spectroscopy show that nephrite colours depend upon $Cr^{3+}$ and $Fe^{2+}$-ions taking distorted octahedral positions instead of $Mg^{2+}$ions. The striking nephrite viscosity comes from the fibre-blasted microstructure. Some nephrite specimen with a "downlike" structure can withstand a pressure of 12000 kg/cm$^2$ (our data).

Nephrite is formed as a result of infiltration-diffusion calcium metasomathose along the antigorite fibre-blasted serpentinites on the contact with apogabbro or apogranitic alumosilicate metasomatites. The role of granitoid and gabbro dikes is to form halos of recrystallized serpentinites at the exocontact with nephrite-like structures.

The fine-fibrous nephrite structure results from a pseudomorphic-metastable substitution of antigorite serpentinite.Experiments and calculations make clear that the nephrite forming is short and proceeds at ~500-550°C lying with a high chemical potential of calcium and silicium. Analyses of supply-loss have shown that in the reaction zone there is a supply of only Si and Ca. The kinetic data on hydrothermal synthesis of fibrous amphiboles show the latter to synthesize upon a successive reaction with diopside as an intermediate.

The temperature and pressure drop results in the increase of chemical potentials of calcium and sodium in the fluids. In this way there come to be vesuvianite-grossularite and albite chlorite metasomatite associations. The metastable fibroblasted nephrite aggregates are substituted by wide-prismatic tremolite. Nephrite and rodingite transformation processes go with postintrusive hyperbasite mass dislocation into the upper Earth's crust layers along with a large-scale rock serpentinization, listvenitization and an intensive shaling.

Each nephrite formation and transformation stage is characterized by the behaviour of $Fe^{2+}$and $Cr^{3+}$, the main chromophores. At the initial stage of an incomplete serpentinite transformation there the relict chromespinelide grains do practically not corrode. The nephrite colour takes only after the $Fe^{2+}$content and is of grey-green hues. The high-temperature stage decomposes chrome-spinelides and transfers chrome into a silicate phase. This stage is distinct with bright green nephrites. The next stage (regressive) is up with nephrite recrystallization. The metamorphism facies bears it whether there do form fibrous or prismatic amphiboles. High pressures make amphiboles keep a nephrite structure. Peculiarly, recrystallized nephrites are chromophore-free. It runs like the following: the chromespinelide relicts go completely, then chrome is lost from the silicate phase and gets fixed as chrome-grossulars in alumosilicate metasomatites and then iron moves fully. For the tremolite nephrites of this sort one observes a fine-grained structure, the blue-to-light-grey and white hues are typical.

Each of the known nephrite deposits in the USSR characterizes certain stages of nephrite formation and transformation.

# EMERALDS FROM DECILICIFIED PEGMATITES IN BULGARIA

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Metamorphic rocks (gneisses, amphibolites, marbles) in the north-western part of Ryla-Planina which enclose granites are interbedded or cut by mica-bearing oligoclase pegmatites and rare-metal microcline-albite pegmatites. Hybrid derivatives of rare-metal pegmatites are the desilicified pegmatites which cut ultrabasic rocks, metamorphosed to serpentinites, amphibole-chloritic, actinolite-chloritic or talc-chloritic shales. Desilicified pegmatites have zonal structure. On both sides of the central plagioclase zone there are usually symmetrically located the following reaction zones: plagioclase-phlogopite, phlogopite, amphibole-phlogopite,actinolite, chlorite,talc ones. There have been recognized about 50 mineral species and varieties. Besides the principal rock-forming minerals, constituting individual zones, there were recognized quartz,muscovite, fuchsite, beryl, emerald, chrysoberyl, orthite, columbite, samarskite,yttrotantalite, uraninite, cyrtolite, monazite xenotime, apatite, garnet, rutile, titanite, clinozoisite, gagnite, fluorite, magnetite, ilmenite, hematite, chromite, pyrite, pyrrhotite, galena, chalcopyrite, molybdenite, bismuthinite, bismuth, bismutite, calcite, thomsonite, lomontine,etc.

Beryl occurs predominantly in the plagioclase and plagioclase phlogopite zones in association with quartz, apatite and garnet. The most common forms are m $\{10\bar{1}0\}$, c $\{0001\}$ ; much more rare are s $\{11\bar{2}1\}$ , p $\{10\bar{1}1\}$ , a $\{11\bar{2}0\}$ , 1 $\{21\bar{3}0\}$ . Besides single crystals 1-2 cm to 10-15 cm long and 1.5-2 cm across there occur subparallel intergrowths, radial and sceptre-like aggregates. The colour of beryl varies from light - blue to green and emerald-green colouring are emeralds in the plagioclase-phlogopite and phlogopite zones. Beryls from the desilicified pegmatites belong to the group of alkaline beryls containing $Na_2O$ - 0.9 - 0.95% $K_2O$ - 0.07 - 0.12%, $Rb_2O$-0.2-0.3%, $C_2O$ - 0.055 - 0.077%. Emeralds have higher contents of MgO - about 1% and $Cr_2O_3$ - 0.03 - 0.04%.

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# GEMSTONES IN THE PEGMATITES OF HINDUKUSH,SOUTHERN PAMYRS AND WESTERN HIMALAYAS

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In the mountain systems of the folded frame of the Hindustan shield there are widely spread pegmatites, which have been the sources of gemstones since times immemorial. There are distinguished two pegmatite formations containing gemstones: a)rare-metal pegmatites at medium depths with kunzite, tourmaline, aquamarine, vorobievite; b) deep-seated desilicified pegmatites with sapphire, ruby and dravite.

Pegmatites of different formations greatly differ by their geologic position, age and conditions of formation, this in turn determining the spatial location of deposits and occurrences of gemstones. The deep-seated pegmatites occur among the protrusions of Precambrian foundation, the rare-metal ones mainly in the sequences of Paleozoic and Mesozoic age and in the folded frames of the protrusions.

Gemstones of rare-metal pegmatites are formed at the final stages of the pegmatite process by direct crystallization from pegmatite melt-solutions; sapphire and ruby are formed in the process of metamorphogenous transformation of granite pegmatites (diaphtoresis of granulite substratum under the conditions of amphibolite facies).

Hindukush, Southern Pamyrs, Western Himalayas constitute the largest province of pegmatites with gemstones. By the scale of pegmatite occurences and the complement of gemstones this province is unique and greatly excels other regions. Finds of deep-blue, violet and pink corundum crystals in the south-western Pamyrs, great similarity of Pamyrian corundum plagioclasites to the well-known sapphire deposits in the Himalayas permit regarding the south-western Pamyrs as a new promising region in our country for prospecting jewel-stone varieties of natural corundum.

# FORMATION CONDITIONS OF CHAROITE ROCK-NEW STONES FOR JEWELLERY AND CARVING

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A deposit of charoite rock is localized in the potassium alkaline syenites of the Murun massif (Aldan) of Mezosoic age, which cuts through Archean schists in the southern part, and Cambrian marly limestones and dolomites in the northern part. The following rocks have been recognized as composing the massif: sheets of pseudo-leucite trachytes of limited extent, nepheline,calcilite,pseudo-leucite,aegirine syenties that compose the principal part of the massif, dykes,veins of alkaline pegmatites,pseudo-leucite tinguaites,solvsbergites,grorudites, aegirine granites.

In the zones of tectonic dislocations there are manifested three stages of metasomatosis replacing each other in time:potassium (anorthoclasites),potassium-calcium (charoites),sodium one (aegirinites).Potassium metasomatosis is of areal extent; it resulted in the formation of fine-grained,white,sugar-like rocks--anorthosites.Potassium-calcium metasomatosis was widely manifested,over the anorthoclase of host rocks there developed tinaxite,hydrocanacite and charoite.At this stage there were supplied,besides potassium and calcium considerable amounts of iron titanium that concentrated in tinaxite,as well as of strontium, barium,fluorine and water found in hydrocanacite and charoite.

The temperature of mineral formation at this stage,about 400°C, was determined from gas-liquid inclusions in tinaxite.There is noted a zonality in the distribution of minerals,tinaxitization being developed most widely,while charoitization spread locally. In the external parts of the aureole there are 5-10% of charoite, in the internal parts 50-90%,and within small intervals there occurred the formation of almost monomineral charoite rock--charoitite.Charoitization is developed most intensely in syenites,syenite-porphiries,to a lesser degree in schists and quartzites.

At the stage of sodium metasomatosis sodium and iron were most active,this having resulted in the formation of mpnomineral rocks-aegirinites.

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# TWO TYPES OF BERYLLIUM PEGMATITES WITH GEMSTONES IN NORTHERN MORAVIA, CZECHOSLOVAKIA

J. Stanek, Brno, ČhSSR

In Northern Moravia there occur types of pegmatites with gem-stones. To the first type belong syntectonic pegmatites with parallel texture which lie alongside Varian structures. To the other group belong posttectonic pegmatites which discordantly intrude Varian structures.

The mineralogical composition of the first type includes albite, quartz, muscovite and sillimanite, without any potassium feldspar. Chrysoberyl is a typical mineral of this type. Beryl is very rare, other beryllium minerals are absent. Well differentiated zonal pegmatites with a strongly developed albite zone belong to the other type. Beryl of two generations occurs in these pegmatites. Beryl of the first generation is yellowish of large size, associated with potassium feldspar. The other is smaller, occurring as aquamarine together with sugar-like albite. Aquamarine developed from the recrystallization of yellow beryl. Of other beryllium minerals there were recognized bertrandite, bavenite, euclase and milarite. Chrysoberyl is very rare in this type of pegmatites.

# GEM STONES IN YUGOSLAVIA

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The gem stone deposits in Yugoslavia have not been studied systematically until very recent. And still there is a number of gem stones in Yugoslavia, which have not become known everywhere.

Extremely large beryl crystals were found to occur in the muscovite-microcline stripless pegmatites in granitic rocks of Zhelin, Bukul, Tsera etc. as well as in metamorphic rocks of Serbyan-Mackedonian Massif. They are presumably non-transparent, semitransparent and fissured, being seldom suitable for faceting. It is only in pegmatites from Bukul and Tsera (west Serbia) that there occur individual aquamarine crystals ofjewelry value.

The metamorphic rock complex contains: a) jewelry kyanite from the quartz-kyanite veins of crystalline schists of Pelagonsky and Serbian-Mackedonian Massifs ( in the vicinity of Prokuple city); b) rubies as individual frequently very large but non-transparent crystals and aggregates in dolomitic marbles in the vicinity of the city of Prilepa (Mackedonia); c) the mountain crystal, smoky quartz, citrine, ametyst and hyalophane from Alpine-type veins in Busovach deposit (Central Bosnia) as well as smoky quartz, mountain crystal and adular from the same veins near the city of Kotchani and Byerovo (Mackedonia).

The following gem stones are associated with volcanogene rocks within the Serbian-Mackedonian neoalpine autonomous activation zone: a) precious opal,semiopal and jasper of hydrothermal genesis from the joints and cavities in volcanites of Kratovo - Zletov district (Mackedonia); b) chrysolite in the form of porphyry phenocrysts and granular aggregates in alkaline olivine basalts in eastern margin of Vardarsk zone (South Serbia and Mackedonia); c) ametyst in the form of crystals and druses of hydrothermal genesis from mineralized fractured zones of Pb-Zn Letse deposits (Serbia), Zletovo (Mackedonia) and

from dacite-andesite zone in Blagodat-Sasi (East Mackedonia). The ultrabasites from the inner Dinarides and Vardar zone contain chrysoprase of opal chalcedony composition (in the nickeliferous Crusts of weathering near Ligi, Vrnyachka, Banya, Prishtine. The best chrysoprase of jewelry value is found in Golesh Massif area (near the city of Prishtini).

In the mines near granite and metamorphic rocks there occur rubies, sapphire, beryl, aquamarine, kyanite, almandine of jewelry value. There also occur large deposits of jewelry gem stones and stones of industrial importance, such as rhodonite, amasonite, precious serpentinite, jasper, agate, obsidian, epidote,etc.

# ELECTRON PROBE MICROANALYSIS
# IN MINERALOGY

# ON SOME SOURCES OF ERRORS IN X-RAY SPECTRAL MICROANALYSIS OF NON-CONDUCTING OBJECTS

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The modern practice of quantitative X-ray-spectral microanalysis of non-conducting objects calls for a simultaneous spraying of a thin layer of metal or carbon over the surfaces of studied specimen and standard for the removal of a local charge that arises in the object at bombardment with electrons. A criterion of the optimum thickness of film is considered to be the stable position of a probe on the surface and negligible losses in the film of the intensity of X-rays leaving the object. In a number of papers there were analysed errors of measurements of relative irradiation intensity *resulting from absorption by film.* However, no attention has been paid so far to the fact that the sprayed film changes the coefficient of the inverse reflection of electrons. For taking account of this effect, it is necessary to take, for the correction of atomic number, not a mean atomic number of the specimen Z but an "effective" atomic number:

$$Z_{eff} \sim d^*Z^* + (d\ (E) - d^*)\ \bar{Z}\ ,$$

where $D^*$ and $Z^*$ are the thickness and atomic number of the film material, $d(E)$ is the depth of electron penetration. It should be emphasized *that* $Z_{eff}$ *depends on the acceleration* potential, this dependence being greater at low potentials. For the evaluation of errors caused by this effect in olivines ($\bar{Z}$ = 11.5 - 11.8), enstatite: ($\bar{Z}$ = 11.3 - 11.5), nepheline ($\bar{Z}$ = 11.4) and copper ($\bar{Z}$ = 29) there were sprayed carbon films of different thickness, and currents were measured across specimens at different acceleration potentials in the range of 5 to 50 kV. Using the dependence of current across the specimen on the atomic number, it was found that at the acceleration potential of 15 kV for copper $Z_{eff}$ was 25.5, and for olivine 8 and 15 for films of different thickness. A neglect by this effect results in considerable errors when corrections for the atomic number are made. It should also be noted that in using the published program of making corrections in quantitative microanalysis, account should be taken of the specificity of preparation of non-conducting objects for analyses at a given laboratory.

Another source of errors in quantitative microanalyses of semiconductors and dielectrics is the change of the energy of electrons incident on the specimen caused by a local charge. Using the technique of measurement of the energy change in incident electrons there were investigated some natural minerals and synthesized monocrystals. The results of the measurements are given in Table 1.

Table 1

| *Specimen* | | *Standard* | *Anal.line* | $E_q$*,kV* | E, *keV* |
|---|---|---|---|---|---|
| $PbGa_2S_4$ | | GaAs | Ga$_\alpha$ K | 10.4 | 0.20 |
| $Sm_7Ga_5O_{12}$ | [110] | " | " | " | 0.20 |
| $Sm_7Ga_5O_{12}$ | [001] | " | " | " | 0.18 |
| $Sm_7Ga_5O_{12}$ | [111] | " | " | " | 0.10 |
| *Olivine* | | *Fe* | FeK $_1$ | 7.11 | 0.20 |
| Enstatite | | " | " | " | 0.10 |
| Nepheline | | " | " | " | 0.25 |
| Chromite | | " | " | " | ~/20 |

The neglect by the change in electron energy can result in the measurements of the analysed specimen and standard at different acceleration potentials, leading to considerable errors in the determination of the content of elements. Thus, in measurements of a $PbGa_2S_4$ specimen at the acceleration potential of 15 kV the relative error in the determination of gallium on the GaK$d_1$ line will be about 20%, while the difference in the energy of electrons incident on the specimen and standard will be only 0.2 kV.

