

IMA MEETING '74  
INTERNATIONAL MINERALOGICAL ASSOCIATION  
NINTH GENERAL MEETING

COLLECTED ABSTRACTS

Invited by:  
Deutsche Mineralogische Gesellschaft, DMG  
Technische Universität Berlin, TUB

Sponsored by:  
Der Senat von Berlin  
Bayerisches Staatsministerium für Unterricht und Kultus  
Deutsche Forschungsgemeinschaft, DFG

C o n t e n t s

ABSTRACTS OF PAPERS PRESENTED AT BERLIN

<u>Main Sessions:</u>	3
Pegmatites and Pegmatite Minerals	5
Fluid Inclusions in Crystals	23
Secondary Minerals in Ore Deposits	39
Gem Minerals and Gemology	49
<u>Symposia:</u>	61
Commission on Ore Microscopy	63
Commission on History and Teaching	69
Commission on Mineral Data and Classification	73
<u>Open Sessions:</u>	75
Silicates	77
Mineral Properties and Mineral Occurrences	89
Petrology I	103
Sulfides	113
Unclassified Papers	119

ABSTRACTS OF PAPERS PRESENTED AT REGENSBURG

<u>Main Session:</u>	125
Mineral Genesis and Crystal Growth	127
<u>Symposia:</u>	141
Commission on Cosmic Mineralogy	143
Thermodynamics in Exp. Mineralogy and Petrology (IUGS-Commission on Experimental Petrology)	155
Mineral Physics (Inter-Union Commission on Geodynamics, WG 5)	177
<u>Open Sessions:</u>	185
Petrology II	187
Joint Session IMA-DMG: Technical Mineralogy and Applied Crystallography	195
<u>Author Index</u>	201

ABSTRACTS OF PAPERS PRESENTED AT BERLIN

Main Sessions:

Pegmatites and Pegmatite Minerals	
Thursday, September 12, 1974	
Part I, Chairmen: B. Shmakin A. Forster	
Part II, Chairmen: E.W. Heinrich H.U. Bambauer	
Fluid Inclusions in Crystals	
Friday, September 13, 1974	
Part I, Chairmen: E. Roedder E. Seeliger	
Part II, Chairmen: G. Gottardi W. Eysel	
Secondary Minerals in Ore Deposits	
Saturday, September 14, 1974	
Chairmen: B. Fojt G.C. Amstutz	
Gem Minerals and Gemology	
Saturday, September 14, 1974	
Chairmen: P.C. Zwaan H. Bank	

Main Session: PEGMATITES AND PEGMATITE MINERALS  
Introductory lecture  
GRANITIC PEGMATITES AND THEIR MINERALS:  
SELECTED EXAMPLES OF RECENT PROGRESS

P.Cerný, Winnipeg, Canada

The pace of systematic investigation of granitic pegmatites has slowed in the few past decades but considerable progress has been made in the crystal chemistry of some minerals and in petrological interpretation based on experimental work. Recent developments in the mineralogy of pegmatites will be shown on examples of the Fe, Mn, Ta, Nb oxides, phosphates, lithium micas, and pollucite.

Advances in pegmatite petrology will be demonstrated on the Jahns-Burnham and Stewart models, primary vs metasomatic assemblages, lithium aluminosilicates, feldspar chemistry, and the graphic granite problem. A review of the petrography and mineralogy of the giant Tanco pegmatite in southeastern Manitoba will be presented. The pegmatite, the world's largest deposit of tantalum, cesium, and refractory-grade spodumene, displays many characteristics supporting recent petrological theories, but it also shows some puzzling phenomena which are yet to be explained.

E.W.Heinrich, Ann Arbor, Michigan, USA

In homogeneous (unzoned), granitic, lithium pegmatites (Type I) high-iron spodumene is the sole representative of lithium. Increasing structural complexity of pegmatites is accompanied by increasing diversity of lithium mineralogy. Zoned pegmatites (Type II) rich in lithium contain zonal assemblages that include low-iron spodumene, petalite, triphylite-lithiophilite, and amblygonite-montebbrasite, singly or in various combinations. Zoned pegmatites with superimposed replacement (secondary) units (Type III) can contain the additional lithium species: lepidolite, zinnwaldite and lithium tourmalines. In addition, this third complex class of pegmatites commonly is characterized by the presence of a variety of hydrothermal "decay" products that contain lithium:

From petalite: spodumene + 2 quartz intergrowth  
("petamene", "spodulite", "squi")

From spodumene: eucryptite + albite — Li mica + albite  
("cymatolite")

cookeite  
bikitaite  
Li-clay minerals

From triphylite: tavorite

From amblygonite: palermoite, bertossaite, lithiophosphate  
Lithium minerals formed exogenically in the metasomatic wallrock haloes of pegmatites that contain primary spodumene are lithium biotite and the lithium amphibole, holmquistite.

In contrast, in alkalic-granitic and nepheline-syenitic pegmatites, lithium is represented by the lithium micas, taeniolite, polyolithionite and protolithionite, by lithium amphiboles (including Li-riebeckite), and by the fluoride, cryolithionite. In these petrologic categories of pegmatites discrete lithium species are restricted to structurally complex (Type III or "fully differentiated") pegmatites.

I.V.Bussen, E.M.Eskova, A.P.Khomyakov, Yu.P.Menshikov,  
A.N.Merkov, E.I.Semenov, Moscow, USSR

Pegmatites of agpaite nepheline-sodalite syenites, rich in sodium, were earlier known in Greenland (Ilimaussaq) and Kola peninsula (Lovozero, Khibina). But these pegmatites on the surface were intensively changed. During last years new bodies of pegmatites have been found and investigated by the authors in deep part of Lovozero massif, much lower of water penetration zone. These pegmatites appeared to contain a lot of minerals, which are unusually rich in sodium and readily change and dissolve in water. Extra-ordinarity of these peralkalic pegmatites is emphasized by the finding of 11 new sodium and rare-metals silicates by the authors:

Ilmajokite	$\text{Na}_2\text{Ti}[\text{Si}_3\text{O}_9] \cdot 4\text{H}_2\text{O}$
zorite	$\text{Na}_2\text{Ti}[\text{Si}_3\text{O}_9] \cdot 3\text{H}_2\text{O}$
penkvilksite	$\text{Na}_4\text{Ti}_2[\text{Si}_8\text{O}_{22}] \cdot 5\text{H}_2\text{O}$
kazakovite	$\text{Na}_6\text{H}_2\text{Ti}[\text{Si}_6\text{O}_{18}]$
vuonnemite	$\text{Na}_{11}\text{TiNb}_2[\text{P}_2\text{Si}_4\text{O}_{25}\text{F}]$
bornemanite	$\text{Na}_{12}\text{Ba}_2\text{Ti}_5\text{Nb}_2[\text{Si}_8\text{P}_2\text{O}_{44}]$
laplandite	$\text{Na}_4\text{CeTi}[\text{PSi}_7\text{O}_{22}] \cdot 5\text{H}_2\text{O}$
saghinite	$\text{Na}_3\text{Ce}[\text{Si}_6\text{O}_{15}] \cdot 6\text{H}_2\text{O}$
umbozerite	$\text{Na}_3\text{Sr}_4\text{Th}[\text{Si}_8\text{O}_{23}(\text{OH})]$
lovdarite	$\text{Na}_3\text{KBe}_2\text{Si}_6\text{O}_{12}(\text{OH})_8$
raite	$\text{Na}_4\text{Mn}_3[\text{Si}_8\text{O}_{21}] \cdot 10\text{H}_2\text{O}$

Peralkalic pegmatites and hydrothermalites (ussingite, natrolite) concentrate near foyaite and malignite horizon which is also extremely rich in sodium, rare and volatile components. Nearly horizontal pegmatite layer has thickness up to 1,6 m and length more than 26 m. Outer pegmatite zone (~0,5 m) consists of big crystals of microcline, sodalite, arfvedsonite, aegirite, eudialyte. Central zone (and apophyse) is mainly natrolitic. Natrolite (and analcite, ussingite) also form small hydrothermal veins with similar mineralization. In addition to our new minerals mentioned above nearly 50 other rare minerals were found here.

PETROGENESIS OF THE GRANITE-PEGMATITE-SYSTEM  
IN THE NORTHERN END OF THE PIKES PEAK BATHOLITH, COLORADO

W.B. Simmons, New Orleans, and E.W. Heinrich, Ann Arbor, USA

A distinctive cluster of well-zoned pegmatites occurring near the northern margin of the Pikes Peak batholith in Jefferson County, makes up the South Platte pegmatite district. The whole assemblage constitutes a well-defined granite-pegmatite system. The major petrologic units are: 1) granite; 2) quartz monzonite; 3) pegmatite; 4) aplite dikes; 5) xenoliths of biotite gneiss, granitic gneiss, and associated aplite; 6) quartzite dikes; 7) Idaho Springs Formation; and 8) high-level Tertiary gravel. The granite occurs as an outer zone of the batholith and surrounds the interior-zone quartz monzonite.

Normative analysis indicates that the granite and Q-monzonite formed from liquids of essentially similar composition, their differences being principally modal. Ab-Or-Q and Ab-Or-An-(SiO<sub>2</sub>) plots fall close to the minimum-temperature-melt compositions in both systems. Plots of Ab/An and Ab/Q ratios versus P-T data for experimental water-saturated melts indicate that the granite crystallized under lower P<sub>H<sub>2</sub>O</sub> conditions than the Q-monzonite.

The district is characterized by over 50 large concentrically zoned, nearly vertical pegmatites, which all occur within the pluton rather than marginal or exterior to it. In shape and external structure, two end-member types are distinguishable: (1) vertical pipe-like bodies with essentially circular plans; (2) vertical to steeply dipping, thick ellipsoidal lenses. Pegmatites of the central group are restricted to elevations between 6800 and 7800 feet within the granite, forming a clearly defined level of pegmatites. The concentric internal zonation consists of the idealized sequence: 1) very poorly developed border zone (usually absent), 2) wall zone of biotite graphic granite, 3) outer-intermediate zone of giant biotite crystals (rarely present), 4) intermediate zone of microcline-perthite, 5) core-margin zone of green fluorite, 6) large core of massive quartz or quartz-microcline, 7) secondary replacement units, containing albite, fluorite, rare-earth minerals and hematite. Fractional crystallization of the Pikes Peak magma resulted in water-enriched liquid segregates of residual fluids which became the parent fluid from which the pegmatites crystallized.

NEPHELINE PEGMATITES IN THE BANCROFT AREA, ONTARIO CANADA

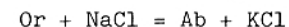
G.M. Anderson, G. Sylvester and E.J. Reeve, Toronto, Canada

A narrow, discontinuous belt of syenite and nepheline syenite gneisses extends for over 160 km in northern Ontario, through the town of Bancroft. Within the nepheline-bearing gneisses there occur several large (50-100 m) pegmatite bodies consisting almost entirely of albite-oligoclase, nepheline and biotite. Two pegmatites and their adjacent gneisses in the York River area have been diamond-drilled and studied in detail.

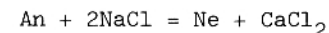
The gneisses and unzoned pegmatites have rather simple mineralogy with no unusual trace element concentrations and no rare mineral occurrences. Plagioclase is generally unzoned, shows two generations, and ranges from about An<sub>1</sub> to An<sub>30</sub>. Nepheline compositions cluster around Ne<sub>77</sub>Ks<sub>21</sub>Qz<sub>2</sub>. Microcline is minor and ranges from about Or<sub>70</sub> to Or<sub>95</sub>.

The bulk compositions of the pegmatites are Ne<sub>67</sub>Ks<sub>11</sub>Qz<sub>22</sub> and Ne<sub>50</sub>Ks<sub>10</sub>Qz<sub>40</sub> (CIPW norms) and gneiss compositions are similar but highly variable. These compositions cannot be derived by differentiation of known igneous rock compositions, nor can they represent partial melting of the host gneisses unless unrealistically large degrees of melting are postulated.

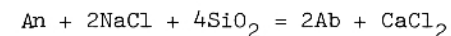
Many of the compositional and textural features of these rocks can be explained by the hypothesis that post-metamorphic ion-exchange reactions between quartz-poor feldspathic gneisses and NaCl-rich brines have taken place. The reaction:



depleted the rocks in Or content (thus the strange pegmatite compositions) and the reaction:



produced nepheline. These reactions result in a second generation of plagioclase higher in Ab. In the presence of quartz the reaction:



enriches the rock in Ab and depletes it of quartz. The occurrence of sodalite sporadically throughout the belt shows that NaCl was present.

A NEW CALCIUM ZIRCONIUM SILICATE - ARMSTRONGITE,  
ARMSTRONGITE - ELPIDITE ISOMORPHIC SERIES AND MINERAL  
PARAGENESIS OF ZIRCON MINERALS IN ALKALINE GRANITE  
PEGMATITES

N.V.Vladykin, V.I.Kovalenko, I.L.Lapides, Irkutsk, USSR

A new mineral - armstrongite,  $\text{CaZr}[\text{Si}_{15}\text{O}_{15}]\cdot 2,5\text{H}_2\text{O}$ , was found in agpaitic alkaline granites and pegmatites of Han-Bogdo massif in Mongolia and named in honour of N.Armstrong - the first man who had set foot on the Moonland.

Han-Bogdo massif is a part of South-Gobi alkaline rock belt and is composed of arfvedsonite granites. Numerous ekerite and pegmatite dikes contain elpidite as rockforming mineral (up to 20%). Practically all known elpidites were of sodium composition and it seemed to be no isomorphism in this group of minerals. As CaO content in Han-Bogdo elpidites was 1-3,5% armstrongite appeared to be the pure calcium analogue of elpidite. We assume the occurrence of elpidite-armstrongite isomorphous range with their limited miscibility. Decreasing of density, increasing of refractivity and lowering of symmetry from orthorhombic system to monoclinic system was found in the elpidite-armstrongite range. Polysynthetic twinning was found in armstrongite. Asymmetric isomorphism ( $2\text{Na} \leftarrow \text{Ca} + \text{vacancy}$ ) seems to occur in this case. The presence of alkali controls the structural positions of water and dehydration. Three energetically different water positions and zeolite-like character appear to be revealed in this mineral group during thermographical and IR investigation. Zirconium of Han-Bogdo massif is concentrated mainly in armstrongite-elpidite minerals which are typomorphic minerals of alkaline granites in general. They are associated with accessory synchisite, monazite, rare-earth sphene, neptunite, spherulite of zircon, native gold, and yellow titanosilicate.

TRIPHYLITES AND LITHIOPHILITES FROM THE GRANITE PEGMATITES  
OF KITEE AND TOHMAJÄRVI PARISH, E-FINLAND

Pekka Kallio and Reijo Alviola, Haukilahti, Finland

A pegmatite bearing rare element minerals was discovered in the Kitee-Tohmajärvi area in 1971. In 1972 and 1973 about 500 pegmatites were studied. Beryl was found in about 80 pegmatites and Li-minerals in 14 pegmatites. None of the pegmatites proved to be economically important. The pegmatites are associated with the tourmaline-bearing Kitee granite; they occur in Karelian micaschists, quartzites, black schists and amphibolites. According to radiometric determination (U-Pb-age from zircon) the age of the pegmatites is 1810 m.y. Microcline, albite (including cleavelandite), quartz, muscovite and black tourmaline are the main minerals. Beryl, garnet, apatite (often hydroxylapatite) and Fe,Mn-phosphates are common. Arsenopyrite, löllingite, pyrite, pyrrhotite, sphalerite, uraninite and columbite are also met with, but in minor amounts. Green and red tourmaline, montebasite, spodumene, cassiterite and lepidolite occur in only a few pegmatites.

Fe,Mn-phosphate crystals or nodules were found in 14 pegmatites. The biggest nodules are 30-50 cm in diameter; usually the nodules measure 1-3 cm. The most common Fe,Mn-phosphates are triphylite-lithiophilite, sicklerite, heterosite and alluaudite. In some pegmatites triphylite is the primary mineral of the big nodules, in other lithiophilite.

In the big nodules triphylite is covered by concentric shells of alteration products. Greenish grey triphylite is surrounded by brown ferrisicklerite, while the outermost shell consists of green vivianite and yellow ludlamite or purple heterosite. The border between ludlamite and vivianite is gradational; other borders are sharp.

The lithiophilite nodules consists of Ca-poor lithiophilite interlaminated with a Ca-Mn-Fe-phosphate (electron microprobe analysis). The X-ray diffraction powder photographs indicate that also the interlaminating mineral is lithiophilite. Both minerals have been partly altered into alluaudite and triplidite.

A NOTE ON SCORZALITE FROM ZENAGA PLAIN PEGMATITES, ANTI-ATLAS, MOROCCO

A.M.Fransolet, Liège, Belgium

In the phosphates from the precambrian pegmatites outcropping in Zenaga Plain (Anti-Atlas, Morocco), scorzalite frequently occur.

On account of the very fine grained shape and the mixture of muscovite, apatite, hematite, quartz and also mitridatite, the accurate determination of scorzalite is not easy. It is characterized by a unit-cell dimensions measurement and by a DTA curve. A qualitative test by microprobe shows a higher content in Fe with regard to Mg.

In the Angarf-Sud pegmatite, the phosphates have a zonal structure. A core of gray triphylite, widely replaced by green alluaudite, is fringed by reddish fine-grained apatite. The more important secondary phosphates are: barbosalite, tavorite, melonjosephite, hureaulite and whitlockite. Quartz and mainly pyrite are also associated. If muscovite occurs in this assemblage, it is systematically accompanied by scorzalite and fringed by apatite.

Investigations of this blue phosphate under microscope show an interesting paragenesis. Scorzalite replaces muscovite and is inserted in its cleavage. Hematite and fine grained apatite are also present in the cleavage. Some quartz also crystallizes following this direction. Sometimes, the structure is cutted by mitridatite veinlets.

In the Tazzarine-Est pegmatite, scorzalite is embedded in heterosite. It replaces patches of muscovite completely; the structure is still remaining.

From these observations it seems that scorzalite forms under a low oxygen fugacity, probably immediately after magnesian triphylite and before alluaudite and apatite. The solution, rich in phosphorus, ferrous iron, with a little magnesium, reacts with mica that gives aluminium;  $\text{SiO}_2$  and K are released. So it is not necessary to evoke a metasomatic process to explain presence of aluminium and, a recurrence phenomenon to explain ferreous iron and magnesium.

PHOSPHATE MINERALS FROM PEGMATITES OF THE NORTHEASTERN BRAZIL

R.Rodrigues da Silva, Recife, Brazil

Typical zoned granite pegmatites of the heterogeneous type, of the Northeastern Brazil have been investigated for their phosphate and associated mineral content.

The pegmatites under consideration occur in the States of Paraiba and Rio Grande do Norte, near the cities of Equador, Parelhas, Pedra Lavrada, Picos, etc. Besides those of the normal beryl-tantalite pegmatites the following minerals appear:

arrojadite, barbosalite, beraunite, chavesite, huréaulite, leucophosphite, metastrengite, mitridatite, scorzalite, tavorite, vivianite and others.

Detailed description of the occurrences, chemical analysis, physical properties, X-ray data (diffractometry and spectrography), thermal analysis (DTA and TGA) are given for these minerals.

W.L.Roberts, South Dakota, and George Rapp, Minnesota, USA

The Tip Top pegmatite contains thirty-seven mineral species, twenty-two of which are phosphates. Of these only two, triphylite and montebbrasite, crystallized as primary minerals in the late magmatic stage of crystallization. The other twenty phosphate species are secondary minerals formed as alteration products from the disintegration of large triphylite masses in the presence of residual pegmatitic hydrothermal fluids.

The mechanisms contributing to the formation of this large secondary suite are solution, alkali leaching, oxidation, hydration, hydroxylation and Ca/Mg metasomatism. The secondary phosphates formed by one or more of these mechanisms are: ferrisicklerite, heterosite, mitridatite, laeuite, ludlamite, bermanite, rockbridgeite, hureaulite, fairfieldite, collinsite, jahnsite, robertsite, segelerite, whitlockite, leucophosphate, vivianite, hydroxyapatite, fluorapatite, carbonate-apatite, and tavorite. New chemical and trace chemical data on these secondary phosphates are included.

Paul Brian Moore, Chicago, USA

A monograph is nearing completion which exhaustively treats the primary and secondary phosphates found in pegmatites, excluding the complex uranyl phosphates whose chemistry is as yet unresolved. Ninety-eight species are included. The study involves a complete collection of references, crystal drawings, crystal-chemical characters, optical properties, paragenetic settings and occurrences. Some salient features include:

1. Nine species new to science (jahnsite, segelerite, robertsite, foggite, whitmoreite, goedkenite, and three awaiting approval by IMA).
2. Revisions of the crystal chemistry of xanthoxenite, azovskite, souzalite.
3. Crystal drawings of the nine new species, dufrenite, mitridatite and xanthoxenite.
4. Crystal structures of mitridatite, jahnsite, montgomeryite, whitmoreite, xanthoxenite, palermoite and stewartite.
5. A general paragenetic-crystal chemical outline stressing the crystal-chemical basis of the associations.



ACCESSORY MINERALIZATION AND GEOCHEMICAL SPECIALIZATION OF  
MUSCOVITE PEGMATITES OF DIFFERENT REGIONS

B.M.Shmakin, Irkutsk, USSR

The most characteristic (typomorphic) accessory minerals of muscovite pegmatites are the tourmaline of dravite-buergerite series, the garnet with the predominance of almandite and the fluorine apatite. But such accessory minerals as beryl, uraninite, zircon, allanite, monazite are only in some regions or in some veins. Accessory columbite and cassiterite can be in pegmatites of transition raremetal-muscovite specialization, and when the latest albitization takes place in muscovite pegmatites.

Among the element-impurities Ba, Sr, Rb and Cs show the most regular behaviour. The very high content of the first two elements and the low content of Rb and Cs are characteristic for early generations of potassium minerals in typical muscovite pegmatites. Along with the transition to raremetal-muscovite pegmatites one can see the decreasing of Ba and Sr but the increasing of Rb and Cs. As a result the ratios Ba:Rb, Sr:Cs, etc. in early generations of potassium minerals are good indicators of pegmatite specialization. The content of Ti in micas of typical muscovite pegmatites is maximal, but contents of Nb, Ta, Sn, F are minimal and then the figure of Ti:Nb ratio in biotite and muscovite can be the geochemical indicator of pegmatite specialization too.

Be-content in rockforming minerals is in good correlation with the quantity of accessory beryl in pegmatites. It is not accurately connected with the geochemical specialization. The same can be said on Li and Rare Earths contents. But all these elements and their correlations especially show regular behaviour in processes of postmagmatic replacement of pegmatites.

The presence of typomorphic accessory minerals and the concentration level of element-impurities depend on conditions of formations, first of all - on pressure and composition of volatile components. But contents of other elements and minerals depend on some additional factors. The composition of wall rocks is among these factors.

MUSCOVITE OF THE PEGMATITES OF NORTHERN PORTUGAL AND ITS  
GEOCHEMISTRY

Ana M.R.Neiva, Coimbra, Portugal

The muscovite from pegmatites has tabular habit, with greater basal spacing than the muscovite from parental granites. There is a muscovite like feathers which is later and has greater basal spacing than the muscovite of tabular habit. Quantitative determinations of major and trace elements of nineteen muscovites from pegmatites and eleven muscovites from parental granites are given.

The trend of fractionation granite muscovite → pegmatite muscovite is clearly defined based on trace elements and trace element/major element ratios.

Correlation between some elements were found.

Considering the importance of tin-tungsten mineralization in Northern Portugal, the study of muscovite shows the affinity of Sn for F. Lithium and rubidium also accompany the increase in Sn in the muscovites from pegmatites, while Sn and Ti vary inversely. W and Mn increase together and they are more concentrated in the muscovites from pegmatites.

The muscovites from pegmatites which cut schists are poorer in Cl, F, Sn, Li, Ni, Cu, Bi, Ba than the muscovites from pegmatites related to the same parental granite, which they cut.

DISTRIBUTION OF Sr-ISOTOPES, K/Rb, AND Rb/Sr RATIOS IN  
FELDSPARS AND MICAS FROM PEGMATITES AND ADJACENT ROCKS

J.Rimsaite, Ottawa, Canada

Distributions of K, Rb, Sr, and Sr-isotopes  $Sr^{86}$  and  $Sr^{87}$  were studied in minerals from three Canadian Li-pegmatites and syenite- and granite-pegmatites. The Li-pegmatites contain variable quantities of beryl, pollucite, spodumene, or tourmaline. One pegmatite is associated with commercial Nb-Ta deposit, and the others, molybdenum and uranium occurrences. The syenite-pegmatite is in a Ni-Cu mine. All pegmatites are of Precambrian age and exhibit prominent replacement textures. The highest concentrations of Rb and F are in lepidolites that replace beryl and spodumene during the late pegmatitic hydrothermal phase. These lepidolites contain very little (less than 1 ppm) or no common Sr, in contrast to the pegmatitic albite which contains very little Rb (3.6 ppm). The relationships found between K, Rb, Sr common ( $Sr_c$ ) and Sr radiogenic ( $Sr_{Ra}$ ) in minerals from the pegmatite and from adjacent rocks are summarized in the following table:

Origin	Mineral	K/Rb	Rb/Sr <sub>c</sub>	Rb <sup>87</sup> ppm	Sr <sup>86</sup> ppm	%Sr <sup>87</sup> Ra	Sr <sup>87</sup> Ra/Sr <sub>c</sub> <sup>87</sup>
<u>Li-pegmatite</u> hydrothermal phase	Lepidolite	2.5- 6	7000- 15000	4000- 9300	0.0- 0.1	99	2250
<u>Li-pegmatite</u> main phase	Al, Li-micas	10- 15	4000- 6000	1400- 2200	0.3- 0.8	95- 98	500- 1000
" "	Biotite & Microcline	20	100- 730	1100- 1500	0.5- 2.2	40- 70	10- 25
<u>Li-pegmatite</u> initial phase	Na-feldspar antiperthite	40	9	38	1.5	10	1.6
Gneiss & Skarn	Biotite	110- 160	30- 150	26- 62	0.4- 0.5	25- 35	1.1- 2.5
Metavolcanics Metagreywacke	Biotite	300- 350	8- 20	120- 160	1.1- 1.3	7- 15	7
Micas assoc. w. serpentine	Muscovite Phlogopite	500	3	50- 150	2- 5	2.5- 9	0.5- 1.5
Syenite- pegmatite	Microcline perthite	400	0.5	60	46	0.17	0.024
"	Albite	2250	0.005	0.98	65	0.00	0.0
"	Biotite	160	97	120	0.44	25	1.8

LITHIUM - ALUMINUM MICAS FROM SOUTH WEST AFRICAN PEGMATITES

C.T.Logan, Johannesburg, South Africa

Chemical and X-ray data are presented for a series of lithium-aluminium micas collected from various points within lithia-rich South West African pegmatites.

The relation of structural type to compositional variation and the environment of crystallisation is considered. Temperature and pressure appear to have played a minimal part in determining which polymorph crystallised, and the structural type of mica occurring in these pegmatites provides a reliable estimate of lithium-mica composition between wide limits.

A PRELIMINARY STUDY OF TIN MINERALISATION IN BIHAR PEGMATITES,  
INDIA

N.K.Mukerjee, Varanasi, India

Several occurrences of tin deposits are known from different States of India, namely Bihar, Rajasthan, Gujarat and Karnataka. But none of them has so far been proved to be of commercial importance. On the face of acute shortage and steadily increasing demand of the metal in India, it has become imperative to undertake an intensive study of their geological and economic aspects.

The present paper, mainly dealing with the occurrences in Bihar, comprises of two parts. The first one records the different cassiterite deposits in the districts of Hazaribagh, Gaya, Ranchi and Singhbhum, and supplies short descriptions. In the second part, detailed investigations of the deposit in the neighbourhood of Chhakkarbendah have been incorporated.

The Chhakkarbendah occurrence is situated about 8 km south of Deo in Gaya District of Bihar. The prospective region consists of Archaean granite-gneisses, various types of schists occasional amphibolites as country rocks which have been intruded by later pegmatites and aplites. The mineralization is restricted to the schistose rocks represented by garnetiferous quartz-sericite-biotite-muscovite-schist and quartz-sericite-sillimanite-schist, which occur dominantly in two bands running more or less north-south along the eastern flank of the local hill range. The following rocks, namely (1) Quartz-tourmaline rock, (2) Garnet-cassiterite rock, and (3) Magnetite-cassiterite rock - are richly stanniferous and these are usually found enclosed along the foliation planes of the above-mentioned rocks.

The occurrence of tin is believed to be present in two phases, firstly as a separate phase of cassiterite occurring as very tiny or micro-granular disseminations, and secondly as a dispersed phase replacing divalent iron in biotite, almandite, etc. The cassiterite content of the rocks varies widely, but it is about 1,5 % in richly mineralized zones. In the light of the detailed petrography of the various lithological units, it is believed that the formation of cassiterite in the Chhakkarbendah region is genetically connected with pegmatitic activity which had been so widespread in the Bihar-Mica-Belt.

COMPOSITE ALBITITE-APLITE AND PEGMATITE FROM MANSEHRA AND  
BATGRAM AREA OF HAZARA DISTRICT, PAKISTAN

Muhammad Ashraf, Lahore, Pakistan

Composite albite-aplite and pegmatite bodies have been discovered from the granitic complex of Hazara district for the first time. On the basis of field and laboratory investigations the following types of composite bodies have been discovered:

- I) Pegmatitic-albite, albite-aplite, albite-microcline-aplite/pegmatite
- II) Fine to medium-grained albite, layered-albite and layered-aplite, and albite-pegmatite
- III) Pegmatitic-albite, medium-grained-albite
- IV) Pegmatitic-albite, medium-grained-albite, albite-aplite
- V) Pegmatitic-albite, medium-grained-albite, albite-aplite, albite-(microcline)aplite
- VI) Pegmatitic-albite, medium-grained-albite, albite-(microcline)aplite
- VII) Albite-(microcline)-aplite/pegmatite, fine-grained and pegmatitic albitites (xenoliths)

These bodies occur in the interior zone of the granitic complex and are very simple in composition. Genetically the albitites are thought to be products of high water vapour pressure of more than 10 Kilobars, but as the vapour pressure decreased gradually the trapped liquids in fissures started crystallizing albite-aplite, albite-(microcline)-aplite/pegmatite, and albite-microcline-aplite/pegmatite depending on the favourable conditions.

PRECIOUS STONES PEGMATITES IN SOUTH AFRICA AND SOUTH AMERICA,  
AND THE CONTINENTAL DRIFT THEORY

H.Strunz, West-Berlin (see page 60)

Main Session: FLUID INCLUSIONS IN CRYSTALS

Introductory lecture

G.Deicha, Saint-Germain-en-Laye, France

The study of gas and liquids trapped in syngenetic as well as epigenetic cavities of minerals has been widely developed in recent years. The sessions of the Commission on ore-forming fluids in inclusions (1) held during I.M.A. Meetings in Japan (1970) and Canada (1972) gave proof of the importance of this subject.

Essentially new trends in the investigation of various kinds of microscopical and submicroscopical fluids or solid inclusions are reflected in recent publications (2, 3 and 4). Practically every regional meeting of mineralogists deals with this matter, for instance in Europe in autumn 1973 the Joint Session (Paris) of the English and French Mineralogical Societies, the Symposium on Inclusions (Milano), sponsored by the Italian Mineralogical Society with an active French and Swiss participation, the annual meeting (Frankfurt/Main) of the German Mineralogical Society, the 4th Russian Symposium on Thermobarogeochemistry (Rostov/Don).

Mass spectrometry, electron and ion probe as well as neutron activation analyses of the trapped matter are now combined with heating-, freezing-, and crushing-stage experiments, decrepitation and investigation of the host cavities by replica electronmicroscopy or direct scanning electron fractography.

Thanks to the expansion of such researches nearly all parts of the Mineral Realm are concerned and more light is thrown on the crystallogenesis in rocks, ore deposits and gem occurrences.

- (1) For the activities of this Commission (C.O.F.F.I./I.A.G.O.D. see: Fluid Inclusions Research-Proceedings of C.O.F.F.I., U.S. Geological Survey, Washington, annual issues since 1968.
- (2) Gas und Flüssigkeitseinschlüsse in Mineralien (1970). Schweiz.Mineral.Petr.Mitt.Bd. 50, 208 p.
- (3) ROEDDER E.: Composition of Fluid Inclusions (1972) - U.S. Geol.Survey.Prof.Paper 440 JJ, 164 p.
- (4) ERMAKOV N.P.- Geochemical Systems of inclusions in minerals (1972) Ed."Nedra", 176 p., Moscow.

