# SYMPOSIUM 1 : Sheet silicates

Chairman / Editor : J. Konta

Saturday, August 31, 1968

PROGRAM

9.00- 9.05 Chairman: Opening remarks.

9.05- 9.15 Whittaker E.J.W. (Oxford, United Kingdom):
Relationships among sheet silicates, and some "missing" species.

9.20- 9.30 Strens R.G.J. and Robbins D.W. (Newcastle upon Tyne & Rochdale, United Kingdom):
Polarised absorption spectra of trioctahedral micas.

9.35- 9.45 Seifert F. and Schreyer W. (Bochum, Germany):
Synthesis and stability of micas in the system $K_2O-MgO-SiO_2-H_2O$ and their relations to phlogopite.

9.50-10.00 Sunagawa I., Endo Y., Daimon N. and Tate I. (Tokyo and Nagano-shi, Japan):
Nucleation, growth and polytypism of fluor-phlogopite from vapour phase.

10.05-10.15 Rimsaite J. (Canada):
Natural and laboratory fused phlogopite.

10.20-10.30 Starkey J. (London, Canada):
On the relationship between the chemical composition and X-ray diffraction pattern of biotite.

10.35-10.45 Serratosa J.M. and Johns W.D. (Madrid, Spain and St.Louis, U.S.A.):
Infrared study of alkyl-ammonium vermiculite complexes.

10.50-11.00 Liberto de Pablo (Mexico City, Mexico):
The system of kaolinite - nonordered kaolinite - - metahalloysite - endellite. Morphological and structural relations.

11.05-11.15 Munsuz N., White J.L. and Baumgardner M.F. (Lafayette, U.S.A.):
Estimation of mica content of clays using the intensity of the (005) X-ray reflection.

INTERNATIONAL MINERALOGICAL ASSOCIATION

## Sixth General Meeting

# ABSTRACTS

PRAGUE 1968
August 30 - September 5

11.20-11.30 Čičel B. and Novák I. (Bratislava, Czechoslovakia):
Unusual acid attack of montmorillonite.

11.35-11.45 Rustom M.A. (Allepo, Syria):
Study of clays from Charentes, France and from Syria using the X-ray fluorescence.

11.50-12.00 Frank-Kamenetzky V.A. (Leningrad, Soviet Union):
Mixed-layer structures of clay minerals as products of the synthesis and natural formation.

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14.00-14.10 Krumm H. (Frankfurt, Germany):
Recent clay-mineral sedimentation in Persian Gulf.

14.15-14.25 Caillère S. and Morre-Biot N. (Paris, France):
Mineralogical study of the chlorites found in the Carboniferous lavas.

14.30-14.40 Thorez J.L.M. (Liège, Belgium):
Mixed-layer and other clay minerals formed by degradation of the sedimentary rocks in Belgium.

14.45-14.55 Bourguignon P. (Liège, Belgium):
Mineralogy of the argillaceous residues after the Dinantian limestones.

15.00-15.10 Böhmer M., Gerthofferová H. and Kraus I. (Bratislava, Czechoslovakia):
Clay minerals in hydrothermally altered zones in central Slovakian neovulcanite region.

15.15-15.25 Melka K. and Vybíral J. (Praha, Czechoslovakia):
Fe-phyllosilicates in the submarine exhalation deposits of the Moravian Devonian.

15.30-15.40 Schneider H. (Dresden, Germany):
Nickel-bearing chlorite from the nickel hydrosilicate deposits, Saxony.

15.45-15.55 Lopes-Vieira A. and Zussman J. (United Kingdom):
The crystal structure of the mineral zussmanite.

# INTERNATIONAL MINERALOGICAL ASSOCIATION

## Sixth General Meeting

## ABSTRACTS

PRAGUE 1968
August 30 - September 5

# OPEN SESSION

Chairman / Editor : Prof.H.G.Winkler

September 2, 1968

PROGRAMME

## MINERALOGY

8.30 - 8.40 H.J.Kisch (Leiden) :
Magnesio-cummingtonite : A new Ca-poor magnesian clino-amphibole from New South Wales.

8.45 - 8.55 A.Mottana (Milano) :
Amphiboles in eclogitic rocks : their chemistry and relationships to the other mineral constituents.

9.00 - 9.10 A.D.Edgar, A.Mottana and N.D.MacRae (London, Canada) :
The chemistry and cell parameters of omphacites and related pyroxenes.

9.15 - 9.25 W.G.R. de Camargo (S. Paulo) and C.R.Leite (Araraquara) :
Inclusions in Brazilian diamonds : olivine.

9.30 - 9.40 H.O.A.Meyer (Washington) :
Geochemistry of mineral inclusions in diamand.

9,45 - 9.55 L.Žák (Praha) :
Melanophlogite from Chvaletice, Bohemia.

10.00 - 10.10 A.S.Povarennykh (Kiev) :
Principles of scientific nomenclature of minerals.

10.15 - 10.25 S.Ueda, M.Koizumi and S.Kume (Osaka) :
Synthetic experiments of germanate albite and anorthite under pressures.

10.30 - 10.40 A.Traveria-Cros and J.M.Amigo (Barcelona) :
Etude quantitative de la transformation thermique de l'esphalerite.

10.45 - 11.00 Coffee break

PETROLOGY - MINERALOGY

11.00 - 11.10 M.P.Atherton (Liverpool) :
Zoned garnets and metamorphism.

11.15 - 11.25 B.W.Evans (Berkeley) :
Composition of scapolite by electron probe microanalysis.

11.30 - 11.40 E.Wm.Heinrich and D.G.Moore (AnnArbor) :
Metasomatic potash feldspar rocks associated with alkalic igneous complexes.

11.45 - 11.55 P.Černý (Praha) :
Mineralogy, petrology, and decent of two pegmatite types from West-Moravian ultramafites.

12.00 - 12.10 M.Font-Altaba and J.Montoriol-Pous (Barcelona) :
Crystallization conditions of salt minerals in Catalonian deposits (Spain).

12.15 - 12.25 J.J.Dubois (Liège) :
Determination quantitative de dolomite, calcite et quartz dans une roche carbonatée par difraction de rayons X.

12.30 - 12.40 S.Bhattacharji(New York) :
Mechanics of flow differentiation in ultramafic and mafic rocks

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CRYSTALLOGRAPHY - CRYSTALCHEMISTRY

14.30 - 14.40 R.Rath (Hamburg) :
Neue Ergebnisse zur Kenntnis optischer Achsenbilder.

14.45 - 14.55 Y.Endo and I.Sunagawa (Tokyo) :
Positive and negative crystals of pyrite.

15.00 - 15.10 A.Pabst (Berkeley) :
Multiple orientations in the topotaxy of $MgO$ on $MgF_2$.

15.15 - 15.25 I.Krstanović, S.Djurić and P.Ilić (Beograd) :

Further X-ray study of zircon.

15.30 - 15.40 G.V.Gibbs and P.H.Ribbe (Blacksburg, Virginia) :

The crystal structures of the humite minerals, I. norbergite.

15.45 - 15.55 J.Hrušková (Praha) :

On the crystal structure of samsonite, $2\ Ag_2S\ MnS\ Sb_2S_3$.

16.00 - 16.15 Coffee break

16.15 - 16.25 P.B.Moore (Chicago) :

Studies on complex silicates : the crystal structures of kornerupine ( with J.M.Bennett), sapphirine, joesmithite, leucophoenicite, and a new mineral.

16.30 - 16.40 W.M.Meier and H.Villiger (Zürich and London) :

Least squares refinement of interatomic distances in framework structures

16.45 - 16.55 R.G.J.Strens (Newcastle upon Tyne)

Bond length - bond strength correlations in silicates.

17.00 - 17.10 H Katscher (Kiel) :

The crystal structure of the high temperature form of $BaSi_2O_5$.

17.15 - 17.25 R.S.Boorman and J.K.Sutherland (Frederictown, Canada) :

The $ZnS-In_2S_3$ binary 1064° to 500°C.

17.30 - 17.40 A.Preisinger (Wien) :

Crystal structure of prosopite, $CaAl_2(F,OH)_8$.

September 3, 1968

## PETROLOGY - MINERALOGY

14.30 - 14.40 M.C.Gilbert, S.W.Richardson and P.M.Bell (Washington) :

Andalusite - sillimanite - kyanite equilibria.

14.45 - 14.55 P.M.Bell (Washington) :

Experimentally determined relationships with omphacite.

15.00 - 15.10 D.Ganguli and P.Saha (Calcutta) :

Synthetic epididymite.

15.15 - 15.25 F.J.Eckhardt (Hannover) :

Differentiation and spilitization of permian basalts in Northwest Germany

15.30 - 15.40 J.M.Moore (Ottawa) :

Metamorphic zoning in thor-odin gneiss dome British Columbia, Canada.

15.45 - 15.55 E.Roeder (Washington) :

Varvelike banding of possibly annual origin in celestite crystals from Clay Center, Ohio, and similar occurrences.

# SYMPOSIUM II : Crystal Field Theory

Chairman / Editor: Prof.W.S.Fyfe

September 3, 1968

PROGRAMME

9.00 - 9.10 Chairmans remarks (W.S.Fyfe).

9.15 - 9.25 G.M.Bancroft (Cambridge, U.K.) :
Quantitative site populations in silicate minerals by Mössbauer spectroscopy, and a possible geothermometer.

9.30 - 9.40 G.M.Bancroft, R.G.Burns and F.J.Prentice (Cambridge and Oxford, U.K. and Wellington, New Zealand) :
Distributions of iron cations in alkali amphiboles by Mössbauer and infrared spectroscopy.

9.45 - 9.55 S.Shin, F.Kanamaru and M.Koizumi (Osaka, Japan) :
Mössbauer spectra of perovskites of the system $Ca_2Fe_2O_5$ -$SrFeO_3$.

10.00 - 10.10 R.Burns (Oxford,U.K.) :
Site preferences of transition metal ions in silicate crystal structures

10.15 - 10.25 P.Henderson, I.M.Dale (Glasgow,U.K.) :
The partitioning of manganese,cobalt and nickel between olivine crystals and the groundmass of selected basic igneous rocks.

10.30 - 10.40 Y.Matsui, B. Banno (Tottori-Ken and Tokyo, Japan) :
Partition of divalent transition metals between coexisting ferromagnesian minerals.

10.45 - 11.00 Coffee break

11.00 - 11.10 E.H.Nickel (Ottawa,Canada) :
The application of ligand-field concepts to an understanding of the structural stabilities and solid solution limits in sulphides and related minerals.

11.15 - 11.35 R.G.J.Strens (Newcastle upon Tyne,U.K.) :
Calculation of the crystal field splittings of the d-orbitals of transition metal ions in distorted coordination polyhedra.
and
Pressure-induced spin-pairing in iron (II) minerals

11.40 - 11.50 S.Ghose, P.Schindler (Chicago and Argonne, U.S.A.) :
Distribution of $Mn^{2+}$ in trace amouts in diopsides and dolomites by electron spin resonance.

12.10 - 12.35 S.S.Hafner, M.Raymond (Chicago, U.S.A.) :
Self-consistent ionic field gradients at the Al sites in kyanite and andalusite.

12.10 - 12.20 R.Coy-Yll (Quebec, Canada) :
Some aspects of mineralsCathodoluminescence.

12.25 - 12.35 P.M.Bell (Washington) :
A theoretical approach to pressure, energy and crystal field.

12.40 Concluding remarks

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SYMPOSIUM I: Sheet Silicates
Chairman / Editor: Prof. J. Konta

August 31, 1968

# AUTHORS´ ABSTRACTS
## in alphabetic order

# CLAY MINERALS IN HYDROTHERMALLY ALTERED ZONES IN CENTRAL SLOVAKIAN NEOVOLCANITE REGION

M. Böhmer, H. Gerthofferová and I. Kraus
/Czechoslovakia/

The ore veins in the district of Kremnica and Štiavnica caused intense alteration of wall rock. We can trace altered complexes of volcanic rocks at several places in the whole central Slovakian neovolcanite region. Detailed study of clay minerals has shown two types of alteration in these zones.

The first group includes alterations caused directly by ore-bearing hydrothermal solutions. They manifest around the ore veins by whitening of rocks and variable grade of argillization. Clay minerals characteristic of this alteration are hydromicas of dioctahedron type and kaolinite. In most cases both minerals appear together. Sporadically they are present in monominerals. Another present typical mineral is jarosite. We have ascertained that extent and intensity of alteration are directly connected with the character of mineralization. In principal vein system of the Kremnica district ore field alteration was very strong. Near later low-thermal mineralization in marginal part of the Kremnica district kaolinite with small admixture of diaspore in the shape of thin /1-3 mm/ veinlets appears in groundmass of altered andesites.

The second type of alteration has been ascertained at several places in the region of central Slovakian neovolcanites. It is of regional character and shows in contrast to the preceding type different mineralogical composition of clay component. There are propylitized mainly pyroxene andesites, often in whole extent argillitized in various grade. Predominant clay mineral is montmorillonite. In the part of studied profiles with indications of mineralization kaolinite arose first. Zonality in vertical distribution of clay minerals has not yet been ascertained to depth of 500 m.

From above mentioned follows that in central Slovakian neovolcanite region in hydrothermally altered zones kaolinite in association with hydromicas usually indicated mineralization. Alteration of regional character, where montmorillonite predominates was not directly connected with the effect of ore bearing hydrothermal solutions and could be caused by several factors.

# MINERALOGY OF THE ARGILLACEOUS RESIDUES AFTER THE DINANTIAN LIMESTONES

P. Bourguignon

(Liège, Belgium)

The Dinantian limestones from the Dinant basin yield, after alteration,brown-reddish clay which forms paleosol (terra fusca) and is sometimes overlain by leached brown soil developed on the loess.

In this intricate pedological environment the mineralogical association of the decalcified clays is determined by X-ray study of about fifty samples.

In pure state these formations are characterized by strongly open illite and by kaolinite which is accompanied by chlorite.

The swelling interstratifications of the type 10-(10-14 M)Å appear in small amount in two places of the profile.When clay is overlain by less, a contamination by loess intercalations occurs, and the clay contains a higher proportion of loess.

In the second place, in the immediate vicinity of the limestone, the swelling interstratification can be traced systematically in the samples which occasionally show the highest sorption capacities.

The last mentioned case is interpreted as a result of the existence of a thin zone at the contact with limestone, which is characterized by a confined milieu.

This distribution of clay minerals helps to understand better the alteration of limestones.

A hypothesis has been expressed as to the origin of different minerals.

# MINÉRALOGIE DES ARGILES DE DISSOLUTION DES CALCAIRES DINANTIENS

F. Bourguignon
/Liège, Belgique/

Les calcaires dinantiens du bassin de Dinant donnent par altération une argile brun-rougeâtre qui constitue un paléosol /terra fusca/, éventuellement surmonté d'un sol brun lessivé développé sur loess.

Dans ce contexte pédologique complexe, l'association minéralogique propre aux argiles de décalcification est définie par examen diffractométrique, sur une cinquantaine d'échantillons.

A l'état pur, ces formations sont caractérisées par une illite très ouverte, et une kaolinite accompagnées très accessoirement de chlorite.

Des interstratifiés gonflants du type 10- /10 - 14 M/ Å interviennent en faible quantité mais en deux sites précis des profils. Lorsque l'argile est surmontée de loess, il y a contamination par les interstratifiés propres à cette dernière formation et l'argile en contient alors une plus forte proportion.