## INFLUENCE OF ELECTRIC CONDUCTIVITY OF MINERALS ON MICROPROBE

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The microprobe analysis of typomorphic minerals must be especially precise and sensetive when it comes to studying the dependences of stoichiometric features on the forming conditions. For example, a definition of the temperature of arsenopyrite formation (precision - 50°C) demands 0,5% rel. precision in determination of As and S. As it had been shown in our previous work , the conductive coating of a sample does not wholly preclude the influence of the negative volume charges, accumulated in the region of probing. Its effect is translated in decreasing depth of electron penetration, in a redistribution of the current of the absorbed electrons between the sample proper and the coating (the latter receives more) and in a drop of the working voltage E by a $\Delta$E value. The relative value $\Delta E/(E-E_x)$ depends on the energy of excitation in the series, where the analytical line $\lambda_x$ to the examined element belongs. If not considered and corrected, this effect may result in overestimating the contents of the elements with small $E_x$ (S in sulphosalts, Si in silicates, Pb in polarite, etc.), the total being understated. For instance, in sphalerite having a low conductivity, the total value drops to 92% and the atomic content rises by 8% as compared to that of a conductive sample. In a scheelite analysis the nominal working voltage E=20 kV dropped to such extent that tungsten's series did not excite ($E_x$ = 12 kV). CaK$\alpha$ and WM$\alpha$ analyses with $CaF_2$ standards misrepresented the Ca-W correlations. The present work gives the results of an experimental study of isochromates of a characteristic X-ray mineral spectrum compared to standards. We have elaborated a technique of finding corrections taking into account the displacement of isochromates (depending curves of specific intensity of the analytical lines v. voltage). This technique consists of a comparison of isochromate of the conductive standard with the hypothetic line of the sample. Then the first approximation of a displacement must be found as well as the hypothetic specific intensity of the standard, the displacement being considered. The iterative fits when there is a fitting for concentrations in successive approximations. This method is proved to be effective in analyses of chalcopyrite, fahlore, famatinite, emplektite, magnetite garnet and chromite. The decrease of the electron penetration is experimentally proved in analysis of corundum in comparison with Al 100% by isochromates ALK$\alpha$, ALK$\beta$, $ALK_{short}$ and $ALK_{long}$ ("short" and "long" refer to the wave length on both sides of K-edge of the Al absorption.

## DEPENDENCE OF X-RADIATION INTENSITY ON ELECTRON INCIDENCE ANGLE

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The method of a quantitative microanalysis at the arbitrary incidence angle of an electron probe onto a sample plays an important role when studying admixture contents on various faces of minerals by means of an X-ray spectrum microanalysis. To work out such methods there has been carried out a theoretical and experimental study of the characteristic radiation intensity dependence on electron incidence angle to the sample.

The calculations carrried out on the basis of ZAF technique take into account the energy distribution of the non-elastically reflected electrons which were obtained on the basis of experimental distribution for transmitted electrons, there have been determined expressions for R-backscattering factor as well as for $\Phi(\rho z)$-function of depth distribution of an ionization number in a massive sample at an arbitrary angle of an electron probe incidence on a sample. The $\Phi(\rho z)$ expression is then applied to modification of Philibert's absorption function.

There has been designed an attachment to a microanalyzer to study experimentally the dependence of X-radiation intensity upon an incidence angle. The attachment provides the change within a wide range of an electron incidence angle onto a sample while an X-ray take-off angle being kept unchanged.

# PECULIARITIES OF THE TECHNIQUE OF QUANTITATIVE MICRO-X-RAY-SPECTRAL ANALYSIS OF TANTALO-NIOBATES AND STANNOUS TANTALATES

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Local X-ray spectral analysis (LXRSA), being very laboursome requiring lengthy calculations, calls for the use of an electronic computer (EC) or for the simplification of calculation formulas, so that the whole procedure is reduced to elementary measurements according to previously prepared diagrams. In the first case, the maximum effectiveness is attained when an EC is available directly in the LXRSA group. In the second case, special calculations, which would give grounds for use of approximation formulas are needed for the discussed system.

The present paper shows that for tantalo-niobates which contain such oxides as $Ta_2O_5$, $Nb_2O_5$, MnO, FeO, $SnO_2$, the technique of graphic determination of the correction factor "F" which takes into account the interaction between electrons and X-ray irradiation and the substance of specimen and standard may be recomended.

The technique is based on the use of approximate definition of "F" in an N-component system, suggested by Lachance and Traill:

$$F_i = 1 + \sum_{j=1}^{N} \delta ij \quad C_j$$

where $\delta$ ij is the tangent of the inclination angle of linear function $F_{ij}$ from concentration $C_j$ in a binary system $i = j$ These quantities for the oxide pairs in tantalo-niobates have been calculated by the method of I.B. Borovski and V.I. Rydnik for the acceleration potential of 20 kV and for two angles of departure of X-rays from specimen ($20^\circ$ and $40^\circ$). $F_i$ for a corresponding oxide is determined by graphic summing according to previously prepared diagrams containing families of lines. The possibility of approximation of $F_j(C_j)$ by a linear function depends on the absence of a correction for fluorescence in the discussed system.

The suggested technique has been approved in tests on different model compositions. It has been found that the relative difference between $F_j$ found by the graphic method and that of calculated by EC according to the method of I.B. Borovski and V.I. Rydnik does not exceed 3% being less than 1% in the majority of cases.

The time expended for the determination of all $F_i$ in a five - component system does not exceed 5 min., which is comparable to the time of $F_i$ calculation by a PDP-8F EC (about 1 min.).

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# ON MINERAL HEATING WITH ELECTRON PROBE

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For temperature estimation of the samples under the action of the electron probe, a method taking into account heat generation in a cylindrical volume is proposed.

The radius of the cylinder is taken equal to the probe size on the sample surface plus the lateral path of electrons, and the height is taken equal to the depth of complete penetration of electrons into the substance. The method allows to calculate the temperature distribution by the depth, and to find the minimum thickness of the polished section at which no melting of the resin pasting the sample to the slide takes place.

For various working conditions the heating temperatures for 43 minerals with known thermophysical characteristics have been calculated. By the data obtained, a simple empirical formulae has been derived and the ways of heating sample reduction has been determined.

# DETECTABILITY LIMITS AND THE MINOR AND TRACE ELEMENT ANALYSIS OF ROCK-FORMING MINERALS USING AN AUTOMATED ELECTRON MICROPROBE

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Trace and minor elements in some-rock-forming mineral systems (olivines, pyroxenes, Fe-Ti oxides, feldspars, etc.) are important indicators of their host rock petrogenesis. Their concentrations and their intraphase distributions can provide constraints on parental magma composition, temperatures of crystallization from the melt, cooling histories, subsolidus equilibration temperatures and pressures, diffusion rates, etc.

We have developed criteria for the dtermination of minor and trace element abundances in conjunction with routine, on-line mineral analysis and have incorporated these criteria in a subroutine for minor and trace element analysis. Variables include accelerating potential, beam current, analysis time, and number of replicate analyses. Matrix effects are unimportant at low concentration levels; however, corrections for the x-ray continuum are important and great care must be exercised in determining and correcting for this contribution to the signal.

Selected results, summarized in Table 1, indicate that we are able to detect and quantitatively analyze certain elements in concentrations as low as a few tens of parts per million. Each value is for a single analytical point. Errors are calculated from counting statistics at the 99% confidence level, and give an indication of the precision of an individual analysis.

Table 1

| | | n = 2 | n = 12 | n = 24 | Independent Analysis |
|---|---|---|---|---|---|
| Olivine<br>(B58) | Ni | C 3224 ± 748 (ppm)<br>$C_{DL}$ 1084 (ppm) | 3227 ± 19<br>28 | ---<br>--- | 3140<br>(E.S.) |
| Pyroxene<br>(B168) | Cr | 2861 ± 902<br>1276 | 2850 ± 18<br>25 | | 2942<br>(E.S.) |
| Plagioclase<br>(Lake County) | Fe | 2987 ± 24<br>37 | 2987 ± 14<br>18 | 2989 ± 7<br>11 | N.A. |
| Green Glass<br>Sphere, 15426 | Ni | 170 ± 194<br>285 | 168 ± 11<br>16 | ---<br>--- | 170<br>(E.S.) |
| Orange Glass<br>Sphere, 74220 | Ni | 20 ± 885<br>1301 | 23 ± 12<br>17 | ---<br>--- | <5<br>(E.S.) |

Analytical conditions: 30 kv and 1800 μamps beam current.

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# QUANTITATIVE MICROPROBE ANALYSIS OF SODIUM IN SEVERE ABSORBING MATRIX. THE EFFECT OF THE ACCELERATION POTENTIAL

**J.G. Ronsbo, Copenhagen, Denmark**

Quantitative microprobe analyses of vitusite ($Na_3(Ce,La)(PO_4)_2$) from the Ilimaussaq alkaline intrusion (South Greenland) are presented with special attention to the sodium determinations. The microprobe results are compared with the results of wet microchemical analysis.

The sodium determinations have been performed using acceleration potential from 4.0 to 25.0 kV. The results show clearly that the calculated sodium content depends on the acceleration potential level when using common ZAF-correction procedure, i.e. when the absorption correction is based on the simplified Philibert formula. For the two mentioned acceleration potentials the calculated sodium content is 17.05 and 19.60 wt% Na, respectively. The results of the wet microchemical analysis is 17.20 wt% Na.

The sodium contents distinct dependence on the acceleration potential level is substantially reduced by applying the full Philibert formula in the absorption correction. This change allows the surface ionization to be calculated.

In the present investigation, the surface ionization has been calculated by using the empirical expression $R_o = 1 + 2.8 (1 - 0.9/U)$, as proposed by Reuter.

The results for applying the complete Philibert formula in the absorption correction are presented for different expressions of sigma and h.

# APPLICATIONS OF ENERGY DISPERSIVE ELECTRON MICROPROBE ANALYSIS IN STUDY OF MINERALS

D.G.W. Smith, Edmonton, Canada

Si(Li) detectors for electron microprobes have been commercially available for about a decade. However, only recently has the analytical potential of such instrumentation started to become widely recognized. The principal advantages of energy dispersive analysis (EDA) are convenience, cost and speed. Because of the stability of a well maintained and adjusted EDA system and its extreme simplicity of operation, it may be used with complete success by persons with little or no training in microanalysis. The cost of a complete energy dispersive spectrometer is still a fraction of that of a fully equipped wavelength dispersive system capable of performing comparable analyses in the same period of time. EDA permits the entire X-ray spectrum to be sampled at one time and hence all elements to be determined simultaneously. This feature, coupled with the extreme system stability and insensitivity to wear and tear (because there are no moving parts) works towards improved speed, precision and accuracy. Sensitive samples that are relatively easily degraded by an electron beam, such as zeolites, feldspars, clays and carbonates, can usually be more successfully analysed by EDA. This is so because the probe current can often be reduced by more than an order of magnitude relative to that required in wavelength dispersive analysis (WDA), as a result of the high detector collection efficiency. Also, in many situations, the beam can be defocussed, or rastered over a small area. This reduces damage by decreasing the electron flux/unit area, without causing the spectrometer defocussing effects that would result in WDA. This is also an advantage when obtaining X-ray scanning images by EDA.

Used in the simplest fashion, EDA is an invaluable asset in mineral identification, distinction between several possible species or varieties often taking only a matter of seconds. In a similar way it can prove invaluable in the accurate petrographic description of rocks. An extension of this qualitative role, using a computer to control instrument operation and process data, permits accurate, automated, modal analysis to be carried out in a manner analogous to the point counting procedures of optical microscopy. In compositionally simple mineral series such as the alkali feldspars or the olivines, semi-quantitative determinations, at least as accurate as those obtained by all but the most elaborate and time-consuming optical techniques , can be made in less than a minute, using only a desk calculator to process data.

Rapid and fully quantitative EDA of a wide range of minerals, has been made possible by recent advances in instrumentation and the development of sophisticated computer software. The accuracy achievable for major and minor elements is comparable to that of the well established WDA. Detection limits as low as 0.05% can be routinely achieved for most elements, although accuracy falls off seriously at these low levels. The core of a successful and versatile procedure for quantitative EDA is the data reduction program. In addition to integrating peak intensities and making full matrix corrections (atomic number, absorption, characteristic and continuum fluorescence), such computer software must accurately calculate sample background throughout the spectral energy range, strip escape peaks, make deadtime corrections, deal regorously with complex overlap possibilities determine system resolution, correct for miscalibration in the energy of spectra acquired and take into account any fluctuations in probe current during analysis. Necessarily, software which can perform all these tasks satisfactorily is rather large and complex and few suitable programs are available. The FORTRAN IV program "EDATA" has been designed for this purpose and has been tested in continuous use over a period of nearly three years. The program has been slightly modified by one Canadian laboratory using overlaying techhiques and disc storage, to operate on a dedicated mini-computer that also exercises simultaneous operational control over two microprobes and an X-ray fluorescence analyser.

# ELECTRON MICROPROBE ANALYSIS OF CLAY MINERALS

D.G.W. Smith and P.A. Cavell, Edmonton, Canada

Clay minerals, a particularly widespread and abundant group, have remained virtually unexplored by electron microprobe analysis perhaps because of the numerous analytical problems that are encountered. A microprobe mount should be flat, solid and conductive. Fine grained powdered materials, such as clay, cannot be made conductive by the deposition of the usual carbon film. Clay minerals have variable $H_2O$ and (OH) contents and these species cannot be analysed by the microprobe; they may be calculated on various criteria during data processing. Impurities such as quartz and feldspar, are commonly mechanically mixed with clays and must be excluded to obtain the true clay mineral composition. Clays can readily adsorb and exchange various ions and thus are sensitive to the preparative treatment preceding analysis.

The analytical procedures described below were developed using samples of the A.P.I. reference clays. These have been extensively characterized previously (A.P.I. Research Project 49). The $<1$ µm size fraction is obtained by standard setting techniques following disaggregation in distilled water and dispersal with a known and controlled amount of $(NaPO_3)_6$. A portion of this size fraction is mixed with a known amount (normally 10-20 wt%) of colloidal graphite. This mixture is deposited on a porous ceramic disc using a specially designed suction apparatus. After being washed with distilled water, sample discs are removed, allowed to stand for 5-10 min., inverted on a fluorotelomer-coated glass slide and left to air-dry completely. The resultant samples are electrically conductive, flat and ready for analysis.

The clays are analysed by energy dispersive techniques while rastering the electron beam over an area of approximately 125x 125 µm$^2$. A single analysis for 22 elements (Na-Zn incl., plus Zr & Ba) is carried out in approximately 500 sec. and the data then transferred to casette tape for subsequent computer reduction. Samples are not damaged by analysis and thus may also be used for X-ray diffraction investigations, should these prove desirable.

The FORTRAN IV computer program "EDATA", corrects raw analytical data for background, overlap, escape peaks, etc., and for all ZAF (matrix) effects. The effects of the known amount of graphite present are computed by assuming homogeneity. The water content of the clays is determined by difference. Opportunities are provided for an $Fe^{2+}:Fe^{3+}$ ratio to be inserted into the program, along with any available information on the concentration of other elements, such as Li, which may be present but which cannot be analysed. Additional corrections are applied for any impurities in the colloidal graphite and for phosphorus which most clays absorb to some extent from the dispersant.