THE APPLICATION OF MACRO- AND MICRO-CINEMATOGRAPHY IN THE STUDIES OF THE CRYSTALS' AND GEMS' INCLUSIONS, PARTICULARLY THE FLUID INCLUSIONS - Colour-Sound-Film

E. Bettetini, Nice, France

The mutual crystallographic orientation of host and guest, that is endotaxy, makes it possible to ascertain the authenticity of gems and precious stones by their solid inclusions.

The fluid inclusions are the distinctive mark of the liquid and gaseous phases which were present during the genesis and the evolution period of the minerals and the rocks.

Under the effect of heat one can observe in certain internal cavities of the minerals an ebullition; such as an "operation of the open heart" which gives the impression of a beating heart. An inward world animates itself agitating sometimes other solid inclusions floating within the fluid or gaseous realm.

Thus, many most peculiar and highly interesting features can be observed, such as:

- Passage from the liquid to the gaseous state and vice-versa
- Disappearance and reappearance of retreating bubbles
- Separation of the CO<sub>2</sub> into two phases
- Movements of a minute solid particle to a bubble which accurately changes position according to the variations of the intensity of luminosity.

FLUID INCLUSIONS IN QUARTZ-CRYSTALS FROM ORPIERRE (HAUTES ALPES, FRANCE) AND RÉMUZAT (DRÔME, FRANCE)  
Coloured film

Roger Martin, Nyon, Switzerland

The Oxford marls with their characteristic levels of calcareous concretions have suffered low metamorphism of anchimorphic grade, accompanied by structural deformations due to the regional tectonic events.

During these deformations the concretions have been flattened, and their opening cracks of perhaps even diagenetic origin gave way to growth of quartz-crystals of a very peculiar morphology which is probably due to the presence of hydrocarbons during their growth (MARTIN 1973). The quartz-crystals are very rich in vacuoles of growth and fluid inclusions, which all contain besides water different hydrocarbons of gaseous, liquid or solid consistence. Sometimes, clear yellow or red-brown coloured oil contains small drops of denser oils or even organic particles. In the quartz-crystals of Orpierre water may be completely absent, and inclusions are composed essentially by "oily" and gaseous substances.

The meaning of the film technics is to show how complicated the behaviour of fluid inclusions is during heating, cooling or rotation of the samples.

During the changing conditions between 18<sup>o</sup>-50<sup>o</sup>C the following events are observed: formation of eddies, change of viscosity, convection-currents, homogenization of phases, unmixing of phases with retro-boiling, attraction or repulsion of particles.

- DEICHA, G. (1970): Le degré de liberté des solutions géochimiques. SMPM 50, 25-35.
- MARTIN, R. (1973): Morphologie des quartz de la zone d'Orpierre (Hautes-Alpes, France). Schweizer Strahler 3, 101-118.
- TOURAY, J.C. & JAUZEIN, A. (1967): Inclusions à méthane dans les quartz des "terres noires" de la Drôme C.R.Acad.Sc.Paris, 264, 1957-1960.

LIQUID AND GASEOUS HYDROCARBON INCLUSIONS IN QUARTZ MONO-CRYSTALS FROM "TERRES NOIRES" AND "FLYSCH À HELMINTHOIDES" (FRENCH ALPS): A MINERALOGICAL INVESTIGATION

Jean-Claude Touray and Jacques Barlier, Orléans, France

Gaseous and liquid hydrocarbons trapped by quartz monocry-  
stals from septaria (Terres noires) or fissure veins (flysch  
à helminthoides) exhibit various appearances under the micro-  
scope. The present paper is concerned by an optical study of  
organic inclusion fluids upon heating and freezing stages  
and relates to about a thousand of inclusions. In the range  
-150°C to +200°C were determined

- melting temperatures of paraffins
- partial homogenization temperatures,  
should the occasion arise
- total homogenization temperatures.

When possible in those water-poor samples, thermometric  
and cryoscopic investigations have been made.

The quartz crystals were collected in two domains that one may  
distinguish by a microreflectometric study of the disseminated  
organic material in rocks. Their frontier-line orientated gross-  
ly NW-SE passes near Barles. As indicated by the temperature-  
reflectance curves, this limit is an imprint of a 180°C - 200°C  
paleo-isotherm; westward temperatures are lower (155°C to  
175°C) and eastward they are higher (210 to higher than 230°C).

Amongst the differences between organic inclusions trapped by  
the quartz from the two domains one may notice.

- An eastward decrease of the homogenization temperatures  
of the one phase gaseous inclusions probably explained by  
an increase of their density and perhaps by an increase of  
the CH<sub>4</sub> amount, compared with other light alcanes.
- An eastward decrease of the homogenization temperatures  
of the "petroleum" bearing inclusions possibly depending  
on a pressure increase.

Such oppositions reinforced by data from aqueous inclusions  
may be explained by diagenetic against anchimetamorphic growth  
of the quartz monocrytals.

CAVITIES AND INCLUSIONS IN QUARTZ FROM KING SALOMON MINES  
(MENE'ITYEH). SOME ASPECTS OF THEIR STUDIES UNDER THE SCANNING  
ELECTRON MICROSCOPE

J.Rasumny, Orsay, France

Observations under the scanning electron microscope done in  
the geological laboratory of the "Museum d'Histoire Naturelle  
de Paris" have enabled to study the quartz of this copper  
occurrence. The obtained electron fractographies have shown,  
besides the intragranular inclusions in quartz crystals, al-  
ready described from other localities by various authors  
(J.VERDIER et al.: The distribution of epigenetic fluid in-  
clusions as evidence of rock microfissuration. - Symposium  
Soc. International Mecanique des Roches, Nancy, 1-10, fig.7-8)  
also intergranular cavities, as well as contacts between quartz  
and other minerals (under magnifications going over 20.000).  
Some conclusions are drawn as to the possibilities of capil-  
lary circulations of ore forming fluids.

AN INDEPENDENT CHECK ON THE VALIDITY OF THE PRESSURE  
CORRECTION IN INCLUSION GEOTHERMOMETRY, USING  
HYDROTHERMALLY GROWN QUARTZ

Otto C.Kopp, Oak Ridge, Edwin Roedder, Washington, USA

Primary fluid inclusions were studied in synthetic quartz crystals (~1 cm) grown in static thermal gradients from 0.5N CsOH or RbOH (partial fill 62-75 %) at 0.8-1.8 kb and 377-470°C. Inclusion homogenization temperatures ( $T_H$ ) were determined blind, corrected for known pressure to yield trapping temperatures ( $T_T$ ), and compared with laboratory growth temperatures ( $T_G$ ) in order to evaluate the validity of inclusion thermometry when pressure corrections ( $P_C$ ) are large:

$T_G$ (est.)(°C)	411	411	394	452	462	400	447	380	399
$T_H$ (°C)-	327	319	281	320	329	315	297	314	306
$P_C$ (est.)(°C)	90	111	122	140	127	87	168	77	115
$T_T$ (est.)(°C)	417	430	403	465	456	402	465	391	421
$\Delta T$ ( $T_T - T_G$ )(°C)	+6	+19	+9	+13	-6	+2	+18	+11	+22

In spite of relatively large values for  $P_C$ ,  $\Delta T$  is relatively small.  $\Delta T$  is the sum of the following errors, only part of which can be evaluated with any precision: 1) Errors in measurement and interpolation of  $T_G$  in the bomb at the crystal face; 2) Errors in measurement of  $T_H$  (here probably  $\pm 2^\circ\text{C}$ ); 3) Errors in calculating  $P_C$  (here probably  $\pm 5^\circ$ ); 4) Errors known to be intrinsic to the  $T_H$  method, such as bubble surface tension and host mineral expansion on external pressure release and on internal pressure increase (here probably  $<1^\circ\text{C}$ ); 5) Errors suggested by others to be intrinsic to the method, such as trapping nonrepresentative fluid (unknown magnitude). We believe that (1) is probably the major source of discrepancy here, and that these data prove that if the solution composition is known adequately, pressure corrections can be large and still permit relatively accurate thermometry by means of inclusions.

ENDOSCOPICAL STUDY ON SOME CARBONIFEROUS DETRITAL  
SEDIMENTS FROM WEST-CENTRAL SINAI, EGYPT

Mahmoud M.Kholief, Cairo, Egypt

Inclusions were investigated microscopically in about 60 preparations of quartz grains from the Carboniferous detrital sediments of west-central Sinai. The inclusions are either solid or fluid-gaseous of primary and secondary origins. Many of the inclusions, especially the solid ones, have their impressions on the surface morphology of quartz grains. The nature and the mode of distribution of the inclusions indicate that the source rock was mainly effusive acidic and microgranitic. Subsequent tectonic effects resulted in a fissuring system and the penetration of secondary inclusions.

GASES RELEASED FROM NATURAL AND SYNTHETIC DIAMONDS BY CRUSHING UNDER HIGH VACUUM AT 200°C, AND THEIR SIGNIFICANCE TO DIAMOND GENESIS

A.A.Giardini and C.E.Melton, Athens, Georgia, USA

Thirty-eight natural diamond samples (21: 0.1 to 2.1 ct. each, Arkansas, U.S.A.; 16: 0.1 to 4.5 ct. each, Africa; one 2.5 ct., Brazil) were crushed in the inlet of a research mass spectrometer at  $10^{-9}$  torr and 200°C. Six 36-mesh Gen. Electric synthetic diamond samples (2 from regular production, 4 from a new high pressure and temperature process) also were crushed. Most diamonds contained totally enclosed solid inclusions. All samples released gas. The average (and range) of gas composition (vol.%) from natural diamonds and from commercial synthetics shows the table.

	Arkansas	Africa	Brazil	Average	Comm. synth.	New proc.
H <sub>2</sub> O	32.9(2.9-75.7)	34.5( 0-85.1)	85.1	34.43	----	25.8
H <sub>2</sub>	24.1(1.5-40.4)	21.6( 1-59)	1.6	22.49	33.2	26.2
CO <sub>2</sub>	22.6(5.3-37.7)	15.2( 2-28.1)	5.4	18.91	12.1	17.4
CO	3.6(0.4- 9.4)	7.6( 0-45.8)		5.78	----	----
N <sub>2</sub>	7.4( 0-87.2)	14.0( 0-80)	1.7	9.96	----	5.1
CH <sub>4</sub>	8.4(0.9-25.1)	6.1(0.5-18.3)	4.0	7.32	54.7	24.8
C <sub>2</sub> H <sub>4</sub>	-----	0.1( 0 - 0.7)	0.2	0.08	----	----
C <sub>3</sub> H <sub>6</sub>	-----	0.2( 0-2)	---	0.09	----	----
CH <sub>3</sub> OH	0.3( 0- 5.2)	-----	---	0.17	----	----
CH <sub>3</sub> CH <sub>2</sub> OH	0.4( 0- 3.2)	0.5( 0-3)	0.1	0.33	----	----
O <sub>2</sub>	-----	0.2( 0-1.9)	1.9	0.14	----	----
Ar	0.3( 0- 1.3)	0.2( 0-1.2)	0.05	0.3	0.05	0.6

The ratios of average (and range) of gas volume (STP) to diamond sample volume =  $4.2 \times 10^{-3}$  (1.8 - 18.5,  $\times 10^{-3}$ ) Arkansas;  $3.5 \times 10^{-3}$  (0.02 - 15.7,  $\times 10^{-3}$ ) Africa;  $0.3 \times 10^{-3}$  Brazil.

Except for N<sub>2</sub> (once, Arkansas), and for H<sub>2</sub>O and N<sub>2</sub> (once each, Africa), H<sub>2</sub>O, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> always were present. O<sub>2</sub> was found only in a few diamonds of cube form. The gas difference in natural diamonds and commercial synthetics indicates a different formation environment. A thermodynamic interpretation of diamond genesis with various models of the C-H-O system has been carried out. Results can be interpreted qualitatively on the basis of a gas-solid reaction mechanism.

IN SITU MEASUREMENTS OF THE REFRACTIVE INDICES OF LIQUID AND GASEOUS INCLUSIONS IN MINERALS

Harry Micheelsen, Copenhagen, Denmark

The refractive indices of the gas, liquid and mineral contents of inclusions in minerals can often be measured in situ by a conoscopic method on the ordinary polarizing microscope using a slightly modified condenser. The principle of the method is that a narrow beam of light can be totally reflected on the surface of an inclusion. This can be observed by means of the Bertrand lens. The incident beam is tilted away from the microscope axis until the limiting angle of total reflection is reached; if the angle of tilt becomes too large the reflection will disappear. The tilt is obtained by manual movement of a pinhole plate placed just on top of the fully opened aperture iris-diaphragm of the condenser. Some degree of training is needed to get reproducible determinations of the limiting angle. The angles of tilt of the incident beam and of the reflected beam are measured by means of a grating ocular.

The ratio between the refractive index of the inclusion and that of the host mineral is calculated from the two angles of tilt. Large single inclusions with approximately plane surface give better results ( $\pm .002$  to  $.012$  depending on  $n$ ) than groups of small inclusions ( $\pm .01$  to  $.05$ ). Solid-solid grain boundaries can also be measured in petrographic thin sections, but care is needed to distinguish between refraction and reflection.

Inclusions in rock crystal from a quartz vein in alkali granite from the Ilimaussaq intrusion, South Greenland, show in this way the presence of several phases, here given as  $n_D$ - values and a tentative identification:

$n = 0.99$ - air	$n = 1.432$ - fluorite
$n = 1.19$ - liquid CO <sub>2</sub>	$n = 1.452$ - ?
$n = 1.24$ - light hydrocarbon liquid	$n = 1.478$ - 1.500 natrolite
$n = 1.34$ - cryolite	$n = 1.517$ - immersion oil
$n = 1.367$ - NaCl solution	$n = 1.534$ - albite
$n = 1.398$ - mirabilite	$n = 1.543$ - halite



THE CARBON ISOTOPIC COMPOSITION OF CO<sub>2</sub> IN FLUID INCLUSIONS

Jochen Hoefs, Göttingen, Germany (FRG)

CO<sub>2</sub> from fluid inclusions is extracted through decrepitation in vacuum. Two sets of samples have been analyzed:

1. Quartzes from the granulite facies of Norway
2. Olivines from xenoliths in basic and ultrabasic rocks from various localities.

The  $\delta^{13}\text{C}$ -values of the quartzes showed a variation range of -5 to -22 ‰ relative PDB. The majority of the analyzed samples varied between -5 and -8 ‰, favouring a deep-seated (juvenile) origin. The CO<sub>2</sub> from the olivines showed a very strange isotopic composition,  $\delta^{13}\text{C}$ -values, in general, varied between -20 and -28 ‰. Some speculations will be given about the controversial meaning of this isotopically light carbon.

FLUID INCLUSIONS IN CHARLEVOIX CRYPTOEXPLOSION STRUCTURE ROCKS (QUÉBEC - CANADA)

Maurice Pagel and Bernard Poty, Vandoeuvre-les-Nancy, France

Two main kinds of fluid inclusions related to the genesis of the cryptoexplosion structure have been recognized in Charlevoix area:

Numerous minute fluid inclusions which are located in planar deformation structures. The fluid phase of these inclusions is essentially aqueous and the ratio H<sub>2</sub>O liquid/H<sub>2</sub>O vapor is quite variable. However, a large number of these inclusions contain only vapor. There are evidences of necking down for many inclusions. Salinity, estimated from microthermometry measurements, varies from 1 weight percent equivalent NaCl to saturation at room temperature.

Inclusions of the other kind occur as clusters, mainly in quartz of breccias, in quartz relicts from rocks which are almost entirely recrystallized and also in milky quartz from "Mont des Eboulements". These inclusions contain H<sub>2</sub>O vapor, though a few show also low salinity aqueous solution.

Besides these features, older aqueous or CO<sub>2</sub> rich inclusions (CO<sub>2</sub> rich from high grade metamorphic rocks and anorthosites) have undergone morphological, physical and chemical changes related to the cryptoexplosion. The modifications are due mainly to microfracturing of quartz but also to decrepitation, followed by healing, at high temperatures.

The great extent of low density water bearing inclusions indicates high temperatures and low pressures during their formation. In addition, lack of CO<sub>2</sub> associated to the cryptoexplosion as confirmed by microthermometry, crushing and gas chromatography, is rather contradictory with a volcanic process. Necking down in planar decorated features indicates that temperature decreased during healing after the shock. Heterogeneous chemical composition of the aqueous solutions show a complex history of mixing. Finally the decreasing abundance of transformed and gas inclusions towards the margin of the structure gives us new and supplementary criteria to the meteoritic hypothesis retained for this structure (RONDOT, 1968).

TEMPERATURE GRADIENTS AND ORE DEPOSITION IN THE  
NORTH PENNINE OREFIELD

F.W.Smith & R.Phillips, Durham, U.K.

Measurements on fluid inclusions in fluorite have been used to establish transverse, longitudinal and vertical temperature gradients in the PbS - ZnS - CaF<sub>2</sub> - BaSO<sub>4</sub> bearing veins of these Hercynian age deposits.

Vertical gradients varying from 0.1°C/m at 500 m depth to 0.5°C/m near surface are found, with formation temperatures ranging from 195 to 130°C.

The significance of these results in understanding the mode of formation of the ores is discussed.

FLUID INCLUSIONS IN SOME GANGUE MINERALS FROM DEPOSITS IN  
SOUTHERN FRANCE

C.Gritti-Baudracco, Toulouse, France

The laboratory of mineralogy and crystallography of Toulouse develops since several years determination methods for fluid inclusions in gangue minerals from regional deposits. The techniques used are decrepitochemistry, decrepitoscopy and the hot plate of DEICHA.

Because of its abundance in deposits in southern France (deposit of Pessens, Colombies (Aveyron), Clermont l'Hérault (Hérault) etc.) baryte was selected as example.

Recently the scanning electron microscope allows to show in these samples cavities which are not noticeable by the usual methods.

The different methods described are complementary. Their joint use serves for the determination of the temperature of formation of gangue minerals.

THE REAL NATURE AND CHARACTER OF PEGMATITE-FORMING MELTS-  
FLUIDS REVEALED BY THEIR INCLUSIONS IN MINERALS

A.I.Zakharchenko, Leningrad, USSR

Very problematic features of nature and character of pegmatite-forming melts-solutions and of pegmatite genesis are understood to a extent by studies of original inclusions of these melts-solutions relicts in pegmatite minerals, especially in the fully-differentiated-chamber, partly in quartz, and largely in topaz, beryl, etc.

- 1) In the wall-rock parent granites these are gaseous-solidified inclusions, composed to 90-95 % of crystallized aggregates of minerals, and gases - to 5-10 %. The liquid aqueous phase is lacking, but many hydrides are present. Under heating they are fusing in the range of 800-1000°C.
- 2) In the marginal zones of pegmatites the original inclusions are also gaseous-solidified, but with the increase of volatile content up to 20-35 % of alkali, with appearance of minerals of free growth. Under heating the fusion takes place in the range of 650-850°C with complete solution of volatiles.
- 3) In the inner zones (block, monomineral) a regular decrease of melting aggregate of minerals down to 40-20 %, and increase of liquid-gaseous phases highly saturated in minerals of free growth are observed. Under heating (450-530°C) at first the solutions of minerals of free growth in fluid takes place, and then above 530°C-fusion occurs.
- 4) In the inclusions of the cavity-chamber minerals we observe a complete disappearance of melting aggregate of minerals and transition into very concentrated fluids (minerals of free growth up to 70-60 %).

Thus, the easily fusible melts with accumulation of fluxing fluids and their gradial transition into highly concentrated fluids are the pegmatite-forming agents.

METHOD OF DETERMINATION THE ORIGIN OF SOLUTIONS BY MEANS OF  
ARGON ISOTOPES IN FLUID INCLUSIONS OF MINERALS

V.G.Bogolepov, Alma Ata, USSR

Based on data of argon isotopes  $Ar_{40}/Ar_{36}$  from lunar rocks, delivered by "Apollo 2" and "Luna 16", the ratio for solar wind equals one, but for present-day atmosphere this ratio is 296. It is also a constant in the potassium containing rocks, where all of Ar is represented by the heavy isotope which is formed from  $K_{40}$ . This is borne out by a similar ratio of argon-nitrogen in underground waters and in the air, on agreement of observed and calculated data of concentration and argon pressure in different depth, and data of isotopes of argon.

According to data of argon isotopes in gas-fluid inclusions of minerals and rocks, determined in the laboratory of Kasak Institute of Mineral Resources, two types of solutions are established. Solutions of the first type containing  $Ar_{40}$  are juvenile and produce metamorphism up to granitization, formations in the metamorphic belts of micaceous pegmatites, and quartz veins of the Alpine type. The second type of solutions is characterized by the dominant role of argon from the air (50-100 %). Argon is transported from air into hydrotherms indirectly by way of underground waters. From hydrotherms of this type, in weak metamorphic effusive sedimental rocks of upper structural steps of fold areas, greisen, skarns, and pegmatites as well as waters of some volcanic zones are formed.

PRIMARY LIQUID INCLUSIONS AND EVOLUTION OF FELDSPARS IN  
MAGMATIC GRANITES

V.V.Zalutskii, Irkutsk, USSR

In 1940 D.S.Korzinskii pointed out that feldspars contain abundantly finest inclusions usually taken for pellites. This false pelltization has infrequently been mentioned in literature up to now. The author has investigated plagioclases, potassium-sodium feldspars and anorthoclases containing abundantly pellite like inclusions of the middle paleozoic volcano-plutonic series of the western Trans-Baikal area. Gaseous-liquid inclusions can be detected under microscope magnification of 500-800 x. They are stable while samples are annealed up to 900°C and therefore are regarded as primary inclusions. The analysis of the location of the inclusions and the nature of twinning and disintegration of feldspars enables us to trace their evolution. During twinning and disintegration into phases inclusions open and move out. In the process of the microclinization of the orthoclases the primary inclusions disappear partially or completely.

Main Session: SECONDARY MINERALS IN ORE DEPOSITS  
Introductory lecture

F.V.Chukhrov, Moscow, USSR

In the Soviet geological literature that zone where secondary minerals are deposited is designated as hypergene zone or zone of hypergenesis. The term "hypergene" corresponds in sense to the term "supergene" adopted in the American literature.

On the early and late stages of the Earth's geological evolution conditions for chemical weathering were distinctly different. Prior to the significant amounts of oxygen making its appearance in the atmosphere, the main weathering agents were water and carbon dioxide; in consequence a highly active decay of silicates was going on while sulphides hardly suffered any alteration.

With progress of photosyntheses, the atmosphere was gradually enriched in oxygen, and, as a result, chemical weathering of sulphides started and preceded along with the silicates alteration. - Although a possibility for oxidation reactions existed as long as 3 billion years ago, still their importance increased drastically no sooner than the vegetation emerged into the land, which time is dated Silurian.

Besides abiogenic processes (electrochemical reactions inclusive) affecting the alteration of primary ores, the organic life activity played an important role, as well. Owing to both - oxidation and reduction reactions resulted with these latter leading to the secondary sulphides deposition.

Diversity of mineral association formed within the hypergene ore zone is significantly dependent on those elements which are carried in out from the enclosing rocks - silicium, phosphorus, vanadium, molybdenum, chromium, chlorine etc. Some specific properties of secondary mineral deposition reflect the effect of climate, while the succession in their deposition may fail through changing geological environment in the given ore field.

The ore hypergene zone emplacement is intimately connected with the rock alteration and the eluvial material accumulation, this latter being termed crust of weathering.

## OXIDATION OF SULFIDE ORES AT GRANITE GAP, NEW MEXICO

Sidney A. Williams, Douglas, Arizona, USA

Sulfide ores at Granite Gap occur in Paleozoic limestones adjacent to the Granite Gap "granite", a coarse grained biotite quartz monzonite. Mineralization is directly related to quartz latite granophyre dikes contemporaneous with the "granite". Thermal zoning of ores and wallrock alteration relates both to the dikes and to the thermal aureole surrounding the granite. Sulfides occur in crushed zones and favorable beds in limestones with phlogopite and epidote. Primary sulfides are pyrite, pyrrhotite, galena, sphalerite, chalcopyrite and arsenopyrite. Traces of matildite occur in the galena.

Oxidation has been severe for a depth of up to 75 meters. Most ores were arsenic-free and oxidation has first produced linarite-chlorargyrite-anglesite-cerussite, then rosasite-chrysocolla-hemimorphite-malachite. With groundwaters alkaline and at higher Eh, minerals such as murdochite and tenorite formed. Only Zn and Cu migrated, resulting in fractures and caves lined with malachite or rosasite and hemimorphite.

Sulfide ores identical to those described above but carrying arsenopyrite as well have oxidized in situ. Paragenetic study indicates that only minerals in the system  $\text{Fe}_2\text{O}_3$ - $\text{PbO}$ - $\text{As}_2\text{O}_5$  formed, and in order of increasing  $\text{PbO}:\text{Fe}_2\text{O}_3$  ratios. Only when all  $\text{Fe}_2\text{O}_3$  was precipitated did  $\text{CuO}$  enter the system and, lastly,  $\text{ZnO}$  is involved and replaces  $\text{CuO}$  progressively. A constant excess of  $\text{PbO}$  with respect to  $\text{As}_2\text{O}_5$  held the system within the area bounded by hematite-beudantite-mimetite-anglesite. The transition of anglesite to cerussite coincided with the entry of  $\text{CuO}$  into the system.

## THE FERRIC SULFATES DEPOSITS IN CENTRAL DESERT OF IRAN

J.P. Berthelon and F. Cesbron, Paris, France,  
and M. Sadrzadeh, Tehran, Iran

The systematic study of several sulfate rich areas, undertaken recently in Iran, permitted to discover some paragenesis very rich in ferric sulfates and very similar to those encountered at Chuquicamata (Chile) and San Rafael Swell (Utah). These deposits were formerly worked for "alums", employed as mordant in wool-dyeing.

The most interesting of them, near Saghand (province of Yazd), constituting a 12 meters thick oxidation zone, results from alteration of pyrite abundantly disseminated in more or less pelitic schists in contact with a intrusive body.

The following paragenesis is observed:

- a) in the lower level: pyrite, szomolnokite, roemerite, coquimbite, metavoltine and voltaite,
- b) in the upper level: amarantite, hohmannite, magnesio-copiapite, butlerite and parabutlerite, jarosite, fibroferrite.

Aluminium sulfates are quite abundant: tamarugite and halotrichite in the lower part, alunogen and the new mineral khademite,  $\text{Al}(\text{SO}_4)(\text{OH})\cdot 5\text{H}_2\text{O}$ , in the upper level.

Thermal analysis curves and unit cell of these minerals, particularly alunogen, szomolnokite and khademite, were determined. According Posnjak and Merwin's synthesis, most of these minerals can be formed only in very concentrated sulfuric solutions, corresponding to the desertic climate in this part of Iran.

ON THE PROBLEM OF GLOCKERITE AS A SECONDARY MINERAL  
OF ORE DEPOSITS

Bohuslav Fojt, Brno, CSSR

E.F.Glocker in 1853, has described basic and hydrous ferric sulphate, which was later named by F.Naumann (in F.Zirkel, 1901) as Glockerite. As early as in 1909 F.Cornu drew attention to the fact that it is not a new mineral, but only limonite with adsorbed sulphuric acid. This opinion is supported by most of the contemporary authors, although some take it still for ferric sulphate.

A number of samples of the mentioned secondary products was taken from the original Glocker's locality - Alt-Hackelsberg mine - on the occasion of new researches in the region of Zlaté Hory (previously Cukmantl), Czechoslovakia. Stalactite and stalagmite formations of "glockerite" were slowly dried at room temperature. Then they were subjected to chemical, X-ray and thermal analysis and studied by infrared spectroscopy. It was established by these methods that the studied material is roentgenometrically amorphous at 20°C and a significant recrystallisation takes place at about 560°C. It was not possible to find out unambiguously whether the studied matter contains hydroxyl group or not. The sulphate anion is firmly bound and it is not mostly connected with sorption of H<sub>2</sub>SO<sub>4</sub>. The "glockerite" formations arise there where the pH-value is about 4,5 and locally to 1,5, in small stagnant basins of deserted pyrite dumps.

Other secondary compounds of iron, e.g. matter corresponding to "hydrohematite", limonite, siderogel, rarely also hisingerite and karpnosiderite, and of aluminium, namely allophane, kliachite and gibbsite, occur together with "glockerite".

HYDROTHERMAL POTASSIUM FELDSPAR AT BODIE, MONO COUNTY,  
CALIFORNIA, AND ITS USE IN DETERMINING THE AGE AND CONDITIONS  
OF ORE DEPOSITION

Ch.W.Chesterman, San Francisco, M.L.Silberman, R.A.Koski and  
B.P.Fabbi, Menlo Park, California, USA

Hydrothermal potassium-feldspar (or "adularia") occurs in gold and silver-bearing quartz veins and in hydrothermally altered dacite wall rocks of Pliocene age in the mines at the Bodie mining district, Mono County, California. Chemical and X-ray analyses of vein adularia indicate a composition of 95 to 98 percent orthoclase. Optical, physical, and X-ray crystallographic properties of the feldspar are consistent with those of high temperature sanidine.

The potassium feldspar is of hydrothermal origin and developed late in the volcanic history of the Bodie Hills volcanic field during a period of intense potassium-silicate hydrothermal alteration and gold and silver deposition between 8.6 and 7.1 m.y. ago. Chemical analyses of the feldspars, O<sup>18/16</sup> isotope analyses of the feldspars and associated vein minerals, quartz and calcite, and O<sup>18/16</sup> and D/H analyses of fluid inclusions in these minerals indicate that ore formation occurred within a temperature range of 215<sup>o</sup>-245<sup>o</sup>C from a very dilute solution of meteoric origin, of constant K/Rb, O<sup>18/16</sup>, and D/H. K and Rb metasomatism of the wall rocks occurred principally by replacement of the pre-existing minerals by hydrothermal potassium-feldspar.

## SECONDARY MINERALS IN SCHEELITE DEPOSITS IN NORTHERN BRAZIL

A. Bhaskara Rao, Brasilia, Brazil

During the last fifteen years, the author and his associates emphasized the effective participation of hydrothermal solutions in the mineralisation of scheelite deposits in the Borborema Metallogenetic Province of NE Brazil. The mineralogical studies have revealed several minerals, and their origin is attributed either to hydrothermal solutions at low temperatures (final phases) or to meteoric waters. The secondary minerals, thus far recorded, are listed below:

Apophyllite, aragonite, bismutite, chrysocolla, chalcodony, chabasite, calcite (sugary), chlorites, covellite after chalcocite, cuprite, Fe-hydroxides and goethite, gypsum (selenite), heulandite, huntite, jasper, malachite, Mn-hydroxides, montmorillonite, mordenite, pinguite (chloropal), stilbite, tungstite, turquois and uraniferous opal.

The scheelite deposition is mainly in calc-silicate rocks (skarns). Minerals such as garnets (grossularite and andradite mixtures), epidote, hornblende, diopside and scapolite show incipient alteration, resulting in corrosion and occasional partial pseudomorphism. Huntite, found only in mine dumps, is considered as derived from Mg-rich calcites through leaching and subsequent deposition. Gypsum is characteristic in occurrence, found as large plates in solution cavities in the host rocks.

## THE DEVELOPMENT OF MAGNETITE AND ITS ALTERATION PRODUCTS IN SOME PRECAMBRIAN IRON FORMATIONS

T.M. Han, Ishpeming, Michigan, USA

Magnetite is or was present as one of the principal iron-containing minerals in most of the Precambrian iron formations. Its stability varied with the postdepositional history of the iron formations. This is indicated by its textural relationships with other coexisting minerals, and the differences in composition and magnetite distribution along the same iron formation band. The objective of this paper is to describe such textural and structural features which lead to the conclusion that magnetite in the iron formations may replace or be replaced by other minerals through various geological processes under different conditions.

During the diagenesis and the incipient stage of metamorphism, the magnetite in the oxide and carbonate iron formations is stable and trends to replace other minerals, while that in some of the silicate iron formations may be altered to iron-rich carbonates. Under moderate metamorphic conditions, it may be replaced by specular hematite in the oxide iron formations and by amphiboles in the silicate iron formations. In the more highly metamorphosed iron formations, it appears to have been formed at the expense of specular hematite.

Diabasic dikes in some iron formations were not only responsible for the pseudomorphic reduction of some hematite to magnetite, but also for the alterations of the pre-existing magnetite to pyrite, siderite, and chlorite along or near the dike-iron formation contacts. The most interesting and significant feature is the progressive decrease in quantity, grain size, and degree of crystallinity of the magnetite toward these dikes.

Under supergene conditions, the magnetite, almost as a rule, alters to martite and rarely to goethite and siderite. At the advanced stages of oxidation the martite grains may either be replaced by goethite or modified by the overgrowth of hematite crystals on their peripheries.

MINERALOGICAL AND GENETIC SIGNIFICANCES OF NSUTITE IN  
SUPERGENE MANGANESE OXIDE ORES

Soo Jin Kim, Seoul, Korea

Nsutite is the naturally occurring equivalent of a specific form of synthetic  $\gamma\text{-MnO}_2$ . Its occurrence is confined to the supergene manganese oxide deposits. It is most abundantly found in the oxidation products of manganese carbonate protore. It occurs in close association with birnessite, todorokite and pyrolusite.