En second lieu, au voisinage immédiat de la roche calcaire, on observe systématiquement un interstratifié gonflant, dans des échantillons qui, par ailleurs, présentent les capacités de sorption les plus élevées.

Ce dernier cas est interprété comme résultant de l'existence d'une mince zone au contact du calcaire, caractérisée par un milieu confiné.

Cette répartition des minéraux argileux concourt à une meilleure compréhension de l'altération des calcaires.

Une hypothèse est émise quant à la provenance des divers minéraux.

# MINERALOGICAL STUDY OF THE CHLORITES FOUND IN THE CARBONIFEROUS LAVAS

S. Caillére and N. Morre-Biot

(Paris, France)

Mineralogical study of the chlorites found in a series of volcanic rocks encountered by various borings in the northern France shows that whatever be the nature of rocks, chlorites belong to the group of penninites, but their number is large, ranging from magnesium-rich types to iron-rich types.

Their composition reflects the composition of the surrounding rock whose last phase of crystallization they represent.

# ETUDE MINÉRALOGIQUE DE CHLORITES RENCONTRÉES DANS DES LAVES CARBONIFÉRES

S. Caillére et N. Morre — Biot
/Paris, France/

L' étude minéralogique de chlorites trouvées dans une série de roches volcaniques rencontrées par divers sondages effectués dans le nord de la France montre que quelle que soit la nature des roches, les chlorites appartiennent au groupe des pennines mais elles se répartissent dans un éventail assez large allant des types magnésiens aux types trés ferriféres.

Leurs compositions reflétent celles des roches englobantes dont elles représentent la derniére phase de cristallisation.

# UNUSUAL ACID ATTACK OF MONTMORILLONITE

B. Číčel, and I. Novák
/Bratislava, Czechoslovakia/

The acid attack of montmorillonites has been described by several authors as a first order reaction. This is valid for most montmorillonites. Investigating the samples from Draňany /Czechoslovakia/ and Ginovec /Jugoslavia/ we found that the formal description of the reaction kinetics is of the zero order. There is good agreement between the structural formula constructed with the aid of chemical analysis data and the data obtained by the acid attack studies. The sequence of atoms elution from the structure is the same as in the case of first order reactions.

The model of acid attack of montmorillonite structure, as it has been devised on the basis of a great number of experimental data, shows that the evaluation of destruction kinetics performed on the basis of kinetics equations for reactions in solution is only formal and the apparent reaction order is given by the particle size distribution of the material.

# MIXED-LAYER STRUCTURES OF CLAY MINERALS AS PRODUCTS OF THE SYNTHESIS AND NATURAL MINERAL FORMATION

V.A. Frank-Kamenetsky
(Leningrad, U.S.S.R)

In the crystallochemistry and mineralogy of clay formations, like layered silicates, the mixed-layer structures are typical and unique examples of defect formations. The recent development of "basal X-ray study" of clay minerals together with diffractometry made it possible to establish a great variety of ordered and nonordered mixed-layer structures in natural clays and to find some connections between their regional and radial distribution and the conditions of their origin. The experimental investigation of the conditions of origin and alteration of mixed-layer structures of various types in the clays under the influence of mineralized solutions at various temperatures and pressures have shown that the formation of mixed-layer structures is, in fact, influenced by the composition of solutions instead of being controlled by the thermodynamic conditions which largely are responsible for the origin of the defects of other types (nonordered layers, dislocation defects etc.) and for the kinetics of the transformation of phases. The correlation of the laws established by the investigation of natural and synthetized mixed-layer formations, makes it possible to find, in spite of the paucity of data, many features of the conditions of formation of single types of mixed-layer structures which are common both in nature and in laboratory. The mixed-layer structures seem to be unbalanced phases which originate in the process of the transformation reconstitutions of clay minerals under the conditions of epigenesis and early stages of metamorphism. These transformations take place in solid state inheriting individual features of structural similarity and are controlled by the chemism of the environment, however, they depend also on other factors. In connection with this the problem of mixed-layer structures is of genetic importance, making it possible to display the genetic factors of diagenesis and of initial metamorphism.

# СМЕШАННОСЛОЙНЫЕ СТРУКТУРЫ ГЛИНИСТЫХ МИНЕРАЛОВ, КАК ПРОДУКТЫ СИНТЕЗА И ПРИРОДНОГО МИНЕРАЛООБРАЗОВАНИЯ

В.А. Франк - Каменецкий
/Ленинград, СССР/

В кристаллохимии и минералогии глинистых образований, как слоистых силикатов, смешаннослойные структуры являются типичными и уникальными примерами дефектных образований. Развитие в последнее время "базальной рентгенографии" глинистых минералов в сочетании с дифрактометрией позволило выявить в природных глинах большое разнообразие упорядоченных и неупорядоченных смешаннослойных структур разных типов и наметить некоторые связи между их региональным и радиальным распространением и условиями образования. Экспериментальные исследования в области установления условий образования и преобразования в глинах смешаннослойных структур разных типов под влиянием минерализованных растворов при разных температурах и давлениях показывают, что формирование смешаннослойных структур в основном связано с воздействием состава растворов, а не с термодинамическими параметрами, которые оказываются в большей степени ответственными за возникновение дефектов иных типов /разупорядоченность слоев, дислокационные дефекты и проч./ и кинетику преобразования фаз. Сопоставление закономерностей, выявленных в результате исследования природных и синтезированных смешаннослойных образований, позволяет уже теперь, несмотря на недостаточность данных, найти много общего в условиях формирования отдельных типов смешаннослойных образований в природе и в лаборатории. Смешаннослойные структуры являются неравновесными фазами, которые возникают в процессе трансформационных преобразований глинистых минералов в условиях эпигенеза и ранних стадий метаморфизма. Осуществляясь в твердом состоянии при унаследовании отдельных черт структурного подобия, эти преобразования в основном определяются химизмом среды, но зависят и от других факторов. В связи с этим проблема смешаннослойности преобретает вполне определенное генетическое значение, давая возможность выявлять генетические факторы диагенеза и начального метаморфизма.

# RECENT CLAY-MINERAL SEDIMENTATION IN THE PERSIAN GULF

H. Krumm

/Frankfurt, German Federal Republic/

149 samples from the surface of recent sediments off the Persian coast towards the central axis of the Persian Gulf and from the Gulf of Oman, 17 samples of suspended inorganic matter from the same areas and 4 samples of suspended matter from the rivers Euphrates and Tigris have been investigated in bulk by means of X-ray, optical methods, electron microscopy and DTA.

As already known, the clay content decreases from the deeper parts of the sedimentation basin near the Persian coast and the amount of carbonates increases towards the shallow areas near the coast of the Arabian peninsula. Possible sources for -land derived clay material are:

1) discharge of many smaller rivers from the Zagros ranges /Persia/, which mostly are reported not to be perennial,
2) suspended sediment load of the river Karun /from the Persian ranges to Shatt el Arab/ and Shatt el Arab as confluent of Euphrates and Tigris with the united sediment load of these big streams, reaching from the Taurus mountains through Mesopotamia on to the Persian Gulf,
3) wind-transported sediments from the Arabian peninsula /dust samples have been taken and partially investigated/.

The combined investigation of recent sediments, suspended matter and dust samples gave evidence for source, transport and sedimentation of some of the clay minerals present in the recent sediments of the Persian Gulf.

Palygorskite in suspension is limited to the northern parts along the Persian coast, in sediments the frequency is highest in this area. As it is not to be the source has to be sought in Zagros range rivers.

Mica and illite give increasing patterns of frequency towards river mouths, also kaolinite and chlorite.

Montmorillonites are enriched 1) at river mouth-areas and 2) in the open gulf in local deeps as well as at shallows. The distribution mechanism is not fully understood.

Mixed-layer minerals are quite abundant in the suspended matter, also from Mesopotamia, but seem to be less frequent in the recent sediments.

Generally strong evidence is given for detrital origin and transport sorting of clay minerals in a land locked sea like the Persian Gulf.

# THE CRYSTAL STRUCTURE OF THE MINERAL ZUSSMANITE

A. Lopes-Vieira and J. Zussman

/U. K./

The structure of zussmanite was described in outline in a short communication to the Mineralogical Magazine /1967, vol. 36, pp. 292-293/. The present paper will give more detail concerning both the determination and description of the structure. Bond lengths and bond angles will be given and interesting features of the structure will be discussed.

# Fe-PHYLLOSILICATES IN THE SUBMARINE EXHALATION DEPOSITS OF THE MORAVIAN DEVONIAN

K. Melka, J. Vybíral
/Praha, Czechoslovakia/

The Devonian Vrbno Group in the Jeseníky Mountains is noted for occurrences of ferrous and non-ferrous metals. The former continue into the buried area of the Upper Moravian Basin where they were exploited. In this paper some new opinions on the geological setting of this area are discussed and the results of the detailed mineralogical investigation of iron-bearing phyllosilicates are presented. The deposits of these ores occur in the top layers of the anticlines /localities Medlov, Králová, Western Benkov area/ which are built of volcanites, limestones and pelitic sediments of Eifelian-Frasnian age and of the flysch envelope of the Andělská Hora Formation. They are associated with the volcanism of submarine hydrothermal exhalations. The relationship between the acid hydrotherms and the alkaline carbonate environment played a decisive role in the development of various types of ores. Either magnetite-hematite ores strongly siliceous up to jaspers arose or Fe-phyllosilicates with magnetite originated. From the mineralogical point of view special attention has been paid to Fe-phyllosilicates which were, therefore, subjected to a detailed laboratory examination.

Of Fe-phyllosilicates chlorites /designated by various names as, for instance, moravite, mackensite, viridite etc./

and stilpnomelanes have sofar been known. The chlorites have been identified by us as thuringites in accordance with the classification suggested in 1965 by one of the authors. In the rocks surrounding the deposits proper clinochlor-ripidolites have been established. Stilpnomelane has been identified as ferro-stilpnomelane. Minnesotaite and greenalite have been described for the first time from here.

Attention is called to the occurrence of an interesting mineral assemblage of this area, which resembles that reported from the iron ore formation of the Mesabi Range, Minnesota, at the Lake Superior. The occurrence of this assemblage points to a low-temperature origin of deposits.

# ESTIMATION OF MICA CONTENT OF CLAYS USING THE INTENSITY OF THE /005/ X-RAY REFLECTION

N. Munsuz, J. L. White and M. F. Baumgardner

/Lafayette, U.S.A./

The estimation of the mica content of sediments by x-ray diffraction techniques is difficult because the intensity of the /001/ reflection of mica varies with chemical composition as well as with the degree of crystallization. In addition, the /001/ reflection of small amounts of mica may be obscured by the shoulders of intense peaks originating in the 14-16 A region. Calculations show that the effects of variation in chemical composition are minimal for the /005/ reflection. Synthetic mixtures of dioctahedral mica from three sources were prepared and the effects of concentration and diluent on the x-ray diffraction intensities of the /001/, /002/, /003/, and /005/ reflections of oriented specimens were studied. The standard curves were essentially linear up to 50 percent mica. Departure from linearity appeared to be due to particle interactions and consequent changes in orientation. Addition of diluents which increased the viscosity of the suspensions improved the linearity of the intensity-concentration relationship. Application of the technique is illustrated by examples from a study of the chemistry of potassium in soils.

# THE SYSTEM OF KAOLINITE - NONORDERED KAOLINITE - METAHALLOYSITE - ENDELLITE.

## MORPHOLOGICAL AND STRUCTURAL RELATIONS

L. de Pablo
(Mexico City,Mexico)

X-ray diffraction,microscope, and electron diffraction studies have been used to determine the morphological and structural relations between kaolinite,nonordered kaolinite, metahalloysite and endellite. The crystals of kaolinite,hexagonal or irregular, with pseudohexagonal symmetry $C_6$ and without defects observable by electron diffraction enroll according to variable angles of their axes <u>a</u> and <u>b</u> into crystals with longer curved axis, with longitudinal margins which are direct, undulated or transversely elliptic and with the zones of various electron absorption. In the process the symmetry $C_6$ is maintained and no tension or the displacement glidings of layers have been found.

With the acetate the reflection 001 shifts from 7.35 Å to 13.75 Å which after dehydration is displaced to 7.35 Å and is stable. The initially enrolled crystals unroll into irregular plates which do not roll and whose diffraction is normal $C_6$. This is conditioned by the mechanism of the reaction or it is due to the fact that the enrolling is not permanent, that it neither results from translation or tension in the structure nor could it be attributed to the repulsion of ions or to the different dimensions of layers.

Originally metahalloysite crystallized in tubular plates which are often parallely shifted perpendicular to longer axis of the tubes. It is monoclinic $C_{2v}$, the reflection 060 is very intensive and the reflections perpendicular to b are weakened. This manifests itself by variable angles of the longer axis of the tubes but the values ± 33° are dominant. With the acetate, the reflection 001 shifts to 13.70 Å and after dehydration and when treated with glycol to 10 Å. The crystals of initially even plates do not change under the effect of glycol and show sometimes slight deformation.

The calculation of intensities for electron diffraction of the groups $C_{2h}$ - 2/m and $C_s$ - m indicates that the latter is in accordance with experimental data.

Judging from the properties and various characteristics it can be concluded that there are no continuous transitions from kaolinite to endellite nor are there two systems kaolinite - nonordered kaolinite and metahalloysite - endellite.

# SISTEMA CAOLINITA - CAOLINITA DESORDENADA - METAHALOISITA - ENDELITA. RELACIONES MORFOLOGICAS Y ESTRUCTURALES

L. de Pablo
/México, México/

Las relaciones morfologicas y estructurales entre caolinita, caolinita desordenada, metahaloisita y endelita son estudiadas por difracción de rayos X, microscopía y difracción electronica. Cristales de caolinita, hexagonales o irregulares, de simetria pseudohexagonal $C_6$ y libres de defectos visibles por difracción electronica, se enrrollan, a angulos variables de sus ejes a y b, a cristales de eje longitudinal curvo, bordes longitudinales rectos u ondulados, transversales elipticos y con zonas de absorción electronica diferente. En el proceso, se mantiene la simetria $C_6$ y no se observan tensiones o desplazamientos de las capas.

Con acetato, 001 se mueve de 7.35 Å a 13.75 que, al secar, se desplaza a 7.35, estable. Los cristales, originalmente enrrollados, se desenvuelven a placas irregulares que ya no se enrrollan de nuevo y cuya difracción es $C_6$ normal. Ello presume un mecanismo de reacción e implica que el enrrollamiento no es permanente ni consecuencia de translaciones o de tensiones en la estructura, sino posiblemente causado por repulsiones ionicas o por diferencia de dimensiones entre las capas.

Metahaloisita es de cristalización tubular concentrica original, frecuentemente desplazada paralelamente al eje longitudinal recto. Es monoclinica $C_{2v}$, 060 muy intensa y corrimiento de las reflexiones perpendicularmente a b. Este se presenta a angulos variables del eje longitudinal pero predominan valores de ± 33°. Con acetato, 001 se desplaza a 13.70 Å y, secada y tratada con glicol, se mantiene en 10 Å. Los cristales originalmente tubulares rectos, no varian con el tratamiento y permanecen como tales, mostrando cuando mas una ligera deformación.

El calculo de las intensidades para difracción electronica de los grupos $C_{2h}$- 2/m y $C_s$- m indica que este ultimo esta de acuerdo con los datos experimentales. Se concluye que no hay una transición continua de caolinita a endelita sino que son dos sistemas, caolinita - caolinita desordenada y metahaloisita - endelita, de propiedades y caracteristicas diferentes.