A test of the precision of the method was carried out on 20 separately prepared discs of the well known Fithian illite. Two areas on each disc were analysed and the results treated statistically. The average result from the 40 analyses is given below in element wt%, after recalculation water, carbon and phosphorus free to 100%. Standard deviations (SD) for the group of analyses and standard error (SE) for the average result are also shown: Na=0.07, SD=0.04, SE=0.01; Mg=1.46, SD=0.03, SE=0.004; Al=14.17, SD=0.06, SE=0.01; Si-25.96, SD=0.06, SE=0.01; K=5.65, SD=0.04, SE=0.006; Ca=0.86, SD=0.05, SE=0.008; Ti=0.46, SD=0.03, SE=0.004 Fe=4.60, SD=0.06, SE=0.01; O(calculated)=47.76, SD=0.03, SE= 0.004; P(adsorbed)=0.50, Sd=0.04, SE=0.006. Inter-and intra-sample variances were not found to be significantly different.

The technique outlined above has now been successfully applied to a wide range of other clays including members of the kandite, smectite and palygorskite groups. It should have many applications in clay mineralogy including mineral identification, the study of diagenetic processes producing and modifying clays, investigations of variations in clay mineral compositions within and between different sedimentary environments, and the study of the mechanical behaviour of clays in different natural environments. Beyond the earth sciences, there are many potential applications in fields such as soil science, forensic science and ceramics. The general technique for preparing and analysing powdered samples by means of the microprobe may well be applicable in a much wider sphere.

## THE ARSENIDES STUDY BY ELECTRON MICROPROBE ANALYSER

B.Fojt, Brno, CSSR

The deposit Zálesí in Silesia (ČSSR) is the representative of the so-called "five-element association" of the Jáchymov type. In its second development stage the arsenides of iron, nickel and cobalt can be found here as predominant mineral components.

The zoned development, the microscopic alteration of components near one another by their behaviour in the reflected light,fine intergrowths and metasomatic phenomena did not enable to carry out research by classical methods. Therefore, the electron microprobe analyser was successfully used for the solution of the paragenetic problems.

The obtained results allowed one to make a skeleton reconstruction of the chemism of the crystallization surroundings and its development as the complex of mono-, di- and triarsenides are concerned. The general development of the chemismus is characteristic of the decreasing influence of Ni and As towards the crystallizationally younger components. In the connection with this phenomenon the role of Co and especially of Fe and S relatively increases which is indicative of the passage to the latest sulphide stage. Based on quantitative observation of the elements in polymineral zoned layers is the opinion on the character of metasomatic phenomena and newly originated reactional combination of the given system Fe-Ni-Co-As-S.

## APPLICATION OF ENERGY-DISPERSIVE SPECTROMETER FOR THE X-RAY ELECTRON PROBE MICROANALYSES (EPMA) OF MINERALS

I.G. Lyapitchev, A.G. Sysoev, Leningrad, USSR

Methods of X-ray EPMA for the quantitative analysis of complex specimens with energy-dispersive spectrometer (EDS) proposed by some authors (F.H. Schambler, C.E. Fiori et al.) have some peculiarities: for getting reliable intensities, it is necessary to know some parameters depending on particular characteristics of EDS and to give solid state analytical conditions.

In the All-Union Geological Institute there was developed method of EPMA for silicate minerals, independently, on particular peculiarities in EDS. The results of testing the EPMA on a number of minerals are presented.

## ELECTRON MICROPROBE DETERMINATION OF TRACE ELEMENTS IN MINERALS

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The dependence of the detection limit for various elements on different microanalytical conditions was investigated.

Minimum limit of detection for Na was obtained at electron beam energy 5-10 keV. For a number of elements from K to Zn the minimum limits of detection are within 18-23 KeV. Rb, Y, Zr (analytical L-lines) have minimum limits of detection at the electron beam energy 10-15 KeV.

The investigation was carried out by electron microprobe JXA-5A (JEOL). The data involving the dependence of the detection limit on the analytical conditions were compared with theoretical computations.

Explanation of various detection limits and suitable conditions of the trace element microanalysis are suggested.

## MICROPROBE ANALYSIS OF THE PLATINUM GROUP MINERALS

I.P. Laputina, Moscow, USSR

The correctness of microprobe analysis acquires a particular value while exploring the composition of the platinum group minerals, their stehiometry and the limits of the isomorphic substitution. The essential distinction of values of the mass attenuation coefficients in the longwave range of spectrum according to different authers, the influence of the atomic number and fluorescence by characteristic lines for a lot of combinations of the elements bring significant uncertainties in the accuracy of the measured concentrations.

One can explore the influence of these factors only with the help of specimens of definite compositions. For this, some artificial specimens were selected in which the effect of the absorption of the atomic number and fluorescensence due to characteristic lines were great. The compositions of the binary alloys in the systems Pt-Rh, Pd-Sn, Au-Ag and in the specimens PdAg, AuPd(40), PtS, Pt(Fe,Ni,Cu) were studied; accelerating voltage was from 7 to 30 kv. The calculations were carried out according to Z A F program with different values of the mass absorption coefficients and of other parameters. A plot of k/c as a function of k for each measured x-rays line shows the precision of single measurements. Plottings of experimental intensity ratios (as well as the calculating concentrations of the measured elements and the values of corresponding corrections) as a function of accelerating voltage were performed for each alloy. The differences between $c_{cal}$ and $c_{tr}$ give an indication of the accuracy of the theorethical correction procedures which are widely used at present.The plot of the ratio $I_{sp}/ I_{st}xii_{sp}/ i_{st}$ as a function of $E_o$ was extrapolated to the excitation potential. This allowed to determine one more value of concentration of the elements in the specimens.

The investigations were carried out with the Electron Microprobes having 18°,40°,75° take-off angles. The correction values for the absorption, the atomic number and fluorescence for the same specimen differ from one Electron Microprobe to the other. The comparison of the results permits to determine more correctly the contribution of the separate effects into the summary mistake of the measuring concentrations and to establish optimum conditions to analize minerals of the platinum groups with different compositions.

## COMPLEX MICROPROBE AND SPECIAL MICROSCOPIC INVESTIGATION OF HIDDEN CRYSTAL INCLUSIONS

O.B.Dudkin, L.I. Polejaeva, J.A. Pachomovsky, Apatites, USSR

The microprobe and special microscopic analysis of one and the same polished specimens carried out in turn allow one to decipher the composition of crystallitic aggregates with the large degree of accuracy. The microprobe investigation of specimens was carried out with the electron microprobe analyser MS-46.

The complete quantitative chemical composition was calculated with the computer "Nairy-2". Microscopic investigations (magnification up to 1500) were fulfilled in dark field with crossed nicols (reflected light) with the microscope Nu-2 and intense sources of light. Under these conditions the form, size, transparence, colour, double refraction of mineral particles and at the same time the trace of the electron probe were observed.

In this work the complex phase composition of the apatite-francolite inclusions in the carbonatites was deciphered, the apatite-orthoclase inclusions in the lujavrits were determined and the presence of micro-inclusions of the apatite in the rock-forming silicates of the Hibiny rocks was proved.

## FLUORESCENT EXCITEMENT EFFECT IN THE DEFINITION OF ELEMENT CONCENTRATIONS IN INTERGRANULAR CONTACTS

A.I. Tsepin, Moscow, USSR

As a distinction from the primary X-radiation excited in a limited volume (several mcm$^3$) the secondary (fluorescent) radiation is usually excited in greater volumes and farther away from the point of incidence of the electron beam (up to 100mcm and even more). When one analyses homogeneous lengthy minerals, the two above-mentioned types of radiation are excited in the investigated mineral. In this case the contribution of fluorescent radiation in total intensity of analytical line can be calculated by means of putting the correction factor related to the characteristic fluorescence.

However, when small inclusions of one mineral in another are analysed, or when measurements are done near the contact of different minerals, it may be possible that the primary radiation is induced only in the mineral under study, whereas the secondary one - in the neighbouring mineral as well. The correction programm does not take into account the above mentioned additional radiation from the neighbouring mineral. The smaller are the analysed grains and the nearer is the sampling point to the minerals contact, the greater is the additional radiation. The neglect by the additional radiation may lead to considerable errors in the determination of the element concentrations. It is especially important when studying diffusional redistribution of the elements between the minerals in contact.

In this article there are found quantitative contributions of the fluorescent radiation for a number of elements ($FeK_{\alpha}$, $CuK_{\alpha}$, $ZnK_{\alpha}$, $CaK_{\alpha}$, $AuL_{\alpha}$, $BiL_{\alpha}$, etc.) in various mineral combinations and for different distances of the analysed point from the mineral boundary. For example, the fluorescent radiation of the FeK line for tennantite-pyrite contact gives an apparent rise of the Fe-concentration in tennantite up to 1.5 w.p.c.

Diffusion in fahlerz contacts with other minerals (pyrite, chalcopyrite, sphalerite, bornite, etc.) has been studied as subject to the mineral forming conditions. There also have been calculated contributions from diffusion and fluorescent excitement into the patterns of redistribution of the elements between the mentioned minerals.

## AUTOMATIC QUANTITATIVE ANALYSIS OF MINERALS USING Si DETECTOR AND CAMAC INSTRUMENTATION

J.C. Rucklidge, Toronto, Canada

A basic ETEC AUTOPROBE consisting of X-Y-Z stage, refracting optical microscope, electron gun and column and KEFEX Si X-ray detector has been interfaced to a PDPII/10 mini-computer through CAMAC interface modules. The Si detector is mounted in a position normally occupied by a crystal spectrometer, and is thus able to approach the specimen very closely. In this position extreme sensitivity is obtained, giving 3000 cps from the detector at probe currents of about 10$^{-10}$A. Sample damage and diffusion of alkalies due to beam loading is thus effectively eliminated. Suites of points for analysis can be pre-selected and stored in a disc file which is subsequently replaced and the data collected automatically. Data are reduced on the minicomputer by a sophisticated program Smith a. Gold, 1976 specifically designed for data from Si detectors and applied to mineral compositions. High quality analyses are obtained for 22 elements for each point. The ease of acquiring quantitites of the data easily allows trends to be seen and statistical tests to be made of geological materials.

# ON THE TECHNIQUE OF QUANTITATIVE ANALYSIS OF OXYGEN IN SOME GROUPS OF MINERALS

A.S. Avdonin, N.I. Chistiakova, V.S. Soloviev, Moscow, USSR

The quantitative analysis of oxygen is often necessary in the study of minerals. The determination of this element along with some others, was carried out on iron minerals (magnetite, hematite, goethite), tin (cassiterite, hydrostannates) molybdenum , on quartz, uraninite and others, with the aid of a "Camebax"microanalyzer.

Principal problems of the analytical technique are discussed. Specimens were sprayed with copper. The assessment of the amount of relaxation of $K_\alpha$ oxygen line ( $\lambda = 23.6 \mathring{A}$ ) in the sprayed layer was done on the line $TiL_\alpha$ ( $\lambda = 27.39 \mathring{A}$ ). The value is 10-15%. The coefficient of intensity variation for the most remote areas of the sample is within 0.7 - 1%. There was recognized no displacement of the maximum for lines in the spectrum for the listed minerals. The optimum operation potential was 10-15 kV, probe current - 70-150 nA. Anhydrous minerals and those containing water in the form of (OH) remain stable under these conditions.

The results obtained were compared with the methods of correction calculations suggested by Borovsky-Rydnuk, Philiber-Heinrich and the present one with Ruste's modification. In the latter case $\bar{n}$, $\bar{\sigma}_0$ , $\bar{\sigma}_L$ parameters for the samples of complex composition were determined as $\bar{n} = \sum_i n_i c_i$; $\bar{\sigma}_0 = \sum_i \sigma_0 c_i$; $\bar{\sigma}_L = \bar{\sigma}_0 \cdot 10/E_0^{\bar{n}}$

Absorption coefficients used were taken from Henke. It has been shown that when a standard was selected from the same group as the analysed minerals, the errors of analysis for minerals with an average Z exceeding 10, were caused mainly by experimental data and incorrect values of the absorption coefficients, and not by the choice of the method of correction calculations.

The results of mineral analyses are given. The reproducibility of the determination of oxygen in oxides of iron with the change of all operations of specimen preparation is 0.6 - 2%, for uraninites 5-10%. The results obtained agree well with the data of chemical analyses. The correctness of uraninite analyses was assessed by the oxygen coefficient.

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# ELEKTRON-PROBE INVESTIGATION OF BAUXITES

L.S. Dubakina, K.S. Ershova, O.V. Scherbak, Moscow, USSR

The quantitative determination of chemical and shaft composition of bauxite minerals is one of the tasks, without solving of which it is impossible to work out the optimal scheme of technological treatment of ores. One of the most perspective method of investigation of mineral composition and of the character of mineral aggregates in ores is the electron-probe analysis.

The composition of bauxites minerals: boehmite, gibbsite, diaspore, caolinite and shamosite was investigated along with the form of presence of some accompanying elements. It is established that the composition of the investigated minerals is constant and that the accompanying elements are in the form of admixture of other minerals.

The determination of water in these minerals was carried out by the exchange of intensivity of analytical line $K_\alpha$ Al according to the hydration of these minerals under the electron probe. The relative error of determination is not greater than 10-15%. The investigations were carried out at the working voltage of 20 kV and specimen current of 40-50 nA.

The artificial crystal of corundum and the metallic Al were the standards and they were prepared with simultaneous coverage with carbon.

## THE OPTIMIZATION OF METHROLOGICAL CHARACTERISTICS IN ELECTRON PROBE MICROANALYSIS OF ROCK-FORMING SILICATE MINERALS

V.A. Cherepanov, A.G. Sysoev, I.D. Makedon, Leningrad, USSR

The value of the mineralogical application of the electron probe microanalysis of rock-forming silicate minerals is determined by the lowest limit of detecting the concentration of chemical elements, not exceeding 0,01 of the crystallochemical coefficient and with accuracy of determination of concentration no more than 5% (relative).

The elaborated method of optimisation includes the system of standard samples, the method of analysis of errors of both the method and problem, and the programme of computing the experimental data of contents of chemical elements, methodological characteristics and evaluations of longitudinal and transverse locality.

The proposed method contains a new algorithm for computing the correction factors and for evaluation of adequacy of any algorithm.

## MICROPROBE ANALYSIS OF FLUORINE IN MINERALS

P. Suddaby, London, England

Elements with atomic numbers less than that of sodium are not normally analysed quantitatively in the electron microprobe. This is partly due to the experimental difficulties but also because many of the input parameters required for the matrix correction procedures are poorly known. The analysis of fluorine is important in minerals such as amphiboles, apatite, tourmaline, etc. Data are presented on the analysis of fluorine in a variety of minerals and the effects of using different matrix correction models and input parameters are discussed.

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## USE OF THE ELECTRON MICROPROBE IN MEASURING SOFT X-RAY SPECTRA OF FERROUS SILICATES

Charles G.Dodd and Paul H. Ribbe, Blacksburg, USA

Energy gaps and electrical conductivities in the ferrous silicates, $Fe_2SiO_4$ and $FeSiO_3$, depend primarily on Fe-O bonding and may be studied by ultraviolet and soft X-ray spectrometer, we have measured Fe $L_{II-III}$ X-ray band spectra under conditions of "minimal" ($I_4$, at 4.0 keV) and "high" ($I_{10}$, at 10.0 keV) self absorption to determine 3<u>d</u> orbital energy levels, to delineate <u>d</u> states in the valence band, and to construct band gap models. Absorption spectra, $I_4/I_{10}$, were computed to determine vacant orbital levels in the gap. A difference function ($I_4-I_{10}$) has been proposed to identify X-radiation at photon energies above the measured $L_{III}$ absorption edge, including high-energy, double-vacancy satellites and radiative transitions involving the anti-parallel $d^6$ electron in the ground state. The proposed band gap model for $Fe_2SiO_4$ includes an intrinsic transition of 6.5 eV and an energy gap of 7.8 eV. The 3d orbital energy level electronic structures are in general agreement with levels computed by Tossell <u>et</u> <u>al</u>.(1974) for $FeO_6^{10-}$ in FeO. A high-energy, double-vacancy satellite was found at ∼ 710.7 eV, and is presumed to originate from an $L_{III}$ $M_{II,III}$ initial state. The intensity of these satellites for the ferrous silicates and other iron compounds, and corresponding Fe $L_{II}/L_{III}$ intensity ratios are correlated with differences in band gap magnitudes and gap structure.