Nsutite is formed by various modes of formation; crystallization from true solution, colloidal precipitation and replacement. Ores formed by replacement are most abundant. Replacement of other hydrous manganese oxides by nsutite results in the shrinkage phenomena. Shrinkage cracks are not the evidence of colloidal origin of the mineral, but of dehydration and volume change in the replacement.

All the textural relations of nsutite with associated oxides indicate that it is formed diagenetically at the last stage or high oxidation stage of oxide ore formation in the supergene environment. The textural importance of nsutite in the supergene manganese oxide deposits is that all the previous textures of the ores are destructed by and newly formed by nsutite. The presence of nsutite indicates the dehydration environment of formation under the high Eh and pH.

X-ray, thermochemical and infrared absorption spectroscopic characters as well as the phase relations of nsutite to other  $\text{MnO}_2$  phases are also discussed.

CRYSTAL CHEMISTRY OF HYPERGENE MINERALFORMING PROCESS

A.S.Povarennykh, Kiev, USSR

1. Hypergene mineralforming process being characterized by low values of T and P of surroundings is notabled for minerals with little strength of interatomic bonds; these minerals are stable only in the present conditions.

2. The little strength of bonds in minerals is reached by two main modes: by increase of size and coordination number of cations, and for small and high-valent atoms by including to the sphere of their coordination of anions  $\text{OH}^-$  and water molecules.

3. This is the specific feature of composition and structure of hypergene minerals, which by the number of species in some classes predominate over hypogene minerals, being often unique by own crystal chemical peculiarities.

4. Hypergene minerals are formed at the expense of hypogene ones by means of their change, distortion and transformation and arise either direct in situ (pseudomorphoses and relicts) or are deposited in other place with transfer of substance.

5. The main elements building hypergene minerals are the following: cations - Na, K, Mg, Ca, Ba, Cu, Zn, Pb, As, Sb, Bi, Al, Fe, Mn, V, U; radicals and anions -  $\text{BO}_4$ ,  $\text{SiO}_4$ ,  $\text{PO}_4$ ,  $\text{BO}_3$ ,  $\text{SO}_4$ ,  $\text{WO}_4$ ,  $\text{CO}_3$ ;  $\text{AsO}_4$ ,  $\text{VO}_4$ ,  $\text{SeO}_4$ ,  $\text{CrO}_4$ ,  $\text{MoO}_4$ ,  $\text{SeO}_3$ ,  $\text{TeO}_3$ ,  $\text{NO}_3$ ,  $\text{IO}_3$ ; O, F, Cl, OH;  $\text{H}_2\text{O}$ .

6. Into the composition of the minerals of hypergene process enter both radicals typical for hypogene conditions (formers seven in the previously row) and forming themselves solely at the hypergene surroundings with high oxygen potential (nine last radicals). Combination of them with different cations is unequal and is submitted to definite regularities.



Main Session: GEM MINERALS AND GEMOLOGY  
Introductory lecture  
WHERE GEMSTONE RESEARCH STANDS TODAY

E.J.Gübelin, Lucerne, Switzerland

The present situation in the science of gemstones and of gemstone research is determined by four principle factors:

a) The discovery of new gems or gem varieties

During the last 30 years gemmologists have discovered several new gems: taaffeite, sinhalite, painite, ekanite, as well as the longknown minerals amblygonite, zoisite (tanzanite), jere-mejewite etc. as new gemstone varieties.

b) New methods of testing and research

Of the traditional testing methods refractometry, spectroscopy and microscopy the latter two have developed to high importance. The absorption spectroscopy may serve as a criterion to determine, e.g. whether or not a green beryl is an emerald. Infrared absorption spectra of polarized radiation seems to become important for the distinction between certain imitations (emerald) or treated stones (turquoise) and their natural counterparts. The study of inclusions in gemstones, possible by means of X-ray fluorescence and the electron microprobe, enables gemmologists to distinguish between natural gems and their imitations and to recognize diagnostic features typical of certain sources.

c) The manufacture of simulating products, artificial colouration and their distinction from natural gems

Since 1945 there has been a spate of synthetic stones and artificial products the gemmologists have to deal with. Many of these materials originally have been produced as a result of experiments in the field of electronics and space-age programmes or in laser techniques.

Particle irradiation to improve or change the colour of gem materials is wellknown and is mainly applied to diamonds. The majority of "bombarded" diamonds display conclusive spectra in the visible and the short wave end of the infrared region.

d) The application of gemmological knowledge to commercial use and benefit

The accumulation of knowledge gained from gemmological studies and trade practice lead to commercial application of gemmology for more accurate grading methods judging the qualities of gems.

## FLUID INCLUSIONS AND GEMOLOGY

Jean-Paul Poirot, Paris, France

The inclusions we find in a crystal give a good idea of the paragenesis of this crystal. Therefore the study of inclusions is of very high importance for the jeweller. He has so the proof that a crystal is artificial or natural, and in this last case, from what type of ore it comes. Of particular interest are the observations of fluid inclusions in gems and their imitations.

## SURFACE MICROTOPOGRAPHY AS A TOOL OF DISTINGUISHING NATURAL AND SYNTHETIC CRYSTALS

I. Sunagawa, Sendai, Japan

Since natural and synthetic crystals of the same mineral species grow under different environmental conditions and with markedly different growth speeds, some of their physical properties are different to such extent as to serve to discriminate between the two by conventional methods. This is the basic idea for the identification of natural and synthetic gemstones. Specific gravity, refractive indices, inclusions, etc. have been used for this purpose.

Differences in growth history may appear as differences of macro-morphology (external forms of crystals) and micromorphology (surface microtopography of crystal faces) as well, or even more clearly than in physical properties such as refractive indices, inclusions, etc. In this paper, several examples will be presented how surface microtopographs are different between natural and synthetic crystals, as well as among natural crystals of different origins, or among synthetic crystals grown by different methods. Examples to be demonstrated are diamond, emerald, corundum, and others.

QUALITATIVE STUDY OF FLUORESCENCE AND PHOSPHORESCENCE OF  
CUT DIAMONDS

L.Monés Roberdeau and J.M.Bosch-Figueroa, Barcelona, Spain

Study of the luminescence of "Commercial White" and "Top Silver" diamonds. The samples studied were selected from several lots of cutted stones. Their weight lies within the range from 0.35 to 0.75 carats, and they belong to the pure or V.V.S. qualities.

A mercury lamp HBO 200 W/4 with the excitation filter VG1, Carl Zeiss, was used as source of illumination.

For the realisation of this investigation an original Monés-Bosch chamber was constructed.

The description of the apparatus precedes the examination of first results. For the quantitative determination a photomultiplier EMI-9592, A-S, was assembled with an S-10 cathode. The G G 17 uranium glass, Carl Zeiss, was used as standard.

The relative intensity of fluorescence was measured each 15 nm from 405 to 750 nm with the interference filter Veril-S-200, Schott. With these measurements the dispersion curves were established.

THE "ALEXANDRITE EFFECT" IN CHROMIUM AND IRON-BEARING CORUNDUM

Hermann Harder, Göttingen, Germany (FRG)

Some very rare fancy sapphires from Ceylon, Burma and Australia show an "alexandrite"-effect of changing colour from blue-greenish to red-violet in response to a change of observation from daylight (more bluish) to incandescent light (more yellowish). X-ray fluorescence investigations of these fancy sapphires have shown that chromium together with iron in some ratios are responsible for this colour changing. These sapphires contain a high content of iron (0.03-0.3 % Fe) and a medium content of chromium (0.003-0.1 % Cr). - Only chromium or only iron substituting for aluminium in the corundum lattice lead to the red colour of ruby or to blue, green or yellow colours of sapphires. Natural blue, green or yellow corundums do not contain transition metals other than iron in amounts sufficient for colouration and the variation in colour is thought to be due to the ratio between di- and trivalent iron decreasing from blue to yellow. Chromium along with iron and vanadium are responsible for all the colours of the rubies. The Cr:Fe ratio in the ruby may be varying from 1 : 0.1-2. - Only those corundums which contain chromium and iron in the ratio 1 : 5-30 show this "alexandrite" effect. A combination of the adsorption part of chromium and that of the iron leads to a resulting adsorption similar to the "alexandrite" adsorption conditions.

MICROMORPHOLOGY COMMENTS ON THE IRIDESCENT CLOUDY BEHAVIOUR  
OF ROSE QUARTZ (TSAOBISMUND, SW-AFRICA)

Heinrich Newesely, West-Berlin, Germany

South West African pegmatites hold within their zonal veins rose quartz occurrences, with peculiar striations and some parallel line work on fracture faces, and with an iridescent cloudy behaviour. Electron micrographs from the surfaces demonstrate the visible striation texture to be resolvable in a finely lamellated microtexture with preferential orientation in the [0001] zone as proved by X-ray swivel recording.

Light scattering interferences on these textural inhomogeneities lead to the iridescent and cloudy effects analogously to a well known behaviour of similar microlamellated materials.

Rutile inclusions - even scarcely detectable with the electron microscope from the hydrofluoric acid residue - here don't seem to implicate opalescent luster, but represent casual segregation of the color inducing lattice substitution centers of titanium. X-ray fluorescence analyses from the residue material ensure the presence of iron and copper, zinc, manganese and titanium but these latter ones in the micrometre scale, and corroborate further the assessment of a dispersed scattering of minor components.

PHYSICAL AND OPTICAL PROPERTIES OF GEMOLOGICAL VARIETIES  
OF GARNET

M.Arbuties Andreu & J.M.Bosch-Figueroa, Barcelona, Spain

The physical properties of the following garnets were studied: almandine, green transparent grossular, and hessonite. The samples of gem quality were selected coming from three different localities.

The refractive index, the density and the microhardness of all samples were measured. The colour was established according to the C.I.E. system by measuring the transparency and the reflectance each 20 nm from 410 nm to 680 nm.

William G. Rolim de Camargo and J.B. de Madureira,  
Sao Paulo, Brazil

This paper has the main purpose of identifying isomorphous terms of garnets, by the use of triangle diagrams, which give an approximate idea of the chemical composition of a garnet sample, without the data of chemical quantitative analysis. Three physical properties ( $\Delta 2\theta$ ,  $n$  and  $D$ ) are associated to the chemical composition, being necessary only to know the values of such three physical parameters, in order to classify the garnet type.

In the proposed diagrams only the physical constants of those garnet types are given the occurrence of which in nature is relatively abundant (almandine, andradite, grossular, pyrope, spessartine) and such constants are related to the molar chemical composition. The use of  $\Delta 2\theta$ , instead of  $a_0$ , is a tremendous advantage of the method, since the usual determination of the unit cell dimensions is both tedious and time-consuming.

Drawing of triangle charts has been possible through proof of linearity of  $\Delta 2\theta$  in function of chemical composition. The two-dimensional triangle diagrams make much easier the manipulation and the view of the plotted garnet, which is not the case for the tridimensional tetrahedron representation (Winchell, 1951). The diagrams could be used for the large majority of garnets (83 %).

G. Amthauer and F. Rost, Saarbrücken, Germany (FRG)

Grossulars with gemstone quality from Tanzania have green or brown colours, ranging from greenish to emerald-green in the green series and from yellow to red-brown in the brown series. Within these two series several fractions could be separated by visual inspection. These fractions were analysed by X-ray fluorescence and spectrographic methods and their cell edge was determined by Guinier X-ray method with pure Si as standard. Absorption-spectra were measured on thin polished plates and compared with the chemical analyses, so that absorption bands could be assigned to the transition elements Cr, Mn, Fe.

The green grossulars have two absorption bands in the red and the blue part of the visible spectrum at about 16350 and 23400  $\text{cm}^{-1}$ , whose intensity is related to the chromium content. Within the green series the chromium varies between 0.02 and 1.45 wt. %  $\text{Cr}_2\text{O}_3$ . The cell edge increases with the chromium content from 11.851 Å (0.02 wt.%  $\text{Cr}_2\text{O}_3$ ) to 11.886 Å (1.45 wt.%  $\text{Cr}_2\text{O}_3$ ). The two bands could be assigned to  $\text{Cr}^{3+}$  in an octahedral ligand field and correspond to the transitions  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  (band at 16350  $\text{cm}^{-1}$ ) and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (band at 23400  $\text{cm}^{-1}$ ). The transition elements Ti, Fe, Mn, and V, which were also analysed in these specimens, have no influence on the absorption spectra of the green grossulars.

The colour of chromium-free brown grossulars is mainly due to strong absorption bands of  $\text{Fe}^{3+}$  in octahedral position at ca. 23000  $\text{cm}^{-1}$  (transition  ${}^6A_{1g} \rightarrow {}^4A_{1g} {}^4E_g$ ) and  $\text{Mn}^{2+}$  in cubic position at ca. 24500  $\text{cm}^{-1}$  (transition  ${}^6A_{1g} \rightarrow {}^4A_{1g} {}^4E_g$ ). There are also some weaker bands of ferric iron in the visible part of the spectrum. The  $\text{Fe}^{3+}$  absorption band corresponding to the transition  ${}^6A_{1g} \rightarrow {}^4E_g$  could be measured in the UV at 27000  $\text{cm}^{-1}$ . There are only small amounts of ferrous iron in the cubic position of these brown grossulars, because the corresponding bands at ca. 4350, 5750 and 8050  $\text{cm}^{-1}$  are very weak. Within the brown colour series the total Fe content (determined as  $\text{Fe}_2\text{O}_3$ ) varies between 1.4 and 3.6 wt. %, the manganese content between 0.37 and 0.87 wt. %  $\text{MnO}$ , without influence on the cell edge of 11.850 Å.

## ZONAL AQUAMARINES: THEIR MINERALOGY, GEOCHEMISTRY AND GENESIS

V.F.Barabanov, Leningrad, USSR

Numerous crystals of beryl from greisen veins and tin-bismuth-tungsten deposits in USSR have been studied. It is established that crystals from veins formed in deep, relatively calm tectonical conditions have a yellow colour and a uniform structure. Crystals from veins formed in superficial, tectonically strained conditions have zonal or rhythmic-zonal composition and properties: colour, refraction of light, double refraction, specific gravity, infrared spectrum, lattice dimensions and varying content of  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{Sc}$ .

Influence of these admixtures of beryl has been observed and it is clear that  $\text{Fe}_2\text{O}_3$  raises the refraction of light of beryl and creates a blue colour in it,  $\text{CaO}$  and  $\text{MgO}$  raises specific gravity of beryl,  $\text{H}_2\text{O}$ , on the contrary, reduces it.

Isomorphism has been established in all structural groups of beryl. A view is been expressed that in  $\text{Si}_6\text{O}_{18}$  rings a replacement of a part of Si atoms by Be and Al atoms can take place and at the same time an equivalent number of atoms of alkaline elements and Ca enters into these rings.

It is supposed that variation in properties and peculiarities in composition of these microadmixture in zonal beryl crystals is caused by the change in crystallizing conditions which is accompanied by periodical boiling up of mineral-forming solution, separation of gas phase, increase in alkalinity of solution and change in its oxidizing properties.

In accordance with this, zonal form of beryls can be considered as an objective criterion of geochemical conditions in formation of raremetal veins.

## A NEW BLUE AXINITE FROM EAST AFRICA

E.A.Jobbins, A.Tresham, B.R.Young, London, United Kingdom

A faceted gemstone from East Africa, probably Tanzania, gives X-ray diffraction patterns for axinite, but shows low optical and physical properties. Electron microprobe analysis shows that in this stone magnesium substitutes for the iron and manganese content of the well-known material from Bourg d'Oisans, France.

PRECIOUS STONES PEGMATITES IN SOUTH AFRICA AND SOUTH AMERICA,  
AND THE CONTINENTAL DRIFT THEORY

H.Strunz, West-Berlin, Germany

A preliminary comparative investigation of the precious stones pegmatites in Minas Gerais and South West Africa reveals great similarities in the sequence of crystallisation, in the zoning of the pegmatites, in the concentration of common and rare elements and in the final hydrothermal recrystallisation of aquamarines, rubellites, verdelites, indigolites, topaz etc. These pegmatites lie in a very straight north south girdle zone of the early South Continent before the beginning of the continental drift. The pegmatites may be slightly older than the drift beginning.

These observations allow a hypothesis of a great mineralogical and geological process: The material of the upper mantle is partial solid, liquid and fluid. Fluid exhalations out of the upper mantle into the crust material must have happened along this girdle zone or hot line. These hydrous infiltrations were accompanied by the immigration or exsolution of hydrophil elements, of K, Li, Be, B, F, etc. These infiltrations and migrations, especially a frontal metasomatic potassium transport, were followed by migmatisation resp. granitisation of crust material. In the late stage of the granite crystallisation, high liquid and fluid masses, rich in rare elements, were concentrated in the roof of the granite bodies and in fractures of the country rocks. Here the pegmatitic minerals crystallised, and in a final hydrothermal recrystallisation the precious stones were produced. This may have been a normal crystallisation sequence, but in the South Continent it possibly was the initial stage for the breaking and drifting of the continents. Later climate was dry in South Africa and wet in South America. Therefore different secondary minerals and different geomorphology were produced. - In combination with tectonics in the front side of both drifting continents and near the rift valleys, also precious stones pegmatites were produced; sometimes chromium was leached out of biotites in the metamorphic rocks, and beryls were modified to very precious emeralds.

Our further work, on pegmatites in both South Continents will try to proof this hypothetic combination and generally the genesis of pegmatites in the light of global tectonics.

Symposia:

Commission on Ore Microscopy

Thursday, September 12, 1974

Chairman: S.H.U. Bowie  
Vice-Chairman: F.M. Vokes  
Secretary: M. Font-Altaba

Commission on History and Teaching

Thursday, September 12, 1974

Acting Chairman: H.E.Wenden  
Acting Secretary: P.Paulitsch

Commission on Mineral Data and Classification

Saturday, September 14, 1974

Acting Chairman: A.Kato  
Secretary: G.T. Faust

EXPERIMENTAL STUDY ON THE PRECISION OBTAINED IN THE  
DETERMINATION OF REFRACTIVE INDICES BY MICROREFLECTOMETRY

B.Cervelle, C.Lévy & M.Pinnet, Paris, France

An investigation on sphalerite consisted in determining their refractive indices by different methods:

1. by classical refractometry, prism method
2. by microreflectometry on a fresh cleavage surface
3. by microreflectometry on two polished sections.

In the cases 2. and 3. the refractive indices  $\underline{n}$  were calculated from:

a) the reflectance  $R_A$  in air,  $n = (1 + \sqrt{R_A}) / (1 - \sqrt{R_A})$

b) the reflectance  $R_O$  in immersion oil with index  $N$ ,  
 $n = (1 + \sqrt{R_O}) / (1 - \sqrt{R_O})$

c)  $R_A$  and  $R_O$  by the relation of Koenigsberger:

$$n = \frac{1/2 (N^2 - 1)}{N \left( \frac{1+R_O}{1-R_O} \right) - \frac{1+R_A}{1-R_A}}$$

The comparison of the values for  $\underline{n}$  from different methods, considering as best values those obtained by classical refractometry, has shown that the relation of Koenigsberger furnished the best results even for a low absorbing mineral as sphalerite. Indeed this method, like every method of double determination, allows to eliminate a part of the disturbing polishing effects which appear therefore less important for they do not influence the determination of the optical constants of opaque minerals by microreflectometry.



OPTICAL STUDY OF MINERALS BY DIRECT METHOD

J.Nogues Carulla, A.Lopez Soler, J.M.Bosch-Figueroa,  
M.Font-Altaba, Barcelona, Spain

The apparatus constructed to take measurements of reflectance by means of a narrow direct beam of light on surfaces is described. The result obtained on polished and cleavage surfaces are given and are compared with those obtained by the microphotometer with normal incidence.

OPTICAL STUDY OF GRATONITE ( $\text{Pb}_9\text{As}_4\text{S}_{15}$ )

J.Besteiro, A.Lopez Soler, J.M.Bosch-Figueroa, and  
M.Font-Altaba, Barcelona, Spain

The refractive index and the coefficient of absorption in the two principal directions of vibration, that correspond to the ordinary ray and to the extraordinary ray, in a section (11 $\bar{2}$ 0) of a sample of gratonite ( $\text{Pb}_9\text{As}_4\text{S}_{15}$ ) from Rio Tinto, has been calculated from the value of reflectance in two mediums of known refractive indexes.

OPTICAL STUDY OF CUPROSTIBITE (Cu<sub>2</sub>Sb)

A.Lopez Soler, J.M.Bosch-Figueroa, Barcelona, Spain,  
S.Karup-Moller, Copenhagen, Denmark,  
J.Besteiro, M.Font-Altava, Barcelona, Spain

By means of a microphotometer the principal reflectances at normal incidence have been measured, in air and in oil, on section (10 $\bar{1}$ 0) of cuprostibite. Measurements were made at intervals of 10 nm from ultraviolet to near infrared. From 700 nm a Nicol prism was used as the polarizer; as monochromators, glass prism and quartz prism were used.

Dispersion curves are given for the reflectances (in air, in oil) and also for the values of the refractive index and the absorption coefficient.

REFLECTANCE MEASUREMENTS IN MONOCHROMATIC LIGHT ON THE BOWIE-TAYLOR COLLECTION OF 103 ORE MINERALS

S.H.U.Bowie, P.R.Simpson and D.Atkin, London, U.K.

The reflectance of 103 ore minerals from the Bowie-Taylor collection, previously measured in white light with a selenium cell photometer against an Elba pyrite standard, has been measured in monochromatic light at four standard wavelengths with a silicon carbide standard and a semi-automated photomultiplier light-measuring system attached to a Zeiss microscope. The identity of all specimens measured in this work has been confirmed by various combinations of X-ray powder diffraction, semi-quantitative X-ray fluorescence, optical emission spectrographic analysis and quantitative electron-probe microanalysis. The reflectance data are presented in tabular form in two different formats: the first contains an alphabetical listing of the mineral species with the mean reflectance at  $\lambda$  546 nm, in the second the mineral species are re-arranged in order of increasing mean reflectance at  $\lambda$  546 nm. In addition, reflectance ranges at  $\lambda$  470, 546, 589 and 650 nm, with white-light and microhardness data from Bowie and Taylor (1958), are included, together with the chemical formula and symmetry; this arrangement is specially suited to the identification of unknown minerals. The white-light values are in general agreement with the new data. The methods of measurement are designed to optimise precision and accuracy in the collection of large amounts of data.

F.M.Nakhla, Cairo, Egypt

Recent study, dealing with reflectivity measurements of polished surfaces of some ore minerals and metals, using the photomultiplier method with monochromatic light having a wave length of 4900 Å, has revealed that reflectivity values are dependent upon primary and secondary factors which are as follows:

- A. Primary Factors include physico-chemical and crystal structure characteristics of the mineral or metal. These factors play a dominant role in determining the reflectivity characteristics of the substance. Among the physical factors, are atomic volume, electronic configuration of the element, number of valency electrons, refractive and absorption indices of the substance. Chemical factors include composition of the ore mineral, as well as isomorphism and solid solutions. Structural factors include type of the crystal structure, pattern and dimensions of unit-cell, nature of chemical bonds and crystallographic orientation. There is an intimate relationship between the crystal structure of a certain metal and its reflectivity index, which is the ratio between reflectivity value of the metal, at a certain wave length, and its atomic volume. Consequently, by knowing the atomic volume and the crystal structure of a certain metal, then it would be possible to deduce its reflectivity value. Reflectivity values postulated for some metals, such as beryllium, manganese and hafnium, at a wave length of 4900 Å, are in close agreement with the measured values.
- B. Secondary factors are mainly related to type of apparatus adopted for reflectivity measurements, polishing technique, and nature of standard material. Among instrumental factors may be mentioned the medium used for reflectivity measurements (air or oil), wave length of monochromatic light, area of measurement, angle of acceptance of the photomultiplier, numerical aperture (N.A.) of objectives and internal reflection of lenses used in the optical system. All secondary factors should be standardized before setting the apparatus for reflectivity measurements.

H.Strunz, West-Berlin, Germany

The first academic course in mineralogy in Berlin started on the First of November in 1770, which may be regarded as the birthday of the Bergakademie Berlin. This Academy, with some interruptions, existed up to 1916, when it was incorporated in the Technische Hochschule Berlin-Charlottenburg (constituted 1879), since 1946 named Technische Universität Berlin.

In 1810 the Friedrich-Wilhelms-Universität zu Berlin was founded, now called Humboldt-Universität, in memory of Wilhelm and Alexander von Humboldt.

The first mineralogists in Berlin were C.A.Gerhard (1770-1789) and L.G.Karsten (1789-1810). Lecturer in chemistry was Martin Heinrich Klaproth (1784-1817), the discoverer of the elements U and Zr (both 1789), Sr (1793), Ti and Ce (1795), who published six volumes on the Chemistry of Minerals (1795-1815).

In 1810 Christian Samuel Weiß became Professor of Mineralogy at the University and Mining Academy (1810-1856). After his translation of Haüy's famous "Traité de Minéralogie" (1801), Weiß discovered the law of rationality by introducing crystallographic axes (Kristallelemente, 1809), which are of basic importance also in modern X-ray crystallography, as well as in physics and chemistry of solids. - His assistant professor for many years and his successor was Gustav Rose (1856-1872) who discovered the minerals albite and anorthite, zinckenite, miargyrite, polybasite, plagionite, fibroferrite, rhodizite, perovskite, astrakanite, samarskite, carnallite, staßfurtite.

The mineralogists following Rose at the University were C.Klein (1880-1908), Th.Liebisch (1908-1921), A.Johnsen (1921-1934), P.Ramdohr (1934-1950) and W.Kleber (1953-1970).

At the Bergakademie and Technische Hochschule followed Ch.E.Weiß (1872-1890), R.Scheibe (1890-1923) and W.Schmidt (1930-1945). Mineralogist and petrologist at the Freie Universität in Berlin-Dahlem (constituted 1948) is K.H.Mehnert (since 1953).

Mineralogy in Berlin, including crystallography and petrology, has a 200 years continuous history, with periods more belonging to mining and metallurgy and others more belonging to chemistry and physics or to modern geosciences.

## HISTORY OF MINERALOGY IN BULGARIA

S. Stoynov, Sofia, Bulgaria

The development of the mineralogical studies in Bulgaria can be divided into four periods, without taking into account the traces of the use of minerals by the time of the tribal society, as well as those ones by the Roman times and the end of the Turkish yoke (18 and 19 centuries). During the first period, which covers the times up to the liberation of Bulgaria from the Turkish yoke, any special mineralogical investigations are not carried out. Information about some minerals can be found in the works of foreign geologists-Ami Boué, Franz Toula etc.

The second period includes the times from the liberation of Bulgaria from Turkish yoke up to the end of the World War I. Just four years after the liberation of our country, in 1882, the first Bulgarian geologist, professor Gueorgui Zlatarski gives a description of 42 minerals in 74 pages. This is indisputably the first book on the mineralogy of Bulgaria. Having in mind the great geological variety of his country, the author prognosticates that many other minerals will be discovered. During the same period, in 1900, the book of Gueorgui Bontchev "A small contribution to the Mineralogy of Bulgaria" is published, where in 10 pages 30 minerals are described.

The third period covers the time between the World War I and the World War II. In 1923, G. Bontchev publishes his book "The minerals in Bulgaria", covering 215 pages. A description is given of 107 minerals, including a lot of crystallographic and optic constants. In 1925 G. Bontchev makes a generalization on the minerals from the Rhodope mountain, giving a description of about 50 minerals.

The fourth period begins after the World War II. This is a period of an intensive development of the mineralogical studies in Bulgaria. The great successes realized during this time are summarized in the book "The minerals in Bulgaria", published in 1964. It is written by a group of Bulgarian mineralogists under the direction of our eminent scientist, academician Ivan Kostov. A description is given of more than 350 minerals in 540 pages.

## ASPECTS OF FORM AND STRUCTURE; THE RENAISSANCE PRELUDE TO CRYSTALLOGRAPHY

C.J. Schneer, Durham, USA

The intellectual foundation for the science of the Renaissance was in Koyre's words "... an unnatural alliance between Plato and Democritus" but the historical genesis of crystallography was in the attempt to locate in the natural world ideal harmonies of form and structure. Renaissance artists and musicians were mathematical physicists in that they worked toward exact sciences of modelling nature. They were also Pythagoreans in that they found in nature the harmonic proportions and geometric forms canonized by the ancients. For Johann Kepler, the results were not only new laws of astronomy but also the connection between the Democritean concept of atomism and the new geometry born out of the five perfect solids of Plato. Always the physicist, Kepler found the celestial harmonies as well as the Platonic solids in natural crystals. Through Descartes, Bartholinus, Hooke, and Steno, the ground was prepared for a natural science of crystals.

Marjorie Hooker, Washington, USA, and Ch. C. Waterston,  
Edinburgh, Scotland

Dr. William Thomson, an English physician in Oxford and a Fellow of the Royal Society, left England in 1790 and took up residence in Italy where he continued his interests in natural history, built up an extensive mineral collection which was considered to be one of the best in Europe, and made valuable contributions to geology and mineralogy. One of his contributions, long unrecognized, was the discovery and first description and illustration of the Widmanstätten pattern, the etching phenomenon found in meteoric iron. In Naples he was known as Guglielmo Thomson and he signed his articles either W. Thomson or G. Thomson, or even simply with the initials W.T. or G.T. It was customary in those times for letters to editors to be signed only with initials. Letters written to other scientists were often quoted and used in their articles, either with or without the writer's initials. Thus, Thomson's writings appeared under a variety of signatures and it was not until 1939 that the Oxford historian, Dr. R. T. Gunther, recognized and published a brief notice on the identity of G. Thomson with William Thomson, formerly of Oxford. This paper will present a list, with explanatory notes, of as many of Thomson's writings as it has been possible to discover and identify.

F. Liebau, Kiel, Germany (FRG)

A suitable classification should on the one hand allow a logical and unequivocal file on individuals to the various pigeon-holes of the system. On the other hand for as many properties as possible a classification should reflect relationships between the individuals.

Since physical, chemical, morphological and many other properties of solids depend on their crystal structures, silicates can reasonably be divided according to two principles:

- (I) the linkage of  $[\text{SiO}_4]$  tetrahedra,
  - (II) the coordination and linkage of cation-oxygen polyhedra.
- While since Machatschki (1928) the linkage of  $[\text{SiO}_4]$  tetrahedra is used to group silicates into neso-, soro-, cyclo-, ino-, phyllo-, and tecto-silicates, Belov has emphasized the significance of the cation-oxygen polyhedra.

A combination between these two principles is found if a subdivision of chain, layer and framework silicates is based on the type of chains of  $[\text{SiO}_4]$  tetrahedra that exist in the silicates concerned. This is due to the fact that the shapes of the tetrahedral chains depend mainly on the size and charge of the cations contained in the silicates. Since on the other hand many mineralogical, chemical and other properties of silicates depend on their cations, a crystal chemical classification of high-polymer silicates based on tetrahedral chain types fulfills very well the conditions demanded from a suitable silicate classification.

The report will be illustrated by an exhibition of structural models.

## AUTOMATIC COLLECTION AND ASSESSMENT OF MINERALOGICAL DATA

M.P.Jones, London, U.K.

The mineralogical data that are now required by geological research workers and by many people in the mineral industry include detailed, quantitative information about the proportions, the sizes, the shapes and the spatial inter-relationships of minerals in rocks and in mineral products.

The paper shows that such information cannot be obtained efficiently by manual measuring methods because the speed at which they operate is much too slow for most practical purposes. Furthermore, both the precision and the accuracy of the manual methods are shown to be, in many instances, too low to provide numerical information of any real value.

The paper proceeds to describe briefly the development of some of the automatic measuring instruments that are now available and which provide rapid, objective data from plane sections of mineral specimens.

Since the raw data provided by these instruments are seldom of direct interest to the mineralogist, details are given of the manner in which these raw data are assessed and are presented in acceptable forms.

The assessment of such data is primarily a stereological problem and the transformation of one-dimensional or two-dimensional measurements into three-dimensional values is discussed in some detail. It is shown that volumetric mineral proportions and sizes, and three-dimensional mineral shapes can be rapidly determined with a high degree of accuracy but that difficult problems still exist in the quantification of three-dimensional spatial parameters such as fabric, texture and mineral liberation.