# NATURAL AND LABORATORY FUSED PHLOGOPITE

J. Rimsaite

/Canada/

Natural occurrence of partly fused phlogopite in an eclogite nodule from a basic rock prompted present study of thermal stability and other chemical and physical properties of mica. The partly fused phlogopite: $(Al_{.03}Ti_{.23}Fe'''_{.24}Fe''_{.74}Mg_{4.37}Mn_{.004})(Si_{6.16}Al_{1.84})\ O_{20}\ (OH_{3.12}F_{.18}O_{.35})(K_{1.73}Na_{.15})$ has a deficient hydroxyl group and contains glassy particles that concentrate mainly along fractures and margins. Samples heated at 6°/min. retain glass inclusions to the temperature of final dehydration, fusion and recrystallization at <u>ca</u> 1150°C. Samples heated 50 hrs at 970°C also recrystallize, and glass particles disappear with decomposition of mica.

Properties of partly fused mica and of its host rock are compared with those of other similar micas from basic and calcic rocks. Dehydration-oxidation phenomena are discussed as a function of losses of hydrogen and water from the hydroxyl group under various experimental conditions. In is concluded that thermal stability of mica is a function of its hydroxyl, flucrine and iron contents, and that naturally occurring partly fused mica provides some data on the conditions of crystallization and cooling of its host rock.

# STUDY OF CLAYS FROM CHARENTES, FRANCE AND FROM SYRIA USING THE X-RAY FLUORESCENCE

M. Rustom

(Allepo, Syrian Arab Republic)

The X-ray fluorescence analysis has obtained - due to its speed and sufficient accuracy - an important place in the control and research laboratories besides the classical methods of chemical analysis which are more precise, however, less rapid.

The present paper deals with the identification and determinatión of the amcunt of principal elements: Fe,Ti,Ca,K,Si,Al in the clays of the Charentes Basin (France) and in the clays from different regions in Syria.

Our work consisted of three parts as follows:

The first part enable us to determine the optimum conditions for the dosing of six elements - Al,Si,K,Ca,Ti,Fe - in clay powder samples.

In the second part we compared the results obtained from powder samples with the results obtained from pressed samples. The statistic calculation confirmed the priority of the method with pressed samples owing to two reasons:

- considerable gain of intensity
- lower dispersion of results.

In the third part the method of outer calibration was used for the dosing of the six elements mentioned in the clays and the results were compared with those of the classical method of chemical analysis.

A simplified formula used for the correction of absorption effects upon Ti and Fe gave us stimulating results.

Generally speaking, this method can be used in other types of raw materials (sands,feldspars etc.) and in ceramic products (faience, porcelain, chamot etc.) giving, in the majority of cases, rapid results with sufficient precision for industrial control. It would enable a more intensive control which cannot be achieved with the classical methods of chemical analysis.

# ETUDE DES ARGILES DES CHARENTES FRANCE ET DE LA SYRIE PAR LA FLUORESCENCE X

M. Rustom
/Allepo, Syrian Arab Republic/

L'analyse par fluorescence X, par sa facilité d'emploi, sa rapidité et sa precision suffisante a pris une place importante à coté des methodes d'analyse chimique classique, plus rigoureuses mais moins fidèles, dans les laboratories de controle et de recherche.

La presente étude est consacrée à la détermination et au dosage des principaux éléments: Fer, Titane, Calcium, Potassium, Silicium, et Aluminium des Argiles du Bassin des Charentes /France/ et de différentes parties de la Syrie.

Notre travail comporte trois parties:

La première partie nous a permis de determiner les conditions opératoires optimales pour le dosage des six éléments Al, **Si**, **K**, Ca, Ti, Fe, sur les échantillons d'argiles en poudre.

Dans la deuxième partie ou nous avons comparé les resultats obtenus sur les échantillons en poudre à ceux obtenus sur des pastilles, le calcul statistique a donné la preference à la methode des échantillons pastillés pour deux raisons:

- un gain notable d'intensité
- une dispersion plus faible des resultats.

Dans la troisième partie nous avons utilisé la methode de l'étalon externe pour le dosage des six elements cités ci-dessus dans les argiles et nous avons comparé nos résultats avec ceux de l'analyse chimique classique.

Une formule simplifiée utilisée pour la correction des effets d'absorption sur le Ti et le Fe a donné des resultats encourageants.

D'une manière générale nous pouvons dire que cette methode applicable à d'autres types de matières premières /sables, feldspaths, etc.../ et de produits céramiques /faiences, porcelaines, chamottes, etc..../ donne, dans la plupart des cas, des résultats rapides et d'une exactitude satisfaisante pour le controle industriel. Elle permettrait en effet un controle plus intensif que ne peuvent fournir les méthodes d'analyse chimique classique.

# INFRARED STUDY OF ALKYL-AMMONIUM VERMICULITE COMPLEXES

J. M. Serratosa, and W. D. Johns
*

A series of octyl-ammonium vermiculite complexes with different 001 periodicities has been studied by infrared spectroscopy. In each case infrared spectroscopy affords informatio on the hydrogen bond between these groups and the strength of the $NH_3$ groups and the silicate oxygen surfaces.

The infrared results are discussed in relation to the structural models deduced from X - ray analysis.

*/Madrid, Spain and St. Louis, U.S.A./

# NICKEL-BEARING CHLORITE FROM THE NICKEL HYDROSILICATE DEPOSITS, SAXONY

H. Schneider

(Dresden,German Democratic Republic)

Although Ni-bearing chlorite is often described in notable textbooks (Strunz, Ramdohr, Betechtin), there has so far been no uniform opinion as to its correct assignment,and its existence is doubtful.

The mineral from the nickel ore deposits in the Saxonian Granulitgebirge is described by Jubelt under the name Ni-chlorite.The present author has established that this mineral is mostly Ni-bearing vermiculite and vermiculite-chlorite inter - stratifications. Only one sample was found to be chlorite. The data of the chlorite mentioned are as follows:

Chemical analysis (weight percentage) :33.32 $SiO_2$; 13.23 $Al_2O_3$;
2.92 $Fe_2O_3$; 3.10 FeO; 1.11 NiO; 33.79 MgO;
14.3 $H_2O^{(+)}$.

Structural formula $(Al_{1.30}\ \overset{\cdot\cdot\cdot}{Fe}_{0.42}\ \overset{\cdot\cdot}{Fe}_{0.50}\ Ni_{0.18}\ Mg_{9.58})$
$/(OH)_{16}\quad(Si_{6.34}Al_{1.66})\ O_{20}/$

| X-ray analysis | hkl | d (Å) | J | |
|---|---|---|---|---|
| | 001 | 14.2 | 38 | |
| | 002 | 7.12 | 100 | |
| | 003 | 4.747 | 77 | $d_{(001)}$=14.2 |
| | 004 | 3.561 | 80 | $d_{(060)}$=1.536 |

The basal reflection did not change when treated with gly - cerine; after heating at 580°C its intensity strongly increased with simultaneous decrease of d to 14.0 Å.

The DTA shows endothermal peaks at 625 and 840°C and exothermal peak at 860°C. Two stages of dehydration (brucite or talc layer) could be established from the thermal gravimetric curve.

Optical data: $n_x$ $(=n_y)$ = 1.579; $x_z$= 1.584;

$n_z - n_x = 0.0048$;

optically positive, 2 V = 41°.

On the basis of the data given the mineral was named by the author as Ni-penninite.

# EIN NICKELCHLORIT AUS DEN NICKELHYDROSILIKATLAGERSTÄTTEN SACHSENS

H. Schneider

/Dresden, Deutsche Demokratische Republik/

Obwohl Nickelchlorite oft beschrieben worden sind, herrscht bis heute in den führenden Lehrbüchern /STRUNZ, RAMDOHR, BETECHTIN/ über die Stellung dieser Minerale noch keine Klarheit, teilweise wird ihre Existenz bezweifelt.

Der Autor dieser Arbeit untersuchte die von JUBELT als Nickelchlorite bezeichneten Minerale aus den Nickellagerstätten im Sächsischen Granulitgebirge. Er konnte feststellen, dass diese Minerale grösstenteils nickelhaltige Vermiculite und Vermiculit-Chlorit-Wechsellagerungen sind. Nur eine Probe erwies sich als Chlorit. Im folgenden werden einige Daten dieses Chlorits mitgeteilt.

Chemische Analyse /Gew.-%/: 33,32 $SiO_2$; 13,23 $Al_2O_3$; 2,92 $Fe_2O_3$; 3,10 $FeO$; 1,11 $NiO$; 33,79 $MgO$; 14,3 $H_2O^{(+)}$.

Strukturformel $(Al_{1,30}Fe'''_{0,42}Fe''_{0,50}Ni_{0,18}Mg_{9,58})$ $/(OH)_{16} | (Si_{6,34}Al_{1,66})\,O_{20}/$

Röntgenanalyse:

| hkl | d (Å) | J | |
|---|---|---|---|
| 001 | 14,2 | 38 | |
| 002 | 7,12 | 100 | $d_{(001)} = 14,24$ |
| 003 | 4,747 | 77 | |
| 004 | 3,561 | 80 | $d_{(060)} = 1,536$ |
| 005 | 2,847 | 20 | |

Der Basisreflex veränderte sich nicht bei Glycerinbehandlung; nach Erhitzen auf 580°C vergrösserte er seine Intensität berächtlich bei gleichzeitiger Abnahme vond auf 14,0.

Die DTA zeigt endotherme Peaks bei 625 und 840°C und einen exothermen bei 860°C. Zwei Stufen der Wasserabgabe Brucit- bzw. Talkschicht/ konnten aus der Gewichtsverlustkurve ermittelt werden.

Optische Daten: $n_x$ (= $n_y$) = 1,579; $x_z$ = 1,584;

$n_z - n_x$ = 0,0048;

Optisch positiv 2 V = 41°.

Auf Grund der angeführten Daten bezeichnete der Verfasser das Mineral als Ni-Pennin.

# SYNTHESIS AND STABILITY OF MICAS IN THE SYSTEM $K_2O$-MgO-$SiO_2$-$H_2O$ AND THEIR RELATIONS TO PHLOGOPITE

F. Seifert and W. Schreyer
/Bochum, German Federal Republic/

A series of alumina-free micas was synthesized hydrothermally in the potassium-poor portion of the above system. One end member of this series has the composition $KMg_{2.5}Si_4O_{10}(OH)_2$, which, because of its octahedral occupancy, is intermediate between the dioctahedral and trioctahedral micas.

From this end member a series of mica solid solutions extends towards more Mg-rich compositions. Although the substitution causing this solid solution is not yet known with certainty, by far the highest yields were obtained along the substitution line 2 Mg for Si, which would invole incorporation of Mg in tetrahedral sites.

At $P_{H_2O}$ = 1000 bars and 620°C the Si-rich end member decomposes to a more Mg-rich mica, the roedderite phase $K_2Mg_5Si_{12}O_{30}$, liquid, and $H_2O$-rich vapor. With increasing Mg--content the thermal stability of the mica solid solutions increases up to 860°C at a composition of about $K_2O \cdot 6.2\ MgO \cdot 7.5\ SiO_2 \cdot x\ H_2O$. This mica disintegrates directly into forsterite + liquid + $H_2O$-rich vapor. The mica phase richest in Mg with a composition of about $K_2O \cdot 6.6\ MgO \cdot 7.2\ SiO_2 \cdot x\ H_2O$ breaks down at 780°C to forsterite, a more Si-rich mica, liquid, and $H_2O$-rich vapor.

This binary series of alumina-free micas forms a complete series of ternary solid solutions with normal phlogopite, $KMg_3Si_3AlO_{10}(OH)_2$. Analyses of some natural phologopites showing Si in excess of 3.0 /up to 3.18/ can be explained through this ternary miscibility range as alumina-defficient solid solutions.

# ON THE RELATIONSHIP BETWEEN THE CHEMICAL COMPOSITION AND X-RAY DIFFRACTION PATTERN OF BIOTITE

J. Starkey
/London, Canada/

Calculations based on a model of the biotite structure indicate that variations in the diffracted X-ray intensities of 00<u>l</u> planes as a function of changes in composition are more pronounced for single crystal specimens than they are for powder specimens. The atomic substitutions which occur within the tetrahedral layer and amongst the large interlayer cations and the anions do not involve atoms differing sufficiently in their scattering factors to produce detectable differences in intensity; their possible effect is further minimized by the limited substitution which occurs. However, the effect on the intensity of 00<u>l</u> reflections by the substitution of iron and manganese for magnesium and aluminium within the octahedral layer is large. On the basis of these calculations determinative curves are drawn relating the intensities of 00<u>l</u> reflections to the composition of the octahedral layer of the trioctahedral micas.

The calculations for single crystal specimens are applied to X-ray diffractometer powder specimens in which the preferred orientation of the mica crystallites has been enhanced. Such powder specimens behave essentially as single crystal specimens as far as the 00<u>l</u> reflections are concerned. The compositions of twelve analyzed micas are determined in this way and the agreement with the chemical analyses is better than 5 %.

The model used in the calculation also permits the computation of the b parameter. It appears that b is largely determined by the aluminium-silicon diadochy in the tetahedral sites.

# POLARISED ABSORPTION SPECTRA OF TRIOCTAHEDRAL MICAS

R.G.J. Strens and D.W. Robbins

/Newcastle upon Tyne, U.K. and Rochdale, Lancs, U.K./

Polarised absorption spectra /1850-25000 Å/ have been obtained for 15 analysed trioctahedral micas containing 0.2 to 6 % $TiO_2$, 0.3 to 6 % $Fe_2O_3$, and 0.4 to 25 % FeO, and including 4 phlogopites, 9 biotites and 2 lepidomelanes.

There are three main contributions to the absorption: they are /a/ charge transfer from oxygen to $Ti^{4+}$, $Fe^{3+}$ and $Fe^{2+}$ in the near ultraviolet; /b/ charge-transfer from $Fe^{2+}$ to $Fe^{3+}$ at the red end of the visible region, and /c/ internal d-d transitions of the $Fe^{2+}$ ion in the near infrared.

Extensive solid solution in the brucite layer caused the $O \rightarrow$ /Fe, Ti/ charge transfer band to broaden, and thus to encroach on the visible region. Titania has a particularly large broadening effect, which is most marked for vibration directions in the plane of the flake, accounting for the reddish colour and strong pleochroism of titanium-rich biotites. The transmission window between the $O \rightarrow$ /Fe, Ti/ and d-d bands is partially blocked by the $Fe^{2+} \rightarrow Fe^{3+}$ band, which absorbs red light and gives rise to the green colour which is characteristi of micas rich in FeO + $Fe_2O_3$, but poor in $TiO_2$. This band is strongly polarised in the plane of the cleavage /$\beta$, $\gamma$/, and it intensifies the pleochroism: its polarisation dependence in the $\beta$ and $\gamma$ spectra is such as to imply a high degree of orderinf $Fe^{2+}$ and $Fe^{3+}$ in the brucite layer.

Application of these findings to other minerals leads to a better understanding of the colour and pleochroism of orthopyroxene, cordierite, tourmaline, alkali amphiboles, hornblendes and most sheet silicates, and also throws light on the mechanisms of electrical conduction in mineral insulators such as mica and the asbestiform amphiboles.