Fe $L_{II}/L_{III}$ intensity ratios are <u>not</u> well correlated with iron oxidation state.

# CONTRIBUTION OF THE ION ANALYSIS TO THE STUDY OF MAGMATIC MELTS TRAPPED INTO LAVA PHENOCRYSTS

R.Clocchiatti* and A. Havette**, Paris, France

Ion microanalysis is a new technique making in situ analyses possible. Sample is bombarded by a beam of primary ions ($Ar^+$, $O_2^+$, $O^-$); the simple and polyatomic ions, thus torn away from matter, are accelerated by an optical system and sorted in mass by a magnetic prism. The instrument is a mass spectrometer which makes it possible:- To visualize during study, or to print on a film, the distribution image of a given element on a 30 to 250 um diameter range. - To calculate isotopic ratios or to quickly obtain a mass spectrum where present elements appear on a 10 to 4.000 um$^2$ range.

Slightly concentrated elements can be detected, for instance: 1 to a few ppm for alkaline and alkaline-earth elements, 10 to 50 ppm for metals from the transition first series, 50 ppm for silicium.

Spatial resolution at the images surface is about 0.5 um; penetration is some tens Angströems deep.

It is possible to obtain quantitative analyses by counting or else from distribution maps by microdensitometry. The instrument utilization is well adapted to the study of melt inclusions on account of their small dimensions ($200 < d < 1$ um). Indeed, through the images taken on all the present elements, the ion analyser makes quite obvious:

A) Heterogeneities in crystalline phases as host minerals, minerals deposited in epitaxy on the walls of cavities proceeding from the host mineral growth upon the included liquids, minerals mechanically trapped before the cavities locking up, so already present into magma (zircon, apatite, sphene, rutile, etc. ...) minerals proceeding from the experimental or natural crystallisation of the included glass (pyroxene, olivine, magnetite, etc. ...).

B) Heterogeneities in vitreous phases as lessened zoned structures in elements entering into the host mineral constitution, resulting from a bad diffusion in the liquid (melt inclusion) - solid interface (walls of the cavity). It is also the case for immiscible liquids proceeding from the last evolution in the filling up of some cavities.

The ion analyser is a tool, complementary to the optical microscope and electron microprobe and absolutely necessary to any advanced chemical study on magmatic liquids trapped in during the lava mineral growth.

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# MICROPROBE STUDY OF ROCK-FORMING AND ORE MINERALS BY THE EXAMPLE OF ALKALINE-ULTRABASIC ROCKS OF MASSIFS IN KOLA PENINSULA

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Microprobe study of rock-forming and ore minerals of alkaline-ultrabasic rocks taking into account the dynamics of crystal growth in coordinates of space and time has allowed to obtain some new data revealing the peculiarities in ontogeny of minerals depending on thermodynamic and physico-chemical conditions of their formation. Moreover, it is possible to determine reliably the stages of mineral-formation and petrogenetic differences in monotypic rocks on the basis of mineral composition.

Thus, titanomagnetites of intrusive complex of rocks are accurately differentiated from that of metasomatic series of rocks by the chemical and phase composition and peculiarities in their change. In titanomagnetites of the primary rocks there has been established higher volume of Ti, Mg and Al admixtures. The difference in their content in titanomagnetites of monotypic rocks (primary and recrystallized) increases gradually in the later series. In each type of rocks the composition and structural peculiarities in titanomagnetites evolve, displaying the stepped character of equilibrium. So in titanomagnetites of recrystallized rocks in the composition of the main phases of the decay structures of ilmenite and ulvöspinel, the Mg content in the late generation increases more and more while in magnetite bases the content of Fe increases progressively. Such conjugated behaviour of these elements is connected with the transition of $Fe^{+2b}$ into $Fe^{+3}$ and with the increase of the portion of magnetite minal and parallel Mg releasing from the composition of magnetite with its fixing in ilmenite and ulvöspinel. The evolution of composition of decay phases and host mineral is in keeping with the Le Chatelier's principle.

The perovskites of magnetic and metasomatic series of rocks display sharp differences by the degree of mineral homogeneity and regularities in the compositional changes especially in the indicative elements such as La, Ce, Nb, Na, etc. There is established the polar character of their behaviour in perovskites of rocks of various genesis. Besides, for perovskites of metasomatic rocks there is displayed the autonomous evolution characteristic of each type. This testifies to repeated display of metasomatic processes conjugated with each intrusive phase.

The evolution of composition is also observed in olivines. The indicator properties display in them both the main elements of Mg and Fe and elements -admixtures of Ca and Mn. The first ones readily react to t-change while the Ca-content correlates with the depth factor. The succession in the displayed metasomatic processes in olivine-bearing rocks is traced by increased Mn - content in olivines.

# MICROPROBE INVESTIGATION OF THE PRODUCTS OF DEVITRIFICATION OF ACID VOLCANITES

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Products of devitrification form the main part of the majority of paleotype acid volcanites. Microgranularity and indistinct individualization of minerals in them highly restrict the application of precise methods for crystallooptic diagnostics. Microprobe methods allow to investigate in clear palish sections concentration and distribution of chemical elements in various structural components of rocks with high exactness and to observe and to fix their morphological pecularities and relations.

It was established that the primary separation of ash particles of some Devonian ignimbrites of Kazakhstan is the result of fragile deformation of glassy mass with the formation of flat fissures in it. The plastic deformation which completed their formation took place due to subsequent partial remelting of material during its bedding. Subtraction and uniform distribution of potassium in peripheral areas of particles accompany the process of remelting. The bordering of their section by cryptogranular aggregate of common potash feldspar bear witness to this.

The obtained data prove the *conception of Fenner(1926), Marshall* (1935) and A.N.Zavaritsky (1947) of the genesis of ignimbrites which at present was rejected by the majority of investigators. *However they do not exclude the possibility of some* other ways of formation which are analogous in composition and structure of rocks.

The use of microprobe in Complex with the traditional analytical methods opens new possibilities in reconstruction of the genesis *of acid volcanites.*

# OPEN SESSION

## *CUMMINGTONITE, OLIVINE, ORTHOPYROXENE, STABILITY FIELDS,* THERMODYNAMIC CHARACTERISTICS

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The phase equilibria in the system $MgO-FeO-SiO_2-H_2O-O_2$ involving the variable+composition minerals (cummingtonite, olivine, orthopyroxene) were experimentally studied at 560-850°C, $P_{H_2O}$ = 1000-9000 kg/cm$^2$. The oxygen fugacity is controlled by oxygen buffers. The lower temperature stability limit for the Opx+Q assemblage was studied with oxygen fugacities fixed with nickel-bunsenite and quartz-fayalite-magnetite buffers. The Cum+Mt and Cum+Ol associations were formed, respectively. The equilibrium temperature of the first reaction is 725, 770 and 780±10°C at P=1000,3000 and 5000 kg/cm$^2$, respectively; the equilibrium temperature of the second reaction is 725 and 735±10°C at P=3000 and 5000 kg/cm$^2$, respectively. Temperature and pressure dependences of the ferruginity (F=FeO/FeO+MgO) changes in the variable-composition minerals were experimentally established. 1. The assemblage Cum+Q+Mt. The F in cummingtonite has been found to decrease with a rising temperature and to increase with a rising pressure. 2. The assemblage Opx+Q+Mt. The F in orthopyroxene rises with both temperature and pressure. 3. The assemblage Cum+Ol+Q. The F in cummingtonite and olivine decreases with a rising temperature and goes up with pressure. 4. The assemblage Opx+Ol+Q. Both olivine and orthopyroxene in this association show a marked increase in F with rising pressure, while a higher temperature results in only a slightly higher values. 5. The assemblage Opx+Cum+Q. Higher temperatures result in lower F in both orthopyroxene and cummingtonite. The effects of pressure on F in the coexisting minerals is not nearly so conspicuous.

The experiments showed that the olivine series minerals approach ideal solid solutions. Orthopyroxene solid solutions show a slight deviation to negative over the 750-850°C range. At 1100°C the deviation becomes signvariable: positive for magnesian compositions and negative for ferrous ones. Cummingtonite solid solutions gave a marked negative departure from ideality, especially over the 600-700°C range.

The data on stability conditions of many mineral associations with cummingtonites, olivines and orthopyroxenes together with thermodynamic characteristics of the mineral solid solutions have made it possible to derive several geothermometers and geobarometers. Furthermore, oxygen fugacity and water partial pressure can also be assessed for metamorphic ferrosilicic rocks.

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## THE Fe-Ni-Co-Cu THIOSPINELS

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The Fe-Ni-Co-Cu members are the most widespread, abundant, and economically important thiospinels. Violarite ($FeNi_2S_4$) and polydymite ($Ni_3S_4$) are common secondary minerals in massive iron-nickel ores; polydymite, siegenite $(Ni,Co)_3S_4$ and linnaeite ($Co_3S_4$) are frequent accessories in vein deposits and stratiform lead-zinc ores; and, linnaeite and carrollite ($CuCo_2S_4$) are important ore minerals in the syngenetic (?) Zambian copperbelt. The distribution of analyses of natural thiospinels and synthesis at 300-500°C reveal that complete solid solution exists in these thiospinels along the joins: $FeNi_2S_4-Ni_3S_4$; $Ni_3S_4-Co_3S_4$; $Co_3S_4-CuCo_2S_4$. Natural Fe-Ni thiospinels extend to greigite ($Fe_3S_4$) even though synthesis of compositions between $FeNi_2S_4$ and $Fe_3S_4$ has not been successful. Fletcherite represents a solid solution from $Cu_{1.1}Ni_{1.0}Co_{0.9}S_4$ to $Cu_{0.7}Ni_{2.1}Co_{0.6}S_4$. The unit cell dimension increases nearly linearly from 9.464Å for $FeNi_2S_4$ to 9.488Å for $Ni_3S_4$; it decreases from 9.488Å for $Ni_3S_4$ through a minimum of 9.392Å at about $NiCo_2S_4$ and then increases to 9.405Å for $Co_3S_4$; it increases linearly from 9.405Å for $Co_3S_4$ to 9.472Å for $CuCo_2S_4$. The unit cell dimension of fletcherite, 9.520Å, is composition independent; that of $Fe_3S_4$ is 9.876Å. Thermal stabilities are: $Fe_3S_4$ -200°C; $FeNi_2S_4$ -461°C; $Ni_3S_4$-353°C; $NiCo_2S_4$ -~800°C; $Co_3S_4$ -680°C; $C_{0.5}Co_{2.5}S_4$ -~880°C; $CuCo_2S_4$ -~600°C. Reflectivities generally parallel the variations in thermal stability. All of these parametres can be interpreted in terms of the electronic structure of the thiospinels.

# MINERAL ONTOGENY AS A METHOD OF DERIVING GENETIC INFORMATION

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At matter organization level "mineral individuum-aggregate" mineral ontogeny investigates generation, growth, change and destruction of mineral individuums and aggregates, their individual history. A systematic analysis of syngenetic stages, diagenesis and metamorphism aids in establishing individual cycles. Polycyclic rocks and ores are dominant in nature. Stadial onthogenetic analysis *(syngenesis, diagenesis and metamorphism) is to* apply to genesis of all rock types and not only sedimentary ones. A systematic application of this method permits one to obtain a comparable and readily coded genetic information. Physical properties of the grain boundaries in the aggregate have been established which cause stereometry of structures. The "Cockseter cell" corresponding to the equilibrium shape of the single-crystal grain in the granoblast aggregate has been investigated. Using the method of measuring the bihedral angles in bimineral aggregates (for example, quartz-apatite) it has been found that the degree of approximation of the boundary framework to equilibrium is quite possible, i.e. indications of paragenesis. Formation of the equilibrial framework of the grain boundaries completes in establishing of the total physico-chemical equilibrium for aggregates. A universal metamorphic equivalent of the primary *growth (syngenetic) aggregate structures is granoblast* structure. The druse ( based on single-crystal or spherolyte), parallel-fibrous, eutectic (platy, rod-like and globular) are self-organizing growth systems, structural-textural characteristics of which practically does not depend on the form of composing minerals.

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# NEW B MINERALS IN SKARNS

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Within the last 20 years a series of B minerals (Ca and Mg-Ca borates and carbonato-borates) have been discovered. They constitute 15 additional mineral species. Found and studied in the Soviet Union, these minerals are registered in the International comission on new minerals and mineral names. The new Ca borate are: calci corite $Ca_2[BO_3BO]_2$ , sibirskite $Ca_2(OH)[B_2O_4(OH)]$ korjinskite $CaB_2.O_4.H_2O$, uralborite $Ca_2[B_4O_4(OH)_8]$ , vimsite $Ca[B_2O_2(OH)_4]$ , hifontovite $Ca_3[B_3O_3(OH)_6]_2.2H_2O$, frolovite $Ca[B(OH)_4]_2$, pentahydroborite $Ca[B_2O(OH)_6]. 2H_2O$, solongoite $Ca_2[B_3O_4(OH)_4]Cl$, olshanskite $3CaO.2B_2O_3.9H_2O$ hexahydroborite $Ca[B(OH)_4]_2.2H_2O$. The new Mg-Ca borates are:kurchatovite $Ca(Mg,Mn)[B_2O_5]$, fedorovskite-rowite $Ca_2(Mg,Mn)_2[B_4O_7(OH)_2].(OH)_4$. They form the range of compositions with varying Mg/Mn and $Mg/Fe^{2+}$ ratios. The new carbonate-borates are sakhaite $Ca_{48}Mg_{16}(BO_3)_{28}(CO_3)_{16}Cl_4(OH)_8.4H_2O$ and borkarite $Ca_4MgB_4O_6(OH)_6.(CO_3)_2$.

This mineral series constitutes a new type of endogenous B mineralisation related in space and genesis to the lime skarns.

The new Ca borates: calciborate, corjinskite, uralborite, vimsite, nifontovite, frolovite, pentahydroborite and hexahydroborite demonstrate a constant relation $CaO:B_2O_3 \approx 1$.It is a new Ca metaborate group characterised by:

-a modification of physical properties of the minerals, depending on their composition. A growth of water content leads to a decrease of density, hardness, refraction index and of the endothermal process temperatures;

-an interdependence between the distribution of certain mineral species in nature and the construction of their B-O complexes, e.g. the prevaled formation of the minerals containing mono-and bi-nuclear B complexes as compared to the other ones, with more complicated anion structures.

## TYPOMORPHISM OF FLUID INCLUSIONS AS INDICATOR OF THE DEPTH OF FORMATION OF HYDROTHERMAL GOLDEN MINERALIZATION

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The data on the depth of hydrothermal ore genesis are necessary for geological practice. In some particular cases the method is needed permitting to make suggestions on the genetic group and depth of formation of mineral associations even by unique findings of gold-bearing mineral parageneses.

The results of investigation of golden-quartz poor sulphidic formation of the abyssal class of East Siberia give evidence for a typomorphic importance of fluid inclusions in the minerals of hydrothermal gold-bearing veins.

Golden deposits of various formations according to investigations of fluid inclusions were formed at various PTX parameters of the process.