### Open Sessions:

#### Silicates

Friday, September 13, 1974

Chairmen: J.V. Smith  
F. Liebau

#### Mineral Properties and Mineral Occurrences

Friday, September 13, 1974

Chairmen: M.H. Hey  
O.W. Flörke

#### Petrology I

Saturday, September 14, 1974

Chairmen: N.V. Sobolev  
K.R. Mehnert

#### Sulfides

Saturday, September 14, 1974

Chairmen: L.G. Berry  
E.F. Stumpfl

#### Unclassified Papers

Saturday, September 14, 1974

Chairmen: C. Frondel  
S.S. Hafner

DISTORTIONS IN THE COORDINATION POLYHEDRA OF M SITE ATOMS  
IN OLIVINES, CLINOPYROXENES AND AMPHIBOLES

M.E.Fleet, Ontario, Canada

Distortions resulting from shared edges in the coordination polyhedra of metal (M) site atoms in olivines, C2/c clinopyroxenes and (Ca),Mg,Fe<sup>2+</sup> amphiboles have been investigated using published crystal structure data. The principal distortions are associated with relative stretching of M-M and M-Si distances, apparently due to repulsive forces between the positively charged atoms. The effective atomic charges on the M atoms are estimated from electronegativity data. In the clinopyroxenes there is qualitative agreement between the apparent magnitudes of the M(1)-M(1) and M(2)-Si repulsions associated with shared edges and the calculated relative electrostatic potentials due to the M atoms, the repulsions decreasing in the sequences, Al > Fe<sup>3+</sup> > (Cr<sup>3+</sup>, In) > Mg > Mn<sup>2+</sup> for M(1) atoms and Ca > Li > Na for M(2) atoms. Also, in Ca amphiboles, in agreement with calculated data, the repulsion due to Mg is apparently greater than that due to Fe<sup>2+</sup>. However, in olivines the repulsion due to Fe<sup>2+</sup> is greater than that due to Mg.

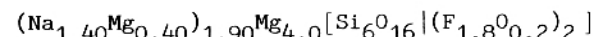
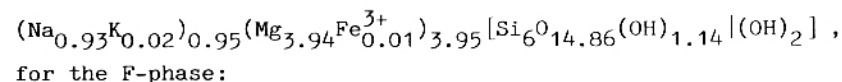
Although the t<sub>2g</sub> orbitals on transition metal atoms must project toward octahedral edges, the coordination octahedra of transition metals do not show a consequent reduction in shared edge-related distortions. Thus, 3d electrons in t<sub>2g</sub> orbitals do not appear to screen the effective atomic charges along M-M and M-Si directions.

ON A NEW TYPE OF CHAIN SILICATES WITH (Si<sub>6</sub>O<sub>16</sub>) RADICAL

V.A.Drits, Yu.I.Goncharov, Moscow, USSR

In studying the processes of mineral formation in the systems Na<sub>2</sub>O-MgO-SiO<sub>2</sub>-H<sub>2</sub>O and NaF-MgF<sub>2</sub>-MgO-SiO<sub>2</sub> fibrous OH- and F-phases have been obtained, respectively, with earlier unknown structural and diffraction characteristics. The composition of the initial components was similar to that of Na-Mg richterite. The synthesis of F- and OH-phases was carried out at temperatures of 400-600°C.

For the OH-phase, a=10.132; b=27.12; c=5.257 Å; β=106°54'; space group C2/c; for the F-phase, a=10.30; b=27.1; c=5.15 Å; β=104°; space group C2/c. The chief feature of the structure of the phases under investigation is that it contains strips of three pyroxene chains connected by common O atoms. In the projection onto the plane (010) the structure of the OH- and F-phases is analogous to those of the monoclinic pyroxenes and amphiboles. The structural model under discussion has been obtained on the basis of an analysis of intensities of reflections from point electron diffraction patterns and building the projections of electrostatic potential. The crystallochemical formula for the OH-phase is:



This shows the possibility of existence of structures with [Si<sub>6</sub>O<sub>16</sub>] strips that are an in-between "link" between layer silicates and amphiboles.

THE CRYSTAL STRUCTURE DETERMINATION OF CHAPMANITE  
SbFe<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>(OH) BY HIGH-VOLTAGE ELECTRON DIFFRACTION

A.P.Zhoukhlistov, B.B.Zvyagin, S.V.Soboleva, L.B.Shlain,  
Moscow, USSR

Two specimens of a rare mineral, chapmanite, from two localities - Cadamdjai (middle Asia) and Snilkov (Czechoslovakia) have been investigated. For the determination of the structure electron diffraction texture patterns obtained at acceleration voltages 350 kV have been used. The unit cell is a = 5,188, b = 8,985, c = 7,696 Å, β = 101°39'. At ρ = 3,8, Z = 2.

The resulting structure obtained by analysis of Patterson and Fourier syntheses and by LS-refinement may be described as consisting of 1:1 kaolinite-like layers with composition Fe<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>(OH) arranged in a sequence  $\delta_6^{\tau_0}\delta_6^{\tau_0}$ . In contrast to the kaolinite case adjacent sheets of neighbouring layers are located with vacant octahedra just over the ditrigonal tetrahedral loops, forming cavities occupied by Sb atoms. Just because of their presence in the interlayers the electrostatically unfavourable layer sequence of the monoclinic structure (Cm) is stabilized.

This structure exhibits pronounced distortions. The tetrahedral bases strongly differ from each other by the edge length. The O atoms of these bases lying in mirror planes m have coordinates z > z<sub>Si</sub> while for others z < z<sub>Si</sub>, that results in a strong tilt of tetrahedra. Under the action of Sb the octahedral apices O,OH approach vacant octahedra and the apices of the outer octahedral surface are occupied by O instead of OH. Furthermore Fe atoms are displaced from the centres of octahedra to the inner O,OH bases.

The structure of chapmanite appears to be the only example of realization of kaolinite-like layers containing Fe<sup>3+</sup> instead of Al, and shows the same difference for 1:1 layer silicates, which exists between micas and pyrophyllites in the case of 2:1 layers.



$A^{2+} [T_2^{3+} T_2^{4+} O_8]$  , FELDSPARS AND DANBURITES:  
THEIR STRUCTURAL AND CRYSTAL CHEMICAL PROPERTIES

H.Kroll and M.W.Phillips, Münster, Germany (FRG)

Both the danburite and feldspar structures can be thought of as being built up of double-crankshaft chains which consist of 4-membered rings of tetrahedra. Two of the adjacent tetrahedra have apical oxygen atoms pointing up (U) and two have those pointing down (D). The apical oxygen atoms serve to link similar four-membered rings.

The differences in the danburite and feldspar structures arise from the manner in which these chains are cross-linked to form the framework. In the danburite structure the successive chains are alternately rotated clockwise and counter-clockwise by approximately  $90^\circ$  whereas in the feldspar structure each chain is rotated approximately  $180^\circ$  from the neighboring chains. In both structures the cross-linking gives rise to a "sheet" of tetrahedra perpendicular to the chain axes. These sheets consist of 4- and 8-membered rings. However, whereas in the danburite structure there is only one type of 8-membered rings having the sequence of tetrahedra UUDUDDUD, the feldspar structure contains two types of 8-membered rings: one with the same sequence of tetrahedra as in danburite and another one in which the sequence is UUUUDDDD. These differences give rise to different coordination polyhedra for the large  $A^{2+}$  cations which lie in cavities between the 8-membered rings of successive "sheets". The coordination number of  $A^{2+}$  cations is 7 in feldspars and 9 in danburites.

Due to the perfect alternation of  $T^{3+}$  and  $T^{4+}$  cations in ordered feldspar structure all linkages are of the type  $T^{3+}-O-T^{4+}$ . This is also the usual case for the danburite type structures, although there is at least one exception: In danburite,  $CaB_2Si_2O_8$  there is a perfect alternation of  $B^{3+}$  and  $Si^{4+}$  within the "sheets", however, within the double-crankshaft chains there are B-O-B and Si-O-Si linkages. Thus although the structure is perfectly ordered, only 75 % of the bonds are of the type  $T^{3+}-O-T^{4+}$ . A discussion of some structures newly refined will be given on the basis of this general description.

ON STRONTIUM FELDSPAR,  $Sr[Al_2Si_2O_8]$

Horst Pentinghaus, Münster, Germany (FRG)

Strontium feldspar, which lies in the middle of the alkaline earth feldspar series  $A^{2+}[Al_2Si_2O_8]$ , where  $A^{2+} = Ca, Sr$  and  $Ba$ , displays intermediate fine-structural properties compared to anorthite,  $Ca[Al_2Si_2O_8]$ , and celsian,  $Ba[Al_2Si_2O_8]$ . For equilibrated anorthite, end-member of the important rock-forming plagioclase solid solution, four classes of reflections are observed by X-ray diffraction methods:

- "a"  $h + k$  even,  $l$  even, which are mainly due to the framework
- "b"  $h + k$  odd,  $l$  odd, which arise from an ordered distribution of Al and Si
- "c"  $h + k$  even,  $l$  odd, as well as
- "d"  $h + k$  odd,  $l$  even, which arise from an antiphase domain structure

However, the rather rare mineral celsian shows only "a" and "b" type reflections. Thus strontium feldspar, obtainable only by synthesis and revealing "a" and "b" and especially "d" type reflections when properly equilibrated with respect to temperature, offers an excellent opportunity to get a deeper insight into the dependence of domain structure formation on the expansion of the feldspar framework. Results based on X-ray single crystal and powder methods as well as on IR spectroscopy and intensity calculations are presented.

Strontium feldspar melts congruently at  $1660 \pm 10^\circ C$ . The metastable hexagonal polymorph of  $SrAl_2Si_2O_8$  can be prepared either by quenching an overheated melt or at lower temperatures under hydrothermal conditions whereas the strontium equivalent of the mineral paracelsian,  $Ba[Al_2Si_2O_8]$ , appears to be the stable low temperature polymorph of  $SrAl_2Si_2O_8$ .

## THE CRYSTAL STRUCTURE OF MAZZITE

Ermanno Galli, Modena, Italy

The crystal structure of mazzite, the natural counterpart of synthetic molecular sieve  $\Omega$ , has been determined from single crystal X-ray data. The space group of mazzite is  $P6_3/mmc$  ( $a = 18.392 \text{ \AA}$ ,  $c = 7.646 \text{ \AA}$ ), hence different from  $P6/mmm$  previously deduced from powder data for phase  $\Omega$ . The structural model proposed by Barrer and Villiger (1969) for the synthetic phase cannot be fit in the space group  $P6_3/mmc$ , hence a new structure has been calculated. The gmelinite cages, which are present in the Barrer-and-Villiger's model, are part also of the new structure but their interconnection is different, because the linked cages are shifted of  $c/2$ .

BARRER, R.M. and VILLIGER, H.: Probable structure of zeolite  $\Omega$ . - Chem.Comm. 1969, 659-660.

## DIMENSIONAL FIT AS THE CONTROL ON ORIENTATION ANGLES OF EXSOLUTION LAMELLAE IN PYROXENES AND AMPHIBOLES

Peter Robinson, Howard W. Jaffe, Amherst, Mass., and Malcolm Ross, Washington, USA

When lamellae of one monoclinic pyroxene or amphibole exsolve within another monoclinic host pyroxene or amphibole, the contacts between lamellae and host develop along planes of best fit between the two structures which are planes of minimal strain. As the differences between the  $a$  and  $c$  lattice parameters of host and lamellae become larger, the differences between the actual contact planes and the rational planes (001) and (100) become larger.

In the case of metamorphic augites with pigeonite lamellae, in which lattice parameters have not changed greatly since exsolution, the orientations of exsolution lamellae are mainly a function of composition, particularly Fe/Mg ratio, and may be predicted from present lattice parameters. The most remarkable confirmation of the dimensional fit theory is obtained from magesian metamorphic augites. Not only are observed angles of exsolution lamellae in close agreement with best fit planes calculated from lattice parameters, but observed slight relative rotations between lattices of host and lamellae are in close agreement with rotations, calculated independently from lattice parameters, that are required to achieve best fit.

In certain slowly cooled igneous augites, in which differences in thermal contraction between host augite and pigeonite lamellae appear to have been large, exsolution took place in as many as three cycles, where the angles of lamellae were appropriate for the relative lattice parameters under the T conditions of that cycle. Study of such lamellae coupled with data on lattice parameters measured at high T and P has some potential as a geothermometer. The cyclical nature of the lamellae suggest that supersaturation, nucleation, and growth was the mechanism by which exsolution took place. Thick initial portions have a consistently different angle from thin later portions, suggesting gradual change in relative dimensions due to differential thermal contraction as lamellae propagated longitudinally through the host crystal.

A COMPARISON OF THE STABILITIES OF OH- AND F-TREMOLITE

M.C.Gilbert, Blacksburg, USA, and G.Troll, München  
Germany (FRG)

The calcic amphibole, OH-tremolite,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , stably dissociates to diopside<sub>ss</sub> + enstatite<sub>ss</sub> +  $\beta$  quartz + vapor at low pressure, and to the same assemblage with  $\alpha$  quartz substituted for  $\beta$  quartz at higher pressure. The breakdown curve changes from a very low  $dP/dT$  at about 550°C, 1 atm to a very steep  $dP/dT$  and a temperature of about 875°C in the pressure range 2 to 5 kb. Above this pressure the curve appears to pass through a maximum and attain a negative slope chiefly because of the compressibility of the vapor. This negative  $dP/dT$  is augmented by the volume change of the  $\beta$  quartz =  $\alpha$  quartz transition at about 11 kb. OH-tremolite stability is limited at higher pressure by the lower volume assemblage diopside + talc, the maximum pressure being about 24 kb at 825°C.

In contrast the stable breakdown of F-tremolite,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2$ , is to the assemblage protoenstatite<sub>ss</sub> + diopside<sub>ss</sub> + fluorite + tridymite at 1 atm and about 1150°C. This reaction has as positive  $dP/dT$  at 1 atm. The slope is modified by the protoenstatite=orthoenstatite change at some unknown low, but higher, pressure. The highest temperature of stability for this amphibole should be about 1175°C at the pressure of the tridymite =  $\beta$  quartz transition ( $\sim 1\ 3/4$  kb). At this transition,  $dP/dT$  becomes negative because the volume change in the  $\text{SiO}_2$  polymorphs results in a negative  $\Delta V$  for the breakdown reaction.  $dP/dT$  is about -340 bars/°C up to the  $\alpha$  quartz =  $\beta$  quartz boundary ( $\sim 24$  kb).

Comparison of stabilities of OH- and F-tremolite indicates that the 600°C difference in their upper thermal stabilities at 1 atm decreases to about 250°C at 24 kb. Thus under some conditions, the effects of fluorine on the temperature of silicate equilibria may not be as dramatic at higher pressure as at lower. On the other hand, whereas OH-tremolite is not stable over 24 kb, F-tremolite appears to be stable to at least 40 kb. Thus fluorine can extend the pressure stabilities of some silicates.

STABILITY RELATIONS OF AMPHIBOLES IN THE TREMOLITE + FERRO-TREMOLITE - ANTHOPHYLLITE - GRUNERITE QUADRILATERAL

K.Schürmann, Marburg, Germany (FRG)

Experimental investigations at different temperatures and water vapor pressures have been made on the joins:

- (1) ferrotremolite - grunerite and
- (2)  $\frac{1}{2}$  tremolite  $\frac{1}{2}$  anthophyllite (TAN) -  
 $\frac{1}{2}$  ferrotremolite  $\frac{1}{2}$  grunerite (FTG)

using common hydrothermal techniques. For 3 investigated compositions of the join (1), grunerite 25, 50, 75, we could find a field of coexisting ferrotremolite and grunerite between 450° and about 550°C and water vapor pressures up to 6 kbars with oxygen fugacities defined by the magnetite-iron and magnetite-wüstite buffers.

At medium pressures (1-3 kbars) and at temperatures between 530° and 580°C the only stable amphibole phase is grunerite coexisting with hedenbergite + quartz +  $\text{H}_2\text{O}$ . Increasing  $P_{\text{H}_2\text{O}}$  (up to 6 kbars) shifts the upper stability curve of ferrotremolite in a rate of about 25°C/kbar to higher temperatures.

First runs on join (2) TAN - FTG at Fe/Fe + Mg-compositions > 40 yielded coexisting actinolites and cummingtonites at temperatures up to 630°C and at  $P_{\text{H}_2\text{O}}$  up to 6 kbars.

UPPER STABILITY OF ORTHORHOMBIC AMPHIBOLES IN THE SYSTEM  
MgO - FeO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> - H<sub>2</sub>O

Th.Hinrichsen, Marburg, Germany (FRG)

Orthorhombic amphiboles of anthophyllite composition are characteristic constituents of metamorphic rocks rich in magnesia. Under high-grade metamorphic conditions anthophyllite becomes unstable and is transformed to H<sub>2</sub>O-free assemblages.

Synthetic aluminous anthophyllites with different Mg-Fe-ratios were investigated experimentally at different temperatures and H<sub>2</sub>O-pressures to determine their stability range. At 6 kb H<sub>2</sub>O-pressure synthetic anthophyllites were found to be stable up to 800°C.

The nature of the high-temperature breakdown assemblages is dependent on the chemical composition and on the H<sub>2</sub>O-pressure. Mg-Fe-anthophyllites containing up to 5 weight-% Al<sub>2</sub>O<sub>3</sub> are transformed to (aluminous) hypersthene and quartz while cordierite is stable in the breakdown products at higher Al-concentrations in the anthophyllite phase.

THE STRUCTURAL AND GENETIC RELATIONS BETWEEN LAYER SILICATES UNDER HYDROTHERMAL CONDITIONS AND SOME PROBLEMS OF THE CLAY MINERALOGY

V.Frank-Kamenetsky, N.Kotov, E.Goilo, A.Tomashenko, Nguen Tat Tram, Leningrad, USSR

The structural and genetic relations between layer silicates were examined by phase transformations of kaolinite, montmorillonite, pyrophyllite, sepiolite, palygorskite under hydrothermal conditions ( $P_{H_2O} = 1 - 2$  kbar,  $T = 150 - 650^\circ\text{C}$ ) with additions of K, Na, Ca, Mg-chlorides, sulphates and carbonates. Practically, all most significant kinds of clay minerals and many unlayered minerals were synthesized. On the base of this material some main problems of genetic mineralogy and petrology of metamorphic processes are discussed.

It was established, that a significant feature of the alterations of clay minerals is their alteration by stages, caused by 3 groups of factors: 1) the thermodynamic factors (P-T-X-pH), 2) the phase stability - unstability, 3) the different velocity of their formation. The rise of temperature up to 200 - 500°C ( $P_{H_2O} = 1 - 2$  kbar) at runs with addition of MgCO<sub>3</sub>, leads to a formation of (Al,Mg)-serpentine and further - forsterite and spinel from kaolinite; from dioctahedral montmorillonite, first of all, there is formed a trioctahedral montmorillonite. The increase of concentration of MgCO<sub>3</sub> (montmorillonite:MgCO<sub>3</sub> = 2:3 in weight) as in runs with kaolinite, leads to a formation of (Al,Mg)-serpentines, and the increase of temperature - to formation of talk, chlorites, forsterite and spinel. The rise of pH of the hydrothermal surrounding up to 7-8, promotes the transition of Al<sup>VI</sup> to Al<sup>IV</sup>. This consequently leads to a formation of kalsilite + leucite, and feldspars + leucite (addition of K<sub>2</sub>CO<sub>3</sub>) from kaolinite and montmorillonite instead of micas. The latter are formed through the beidellite-like and partly ordered mixed-layered mica-montmorillonite phases below pH = 5-6, and with addition of KCL.

All processes examined are realized, as a rule, in the form of transformational reactions, when the structure of initial materials is inherited by the newformed phases. The concrete examples of the alterations of clay minerals by stages might be used as a model system for the investigation of the epigenetic and hydrothermal-metasomatic processes.

H.Minato, H.Kusakabe, T.Yamanaka, M.Utada, Tokyo, Japan

In Japan, many kinds of zeolites from sedimentary rocks are investigated with respect to their mode of occurrence and mineralogical properties. The main varieties of these zeolites are clinoptilolite, mordenite, analcime and laumontite. And these zeolites, associated with plagioclase, quartz, opaline silica and some clay minerals, are formed from the acidic tuffs mainly by diagenesis.

Phase equilibria between these zeolites and plagioclase are studied in order to investigate their stability relationship using hydrothermal method from a view point of solution chemistry. Purified natural clinoptilolite as a starting material is treated with NaOH solution having variable concentrations in a Morey-type reactor. Equilibrium relations in the system of clinoptilolite, mordenite, analcime and albite are obtained in terms of temperature, pressure and pH. One of the results of these experiment is presented in the following table.

pH of NaOH solution	Temperature (°C)	Pressure (bars)	Formed material	pH of reacted solution
10	280	500	clinoptilolite	6.05
12	300	620	mordenite	7.15
13	340	625	albite	11.10
14	380	300	analcime	13.1

Rudolf Allmann, Marburg, Germany (FRG) and  
Gabrielle Donnay, Montreal, Canada

Pauling's logarithmic relationship for covalent and metallic bonds:

$d_n = d_1 - 2k \cdot \log n$  (1947, J.Amer.Chem.Soc. 69, 542; d = atomic distance, n = bond number) may be used for ionic bonds too; as for V-O (Byström & Wilhelmi 1951, Acta Chem.Scand. 5, 1003; Evans 1960, Z.Krist. 114, 257), Mo-O (Åsbrink & Brandt 1971, Chem. Scripta, 1, 169), B-O (Donnay & Donnay 1973, Acta Cryst. B 29, 1417). We prefer the terms bond length L and bond valence v instead of d and n. To get the best fit, the two constants L(1) and 2k (in Å) in

$$(1) L(v) = L(1) - 2k \cdot \log v$$

are chosen for the M-O bonds of the following cations as:

Li 1.262; 1.15 Al 1.644; 0.88 Ti 1.754; 1.12 Zn 1.675; 0.90  
Be 1.374; 0.88 Si 1.63 ; 0.83 V 1.81 ; 0.78 Ga 1.73 ; 0.88  
B 1.366; 0.85 P 1.64 ; 1.10 Cr 1.79 ; 0.78 Ge 1.75 ; 0.75  
C 1.40 ; 0.60 S 1.614; 0.84 Mn 1.75 ; 0.91 As 1.77 ; 0.94  
N 1.41 ; 0.90 K 1.659; 1.30 Fe 1.74 ; 0.88 Mo 1.90 ; 0.76  
Na 1.661; 1.01 Ca 1.896; 0.95 Co 1.655; 0.97 W 1.91 ; 0.82  
Mg 1.636; 0.97 Sc 1.877; 0.81 Cu 1.65 ; 0.91

(Pauling proposed  $2k = 0.60 \text{ Å}$  for all cases). (1) is not very sensitive to the 2k-value (except for strong bonds with  $v > 1$ ), but for a given structure the L(1)-values may need some correction for the individual cations. If for a cation its valence =  $\sum v_{\text{ideal}}$  is known and  $\sum v_{\text{real}}$  deviates from this value, the following correction may be applied:

$$(2) L(1)_{\text{cor}} = L(1) + 2k \cdot \log f, \text{ with } f = \sum v_{\text{ideal}} / \sum v_{\text{real}}$$

The logarithmic function leads to similar results as the potential function.

(3)  $v = v_i \cdot (\bar{L}/L)^p$  (Donnay & Allmann 1970, Amer.Mineral. 55, 1003, and 1972, Acta Cryst. A 28, 108; Brown & Shannon 1973, Acta Cryst. A 29, 266) if one takes  $p = \bar{L}/2k \cdot \log e$ . Some applications of the proposed procedure will be given.

OXIDES AND SULFIDES FROM THE FISKENAESSET COMPLEX, WEST GREENLAND

I.M.Steele, F.C.Bishop and J.V.Smith, Chicago, USA, and B.F.Windley, Leicester, U.K.

The textures and chemistry of opaque phases from the metamorphosed Fiskenaesset igneous complex, west Greenland, were investigated with reflected-light microscopy and an electron microprobe. Magnetite, Cr-magnetite, and ilmenite occur in the lower zones while spinel (near  $MgAl_2O_4$ ), chromite, and rutile predominate in the upper zones. Extensive evidence (e.g. complex exsolution textures and chemical data for coexisting phases) is presented for subsolidus equilibration of opaques to low temperatures, probably in the range of 300 to 600°C.

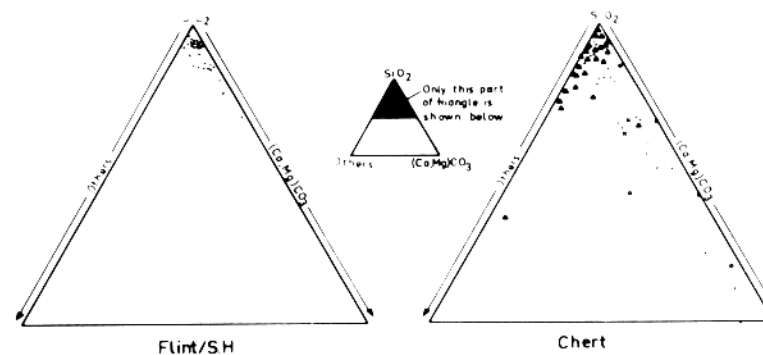
Coexisting spinels outline a probable exsolution gap between  $(Fe,Mg)Fe_2O_4$  and  $(Fe,Mg)Al_2O_4$  which is truncated by entrance of about 40 %  $(Fe,Mg)Cr_2O_4$ . The supposed primary spinels have compositions indicating derivation of the Fiskenaesset complex from a liquid richer in Al than for other well-known layered intrusions.

The sulfide mineralogy is complex, and includes at least the following: pyrrhotite, pentlandite, chalcopyrite, pyrite and cubanite. Detailed parageneses and chemical compositions will be reported and correlated with the oxides. Preliminary observations indicate equilibration to very low temperatures.

COMPARISON "FLINT - CHERT" - BASED ON CHEMICAL DATA

P.Bettermann and D.Ackermand, Kiel, Germany (FRG)

Thirtytwo glacial-flint specimens from eight different deposits in Schleswig-Holstein and the western Baltic Sea have been analyzed for sodium, potassium, magnesium, calcium, aluminum, total iron, silicon, phosphorus, manganese, titanium, adsorptive and chemical bonded water and carbon-dioxide. The results are compared with corresponding published data of flint and chert (as shown for example in the figure below) in order to search for characteristic differences in their chemical composition.



Subsequently an attempt will be made to define the terms: "Flint" - "flints" - "Hornstein" - "chert" - "silix" etc. by means of chemical data and genetic consideration.

In addition optical and electron-optical investigations together with some work on an electron microprobe were made. The aim was to find out the distribution-relations of the analyzed elements and the mineral composition of flint. Beside the main-phase silica in various modifications and crystal-size distributions and beside accessory phases as clay, carbonatic and sulphidic minerals there were found out some interesting silification-phenomena.

## THE MODIFICATIONS OF Mg-Fe-BORACITES

R.v.Hodenberg and R.Kühn, Hannover, Germany (FRG)

Nine samples of Boracites from different occurrences have been found with compositions covering the entire range of Mg-Fe solid solution. The average content of Mn-Boracite in all specimens was 2,6 mol %. The crystals are extraordinary fine twinned and showed cubic morphology with faces (100), (111), (111) and (110).

The crystals were investigated by DTA, optical- and X-ray-methods. In spite of the limited amount of the available material and of their slight inhomogeneity with respect to the composition, the following preliminary observations could be made on the different modifications and their fields of existence:

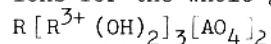
1. All the crystals of the series are cubic above temperatures ranging from 265°C (Mg-rich) to 340°C (Fe-rich).
2. An orthorhombic modification appears below these temperatures, the stability of which extends to room temperature in the case of Mg-rich members.
3. Crystals which contain more than approximately 40 mol % Fe-Boracite, possess an additional - probably monoclinic - modification.
4. In the case of samples with contents of Fe-Boracite between 42 mol % and approximately 90 mol % another monoclinic phase could be observed with quite different optical properties. The transition temperature to this modification is dependent on the mole ratio Mg Fe. It increases with increasing amounts of Fe from 50 up to ca. 220°C.
5. Boracites, very rich in Fe (from ca. 90 mol %) are uniaxial, in analogy to the synthetic Fe-Boracite. In this cases the crystals are trigonal.

## THEORETICAL AND EXPERIMENTAL BASIS OF DISTINGUISHING THE GROUPS OF ALUNITE AND ITS STRUCTURAL ANALOGUES

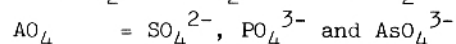
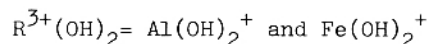
M.A.Kashkai and C.M.Kashkai, Bacu, USSR

34 minerals of different classes - sulfates, phosphates, and arsenates, possessing analogous structures with alunite and jarosite are classified as a "Group of alunite and its structural analogues".

The general chemical formula, reflecting the complex reactive ions for the whole group is expressed as follows:



where R = K<sup>+</sup>, Na<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ag<sup>+</sup>, Rb<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Bi<sup>3+</sup>, Y<sup>3+</sup>, Ce<sup>3+</sup>, Th<sup>4+</sup>, U<sup>4+</sup>,



For formation of crystal structure of alunite type a great importance belongs to hydrocomplexes of aluminium and iron and more likely to ions Al(OH)<sub>2</sub><sup>+</sup> and Fe(OH)<sub>2</sub><sup>+</sup>.

Minerals of the alunite group and their structural analogues have common energy character. Thermodynamical constants of the reactions for the most minerals obtained experimentally are almost similar.

Taking into consideration the complex ions of the system and the variation of their concentration during reaction the common equations is obtained. It is a thermodynamic model of the formation pattern of isostructural minerals of the alunite group. Using the computer program "Alunite" the model gives the possibility to consider simultaneously and separately the role of temperature, pH, concentration of all reacting ions, the influence of ion power of solution on mineralforming reaction.

BASALUMINITE, THE NEW MINERAL OF CZECHOSLOVAKIA

J.Hrusková, Prague, CSSR

In the Ždánice unit which forms part of the flysch zone of the Carpathians, at Nikolčice near Brno (Moravia) on the surface of carbonate concretions in the beds of the Menilitic Formation, a white nodular mineral was found, which was identified as hydrobasaluminite and basaluminite by a detailed study. On the territory of Czechoslovakia, these minerals have not so far been found.

As the main method of identification X-ray diffraction was used. Chemical composition was determined. Under electron microscope, thin flaky transparent crystals, rhombic in shape, with good cleavage, were observed.

In the conclusion of the paper the data on the basaluminite and hydrobasaluminite, obtained by means of X-ray methods, thermal study, chemical analysis and electron microanalysis are summarized.

CLASSIFICATION OF MINERALS OF THE GROUP OF TOURMALINE

V.A.Kornetova, Moscow, USSR

According to their crystallochemical nature, especially the mode of substitution, the following types of tourmalines are distinguishable: schorl, gabiellite ("ferric iron tourmaline"), buergerite, elbaite and jakovlevite. Peculiarities of every type, in their turn, permit to classify all known tourmalines. Analytical diagnosis of valencies of some chemical elements and their position in the structure of tourmalines are of especial significance. The description of a new type - jakovlevite - is given.



XONOTLITE FROM HEGURI, CHIBA PREFECTURE, JAPAN

Akira Kato and Satoshi Matsubara, Tokyo, Japan

Xonotlite from Heguri, Chiba Prefecture, Japan, is monoclinic, space group P2/a,  $a = 17.0217 \text{ \AA}$ ,  $b = 7.3486 \text{ \AA}$ ,  $c = 7.0076 \text{ \AA}$ ,  $\beta = 90.326^\circ$ ,  $Z = 2$  ( $\text{Ca}[(\text{OH})_2|\text{Si}_6\text{O}_{17}]$ ), according to the four-circle goniometric study by Takeuchi and Kudo, Mineralogical Institute, University of Tokyo. Optically biaxial positive,  $2V = 20-25^\circ$ ,  $r < v$  weak,  $n_s \alpha = 1.584$ ,  $\beta = 1.584$ ,  $\gamma = 1.595$  (all  $\pm 0.002$ ); optic plane nearly parallel to  $\{100\}$ ,  $b = Z$ . Chemical analysis by Tiba, Department of Geology, National Science Museum, gives  $\text{SiO}_2$  49.99,  $\text{Fe}_2\text{O}_3$  0.48, FeO none, MnO 0.16, CaO 46.19,  $\text{Na}_2\text{O}$  0.17,  $\text{K}_2\text{O}$  0.02,  $\text{H}_2\text{O}(+)$  2.95,  $\text{H}_2\text{O}(-)$  0.10, sum 100.06 %. Specific gravity 2.70 (meas.), 2.711 (calc.); cleavage  $\{001\}$  perfect. Elongated parallel to  $b$ , dominant faces are (100), (010), (001) and (00 $\bar{1}$ ) observed under the electron microscope.

It occurs 1) as principal fissure-filling material in veinlets cutting an altered dolerite and 2) as accessoric member of veinlets of strontium-bearing tobermorite (SrO 1.65 %) cutting a prehnite-rich greenstone.