# NUCLEATION, GROWTH AND POLYTYPISM OF FLUOR-PHLOGOPITE FROM VAPOUR PHASE

I. Sunagawa, Y. Endo, N. Daimon
and I. Tate
/Tokyo and Nagano-shi, Japan/

Micro-surface structures of cleavage lakes on which fluor-phlogopite crystallites were auto-epitaxially grown were studied using a reflection phase contrast microscope. Four different growth features were observed; i.e. 1/ mono- and multi-molecular growth islands with flat surfaces on which no spirals are observed, 2/ mono-molecular spirals with only a half or small number of turns, 3/ mono-molecular spirals with many turns and wide spacings, 4/ growth pyramids consisting of narrow spaced spirals. From the mode occurrences of these growth features, it is conjectured that near the melt end of the crucible crystallizing particles are supplied in the form of molecules, whereas at the cooler end they are in the form of mono-molecular slices which are formed by the coagurlation of molecules while they are being transported.

The fundamental morphology of mica spirals should be in five-sided form, which is an hexagon truncated one side. The 1M polytype of mica exhibits spirals of this morphology. Other polytypes having zigzag stackings will exhibit different types of interlacings on their spirals. Through morphological analyses of the interlacing patterns, it was possible to identify polytypes of 1M, $2M_1$, $2M_2$, 2O, 3T and other higher orders. It was also noticed that different polytypes coexist near-by on the same cleavage flakes. This suggests that the formation of different polytypes is infered to the kinetic process of crystal growth rather than termo-dynamical factors.

# MIXED-LAYER AND OTHER CLAY MINERALS FORMED BY DEGRADATION OF THE SEDIMENTARY ROCKS IN BELGIUM

J. L. M. Thorez

/Liège, Belgium/

Clay undergo different and significant mineral changes when exposed to weathering agents. Some of these change were revealed by a careful study of the weathering developed on outcrops, galeries and subsurface samples belonging to different sedimentary rocks of Belgium. The rocks are of different ages too; from Revinian to Tertiary. About 200 samples were studied in oriented aggregates.

The mineralogy of the clay minerals vary with the nature of the parent rocks, depth of the surface and with the degree of weathering.

Fresh rocks contain illite and chlorite or illite, chlorite, kaolinite, montmorillonite. The relatively unweathered rocks contain the same assemblage as dominant clay minerals. In the more weathered material, some of the parent material, break progressively dow with the concurrent formation of montmorillonite or kaolinite through possible intermediate stages of random mixed and expansible layer silicates. Those changes are shown on glycolation, Mg - and K - saturations, heating. In many cases, the weathered products still contain a part of the parent clays.

For the examples studied a mechanism of weathering is suggested. A classification and codification of random mixed layer "buildings" are given.

# RELATIONSHIPS AMONG SHEET SILICATES, AND SOME "MISSING" SPECIES

E.J.W. Whittaker

/Oxford, U.K./

The sheet silicates considered include talc, pyrophyllite, common and brittle micas, glauconite, illite, vermiculite and the smectites. Some of their relationships are clarified if the minerals are represented by two parameters - the charge x on the octahedral, and z on the tetrahedral, ions. A plot of z against x puts the ideal minerals on a series of diagonal lines, each corresponding to a different total charge on the inter-layer ions. By representing the dioctahedral and trioactahedral minerals on separate diagrams further relationships become apparent.

Dominant values for inter-layer charge /in the 24 O,OH formula/ are 4 /brittle micas/, 2 /common micas/, 4/3 /e. g. illite/, 2/3 /smectites/ and zero /e. g. talc/. The diagram emphasises the relationship of vermiculite to illite rather than to the smectites, which accords well with its expansibility. The relationship between glauconite and montmorillonite is clarified by the diagram and that of sauconite to the smectites is brought out.

A difference between the dioctahedral and trioctahedral diagrams arises from the higher $Al^{[4]}$ content of clintonite than margarite. The absence of a trioctahedral brittle mica containing less $Al^{[4]}$ is related to the lack of a trioctahedral analogue of paragonite, both due to the excessive size of the inter-layer site unless the tetrahedra are rotated substantially. This requires higher $Al^{[4]}$ in trioctahedral than in dioctahedral micas. It would be inadequate in a sodium phlogopite, but will be adequate in ephesite, which is to be regarded as a common mica related to paragonite as clintonite is to margarite

# OPEN SESSION

Chairman/Editor: Prof. H. G. Winkler

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# AUTHORS' ABSTRACTS

## in alphabetic order

# ZONED GARNETS AND METAMORPHISM

M.P. Atherton
/Liverpool, U.K./

Microprobe analysis of garnets from metamorphic rocks from the Scottish Dalradian reveals strong compositional zoning of Mn, Fe, Ca, Ti and Mg. Comparison of the zonation with that derived for an isothermal model indicates that many garnets grew with a decreasing temperature. Initial nucleation was instantaneous and took place at the maximum temperature reached by the rock. Garnets at the lowest grade on the garnet isograd nucleated in an equilibrium system but were quenched before growth was complete.

From a series of probe traces across the Dalradian, a composite picture of the heating and cooling rates is derived qualitatively. Thus in general the initial heating was rapid and no garnet crystallized till the maximum temperature was reached. This was followed by long slow cooling, during which crystallization and garnet growth continued and annealing took place.

Such results have an important bearing on considerations of the widespread occurrence of non-retrogressed high temperature assemblages in metamorphic terrains and the anomalous age determinations from metamorphic minerals, which may well be due to differing cooling parameters in different parts of the same metamorphic belt.

# EXPERIMENTALLY DETERMINED RELATIONSHIPS WITH OMPHACITE

P.M. Bell

/Washington, U.S.A./

Melting phenomena at high pressures in the system jadeite-diopside are characterized by a two-phase region much the same as that which occurs in albite-anorthite. This permits the assumption that high and low pressure behaviour of this general compositional range in volcanics will be similar. The suggestion of a miscibility gap is observed, which is extremely pressure-sensitive /15°C/kb/. This particular gap probably involves a second-order transition of the order-disorder type and is likely to be the phenomenon characterized by the symmetry change of C2/c to P2 observed by Clark and Papike.

Subsolidus reactions of omphacite ⇄ pyroxene + nepheline + albite demonstrate that the effect of adding diopside to jadeite is extremely slight /less than one kilobar/ up to 20 percent solid solution, the effect becoming stronger to finally complete pyroxene stability with increased solid solution. This concurs with the results of Newton and Smith /their experiments included acmite component/. The conclusion can be drawn that the stability of most natural omphacites will be much the same as that of pure jadeite.

# MECHANICS OF FLOW DIFFERENTIATION IN ULTRAMAFIC AND MAFIC ROCKS

S. Bhattacharji

/New York, U.S.A./

Experimental quasi-scale model studies support the view that the effect of the flow differentiation in causing mineralogical and cryptic zoning, crystal and chemical fractionation of magma leading to the formation of different rock types during their transport from the mantle towards the surface of the crust is more significant than has been previously recognized.

The dynamics of the process/es/ of flow differentiation in viscous and pseudoplastic magma to Bingham body plastic and pseudoplastic magma, containing varying proportion of intratelluric crystals of different sizes, shapes and densities in suspension and settling conditions prior to and during movement, was studied in experimental quasi-scale models. The mechanics of intrusion/s/ and flow differentiation process/es/ of fractionated liquid columns of magma and crystal-mush during movements through circular and parallel plates conduits has also been investigated in experimental models.

In viscous, flow differentiation is facilitated by withdrawal and axial migration of crystals from the walls during movement. Magma flow in presence of magma-floor, high shear gradient, low viscosity and low concentration of intratelluric crystals facilitate axial migration of crystal leading to the fractionation of rock types. In Bingham body plastic-pseudoplastic and elastoviscous crystal or crystal-melt mush, differentiation and intrusion of the mush is facilitated by development of a central plug of crystals with immobilized interstitial fluid surrounded by a lubricating sheet of melt extending to conduit walls. Magnus effect, shear deformation of aggregates of crystals, wall effect and fluid slippage along walls favor withdrawal and axial migration of crystals. Flow barding and flow lineation develop in crystal mass and segregation bandings appear in the marginal melt.

# THE ZnS - $In_2S_3$ BINARY 1064° TO 500°C

R.S. Boorman and J.K. Sutherland

/Frederictown, Canada/

The ZnS - $In_2S_3$ binary has been studied between 1064° and 500°C in evacuated vycor and pyrex glass tubes. This study was initiated to gain information on the substitution of indium in sphalerite which is the common host mineral for this element in nature. Four hexagonal sulphides, $In_2ZnS_4$, $In_2Zn_2S_5$, $In_2Zn_3S_6$ and $In_2Zn_4S_7$ were synthesized. $In_2Zn_2S_5$ and $In_2Zn_4S_7$ are new compounds, the other two having synthesized previously.

Beta $In_2S_3$ coexists with $In_2ZnS_4$ over the temperature range studied, whereas the ZnS end members are in equilibrium with three compounds. $In_2Zn_4S_7$ coexists with wurtzite at 1064° and with sphalerite, below the wurtzite-sphalerite transformation, down to approximately 800°C. $In_2Zn_4S_7$ is not stable below this temperature and $In_2Zn_3S_6$ and sphalerite become the equilibrium pair from 800°C to 645°C. $In_2Zn_3S_6$ is not present below 645°C; instead, $In_2Zn_2S_5$, which coexists with $In_2ZnS_4$ from 1064° to 500°C, becomes stable with sphalerite.

Approximately 14 weight per cen indium is soluble in wurtzite at 1064°C. The indium content in sphalerites decreases from 2.2 per cent at 829°C to zero per cent at 600°C. The cell sizes of these sphalerites also decrease from $5.4129 \pm 0.0003$ Å to $5.4097 \pm 0.0003$ Å, over the same temperature range. Approximately 4.2 weight per cent zinc is soluble in $\beta$ $In_2S_3$ at 1064°C and 4.8 per cent at 744°C.

# INCLUSIONS IN BRAZILIAN DIAMONDS: OLIVINE

W.G.R. de Camargo and C.R. Leite
/S. Paulo and Araraquara, Brazil/

This research proposes to identify the inclusions of Brazilian diamonds, which occur at several areas of the country. A variation of the precession method, introduced by the authors /Camargo, W.G.R. et al., Ciência e Cultura, S. Paulo, Brazil, vol. 19, pg. 254, 1967/ has been successfully applied to the identification of the inclusions. The new procedure scans reciprocal lattice, without the need of several parallel photographs, as in the conventional method. Moreover, there is no need of reorienting the crystals at several positions.

Olivine has been identified as an inclusion in diamonds from the alluvium deposits of Abadia dos Dourados, Minas Gerais State, Brazil. The unit cell dimensions, $a_o = 4.773 \pm 0.006$ Å, $b_o = 10.230 \pm 0.012$ Å and $c_o = 6.013 \pm 0.006$ Å, calculated from the "d" spacings, have indicated the term chrysolite.

The inclusions are dark green in color, prismatic and apparently of curved shape, which is due probably to occurrence of many small faces. The olivine inclusions are randomly oriented, without any topotaxic orientation, as found in other diamond crystals by Giardini, A.A. et al., /Am. Miner. vol. 38, pg. 136, 1953/ and Hartman, P. /Am. Miner. vol. 39, pg. 674, 1954/.

The diamond crystals exhibit anomalous birefringence around the inclusions, probably caused by stresses developed after the growing process. The birefringence eliminates any possibility of a secondary origin for the olivine, as it seems to happen with quartz.

The olivine inclusions indicate a possible correlation of Brazilian diamonds to basic magmas, at least in the investigated area. Researches of other kinds of inclusions are being carried out.

# MINERALOGY, PETROLOGY, AND DESCENT OF TWO PEGMATITE TYPES FROM WEST-MORAVIAN ULTRAMAFITES

P. Černý

/Praha, Czechoslovakia/

Serpentinized alpine-type peridotites that occur in meso- and catametamorphosed rocks of West-Moravian Moldanubicum and in the Svratka anticline occur as irregular to lenticular bodies whose pre-serpentinization schistosity often disagrees with that of the enclosing acid rocks. Serpentinization was post-tectonic, chrysotile + lizardite preserve the framework of the preceding ol + py + px up to ol + en + ho + chl assemblages. Along contacts with ultramafites the acid country rocks are converted to chlorite + saponite, sometimes accompanied by a weak zeolitization.

Abundant pegmatites of the first type compose veins that penetrate fissure systems related mostly to the internal fabric of the ultramafites. The almost unzoned pegmatites grade from aplitic to coarse-grained bodies composed mostly of plg or plg + q; the Kf + plg + q and plg + corundum assemblages are exceptional. The content of accessory minerals is very low. All pegmatites of this type underwent the same Mg-metasomatism ± zeolitization as the country rocks, being often completely replaced by chlorite, saponite, and late cerolite.

Pegmatites of the second type having well developed zoning etc. are rather scarce, and are located in late fractures post-dating regional dynamometamorphism. These pegmatites were found to cross-cut the earlier chloritized pegmatites but are themselves almost unaffected by this Mg-metasomatism.

The first group of the early pegmatites originated during the regional dynamometamorphism and concentrated in the heavily fractured peridotite bodies. After consolidation and regional uplift the ultramafites underwent a slow static serpentinization that chloritized the early pegmatites and adjacent country rocks. In the final serpentinization stages the second group of late granitic pegmatites penetrated the ultramafites along fissures.

# DETERMINATION QUANTITATIVE DE DOLOMITE, CALCITE ET QUARTZ DANS UNE ROCHE CARBONATEE PAR DIFFRACTION DE RAYONS X

J.J. Dubois
/Liège, Belgique/

Une méthode de préparation d'échantillons de roches carbonatées a été développée en vue du dosage de la calcite, de la dolomite, du quartz et éventuellement d'autres minéraux. L'analyse quantitative par diffraction de rayons X est faite sur l'échantillon déposé sur un filtre membrane en une couche mince d'épaisseur monogranulaire /moins de 4 microns/.

Le filtre est déposé sur un support métallique où une cavité a été ménagée, ce qui permet un abaissement de la limite de sensibilité par diminution du bruit de fond. L'homogénéité du dépôt ne nécessite pas l'emploi d'échantillons tournants. La précision de la mesure se situe aux environs de 1 à 7 % relatifs suivant les teneurs.

D'autre part, les analyses élémentaires de Ca, Mg, Si, Fe et Mn ont été effectuées par voie chimique, spectroscopie de rayons X et absorption atomique. Après contrôle de la teneur en Mg dans la calcite par variation de ses paramètres, il apparait une teneur en $MgCO_3$ dans la dolomite, variant de 42 à 49 %.

Translation

# QUANTITATIVE DETERMINATION OF DOLOMITE, CALCITE AND QUARTZ IN CARBONATIC ROCK BY X-RAY DIFFRACTION

J.J. Dubois
/Liège, Belgium/

A method was developed for preparing samples from carbonatic rocks suited for determining the contents of calcite, dolomite, quartz and possibly of other minerals. The quantitative X-ray analysis is carried out in a sample placed on a membrane filter in a thin monogranular layer, its thickness being less than 4 µ.

The filter is placed on a metal holder with a cavity which makes it possible to increase the sensitivity by decreasing background noise. The homogeneity of the sample layer does not require the use of rotating samples. The accuracy of measurement varies between 1 % and 7 % /rel./, depending on the content.