The highest (350-400°) temperatures are characteristic of the mineral associations of the abyssal bodies, the intermediate ones (285-295) characterize the formation of the hydrothermal slightly gold-bearing veins of the hypabyssal class, as to subsurface deposits, they are related with low-temperature fluids (170-195°).

During the formation of gold-bearing veins in abyssal conditions the pressure grew with the depth and for middle depths it was 850-900 atm.

According to the analytical results, the inclusions in the minerals of hydrothermal gold-bearing veins of abyssal class contain carbon dioxide (81.3-95.6%), nitrogen (11.5), methane (4.1-4.7%) and other gases.

The carbon dioxide is the main gaseous component of fluid inclusions of golden deposits. High $CO_2$ concentration in homogenous aqueous mineral-forming solution favours gold migration.

Their heterogenization is accompanied by intensive precipitation of gold (productive stage of mineral formation). Hydrocarbons are often present in gaseous mixture of solutions.

There is the definite dependence between the gold content and the quantitative changes in gaseous components. It is directly proportional for gold and methane, partially for gold and nitrogene and inversely proportional for gold and carbon dioxide.

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## QUARTZ-TRIDYMITE TRANSITION UNDER HYDROTHERMAL CONDITIONS

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The equilibrium temperature for the quartz-tridymite transition was determined at several pressures and a P-T diagram for the reaction was constructed. From this diagram a value for dT/dP of 0.18°/atm. was found. This value for dT/dP is in agreement with an earlier experimental determination but is in disagreement with a value of 0.85°/atm. calculated from thermodynamic data. The disagreement between the two values is probably due to the unreliability of the thermodynamic data for quartz and tridymite. The tridymites formed in the experiments were classified by an x-ray diffraction technique into types M, S and U or mixtures of the three types. A sample of type M tridymite was examined in a transmission electron microscopé. It was found to have a C-repeat of 40A corresponding to a 5H polytype, although fringes with a spacing of about 80A were observed in a dark-field photograph, suggesting the presence of a 10H structure. The possible effects of impurities in the stability of tridymite are discussed.

## CRYSTAL CHEMICAL STUDIES OF SAPPHIRINE

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Sapphirine is a Mg-Al silicate found in upper amphibolite to granulate metamorphic terrains and has recently been described in xenoliths from kimberlites and layered igneous intrusions. The application of experimental work in the $MgO-Al_2O_3-SiO_2$ system to obtain petrogenetic information on numerous recently described sapphirine assemblages is not straightforward because of an incomplete understanding of solid solution, cation ordering, and polymorphism in sapphirine.

Sapphirine exhibits solid solution along the join:

$${}^{VI}R^{3+} + {}^{IV}Al^{3+} \rightleftarrows {}^{VI}R^{2+} + {}^{IV}Si^{4+} \quad \text{where}$$

$${}^{VI}R^{2+} = (Mg,Fe,Mn) \text{ and } {}^{VI}R^{3+} = (Al,Fe,Cr)$$

Fe may be partitioned between $Fe^{3+}$ and $Fe^{2+}$ because ${}^{IV}Al^{3+}$ must equal ${}^{VI}R^{3+}$ to maintain charge balance. $Fe^{3+}/Fe^{2+}$ ratios calculated in this manner agree closely with those determined from Mossbauer studies.

Cation ordering in sapphirine has been studied by neutron and x-ray diffraction on a specimen from Bekily, Madagascar. Refinement of the $P2_1/a$ polymorph with $a$ = 11.284, $b$ = 14.438, $c$=9.955 A, $\beta$= 125.44 gives the following occupancies and mean M-O and T-O distances (in Angstroms).

| | Mean M-O | Al/(Al+Mg) |
|---|---|---|
| M1 | 1.931 | 0.95 |
| M2 | 1.938 | 0.95 |
| M3 | 2.001 | 0.4 |
| M4 | 2.084 | 0.0 |
| M5 | 2.120 | 0.0 |
| M6 | 2.120 | 0.0 |
| M7 | 1.928 | 1.0 |
| M8 | 1.935 | 1.0 |

| | Mean T-O | Al/(Al+Si) |
|---|---|---|
| T1 | 1.757 | 0.9 |
| T2 | 1.652 | 0.0 |
| T3 | 1.709 | 0.5 |
| T4 | 1.755 | 0.9 |
| T5 | 1.756 | 1.0 |
| T6 | 1.735 | 0.7 |

An electron optical study of sapphirine polymorphism on specimens from Wilson Lake, Canada, indicates a triclinic sapphirine polymorph with the aenigmatite structure which contains two sets of deformation induced (010) stacking faults with Burgers vectors 1/2[001] and 1/2 [100]. The [001] faults are associated with the triclinic to monoclinic transition while the [100] faults twin the triclinic polymorph.

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## $FeCl_2 \cdot 2H_2O$, A NEW SALT MINERAL

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In March 1977, a new mineral was observed in a thin sheet between brownish-yellowish nests of rinneite and surrounding secondary carnallite. On a broken surface it appears as a light green fringe, 2 to 4 mm wide.

Chemical and X-ray analyses showed that part of this fringing zone (ca.40%) consists of $FeCl_2 \cdot 2H_2O$.

According to the microscopic results, this new mineral is often developed in thin plates of 0.15 mm or in small fibres. Idiomorphic prismatic crystals up to 1 mm in size have been found sometimes.

The morphology and the optical properties of this new mineral have been determined. Type locality is the 915 m (intermediate) level of the potash mine Salzdetfurth near Hildesheim (Germany).

We would like to name the mineral in honour of Professor Dr. Robert Kühn ROKÜHNITE in acknowledgement to his great merits in investigations of salt deposits.

## THE TERRESTRIAL OCCURRENCE OF WÜSTITE

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The temperature and oxygen fugacity conditions necessary to the formation of wüstite in the system Fe - O are approached in basaltic melts, and local contamination by assimilation of inclusions may lower the oxygen fugacity into the required range. There must also be insufficient $SiO_2$ available for the olivine-producing reaction to proceed to completion. All these conditions can be met by nonsilicate xenoliths in basaltic melts, and wüstite can form as a stable phase.

The paucity of terrestrial occurrences of wüstite may be due not to its lack of formation, but to its lack of preservation; at temperatures below its lower limit of stability it decomposes rapidly, in two recognizable steps. Under conditions of rapid but continuous cooling to below 200°C (over a period of hours to days) the first step generates metastable, stoichiometric wüstite. A slower cooling rate allows decomposition of this intermediate-stage wüstite to iron and magnetite, the stable products of the decomposition.

The mechanism of formation proposed by Walenta (N.Jb.Min.Mh, 1960, 150-159) for non-stoichiometric wüstite from Scharnhausen, Germany, is in agreement with these experimental data. The wüstite thus formed must have been subjected to extremely rapid quenching (minutes) in order to preserve a non-stoichiometric composition.

The formation of wüstite in a massive sulphide - oxide block in a basaltic dyke at Igdlukunguaq, Greenland is also not unexpected. Given the dimensions of the basaltic dyke, and known cooling rates of bodies of this size, however, the preservation of intermediate-stage, metastable, stoichiometric wüstite is surprising; it may be due to the presence of other elements, or to high pressures induced by thermal contraction of the surrounding pyrrhotite masses. Barring preservation under unusual circumstances, one would expect pre-existing wüstite in terrestrial rocks now to be represented by the assemblage iron - magnetite.

## A NEUTRON DIFFRACTION STUDY OF A ONE-LAYER TRICLINIC CHLORITE (PENNINITE)

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A neutron diffraction study of a one-layer triclinic chlorite of the IIb polytype was used to provide first reliable data on the hydrogen bonding system in chlorite minerals.

About 1000 reflexions up to $2\theta = 80^\circ$ were collected on the D 8 four-circle facility at the ILL, Grenoble, in an $\omega/X\theta$ scan mode, resulting in 850 non-equivalent reflexions. The refinement including the site occupancies of the tetrahedral and octahedral positions, anisotropic temperature factors and isotropic extinction parameter gave a final R-factor of 2.4%.

The refined structure shows a distinct regularity of bond lengths and angles within the different sheets preserving the hexagonal and trigonal symmetry respectively but appears to be compressed along c*. The tetrahedral site does not show Si/Al ordering proved by bond lengths and refined scattering lengths. A preferred occupation of aluminium was, however, observed in one octahedral site of the brucite sheet. Talc and brucite sheets are hold together by hydrogen bonds. The three symmetrically independent O-H dipoles are roughly perpendicular to the brucite sheet, but they are significantly tilted towards the respective acceptor oxygen atoms of the silicate sheet. Without hydrogen bond formation the O-H dipoles would be perpendicular to the sheets as observed in the brucite structure itself.

## ON THE GEOCHEMISTRY OF META-BASALTS AND META-RHYOLITES IN THE EARLY PRECAMBRIAN ISUA SUPRACRUSTAL BELT, WEST GREENLAND,

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The Isua supracrustals are exposed in an arcuate belt ca 30 km long and up to 3 km wide, in the Amitsoq gneisses (Allaart, 1976). Both the supracrustals and the Amitsoq gneisses give radiometric ages in the range 3.7-3.8 b.y. (Moorbath et al.,1975). The supracrustals are composed of meta-sediments and metamorphosed volcanic extrusive and intrusive rocks. Meta-basalts are mainly represented by layered tuffaceous amphibolites and massive amphibolites. The latter representing extrusive lavas and intrusive dykes and minor silla (Appel 1977, 1978). Thick horizons of carbonate bearing siliceous schists are believed to represent meta-rhyolites (Allaart, 1976). After deposition, the supracrustals were metamorphosed in lower amphibolite facies and suffered several phases of deformation.

### Chemistry.

The major element distribution in the Isua meta-basalts show the same trends as seen in other Archean meta-basalts (Appel,1978). At present time only a few trace element analyses of basaltic and rhyolitic rocks have been made,see Table 1 where (1)-(3) are massive amphibolites,(4) amphibolite.

| | | (1) | (2) | (3) | (4) |
|---|---|---|---|---|---|
| Co | ppm | 47.8 | 53.9 | 49.1 | 47.4 |
| Ni | ppm | 140 | 160 | 160 | |
| Cr | ppm | 194 | 279 | 290 | 80 |

The amphibolites from the Isua supracrustals analysed so far, show good agreement in their major and trace elements as compared to other Archean meta-basalts. There seems, however, to be a marked difference between the Isua amphibolites and many other Archean meta-basalts in their content of Cr. Whereas the Isua amphibolites have approximately the same or even lower content of Cr as the oceanic tholeiites, do most other Archaean metabasalts have considerably higher content, than that of oceanic tholeiites.

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## CRYSTALLOCHEMISTRY AND SYSTEMATICS OF SIMPLE COMPOUNDS (*ELEMENTS*)

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The identical atoms with a zero difference in electronegativities appears to be the main characteristic of simple compounds in crystallochemistry.

The comparisons of the properties of simple compounds with the covalent bonds and those of molecular crystals show that in both of them the degree of metallicity of bonds increases with the growth of Z with the following jump to the crystals with metallic bond.

The crystals with metallic bond account for more than 2/3 of all simple compounds. That is why the main attention is paid to the genesis of their structures, mechanism of bonding, on the basis of the constitution and properties of their atoms poorly studied as yet. It is shown that:

a) The valence of atoms in metallic crystals should be determined by the energy barriers of ionization potentials.

b) The metallic bond is to be considered as directional, often resonant by nature, with different mechanism in different metals.

c) All phase transitions in metals, determined by the temperature and pressure variations are well explained by the given scheme.

d) The peculiarities in the variations of other metallic simple compounds properties such as melting and sublimation temperatures, sublimation heat, enthropy and so on are in good agreement with them.

e) All these data allow one to understand anew the main peculiarities in their properties and also to make a number of general conclusions concerning the general model of chemical bonding and, among them about the necessity of consideration in all the cases not only of the covalency and ionicity, but also metallicity of bonding, specially taking into account the possibility in number of structures of covalent and metallic components of bonding.

The systematics of simple compounds including minerals is based on the character of their chemical **bonds** and peculiarities in their structure.

## THE BIGGEST DIASPORE CRYSTAL IN THE DOLOMITE MARBLE QUARRY ON SIVEC NEAR PRILEP (MACEDONIA, YUGOSLAVIA)

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Until recent the largest diaspore crystal was found in the dolomite marble quarry Sivec in Macedonia; it was found there in a small diaspore crystals oriented and grown on corundum crystals with the faces: b $\{010\}$ , k $\{130\}$ , y $\{120\}$ , m $\{110\}$ , t$\{221\}$ s $\{111\}$ and p $\{121\}$ . And besides it is a twin according to $\{061\}$ . On $[001]$ -zone faces there is seen a fine vertical striation. The hardness is between $6^1/2$ and 7; the colour is pale bluish-greenish.

Determination of the refraction indices in Na-light by Klein's total reflectometer gave the following results:

Nx = 1.7014 Ny = 1.7220 Nz = 1.7486

The optic axial angle was determined on some cleavage plates by the Berek standard diagram as 2V =(+84) ; (+84) and (+85) .

The absorption curve in the IR-spectral area is measured.

From the yellow transparent diaspore crystals from Newlin (USA) some precious stones were prepared.

Mn-diaspore was found in the manganic deposit Postmasburg (South Africa); its crystals are 8 cm long, 1.5 cm wide and maximum 2 mm thick in the $[010]$ -direction.

## POTASSIC RICHTERITE FROM THE MESOZOIC ALKALI PROVINCE OF THE ALDAN SHIELD

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K-richterite has been established in the Mesozoic alkaline and subalkaline igneous rocks of the western slope of Aldan shield. Its $K_2O$ content ranges from 4.0 to 4.5%. Richterites with similar $K_2O$ content have been found to occur in alkaline igneous rocks only (Prider, 1939; Hernandez-Pacheco A., 1964; Erlank, A. J., Finger L.M., 1970).

We singled out 3 varieties of K-richterites. The first variety is represented by blue-green crystals, up to 3 mm in size, with the well developed prismatic faces. Refractive index Ng ranges from 1.635 to 1.649. CaO content does not exceed 4.0%, while $Na_2O$ content is higher than that of $K_2O$ (up to 5.5%). Iron content is 20 mol.%.

The second richterite variety is characterized by crystals of pale greyish-green colour in the form of thin, frequently bent laths, forming felted or radial-fibrous aggregates. Refractive index Ng 1.632 - 1.621. CaO content is higher: 5.5-6.0%, while that of $Na_2O$ is usually lower than 5.5%, iron content is 10 mol.%.

The third variety is represented by colourless water-transparent crystals in the form of very thin spicular prisms, often with well-developed faces. Refractive index Ng 1.615 - 1.623. These richterites contain the maximum amount of CaO - 6.7% , while their $Na_2O$ content is minimal (4.5%), almost equal to that of $K_2O$. Iron content decreases to 4 mol.%.

Occurences of K-richterite-bearing rocks of different composition and genesis in one of the areas of the Aldan shield's western slope makes it possible to suggest the existence of a peculiar alkaline province. Its peculiarity is confirmed by the occurence of tcharoite rocks, containing "endemic" minerals tcharoite and tinaksite, which have not been found elasewhere so far.

At present, it is difficult to make the conclusions about the processes responsible for the formation of this unusual and rare mineral assemblage, but the data obtained makes it possible to suggest the relation of its genesis to metasomathosis.

## EXPERIMENTAL STUDY OF ZEOLITIZATION IN TUFOGENIC ROCKS

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The distribution of zeolites in tufogenic rocks usually displays a vertical or a lateral zoning which is brought about by various factors such as temperature, alkalinity of the solutions, the depth of burial of the sediments. etc.