HARADAITE,  $\text{Sr}_2\text{V}_2[\text{O}_2|\text{Si}_4\text{O}_{12}]$ , A NEW MINERAL FROM THE NODA TAMAGAWA MINE, IWATE PREFECTURE, AND THE YAMATO MINE, KAGOSHIMA PREFECTURE, JAPAN

Takeo Watanabe, Akita, Japan

& A.Kato, J.Ito, T.Yoshimura, H.Momoi, K.Fukuda

Haradaite,  $\text{Sr}_2\text{V}_2[\text{O}_2|\text{Si}_4\text{O}_{12}]$ , is found from the Noda-Tamagawa Mine, Iwate Prefecture and the Yamato Mine, Kagoshima Prefecture, Japan, as an accessoric member in bedded manganese ore deposits. The chemical analysis by J.Ito on the Yamato material gives  $\text{SiO}_2$  38.38,  $\text{Al}_2\text{O}_3$  0.36,  $\text{TiO}_2$  0.06,  $\text{VO}_2$  26.16, CaO 1.27, SrO 27.08, BaO 4.90, MnO 0.19, FeO 0.12,  $\text{Na}_2\text{O}$  0.01,  $\text{K}_2\text{O}$  0.04,  $\text{H}_2\text{O}(+)$  1.24,  $\text{H}_2\text{O}(-)$  0.20, Pb 0.02, Cu 0.20, sum 100.23 %. Colour bright green, luster glassy. Cleavages,  $\{010\}$  perfect,  $\{100\}$  and  $\{001\}$  distinct. Hardness (Mohs) 4 1/2. Specific gravity 3.80 (meas.), 3.83 (calc.).

It is orthorhombic, space group Ama2,  $a = 7.001 \text{ \AA}$ ,  $b = 14.67 \text{ \AA}$ ,  $c = 5.324 \text{ \AA}$  (Noda-Tamagawa Mine);  $a = 7.001 \text{ \AA}$ ,  $b = 14.64 \text{ \AA}$ ,  $c = 5.312 \text{ \AA}$  (Yamato Mine), respectively. Unit cell content  $(\text{Sr}, \text{Ba})_4\text{V}_4\text{Si}_8\text{O}_{28}$ . Optically biaxial negative,  $(- )2V = 75^\circ$ ,  $r < v$  very strong,  $n_s \alpha = 1.713$ ,  $\beta = 1.721$ ,  $\gamma = 1.734$  (all  $\pm 0.002$ ),  $\gamma - \alpha = 0.021$ ; optic orientation  $a = X$ ,  $b = Y$ ,  $c = Z$ ; axial colours X = colourless to very pale green, Y = colourless to light yellowish green, Z = bluish green.

It occurs with quartz in coarse-grained rhodonite ore at the Noda-Tamagawa Mine and as veinlets cutting manganoan goldmanite-rhodonite ore at the Yamato Mine.

The present name covers the solid solution  $(\text{Sr}, \text{Ba})_4\text{V}_4\text{Si}_8\text{O}_{28}$  with  $\text{Sr}_2\text{Ba}$ , and unnamed natural  $(\text{Ba}, \text{Sr})_4\text{V}_4\text{Si}_8\text{O}_{28}$  found at the Tanohata Mine, Iwate Prefecture and synthetic  $\text{Ba}_4\text{V}_4\text{Si}_8\text{O}_{28}$  are probably isostructural.

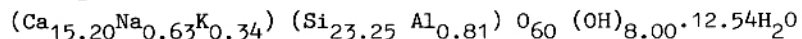
The name is given in honour of Dr. Zyumpei Harada, Emeritus Professor of Hokkaido University, Sapporo.

THE GYROLITE - APOPHYLLITE MINERAL ASSEMBLAGE OF THE  
RANSKO INTRUSIVE BODY (EAST BOHEMIA)

K.Melka, J.Pokorný and D.Ulrichová, Prague, CSSR

This rare assemblage of the secondary minerals together with other alkali-lime minerals found in the mafic and ultramafic rocks of the Ransko-Massif (associated with both copper-nickel liquation magmatic and sulphide copper-zinc ores) has originated by the hydrothermal leaching of the main chemical components of plagioclases.

Special attention in this contribution has been paid to the mineralogical determination of the rare gyrolite - hydrous calcium silicate - which shows a significant 22.3Å X-ray reflection. X-ray microanalysis has shown that the micaceous flakes with pearl lustre separatable from the spherulitic aggregate did not consist of gyrolite only but of the gyrolite alternating with apophyllite intimately intergrown. The structural formula



has been calculated from the chemical analysis of the relatively pure gyrolite. This formula has shown a fair agreement with that which has been calculated from the point X-ray microanalysis.

The special feature of the gyrolite sample from Ransko is characterized by the presence of hydrocarbons. These hydrocarbons have been confirmed especially by the infrared absorption spectroscopy and gas chromatography. The electron and X-ray images which were carried out on the X-ray microanalyser and on the scanning electron microscope have shown that hydrocarbons are concentrated in the channel spaces present in gyrolite.

LITHIUM MICAS FROM JAPANESE PEGMATITES

Kozo Nagashima, Mariko Honda, Junko Iino and Kazuo Harada,  
Tokyo, Japan

Chemical composition, optical and X-ray properties, infrared and far-infrared absorption spectra of the following lithium micas from Japan have been studied.

- (1) Pink Li mica (lepidolite) from Nagatare, Fukuoka Prefecture.
- (2) Pink Li mica (lepidolite) from Sakihama, Iwate Prefecture.
- (3) Pale pink Li mica (lepidolite) from Suisawa, Mie Prefecture.
- (4) Pale pink Li mica from Minagi, Okayama Prefecture.
- (5) Pale brown Li mica (zinnwaldite) from Dairi and Tahara, Gifu Prefecture.
- (6) Pale brown Li mica from Miyazuma, Mie Prefecture.

For comparison, taeniolite, an aluminum free lithium mica, from Kola, USSR, has also been studied. The relationship between lithium content and the polymorphic type will be discussed.

CRYSTALCHEMICAL VARIABILITY OF CHLORITE AND CORRENSITE AS AN INDICATOR OF THEIR GENESIS

A.G.Kossovskaya, V.A.Drits, Moscow, USSR

The crystalchemical features of a number of minerals with sheet structures may convey important information relating to their genesis.

Chlorites. In contrast to the earlier notions that only Fe-chlorites occur in sedimentary rocks, magnesium chlorites have been established to be wide-spread in terrigene-evaporitic deposits. Crystalchemical distinctions of authigenic Mg-chlorites of sedimentary rocks from Mg-chlorites formed on ultrabasites and serpentinites are shown. A group of Fe-Mg-chlorites of sedimentary and magmatic rocks is studied. The pattern of settlement of Al, Mg, Fe in octahedra has been established to be an indicator of the genesis of the chlorites that can be used for "eliminating metamorphism" and diagnosis of para- and orthorocks.

Corrensites. In various types of geological units 28 Å ordered mixed-layer chlorite-montmorillonite minerals have been established to be wide-spread. Four types are distinguished: (1) sedimentary evaporitic complexes; (2) sedimentary coalbearing formations; (3) hydrothermal formations associated with basalts and andesites and (4) metasomatites formed on gabbroids and ultrabasites. The crystalchemical features of the corrensites of all the four types have been identified and their "cognateness" to the chlorites of the corresponding geological environments established.

PARAGENESIS OF FAUJASITE AND PHILLIPSITE AT SASBACH, KAISERSTUHL

R.Rinaldi and J.V.Smith, Chicago, USA

The crystallization sequence in amygdules of limburgite rock is: faujasite (octahedra, some spinel-twins, not present in all amygdules), amorphous coating (mostly hydrated silica-alumina: SiO<sub>2</sub> ~52, Al<sub>2</sub>O<sub>3</sub> ~33 wt. %), phillipsite (radial twinned aggregates in tufts and spherules), calcite and amorphous black material. No evidence was seen for breakdown of faujasite. Not all amygdules contain the complete sequence, suggesting erratic entrance of incoming solutions.

Both faujasite and phillipsite have Si/Al ~2.5 (electron microprobe analyses) and considerable MgO content: mean values are

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Total
faujasite	58.2	18.3	3.0	3.9	1.8	0.2	85.5
phillipsite (fine grained)	56.6	19.5	1.7	4.1	0.4	3.8	86.1
phillipsite (coarse)	62.4	19.1	0.05	4.6	1.9	6.2	94.3

All the specimens were collected in 1969 from one small area of the quarry (with kind assistance of G.Jung). Analyses of random faujasite crystals from mineral collections show different values suggesting variability in the quarry.

The limburgite contains euhedral pyroxene (coarse twinning, oscillatory and hour-glass zoning) and olivine (altered margins) set in a devitrified or glassy matrix.

The data on faujasite are consistent with primary crystallization from solutions entering amygdules, with no breakdown to other phases. The source of the solutions is unknown.

A grant-in-aid from the petroleum Research Fund administered by the American Chemical Society is acknowledged.

QUARTZ-FELDSPAR-CALCITE-H<sub>2</sub>O OXYGEN ISOTOPE GEOTHERMOMETERS:  
NEW EXPERIMENTAL RESULTS FOR 600°C AND GEOTHERMAL DATA  
FOR 250°C

Peter Blattner and G.W.Bird, Lower Hutt, New Zealand

Experimental calibrations of quartz-H<sub>2</sub>O, feldspar-H<sub>2</sub>O, and calcite-H<sub>2</sub>O oxygen isotope 'geothermometers' are available in the literature, and in the case of quartz and calcite have been backed up by partition function calculations. For geological applications of mineral-pair thermometers, calibrations need to be very precise. We have attempted a refinement of earlier experimental studies, placing particular emphasis on the relationships between the isotopic compositions of the solids.

In the experiments at 600°C quartz and alkali feldspar were equilibrated with a common solution and analyzed as pairs. Identical quartz-feldspar oxygen isotope fractionations were obtained for quartz and silicagel starting materials, and for water and 1M KCl solution. For silicagel starting material identical quartz-feldspar fractionations were obtained for fluids of widely differing  $\delta O^{18}$  (reversal runs).

The geothermal data from Boadlands no.7 drillhole are important for quartz and feldspar, which to date have not been equilibrated in the laboratory at low temperatures. The possibility of equilibrium among the geothermal phases, including quartz, is real and is critically discussed.

Significantly improved mineral-pair calibration curves are proposed and are compared with geological data.

## CONDITIONS OF STABILITY AND PARAGENESES OF MERWINITE

N.N.Pertsev, Moscow, USSR

Ca-Mg-orthosilicate merwinite,  $\text{Ca}_3\text{MgSi}_2\text{O}_8$ , occurs only in carbonate hornfels and skarns formed at higher temperatures and shallow depths. The mineral is interesting with a great variety of its assemblages and their carbonization and hydration conditions. Natural equilibrium merwinite assemblages give possibilities to calculate temperatures,  $\text{CO}_2$ -pressures,  $\text{MgO}$  and  $\text{SiO}_2$  activities and some other parameters of their formation.

New experiments at  $p_{\text{H}_2\text{O}}$  more than 250 atm have showed that merwinite converts into dellaite-monticellite paragenesis by hydration. At 1000 and 500 atm of  $\text{H}_2\text{O}$  the mineral decomposes at 710 and 690°C respectively. The merwinite skarns from Iglica (Bulgaria) gives a good example of such hydration reaction.

Carbonization reduces merwinite stability field much more. The mineral can be converted to akermanite-calcite paragenesis at above 820°C and more than 75 atm of  $\text{CO}_2$ -pressures. At lower parameters merwinite can be changed into akermanite + spurrite + monticellite or kilchoanite + monticellite + spurrite.

$T - p_{\text{CO}_2}$ ,  $T - x_{\text{CO}_2}$ , log activity - log activity diagrams of merwinite assemblages help to estimate parameters of formation of its occurrences. The conditions of merwinite paragenesis formation of several occurrences are discussed.

## DISTRIBUTION OF CALCIUM BETWEEN PLAGIOCLASE AND GARNET AND ITS PARAGENETIC SIGNIFICANCE

Roland Gorbatshev, Lund, Sweden

Large changes of volume in reactions relating grossular and anorthite demonstrate that the distribution of Ca between garnet and plagioclase may be employed in geobarometry. In a variety of metamorphic terrains there is good correlation between the Ca-distribution and the pressure environment as suggested by other indicators. The Ca-distribution has been checked for the possible influence of compositional factors like Ca-concentration, cation substitutions and the peristerite solvus, which appear to be of none or minor importance. The influence of the Ca-distribution/pressure relation on the stability of garnet and the paragenetic development of rocks is surveyed.

THERMODYNAMIC REGIME OF METAMORPHISM AND GRANITIZATION

L.L.Perchuk, Moscow, USSR

Mineralogical thermometry and barometry were used to study thermodynamic regime, that is, change in temperature (T), pressure ( $P_s$ ), partial pressure of volatile components ( $P_i$ ) with the depth of metamorphism (M) and granitization (G). The following effect was used as a basis for temperature measurements: the greater the difference in the strength of silicic acid radicals and in the symmetry of natural equilibrium minerals, the higher the degree of redistribution of the two isomorphous components between silicates with T; maximum effects have been noted for hydrous minerals in equilibrium with anhydrous ones. This rule is best shown by the exchange equilibria of ferromagnesian minerals. Based on calibration of this effect, numerous diagrams of the phase relations, "mineralogical thermometers", have been developed. Pyroxene-garnet barometers and a number of diagrams of the  $P_s-X_M$  type allowed the  $P_s$  at M and G to be evaluated. With T and  $P_s$  known, fugacities and partial pressures of the volatile components have been calculated for hydration-dehydration, carbonatization-decarbonatization and oxidation-reduction reactions. The relations between  $P_s$  and the mean values of other thermodynamic parameters at M of terrigenous geosynclines are illustrated in the table.

	$P_s$ kb	1	3	4	5	6	8	10	11
	T°C	-	430	550	615	660	750	820	870
M	$P_{CO_2}$ kb	0,1	0,6	1	1,6	2,2	4	6	7
	$P_{H_2O}$ kb	-	1,5	2,3	3	2,6	1,8	1	0,5
	$lg P_{O_2}$ bar	13,6	16,6	17,3	18,0	18,2	18,6	19,0	19,2
G	$P_{H_2O}$ kb	0,8	2,7	3,5	4,2	4,5	3,5	2,8	2,0
	T°C	725	670	615	615	675	720	785	820

Thermo- and barometry of the pyroxene-garnet inclusions in basaltes and kimberlites indicates the possibility of the temperature maximum to occur in the area of "the waveguide" (h 150 km).

THE CHEMISTRY OF BIOTITES AS A GUIDE TO THE PETROGENESIS OF EL-INEIGI GRANITIC ROCKS, EASTERN DESERT, EGYPT

M.L.Kabesh, M.L.Abdel Khalek and M.A.Heikal, Cairo, Egypt

Biotites recovered from the granitic rocks of El-Ineigi stock in the Eastern Desert, Egypt, have been investigated by chemical methods. The chemical data of 12 newly analyzed biotites are presented and projected on variation diagrams originally constructed by Heinrich and Nockolds, slightly modified by Gokhale. The significance of biotite - the sole mafic in these granites - as an index mineral in the petrogenesis of El-Ineigi granitic complex is discussed.

SPECIFIC FEATURES OF THE MINERALOGY OF ALKALINE  
(NEPHELINE-BEARING) ROCKS

V.I.Gerasimovsky, Moscow, USSR

1. The mineralogy of nepheline syenites is very diverse. Two different groups can be distinguished among the typomorphic minerals of these rocks and related pegmatites and hydrothermalites: one of them is typical of agpaitic nepheline syenites, the other of miaskitic ones. Agpaitic rocks are characterized by wide development of minerals containing sodium and rare lithophilic elements, miaskitic rocks by minerals containing calcium. Such difference is mainly due to peculiarities of melt composition which give rise to these rocks, and in the first place to relative amounts of alkalis and aluminium and the different content of rare lithophilic elements and volatiles.
2. One of the most important characteristic features of nepheline syenites is a joint occurrence in minerals of sodium or calcium with elements defining the specificity of the mentioned rocks: Cl and S (sodalite); F (villiaumite, fluorite); P (lomonosovite, apatite); Nb (murmanite, pyrochlore); TR (rinkite, steenstrupine, apatite); Zr (eudialyte, zircon etc.).
3. The mineralogy and geochemistry of Cl, F, P and S are very peculiar. The bulk of these elements enter the composition of minerals being formed at the magmatic stage.
4. Distribution regularities of rare lithophilic elements and some other (F, Cl, P, S) elements is conditioned by the geochemical history of petrogenic elements. The concentration of rare elements in dark coloured rock-forming minerals, being formed later than leucocratic minerals, is considerably higher and is usually highest in accessory minerals. The latter are frequently found in considerable amounts and sometimes they are rock-forming minerals (eudialyte, lovozerite, etc.).
5. Pegmatite and hydrothermalite minerals are more diverse in comparison with rock-forming minerals. This is due to the fact that many trace elements are accumulated towards the end of the magmatic process, because their isomorphic entrance into leucocratic rock-forming minerals (microcline, nepheline) is impeded.
6. Secondary processes of mineral formation were wide developed at the final formation stages of alkaline rocks and pegmatites, during which water played an important role.

SYNGENETIC CRYSTALLINE INCLUSIONS IN NATURAL DIAMONDS

N.V.Sobolev, Novosibirsk, USSR

Natural diamonds from kimberlites of Yakutia and other deposits of the World contain inclusions of olivine, chromite, garnet, clinopyroxene, enstatite and rutile. Among the newly found evidence of simultaneous growth of inclusions and diamonds are the octahedral faces of numerous inclusions represented by negative diamond octahedra oriented parallel to the external diamond faces.

The results of determination of the composition of more than 100 inclusions from the diamonds of Yakutia and Urals obtained by electron probe technique confirm both the similarity with corresponding kimberlitic minerals and some differences which are most distinct in Cr-rich Ca-poor pyropes and magnesian chromspinelides approximating pure chromites in the composition. It has been proved that garnets and chromites similar to those included in diamonds are present in heavy concentrates of diamantiferous kimberlites.

Examination of inclusions have permitted one to establish the entire series of polymineral combinations in individual diamond crystals and to identify stable parageneses of the ultramafic and basic types which may be considered as primary parageneses of the diamond. To the ultramafic type (with olivine) belong: a) Ca-poor Cr-pyrope + chromite ± enstatite; b) Cr-garnet + enstatite + Cr-diopside; c) Ca-rich Cr-garnet + Cr-diopside. Few of the diamonds contain basic, eclogitic paragenesis of inclusions: Mg-Fe garnet + omphacite ± rutile. The range of these parageneses embrace all possible types of ultramafic and basic compositions with marked predominance, however, of dunitic paragenesis - "a". The study of inclusions justify that diamonds crystallized within the Upper Mantle in the depth ranging between 150 and 200 km in equilibrium with included minerals and the melt in igneous events.

## OSCILLATORY ZONING OF AUGITIC PYROXENES IN PLATEAU BASALTS

S.S. Augustithis, Athen, Greece

Augitic pyroxenes have been found in basaltic lava of the Ethiopian Plateau consisting of up to 250 fine zones.

Microprobe point-analysis by J. Ottemann along a traverse, perpendicular to the zoning of the augitic phenocrysts, shows oscillation in the Mg, Fe and Ti contents of the fine zones.

Often two distinct generations of oscillatory zoned augites have been determined; generation I forms the nucleus and is surrounded by generation II.

The oscillation of Mg is reversed to that of Fe and the Ti coincides rather with the Fe. There is little difference in the Mg percentage and also in the oscillatory percentage fluctuations between the nucleus of the pyroxene, generation I, and the outer augite, generation II. However, a noticeable increase in Ti content is determined in the outer augite (generation II) as compared with the nucleus.

The oscillatory zonal development of the augite phenocrysts seem to result in the formation of "Sand Uhr" structures in some of the studied cases.

In addition, the paper describes the phenomenology of the zonal growths and particularly the anomalies and interruptions in the development of zoning. Also an attempt is made to understand the presence of orientated and at random occurring fine needles in respect to the oscillatory zoning of the pyroxenes.

Furthermore, attention is drawn to the relationship between oscillatory zoning and simple and polysynthetic twinning developed in these augites.

## PARAGENESIS AND PETROGENESIS OF A CORUNDUM-BEARING MARBLE, PAKISTAN

M. Okrusch, Braunschweig, Germany (FRG), T.E. Bunch, Calif., USA  
H. Bank, Idar-Oberstein, Germany (FRG)

In the northwestern part of the Himalaya mountains, Pakistan, a calcite-marble containing gem-quality ruby has been detected, material of which was submitted to us for gemological and mineralogical investigations.

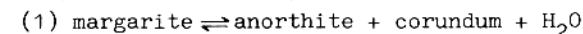
The following mineral assemblages are recognized in the corundum-bearing marble ( $\pm$  tourmaline, sphene, rutile, pyrite, pyrrhotite):

Calcite + corundum  $\pm$  margarite  $\pm$  phlogopite  $\pm$  corundophyllite  
 $\pm$  plagioclase  $\pm$  hornblende;  
calcite + corundum + spinel + phlogopite + corundophyllite;  
calcite + spinel + phlogopite.

Microprobe analyses of the prominent minerals are presented.

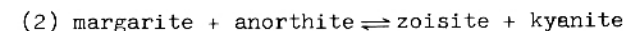
P-T conditions of metamorphism can be estimated using the experimental data in the system  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O} - \text{CO}_2$  (e.g. Storre, 1973).

The uppermost stability limit is given by the reaction.



which proceeds at about 500°C (2 kb water pressure) and 600°C (6 kb) according to the investigations of Velde (1971), Chatterjee (1971) and Storre and Nitsch (1974).

An upper pressure limit is given by the reaction



at about 9 kb (Storre, 1973).

Judging from the stable occurrence of margarite and of the assemblage calcite + anorthite, the mole fraction of  $\text{CO}_2$  in the fluid phase must have been confined to rather low values within a very limited range, e.g., at 2 kb total pressure,  $X_{\text{CO}_2}$  would range between 0.02 and 0.13 (Nitsch and Storre, 1972; Storre and Nitsch, 1972).

### References

- CHATTERJEE, N.D. (1971): *Naturwissenschaften* **58**, 147.  
NITSCH, K.H., STORRE, B. (1972): *Fortschr. Mineral.* **50**, Bh.1, 71.  
STORRE, B. (1973): *Fortschr. Mineralogie (im Druck)*.  
STORRE, B., NITSCH, K.H. (1972): *Contr. Mineral. Petrol.* **35**, 1.  
----- (1974): *Contr. Mineral. Petrol.* **43**, 1.  
VELDE, B. (1971): *Mineral. Mag.* **38**, 317.



CHANGE IN PHYSICAL PROPERTIES OF COALIFIED AND GRAPHITISED  
PHYTOCLASTS WITH GRADE OF METAMORPHISM

C.F.K.Diessel and R.Offler, Newcastle, Australia

Phytoclasts are dispersed plant fragments which occur together with inorganic detritus in sediments and their metamorphic counterparts. Because of their origin and composition the organic particles are subjected to the same post-depositional changes that lead to the formation of coal and eventually graphite. In this paper the results of microscopic reflectance measurements, differential thermal and X-ray diffraction analyses of coalified and graphitised phytoclasts from two Australian fold belts are presented and related to the respective metamorphic grades of the host rocks. Further comparisons are made with samples from other continents.

The results show that from the zeolite facies to the lower greenschist facies, phytoclasts occur in coalified form with the various coal macerals being clearly distinguishable under the microscope. The main physical expression of the progressing anthracitization is an increase in mean maximum reflectance to approximately 7 % (in oil). Rocks from the upper portion of the chlorite zone of the greenschist facies contain both coalified and graphitised phytoclasts. In the coalified portion only inertodetrinite remains unaffected while all vitrinite has disappeared and appears to be represented by several graphite varieties. Within the biotite zone, all phytoclasts have been converted into graphite which in the amphibolite facies experiences an increasing lattice perfection. This is shown by a rise in both maximum reflectance up to approximately 15 % (in oil) and optical anisotropy, by an increase in intensity of the (002) X-ray reflection at 3.35-3.36Å, and by a rise of the exothermic peak temperature from 500°C to 660°C. The nature of the transformation of coal into graphite, as well as the significance of the relationship between metamorphic grade and the changes that occur in graphite are discussed.

ARSENIAN VARIETIES OF BRAVOITE AND PYRITE

T.N.Shadlun and N.V.Troneva, Moscow, USSR

During the last years new data concerning the chemical composition of iron disulfides become available from lead-zinc deposits, deposits of Ag-arsenides, and hot springs in regions of volcanic activity.

Additional to some Co and Ni various amounts of As have been determined. The variability of As content allows the division into two groups: arsenian (less than 1 % As) and arsen-pyrites or arsen-bravoites resp. (more than 1 % As).

A high As content was detectable by microprobe in bravoites from Sedmotshislenizi, Bulgaria (8.2 - 13.8 %) and from Silverfield, Ontario (8.7 %). Pyrites from the same provenance also have an extraordinary high As content (0.88 - 5.2 %). Those As containing (or As-Co-Ni-containing) iron disulfides microscopically show a reniform, fine concentric zonality. In reflecting light such zones with the highest content of the elements mentioned above have yellowish-white colors with rose tinge.

The anionic content of As and S as well as the cationic content of Co, Ni, Fe is explained by isomorphic substitution.

GENETIC SIGNIFICANCE OF THE ZONING OF BRAVOITE AND  
SPHALERITE

J.Mincheva-Stefanova, Sofia, Bulgaria

Two types of zoning in the crystals of minerals are discerned: a polygeneration and a monogeneration one. The former results when crystals of the earlier generations of a given mineral are regularly overgrown by a crystal or crystals of its later generations. It is typical of minerals from high- and medium-temperature deposits. The crystals of the individual generations in the polygeneration type may also be zoned. The monogeneration type of zoning caused by the non-uniform chemical composition of the mixed crystals is of special interest. The development of this type of zoning exhibits varying trends depending on the physico-chemical conditions under which it is formed in accordance with the crystallochemical and structural relations between the main components in the mixed crystals. Therefore, it may be used as a genetic criterion.

The phenomenon is exemplified by the widely occurring zoning in bravoite and sphalerite crystals.

Bravoite represents mixed crystals of the three components of the ternary system  $\text{FeS}_2\text{-NiS}_2\text{-CoS}_2$ . Its zoning is controlled by the relative concentration of the respective metal ions in the solution. Generally, the formation of mixed crystals takes place in neutral solutions and the variation of the chemical composition of the successive zones is accounted for by the solubilities of the three disulphides.

Sphalerite crystals frequently exhibit both types of zoning. Its monogeneration zoning greatly restricts the possibility of using sphalerite as a "geobarometer" and "geothermometer". This type of zoning shows two basic trends - either towards decreasing, or towards increasing of the iron content from the central to the outer crystal zones. The latter case is rare and is observed when high- and medium-temperature cleiophanes have been formed under conditions of raised Eh.

THERMAL CHANGES OF PYRRHOTITE

Goro Shibuya, Yamaguchi, Japan

Many natural and synthetic pyrrhotites showing various chemical compositions have been investigated to know the changes on heating up to  $650^\circ\text{C}$  in vacuum and in air by main means of differential thermal analysis, magnetic balance and X-ray powder diffractogram. On the DTA curve for the paramagnetic hexagonal pyrrhotite treated in air, a small exothermic peak at  $\gamma$ -anomaly point,  $220^\circ\text{C}$ , and a plateau-like exothermic reaction starting from  $\beta$ -transition point,  $320^\circ\text{C}$ , following a very remarkable endothermic peak centered at  $580^\circ\text{C}$  were recognized. Besides, if the specimen is heated up to about  $200^\circ\text{C}$ , the magnetic character turns abruptly from paramagnetism to ferrimagnetism. Being ferrimagnetized at once, the specimen can not restore the original paramagnetism by any heat-treatments thereafter. The cause of the ferrimagnetization is not based upon the formation of magnetite or ferrimagnetic monoclinic pyrrhotite, judging from the results of thermo-magnetic experiments. The author here presents a new idea that the formation of co-called "ferrimagnetic oxidized pyrrhotite" is supposed due to a reaction:  $\text{FeS}_{1+x} \xrightarrow{+O_2} \text{Fe}(\text{S}_{1+x} \cdot \text{O}_y)$ , where  $x + y = 0.14$ . It retains a hexagonal symmetry as well in the X-ray powder diffractogram. If the heating-experiment is applied higher than  $320^\circ\text{C}$ , it is surmised that the ferrimagnetic hexagonal phase changes to "ferrimagnetic monoclinic oxidized pyrrhotite" which may solve oxygen at its extreme in the pyrrhotite structure. The remarkable endothermic peak centering about  $580^\circ\text{C}$  means the generation of  $\text{SO}_2$  gas with simultaneous formation of magnetite. The thermal changes of the synthetic pyrrhotite, which has nearly the same composition as the natural pyrrhotite, measured by use of Arnold's X-ray determinative curve are very poor in general compared with the natural specimen.

HOMOLOGOUS SERIES OF SULPHOSALTS (COMPLEX SULPHIDES)

N.N.Mozgova, Moscow, USSR

In the isochemical sulphosalt groups there are homologous series of compounds, which are characterized as follows: 1) Every series corresponds to some interval of compositions and is represented by a totality of compounds. Metal and semimetal contents of these compounds are in inverse ratio and their sum to sulphur ratio changes in desultory way. Sometimes the adjacent members are very similar and composition of the series changes almost continuously. As a rule in each interval there are more natural compounds than the number of the known mineral species. In this connection problem of their names arises. 2) The changing composition of the series is accompanied by their regular structural alteration. Two of the unit cell parameters keep constant over the whole series while the third one increases along with the growth of the relative metal amount. This increase can be a multiple of the unit cell length and then the series members have different superstructures. A similar dependence is revealed for the goniometric relationship of axes. X-ray powder patterns of all members of one series are very similar, but have some light regular differences mainly in the field of small reflection angles (splitting of some reflections, their insignificant shifts and change of intensity). The lesser is the difference in composition of members the closer are their powder patterns. 3) The physical properties of series members change regularly, gradually along with alteration of their composition. 4) Regular intergrowth of members of single series are very characteristic and have been formed during exsolution as a result of ordering.

Such series can be considered as series of ordered bertholide phases (WEDSLEY, 1971) and may be taken as basis for a rational classification of these minerals.

THREEDIMENSIONAL INTERGROWTH OF ORE MINERALS IN PEGMATITES:  
EXAMPLE FOR APPLICATION AND VALIDITY OF A GEOCHEMICAL VOLUME-RULE

Heiko Rabe, West-Berlin, Germany

Separated special paragenesis of sulphides, phosphates and silicates in pegmatites of the type Hagendorf/Opf. are differing in its trace element contents as a result of selection. In the sulphides, and for example in sphalerite, many trace elements cannot be explained by diadochy. Replacement of Zn by Bi or Ag probably cannot be assumed. Therefore a geochemical volume-rule seems to exist: Under conditions of high pressures in presence of fluid components and in overcritical pT-range, guest elements will be integrated in form of anomalous-solid-solutions in host-crystals.

During the decomposition exsolution bodies with nearly coincident cell volumes are originated and diataxy (= threedimensional orientated intergrowth) is resulting. - ZnS e.g. includes crystals of Bi and compounds like  $AgBiS_2$ ,  $Bi_2S_3$ , etc., and nearly all trace elements are fixed in this way in the host-lattices.

Crush-structures as usually common in the neighbourhood of inclusions of Bi are not to be observed in sphalerite. This shows that the stress in coherent lattice-planes becomes compensated by diataxy. Deformations of the host-crystal keep small and are comparable with those in mosaic-crystals. If exsolution bodies different in chemical composition appear in diataxy with one and the same host, each guest can be in diataxy with each other guest. The metrical relationship of host and guest derivable from the volume-rule could be verified for the first time by ore microscopy, using the Laves-Ernst-Compensator for determination of the main directions of optical properties for anisotropic opaque exsolution bodies of FeS,  $Bi_2S_3$ ,  $AgBiS_2$ , Bi etc. Observed examples of diataxy in Hagendorf are:

	ZnS	FeS	Bi <sup>1)</sup>	$Bi_2S_3$	$AgBiS_2$
planes of intergrowth	110	(00.1)	( $\bar{1}21$ )	(010)	(100)
zone axis with equivalent positions of host and guest	110	00.1	210	010	100
	$\bar{1}10$	01.0	$\bar{1}\bar{2}\bar{1}$	001	010
	00 $\bar{1}$	21.0	$\bar{1}\bar{1}3$	$\bar{1}00$	00 $\bar{1}$

1) indexing refers to pseudocubic cell:  $a_{rh} = 6.56 \text{ \AA}$ ;  $\alpha = 87.4^\circ$

THE CRYSTAL CHEMISTRY OF SELENIUM AND TELLURIUM MINERALS,  
A COMPARISON WITH SULFUR MINERALS

Josef Zemann, Vienna, Austria

Selenium and tellurium have the same configuration of the outermost electron shell as sulfur; therefore, Se- and Te-compounds often show crystal chemical similarities to S-compounds. However, the increasing effective radii and the decreasing electronegativities with increasing atomic number, as well as an increasing preference of the 4-valent oxidation state as compared with the 6-valent oxidation state with increasing atomic number cause quite remarkable differences in the crystal chemistry of tellurium minerals as compared with sulfur minerals, selenium showing an intermediate behaviour.