The contents of Ca, Mg, Si, Fe and Mn were also analyzed chemically, by X-ray spectroscopy and by atomic absorption. On the basis of estimating the Mg content in calcite by changes of its lattice parameters the $MgCO_3$ content in dolomite varies from 42 % to 49 %.

Translated by A. Kotyk

# DIFFERENTIATION AND SPILITIZATION OF PERMIAN BASALTS IN NORTHWEST GERMANY

F. J. Eckhardt

**/Hannover, Germany/**

Deep borings made possible the investigation of thick volcanite masses in the Permian. As a result of microscopie examinations these rocks are to be regarded as spilitized basalts. For the process of spilitization the following observations are of importance:

/1/ The phenocrysts are the only plagioclases which are saussuritized. They now have a seam of albite corresponding, in its optical data, to the alvites which also from the matrix and the filling of fine veinlets.

/2/ Ilmenite skeletons always have a seam of sphene.

/3/ After the consolidation of the rock the matrix consisted of glass.

This iddicates that the vasaltic melt, after crystallization of the first minerals /basic plagioclase and ilmenite/ underwent a change of condition and was rapidly crystallized.
An evaluation of the chemical analyses facilitates an arrangemant of projection points in the variation diagram. As starting point for a differentiation a low-alkaline basaltic melt may be assumed. The good orientation of projections points in the variation diagram furthermore permits the conclusion

that in this case the spilitization was an isochemical process. This will be discussed.

# THE CHEMISTRY AND CELL PARAMETERS OF OMPHACITES AND RELATED PYROXENES

A.D. Edgar, A. Mottana and N.D. MacRae
/London, Canada/

In an attempt to relate the chemical compositions of omphacites and related pyroxenes to their recalculated mineralogical compositions and origins, chemical analyses and cell parameters of 47 pyroxenes have been determined, or taken from the literature. Approximately two thirds of these analyses may be considered first class, the remainder being of doubtful or unknown quality. Twenty of the analysis are given for the first time, including 16 samples determined on the MAC-400 electron microprobe. Cell parameters, determined by x-ray powder diffraction techniques, have errors of ± 0.1 % for the majority of the samples, although for some samples taken from the literature the errors are unknown.

A number of methods of recalculation of the omphacite analysis into standard end-member molecules have been attempted. Most methods require recalculation into 5-12 end members which makes them geometrically unfeasible for correlation with their cell parameters on a planar surface. However, correlation with combinations of 3 end-member molecules, including diopside and jadeite the two most important end-members of omphacites, can be made using triangular diagrams. It can be shown that for some of the methods of recalculation further reduction to the diopside and jadeite end-

-members by projection from the third component can be made and still result in an accurate /± 5 %/ estimation of the chemical composition of the omphacite from its cell parameters. The relative merits of the different recalculation methods are considered. From the projections of the cell parameters and chemistry of the samples some prediction of the conditions of formation of the rock of the omphacite can be made.

# POSITIVE AND NEGATIVE CRYSTALS OF PYRITE

**Y. Endo and I. Sunagawa**
/Tokyo, Japan/

More than ninety-five percent of natural pyrite are positive crystals in the sence that their {210} faces show striations parallel to ⟨001⟩, whereas negative crystals showing striations parallel to ⟨010⟩ are extremely rare. However, it is a general tendency that where negative crystals are in negative form. It is the purpose of the present study to clarify how negative crystals are formed and what is the difference between positive and negative crystals in connection with their formation. For this, surface structures of {210} and {100} faces, variation in the frequency of appearance of different crystal habits according to grain sizes, internal zonal structures as well as characteristics of modes of occurrences were studied on the so-called negative crystals of pyrite from a few Japanese localities. Surface structural studies of these crystals revealed that negative {210} faces show freely developed growth pyramids elongated paralled to ⟨010⟩, whereas positive {210} faces show striations consisting of steps of growth layers on {100}. This shows that positive {210} faces are formed by piling up of the edges of growth layers on {100} faces, whereas negative {210} faces are formed by spreading of their own growth layers. It is also that that crystals change their habits from cubic to pentagonal as they grow larger, and that {210} faces of smaller crystals show positive **striations**, whereas negative striations can be observed only among larger pentagonal crystals, Zonal structures of these crystals revealed by chemical etching also showed that the larger negative crystals consist of inner core and outer thin crust, ehile smaller positive crystals have no outer crust. The outer thin crust corresponds to the zone formed by growth layers on $\{210\}$ faces. From these results, it is considered that pyrite crystals grow at first as positive crystals and only at the latest stage negative crystals appear, and that the positive crystals are formed when growth layers develop mainly on $\{100\}$ faces, whereas the negative crystals are formed only when growth layers can develop freely on the $\{210\}$ faces.

# COMPOSITION OF SCAPOLITE BY ELECTRON PROBE MICROANALYSIS

W. Evans

/Berkeley, U.S.A./

The ability to analyze scapolite clear of inclusions shows that MgO in scapolite seldom exceeds 0.05 %, $TiO_2$ 0.01 %, FeO 0.15 %, and MnO 0.02 %. The ratio of Ca + Na + + K + Ba + Sr + Mg + Fe atoms to Si + Al atoms in fourteen scapolites analyzed in detail is 1:3, with a variation of less than ± 1 %.

In metasediments from areas of progressive regional metamorphism, the compositions of coexisting scapolite and plagioclase generally show evidence of mutual equilibrium. In the biotite and garnet zones, albite or oligoclase, or both, coexists with a scapolite typically $Me_{40}$. At higher grades of metamorphism $Me_{60}$ coexists with $An_{30}$ and $Me_{75}$ with $An_{40}$.

# CRYSTALLIZATION CONDITIONS OF SALT MINERALS IN CATALONIAN DEPOSITS /SPAIN/

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/Barcelona, Spain/

The study of 135 samples collected from the salt deposits of Suria, Cardona and Balsareny /Barcelona, Spain/, is given. The following techniques were applied: difractometry, optical spectrography and decrepitometry. From data obtained, the variations of the parageneses in the different layers and the distribution of the minor elements in these layers are established, The different temperatures of crystallization in the layers of sylvine and halite were calculated.

With the study of time and the connection between variations of the parageneses, distribution of minor elements and different temperatures of crystallization, the conditions of deposition and type of deposits are deduced. According to the present work, these deposits formerly considered as only very weakly metamorphosed have andergone a very strong metamorphism.

# SYNTHETIC EPIDIDYMITE

D. Ganguli and P. Saha
/Calcutta, India/

Very thin, micaceous cleavage flakes of epididymite, $NaBeSi_3O_7/OH/$, were synthesized hydrothermally from mixtures containing different proportions of $Na_2CO_3$ /$>$40 % by wt./ and natural beryl at 600° ± 5°C and 30.000 ± 500 psi. The synthetic flakes of this orthorhombic mineral showed distinct hexagonal outlines, comparable to the pseudohexagonal and micaceous /001/ cleavage flakes studied by Pobedimskaya and Belov /1960/. Average refractive index, 1.577 ± 0.002, was quite high compared to the normal values of 1.54 - 1.55, birefringence being practically nil; it was suggested that the difference could be caused by incorporation of constituent cations /e.g., $Al^{3+}$/ and impurity cations /$Fe^{3+}$, $Ca^{2+}$, $K^+$ etc./ of the natural beryl used, as well as some autoclave impurities, in epididymite structure. However, due to intimate growth of analcite along the cleavages, it was not possible to separate a pure epididymite fraction for analysis. The isotropic analcite grains probably accounted for most of the aluminium released from beryl. X-ray powder pattern of this composite material, apart from containing nearly all the major peaks of these two minerals, recorded also some unidentified lines. Alteration of beryl to epididymite and analcite-epididymite association are already known in alkalic pegmatites, and the present experiments indicated an unusually soda-rich environment for such associations.

The complete decomposition of beryl to epididymite and other phases in an alkaline atmosphere was noteworthy in view of the fact that natural beryl stubbornly resisted decomposition in neutral hydrothermal environment.

# THE CRYSTAL STRUCTURES OF THE HUMITE MINERALS: NORBERGITE

G.V. Gibbs and P.H. Ribbe
/Blacksburg, U.S.A./

The crystal structure of norbergite, $Mg_3SiO_4F_{1.8}/OH/_{0.2}$, from Franklin, N. J. /$\underline{a}$ = 4.71; $\underline{b}$ = 10.27; $\underline{c}$ = 8.72 Å; Pbnm, $\rho$ = 3.228 g./cc./ was refined to R = 0.07 by least-squares methods using 800 intensities recorded with a scintillation counter on a Weissenberg diffractometer. Important interatomic distances are tabulated below.

| | Mean Bond Length /Å/ | | Description |
|---|---|---|---|
| | F | O | |
| Si- | ----- | 1.628 | tetrahedral distances |
| Mg- | 2.010 | 2.124 | octahedral distances |
| O- | ----- | 2.561 | edges shared by tetrahedra, octahedra |
| O- | ----- | 2.740 | unshared tetrahedral edges |
| F- | 2.675 | ----- | shared octahedral edge |
| O- | ----- | 2.821 | shared octahedral edges |
| F- | 2.899 | 2.994 | unshared octahedral edges |
| O- | 2.994 | 3.135 | unshared octahedral edges |

Taylor and West /1929/, recognizing similarities between norbergite and olivine, proposed a structure based on a hexagonal closepacked array of anions in which half the octahedral sites are filled by Mg and one-twelfth tetrahedral sites by Si. However, they described the structure as alternating layers of

$Mg_2SiO_4$ and $Mg/F,OH/_2$, whereas in fact the key structural units are not "layers" but zig-zag chains of edgesharing octahedra, just as in olivine. The normalized volume of norbergite is less than that of forsterite because of the coupled substitution of 4 /F/ + vacancy for 4 /O/ + Si which is accompanied by a decrease in polyhedral distortions in norbergite. The table shows that the interatomic distances involving fluorine are $\sim$ 0.1 Å shorter than corresponding distances involving oxygen and that the distortion of polyhedra can be explained qualitatively in terms of Pauling's rules.

Fluorine is ordered in the close-packed array and is bonded to three Mg atoms, unlike oxygen which is bonded to three Mg and one Si. This explains the fact that the isotropic temperature factors of the oxygens are several times smaller than that of fluorine.

# ANDALUSITE-SILLIMANITE-KYANITE EQUILIBRIA

M.C. Gilbert, S.W. Richardson and P.M. Bell
/Washington, U.S.A./

Each of the reactions kyanite ⇄ sillimanite, kyanite ⇄ andalusite and andalusite ⇄ sillimanite has been studied hydrothermally in the presence of about 5 % quartz in the range 600-850°C. Both internallyheated and cold-seal gas-medium apparatus were employed. Reaction direction was determined by comparison of ratios of X-ray intensities on a diffractometer. The experiments used to establish each of the equilibria involved only the appropriate two polymorphs.

The equation for the kyanite-sillimanite transition is

$$P/Kb/ = 0.0243\ T\ /^{\circ}C/ - 9.63.$$

The equation for the kyanite-andalusite transition is

$$P/Kb/ = 0.0107\ T\ /^{\circ}C/ - 1.173.$$

The intersection of these curves at 5.5 Kb and 622°C defines the triple point although there is a considerable region of uncertainty because of the modest angle of intersection. Application of the high temperature molar volume data of Skinner, Clark and Appleman and the slopes of the two transitions above permits the andalusite-sillimanite transition to be calculated as

$$P/Kb/ = -0.0243\ T\ /^{\circ}C/ + 20.59.$$

Our experiments involving the andalusite ⇄ sillimanite reaction are so far consistent with this equation.

The results presented here differ from those previously published.

# METASOMATIC POTASH FELDSPAR ROCKS ASSOCIATED WITH ALKALIC IGNEOUS COMPLEXES

E. Wm. Heinrich and D. G. Moore

/Ann Arbor, U.S.A./

Anchimonomineralic potash feldspar rocks /"orthosite, alkorthosite, orthoclasite, perthosite, trachyte, feldspathic breccia"/ are widespread components of alkalic-carbonatitic complexes or provinces in many localities /e.g., Alnö, Sweden; Mbeya, Tanzania; Chilwa Island, Malawi; Rufunsa Valley, Zambia; Wet Mountains, Colorado, U.S.A./. Textures vary from granitoid to trachytoid to fragmental. Where associated directly with carbonatite, these rocks are generally older, but locally rheomorphic /?/ dikes trangress carbonatite. They occur as 1/ units complexes, 2/ in wall rocks adjacent to complexes, 3/ as veins, dikes, pipes, and linear zones apart from complexes but within alkalic provinces.

Commonly red /"burnt rock"/ owing to abundant minutely disseminated hematite, the rocks also may contain concentrations of rare earths and thorium /as thorite/ and normally are markedly radioactive.

The feldspars are turbid /owing to dusty hematite/, show fine "gridiron" twinning, and may have relict cores of clear, older feldspar. X-ray determinations of their Na contents /using the $\bar{2}01$ d-spacing and correcting for structural state/ indicate that they contain usually less than 3 mole per cent albite. Structural state $\Delta = 12.5\,[d/1\bar{3}1/]$, studies show that they are near-maximum microclines with a usual range for $\Delta = 0.85 - 0.92$. Further evidence of their low-temperature genetic environment is advanced by the co-presence of chalcedony, opal, and Schachbrett albite, and associated fluorite, barite, and quartz crystals.

The rocks were formed by potash metasomatism, and are variants of fenites, representing a relatively high-level type of alteration associated especially with complexes displaying sub-volcanic or hypabyssal characteristics. The Laacher See sanidinites are their high-temperature analogs.

# ON THE CRYSTAL STRUCTURE OF SAMSONITE, 2 $Ag_2S$ MnS $Sb_2S_3$

J. Hrušková

/Praha, Czechoslovakia/

The crystal structure of samsonite /sulphur salt of Ag, Mn, Sb/ from Andreasberg, Harz has been carried out on a single crystal of this mineral. The rotation and zero - layer Weissenberg photographs have been taken for all three crystallographic axes as well as equiinclination photographs about /001/ axis. Visually estimated intensities of reflections have been used for calculations of projections of Patterson function along three crystallographic axes and of Patterson - Harker sections $\left(x\ \frac{1}{2}\ z\right)$ and $\left(\frac{1}{2}\ y\ \frac{1}{2}\right)$. The interpretation of these syntheses led directly to the determination of the positions of heavy atoms in the unit cell of samsonite. These positions served for construction of projections of minimum function along /001/ and /010/ axes. The first projections of electron density along /001/ and /010/ axes were calculated with structure factore whose signs were already reliably determined from heavy atom positions.

All atome except Mn lie in general fourfold positions of the space group P $2_1/n$. Mangenese atoms lie one of the four twofold positions of this space group. The presence of two atomic poyyhedra - the pyramids $SbS_3$ and slightly deformed octahedras $MnS_6$ - are the most characteristic feature of the crystal structure of samsonite. The $SbS_3$ group is a low pyramid with Sb at the vertex and three sulphur atoms at the basal corners.

The manganese atoms are situated in one of four two-fold positions in centres of symmetry and lie between octahedral groups of sulphur atoms. All three sulphur atoms in $SbS_3$ pyramid are crystallographically different from each other and belong to different $MnS_6$ octahedra.