The experimental investigation was performed in a thermogradient autoclave within a temperature interval 110-260°C in NaOH and KOH solutions and at glass:solution ratio = 1.3 : 1. From the glass with rhyolitic composition (perlite and pumice) the following minerals were synthetized: analcite, phillipsite, mordenite and clinoptilolite. The glass with basaltic composition yielded analcite, phillipsite, zeolite Na-P and tobermorite. The mixture of basaltic glass and opal gave rise to analcite, mordenite and clinoptilolite.

In addition the influence of temperature and chemical composition on zeolite reactions with the addition and removal of silica was studied. As a result the following species were obtained: feldspars, analcite and mordenite from clinoptilolite, erionite, chabazite and phillipsite. Clinoptilolite was also synthesized from a mixture of phillipsite and 30% biogenic opal.

The role of the temperature, the chemical composition of the glasses and of the pore solutions, the grain size and the permeability of the rocks for the appearance of zeolite zoning in volcanic tuffs was estimated. The experimental results are compared with data known for natural deposits.

## SUBSOLIDUS RELATIONSHIP BETWEEN BASALTIC, GRANITIC AND ALKALINE HAPLOSYSTEMS AT ELEVATED $P_{H_2O}$ -T - PARAMETERS

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In the modern petrology the problem of genetic relationship between the basic, acid and alkaline rocks is very important and actual. In this connection the present work deals with the modelling of the deep interrelations of basic rocks with acid and alkaline ones at subsolidus stage. The Pl of haplobasaltes is unstable at $P_{H_2O}$ = 1kbar, T = 600°C in the presence of $Na_2CO_3$ - solutions of 0.1M concentration and transforms into Ne. Cancrinite forms in 0.5M solution of $Na_2CO_3$ at the same $P_{H_2O}$ - T conditions. *It is observed the high stability of diopside in the* Na-carbonate medium. This mineral transforms into amphibole of richterite type in the presence of solutions of 0.5 - 5M concentrations. The sodic carbonatites form in the 5M solutions of $Na_2CO_3$. The coexistance of $Na_2CO_3$ (0,5M) and NaCl(1M) in the vapour phase does not effect sufficiently upon the synthesis of alkaline mineral assemblage, such as Ne+Cn+Di+Rich. At the same $P_{H_2O}$ - T conditions the Pl-bearing assemblage transforms into Or and Ne in K-carbonate medium, but kalcilite forms from 0.5M $K_2CO_3$ solution. The diopside is unstable in $K_2CO_3$-solutions of $\gtrsim$0.75M and Woll + Phl are formed instead of it. The addition of $P_2O_5$ to the 5M solution of $K_2CO_3$ lead to formation of Ap+Lc+Or and to the disappearance of Woll. The experiments with Na-K-solutions where $K_2CO_3/Na_2CO_3$-relations are of 1/3, 1/1, 3/1 show that according to its total concentration, the newly-formed phases are Ne, Cn, Amph, Pl, Or, Ks, Woll, Di and Phl. The transition from the haplogranitic system to the alkaline one with formation of Ne and Cn is realised in solution of $N_2CO_3 \sim 1.5$M at $P_{H_2O}$= 1 - 1.75 kbar and T = 600 - 700°C.

This data provides the model for the origin of alkaline rocks in subsolidus stage. The interreaction of alkaline carbonate fluid with basic and acid rocks in the process of differentional degazing and dehydration of mantle may lead to the appearance of al -

kaline rocks on the depth, for example, in the rift zones. The next melting of this metasomatic rocks would lead to the formation of various series of magmatic rocks containing Ne,Lc,Ks. The metasomatic process of the formation of alkaline rocks, as described above, would simplify the origin of some its types by means of common mechanisms of partial melting and crystallizational differentiation.

## MALACHITE-CERUSSITE-PYROMORPHITE MINERALIZATION FROM BROWN'S DEPOSIT, NORTHERN TERRITORY, AUSTRALIA

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A description of the mineralogy and general geology of an unusually rich deposit of oxidised copper-lead mineralization to occur within five metres of the surface in semi-tropical terrain of Northern Australia. Brief accounts are given of two mechanised excavation of the site in 1973 and 1977, made for the purpose of research and for collecting and preserving the specimens.

Geological factors which have influenced formation of massive malachite, cerussite and pyromorphite are the presence of adjacent underlying carbonate rocks, and a shallow seasonally fluctuating water table in a region of high rainfall. Mineralogical peculiarities of the site are discussed and comparisons made with material from other world localities. Geochemical factors are suggested which may have contributed to the formation of certain crystal habits.

## CORRELATION OF SKELETAL CRYSTAL MORPHOLOGY WITH GROWTH CONDITIONS

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The paper presents the results of the experimental material on the growth of skeletal crystals of potassium aluminium sulphate in the gravity segregational solution. Several stages of the skeletal crystal and the subsequent development of funnel and box formations were followed.

The crystallization process was produced in isothermal conditions by evaporating the solution without adding it. The inflow of the concentrated solution to the growing crystal was performed mainly from the upper layer. According to the holographic interferometric data, the solution is characterized by a progressive change in the intensity of bands in the crystallizer with an abrupt intensity in the upper layers.

The crystals grown in such a solution on different hypsometric levels turn out to be morphologically different. For the crystals more remote from the surface of the solution an equal development of the faces III , 110 and 100 is characteristic. With the approach of the phase boundary (i.e. the layer of the locally oversaturated solution) to the rear faces, an intensive crystallization process is seen on the boundary of "crystal-solution-air" phases with the clear predominance of the radial growth over that of the tangential due to the growth of edges (III):(III), (III:(110) and (III):(100). The bench forms were formed here with the development of complex radial surfaces in the trace of every edge. The growth was seen not only along the edges but along the tops as well. With further movement of the boundary of the "solution-air" phase relative to the crystal-substratum, translation of the edge - top growths helps to formation of a hollow funnel carcass. In case of a repeated immersion of the skeletal funnel crystal, the elements of edge forms grow into facial with the formation of box forms. The resultant forms are a combination of internal and external skeletons.

In the paper there are given data on the correlation between the external symmetry of the crystal and the crystal forming media determined with the holographic interferometeric technique. Observations of the formation of skeletal forms help to understand the peculiarities in the growth of natural skeletal crystals (which widely occur, for example, in the open voids of hydrothermal deposits and mineral bodies of metasomatic origin).

## ABOUT EVOLUTION OF THE FRAMBOIDAL PYRITE

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On the framework of natural crystal growth in a diagenetic environment, the study of numerous pyritic formations allows one to suggest the evolution of the crystals from the framboidal stage to the classical crystalline form.

After studying polished sections of various regions and specially the *rich collection found in the Kimmeridgian of Boulogne-sur* Mer (Pas de Calais-France) one can show that the internal organization of the framboid evolves, in some cases, to the appearance of crystalline forms.

When such framboids aggregate, they are able to arrange themselves following some laws of symmetry and in this way become crystals of a larger size.

Numerous photographs illustrate the progression of this phenomenon.

## THE HEATH BEHAVIOUR OF THE CATION EXCHANGED ZEOLITES WITH THE STILBITE FRAMEWORK

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Li-, Na-, K-, Rb-, Mg-, Ca-, Sr-, Ba-, La-exchanged forms were obtained from natural samples of stilbite, stellerite and barrerite. The heat behaviour of these exchanged forms is characterized by a framework contraction normally followed at a higher temperature by the destruction of the lattice. In this work the variation of $d_{(020)}$ value was recorded with an X-ray diffractometer with a high temperature attachment. In all samples the extent of the framework contraction and the temperature of the lattice destruction depend on the exchangeable cation: except for one Li-form and for all Ba-forms, the extent of contraction decreases and the destruction temperature increases with increasing ionic radius of the exchangeable cation. The different Si/Al ratio of the samples influences the heat behaviour of the exchanged forms: a higher Si content makes the framework harder to destroy.

## GEOCHEMICAL ASPECTS OF UPPER MANTLE ORIGIN OF ANDESITES OF THE YOUNG VOLCANIC CONE OF COTOPAXI

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Detailed geochemical study of 27 samples of andesites of the young volcanic cone of Cotopaxi has shown them to represent distinctly different types of these rocks when compared with that characteristic of the Central Andes Formation as reported by Pichler and Zeil. It is, therefore, suggested that there are at least two subtypes of Andes andesites, genetically linked with the crustal fragments of South American continental plate margins, displaying different slopes of Benioff zone. In accordance with geophysical models, all the obtained geochemical data indicate that the recent north Andes andesitic magmas originated from the Upper Mantle material.

# SOME ASPECTS OF THE DEVELOPMENT OF THE MINERALOGY OF ORGANIC COMPOUNDS

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Knowledge of the composition and properties of organic minerals dates mostly from the end of the 19th century. Attempts of their classification undertaken in major summaries (Dolter, 1931; Orlov, Uspensky, 1936; Tschirch, Stock, 1936) lack sufficiently full and uniform characteristics of the studied objects and were not based on any leading diagnostic principles. These objects having seemed "beyond the grasp of the mind", there developed by the middle of the 20th century a tendency to recognize only natural crystalline formations (Winchell,1949; Bulakh,1977) as objects of mineralogy, and in some extreme cases to regard crystals of non-biogenetic genesis as such objects (Povarennykh, 1966).

At present such limitations are hardly warranted, since on the basis of the concept of different geologic levels of the organization of substance (matter) there is no science, besides mineralogy, which encompasses all objects of the mineral (conditionally: molecular and supermolecular) level of organization . Such an approach to the determination of the objects of mineralogy was postulated earlier by V.I.Vernadsky and has been reflected in the works of A.G.Betekhtin, D.P.Grigoriev, E.K. Lazarenko, F.V. Chukhrov and some others.

The above considerations furnish every reason for the inclusion of organic compounds, products of geologic(and space) processes among the objects of mineralogy. The organic minerals, as well as the inorganic ones, contain extremely regular and irregular units: crystals and amorphous bodies. The difference between these two systems of minerals consists in the majority of organic minerals being represented by regular structures, while the irregular ones are of a definitely minor importance in the physico-chemical environment of the outer shell of the Earth's crust. The opposite correlation is observed for the organic minerals. The nature of this difference is determined by the chemical peculiarities of carbon. Insofar as the overwhelming majority of organic minerals is formed by polycondensation and/or copolymerization, they represent extreme and/or intermediate members of transitory series which can be identified with mineral species, with both diverging and closed limits of variability. These two systems, gigantic in volume (and importance) can also produce intermediate compounds.

The best studied among the known organic minerals are their few crystalline represntatives. Incomparably less studied are the amorphous ones (mainly those of polymeric structure).Nevertheless, the ontogenetic approach to the study of these objects has proved highly fruitful, and so has the research with the aid of a complex of modern physical methods.

One of the main objectives of mineralogical study of the physically isolated organic compounds of the Earth's crust is the recognition of correlation between their composition,structure and properties as well as of the geologic factors causing their formation and changes. The solution of this problem would be of scientific and practical importance, since it would open up new possibilities for the use and processing of mineral raw materials. However, before starting this work, it is necessary to do the following. 1) to revise organic matter that is known to-day and to accumulate new analytical data; 2) to reveal the transitory series of organic minerals; 3) to draw up a classification based on structural-chemical features.

## HYDROTHERMAL EQUILIBRIA IN LANTHANIDE OXIDE-WATER SYSTEM

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The results of Shaffer and Roy (1959) on the hydrothermal equilibria in the systems $La_2O_3$-$H_2O$, $Nd_2O_3$-$H_2O$, $Sm_2O_3$-$H_2O$ showed that polymorphic forms of oxides of rare earths are stable under hydrothermal conditions, suggesting the hydrothermal method as a promissing technique for growth of single crystals of polymorphic forms of these oxides, for characterisation. But such an attempt was hindered for want of phase diagrams in most of the $Ln_2O_3$-$H_2O$ systems, in order to establish the stability fields of oxide phases.

Phase diagrams for the systems $Ln_2O_3$-$H_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu) are now constructed in the pressure range of 5000-25000 PSI and temperature range of 200 to 900° C. Within the present experimental limits, Ln $(OH)_3$ hexagonal and LnOOH monoclinic are the only two stable phases from Pr to Ho. The cubic oxide phase (C-$Ln_2O_3$) is stable for Er, Tm, Yb and Lu but there is no evidence of an oxide field in the system of lighter rare earths.

The present results however contradict the report of Shaffer and Roy (1959) who have identified stable fields of C and B type oxides in $Sm_2O_3$-$H_2O$ and $Nd_2O_3$-$H_2O$ systems, which descrepancy may be attributed to the contamination of $CO_2$, $NO_3^-$, $Na^+$ and also reactor material, in the substrate used by them.

The cubic oxide phases of Erbium, Thulium and Ytterbium have been grown using different mineralisers, NaOH, $NaNO_3$ and $HNO_3$, which have shown substantial effect on the morphology of the grown oxide crystals.

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## THE EOSPHORITE-CHILDRENITE SERIES IN BURANGA PEGMATITE (RWANDA, AFRICA).

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Although the presence of the eosphorite-childrenite series has been previously reported in the famous Buranga pegmatite, a recent detailed investigation of the phosphate assemblages from that pegmatite has allowed to precise that occurrence considering both mineralogical and genetical view-points.

The mineralogical nature of the eosphorite-childrenite series, recognized by X-ray diffraction, is optically and/or chemically specified. So, the following Fe/Mn+Fe ratios of $(Mn,Fe)AlPO_4(OH)_2 \cdot H_2O$ are recorded in different associations: Fe/Fe+Mn =0.20, 0.33, 0.55, 0.85. The chemical analyses have been performed by the election microprobe and sensitive variations of Fe/Mn appear into a few well-developed crystals. Optical measurements are not easy because of the heterogeneity of such material; moreover pleochroic phenomena are also irregular in isolated grains. These optical data tend to compare with similar phenomena observed for the transformation of reddingite in landesite. If an auto-oxida*tion process may be suggested into crystals of* $(Mn,Fe)AlPO_4(OH)_2 \cdot H_2O$ without important structural modifications, the problem is to know if the auto-oxidation is realized following either $[Fe^{2+}(OH)]^+ \rightarrow [Fe^{3+}O]^+ + 1/2\ H_2\nearrow$ or $[Fe^{2+}(H_2O)] \rightarrow [Fe^{3+}(OH)^-] + 1/2\ H_2\nearrow$. Anyway, the problem of oxychildrenite is raised up again in spite of the paucity of material forbiding chemical distinction of ferrous and ferric iron.

*In order to approach the genetical question, different observa*tions show that phosphate minerals from the $(Mn,Fe)AlPO_4(OH)_2 \cdot H_2O$ series growth up in close relationship with former phases that obviously provide Al by very late alteration. Most occurrences of eosphorite or childrenite in Buranga pegmatite exhibit that mineral in contact of lithiophilite with microcline or of Al-bearing alluaudite (rich in sodium too) with albite. Although the Fe/Mn ratios in the primary (or so-called) phases and in the terms of the $(Mn,Fe)AlPO_4(OH)_2 . H_2O$ series are different, the values of these ratios in the eosphorite-childrenite series seem to be influenced by the Fe and Mn contents of the former minerals.

In the evolution of $Li(Fe,Mn)PO_4$ phases, the formation of eosphorite or childrenite could appear after the development of hureaulite-barbosalite paragenesis, not because of the variation of Fe/Mn ratio. In fact that variation has no genetical signification, eosphorite and childrenite being the result of a reaction between Al-bearing silicate and a solution containing phosphorus in a phosphoric acid form probably. The presence of $H_2O$ as water *molecule indicates that such minerals are rather late in the evolution* sequence.