Examples:

- (1) Tellurium can substitute sulfur in sulfides, but it can also form a pyramidal  $\text{TeS}_3$ -group, as in the fahlores, where it substitutes for Sb and As, resp.;
- (2) sulfites seem to be unknown among minerals, but in the oxidation zone of tellurium deposits, Te(IV)-minerals - and not Te(VI)-minerals - definitely dominate, and perhaps even occur exclusively.

Yu.V.Kazitsyn, Leningrad, USSR

Two main types of metasomatic processes are distinguished. The former take place under progressive conditions (granitization, regional skarning etc.) the latter - under regressive ones (near-ore rocks of hydrothermal deposits). Mechanism of metasomatic mineral formation is determined in both cases by the formation of replacement pseudomorphs under the conditions of differential mobility of components and constancy of the geometrical volume. In a general case when mineral A with the volume V being replaced, inert-pseudomorph mineral with the volume Vn and defect of the volume  $\pm \Delta V$  are formed. The latter is either compensated by a released mineral with the volume Vo by precipitated mineral with the volume Vk and a displaced mineral with the volume Vb, or it remains unfilled.

On condition of an obligatory conformity of the volume of final products is, as a rule, not equal to the mass of the initial ones. The structure looseness, mean atomic density and isomorph capacity of lattices of the initial mineral and products of pseudomorphism also vary depending on a type.

In the course of granitization the replacement of basic plagioclase and amphibole by orthoclase is a leading process. The replacement takes place with increasing of a resultant volume and structure looseness of newly formed products. Mean atomic density decreases when the average mass of atoms being increase. According to data of microprobe investigations isomorph capacity of metasomatic new formations decreases.

Under the conditions of regressive metasomatism of near-ore transformations pseudomorphism takes place with decreasing of structure looseness of lattices, the average mass of newly formed products decreases, and the mean atomic density increases.

Ivan Kostov, Sofia, Bulgaria

In addition to zonalities concerning mineral species and trace elements in the composition of minerals, zonality after morphology of crystal forms of minerals and kind of mineral aggregates is considered of no lesser significance when the interpretation of mineral deposition is concerned. The three types of zonalities, mineralogical, geochemical and morphological, are supplementary and should have to be account always together.

The morphological zonality comprises (a) variation of crystal habits of a mineral and richness of its combination forms coupled with observations on size and degree of perfection of its crystals, and (b) if no crystal forms are presented, variation of mineral aggregates, again paying attention to the morphology ('pseudomorphology') of the separate individuals, their size and pseudosymmetry, as well as their spatial arrangement. Rate of crystallization, temperature and admixtures on one hand and kind of crystallization locus on the other are of primary importance for the development of minerals with changing morphology. From detailed observation on the distribution of the different morphological types of a mineral can thus be gathered direct evidence about the condition of crystallization in a mineral deposit.

The morphological zonality can be normal or reverse, depending on the trend of the crystallization rate. Recurrences due to changing conditions of crystallization may lead to telescoping of different crystal habits and aggregates. It can be further local, regional, concentric, linear, vertical, horizontal, etc.

A STUDY OF THE IRON ORE DEPOSITS OF KUDREMUKH,  
KARNATAKA STATE, INDIA

C.Naganna, B.S.Shivakumar and N.B.Nagesh, Bangalore, India

Kudremukh Iron ore deposit, which is regarded as one of the largest Iron ore deposits in Asia, with proved reserves of about 600 million tons of good grade ore, has been studied, in respect of the ore mineralogy and the mineral paragenesis. The Iron ore formations are a part of the Pre-cambrian schistose formation called the Dharwars, consisting of banded magnetite quartzite, chlorite schist, coarse grained amphibolite and fine and coarse grained hornblende schist.

The formations are tectonically folded into an overturned asymmetrical fold. The youngest banded magnetite quartzite assumes varying thickness, in different parts of the region as one moves across the folds. Through a prolonged process of weathering ore concentration has been brought about in the weathered zone, which varies in depth from place to place, depending on the structural and geomorphological facilities for the circulation of ground water.

Through a detailed study of the ores drawn from different depths in the weathered zone and beyond, the presence of ore minerals like magnetite, martite, specularite and haematite, is established.

Further, the occurrence of sulphide minerals like pyrite, chalcopyrite and pyrrhotite along with the iron ore minerals is recorded. The mineral paragenesis of these minerals and the origin of these minerals are discussed.

A NEW METHOD TO DETERMINE THE REFRACTIVE INDEX OF LIQUIDS  
TO ANY AMOUNT

E.Seeliger, West-Berlin, Germany

The method, practised by Duc de CHAULNES, SORBY etc., for determination of refractive indices of isotropic or an<sup>i</sup> isotropic plan-parallel glass- or crystal-plates with the microscope will not be used to-day and seems to be only of historical interest.

But in course of time the tube lifting mechanics of microscopes were developed to a high degree of accuracy. In combination with the BECKE-method this old method to-day is useful to determine the refractive index of liquids in general and especially of liquids with high or very high n-values in a very short time.

Test-slides are fine glass grains, embedded in air under a cover glass. A drop of a liquid (as used for the immersion liquid-method) must be brought into the room between the front-lense of the objective and the test-slide after having focussed a single glass grain in air by BECKE-line. Because the liquid layer can vary its thickness, when lifting the tube, the thickness of liquid-layer depends only from n; as the amount of tube lifting too.

A mechanic counter should be used. To held the error small, it needs to determine a test curve of the fine lifting mechanics for each instrument and to select usefull objectives, which seem to be best if of medium power (25 - 40) and medium aperture (0,5 - 0,7). Best results in measuring are in the range of  $n \pm 0,003$ .

DETERMINATION OF VOLUME CHANGE OF MELTING AT HIGH PRESSURE

P.W.Mirwald, München, Germany (FRG), and G.C.Kennedy,  
Los Angeles, USA

A method for measuring volume change associated with melting has been developed for solid medium piston cylinder apparatus. A first study to 40 Kb was conducted on metal melting curves. In order to explore this method over a wide temperature range (100 - 1200°C) sodium, lead and silver were selected as samples. The pressure vessel used has a bore diameter of 1.25 cm. A low friction cell recently developed for melting curve determinations was modified for this study to accommodate samples of volume up to 0.3 cm<sup>3</sup>. This new cell permitted observation of these small volume changes by sensitive monitoring of piston displacement and associated pressure change while slowly heating through melting. A differential thermoanalyse (DTA) arrangement was used to monitor sample melting and thermal gradients. Results at 40 Kb for the three metals studied show a substantial decrease of volume change on melting compared with the one atmosphere value: 70±10 % for sodium, 60±10 % for lead and 50±10 % for silver. This implies considerable decreases in the change of entropy of melting.

ABSTRACTS OF PAPERS PRESENTED AT REGENSBURG

Main Session:

Mineral Genesis and Crystal Growth

Tuesday, September 17, 1974

Part I, Chairmen: C. Guillemin  
H.v. Philipsborn

Wednesday, September 18, 1974

Part II, Chairmen: I. Sunagawa  
K. Weber

Main Session: MINERAL GENESIS AND CRYSTAL GROWTH  
Introductory lecture  
HYDROTHERMAL GENESIS OF MINERALS

J.Wyart, Paris, France

Hydrothermal genesis of minerals - a review of the role of water at high temperatures and pressures in the genesis of minerals is given. At first the experiments have been made in mineralogical laboratories. The importance of crystals in different industries, which can be prepared only from aqueous solutions at high temperatures and pressures has been at the origin of accurate thermodynamical measures of the properties of these solutions. The results have been very useful for the explanation of the origin of different minerals. Examples are given for some sulfides, oxides, silicates, and among them feldspars.



S.D.Scott, Ontario, Canada

Standard methods of synthesis and determination of stability relations among refractory sulfide minerals are often frustrated at low temperatures by the failure to achieve equilibrium. This inertia towards reaction can be easily overcome by recrystallizing the sulfides in appropriate aqueous solutions over small (usually 10-15°C) temperature gradients. In practice, the powdered sulfide charges and aqueous solution are sealed into gold tubes and heated in a specially-designed, stainless steel pressure vessel along which a linear temperature gradient is applied. The sulfides are dissolved at the hotter (usually bottom) end of each tube and transported by convection to the cooler (top) end where slow precipitation of crystals takes place. Because of the very small temperature gradients at the site of crystallization, the precipitating phases are at or near equilibrium with the aqueous solution and with each other. This technique has the advantages of producing large, chemically-homogeneous crystals of refractory sulfides suitable for single crystal x-ray study from assemblages equilibrated at temperatures (100° - 700°C) and pressures (0 - 10 kb) of geological interest. As well, sulfur fugacity which is an important variable in most sulfide reactions can be varied continuously over many orders of magnitude by carefully controlling the  $f_{O_2}$  and pH of the aqueous solution.

The hydrothermal method has been used to (1) synthesize single crystals of cinnabar, sphalerite, wurtzite, hexagonal and monoclinic pyrrhotite and pyrite of high purity and perfection; (2) examine the growth mechanics and kinetics of single crystal sphalerite and wurtzite; (3) measure the partitioning of trace elements and of sulfur isotopes among sphalerite, galena, pyrrhotite and pyrite; and, (4) determine equilibrium phase relations in portions of the mineralogically-important systems Fe-S and Zn-Fe-S at low temperatures and at high pressure which were unattainable in previous studies.

C.T.Prewitt and V.Rajamani, New York, USA

As part of a study of transition-metal sulfides, crystals of  $Co_9S_8$  (pentlandite structure),  $Co_{1-x}S$  (jaipurite), and  $Ni_{3+x}S_2$  (heazlewoodite) have been grown in a multi-zone furnace using iodine-vapor transport techniques. The crystals of  $Co_9S_8$  are of excellent quality, show well-developed faces, and have been used for diffraction studies of the pentlandite-type structures. Those of  $Co_{1-x}S$  are not as good and give precession photographs with somewhat diffuse diffraction spots. A few crystals show exsolution features. Morphologically, the  $Ni_{3+x}S_2$  crystals appear to be single and of good quality, but the diffraction patterns are very poor, indicating a possible phase transition in cooling.

In addition to the X-ray examination mentioned above, the crystal morphologies have been simulated using computer graphics techniques similar to those first proposed by Keester and Giddings (1971) and Schneer (1973). This allows complete determination of Miller indices, Wulff vectors, and axial ratios which can be used to determine relative growth rates of crystal faces and to compare crystals grown under different experimental conditions.

DETERMINATION OF THE SPECIFIC FREE SURFACE ENERGY OF  
ENERGETICALLY HETEROGENEOUS SINGLE CRYSTAL FACES

W. Bayh and M. Sellschopp, Tübingen, Germany (FRG)

In a previous paper (Z. Kristallog. 132 (1970) 443) we showed that it is possible to determine the specific free surface energy,  $\gamma_s^{hkl}$ , of single crystal faces by measuring the contact angle,  $\theta^{hkl}$ , and the surface tension,  $\gamma_L$ , of a sessile drop resting on the substrate to be examined. Combining YOUNG's equation and ANTONOW's rule the specific free surface energy will be given by:

$$\gamma_s^{hkl} = \frac{1}{2} \gamma_L (1 + \cos \theta^{hkl})$$

A special problem results from energetic surface heterogeneity caused by patchwise adsorption of vapor molecules. In this case the substrate surface will consist of high-energy regions (clean crystal surface) and low-energy regions (adsorption layer), and hence a contact angle hysteresis will be caused. Therefore one has to distinguish between advancing contact angles,  $\theta_A$ , and receding contact angles,  $\theta_R$ , for drops which are advanced or receded, respectively, over the solid surface. According to the theoretical treatment of JOHNSON and DETPRE (J. Phys. Chem. 68 (1964) 1744) those angles should be equal to the intrinsic contact angles of low-energy regions and high-energy regions, respectively.

In order to test this theoretical treatment an apparatus was constructed which allows to measure advancing and receding angles in high vacuum. With this method a vertical crystal plate is dipped into a liquid and slowly moved downward and upward in which cases the liquid advances or recedes over the solid surface. By simultaneous measurement of the capillary rise during the time in which the plate is moving, and of the liquid surface tension, the contact angles  $\theta_A$  and  $\theta_R$  could be determined using capillary theory. The results obtained so far with alkali halide cleavage plates covered with water molecules, and with mercury as wetting liquid confirm the predicted thermodynamical significance of contact angle hysteresis.

QUANTITATIVE ANALYSIS OF PLAGIOCLASE CRYSTAL HABIT IN A  
RHYOLITE LAVA FLOW

Richard Haefner, New York, USA

Although mineralogists have studied the size and shape of the unit cells of crystals for many years, relatively few attempts have been made at quantitatively studying the overall size and shape (crystal habit) of crystals.

Andesine phenocrysts from a single rhyolite lava flow in the Dublin Hills, near Death Valley, Calif., were chosen for analysis. Crystal lengths (a-axes) and widths (b-axes) were measured in phi units in 24 randomly oriented thin sections, which were spaced along the length of the flow's exposure and near the top, middle, and base of the flow. Lengths and widths are measures of crystal size; their ratios b/a are measures of shape. Frequency distributions of a-phi and b/a do not differ significantly from the expected normal distributions. The distribution of b-phi, however, is a relatively poor fit to the normal distribution, perhaps reflecting a bias in the sampling procedure, or the sampling of two populations of b-phi axes. These two populations may represent broken and unbroken crystals.

Correlation of b-phi with a-phi reveals that broken crystals differ from unbroken crystals; b-phi and a-phi of broken crystals are not significantly correlated. As axes of the total group of sampled crystals are highly correlated ( $r = .81$ ), it is inferred that few crystals were broken during the eruption and emplacement of the lava flow. The common occurrence of crystals in swirls of groundmass laminae suggests that most crystals were simply rotated between shear planes in the moving lava.

Regression of b-phi vs. a-phi reveals that the crystals changed shape significantly as they grew: small crystals in thin section are elongate ( $b/a = .21$  at  $+4$  a-phi), whereas large crystals are nearly equant ( $b/a = .81$  at  $-1$  a-phi). The rate of change of shape, b/a, is given by the slope of the regression line: a-phi =  $-.37 + .75$  (b-phi), which amounts to 0.12 per unit of a-phi.

Analyses of variance and covariance reveal no evidence that crystal shape or size varies either laterally or vertically within the lava flow. - This result contrasts with recent observations of some rhyolitic ash-flow deposits.

C.F. Woensdregt, Leiden, Netherlands

The following Periodic Bond Chains according to the theory of Hartman and Perdok can be distinguished in the potassium feldspar structures:

$[001]$ ,  $[\frac{11}{22}0]$ ,  $[\frac{11}{22}1]$ ,  $[100]$  and  $[010]$ .

F(lat)-faces growing slowly are:

$\{110\}$ ,  $\{001\}$ ,  $\{010\}$  and  $\{201\}$ .

Calculations of surface energies in an electrostatic model show, that the growth form of potassium feldspar consists only of  $\{110\}$ ,  $\{001\}$  and  $\{010\}$ . This growth form is very similar to crystals found in alpine veins (adularia) and in lacustrine deposits (Olduvai, Green River and Barstow).

Kenneth L. Keester, Aachen, Germany (FRG)

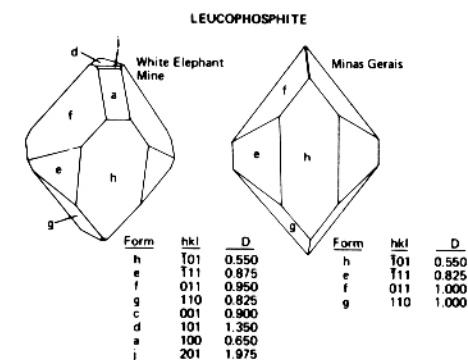
A quantitative description of the morphology for various secondary pegmatite phosphate minerals has been derived by a novel method utilizing interactive computer graphics. The method uses a Fortran program written for an IBM 2250 graphics display terminal. The input parameters are cell constants, crystal class, and a set of hkl's describing closed, convex polyhedra. A parameter called "D" must also be specified for each form. The D parameter is interactively varied so as to duplicate the external appearance of the real

crystal. D is a vector from the origin, normal to the crystal face.

The output is crystal drawings, either photographed directly from the cathode ray screen or drafted by a drum-  
pen plotter. The significant aspect of this

study is that a numerical description of habit is obtained in terms of meaningful values. The set of D values characterize relative growth velocities for each hkl form and are related to surface free energies.

The minerals studied were: laueite, reddingite, ludlamite, whitlockite, vivianite, hureaulite, augelite, strengite, metastrengite, bjarbyite, and leucophosphate from localities in the Black Hills, New England, Minas Gerais, and Hagendorf. Crystal drawings are presented and compared with different pegmatites or contrasting environments, e.g. hydrothermal ore veins. An example of typical results is given above.



MORPHOLOGICAL RELATIONSHIPS BETWEEN HEMATITE CRYSTALS AND  
ETCH FIGURES

Christiane Baltzinger and R. Baro, Metz, France

The shape and the development of etch figures formed on crystals of hematite, not only depend on the type of the faces, but also on their perfection and their growing conditions.

We have etched with boiling HCl 6N hematite crystals from Elba, Brazil, Mexico, and synthetic crystals. The observations have been made by means of optical and electronic microscopes.

Certain directions, that can be related to the lattice, characterize the etch figures. However, those directions do not appear at random frequency but depend on the density of the "molecules" on the corresponding row.

We have studied more particularly the most stable face, that is to say, the one parallel to a plane of the morphological rhombohedron. The values of the bonding energies between the ions of the crystal allow to justify for the frequency of the presence of certain directions. The probability is based upon the predominance of the bonds between the closest "molecules" of the morphological rhombohedron.

In generalizing to other faces with different types of symmetry, a mechanism of etching of hematite crystals can be suggested.

QUARTZ INTERGROWTH PIERCING (120) FACES OF ILVAITE CRYSTALS

Yukio Takano, London, United Kingdom  
T.Nishida and Y.Endo, Tokyo, Japan

Beautiful black crystals of ilvaite of vitreous lustre were collected in the Kamioka mine, Japan. They were found in skarn druses, associated with quartz-hedenbergite and calcite crystals. Crystals show  $\underline{g}$  (120),  $\underline{m}$  (110),  $\underline{o}$  (111) and  $\underline{r}$  (101) faces. Prismatic faces  $\underline{g}$  and  $\underline{m}$ , and pyramidal faces  $\underline{o}$  and  $\underline{r}$  are similarly striated in the directions of the edges of  $\underline{b}$  (010) faces, where these are missing.

Prismatic faces  $\underline{g}$  are the most developed forms in these crystals and consist of several domains, which have slightly different orientations to each other. In each domain there are many growth layers elongated in the direction of the  $\underline{c}$ -axes, and on the boundaries of the domains there are many growth pits. Many prismatic crystals of quartz pierce  $\underline{g}$  faces of ilvaite crystals. According to observations with the scanning electron microscope and Laue photography, in some cases one of the  $\underline{a}$ -axes of intergrowth quartz crystals are oblique by  $2-15^\circ$  to the  $\underline{c}$ -axes of ilvaite crystals instead of having the  $\underline{c}$ -axes of the former in the direction on the  $\underline{a}$ -axes of the latter. In other cases the  $\underline{c}$ -axes of quartz are oblique by about  $18^\circ$  to the  $\underline{a}$ -axes of ilvaite, instead of having one of the  $\underline{a}$ -axes of the former parallel to the  $\underline{c}$ -axes of the latter.

Crystals of intergrown quartz had the same habits as their elongated outcrops, without contracting inside the walls of the ilvaite crystals. These are extraordinary intergrowths. The contact relation is discussed in connection with the crystal growth of  $\underline{g}$  faces of ilvaites, which are the primary growth faces.

THE GROWTH ASPECT OF POLYMORPHISM/POLYTYPISM IN SYNTHETIC  
MICAS OF PETROLOGICAL INTEREST

A. Baronnet, Marseille, France

By means of conventional techniques of hydrothermal synthesis, the most important tri- and dioctahedral end-members of the mica group are crystallized from their respective stoichiometric oxide mixtures under various P,T conditions and run durations. The self-nucleated crystallites obtained are carefully examined using decoration and shadowing microtopographic methods of electron microscopy. Thus, the different mechanisms by which the {001} form may grow are shown: layer-by-layer growth is regularly followed by Frank's spiral mechanism when the crystals are grown in "wet" conditions. The interpretation of the more or less complex spiral growth patterns leads to the knowledge of the layer-stacking sequences (L.S.S.) involved in the exposed ledges of the associated screw dislocations i.e. of the generated polytypes.

Furthermore, in the case of high strength grown-in dislocations, we demonstrate that the short period substructures, on which the L.S.S. are based, correspond to the mica basic structures. These basic structures, which are polymorphs in the usual sense, were growing during the earlier nucleation and layer-growth stages. The nature as well as the number of the various polymorphs and polytypes found on the investigated mica species are reported. It is shown that the widespread short period L.S.S. of micas may be either polymorphic or polytypic structures, depending on their growth mechanisms. Moreover, the fact that long period L.S.S. of these synthetic crystals are generated from spiral growth strongly suggests that this latter growth process may originate natural complex polytypes too.

GROWTH MECHANISM OF SOME CLAY MINERALS

I. Sunagawa, Y. Koshino, M. Asakura and T. Yamamoto,  
Sendai, Japan

To investigate the growth mechanism of some clay minerals, gold decoration method of electron microscopy was applied to kaolinite, dickite, nacrite, sericite, and chlorite of different origins. A small amount of gold was evaporated onto the samples which were heated at about 400°C in vacuum of  $10^{-5}$  Torr, followed by carbon coating. The samples were then dissolved in HF solution to obtain carbon coated foils for observations under the electron microscope. Since gold crystallites are preferentially nucleated along the growth steps of mono-molecular heights if adequate amount of gold is evaporated, microtopographs of as-grown surfaces of such tiny crystals as clay minerals can be investigated in detail, which otherwise is almost impossible to study.

It was found that all crystals, which have been investigated so far, of kaolinite, dickite, nacrite, sericite and chlorite formed by hydrothermal metasomatism exhibit beautiful growth spirals of various types, definitely proving that they were grown by spiral mechanism. This in turn suggests that these crystals should have been grown from solution phases, and not by solid state crystallization. Various interlacing patterns are also universally seen on the corners of growth spirals of dickite, nacrite and sericite, but not on kaolinite. On the basis of morphological analyses of the interlacing patterns, it was possible to deduce the stacking modes of unit layers in each structure, thus identifying polytypes.

Sericite and chlorite in metamorphic rocks exhibit quite different surface microtopographic characteristics from those formed by hydrothermal metasomatism, suggesting that the growth mechanism of crystals in regional metamorphic environment is somewhat different from that in hydrothermal metasomatic environment. However, these crystals also exhibit mono-molecular growth layers, showing that they were formed by layer-by-layer mechanism, which in turn proves the growth from solution phases.

INVESTIGATION OF PHYSICOCHEMICAL CONDITIONS OF NATIVE GOLD DEPOSITION

M.S.Sakharova, Yu.A.Batrakova, S.K.Ryakovskaya, Moscow, USSR

Process of gold accumulation on sulfide minerals from water gold-containing solutions and Au-Ag systems in the temperature interval from 20 to 80°C and normal pressure have been experimentally studied. It has been established that the process of Au deposition on sulfides take place due to electrochemical interaction of Au-containing solution and minerals. There has been shown the dependence of this process on electrochemical properties of minerals in particular on their positions in the row of tension. Cathodic and anodic processes occurring on pyrite, pyrrhotite and galena were studied by the polarisation curves method for the elucidation of the gold deposition kinetics. The high electrochemical activity of pyrite and the possibility of gold being deposited on it in the wide interval of Eh(+820 - -200mv) has been confirmed. The narrower interval of Eh during gold deposition on pyrrhotite (+720 - +40mv) and galena (+380 - +50mv) has been found. The codeposition of Au and Ag out of Au-Ag systems has been studied and solid Au-Ag solutions identical with native gold have been produced. The dependence of the composition of this solid solutions from an Au-Ag ratio in water solutions has been studied. Experimental data explain the close connection of gold with pyrite in natural deposits. They can be used for the determination of physicochemical conditions and a mechanism of native gold formation during hydrothermal process.

THE "STRUCTURE" OF HYDROTHERMAL SOLUTIONS AND THE GROWTH OF CRYSTALS

I.G.Ganeev , USSR

The theory of mineral genesis and growth of crystals is based partially on hydrothermal synthesis with its typical temperature gradient. In general it is assumed that the growth of crystals is the result of the formation of oversaturated solutions. The hydrothermal synthesis of quartz and corundum however shows that this is necessary but not sufficient for the growth of crystals.

The temperature gradient of electrolyte solutions (NaCl, NaF, Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>) shows a differentiation of acid and alkaline solution caused by the hydrolysis of the salts. There exists a direct dependence of the composition of the solution on the temperature and the temperature gradient.

From these results a model for hydrothermal growth of crystals is deduced. The material is dissolved in a lower alkaline zone, the solution migrates upwards where it is hydrolyzed by the acid solution whereby the material crystallizes.

This model is verified by the cinetics of hydrothermal growth of quartz and corundum depending on the temperature gradient. The process described is probably the same in natural crystallization of minerals.

Symposia:

Commission on Cosmic Mineralogy

Tuesday, September 17, 1974

Chairman: D.P. Grigoriev  
Secretary: K. Keil

Thermodynamics in Experimental Mineralogy and Petrology  
(IUGS-Commission on Experimental Petrology)

Tuesday, September 17, 1974

Part I: Chairmen: W.S. Mackenzie  
W. Schreyer

Wednesday, September 18, 1974

Part II: Chairmen: P.J. Wyllie  
E. Althaus

Mineral Physics

(Inter-Union Commission on Geodynamics, Working Group 5)

Tuesday, September 17, 1974

Chairmen: O.L. Anderson  
R. Leckebusch

## COMPOSITION, ORIGIN AND IMPLICATIONS OF LUNAR GLASSES

Klaus Keil, Albuquerque, New Mexico, USA

At least two types of glasses have been recognized in lunar samples, those of igneous and those of shock origin. Others (e.g. the orange glass of Apollo 17) are of uncertain origin, and are interpreted as being formed by fire-fountaining or by impacts into a liquid lava lake. Igneous glasses, for example, occur in the interstices of mare basalts and are interpreted as in situ late stage differentiation products, sometimes representing two immiscible liquids, one iron- and one silica-rich. Glasses of shock origin are the rare diaplectic variety (formed by solid state transformation of plagioclase), and the common shock-melted glass fragments and beads that are abundant constituents of the loose fines and breccias.

Here, textures, physical properties, and compositions of glasses are reviewed in an attempt to unravel their origin. In particular, emphasis is given to the shock-melted glasses and it will be shown that, although they sometimes represent mixtures formed in the regolith and are slightly affected by vapor fractionation and condensation, most appear to be the compositional equivalents of major lunar mare and highland rock types. In fact, most major lunar rock types [e.g. mare basalts; ANT(anorthositic-noritic-troctolitic rocks); alkalic high-alumina basalt (KREEP); low-alkali high-alumina basalt; peridotite] are represented among the shock-melted glasses. Together with lithic fragments, rake samples, and hand specimens, glasses are valuable indicators of the petrogenetic history of the moon, lending additional support to the proposition, that lunar petrogenesis can be explained in terms of the following four basic events or processes: (1) differentiation of at least the outer part of the moon, with creation of the cumulate feldspathic crust and deeper, more mafic layers; (2) a melting or remelting event which produced KREEP basalt and perhaps other similar materials from the feldspathic part of the crust; (3) intense bombardment by planetesimals and/or meteorites which fragmented, dispersed, mixed, and locally remelted the cumulate rocks and KREEP materials; (4) a melting or remelting event which produced mare basalts from the mafic rocks in the interior, most likely from the residual iron-rich, radioactive-element-rich fraction of the early differentiation.



DIAPLECTIC MINERALS, GLASSES AND HIGH-PRESSURE PHASES FROM  
IMPACT STRUCTURES OF THE USSR

V.L.Masaitis, Leningrad, USSR

On the USSR territory diaplectic minerals, diaplectic glasses and high-pressure phases at the first time were found in Popigaian astrobleme in 1970 and following years. After that diaplectic minerals and glasses were discovered in some other round morpostructures the genesis of which was not clear. According to the known geological data it is possible to recognize these ring structures as astroblemes: Puchez-Katunki, Kara, Boltys, Kaluga, Jänisjärvi, Iljinzy, Mishina Gora, Rotmistrovka. Their diameters are from 2 to 80 km.

Diaplectic minerals and diaplectic glasses are found in shock-metamorphosed crystalline rocks included as fragments in different types of breccias or forming the fractured base of impact structures and also in impactites of all named astroblemes. Diaplectic minerals are quartz, feldspars, pyroxenes, amphiboles, biotite and other having fractures, cleavage, planar features, shock twinning, and kink bands. Diaplectic glasses (tectomorphic minerals) have the composition of quartz and feldspars, they are often recrystallized due to the influence of high resistant temperature.

In impactites of Popigaian astrobleme there were found high-pressure phases - coesite and diamond. Coesite is included in quartz diaplectic glass, due to the action of heat it was partly inverted to crystobalite and quartz. Products of the same inversion were observed in shocked rocks of some other astroblemes. Diamond with lonsdaleite originated due to polymorphic transformation of graphite from the crystalline rocks of the base of astrobleme.

The investigation of some transformations of minerals and the comparison with the experimental data allow to draw a conclusion about the dynamic and temperature conditions in the impact structures of cosmic origin.

THE ROCHECHOUART-CHASSENON IMPACTITES: A PROGRESS REPORT

F.Kraut, Paris, France

A study of the spatial distribution of the rocks directly related, or owing their specific properties, to impact effects in the Rochechouart-Chassenon area show that they are restricted inside a ring 13 km in diameter. The breccias of highest shock grade are located in the central parts of the ring, between the localities of Babaudu and Valette.

Shock-effects, through mineralogical evidence, are seen to increase upwards, from the shatter cone zone in the structure basement. Are successively observed from the bottom:

- 1) breccias in which the constitutive crystals show no evidence of deformation or modification process;
- 2) breccias on an upper level in which the mineralogical properties are indeed affected but where crystals are still present as individual entities;
- 3) and rocks on top in which crystals have welded into a fusion glass.

This sequence is especially conspicuous on micrographic documents.

## NEW RESULTS ON THE ORIGIN OF THE RIES CRATER

W.v.Engelhardt, Tübingen, Germany (FRG)

From July 1973 until January 1974 a new hole has been drilled, 1206 m deep, within the central basin of the Ries crater. A complete series of cores has been obtained of 324 m lake sediments and 882 m crater filling breccias. Based on a first examination of these cores and recent investigations on the petrography of crystalline Ries breccias a summarizing report will be given on the structure of the crystalline basement before the Ries event, the formation of the primary crater and its later modification.

## RIES CRATER BRECCIAS AND PLANETARY IMPACT FORMATIONS

D.Stöffler, Tübingen, Germany (FRG)

As the lunar Apollo missions revealed new evidence for the existence of large and even global impact-produced ejecta formations formed in the early lunar history, the study of the geologic-petrologic properties and the origin of various types of impact breccias at large terrestrial craters have become more and more important for some basic problems of the early geological evolution of the terrestrial planets.

At the Ries crater, Germany, which is the only major terrestrial impact structure where most of the ejecta blanket is reserved and available for unlimited investigation (contrary to lunar and meteoritic breccias) two quite different types of breccias are most conspicuous in the ejecta blanket: a lower, weakly shocked, more or less continuous breccia unit called Bunte Breccia which represents the upper 700 - 800 m of the pre-crater section (predominantly Mesozoic sediments), and a upper, highly shocked, discontinuous and much thinner breccia unit called suevite which originates from a deeper and more central part of the crater (predominantly crystalline rocks). The following properties were measured on both breccias: grain size distribution, petrographic modal composition, degree of shock metamorphism of the constituent particles as well as geological setting, distribution and volumetric properties with respect to the crater size and topography. These properties and experimental and theoretical data from high-velocity impact cratering suggest that Bunte Breccia was ejected continuously through ballistic trajectories during the time of crater growth whereas suevite seems to be formed essentially by a fallback mechanism of later high angle ejecta which got mixed with vapourized rock material.