# THE CRYSTAL STRUCTURE OF THE HIGH TEMPERATURE FORM OF $BaSi_2O_5$

H. Katscher

/Kiel, Germany/

ROTH and LEVIN /1959/ pointed out, that the mineral sanbornite, $BaSi_2O_5$, transforms at about 1350°C a high temperature form. Single crystals of this high temperature form were synthesized by solid state reactions at about 1400°C using $BaCO_3$ and $SiO_2$ as starting materials. The quenched phase is stable at room temperature. The lattice parameters are

$a = 23.27$ Å, $b = 4.67$ Å, $c = 13.64$ Å, $\beta = 97.8$ Å

The unit cell contains 12 /$BaSi_2O_5$/. The space group is C2/c. The structure was elucidated by Patterson, electron density, and difference syntheses. The anion of this silicate is a sheet which can be built up by zweierketten, i. e. chains with two tetrahedra in the identity period of the chain /nomenclature after LIEBAU, 1962/. The chains are connected through linkage of corners of tetrahedra and run parallel [010]. The barium cations connecting the silicate sheets form undulating layers.

# MAGNESIO-CUMMINGTONITE: A NEW Ca-POOR MAGNESIAN CLINO-AMPHIBOLE FROM NEW SOUTH WALES

H.J. Kisch

/Leiden, Netherlands/

A cummingtonite with $\frac{Mg}{Mg+Fe+Mn}$ /atomic ratio/ = 0.81 occurs in a cummingtonite-hornblende-chlorite rock from Cooma, NSW, Australia. The structure formula /calculated on a basis of 23 oxygens is

$$Na_{0.09}(Ca_{0.19}Mg_{5.45}Fe^{2+}_{1.23}Mn_{0.04}Fe^{3+}_{0.00}Ti_{0.01}Al_{0.07})_{6.99}$$
$$[(Si_{7.83}Al_{0.17})_{8.00}O_{22}|(OH)_2].$$

The unit-cell constants are $a_0$ 9.49 Å, $b_0$ 18.00 Å, $c_0$ 5.30 Å, $\beta$ 102.0°, $V_0$ 886 $Å^3$, the refractive indices $\alpha_{Na}$ 1.621, $\gamma_{Na}$ 1.644. These values, when plotted against the $\frac{Mg}{Mg+Fe+Mn}$ ratio, fit the extrapolations towards $Mg_7/Si_8O_{22}|(OH)_2/$ from recently published determinative curves for the cummingtonite series.

Ca-poor magnesian amphiboles are predominantly orthorhombic: anthophyllite. The most magnesian cummingtonites known thus far have $\frac{Mg}{Mg+Fe+Mn}$ ratios around 0.7. Presence of calcium and manganese has been claimed to stabilize cummingtonite as against anthophyllite. The Cooma cummingtonite and most other published cumingtonite analyses with $\frac{Mg}{Mg+Fe+Mn} > 0.5$ show 0.10-0.40 Ca per formula unit. However, many contain less than 0.10 Mn per formula unit, though their $\frac{Mg}{Mg+Fe+Mn}$ ratios are consistently higher than in the associated Ca-rich amphiboles. These low Mn-contents apparently do not preclude monoclinic symmetry.

There is no name for the magnesian end-member of the cummingtonite series: "kupfferite" is discredited /Sundius, 1931). Maintaining the subdivision of the cummingtonite series at $\frac{Mg}{Mg+Fe} = 0.5$, the author proposes to revive Tilley's (1939) name magnesio-cummingtonite for this end-member and for cummingtonites with $\frac{Mg}{Mg+Fe} > 0.5$. Grunerite is reserved for members with $\frac{Mg}{Mg+Fe} < 0.5$, while cummingtonite continues as name for the whole series.

# FURTHER X-RAY STUDY OF ZIRCON

I. Krstanović, S. Djurić and P. Ilić
/Beograd, Yugoslavia/

X-ray study of zircon /$ZrSiO_4$/ have been undertaken in order to obtain better understanding of the process of metamictization in this mineral. To detect possible anisotropic changes of unit cell dimensions in radiation damaged crystals, we have measured unit cell dimensions of ten zircon crystals with the uranium content ranging from 0.1 to 1.1 % and exhibiting different degree of metamictization. The measurements from powder and single crystal photographs confirmed that, during the process of metamictization, the zircon lattice expands anisotropically as far as a and c axis are concerned. We were however unable to detect anisotropic expansion of $a_1$ and $a_2$ axis - within the limit of experimental error. Three dimensional intensity data, from two zircon crystals showing different degree of metamictization were chosen for counter technique. Full-matrix least square program and three cycles were used to refine positional and thermal parameters of oxygen atom. The following values were obtained:

$x = 0.064 \pm 0.001$ $z = 0.194 \pm 0.001$

and B = 1.8. No significant change from two set of data were found. Unit cell data were also used for the calculation of the absolute age. When these results were compared with those obtained by isotope uranium-lead and lead-lead method, they were found to be generally lower compared with the isotope ages.

# LEAST SQUARES REFINEMENT OF INTERATOMIC DISTANCES IN FRAMEWORK STRUCTURES

W. M. Meier and H. Villiger

**/Zürich, Switzerland and London, U.K./**

The values of bond lengths are in most instances reasonably well known and can be predicted with some certainty. The direct use of this information in structure analyses has been found particularly useful in studies of aluminosilicate structures. The interatomic distance D is a function only of the coordinates of the atoms involved and the unit cell constants. With framework structures it is found that the number of crystallographically independent interatomic distances exceeds the number of coordinates to be determined. Therefore, given an approximate initial solution, it is possible to compute the coordinates of framework atoms by means of least squares adjustments of interatomic distances to prescribed values. The refined coordinates found thereby define an idealized structure with respect to prescribed interatomic distances /and fixed unit cell constants/ which will be called the <u>D-structure</u>. In some instances, an alternate idealized structure, the <u>R-structure</u>, having specified <u>ratios</u> of interatomic distances can generated using a similar least squares procedure. A general computer program has been developed both for D- and R-refinements.

The main applications of D-refinement are:

1/ The calculation of reasonably accurate trial coordinates.

In our work on tectosilicates we have found that whenever

D-refinement has not proceeded, either the trial structure or the assumed symmetry has been incorrect.

2/ The refinement of pseudosymmetric structures /lowering of the symmetry in structure determinations/.
Fourier maps of the initial high-symmetry structure yield the magnitudes but not the signs of the atomic desplacements from the high-symmetry positions. The probable signs of the displacements may be obtained by D-refinement.

D-structures are also of interest for comparative studies of structure refinements.

Actual examples and applications in the field of mineral structures will be discussed.

# GEOCHEMISTRY OF MINERAL INCLUSIONS IN DIAMOND

H. O. A. Meyer

/Washington, U.S.A./

Minerals of several different types /e.g. olivine, garnet pyroxene/ occur as inclusions in diamond. In many cases the diamond has insulated these inclusions from subsequent chemical alteration. The mineralogical and chemical information that may be obtained from these inclusions bears directly on the compositon of the upper mentle, specifically that region in which diamonds originate.

Groups of selected inclusions have been chemically analysed after removal from the diamond host. The analyses obtained will be presented and discussed and comparsion between these iclusions and kimberlite minerals made; for example: The olivines average 93 % forsterite and are extremely uniform in major and monor element concentration. Conversely, the garnets show extreme variation. Pyrope garnets rich in chromium predominate. The calcium content is too small to accommodate all the chromium as uvarovite and approximately 28 % of the Hanléite $[Mg_3Cr_2(SiO_4)_3]$ end-member occurs. These garnets are among the most magnesium rich yet discovered /~ 24 % MgO by weight/. However, other garnet inclusions are iron rich /almandine/ and in these chromium occurs only as a minor element. The monor element content of the analysed inclusions indicates a gross similarity to the minor element content of minerals from ultramafic rocks as opposed to eclogites.

# METAMORPHIC ZONING IN THOR-ODIN GNEISS DOME
# BRITISH COLUMBIA, CANADA

J. M. Moore, Jr.
/Ottawa, Canada/

Thor-Odin gneiss dome, part of the Shuswap metamorphic complex, consists of a migmatitic core mantled by isoclinally folded, heterogeneous metasedimentary rocks containing abundant granitoid lenses and layers. Supracrustal rocks surrounding the dome are in the greenschist facies. Metamorphic grade rises inward to upper amphibolite facies /sillimanite-orthoclase subfacies/ in a large area including the core of the dome. In pelites the disappearance of staurolite and kyanite, upgrade, approximately coincides with the first appearance of sillimanite and potassic feldspar with muscovite, and marks the outer limit of abundant /anatectic ?/ granitoid roks. Kyanite, sillimanite and andalusite coexist in some rocks at the top of the staurolite zone. In and near part of the core, kyanite reappears with sillimanite, and both minerals are mantled by corundum and cordierite /locally with andalusite/.

These relations imply that the last pervasive recrystallization took place at slightly higher pressure and temperature than the aluminosilicate triple point. Later local reaction accompanied continued diapirism and regional uplift.

# STUDIES ON COMPLEX SILICATES: THE CRYSTAL STRUCTURES OF KORNERUPINE /WITH J.M. BENNETT/, SAPPHIRINE, JOESMITHITE, LEUCOPHOENICITE, AND A NEW MINERAL

P.B. Moore

/Chicago, U.S.A./

Kornerupine, a 16.100 /2/, b 13.767 /2/, c 6.735 /2/ Å, Cmcm, Z = 4, has 18 atoms in the asymmetric unit. Its structure includes walls of Al-O octahedra and chains of Mg-O and Al-O octahedra fused to the walls to form dense slabs parallel to b $\{010\}$. These slabs are held together by $/Si_2O_7/$ doublets and $/Al_2SiO_{10}/$ triplets. The crystallochemical formula is

$$Mg^{VI}{}_2Mg^{VI}Al^{VI}{}_6/Si_2O_7//Al_2SiO_{10}/O_4/OH/.$$

Sapphirine, a 11.26 /1/, b 14.43 /1/, c 9.95 Å, β 125°20′, $P2_1/a$, Z = 4, has 34 atoms in the asymmetric unit. The oxygen atoms are cubic close-packed. Octahedral walls of three and four octahedra in width run parallel to the c-axis. The walls are held together by a new kind of $/T_6O_{18}/_\infty$ tetrahedral chain which also runs parallel to the c-axis. The crystallochemical formula is $M^{VI}{}_8O_2/T^{IV}{}_6O_{18}/$.

Joesmithite, a 9.88, b 17.87, c 5.227 Å, β 105°40′, P2/a, Z = 2, is a new mineral from Långban, Sweden. There are 23 atoms in the asymmetric unit. It is an amphibolelike structure consisting of pyroxene chains and insular tetrahedra. The crystallochemical formula is

$$/Pb, Ca, Ba/Ca_2Fe^{+3}/Mg, Fe/_4[Si_2O_6]_2[Si/O, OH/_4]_2/OH/_4.$$

Leucophoenicite, a 10.95, b 4.831, c 11.43 Å, β 104°30', $P2_1/a$, $Z = 2$, has 13 atoms in the asymmetric unit. This is one of several polytypes. The oxygen atoms are h. c. p. and the octahedral populations define a new kind of chain related to the olivines by a simple algorithm. One set of $/SiO_4/$ tetrahedra is disordered. The crystallochemical formula is

$$Mn_7\,[SiO_4]_2\;[/SiO_4/_{1/2}\,/H_4O_4/_{1/4}]_2\;.$$

New mineral, a 9.68, b 14.77, c 5.14 Å, β 101°30', $C2/m$, $Z = 2$, a new mineral from Långban, is an amphibole-like structure telescoped along the b-axis. Its crystallochemical formula is $Ca_3/Mg,Fe/_4/SbO//Si_2O_6/_2O_4/OH/$.

# AMPHIBOLES IN ECLOGITIC ROCKS: THEIR CHEMISTRY AND RELATIONSHIPS TO THE OTHER MINERAL CONSTITUENTS

A. Mottana

/Milano, Italy/

Amphiboles, coexisting with sodic pyroxenes and garnets in eclogites and related rocks, have been chemically analysed and by electron microprobe. Their x-rays properties have been investigated by powder diffraction techniques, and their cell parameters determined using a least squares program written for the I.B.M. 7040 computer. On the basis of the chemistry and structure of the amphiboles of the present study, and those of compositions taken from the literature, amphiboles of eclogitic rocks fall into the following groups:

| | Si | Al | Ti | $Fe^{3+}$ | $Fe^{2+}$ | Mg | Ca | Na | K |
|---|---|---|---|---|---|---|---|---|---|
| 1. Alkali-amphiboles | | | | | | | | | |
| a) glaucophane | 7.89 | 1.69 | 0.04 | 0.28 | 1.05 | 1.99 | 0.19 | 1.75 | 0.02 |
| 2. Subcalcic amphiboles | | | | | | | | | |
| a) Ca-glaucophane | 7.43 | 1.75 | 0.03 | 0.31 | 1.09 | 2.51 | 1.02 | 1.25 | 0.05 |
| b) barroisite | 7.01 | 1.83 | 0.04 | 0.49 | 1.05 | 2.72 | 1.21 | 1.06 | 0.08 |
| 3. Calcic amphiboles | | | | | | | | | |
| a) carinthine | 6.32 | 2.44 | 0.11 | 0.33 | 0.72 | 2.89 | 1.52 | 0.82 | 0.15 |
| b) hornblende l. s. | 6.32 | 2.50 | 0.11 | 0.36 | 1.12 | 2.79 | 1.72 | 0.56 | 0.15 |
| c) "smaragdite" l. s. | 7.73 | 0.52 | 0.01 | 0.19 | 0.58 | 2.24 | 1.75 | 0.49 | 0.01 |

From their cell parameters, some of the subcalcic amphiboles are related to the alkali amphiboles, others to the calcic ones. Statistically, primary and secondary horblendes do not show significant differencies. Their composition is intermediate between that of amphiboles from granulites and those of kyanitebearing amphiboles.

The distribution of major elements between amphiboles and their coexisting phases has been studied. Ca and Na are equally partitioned /$K_{D_{Na}}^{ho-cpx} = 1.0$/ in all but the Glenelg-type eclogites /$K_{D_{Na}}^{ho-cpx} \sim 2.5$/ . Mg and $Fe^{2+}$ are distributed according to $K_{D_{Fe^{2+}}}^{ho-cpx} = 1.4$ in eclogites from amphibolite facies terrains; $K_D = 1.65$ from granulite facies terrains and $K_D \sim 2.2$ in igneous eclogites. The eclogites from glaucophane schists have somewhat scattered distribution coefficient. $Fe^{3+}$, Ti and Al are partitioned in all the rocks according to a $K_{D_{Fe^{3+}}}^{ho-cpx} = 0.55$, but show a large mean deviation. The Ca, $Fe^{3+}$ and Al content of the garnet does not affect the partitioning of the correspondent elements between pyroxene and amphibole. Only $Fe^{2+}$ and Mg seem to affect significantly at hte same time the three phase association.

# MULTIPLE ORIENTATIONS IN THE TOPOTAXY OF MgO ON $MgF_2$

A. Pabst

/Berkeley, U.S.A./

MgO formed from single crystals of $MgF_2$ by pyrohydrolysis makes a layer over the surface with excellent orientation. Six crystallographically distinct orientations have been found. In each case the MgO is twinned on (111) and additionally comparable orientations related by the symmetry operations of $MgF_2$ may appear, a multiplicity of orientations on a single specimen.