In the brasilianite-trolleite assemblage from Buranga pegmatite, little vacuoles show tiny crystals of childrenite. It is now difficult to infer that it is an alteration product of Al-rich *alluaudite. The interest of that occurrence is to present the oxidation* process of childrenite into pink variscite and limonitic oxides.

A reaction may be assumed:

$$2\left[Fe\ AlPO_4(OH)_2 . H_2O\right] + 1/2\ O_2 + 3H_2O \rightarrow 2\left[AlPO_4 . 2H_2O\right] + 2\ Fe(OH)_3 .$$

In conclusion, the chemical composition of phosphate minerals of the eosphorite-childrenite series is tributary of the composition of mother phases that control the value of Fe/Mn ratio. The presence of Al is in close connection with the presence of microcline or albite altered by late hydrothermal or supergene solutions rich in phosphorus. That genetical process demonstrates that most Al-bearing phosphates, such as scorzalite too,find Al in a former phase of the pegmatite.

# DEFORMATION AND RECRYSTALLIZATION OF OLIVINE STRUCTURES IN HYPERBASITES OF OPHIOLITIC ROCKS OF SOUTHERN SIBERIA

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Deformation mechanism of ophiolite hyperbasites is manifested *in the morphotypes of olivine structures.*

There are two structural types: dislocational and recrystallizational ones. Dislocational structures are those characterized by the following features: 1) Slip systems 100 010, OKL 010; 2) Cleavaging on (010), (100),etc., 3) Plastic bending of crystals: *a) development of S-cleavage; b) microfolding of cleavaged* grains; 4) Plastic fracturing of cleavaged grains. As for the recrystallized structures the following features are characteristic of them; 1) Blastoporphyric texture-relict of primary individuals of olivine on the background of fine-grained aggregate of new grains; 2) Mosaic (polygonal) balanced structure of unstrained grains; 3) Primary recrystallization structure connected with the increase of individual neoblasts, growing at the expense of deformed grains; 4) Secondary recrystallization structure-heterogranoblastic microstructure of unstrained olivine aggregates; 5) The annealing microstructure - the rise of normally oriented subgrains in situ; 6) Turbulent plastic flow structure - polygonal aggregate of crystals of long-prismatic habitus with isometric olivine grains in the interstices. The stress-recrystallizational structures known for oriented growth of olivine grains due to stress are of specific type.

It has been found that the dislocation of olivine structures is mainly typical of hyperbasite massifs in the areas of Paleozoic folding,while recrystallization structures are distributed in the massifs which are closer to the ledges of Proterozoic basement.

# ON THE PROBLEM OF SYSTEMATICS AND IDENTIFICATION OF METAMICT MINERALS

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Minerals may exist in different degree of metamictization. There are the metamict samples with the small disturbance of long-range order in position of atoms and the metamict samples with completely destroyed lattice in which "the memory" about original crystalline structure is absent. At the same time the minerals above can keep the chemical composition quite similar to their premetamict state or undergo the secondary chemical alteration in initial cationic composition in parallel with the metamict desintegration.

Metamict minerals which are able to restore their original crystalline structure in the course of special heat-treatment can be thought as a metamict varieties of the corresponding crystalline forms. The systematisation and identification of such metamict forms may be performed according to the same criteria, which are usually used to the crystalline ones.

In the case when the metamict specimen in the course of heat-treatment at the moment of transformation of metamict substance to crystalline state gives a number of crystalline products or one but being the result of crystallisation of only part of metamict material, it could not be considered as a variety of any crystalline mineral and such mineral form could be the amorphous product of complete metamict disintegration of the initial mineral (in case of identical chemical composition, this newformer and premetamict mineral) or the amorphous product the metamict and secondary chemical alteration as well (in the case of changed cationic composition).

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# PLAGIOCLASE PHENOCRYSTS IN RECENT VOLCANITES FROM KAMCHATKA AND KURIL ISLANDS. TEMPORAL AND SPATIAL RANGES OF THEIR GROWTH

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The results presented in the report have been obtained by the authors during recent eruptions in the Kamchatka and Kuril Isles, viz. Alaid volcano (1972), Tyatya volcano (1973), Karimsky volcano (1970-1971) and the Large Fissure Tolbachik eruption (1975-1976). Some previoulsy published data on Karymsky (1962 - 1965), Klyuchevskoy (1945,1966 and 1974) and Bezymyanny volcano (1956) eruptions have been taken into consideration.

When explosion activity and lava debit are maximal the amount of plagioclase phenocrysts is the lowest, the anorthite content is the highest and the structural state is more disordered. The early portions of volcanites are often subaphyric.

The bombs show the lower plagioclase phenocryst content as a rule than the synchronous lavas. In the fluent Tolbachik lavas the amount of plagioclase phenocrysts varies directly with the duration of liquid occurrence within the moving lava flow, lava tubes, or lava pockets within the newly-born lava field. No dependence of phenocryst amount on the bulk chemical composition have been found.

The authors believe that the substantial part of plagioclase phenocrysts have originated under near-surface conditions or , during the Tolbachik eruption, on the surface within the active lava flows. Phenocrysts have been derived partly or completely from the very portion of lava in which we find them.

# COMPOSITIONAL AND STRUCTURAL TRANSFORMATIONS IN APATITES OF PHOSPHORITE ROCKS UNDER THE ACTION OF WEATHERING AND CATAGENESIS IN THE LIGHT OF NATURAL AND EXPERIMENTAL DATA

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Analyses of apatites of phosphorite rocks catagenetically altered (at 5-10 km depth) have shown certain similarity in their composition and fine-crystal structure. Low $CO_2$ is typical of these apatites as well as low water (in form of $H_2O$) and sodium, while categenetically unaltered apatites contain the above components in varied amounts, the variations being very high. Catagenetically altered apatites are specified by high degree of perfection of their crystalline structure (large size of blocks of coherent dispersion and lower microdistortion value). The effect of catagenetic factors in laboratory conditions, such as temperature and pressure, results in the escape of the above mentioned components from the structure improving thus the degree of perfection of their crystalline structure. Formation of calcite from the products of original apatite decomposition proceeds under the compatible action of both temperatures and pressures.

Under weathering conditions (in nature) and influence of agressive media, superfine powdering, fluorine, calcium, phosphorus escape in this succession from apatite structure. These processes are also accompanied by lowering the degree of perfection of the crystalline structure of apatite (smaller size of blocks of coherent dispersion, greater microdistortions).

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# MANGANESE HALOES SURROUNDING PRECAMBRIAN BASE METAL DEPOSITS: A MICROPROBE INVESTIGATION

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Electron microprobe analyses of mineral associations in amphibolite facies host rocks of stratabound base metal deposits within the 1200 m.y. Kibaran orogenic belt of **Southern** Africa have been performed in order to elucidate possible compositional variations which may escape detection by conventional microscopy and bulk analysis. Rocks investigated include banded iron formation, garnetiferous quartzites, micaschists, garnetgrunerite-magnetite-rocks, amphibolites as well as various types of sulphide ore. The occurrence of barite in upper portions of the stratigraphic sequence is of genetic interest, especially as the constituent sediments may have been deposited during 2600 m.y. Kheis times.

Manganese emerged as a significant constituent of garnets (5-40% MnO), pyroxenes (5%), amphiboles (2%), stilpnomelane (11%) and also of sphalerite (7%) and magnetite (4%). There is a distinct increase in the MnO-content of garnets when the sulphide zone is approached from either hanging-wall or footwall. This contrasts distinctly with mineral compositions in iron formation not associated with base metal mineralization (Itchen Lake, Canada; Bostock 1977).

It is concluded that metamorphism ($\sim 600^{\circ}C$, 3-4 kb) in the area investigated was largely isochemical and did not involve transport beyond the mm-scale. The distribution pattern of manganese is interpreted as a primary depositional feature within a volcano-sedimentary environment. There are compositional similarities (silicate, oxide, carbonate and sulphide facies) not only with other stratabound deposits of various geological age, but also with recent metalliferous muds in the Red Sea.

# ORE FORMATION IN FUMAROLIC ENVIRONMENTS AND THEIR SIGNIFICANCE FOR THE GENESIS OF EXHALATIVE SULFIDE-DEPOSITS

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On the Eolian island of Vulcano, Italy and in volcanic hot lakes of the Nasu volcanic zone of Hokkaido, Japan, present-day formation of massive and disseminated sulfur and sulfide deposition takes place. Fumarolic gases of comparable chemical composition in both areas produce the ore formation. Four different stages of the fumarolic activity, which may be regarded as steps in a continuous process and which may under favorable conditions lead to the formation of sulfide deposites, may be distinguished. The different stages depend on the Eh-pH conditions in the rocks and in the sedimentary environment, and are determined by the interaction of the reducing, acidic fumarolic gases with oxygenated surface or lake water.

1. stage: decomposition of volcanic rocks by hot, sulfuric acid.
2. stage: formation of disseminated sulfides in hydrothermally altered volcanic rocks.
3. stage: precipitation of sulfide and native sulfur in a strongly acidic environment.
4. stage: precipitation of sulfides only in a weakly acidic environment.

R-mode factor analytical studies were made of 144 sediment samples from the different environments, analyzed for Cu, Zn, Pb, Co, Ni, Mn, Cr, Fe, As and S. The results show the diverse behaviour of the analyzed elements under the different fumarolic conditions.

On the basis of these investigations a theoretical model for the genesis of exchalative sulfide-deposits is postulated. This model provides us with a genetic explanation for the different ore types, as they are known from fossile exhalative sulfide-deposits.

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# FLUOR DETERMINATIONS IN MINERALS, ROCKS AND RAW-MATERIALS

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Fluor contents in rocks, minerals and raw-materials are not only of great interest for geochemical investigations, but are very important for environmental sciences, due to air pollution, if fluor-containing materials are used for industrial products.

The analysis of fluor includes two steps, firstly to bring the fluor into solution, and secondly the determination with a direct method, i.e. ion-sensitive method.

There is used a combined procedure by melting the 100 mesh sample *powder (0,05-0,4g) with 5 to 10 fold quantity of sodium/potassium*-carbonate in special platine/iridium crucibles and following destillation with overheated waterstream and F-free sulfuric acid. *The destillate is mixed with an equal proportion of TISAB-solution* and the F-content is determined with the Fluoride specific ion electrode.

With this method the geochemical reference sample, granitic rocks from Schwarzwald and Bavaria-Forrest, minerals and raw-materials (i.e. clays, feldspars etc.) were analysed.

The F-contents vary from low concentrations(100-300 ppm) in basic rocks to higher concentrations (0,1-0,5%) in granitic rocks and to very high concentrations in some minerals, i.e. sepiolites, micas (1-3%).

It is worth mentioning here *that in Kaolin clays and China clays* of different deposit types a wide concentration-range from 100 to 3000 ppm F was found. These variable concentrations could be brought in connexion with the different genetical conditions of the clay-deposites, more so since a good correlation between the F-and Rb-concentrations was observed in these Kaolin and China clays.

# PETROLOGY OF ULTRAMAFIC MASSES IN AND AROUND THE MAIZURU ZONE, SOUTHWEST JAPAN

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In and around the Maizuru Zone, inner zone of South-**West** Japan, two types of ultramafic masses of different origin occur (Kurokawa, 1972). One (type I) is ultramafic tectonite and the other (type II) is cumulus one crystallized from gabbroic magma. Cumulus one forms a small layered complex with gabbroic rocks and both harzburgite and wehrlite are found in a tectonic type. Ultramafic tectonites are found in the Sangun metamorphic terrain along the northern outside of the Maizuru Zone. They mainly consist of serpentinized dunite, but also accompany harzgurgite, lherzolite, clinopyroxenite, amphibolitic rocks and gabbro. As for the Ǒeyama (Kõmori) ultramafic mass, rather large amount (about 15% of the whole mass) of clinopyroxenite and amphibolitic bodies are recognized, and in the latter, relictic staurolite and kyanite are found (Kuroda et al., 1976). Clinopyroxene of clinopyroxenite is characteristically low in $Al_2O_3$ (0.58 - 1.69%) content as compared with that in lherzolite (3.27-3.88%). Rock facies variation in clinopyroxenite and amphibolitic bodies are remarkable from olivine-clinopyroxenite, clinopyroxenite to metagabbroic facies. Mg/Mg+Fe varies according to the rock facies variation; 0.874 to 0.500 in whole rock chemistry and 0.819 to 0.529 in the amphibole chemistry. Meanwhile, dunite and lherzolite are monotonous in rock facies and chemical variation. Equilibrium temperature of lherzolite estimated by Opx-Cpx pair (Wood and Banno, 1972) is 1140±60°C. Thus, it is supposed that the Oeyama mass was once risen to 1140°C, when dunite remained as refractory phase, while clinopyroxenite and amphibolitic rocks once crystallized from melt or segregated material.

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# ON THE GEOCHEMISTRY OF ULTRABASIC ROCKS IN THE EARLY PRECAMBRIAN ISUA SUPRACRUSTAL BELT, WEST GREENLAND

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The Isua supracrustal belt is found within the Amîtsoq gneisses ca. 150 km northeast of Godthab, West Greenland. It outcrops in a ca. 30 km long and up to 3 km wide arcuate belt (Allaart, 1976) The supracrustals as well as the Amîtsoq gneisses give radiometric ages in the range of 3.7 - 3.8 b.y. (Moorbath et al., 1975). Rb-Sr dating of gneiss veins found in the supracrustals show that the Amîtsoq gneisses are younger than the supracrustals (Moorbath et al., 1977).

The supracrustal belt consists mainly of meta-sediments and metamorphosed basaltic and rhyolitic rocks. The sediments are mainly represented by quartzites, carbonates, a banded iron-formation and an extensive horizon of garnet-staurolite schists. In addition, lense shaped intrusions of ultrabasic rocks are found within the supracrustals. The supracrustals have suffered lower amphibolite facies metamorphism and have been folded isoclinally at least twice.

The majority of the ultrabasic rocks, especially on the outer part of the belt, are layered talc-actinolite-chlorite schists. On the inner part of the belt there are some ultrabasic rocks consisting of forsterite (Fo 90). The olivine crystals vary from medium to coarse grained (0.1 - 30 mm) and random orientation is common. The matrix is mostly altered to antigorite and serpentine.

Separates of the olivine are rich in Cr (360 ppm), Ni (4000 ppm) and Sc (3.8 ppm) compared to olivine from lherzolitic nodules.

The Re patterns are remarkable high. This indicates that the parent liquid of this olivine was derived from a mantle, where garnet is not a dominant phase. Attempts to reconstruct the composition of the original parent magma are demonstrated. Limitations on the composition of the archean mantle, the source of this primitive magma, are given.

# SPOTTED STRUCTURES IN THE PURNAMOOTA ROAD GNEISS, BROKEN HILL, NEW SOUTH WALES, AUSTRALIA

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Spotted eye-like structures, composed of biotite mantled by quartz and feldspar, occur in a quartzofeldspathic gneiss located about 8 km north of Broken Hill. The spots are believed to have developed from an originally homogeneous gneiss with the following mode: quartz 34 (per cent by volume), plagioclase 24, K-feldspar 17, biotite 20, muscovite, garnet and opaques 5. The spotting process has produced a "matrix gneiss (quartz 35, plagioclase 29, K-feldspar 12, biotite 22, muscovite and garnet 2) holding quartz-feldspar mantles (quartz 41, plagioclase 37, K-feldspar 20, muscovite 2) which surround clots of biotite and minor ilmenite. The spots have a felsic mantle to mafic clot ratio of 4:1. The shape of the eye-like structure appears to be that of a distorted prolate spheroid with its axis close to the foliation plane of the gneiss; the biotite clots form another internal prolate spheroid with its axis set at approximately 70° to that of the enveloping quartz-feldspar mantle.