The possible analogy of these breccias and their mechanism of formation to lunar surface metabreccias such as the Fra Mauro formation will be discussed with respect to petrographic and grain size data of Apollo 14, 15 and 16 breccia samples.

IN SITU X-RAY FLUORESCENCE ANALYSIS OF THE MARTIAN  
SURFACE FINES: THE U.S. 1975-76 VIKING MISSION

Benton C. Clark, K. Keil, A. K. Baird, H. J. Rose and P. Toulmin

Two spacecraft will be soft-landed on the surface of Mars as part of the Viking mission to explore this planet in 1976. These two landers plus the two orbiters which accompany them contain scientific payloads which are unprecedented in the U.S. planetary exploration program, both for the breadth of the investigations (life detection, organic chemistry, geochemistry, geomorphology, seismometry, meteorology, soil physical and magnetic properties, radio science, atmospheric water vapor distribution, and soil thermal properties and state) and the sophistication of the instruments which accomplish these measurements.

Although the primary mission is the search for life, sufficient instrumentation is included to allow a comprehensive analysis of the nature of regolith. Fines (<2mm) and bulk samples of coarse material (2-10mm) will be analyzed by an X-ray fluorescence spectrometer instrument employing radioisotope sources and energy-dispersive spectral measurements to identify major, minor and high-trace element components. In typical geological specimens, the elements detected are magnesium, aluminum, silicon, potassium, calcium, titanium, iron, rubidium, strontium, and zirconium. All other elements in the periodic table are also detectable if present in sufficient amounts (typically 50 to 1000 ppm), except the very light elements: hydrogen through sodium. In addition, the effects of particle size for inhomogeneous specimens has received preliminary evaluation.

Conclusions of geologic significance will require the evaluation of these geochemical results in the context of the results of other experiments: imagery will provide spectral data in 3 visible and 3 infrared bands, with structural data down to a resolution of 1 mm; organic analysis will provide semiquantitative data on water content, carbonates, and other thermally-labile compounds; magnetic and physical properties studies will provide important bounds on the possible mineralogies; and orbital data on landing site, morphology and infrared spectrum will greatly aid in the definition of the geologic setting.

ELECTRON MICROPROBE EXAMINATION OF INHOMOGENEITIES IN TEKTITES

Stanley V. Margolis and Virgil E. Barnes, Austin, Texas, USA

Barnes pointed out at a Western Meeting of the American Geophysical Union that all exposed tektite surfaces have been etched and that the only original tektite surfaces remaining have been preserved where australite flanges have been tightly welded to the body of the tektite (Tr. AGU, 43, 466, 1962). Petrographic study of plates cut from australites show that a thin zone at the surface of the body of tektites beneath flanges is composed of glass having a much wider range of refractive index than the body of the tektite as a whole. This thin inhomogeneous zone was dragged into flanges at the time australites were ablated and because of this flanges have a similar degree of inhomogeneity. Refractive index reflects composition; therefore, the wider the range of refractive index the wider will be the range in composition.

When the range of composition has been determined more will be known about the character of the fiery mist through which australites were propelled while they were still molten, and this in turn will give information about the impacted surface from which all of this material came. Inhomogeneity in the layered Muong Nong-type tektites is also being investigated; and an inventory is being made of detrital mineral inclusions and their melt products found in Libyan Desert glass.

## RECENT RESULTS OF THE INVESTIGATION OF MOLDAVITES

Rudolf Rost, Prague, CSSR

The report is based on all significant papers of the author and of other scientists dealing with the Czech and Moravian moldavites which appeared in the last 5-10 years.

According to V.Bouška, J.Konta, K.Žebera etc. the earliest sediments are Upper Miocene in age. A smaller part of tektites occur in (or close to) the primary strewn field of their fall from the atmosphere. The majority of other moldavites were later redeposited by water. Two moldavites were found on the northern margin of Prague in the terrace gravels of the Vlatava river. One noteworthy double moldavite described by V.Bouška and R.Rost has recently been found in the classic area of moldavites S of České Budejovice. The surface of moldavites was also studied by scanning microscope. Since 1973 moldavites have been mined for jewellery purposes. An approximate calculation of the total amount of moldavites made in 1968 was confirmed as correct. According to J.A.Dolgov and his co-workers (1969) small bubbles in moldavites enclose a weak vacuum with the content of CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, noble gases etc. (H<sub>2</sub>S or SO<sub>2</sub>).

Micromoldavites have so far not been found in Czechoslovakia. The fragments of volcanic glasses encountered in Tortonian sediments in Lipník and Bečvou (Moravia) cannot be identified as micromoldavites or as glasses from the Bavarian molasse.

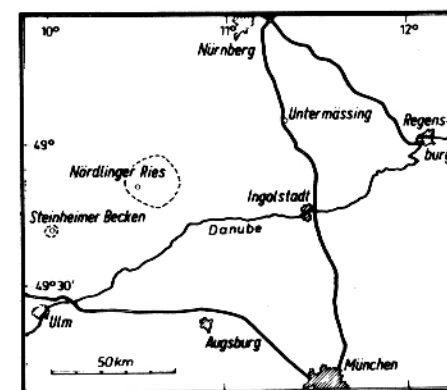
The Ries crater is regarded as a source of Czechoslovak moldavites by J.Konta and V.Bouška from the Charles University, Prague. These two scientists along with W.Gentner, E.David etc. assume that a part of rock material was transformed into gas and thus separated from the glass of the Ries crater.

## THE METEORITE OF UNTERMÄSSING

H.Strunz, West-Berlin, Germany

May I call the attention to a meteorite which was found in 1920 near Untermässing in Bavaria, 60 km ENE of the Ries, in a straight direction Steinheim-Nördlingen-Untermässing-Prague. This iron meteorite has the weight of 70 kg (Acta Albertina Ratisbonensia 20, 1951/52); it is an octahedrite, as mentioned by Heide, 1957 (Kleine Meteoritenkunde, p.129).

The meteorite belongs to the "Naturhistorischer Verein" in Nürnberg, and after the museum was completely burned down during World War II, we found it in the cellar in 1948 as the only conserved object of the earlier collections. It has the form of a rather exact rotation ellipsoid. It was completely undamaged and we were allowed to saw off a 188 grams specimen. This specimen now is in "Staatliches Forschungsinstitut für Angewandte Mineralogie" in Regensburg, and some years ago we got from there a 1.96 grams sample to Berlin for a polished section. According to E.Seeliger in our institute in Berlin, it is a rather finegrained octahedrite, with much more plessite than kamacite and taenite; about 1.5 vol% are schreibersite. Also cohenite, graphite, and chromite inclusions in the schreibersite have been observed. A microprobe investigation is in progress. At the present I only will express the opinion that this meteorite may be a part (or a little brother) of the unknown huge meteorite, responsible for the Ries impact.



THE METEORITE "DOR EL GANI" (INCLUDING A CONTRIBUTION OF  
THE ORIGIN OF WIDMANSTÄTTEN STRUCTURE)

A.Mücke, E.Seeliger and E.Klitzsch, West-Berlin, Germany

The meteorite "Dor el Gani" was found in 1972 in the southern foreland Dor el Gani (16° 02 E; 26° 5730' N; Sahara).

The shape of the Fe- Ni- meteorite (weight 2575 g) points to a monotonous flight within the atmosphere of earth. This part of the meteorite which pointed towards the earth during the flight has been heated by friction of air, resulting in a heat shield which flow towards the back of the meteorite (heat shadow). By a bulge the heat shield is connected with the concave, scarred developed back part of the meteorite.

The chemical composition is 92.4 weight % Fe and 7.35 % Ni. Traces of Co, Cu and Zn are present. The structure is octahedric with wide kamacite lamellae.

Finally the origin of Widmanstätten structure will be discussed based on results from 1. Fe- Ni- melts and

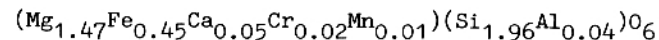
2. Fe- Ni- alloys heated above the Curie point.

1. and 2. were cooled under conditions of free fall.

CRYSTALLOGRAPHIC STUDIES OF A BRONZITE  
IN THE JOHNSTOWN ACHONDRITE

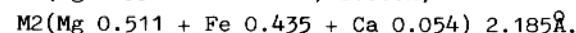
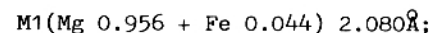
Masamichi Miyamoto, Hiroshi Takeda and Yukio Takano,  
Tokyo, Japan

X-ray studies of a bronzite in Steinbach, a stony-iron meteorite, show an exceptionally high degree of Mg-Fe ordering of the M1 and M2 sites, compatible with slow cooling that have been deduced for the development of Widmanstätten structure in the 700-500°C range<sup>1</sup>. This paper deals with an orthopyroxene (U.S.N.M. No.746) in Johnstown. The chemical and crystallographic data are:



(analysis by A.M.Reid); a 18.276(7) b 8.861(4) c 5.201(3).

The crystal structure has been refined in space group Pbca by the least-squares method using X-ray intensities measured by a diffractometer with MoK $\alpha$  radiation and graphite monochromator. The residual was 0.045 for 948 observable reflections. The determined site occupancies and the mean bond distances are:



The distribution coefficient  $k = (\text{Fe}/\text{Mg})_{\text{M1}} / (\text{Fe}/\text{Mg})_{\text{M2}} = 0.054$ , suggests that the hypersthene achondrite underwent slow cooling process similar to that of Steinbach.

The anisotropic temperature factors were not as large as those expected from the presence of weak diffuse streaks<sup>2</sup>, which have been interpreted to have been produced by Ca-rich GP zones as was found in the Stillwater orthopyroxene by an electron microscope<sup>3</sup>. The fact is also compatible with slow cooling and may be useful in deducing the cooling rate of this group of meteorite.

1. Reid, A.M., Williams, R.J. and Takeda, H. (1973) *Meteoritics* 8, 66. Takeda, H. (1973) Abstr. Annual meeting, Miner. Soc. Japan.
2. Takeda, H. (1972) Abstr. Geol. Soc. Amer. 4, 684, Minneapolis.
3. Channpness, P.E. and Lorimer, G.W. (1973) *J. Meteor. Sci.* 8, 467-474.

TAURUS-LITTROW TiO<sub>2</sub>-RICH BASALTS: OPAQUE MINERALOGY AND  
GEOCHEMISTRY

Ahmed El Goresy, Paul Ramdohr, Olaf Medenbach, and  
Heinz-Jürgen Berhardt, Heidelberg, Germany (FRG)

Two distinct major rock types with different crystallization paths were recognized among the TiO<sub>2</sub>-rich basalts of the Taurus-Littrow site: a) Type I with the following crystallization sequence: Ulvöspinel + minor olivine → armalcolite → titanaugite + pigeonite → ilmenite → plagioclase + cristobalite. b) Type II with the following crystallization path: Ulvöspinel + olivine → armalcolite → ilmenite → titanaugite → plagioclase + tridymite. Of the studied basalts, samples 70035, 70017, 79155 and numerous lithic fragments in 74242 belong to type I, whereas samples 70215, 72015, 74275, 74243, and the majority of lithic fragments in 74242 belong to type II. Tan armalcolite was only encountered in type I rocks and gray armalcolite is confined to type II rocks. Numerous electron microprobe analyses of both armalcolite types indicate a compositional bimodality, whereby the gray variety shows higher MgO and Cr<sub>2</sub>O<sub>3</sub> contents than the tan armalcolite.

Secondary ilmenite rims around armalcolite are formed by one or a combination of the following processes: a) reaction between basaltic liquid and armalcolite b) reaction between armalcolite and ulvöspinel c) reaction between Fe<sup>0</sup> and armalcolite d) breakdown of armalcolite to ilmenite + rutile e) overgrowth of precipitating ilmenite around armalcolite. Reaction b was not reported before from the lunar samples. Reactions a, b, and c cause a strong partitioning of Mg and Cr between armalcolite and ilmenite with preference of these elements to armalcolite. From reaction b, a secondary titanian aluminian chromite with a composition different from secondary chromites formed by subsolidus reduction of ulvöspinel is also generated. The majority of secondary ilmenites formed by reactions a and b could be distinguished from coexisting primary ilmenites since these secondary ilmenites show higher Cr<sub>2</sub>O<sub>3</sub> concentrations. A unique lithic fragment consisting of major metal + chromite + minor silicates was encountered in sample 74242. This fragment probably originated from a metal rich lense of a late differentiate in the Apollo 17 landing site.

THERMODYNAMICS IN EXPERIMENTAL MINERALOGY AND PETROLOGY

S y m p o s i u m

Sponsored by the IUGS-Commission on Experimental Petrology

HIGH-TEMPERATURE SOLUTION CALORIMETRY WITH APPLICATION TO  
PRESSURE-TEMPERATURE STABILITY RELATIONS IN REFRACTORY SYSTEMS

O.J.Kleppa and R.C.Newton, Chicago, USA

The methods of solution calorimetry yield heat of formation data on minerals which make possible thermodynamic calculations of the temperature-pressure stabilities of minerals and mineral assemblages. These data are valuable because they provide checks on experimentally-determined P-T stability curves of minerals. Moreover, in two classes of systems the thermochemical method may be the only reliable means of determining equilibrium relations. These are phase relations, especially of hydrous minerals, at very low temperatures, as, for instance, the blueschist assemblages, and phase relations of anhydrous minerals at moderate temperatures which form in the deep crust and upper mantle under conditions of very low water pressure. In the first case, reaction kinetics in the range below 400°C may be too slow to obtain reversal of equilibria in feasible laboratory times even in the presence of an aqueous flux. In the second case a high pressure aqueous flux may create micas, amphiboles or melt and so obscure the desired anhydrous relations.

Newly developed methods of high temperature oxide melt solution calorimetry have provided thermochemical data pertaining to the problem of anhydrous mineral stability at moderate and high temperatures. In this method a calorimeter solvent of molten lead borate is used at temperatures of 700° - 1100°C. Many refractory minerals in the system CaO - MgO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> dissolve readily in this melt. Some of these are quite insoluble in HF, and so, have not yielded to low-temperature aqueous calorimetric methods. Heats of formation for spinel, aluminum silicates, and minerals in the system MgO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> have been determined by the new technique. For some of these minerals no previous reliable data existed. New heat of formation data for several refractory phases are tabulated below.

Subsolidus phase relations in the system MgO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> in the range 400°C - 1500°C and 0-30 kilobars have been compiled, making use of the new thermochemical data, along with available experimental work. Several principal conclusions have resulted:

- 1) The solution of Al<sub>2</sub>O<sub>3</sub> in enstatite is very nearly accounted for thermochemically as ideal solution of the Mg-Tschermak's molecule. Many equilibria involving aluminous enstatite are strongly curved owing to the high entropy of Al<sub>2</sub>O<sub>3</sub> mixing in enstatite.
- 2) The stability relations of sapphirine are highly variable from sample to sample. The disordered 2:2:1 form which may be prepared at high pressures has an absolute lower stability limit of about 700°C. The natural ordered 7:9:3 form has a much lower absolute stability temperature limit.
- 3) Cordierite, both synthetic and natural, has an upper pressure limit of about 8 kilobars.
- 4) The lower-pressure stability boundary of pyrope has a  $\frac{dP}{dT}$  slope of 15-18 bars/°C over the range of conditions considered. Minimum stability pressure is about 14 kilobars.

PREDICTION OF PHASE DIAGRAMS WITH THERMOCHEMICAL DATA DEDUCED FROM LIMITED EXPERIMENTAL PHASE EQUILIBRIUM DATA

E.J.Essene, Ann Arbor, Michigan, USA

No abstract submitted

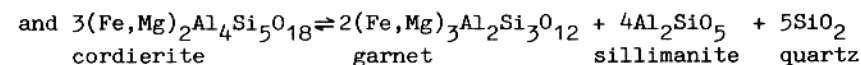
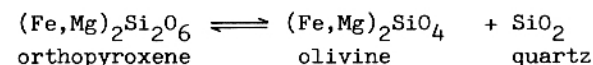
THE APPLICATION OF THERMODYNAMICS TO SUBSOLIDUS EQUILIBRIUM INVOLVING SOLID SOLUTIONS

Bernard J.Wood, Manchester, U.K.

Experimental data on either simple or complex systems cannot be directly applied to rocks without an understanding of the mixing properties of solid solutions. Many equilibria in systems involving complex solid solutions can be quantitatively calculated from experimental data on simple systems by using appropriate thermodynamic models of the solid solutions involved. The application of solution models to the subsolidus regions of a number of systems of petrological interest will be discussed. Examples will be drawn from the following:

(a) Systems involving Fe-Mg solid solutions

The effect of varying Fe/Mg ratio on reactions involving ferromagnesian silicates will be considered. The reactions:



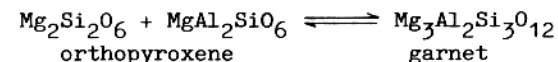
will be taken as examples.

The distribution of Fe<sup>2+</sup> and Mg<sup>2+</sup> between coexisting minerals and the dependence of partition coefficients on temperature, pressure and composition will also be discussed.

(b) Systems involving limited solid solutions

Examples to be considered will include

1. K AlSi<sub>2</sub>O<sub>6</sub> - SiO<sub>2</sub> solid solutions
2. CaMgSi<sub>2</sub>O<sub>6</sub> - Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> solid solutions
3. Experimental data on the reaction:



are consistent with a simple model of Mg-Al mixing in orthopyroxene. Experimental data on more complex orthopyroxene-garnet pairs are consistent with the data on the Mg-Al system and with simple models of Mg-Fe-Ca-Al orthopyroxenes and Ca-Mg-Fe garnet solutions.

THERMODYNAMICS OF ELEMENT DISTRIBUTION IN EXPERIMENTAL MAFIC SILICATE-LIQUID SYSTEMS

P.L.Roeder, Kingston, Canada

Thermodynamic models used to describe the equilibrium between crystalline phases and the basic or ultrabasic silicate liquids found in nature have not been very successful because of the chemical complexity of the phases. The major effort in this field has been in developing empirical freezing point depression and chemical exchange equations from experimental and field data. Freezing point depression equations are necessary in order to predict the temperature of crystallization of a phase when the amount of various species present in the liquid is known. The chemical exchange equations are useful for predicting the composition of crystalline phases as a function of temperature and the ratio of species in the liquid. Equations describing the equilibrium between crystals and liquid are considered for olivine, plagioclase and spinel.

The equilibrium between olivine and basic liquid can be described by empirical freezing point depression equations. These equations are affected by changing liquid composition, for example increasing alkalis in the liquid decreases the solubility of both magnesium and ferrous iron relative to olivine. Because of the similarity of the magnesium and ferrous iron species in the liquid both are affected in a similar fashion. Thus the ratio of activity coefficients is essentially constant and the chemical exchange equilibrium as expressed by the distribution coefficient is insensitive to changes in temperature and liquid composition.

Chemical exchange equations have been written (Kudo and Weill and Mathez) for the plagioclase-liquid equilibrium and these unlike the olivine-liquid equilibrium have a fairly large temperature coefficient and thus they are useful as a geothermometer. Presumably the large temperature coefficient is because of relative differences in Al and Si polymerization in the liquid as a function of temperature.

Equations describing the spinel-liquid equilibrium have to take into account the complex nature of the spinel solid solution. This solution is far from ideal and thus the  $Mg^{+2}:Fe^{+2}$  ratio in the spinel is sensitive not only to this ratio in the liquid but to the ratio of  $Fe^{+3}$ ,  $Cr^{+3}$ ,  $Al^{+3}$  and  $Ti^{+4}$  in the spinel structure.

THERMODYNAMICS OF EXPERIMENTAL SUB-SOLIDUS SILICATE SYSTEMS INCLUDING MIXED VOLATILES

G.B.Skippen, Ottawa, Canada

The application of thermodynamic theory to mixed volatile systems generally presumes that natural systems approach a state of chemical equilibrium. Experimental data can then be used to construct petrologic models that are based on the equation.

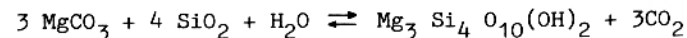
$$\sum_i v_i \mu_i = 0$$

where  $v_i$  and  $\mu_i$  are the stoichiometric coefficient and the chemical potential of each component,  $i$ , in an equilibrium. In many experimental studies where the phases involved consist of a single component, it has been customary to make no distinction between components and phases. In mixed volatile systems, at least one of the phases, the fluid, contains two or more components and it is necessary to recognize that the energy balance in the above equation exists among components rather than phases.

A convenient relationship for consideration of experimental data can be derived from the above equation.

$$\frac{d \ln K}{d 1/T} = \frac{-\Delta H^{\circ}_R}{R}$$

The equilibrium constant,  $K$ , in this equation must be measured experimentally for each independent equilibrium under consideration. There exist four distinctly different methods for measuring  $K$  in mixed volatile systems: (1) The calorimetric method. (2) The extent of reaction method. (P.Metz) (3) The gas analysis method. (H.Greenwood, W.Johannes) (4) The solid-phase buffer method (H.Eugster). The consistency of results obtained by each of the four methods can be demonstrated by data for the equilibrium.



A review of additional experimental data for a typical mixed volatile system,  $CaO-MgO-SiO_2-CO_2-H_2O$ , indicates sufficient data to calculate a model for siliceous carbonate rocks. The model expresses the stability field of common mineral assemblages as functions of temperature, total pressure, fluid composition, and carbonate phase composition.



## THERMODYNAMICS OF MELTING IN EXPERIMENTAL SILICATE-VOLATILE SYSTEMS

C. Wayne Burnham, Pennsylvania, USA

The thermodynamics of melting in rock-forming silicate-volatile systems was first elucidated by Goranson (1938) using experimentally determined phase equilibria in the systems  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  and  $\text{KAlSi}_3\text{O}_8\text{-H}_2\text{O}$ . In the ensuing 36 years, and especially in the past 17 years, several efforts have been made to deduce thermodynamic relations in these systems from experimental data on melting and solubility relationships. These efforts have met with only limited success due largely to lack of fundamental thermodynamic data on the pure phases and to rather large uncertainties on the slopes of experimentally determined phase boundaries. Within the last five years, however, the experimental and thermodynamic data necessary to calculate phase equilibrium relations in many rock-forming silicate- $\text{H}_2\text{O}$  systems have become available. Unfortunately, data on volatiles other than  $\text{H}_2\text{O}$  are insufficient for a comparably rigorous thermodynamic analysis of their role in the melting of rock-forming silicates.

The system for which the most data are available is  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ . Published thermodynamic data on  $\text{H}_2\text{O}$  and  $\text{NaAlSi}_3\text{O}_8$  glass, combined with experimental  $\text{H}_2\text{O}$  solubility and P- $\bar{V}$ -T data, provide the basis for calculation of the pressure, temperature and compositional dependence of the thermodynamic functions for both the  $\text{H}_2\text{O}$  and  $\text{NaAlSi}_3\text{O}_8$  components in the melt phase. The chemical potential function for the  $\text{H}_2\text{O}$  and  $\text{NaAlSi}_3\text{O}_8$  components, when combined with published thermodynamic properties of albite and  $\text{H}_2\text{O}$ , enable calculation of the phase relations in this system as a function of pressure, temperature and composition. The calculated and experimental phase relations agree within experimental error up to 10 kilobars for all  $\text{H}_2\text{O}$ -bearing compositions.

The fugacity ( $f_w^m$ ) or activity ( $a_w^m$ ) of  $\text{H}_2\text{O}$  in the melt phase has been found to vary linearly with the square of its mole fraction ( $X_w^m$ )<sup>2</sup> for values of  $X_w^m \leq 0.5$ , on the basis that one gram formula weight (GFW) of  $\text{NaAlSi}_3\text{O}_8$  constitutes the

effective mass of anhydrous melt that interacts with one GFW of  $\text{H}_2\text{O}$ . For  $X_w^m > 0.5$ ,  $f_w^m$  varies exponentially with  $X_w^m$ ; thus, Henry's law for a dissociated solute is obeyed for  $X_w^m \leq 0.5$ , but not at higher values of  $X_w^m$ .

These relationships, as well as other lines of evidence, are consistent with a solution model for  $\text{H}_2\text{O}$  in  $\text{NaAlSi}_3\text{O}_8$  melts that involves two types of reaction. For the first GFW of  $\text{H}_2\text{O}$ , the solution reaction may be represented by  $\text{NaAlSi}_3\text{O}_8 + \text{H}_2\text{O} = \text{AlSi}_3\text{O}_7(\text{OH}) + \text{NaOH}$ ; additional  $\text{H}_2\text{O}$  then enters the melt by the reaction,  $\text{AlSi}_3\text{O}_7(\text{OH}) + n\text{H}_2\text{O} = \text{AlSi}_3\text{O}_{7-n}(\text{OH})_{2n+1}$ .

The extension of this simple solution model to aluminosilicate melts of more complex composition, such as igneous rock melts, requires proper definition of the mass of melt that is equivalent to one GFW of  $\text{NaAlSi}_3\text{O}_8$  in its interaction with  $\text{H}_2\text{O}$ . This has been done for several rock compositions, ranging from tholeiitic basalt to Li-rich granite pegmatite, for which experimental data are available on the solubility of  $\text{H}_2\text{O}$  in these melts. These solubilities, when recast on a molal basis equivalent to  $\text{NaAlSi}_3\text{O}_8$ , are all identical within experimental error throughout the pressure range covered.

These results confirm the general validity of the proposed reaction model and establish the system  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  as a quantitative thermodynamic model for hydrous magmas of widely different compositions. Thus, it is now possible to calculate the phase relations in many rock-forming silicate systems that would be difficult to determine experimentally.

MELTING RELATIONS IN SILICATE SYSTEMS WITH WATER AND  
CHLORIDES

I.D. Ryabchikov, Moscow, USSR

1. The data on dissociation of alkali halides in supercritical aqueous solutions and thermodynamic treatment of phase diagram for the system  $\text{NaCl-H}_2\text{O}$  show that both  $\text{H}_2\text{O}$ -rich vapour and  $\text{NaCl}$ -rich liquids in this system are close to ideal solutions (above ca.  $500^\circ\text{C}$ ).

2. The miscibility gap between vapour and chloride-rich liquid at relatively low pressures (below 1.5 kb at the temperatures of granite solidus) is substituted at higher pressures by compositional range where the properties of fluid phase gradually change from those of aqueous vapour to chloride melt with almost constant activities of components. This is corroborated by the experimental data on chloride distribution between water-chloride fluid and granitic melts at  $800^\circ\text{C}$  and 2 kb.

3. Very low solubility of chlorides in acid silicate melts (Kilinc, Burnham, 1972; Ryabchikov, Wall, Burnham, 1974) and rock forming silicates in aqueous solutions together with the discussed above properties of high temperature water-chloride mixtures (exsolution at lower pressures and transitional range at higher pressures) causes the solidus temperatures and solubility of water in silicate melt in the systems rock forming silicate - chloride - water to be nearly identical with those in boundary system silicate - water up to very high concentrations of chlorides in the bulk composition. This is demonstrated by experimental data on the system granite - chlorides - water (Ryabchikov, Hamilton, 1971).

STUDIES OF MINERAL REACTIONS BY HIGH TEMPERATURE SOLUTION  
CALORIMETRY

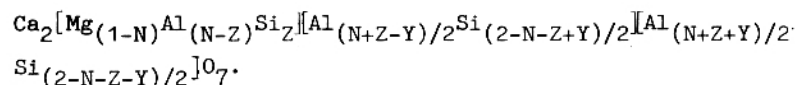
Alexandra Navrotsky, Tempe, Arizona, USA

High temperature solution calorimetry, using molten oxide solvents in a calvet-type twin microcalorimeter at  $700\text{--}800^\circ\text{C}$ , has been applied to the study of a number of solid state reactions in silicates and other oxides. This method has the advantage of requiring quite small amounts of sample; only 300-400 mg of a given phase usually are sufficient. Data are presented on the enthalpy of the olivine-spinel transition in nickel orthosilicate and on the enthalpies associated with partial Al-Si disordering in sillimanite. Development of calorimetry of iron and manganese minerals under atmospheres of controlled low oxygen fugacity is discussed.

THERMODYNAMIC AND CRYSTALLOGRAPHIC PROPERTIES RELATED TO  
Al-Si-Mg ORDERING IN  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$  MELILITE CRYSTALLINE  
SOLUTIONS

D.R.Waldbaum (deceased on 11 April, 1974) and J.A.Woodhead  
Princetown, New Jersey, USA

Equations for the configurational entropy and homogeneous equilibria in  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$  melilites have been derived for two sets of constraints that do not permit Mg on the smaller  $T_2$  sites: (1) When the  $T_2$  sites are topologically equivalent one ordering parameter,  $Z \equiv N_{\text{Si}(T_1)}$ , and one composition parameter,  $N \equiv 1 - N_{\text{Mg}(T_1)}$ , are required and the ordering is non-convergent. (2) When the  $T_2$  sites are not equivalent an additional ordering parameter,  $Y \equiv N_{\text{Si}(T_{2a})} - N_{\text{Si}(T_{2b})}$ , is required and the additional ordering is convergent. For any given melilite, the configurational entropy decreases as Y increases. The structural formula for such a melilite is



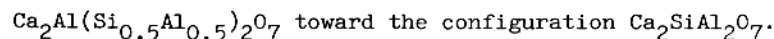
The first set of site constraints correspond to  $P4_2/m$  symmetry. Analysis of this (tetragonal) melilite structure shows that changes in the size of the  $T_1$  and  $T_2$  tetrahedra distort the structure causing changes in the cell parameters  $\underline{a}$  and  $\underline{c}$  (measured at room temperature), where differences between  $\underline{a}$ ,  $\underline{N}$ ,  $\underline{Z}$ , and  $\underline{c}$  for any two melilites in N-Z space are given by:

$$\Delta \underline{a} = -0.162\Delta \underline{N} - 0.098\Delta \underline{Z} \quad (1)$$

and

$$\Delta \underline{c} = 0.055\Delta \underline{N} + 0.102\Delta \underline{Z} \quad (2)$$

Thus as the mol fraction of Si on  $T_1$  increases,  $\underline{c}$  increases and  $\underline{a}$  decreases. In pure  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , this can be due only to Al-Si disordering from the configuration



Cell parameters of quenched synthetic  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  gehlenites annealed between 600 and 1530°C vary with annealing temperature such that  $\underline{a}$  decreases and  $\underline{c}$  increases with temperature. These observations are consistent with the effects of

Al-Si disordering predicted by the structure analysis. A maximum value of  $0.04 \pm 0.01$  for Z at 1590°C (melting point of gehlenite) is inferred from the data. Assuming the vibrational entropy to be independent of degree of order, we obtain:

$$T(^{\circ}\text{C}) = 5300 \left[ \ln \left( \frac{1-Z}{Z} \right) - 2 \operatorname{arctanh} Z \right]^{-1} - 273.15 \quad (3)$$

which relates degree of order - and thus change in cell dimension - with equilibration temperature. These results confirm that at least 2.755 and possibly as much as 3.08 cal mol<sup>-1</sup>K<sup>-1</sup> must be added to the currently accepted entropy data for gehlenite. Annealing studies such as the above can be used as a simple method for self-calibration of any natural iron-free melilite as a single-phase geological thermometer. This method requires extremely high precision and accuracy in determining cell parameters.

V.N.Zyrianov, L.L.Perchuk, Moscow, USSR

As a result of the experimental study, the K and Na distribution between nepheline (Ne) and high and low alkali feldspars (Fsp) at high temperatures (T) has been defined. Systems of the type mineral - aqueous solution of the alkali chlorides (K,Na)Cl<sup>aq</sup> were studied at 1000 kg/cm<sup>2</sup> pressure, while to study the systems mineral - alkali chloride melts (K,Na)Cl<sup>m</sup> sealed quartz tubes and saturated vapor pressure were used (Table).

Experimental work undertaken to study the distribution of K and Na between the equilibrium phases at high temperatures (°C)

Ne <sub>ss</sub>	Fsp <sub>ss</sub> <sup>l</sup>	Fsp <sub>ss</sub> <sup>h</sup>	(K,Na)Cl <sup>aq</sup>	(K,Na)Cl <sup>m</sup>
Ne <sub>ss</sub>	400-1000°	500-1100°	400-500°	800-1100°
Fsp <sub>ss</sub> <sup>l</sup>		500-1000°	400-500°	800-1000°
Fsp <sub>ss</sub> <sup>h</sup>			500-700°	800-1100°

The isotherms of alkali distribution between all the phases of the systems under study were determined. Based on the thermodynamic interpretation of the experimental data, energy of mixing for each phase was estimated and diagrams of the phase relations, Ne-Fsp<sup>h</sup> and Ne-Fsp<sup>l</sup> (mineralogical thermometers) were constructed. They proved to be effective but in the sodic region of compositions for both intrusive and subvolcanic and volcanic rocks.