The orientations are determined by the $MgF_2$ surface which is oxidized. If this is a /110/ cleavage the MgO formed has /112/ or, less commonly, /111/ parallel to /001/ of $MgF_2$ and $[\bar{1}10]$ normal to the nucleation surface in both cases. If the nucleation surface is a cut surface parallel or nearly parallel to /120/ then also /112/ or, less commonly, /111/ of MgO is parallel to /001/ of $MgF_2$ and again $[\bar{1}10]$ of MgO is normal to the nucleation surface.

When other surfaces are oxidized these and subsidiary orientations may occur and oxidized specimens with surfaces originally cut close to /001/ of $MgF_2$ show prominent orientation of another sort.

From the known structures it is clear that there must be a volume shridkage of 43 % but oxidized crystals show no visible dimensional change. Berman balance determinations on fully oxidized fragments indicate a porosity of at least 34%. The openness of the oxide crust is obscured in microscopic view by its finely fibrous character. Determination of the mechanism of formation of such an open-textured, well-oriented, crust must be in terms of adjustments in the cation arrangement. This has been accomplished by Dr. Marcus Borom and his results are being presented elsewhere.

# PRINCIPLES OF SCIENTIFIC NOMENCLATURE OF MINERALS

A. S. Povarennykh

/Kiev, U.S.S.R./

Present nomenclature of minerals is inconsistent and reflects the tradition of naming after persons or locations. Rational names which reflect chemical composition or internal structure are seldom proposed. Similar proper names are proposed for mineral varieries and mineral species. The names of polymorphic forms have no common base and are inconvenient to remember and associate. The following principles of scientific nomenclature of minerals are proposed for discussion:

/1/ The name of a mineral species should be constructed on a chemical and structural basis and should always reflect both the electropositive elements and the electronegative elements or radicals that characterize the species.

/2/ The name should begin with the symbols of the electropositive elements, following each other in succession, and ending with a suffix characterizing the electronegative elements or radicals, for instance, -oxide indicates and oxide, -sulite a sulfide, -silite, a silicate, -phite, a phosphate, etc.

/3/ The names of polymorphs should differ from one another only by prefixes, expressing the crystal system, which are placed before the name of the main species: for instance, quartz and hexaquartz; atacamite and clinoatacamite; cristobalite and cubocristobalite, etc.

/4/ The names of chemical varieties are constructed from the name of the mineral species by addition of a prefix, separated by a hyphen, to show admixture of a chemical element; for example, Fe-sphalerite, Cr-corundum, Cu$^{+2}$-scheelite, etc. Structural varieties are indicated by an upper-case letter following the species name and separated by a hyphen, to show the crystal system, as, for example, wurtzite-2H, wurtzite-3R, biotite-6T, muscovite-2$M_1$, etc.

# CRYSTAL STRUCTURE OF PROSOPITE, $CaAl_2(F,OH)_8$

A. Preisinger
/Wien, Austria/

Prosopite from Colorado, USA is monoclinic with $a = 6.69$ Å, $b = 11.11$ Å, $c = 7.32$ Å, $\beta = 94.5^\circ$, 4 $CaAl_2(F,OH)_8$, space group C 2/c. The structure was determined by Patterson and Fourier synthesis using three-dimensional diffraction intensities on Weissenberg photographs with filtered Cu-K radiation and was refined by least squares. It is a new type of structure composed of chains of edge-linked /$AlF_2(OH)_2$/ octahedra. Al is coordinated by 2 F and 4 OH groups, Ca by 6 F and 2 OH groups.

# NEW REMARKS TO THE KNOWLEDGE OF OPTIC-AXES FIGURES

R. Rath

/Hamburg, Germany/

The equations of the isogyres and the isochromates of biaxial crystals are of the most common form and the 6th or the 4th degree /RATH, Neues Jahrbuch für Mineralogie, Abh. and Mh., 1968/. Starting from these equations

1./ - as to the isogyres - a from of the equation is derived using parameters, which is more convenient for use

2./ - as to the isochromates - the points of disappearence of these curves and intensity profiles through the optical axis are shown.

# VARVELIKE BANDING OF POSSIBLY ANNUAL ORIGIN IN CELESTITE CRYSTALS FROM CLAY CENTER, OHIO, AND SIMILAR OCCURRENCES

E. Roedder

/Washington, U.S.A./

Some celsstites from vugs in Paleozoic dolomites at three localities show a rhythmic, paired banding that may be to of annual origin. This is visible as perfectly straight, parallel, alternately darker and lighter appearing bands, mainly parallel $\{210\}$, in polished plates or even through clear crystal faces at moderate magnification with wellcollimated transmitted light. Although the thicknesses of the individual bands and of band pairs vary widely within a given crystal, these thicknesses are very uniform for sequences of hundreds of pairs. Individual pairs range from 3-70μm total width, and may be traced laterally without thickness change for 0.5 cm; some continue over former crystal terminations. They are visible owing to minute differences in index of referaction between the constituent parts /proven by examinations under Nomarski interference contrast/. These differences arise from a variable amout of substitution of barium for strontium /proven by electron microprobe/. Banding is also outlined by rows of secondary fluid inclusions in healed fractures, one in each pair; this indicates variation in solubility of the constituent parts. Almost no banding was found in the associated vug minerals, but more sensitive tests may be required to detect it.

It is proposed that the warm brine from which these celestites grew was diluted with surface meteoric water that varied in composition or amount over a yearly cycle, causing the compositional banding. If the band pairs are truly annual that is, they are "varves", they yield valuable rate data on diagenetic processes and the hydrologic regimen, and should be searched for in other samples.

# BOND LENGTH - BOND STRENGTH CORRELATIONS IN SILICATES

R. G. J. Strens

/Newcastle upon Tyne, U.K./

Semi-empirical relationships have been derived between the length and strength /measured in electrons/ of Si-O, Al-O, Ti-O, $Fe^{3+}$-O and $Fe^{2+}$-O bonds in oxide and silicate minerals. Application of the resulting bond length - bond strength curves enables a detailed picture to be obtained of the balance of forces acting on each atom in structures such as those of andalusite, sillimanite, jadeite and orthoferrosilite, in which Pauling s electrostatic charge balance fails.

Differences /$\Delta$/ between the lengths of from silicon to bridging /$O_b$/ and non-bridging /$O_n$/ oxygens is complex silicate anions have been used as evidence in support of a theory of $\pi$-bonding in silicates, but all structures so far examined have weak bonds to bridging oxygens from anions other than silicon, which necessarily lengthns the Si-$O_b$ bonds relative to the Si-$O_n$ bonds. Examples are the Na-$O_b$ and Fe-$O_b$ bonds in sodium metasilicate and orthoferrosilite respectively, for which the bond length - bond strength curves predict:

| | | | | | | |
|---|---|---|---|---|---|---|
| Na-$O_b$ | 0.15e | Si-$O_b$ | 0.85e | Si-$O_n$ | 1.15e | $\Delta$ 0.09Å |
| Fe-$O_b$ | 0.10e | Si-$O_b$ | 0.90e | Si-$O_n$ | 1.10e | $\Delta$ 0.06Å |

compared with observed $\Delta$ values of 0.080 and 0.054Å respectively.

The curves also provide evidence increasing covalency with decreasing bond length, and suggest an explanation for the reduction in mean Si-O distances on passing from orthosilicates to framework silicates.

# ETUDE QUANTITATIVE DE LA TRANSFORMATION THERMIQUE DE LA BLENDE

A. Traveria-Cros et J.M. Amigo
/Barcelona, Espagne/

On a fait l'étude de la transformation thermique de plusieurs échantillons de blende recueillis en distincts gites espagnols /Osor, Cierco...../. L'étude thermique a été faite à l'abri de l'oxygène /dans une atmosphère d'azote/, à température constante et à temps divers, dans un four électrique horizontal avec un dispositif pour le double control de la température /four et échantillon/. La même étude on a fait en identiques conditions en changeant les températures de 700 à 1100°C.

Les pourcentages de la transformation ont été determinés par la diffraction des rayons X, en établissant un rapport entre le pourcentage du fer dans la blende et la température de transformation.

Translation

# QUANTITATIVE STUDY OF THERMIC TRANSFORMATION OF SPHALERITE

A. Traveria-Cros and J.M. Amigo
/Barcelona, Spain/

Several samples of sphalerite collected at different Spanish deposits /Osor, Cierco/ were subjected to a thermic transformation examination. It was carried out in the absence of oxygen /in a nitrogen atmosphere/, at constant temperature and for different periods in a horizontal electric oven provided with a device for duplicate temperature control /oven and sample/. The same study was done under identical conditions for temperature changes between 700 and 1100°C.

The course of the transformation was monitored by X-ray diffraction, the relationship between the iron content in sphalerite and the temperature of the thermic change having been determined.

Translated by A. Kotyk

# SYNTHETIC EXPERIMENTS OF GERMANATE ALBITE AND ANORTHITE UNDER PRESSURES

S. Ueda, M. Koizumi and S. Kume
/Osaka, Japan/

A material with chemical composition same as germanate albite /$NaAlGe_3O_8$/ was submitted to a condition of temperature and pressure up to 1000°C and 25 kb. Microscopic observations showed that the high pressure product was an aggregation of needle-like crystals. Its X-ray differaction pattern was identical with that of cryptomelane and this result is in agreement whit those already reported by Ringwood et al. and also by us. The lattice parameters were obtained to be $a_o$ - 9.64Å and $c_o = 2.86$Å, hence the desity was calculated to be 4.98 $g/cm^3$. Since the density of the product under pressure is higher than that of germanate albite /3.94 $g/cm^3$/, this phase can be called the dense form of germanate albite. It was also confirmed that the dense form reverted to germanate albite on heating at 900°C in air.

In the case of germanate anorthite /$CaAl_2Ge_2O_8$/, no dense form was observed but a high pressure product was proved to be a mixture of germanate grossularite /$Ca_3Al_2Ge_3O_{12}$/ and germanium dioxide /$GeO_2$/ of tetragonal symmetry.

# MELANOPHLOGITE FROM CHVALETICE /E BOHEMIA/

L. Žák

/Praha, Czechoslovakia/

Melanophlogite cubes up to 3 mm in size sit on a thin lussatite layer in a druse cavity of a pyrite-rhodochrosite vein in metamorphosed Mn-carbonate horizon in the Algonkian graphitic pyrite shales. Lussatite consists of a microscopically fibrous low-cristobalite with a high degree of disorder /by X-rays/.

The mineral is optically istropic, a thin outer zone of the cubes is weakly birefringent. The physical constants are: $n^{20}_{Na} = 1.\overset{4}{\cancel{5}}49$, $d^{21}_{21} = 2.005 \pm 0.005$, $a_0 = 26.79 \pm 0.02$ Å. Qual. spectrographic analysis gave Si in essential, Al, Cu, Mg, Mn, Ag, Fe, and P? in insignificant to trace amounts. Infrared absorption curves /400-4.000 $cm^{-1}$, powder/ demonstrated b. o. the presence of some nonaromatic hydrocarbons or hydrocarbon derivatives. By heating for 3 hours at 800°C in the air melanophlogite became smoky transparent, by heating for 6 or 12 hours at 1.000°C it grew black. No opaque carbon inclusions could be observed even at highest microscopic magnifications. The presence of S has not been proved either by qual. chemical or by electron microprobe tests. The $SiO_2$ content, determined semiquantitatively by the electron microprobe, was about 95 %.

The doubling of $a_0$ of the mineral with regard to the Sicilian material /B.J. Skinner and D.E. Appleman, 1963/ was established by both powder /Guinier/ and rotation methods. According to further X-ray and thermal investigations /not yet finished/ a superstructure seems to be a probable explanation of the mentioned doubling.

# SYMPOSIUM II: Crystal Field Theory

Chairman/Editor: Prof. W. S. Fyfe

September 3, 1968

# AUTHORS' ABSTRACTS

## in alphabetic order

# QUANTITATIVE SITE POPULATIONS IN SILICATE MINERALS BY MÖSSBAUER SPECTROSCOPY, AND A POSSIBLE GEOTHERMOMETER

G. M. Bancroft

/Cambridge, U. K./

A method is described for the quantitative estimation of the amount of iron in structurally different cation positions using the computer-calculated area under Mössbauer peaks. For a mineral containing two different types of iron atoms, the area ratio $^{A}2/A_{1} = C^{N}2/N_{1}$, where $N_2$ and $N_1$ are the number of iron atoms per formula unit and C is a constant. For a 36% $Fe^{2+}$cummingtonite, the calculated site populations are in good agreement with those calculated by X-ray crystallography for a cummingtonite of similar origin and iron content. For silicates containing $Fe^{2+}$ and $Fe^{3+}$, the ratio $\frac{N_{Fe^{3+}}}{N_{Fe^{2+}}}$ is in good agreement with those calculated from chemical analysis.

In orthopyroxenes, $Fe^{2+}$ preferentially enters the more distorted $M_2$ position. Mössbauer measurements on metamorphic and volcanic pyroxenes containing about 30 % $Fe^{2+}$ show that the extent of ordering decreases with an increase in the temperature of formation. Using classical thermodynamics, it is shown that the extent of ordering can be used as a possible geothermometer. The advantages and limitations of the metod are discussed critically.

# DISTRIBUTIONS OF IRON CATIONS IN ALKALI AMPHIBOLES BY MÖSSBAUER AND INFRARED SPECTROSCOPY

G. M. Bancroft, R. G. Burns and F. J. Prentice
/Cambridge and Oxford, U. K. and Wellington, New Zealand/

Measurements of the Mössbauer spectra of $Fe^{2+}$ and $Fe^{3+}$ ions in amphiboles and the fundamental hydroxyl stretching frequency in the infrared have enabled the distributions of ferrous and ferric ions to be determined in the M(1), M(2) and M(3) positions of the crystal structures of alkali amphibole minerals.

In crocidolites $Fe^{3+}$ ions predominate M(2) positions, and $Fe^{2+}$ ions are concentrated im M(1) and M(3) positions with preference for M(1) positions. However, a small amount of $Fe^{3+}$ ions also occupies the M(1) and M(3) positions with preference for M(1) positions. The cations in pegmatitic magnesioriebeckites and riebeckites are more randomly distributed than in crocidolites that formed at lower temperatures, showing that site populations are strongly influenced by temperature.

In glaucophanes $Fe^{3+}$ ions again predominate M(2) positions and $Fe^{2+}$ ions are concentrated in M(1) and M(3) positions. However, there is a slight preference of $Fe^{2+}$ ions for M(3) positions. Thus, in the glaucophane-crossite-riebeckite series there is a change in site preference of the $Fe^{2+}$ ion from M(3) to M(1) positions with decreasing $Al^{3+}$ ion content.

Estimations of site populations in silicate structures by the Mössbauer and infrared techniques are more rapid, direct and accurate than conventional x-ray methods. It is also possible to distinguish between $Fe^{2+}$ and $Fe^{3+}$ ions in a crystal structure by the spectroscopic techniques and to estimate $Fe^{2+}/Fe^{3+}$ ratios by Mössbauer spectroscopy. By means of infrared spectroscopy it is possible to identify compositions of individual unit cells in hydroxy-amphiboles and to obtain a semi-quantitative estimate of component unit cells in a crystal structure.

# A THEORETICAL APPROACH TO PRESSURE, ENERGY, AND THE CRYSTAL FIELD

P. M. Bell

/Washington, U.S.A./

The crystal field represents the fundamental energy balance in minerals, and while the effect on crystal chemistry is strong with the transition elements /of particular significance are Fe, Ti/, it is in general important in nearly all geologic processes. The field is changed in intensity with pressure as the interaction of individual electronic fields increases. A known pressure effect can be used to calculate the associated energy change.