The whole-rock chemistry of the homogeneous gneiss and that of the gneiss with spots are very similar as are the compositions of almost all the minerals; for example plagioclase crystals are consistently about $An_{40}$ and alkali feldspar is $Or_{94}\ Ab_6$.

It has been suggested that the biotite in the spots was formed by retrogression of garnet but a more likely origin is best related to metamorphic differentiation. The spots in the gneiss are undoubtedly related to similar structures seen in veins cutting the Purnamoota Road gneiss, and it is tempting to suggest that these veins also formed by metamorphic differentiation. However, a second vein type, without biotite spots but rich in K-feldspar, is regarded as a possible product of anatexis.

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# VESUVIANITE (IDOCRASE) STABILITY IN THE SYSTEM $CaO - MgO - Al_2O_3 - SiO_2 - H_2O$ UP TO 5 KBAR

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Syntheses of vesuvianite have been reported for a wide range of temperature (450 - 720°C) and pressure (0,5 - 10 kbar) conditions (COES, 1955; RAPP and SMITH, 1958; CHRISTOPHE-MICHEL-LÊVY, 1960; CHRISTIE, 1961; WALTHER, 1966; ITO and AREM, 1970), but the stability has not been determined by reversed experiments. ITO and AREM suggested - based on synthesis runs only - an upper thermal stability limit of at least 720°C at 2 kbar water pressures, apparently producing melilite, monticellite, and wollastonite as the breakdown phases.

Investigation of the upper thermal stability limit of a synthetic vesuvianite $Ca_{19}Mg_4Al_{10}Si_{18}O_{70}(OH)_8$ ($a_o$=15.604(2), $c_o$=11.825(3) Å) resulted in the equilibrium conditions: o.2 kbar, 765 °C; 0.5 kbar, 820 °C; 1.0 kbar, 870 °C; and 2.0 kbar, 905 °C at $P_{H_2O}=P_{total}$ (pressure ± 5%, temperature = ± 10 °C). Vesuvianite breaks down to the phase assemblage gehlenite-rich melilite + diopside + wollastonite + $H_2O$; a paragenesis which was found also in natural rocks (e.g. BURNHAM, 1959). In these rocks $CO_2$ often play an important rôle. Preliminary results about the stability of vesuvianite in the presence of $CO_2$ show that at $X_{CO_2} \geqslant 0.5$ vesuvianite is unstable.

In regionally metamorphosed rocks the occurrence of vesuvianite can be limited to lower temperatures by the presence of quartz (e.g. BRAITSCH and CHATTERJEE, 1963). Vesuvianite + quartz breaks down to wollastonite + diopside + anorthite + $H_2O$ along a univariant reaction curve located at 0.5 kbar, 515 °C; 1.0 kbar, 535° C; and 2.0 kbar, 580°C at $P_{H_2O} = P_{total}$ (± 0.05 kbar, ± 5 °C). At 2.0 ± 0.1 kbar, 580 ± 10°C is an invariant point involving grossularite in addition. At higher $P_{H_2O}$ vesuvianite decomposes to diopside + grossularite + $H_2O$. This univariant curve has a negative slope and passes through 3.5 kbar, 515°C and 5.0 kbar, 490°C (± 0.05 kbar, ± 10°C).

## UNUSUAL PHOSPHATE MINERAL ASSEMBLAGES FROM SOUTH AUSTRALIA

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Two occurrences of phosphate minerals from South Australia are being studied. One is at Moculta, near Angaston, about 50 km north of Adelaide; the other is at Iron Knob, on Eyre Peninsula.

The Moculta occurrence - Numerous small deposits of rocks phosphate occur at the base of the Cambrian limestone in South Australia. In the Angaston area, the rocks have been locally metamorphosed, the limestone to a coarse-grained marble. The redistribution of phosphorus, and formation of a number of additional phosphate minerals.

Apatite was the first mineral to crystallize, cementing the brecciated phosphorite, and forming cross-fibre veinlets 1-2 mm wide, and botryoidal coating in vugs. In the absence of iron, crandallite and gorceixite were deposited on the apatite. In the presence of iron, veinlets were subsequently filled with dufrenite and rockbridgeite, while beraunite, cacoxenite and cyrilovite crystallized in vugs. Iron-free phosphates such as variscite, fluellite, and minyulite were formed subsequently, followed by wavellite; the latter three minerals formed transparent idiomorphic crystals up to 2 mm in size. Also occasionally deposited on the fluellite were white pearly flakes of an unidentified calcium aluminium phosphate.

Iron Knob occurrence - Phosphorus leached from the Precambrian iron ore at Iron Knob, South Australia, has resulted in the sporadic occurrence of a variety of phosphate minerals in cracks and cavities. They appear to have been formed above the water table, and generally, only one to three minerals occur together. The mineral assemblages include turquoise-wardite-wavellite, wardite-wavellite, mongomeryite-millisite, mongomeryite-variscite (deep pink), cyrilovite-strengite, apatite-wardite, turquoise-crandallite, gorceixite (pseudomorphs after apatite), and an unidentified zinc aluminium phosphate. The latter mineral occurs as pale brownish yellow aggregates of very small needles.

## AUTHORS INDEX

Abs-Würmbach I. 49
Ackermann H. 173
Afonin V.P. 127
Afanasiev V.P. 18
Agafonov L.V. 55
Akizuki M. 64
Alkhazov V.Yu. 93
Anufriev A.M. 59
Appel P.W.U. 152, 175
Arbunies-Andreu M. 89
Arkhipenko D.K. 25
Arnaudov E. 106
Avdonin A.S. 132
Bagdasarov E.A. 137
Balitsky V.S. 92
Baller Th. 51
Barich L. 154
Barsanov G.P. 63, 65
Belichenko V.P. 104
Belyaeva I.D. 72
Bence A.E. 120
Bilenko Yu.M. 17
Blinov V.A. 65
Botkunov A.I.
Bouška V. 99
Bradinskaya E.M. 71
Bukanov V.V. 101
Bukin G.V. 94
Bulka G.R. 59
Burmakina G.V. 104
Buslaev F.P. 78
Cambel B. 60
Candais M. 80
Carmichael D.M. 40
Cavell P.A. 124
Cervelle B. 80
Chashka A.I. 34
Chelishchev N.F. 69
Chenhall B.E. 176
Cherepanov V.A 134
Chistyakova N.I. 132
Clocchiatti R. 136
Corlett M.I. 150
Cradwell R. 176
Danner W.R. 100
Davidenko N.M. 146
Dele M.L. 87
Dhamelincourt P. 87
Dobretsov N.L. 9
Dodd G. 135
Dokina T.N. 142
Domnina M.I. 157
Donskikh A.V. 157
Doroshev A.M. 46
Dubakina L.S. 133
Dudkin O.B. 129
Edelshtein G.B. 117
Eggler D.H. 5, 19
Erlank A.J. 38
Ermakov N.P. 66
Ershova K.S. 133
Eryomenko G.K. 35
Finger L.W. 53
Fojt B. 126
Flerov G.B. 169
Fleet M.E. 47
Fonarev V.I. 142
Font-Altaba M. 89
Fransolet A.M. 165
Fuess H. 151
Fursenko B.A. 50
Geruvol M.T. 93
Godlevsky M.N. 103
Godovikov A.A. 94, 153

Golovko M.M. 34
Golubev B.F.95
Golubyatnikov D.V. 139
Goncharenko A.I. 167
Graig I.R. 143
Gramenitsky E.I. 65
Grattan-Bellew P.E. 147
Gurkina G.A. 103
Gurney J.J. 8, 15
Gusev G.M. 170

Hariya Yu. 48
Harlow G.E. 26
Harris J.W. 8, 15
Havette A. 136
Hawthorne J.B. 8, 15
Haynes S.J. 98
Hazen R.M. 53
Helmstaedt H. 40
Herzberg C.T. 47
Higgins J.B. 148
Hinrichsen Th. J. 56
Hinze E. 47
Hodenberg R. 149
Hofmeister H. 39
Indelicauto G.J. 120
*Ishbulatov R.A.* 56
Ivanov V.G. 90
Jagoutz E. 152, 175
Jarkovsky J. 60
Joswig W. 151
Kalikov V.N. 95
Kalinin A.A. 46
Kalyujny V.A. 146
Kaminsky F.V. 13
Kano S. 83
Kapitonova T.A. 69
Karmanov N.S. 75
Kazakov L.V. 117
Kashaev A.A. 90
Kazachenko Yu.A. 71
Kepezhinskas V.V. 14
Khanukhova L.T. 24
Kharkiv A.D. 18
Khitarov N.I. 45
Khrenov A.P. 169
Khrenov A.Ya. 35
Kirfel A. 47
Kirikilitsa S.I. 35
Kirkinsky J.A. 50
Kirov G.N. 156
Kiselyova I. 65
Kiziyarov G.P. 33
Klyakhin V.A. 94
Koizumi M. 51
Kolesnik Yu.N. 25
Komkov A.I. 168
Kononov O.V. 65
Konovalenko S.I. 107
Korago A.A. 95
Korolkov G.Ya. 142
*Korolyuk V.N. 67, 119*
Koshchug D.G. 65
Kostrovitski S.I.
Kotov N.V. 157
Kranari G.A. 59
Krendelev F.P. 75
Krištin J. 60
Krivoputskaya L.M. 170
Krochuk V.M. 10
Kudrjavtseva G.P. 63
Kulagina D.A. 155
Kume S. 51
Kupriyanova T.A. 114
Kurat G. 39
Kurokawa K. 174
Kutolin V.A. 55
Kutty T.R. N. 164
Kvashitsa V.N. 10
Laduron D. 68
Langer K. 49
Laputina I.P. 128
Lavrentiev Yu.G. 9, 119
Lashnyova Z.V. 82
Lashnyov I.M. 82
Lazebnik K.A. 155
Lazebnik Yu.D. 155
*Lebedeva S.I.* 72
Lennykh V.I. 31
Lerotoli R.M. 10
Letnikov P.A. 104
Lévy C. 80
Lemina N.M. 170
Lipovsky Yu.O. 101
Lisitsina E.E. 92
Litvin A.L. 36, 56
López-Soler A. 89
Lugovskoy G.P. 118
Lundin A.G. 170
Lyapitchev I.G. 127
Makedon I.D. 134
Maleev M.N. 62
Malinovskii I.Yu. 46
Malkov B.A. 32
Malinko S.V. 145
Malysheva T.V. 20
*McCallum M.E. 5, 19*
McColl D.H. 158
Melnikov E.P. 74
Meyer H.O.A. 6
Mikhailov V.P. 159
Miyamoto Y. 51
Mofolo M.M. 10, 16
Moiseenko V.S. 61
*Nambu M. 83*
Narebski W. 161
Nasanova N.M. 59
Nesterov I.V. 65
Nisamutdinov N.M. 59
Nogteva V.V. 25
Novgorodova M.I.79
Ogorodova L.P.65
Olesch M. 177
Orekhov B.A. 25
Ostrovskaya I.V. 36
Ovchinnikov L.N. 69
Paděra K. 11
Pachomovsky J.A. 129
Palme H. 39
Passaglia E. 161
Paukov I.E.
Pechigargov V.I. 156
Pertsev N.N. 67
Perchuk L.L. 45
Petrovskaya N.V. 79
Petrovsky V.A. 159
Petrusenko S. 106
Phillips E.R. 176
Platonov A.N. 104
Pokhilenko N.P. 29
*Polejaeva L.I. 129*
Polkanov Yu.A. 35
Ponomarenko A.I. 23
Prinz M. 26
*Prouvost J. 160*
Puchkov V.N. 31
Reverdatto V.V. 67
Revin N.I. 45
Reznitsky L.Z. 70
Ribbe P.H. 135, 148
Rickard R.S. 8,15,38
Rjaposov A.P. 50, 170

Rogosin M.P. 157
Rogova V.P. 108
Romanenko I.M. 127
Ronsbo G. 121
Rosinov M.I. 30
Rossovsky L.N. 107
Rucklidge G.C. 131
Rusov V.P. 159
Sachambinski M. 88
Safronov P.P. 61
Samoilov V.S. 90
Sapozhnikov A.N. 90
Savkevich S.S. 96, 162
Scherbak O.V. 133
Schchyritsa A, 146
Schreyer W. 49, 52
Schubnel H.J. 87
Schürmann K.U. 56
Segnit E.R. 178
Sekerin A.P. 104
Serdyuchenko D.P. 37
Sergeev V.N. 73
Sherstobitova L.A. 78
Shinkarev N.V. 157
Slutsky A.B. 45
Smirnoff G.I. 10, 16
Smith D.G.W. 122, 124
Smith C.B. 5, 19
Smyth J.R. 38
Sobolev A.V. 22
Sobolev E.V. 17, 28
Sobolev V.S. 94
Sobolev N.V. 16, 29
Soloviev V.S. 132
Spetsiys Z.V. 23
Spettel B. 39
Stanek J. 109
Struensee G. 149
Stumpfl E.F. 171
Suddaby P. 134
Surkov N.V. 46
Sunagawa I. 121
Superchi M. 91
Suturin A.N. 104
Suturina T.A. 104
Sysoev A.G. 127, 134
Sysoeva L.N. 114
Takenchi Y. 151
Takubo H. 51
Tarasyuk O.N. 34
Tarasyuk L.P. 34
Tareen J.A.K. 164
Tatarinov L.V. 33
Teptov S.N. 75
Terada S. 48
Thoreau J. 68
Topor N.D. 65
Troneva N.V. 36, 116
Tsai H.M. 6
Tsepin A.I. 116, 130
Tsiurupa A.I. 169
Tsukamoto K. 12
Udovkina N.G. 36
Ukhanov A.V. 20
Urasin M.A. 59
Urusov V.S. 27
Vakanjak B. 110
Vakhromeev A.M. 170
Valizer P.M. 31
Vandekirkov Yu.I.169
Vanghau D.J. 143
Vasilyeva Z.L. 77
Vendrell-Saz M. 89
Vinokurov V.M. 59
Vinogradov A.P. 90
Viswanathian M.N. 164
Vladimirov B.M.
Vokhmentsev Ya. 104
Volynets O.N. 169
Vorobjov E.I. 70
Wänke H. 39, 175
Waushkuhu A. 172
Watts J. 178
Will J. 47
Willaime C. 80
Wyllie P.J. 54
Yablokova S.V. 75
Yakovleva L.Yu. 45
Yarosh P.Ya. 78
Yasuda T. 12
Yurgenson G.A. 93
Yurieva A.L. 34
Yurkina K.V.118
Yusupov T.S. 170
Zamaletdinov P.S. 104
Zanin Yu.N. 170
Zaric P. 110
Zavyalova L.L. 71,33
Zharikov V.A. 24, 56
Zhabin A.G. 144

# CONTENTS

High-Pressure Minerals . . . . . . . . . . . . . . 3

Experimental Mineralogy and the Problem of Upper Mantle . . . . . . . . . . . . . . . . . . 43

Inhomogeneities of Minerals . . . . . . . . . . . 57

Gem Minerals and Gemology . . . . . . . . . . . 85

Electron Probe Microanalysis in Mineralogy . . . 113

Open Session . . . . . . . . . . . . . . . . . . . .141

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