Pressure induced polymorphism involves changes in field symmetry and density resulting in a change in the energy balance. During this process electrons raised to higher energy levels in a stepwise way are finally ejected, thereby raising the density. It is therefore theoretically possible to relate pressure with electronic phenomena such as ionization potentials. By the method of Savic and Kasanin, the pressure effect on transitional energy can be calculated for monatomic crystals. For more complicated compositions the significant crystal field changes are considered. Comparisons of pressure and measured crystal field energies form a cross-check. Crudely, one can calculate the energetics of geochemical processes.

# SITE PREFERENCES OF TRANSITION METAL IONS IN SILICATE CRYSTAL STRUCTURES

R. G. Burns

/Oxford, U.K./

The structures of many silicate minerals contain one or more crystallographic positions which may be occupied by transition metal ions. The coordination sites differ in the number, symmetry and type of oxygen atoms, metal - oxygen distances, and extent of distortion from regular octahedral or tetrahedral symmetry. These factors affect the crystal field within each coordination site, and influence the distributions of transition metal ions within a particular structure and between two or more coexisting phases.

Site preferences of individual transition metal ions may be predicted from (a) the mean metal-oxygen distances; (b) effective charges on the oxygen ligands; (c) nature and extent of distortion of the coordination site; (d) effects of neighbouring cations; and (e) sizes of the cations. The predicted enrichments are correlated with available data on cation ordering in silicate structures and ion enrichments in coexisting phases.

/Submitted to the Sixth General Meeting of the International Mineralogical Association, Prague, September 1968/

# SOME ASPECTS OF MINERAL CATHODOLUMINESCENCE

R. Coy-Yll

/Québec, Canada/

The scanning systems of an electron microprobe are being used for the study of local cathodoluminescence in minerals. This study has been initiated in order to gain a better understanding of the solid state physics of natural crystals. The electronic states involved in microcathodoluminescence of minerals can sometimes be interpreted in terms of crystal field theory or in other cases in terms of the band structure theory. However, cathodoluminescent emission must generally be interpreted using more complex models than that used in U.V. excited luminescence.

The cathodoluminescent yield depends on acceleration voltage and current intensity of the incident electron beam, nature of the specimen, kind of activators and interaction between activators and excited atoms of the host lattice. The measured intensity of micro-cathodoluminescence depends strongly on specimen surface topography and on the light optics of the system employed. The interpreting of micro-cathodoluminescence is seriously hindered if information on the chemical impurities and structural features of the mineral under study are unknown.

Cathodoluminescent spectra obtained between 400 nm and 700 nm of quartz, orthoclase, calcite, apatite and benitoite minerals show maxima of intensity at 560 nm, 480 nm, 580nm,

565 nm, and 470 nm respectively. The behaviour of growth and decay curves of cathodoluminescence obtained for these minerals has been studied. Saturation of cathodoluminescent intensity and its variations with incident current intensity and high voltage have been measured. Correlation between cathodoluminiscent data and structural features of the minerals is attempted. The experimental set up used in this study is discussed.

# DISTRIBUTION OF $Mn^{2+}$ IN TRACE AMOUNTS IN DIOPSIDES AND DOLOMITES BY ELECTRON SPIN RESONANCE

S. Ghose and P. Schindler

/Chicago and Argonne, U.S.A./

The electron spin resonance of manganese in diopsides and dolomites show that $Mn^{2+}$ occurs in two different sites in both structures. The parameters for the sites are (in Gauss):

| | Diopside | | | Dolomite | | |
|---|---|---|---|---|---|---|
| | A | D | Q | A | D | a |
| Ca - site | 84 | 453 | 1.3 | $94.6 \pm 0.2$ | $\sim 20$ | ? |
| Mg - site | 91 | 375 | $\leq 0.2$ | $92.97 \pm$ | $151.87 \pm$<br>$\pm 2.0$ | 10.26 |

A denotes the Fermi contact hyperfine interaction, D the crystal field interaction, Q the quadrupole interaction and 'a' the cubic field interaction.

In diopside $Mn^{2+}$ associated with the larger D and Q and small A is assigned to the $Ca(M_2)$-site, which is considerably more distorted than Mg' $(M_1)$. The assignment of $Mn^{2+}$ in dolomite is based on D and A parameters in calcite and magnesite, which are 27.69 G, 94.94 G and 85.45, 92.20 G respectively. The $Mn^{2+}$ parameters in diopside agree very well with those determined by Vinokurov, Zaripov and Stepanov (1964), though our site assignment is reverse of theirs.

Three types of $Mn^{2+}$ distributions have been found in natural diopsides:
(1) Most $Mn^{2+}$ in Ca-site, (2) most $Mn^{2+}$ in Mg-site, (3) all $Mn^{2+}$ in Mg-site. A Californian diopside showing the first type of distribution changes to the second type after heating at 1000°C, while a diopside from New York showing the second type of distribution does not change after heating at 1010°C. The second type of distribution appears to be stable at high temperature.

Dolomites show two types of $Mn^{2+}$ distribution: (1) most $Mn^{2+}$ in Mg-site, (2) all $Mn^{2+}$ in Mg-site. Dolomite from Gabbs, Nevada shows the first type of distribution, while clear dolomite crystals from Binntal, Switzerland show the second type, though they contain approximately equal amounts of Mn (.08 Mn/100 cations).

# SELF-CONSISTENT IONIC FIELD GRADIENTS AT THE Al SITES IN KYANITE AND ANDALUSITE

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The nuclear guadrupole coupling tensors of $Al^{27}$ in the two phases kyanite and andalusite of $Al_2SiO_5$ were analyzed by the ionic model to investigate possible residuals in the tensors due to a non-ionic participation in the predominantly ionic bonds of crystal structures. The tensors had been determined recently by the nuclear quadrupole resonance technique[1,2]. They provide 26 independent second derivatives $V_{ij}$ of the crystal potentials at the 6 non-equivalent Al sites.

The second derivates of the ionic potentials at the Al sites were computed self-consistently taking the ionic dipole and quadrupole moments of oxygen into account[3]. The dipole and quadrupole moments of the cations were neglected. The 20 derivatives of kyanite were fitted to the experimental values by treating the polarizibilities $\alpha_D$ (dipole), and $\alpha_Q$ (quadrupole) of $O^{2-}$ as variables. The "reliability factor" $R = [\sum (V_{ij}^{obs} - V_{ij}^{calc})^2 / \sum (V_{ij}^{obs})^2]^{1/2}$ for the best fit is R = 26 %, and the most probable polarizibilities are $\alpha_D = 1.1 Å^3$, $\alpha_Q = 0.1 Å^5$. An equivalent analysis was performed for the 6 derivatives of andalusite yielding similar results. It should be noted that the point charge model is much too coarse to provide an acceptable fit of the coupling tensors

($R_{pointcharge}$ = 78 %). The approximation is strikingly improved if the contribution of the self-consistent ionic dipole and quadrupole moments of oxygen are added.

About 67 percent of the coupling tensors at the Al sites can be accounted for by the ionic potential distribution. The residual consists of the following contributions:

1. Dipole and quadrupole moments of the cations.
2. Inaccurate coordinates of the atomic center positions.
3. Oxygen octupole moments.
4. Non-ionic participation.

It can be shown that contribution 1 is small. Contribution 2, however, may be considerable. While the crystal structures of kyanite and andalusite are currently regarded as well known we find that the atomic coordinates are still not precisely enough determined to permit an accurate analysis of point 4. Nevertheless, estimates appear to be feasible.

# THE PARTITIONING OF MANGANESE, COBALT AND NICKEL BETWEEN OLIVINE CRYSTALS AND THE GROUNDMASS OF SELECTED BASIC IGNEOUS ROCKS

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Unzoned olivine crystals and co-existent groundmass from certain basic igneous rocks have been analysed for manganese, cobalt and nickel by activation analysis. The determination of manganese and cobalt was carried out by a non-destructive method. Hence it has been possible to analyse the same samples for the three elements.

The groundmass is considered to be compositionally representative of the magma which produced the olivine crystals. From the data the three partition coefficients

$K = \frac{[X]_{ol}}{[X]_{magma}}$ /where $X = Mn$, Co, or Ni/

have been calculated for each assemblage. These partition coefficients are interpreted in the light of crystal field theory: for example, the relationship shown between ln K and octahedral site preference energy of each element is discussed and compared to that expected if crystal field effects were dominant in determining the partition coefficients of these elements.

# PARTITION OF DIVALENT TRANSITION METALS BETWEEN COEXISTING FERROMAGNESIAN MINERALS

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Partition of divalent cations of moderate size /e.g., Ni, Co, Fe, Zn and Mn/ between coexisting ferromagnesian minerals can be expressed by the apparent exchange equilibrium constant as follows:

$$K'^{A.B}_{M.Mg} = /M/Mg/_A//M/Mg/_B$$

where A and B denote phases, and M and Mg represent concentration of divalent ion and of $Mg^{++}$, respectively.

Estimation of ionic radii is itself a complicated problem. From purely empirical point of view, however, ionic radii of sixfold coordination can most plausibly be derived from the unit cell constants of oxides of NaCl structure. If we plot logarithm of $K'^{A.B}_{M.Mg}$ against M-O distance of oxide, nearly linear pattern can be observed, <u>including</u> Mg, in the mineral pairs such as orthopyroxene-clinopyroxene, chlorite-chloritoid, garnet-orthopyroxene and garnet-chlorite.

As is shown by Hush and Pryce /1957/, the M-O distances of transition metal oxides contract as a result of crystal field effect. Thus we may conclude that crystal field effect plays an important role in the partition equilibria through the contraction of effective ionic radii.

A remarkable exception is the pair olivine-orthopyroxene, where fractionation of Ni, Co and Fe cannot be explained by the effective size of ions only. Probably symmetry of cation sites in olivine is far more favourable than that in pyroxene for these ions.

# THE APPLICATION OF LIGAND-FIELD CONCEPTS TO AN UNDERSTANDING OF THE STRUCTURAL STABILITIES AND SOLID-SOLUTION LIMITS IN SULPHIDES AND RELATED MINERALS

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Ligand-field theory has proven to be useful in explaining the structural stabilities and solid-solution limits of the higher sulphides, arsenides, tellurides and selenides of the transition metals. The metals in these compounds are generally in the low-spin state, and therefore the crystal structure adopted by any one of these minerals is that which permits maximum spin pairing of the non-bonding electrons in the $t_{2g}$ cation orbitals. The cations with six or more non-bonding electrons form structures in which complete spin-pairing is achieved without appreciable interaction between cations, as in the structures typified pyrite, marcasite and skutterudite. The cations with fewer than six non-bonding electrons achieve spin pairing by adopting structures in which there is metal-metal interaction, as in the arsenopyrite- and löllingite-type structures. The limits of the solid-solution fields in the ternary systems $FeS_2$ -$CoS_2$ -$NiS_2$, $FeAs_2$ -$CoAs_2$ -$NiAs_2$, FeAsS-CoAsS-NiAsS, and $FeAs_3$ -$CoAs_3$ -$NiAs_3$ are governed by similar considerations.

# MÖSSBAUER SPECTRA OF PEROVSKITES OF THE SYSTEM $Ca_2Fe_2O_5$-$SrFeO_3$

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Samples with the chemical compositions of $/Ca_xSr_{1-x}/FeO_{3-\delta}$ were prepared and then treated at 130 atm of oxygen and 300°C.

These ferrates are classified into two types of crystal structure, cubic perovskite $/ABO_3/$ and orthorhombic brownmillerite $/A_2B_2O_5/$, if we denote A and B as an alkaline-earth metal and iron ions, respectively. Specimens before oxidation fell in the category of $ABO_3$ in the region with x being 0 and 0.2, and of $A_2B_2O_5$ from $x = 0.4$ to 1.0. In the composition ranges with x between 0.4 and 0.6, increasing concentration of tetravalent iron ions led to an eventual change in crystal structure from orthorhombic brownmillerite to cubic perovskite phase, with intense oxidation under high oxygen pressure.

The Mössbauer spectra of these ferrates were measured at room temperature. As for strontium ferrate, no measurable quadrupole splitting was observed for a material after oxidation, while the visible splitting due to tetragonal distortion appeared in the specimen before oxidation which seems to have a significant number of oxygen vacancies.

Another characteristic of the spectrum of strontium ferrate is that this compound has an isomer shift. The amount of the shift is greater than that predicted for a purely ionic behavior due to $3d^4$ configuration.

In addition to the above results, the features of the spectra for the ferrates of the system $Ca_2Fe_2O_5$-$SrFeO_3$ are presented to be discussed in relation to crystal field theory.

# CALCULATION OF THE CRYSTAL FIELD SPLITTINGS OF THE D-ORBITALS OF TRANSITION METAL IONS DISTORTED CO-ORDINATION POLYHEDRA

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Computer programs which are now being developed enable the crystal field splittings of the d-orbital energy levels to be calculated for cations occupying coordination polyhedra which have been subjected to arbitrary (centric or acentric) pseudo-orthogonal distortions.

The method has been used to calculate the energies of the spin-allowed transitions in $d^n$ systems ($n \neq 0, 5, 10$). Excellent agreement has been found observed and calculated transition energies for $Mn^{3+}$ ($d^4$) and $Fe^{2+}$ ($d^6$) in a wide range of distorted octahedra in minerals such as viridine and piemontite ($Mn^{3+}$), and olivine, cummingtonite, cordierite, tourmaline and glaucophane ($Fe^{2+}$). For all but the most strongly distorted octahedra is it found that:

$$8j < 4J < \Delta$$

where $\Delta$ is the $t_{2g} - e_g$ separation in a regular octahedron, and j, J are the $t_{2g}$ and $e_g$ splittings respectively.

The calculations are now being extended to other ions and coordination numbers. The splittings produced by non-orthogonal distortions are less easily found, but it should be possible to obtain approximate solutions.

# PRESSURE-INDUCED SPIN-PAIRING IN IRON /II/ MINERALS

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The rapid increase in crystal-field splitting with decreasing metal-ligand distance implies that high pressures will tend to cause spin-pairing in compounds containing high-spin transition metal ions, and Fyfe has argued /from the reduction in ionic radius on pairing/ that polymorphic transitions of possible geophysical importance should occur in oxide and silicate minerals of iron /II/ at pressures corresponding to depths within the mantle.

For any given metal-oxygen distance,. the nature and magnitude of the crystal-field splittings is determined by the geometry of the coordination polyhedron about the metal ion, and the splittings decrease in the order square-planar > > octahedral > cubic eightfold > tetrahedral. Pressure-induced spin-pairing has so far been observed only in gillespite /square-planar/ under a static pressure of about 50 kb, and in fayalite /octaheral/ at $0 < P < 577$ kb in dynamic experiments. Calculations indicate that spin-pairing should occur in close-packed oxides and silicates at about 350 kb at room temperature, and at about 600 kb, equivalent to a depth of 1400 km, on the geotherm. It is unlikely that any oxide compound will contain low-spin iron at 1atm., and the low magnetic susceptibility of minerals such as deerite and magnetite is attributed to ferrimagnetic effects.

Experiments now in progress are designed to measure the changes in volume, entropy, ionic radius, electrical conductivity and crystal field parameters in $d^6$ systems, and to study the effects of the spin-state equilibria which occur when the energy difference between the low and high-spin forms of a compound is comparable with kT.