S.S.Hafner and T.Yajima, Marburg, Germany (FRG)

The Mg(2+), Fe(2+) distribution over the M1 and M2 positions in pigeonite depends on the thermal history of the mineral. Until this time, the crystal structures of pigeonites from four lunar basalts and one terrestrial andesite have been refined using x-ray diffraction. In addition, the average Fe(2+) site occupancies obtained from Mössbauer spectra of pigeonite separates from six lunar basalts have been reported. The pigeonites studied so far have wollastonite components of 5-11 percent and, with one exception, ferrosilite components of 25-36 percent. The terrestrial pigeonite (Isle of Mull) is more ironrich: Fe=52 percent. This consistent body of data allows the following conclusions:

- (1) The natural Mg,Fe distribution coefficients  $k_n$  vary between 0.045 and 0.14, most frequent values being between 0.08 and 0.11.
- (2) The equilibrium temperatures  $T_n$  of the observed natural distributions are between 520 and 840°C, the differences being indicative of significantly different cooling histories. The temperatures generally correspond to  $T_n$  values of orthopyroxenes from basaltic lava flows.
- (3) The standard Gibbs free-energy difference  $G_E^0(1000^\circ\text{C})$  for the Mg,Fe exchange reaction (4-6 kcal/formula unit) is distinctly higher than the corresponding value of orthopyroxene. However, a significant correlation with the wollastonite component cannot be noted in the data. The nature of the apparently large scatter in the  $G_E^0$  values is not yet understood.
- (4) In contrast to the orthopyroxene series there is no evidence yet that the Mg,Fe distribution in pigeonites with a constant wollastonite component can be interpreted in terms of the ideal solution model. For this, the range in chemical composition studied is too small. The peculiarly low value  $k_n=0.045$  of the Mull pigeonite may possibly point to a strong deviation from ideality.
- (5) For semi-quantitative analysis of the cooling history in terms of heat-flow models the rate constants for the exchange reaction at various temperatures are needed. Preliminary studies show the same order of magnitude as for those of orthopyroxene.

DISTRIBUTION OF IRON AND MAGNESIUM BETWEEN BIOTITE AND A  
SALT SOLUTION

S.Schulien, Marburg, Germany (FRG)

The equilibrium distribution of magnesium and iron between synthetic biotites and coexisting (Mg,Fe)-chloride solutions have been studied in the temperature range from 400° - 700°C under water pressures of 200 - 2000 bars. The experiments were carried out with experimental technique described by HINRICHSEN (1967, 1968). The distribution coefficients and the distribution isotherms, represented in ROOZEBOOM-diagrams have been calculated by using the ideal solution models in a least square refinement. In the temperature range from 700° - 500°C, the distribution isotherms have a hyperbolic shape, which accords with the ideal distribution of iron and magnesium between biotite and salt solution.

Computation of the equilibrium constant K for the ion exchange reaction

$$KMg_3AlSi_3O_{10}(OH)_2 + 3 FeCl_2 \xrightleftharpoons{2m KCl} KFe_3AlSi_3O_{10}(OH)_2 + 3 MgCl_2$$

gives values of 0.055 at 700°C to 0.126 at 500°C, respectively. The plot of ln K against 1/T shows a curve with constant slope between 600° and 700°C. In this temperature range, the heat of reaction ΔH can be calculated by using the van't HOFF equation

$$\frac{d \ln k}{dt} = \frac{\Delta H}{RT^2}$$

ΔH has a value of -8,3 kcal/mole between 600° and 700°C. At 550° and 500°C the temperature dependence curve begins to deviate from linearity.

In some ion exchange experiments the biotite was partly transformed to chlorite. This chloritization of the biotites increases with increasing water pressure and decreasing temperature and decreasing potassium content of the salt solutions.

THE THERMODYNAMIC AND EXPERIMENTAL INVESTIGATIONS OF THE  
OPEN MINERAL SYSTEMS

V.A.Zharikov, I.P.Ivanov, Moscow, USSR

Natural mineral systems are well known as the open systems with perfectly mobile components: Experimental and theoretical studies of (natural) mineral equilibria, the geological interpretation of the data have to be based on the major peculiarities of these systems which involve the intensive parameters being independent equilibrium factors for the perfectly mobile components.

A combined program is the best way to investigate these systems. Such a program should consist of:

- a) prognostic topological study of the systems;
- b) experimental key data acquisition;
- c) thermodynamic calculations of the general diagram of the system;
- d) design of the possible petrogenetic models.

The stated above is illustrated by the results of the experimental study performed by the authors on the aluminosilicate systems, characterized by the perfectly mobile regime of water, carbon dioxide, alkali and pH.

THE ENERGETIC THEORY OF MISCIBILITY GAPS IN MINERAL  
SOLID SOLUTION

V.S.Urusov, Moscow, USSR

The theory of regular solutions established the following simple relations between mixing enthalpie  $\Delta H_m$  and mixing energy Q

$$\Delta H_m = x_1 x_2 Q \quad (1)$$

( $x_1$  and  $x_2$  - molar fractions of components 1 and 2 accordingly) and between Q and critical temperature of mixing  $T_{ct}$

$$T_{ct} = \frac{Q}{2R} \quad (2)$$

(R - universal gas constant). These relations are the basis for the estimation of miscibility gaps of solid solutions.

We have developed the energetic theory of  $\Delta H_m$  and Q using the following general equation:

$$\Delta H_m = E_{s.s.} - x_1 E_1 - x_2 E_2 \quad (3)$$

where E - lattice energy (only for pure ionic solids) or atomisation energy (for majority of minerals) of solid solution ( $E_{s.s.}$ ) and pure components ( $E_1$  and  $E_2$ ). The simple crystal chemical model of solid solution based on two additivity rules: the additivity of interatomic distances (Vegard's rule) and effective atomic charges. With these approximations we obtain from (3) and (1) the next main expression:

$$Q = a(\Delta E)^2 + b\left(\frac{\Delta r}{r_1 + r_2 + r}\right)^2 \quad (4)$$

where  $\Delta E$  is the difference of ionicity degrees of pure components,  $\Delta r = r_1 - r_2$  is the difference of radii of substituent ions (atoms), r is the radii of common structural unit for both of components, a and b are semiempirical parameters.

The greater Q the less the limits of isomorphous substitution in according to equation (2). Therefore we conclude from (4): isomorphous limits at given T the less, the more the ionicity difference (electronegativity difference) and the size difference for the isomorphous atomic pair. The other conclusions from (4) deal with the polarity (asymmetry) of substitutions and the influence of size of common structural unit, r in (4): the larger r, the more extensive the miscibility of the same isomorphous pair of elements.

If the bonding characters of components are similar ( $\Delta E \leq 0.05$ ) the equation (4) approximately becomes:

$$Q = b\left(\frac{\Delta r}{r_1 + r_2 + 2}\right)^2 \quad (5)$$

Parameter b in (5) can be estimated by allowing for some crystal data (molar volume, compressibility and so on). Then we obtain the way for determination of miscibility gaps in many mineral systems (oxides, sulfides, carbonates, silicates and etc.) in good agreement with experimental data. The energetic theory allows to predict the influence of the other components in multicomponent systems and the role of polymorphous transitions.

REGULAR SOLUTION MODEL FOR THE  $\text{Fe}_{1-x}\text{S} - \text{Ni}_{1-x}\text{S}(\text{mss})$   
SOLID SOLUTION

S.D.Scott, A.J.Naldrett and E.Gasparrini, Toronto, Canada

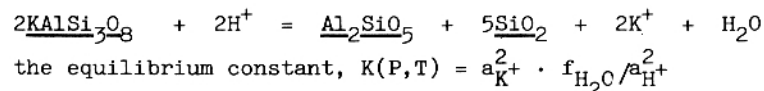
The monosulfide solid solution (mss) of the FeS-NiS-S system extends continuously from the FeS-NiS binary join to more S-rich compositions over a wide temperature range. FeS activities ( $a_{\text{FeS}}$ ) were determined at 930°C for mss by analyzing with an electron microprobe the FeS content of sphalerites which had been equilibrated with the mss in standard evacuated silica tube experiments. Studies on the Zn-Fe-S system have previously shown that between 225° and 1100°C the FeS content of sphalerite is a function only of  $a_{\text{FeS}}$  and this relation is not affected by other elements in sphalerite such as Cu, Cd, Mn or Ni. The sphalerite products contained progressively decreasing amounts of FeS indicating decreasing  $a_{\text{FeS}}$  in the mss passing from stoichiometric FeS (std. state,  $a_{\text{FeS}}=1$ ) to NiS ( $a_{\text{FeS}}=0$ ) and from the FeS-NiS join to more S-rich  $(\text{Fe,Ni})_{1-x}\text{S}$  compositions. Conversely, the Ni content of sphalerite increased systematically across the mss field reaching a maximum of 3.8 mole % NiS on the NiS-S join. The variation of  $a_{\text{FeS}}$  with mss composition fits a regular solution model in which end-member components  $\text{Fe}_{1-x}\text{S}$  and  $\text{Ni}_{1-x}\text{S}$  mix ideally for a given mole % S. The relationship between  $a_{\text{FeS}}$  and mole fraction of FeS in mss ( $x_{\text{FeS}}^{\text{mss}}$ ) is described by  $a_{\text{FeS}} = \gamma x_{\text{FeS}}^{\text{mss}}$  where  $\gamma$  is a function of mole % S in mss as follows: 1.0 at 0 % S, i.e. the solution obeys Raoult's Law on the FeS-NiS join; 0.93 at 5 % S; 0.81 at 10 % S; 0.63 at 13 % S. Variation of  $\gamma$  with temperature is under investigation. The small range in Ni content of sphalerite at 930°C makes it unlikely that  $a_{\text{NiS}}$  can be precisely determined in like manner to  $a_{\text{FeS}}$ . However, we have in progress measurements of  $\text{S}_2$  fugacity ( $=a_{\text{S}_2}$ ) which combined with our  $a_{\text{FeS}}$  data in the Gibbs-Duhem relation will permit calculation of  $a_{\text{NiS}}$ :

THE ORIGIN OF THE ASSEMBLAGE: QUARTZ + AL-SILICATE +  
RUTILE + AL-PHOSPHATE

W.S.Wise, Santa Barbara, California, USA

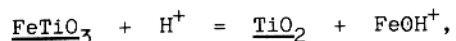
Large bodies of quartz-kyanite or quartz-andalusite occur in several, widely separated localities in the United States and Sweden. These bodies are large enough to be of economic importance, and are characterized by the minerals quartz, Al-silicate (andalusite, kyanite, pyrophyllite), rutile, and Al-phosphate (lazulite, augelite, svanbergite). All the deposits have in common features that are difficult to explain by regional or thermal metamorphism of a sedimentary rock. Some of these features are: massive volumes of rock composed mostly of quartz + kyanite or andalusite with large concentrations of the Al-silicate, pervasive occurrence of rutile as inclusions in all other minerals, rare Al-phosphate minerals in local concentrations, and less common, but persistent tourmaline, topaz, and pyrite.

All of the features of two California occurrences, White Mountains and Cargo Muchacho Mountains, can be explained by an extension of the thermal, ionic equilibria in aluminosilicate assemblages, developed by Eugster (1970, Fortschr.Min.), and  $\text{H}^+$  ion metasomatism, as proposed by Hemley (1964, Econ.Geol.). For example, considering the reaction



can be calculated from available thermodynamic data (Eugster, 1970). Decreases in  $f_{\text{H}_2\text{O}}$  or increases in  $a_{\text{H}^+}$  substantially reduce the stability field of K-feldspar. If one hypothesizes pervasive permeation of  $\text{H}^+$  enriched fluids through a quartz-feldspar meta-volcanic rock, a final assemblage of quartz + Al-silicate can result. If the temperature is above 425°C, andalusite will develop at low pressures and kyanite, at high pressures. Pyrophyllite will form at temperatures below 425°C and in later stages commonly replaces the higher temperature assemblages. The acidic fluid would allow movement of aluminum to form the massive concentrations of Al-silicate, and permit recrystallization of all minerals to large sizes.

In the California occurrences, if rutile forms from ilmenite by a reaction like



the pervasive nature is most easily explained. The early fluids apparently contained sufficient other components to provide fluorine for topaz, boron and fluorine for tourmaline, and sulfur for pyrite.

Later fluids were richer in phosphate and sulfate ions, because Al-phosphate minerals (lazulite, augelite, and trolleite) partially replace Al-silicate along fissures and even later woodhouseite- and alunite-group minerals fill fractures and other cavities.

## EXPERIMENTAL STUDY OF T- $X_{\text{CO}_2}$ LIMITS OF THE ZEOLITE FACIES

I.P.Ivanov, L.P.Gurevich, Moscow, USSR

Laumontite and prehnite stabilities are controlled by temperature and chemical potential of  $\text{CO}_2$  in the fluid, as is shown by topologic analysis of the low-temperature mineral equilibria in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ . The upper temperature limit of the zeolite facies is fixed by decomposition of laumontite into prehnite + montmorillonite + quartz. The replacement of laumontite by the association of calcite + montmorillonite + quartz and kaolinite + calcite + quartz represents the low temperature limit.

Experimental study of the reaction laumontite = prehnite + montmorillonite + quartz at  $P_s = P_{\text{H}_2\text{O}} = 1000$  bars has shown the equilibrium to be established at  $T = 260 \pm 10^\circ\text{C}$ . Equilibrium of reaction laumontite = montmorillonite + calcite + quartz depends on both temperature and  $\text{CO}_2$  content in the solution, its coordinates being  $T = 220 \pm 10^\circ\text{C}$  at  $X_{\text{CO}_2} = 0$ , and  $T = 390 \pm 10^\circ\text{C}$  at  $X_{\text{CO}_2} = 0,1$ . Coordinates of the singular reaction prehnite = calcite + montmorillonite, which represents the lower boundary of prehnite stability field, are  $X_{\text{CO}_2} = 0$ ,  $T = 240 \pm 10^\circ\text{C}$ ;  $X_{\text{CO}_2} = 0,15$ ,  $T = 390 \pm 10^\circ\text{C}$ .

Increase  $P_{\text{CO}_2}$  results contraction of the prehnite and laumontite stability fields and their replacement by clay minerals + carbonate association. These experimental data define the limits of the zeolite facies metamorphism of metabasites at the temperature range  $220\text{-}260 \pm 10^\circ\text{C}$  and very low  $\text{CO}_2$  content in the fluid ( $P_{\text{CO}_2} : P_{\text{H}_2\text{O}} < 0,02$ ). With higher  $\text{CO}_2$  content, substantially non-metamorphosed rocks have been found to transfer directly into the greenschist facies of metamorphism.



EXPERIMENTAL CHECKING OF THERMODYNAMIC DIAGRAMS OF STABILITY OF W, Mo AND Bi MINERALS IN HYDROTHERMAL CONDITIONS

G.P.Kolonin, G.P.Shironosova, Yu.V.Laptev, Novosibirsk, USSR

1. The authors calculated the stability conditions of some principal minerals, such as W, Mo and Bi, and made an experimental attempt to test them as some main elements of these diagrams, in particular, to test the pH effect on the mineral stability.

2. It has been found for tungsten that with increase of alkalinity in sulfide solutions, ferberite is replaced by pyrite with simultaneous entering of tungsten in solution. The specific pH-value for a given equilibrium is mainly determined by the activity of hydrogen sulfide and tungsten ratio. The activity of tungsten in solutions equilibrated with ferberite and pyrite was calculated by the thermodynamic equilibrium constant of corresponding reaction for the given experimental pH and hydrogen sulfide. The calculated values were found to be in good agreement with those for tungsten concentrations chemically determined in the solutions after completion of the experiments.

3. It has been found for molybdenum minerals that intense replacement of powellite by molybdenite in sulfur hydrogen solutions occurs at 300°C at pH ≤ 7, which satisfactorily fits the results of thermodynamic calculations. In these experiments the indicator of sulfur and oxygen volatility was pyrrhotite; this permitted one to plot the experimental conditions on the diagram lg f<sub>O<sub>2</sub></sub>-pH.

4. It was experimentally found that at 250°C in solutions with H<sub>2</sub>S concentration of about 0.05 M bismuthinite was more stable at pH < 8 whereas metallic bismuth was more stable in alkaline conditions. This is also confirmed by the field positions of the phases on the plotted diagram.

MÖSSBAUER STUDY OF IRON IN NATURAL AND SYNTHETIC BIOTITES

H.Annersten, Marburg, Germany (FRG)

Mössbauer spectra are described for chemically complex natural and synthetic trioctahedral micas. The Mössbauer parameters at roomtemperature (see table 1) can clearly distinguish between Fe<sup>2+</sup> and Fe<sup>3+</sup> in the different lattice positions in micas. In spite of the large chemical variations of natural micas the Mössbauer parameters, quadrupole splitting and isomer shift, show small variations.

While natural biotites show no pronounced ordering of Fe<sup>2+</sup> into the two types of octahedral sites. M1 and M2, synthetic Fe-Mg-biotites show a temperature dependence of the ordering of ferrous iron into the different octahedral sites. This feature is discussed in view of the complex crystal-chemistry of micas.

Table 1. Mössbauer parameters of micas in mm/s.

Sample	Site	Coordination	ISOMER*) SHIFT	QUADRUPOLE SPLITTING
Natural biotite	Fe <sup>2+</sup> M1	octahedral	1.03	2.10
	M2	"	1.06	2.56
	Fe <sup>3+</sup> M1	"	0.40	1.20
	M2	"	0.43	0.62
Ferriphlogopite	Fe <sup>3+</sup> Si	tetrahedral	0.17	0.50

\*) Relative to iron metal.

RADIATION INDUCED EFFECTS IN SYNTHETIC  $\alpha$ -QUARTZ  
DOPED WITH Co(II)

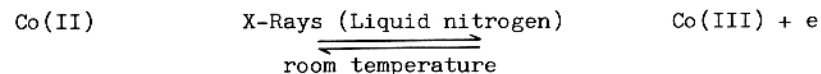
F.Hassan and A.Sacroug, Cairo, Egypt

The optical absorption spectrum of a synthetic  $\alpha$ -quartz single crystal doped with traces of Co(II) ions was measured at liquid nitrogen and at room temperatures. Upon X-irradiation at liquid nitrogen temperature several bands developed. Electronic transitions between the  $^1A_{1g}$  ground state of the octahedrally coordinated Co(III) ion and the  $^1T_{2g}$  and  $^1T_{1g}$  states were identified. These induced absorption bands were found to be unstable and completely disappeared at room temperature.

The results obtained from optical absorption measurements were compared to those obtained using ESR technique.

The possibility of the photo-oxidation of Co(II) to Co(III) at liquid nitrogen temperature in the  $\alpha$ -quartz structure will be discussed.

The following reaction is proposed:



RADIATION CENTRES IN ANHYDRITE

A.S.Marfunin, L.V.Bershov, A.V.Speranskii, Moscow, USSR

Electron paramagnetic resonance (EPR) and luminescence studies of anhydrites from ore deposits of Middle Asia, Norilsk and other regions show that isomorphism and interstitial impurities, vacancies and electron-hole centres in these crystals are the most important features of the anhydrites from different localities.

It is possible to distinguish the radiation (or spectroscopic) varieties of anhydrites.

- 1) The yttrium-containing anhydrites with centres  $Y^{2+}$ ,  $YO_2$ ,  $O_2^{3-} - Y^{3+}$ .
- 2) The rare earth anhydrites with  $TR^{2+} = TR^{3+} + e^-$ .
- 3) The boron-containing anhydrites with free radicals  $BO_2^0$ .
- 4) The phosphorus-containing anhydrite with free radicals  $PO_m^{n-}$ .
- 5) The ozonide ( $O_3^-$ ) and peroxide ( $O_2^-$ )-ion containing anhydrites.
- 6) The thiosulfate anhydrite with  $SSO_3^-$ .
- 7) The anhydrites with oxygen vacancies and radicals  $SO_3^-$ ,  $SO_2^-$ .
- 8) The hydrogen-containing anhydrites with the centres involving hydrogen as compensator.
- 9) The alkali anhydrites with  $O_2^{3-} - K^+$ ,  $O_2^{3-} - Na^+$ .

These varieties correlate with geochemical environment and regional distribution of anhydrites and reflect the thermal and radiation history of the minerals.

D.L.Warburton and S.S.Hafner, Marburg, Germany (FRG)

Two single crystals have been selected for a study of the Mössbauer effect of  $^{57}\text{Fe}$  at the M1 and M2 positions: (1) a natural fayalite (Fa97) from Rockport and (2) a synthetic forsterite (Fa01) with iron enriched to 90 percent  $^{57}\text{Fe}$ . Crystal sections with a thickness of 100  $\mu\text{m}$  have been prepared parallel to (100), (010), and (001). They have been studied at 300, 450, and 600°C.

The quadrupole-split  $^{57}\text{Fe}$ -doublets reveal information about the electric field gradient tensors at the M1 and M2 positions. The tensors generally consist of five independent parameters: the maximum value  $V_{zz}$ , the asymmetry parameter  $\eta$ , and three angles,  $\alpha, \beta, \gamma$ , which describe the orientation of the tensors relative to the crystallographic axes. The splittings of the doublets depend on  $V_{zz}$  and  $\eta$ ; the intensity ratios of the two peaks of the doublets depend on  $\eta$  and  $\alpha, \beta, \gamma$ . For M1  $\alpha, \beta, \gamma$ , are arbitrary angles. For M2 two of the three angles are 0 or 90°.

The M1 and M2 doublets of fayalite are sufficiently resolved so that assignment and analysis of the M2 tensor are possible. In the spectrum of forsterite the low-energy peaks of the doublets overlap so that the intensity ratios cannot be determined completely. However, the analysis is facilitated using two arguments. First, in high-energy peaks of the doublets do not cross over in the olivine solid solution series. Second, the tensors in fayalite and forsterite are not significantly different. The latter argument has been confirmed by lattice summations using the point charge model based on fifteen crystal structure refinements of olivines.

K.Recker and R.Leckebusch, Bonn, Germany (FRG)

Impurity free spessartines are yellow. Natural spessartines always contain impurities in variable amounts and therefore exhibit different colour shades (yellowish, reddish, brownish), which until now have not been explained entirely.

To correlate absorption and luminescence with chemical composition a number of spessartines were investigated by spectrochemical analyses, absorption spectra (350 - 3500 nm), and luminescence spectra (400 - 800 nm). With respect to the results of the chemical analyses the spectra have been discussed under aspects of the crystal field theory.

According to the chemical analyses Mn and Fe are the only absorbing cations in the investigated spessartines. The absorption maxima could be attached correspondingly to  $\text{Mn}^{++}$  and  $\text{Fe}^{++}$  ions (8-fold coordination) and to  $\text{Fe}^{+++}$  ions (6-fold coordination). The different colours of the spessartines are caused by different transparencies and intensities of absorption maxima due to variable  $\text{Fe}^{2+}/\text{Fe}^{3+}$  contents.

The investigated spessartines do not exhibit any luminescence at room temperature, but yellowish crystals, in contrast to brownish ones, luminesce more or less brightly at 77°K under uv radiation. The luminescence spectra show a maximum at 602 nm, which causes a red luminescence colour, and some other maxima in the region between 450 to 500 nm. The maximum at 602 nm is due to  $\text{Mn}^{++}$  ions, the origin of the short wave maxima could not yet be explained. According to experience the absence of luminescence at room temperature is caused by interactions of  $\text{Mn}^{++}$  ions (concentration quenching). The luminescence of the spessartines certainly is suppressed by the relative high iron content (killer effect). At a Mn/Fe rate of about 30:1 the killer effect does not impede luminescence completely, while it does so totally at about 10:1.

PVT EQUATIONS OF STATE FROM ULTRASONIC MEASUREMENTS AT  
VERY HIGH HYDROSTATIC PRESSURES

R.J.O'Connell, Cambridge, Mass., USA

Ultrasonic techniques can provide very precise measurement of the elastic properties of minerals as a function of temperature and pressure. The accuracy is limited by possible systematic errors. Recent developments of technique have permitted one major source of error to be eliminated, namely the effect of bonding an ultrasonic transducer to the specimen. A complete thermodynamic equation of state may be obtained from ultrasonic measurements as a function of temperature and pressure, and thermal expansion and heat capacity at zero pressure. This permits detailed evaluation of theoretical or empirical equations of state. Current measurements to pressures of 40 kilobars in a hydrostatic pressure medium will provide detailed tests of high pressure equations of state and permit refinement of the measurement of high pressure.

MODIFIED GLADSTONE AND DALE CALCULATIONS FOR CARBONATES

A.Pabst, Berkeley, California, USA

The rule of Gladstone and Dale or similar rules are generally used only to calculate mean refractive indices from molar refractivities of components, usually those of the constituent oxides. Bragg (1924) calculated discrete values for  $\epsilon$  and  $\omega$  of calcite and for  $\alpha, \beta$  and  $\gamma$  of aragonite from atomic refractivities by taking into account the influence of neighboring dipoles. Such calculations are complicated and have been little used.

In connection with work on eitelite,  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ , a simple method was devised for calculating expected values of  $\epsilon$  and  $\omega$  for double or multiple carbonates. Molar refractivities are calculated for both the  $\epsilon$  and  $\omega$  rays of the constituent carbonates which are optically negative and either uniaxial or biaxial with small optic angle. If these values are then used in accordance with the rule of Gladstone and Dale, or a comparable relation, to calculate  $\epsilon$  and  $\omega$  of a complex carbonate it is implicitly assumed that the  $\text{CO}_3$  groups in this carbonate are in parallel alignment with their planes normal to the optic axis or acute bisectrix as in the constituent carbonates from which the input data were taken.

The method can be used for predictions in several ways:

- (1) If the calculated indices are close to the observed indices the assumption mentioned is correct.
- (2) If the results of calculation and observation do not agree, especially if the observed birefringence is markedly less than that calculated, it may be concluded that the assumption is not applicable and that the  $\text{CO}_3$  groups in the material are not in parallel alignment.
- (3) The calculations may be used to predict the as yet unknown refractive indices of certain carbonates of known structure.

Examples of each of these types of prediction will be given.

OPTICAL PROPERTIES OF MINERALS DERIVED FROM ATOMIC PROPERTIES

Orson L. Anderson, Los Angeles, California, USA

The variation of the ambient index of refraction,  $n$  of minerals, with their ambient density,  $\rho_0$ , is derived from the equations of motion appropriate to visible optics in a dielectric material. Special consideration is given to the case where oxygen is the main anion.

A number of useful equations relating  $n$  and  $\rho_0$  are derived where the controlling parameters are identified as mass, spring constant, valence, and anion polarizability. For mineral sequences where the mean atomic weight is nearly constant, the relationships between index of refraction and velocity of sound are derived. It is shown that laws controlling the index of refraction are similar to those controlling the velocity of sound systematics in minerals.

Open Sessions:

Petrology II

Tuesday, September 17, 1974

Chairmen: E. Niggli  
H.G. Huckenholz

Joint Session IMA-DMG:

Technical Mineralogy and Applied Crystallography

Wednesday, September 18, 1974

Chairman: K.H. Wedepohl

GEOCHRONOLOGY OF A POLYMETAMORPHIC AND ANATECTIC GNEISS  
REGION: THE MOLDANUBICUM OF THE AREA LAM - DEGGENDORF,  
EASTERN BAVARIA

B.Grauert, R.Hännly, G.Soptrajanova, Zürich, Switzerland

Rb-Sr isotopic analyses of whole-rocks and biotite and U-Th-Pb analyses of zircon and monazite reveal regional metamorphic events for the Ordovician (Caledonian metamorphism) and the Carboniferous (Variscan orogeny), both accompanied by anatexis. The extent of the Caledonian and Variscan anatexis, however, cannot be evaluated so far because the field petrographic criteria are not sufficient to distinguish clearly between early and late Paleozoic anatexites. Evidence for a Precambrian metamorphism has not been found. Rb-Sr whole-rock isochrons obtained on leucosomes and melanosomes of partially molten paragneisses are interpreted as a minimum age of the second, early Variscan anatexis. Concordant and nearly concordant zircon ages (318-335 m.y.) of coarse-grained granites and diatexites are regarded as evidence for an intensive early Variscan granitization and palinogenesis. Concordant zircon ages of diorite dykes, crosscutting the anatexites, establish a lower time limit of 309-312 m.y. for the Variscan anatexis. Rb-Sr ages of biotite (310-290 m.y.) indicate the end of the Variscan metamorphism.

Estimates of the time of sedimentation or diagenesis based on Rb-Sr whole-rock analyses for some metasediment series in the north of the area yield maximum ages of 550 m.y., provided that Rb and Sr migration did not exceed substantially the extent of the outcrops (30-500 m) between the time of diagenesis and the Ordovician metamorphism. Otherwise, an upper limit of 2.0-2.3 b.y., which is the "primary" age of detrital zircons, can be established.

U-Pb SYSTEMATICS OF ZIRCONS DURING THE ANATEXIS OF A  
MOLDANUBIAN PARAGNEISS

D.Gebauer, M.Grünenfelder, Zürich, Switzerland

U-Pb data are reported from zircon suites separated from the following rocks: 1) a biotite plagioclase gneiss, 2) completely molten derivatives of this gneiss (diatexit) and 3) a non - molten calcsilicate gneiss boudin within a nebulitic part of the biotite plagioclase gneiss. All samples were taken within about 30 m of a small quarry in the moldanubian basement of Eastern Bavaria.

The detrital, heterogenous zircons from the small calcsilicate gneiss boudin which contains a waterfree mineral assemblage do not show any new crystal growth after their deposition in contrast to the zircons of the biotite plagioclase gneisses. This fact is explained with the differing water contents of the two host rocks. Nevertheless the zircons from the calcsilicate gneiss suffered a great loss of radiogenic lead during the time of anatexis, about 460 m.y. ago. The zircons of the biotite plagioclase gneiss, however, have again been — in addition to the migmatization 460 m.y. ago — open systems during the following Hercynian metamorphism.

Zircons from the anatectic end-product of the biotite plagioclase gneisses (diatexit) still contain a great amount of inherited, detrital zircons. However, refaceting, overgrowth and new growth of zircon is much more abundant in this rock-type which crystalized from an anatectic melt. The age of these zircons points to the 460 m.y. event which is further supported by Rb-Sr data.

ECLOGITES OF THE BOHEMIAN MOLDANUBICUM

Arnost Dudek and Eva Fediukova, Prague, CSSR

Moldanubian eclogites occurring in connection with peridotites, gneisses and migmatites are distinguished into three main groups on the basis of the chemical composition of coexisting garnet-clinopyroxene pairs, mode of occurrence and petrographical character of the eclogite bodies. According to Fe and Mg partitioning between both minerals, conditions of mineral equilibrium giving rise to individual groups of eclogites are discussed.

ON EQUILIBRATION CONDITIONS OF THE SUDETIC ECLOGITES,  
POLAND

Nonna Bakun-Czubarow, Warszawa, Poland

Gneisses of the Eastern part of the Polish Sudetes include common, plagioclase-free eclogites and transitional oligoclase-bearing rocks, represented by two series: carinthine-eclogite and granulite-eclogite.

Equilibration temperature of the common Sudetes eclogites has been determined by means of geothermometers based on partitioning of elements between coexisting minerals, e.i. by means of Fe<sup>2+</sup>-Mg garnet-clinopyroxene and garnet-amphibole geothermometers, as well as by means of newly calibrated Mn-Mg garnet-clinopyroxene one. The equilibration temperature of the common eclogites ranges from 440 to 620°C.

Load pressure estimated on the basis of the omphacite composition ranges from 7 to 11.7 kb.

The following trace transition elements: Sc, V, Cr, Mn and Ni, which participate in exchange reactions of great sensitivity to the p/t condition changes, have been used as indices of blastesis conditions of eclogites. The concentration of the above mentioned elements together with REE have been applied in searching for primary material of the eclogites.

The results of investigation of the sudetic transitional eclogitic rocks have been used for a tentative elucidation of the discrepancy among the experimentally obtained eclogitization process boundaries.

OPTICAL AND ELECTRON MICROPROBE INVESTIGATIONS OF CHROMITE  
AND OTHER OPAQUE MINERALS IN YUGOSLAVIAN OPHIOLITIC ROCKS

Stanko Grafenauer, West Lafayette, USA

In Yugoslavia there are numerous ophiolitic diapiric or intrusive complexes which on well exposed localities display the entire sequence of these rocks from dunites to pillow lavas. Geographically these rock display increasing Mg enrichment along a traverse running from NW to SE. This enrichment is associated with increase of accessory chromite and with chromite and with chromium ore deposits of considerable magnitude. The enrichment leading to formation of Alpine-type deposits took place at depth mostly as a result of static differentiation. The final position and form was effected through kinetic differentiation during the movement of ophiolites caused by continental drift in Mediterranean.

Primary textures and mineral associations in the chromite ore have been studied and will be discussed. Some cumulate features preserved in Alpine type chromite deposits include certain textures found in stratiform complexes in addition to nodular and orbicular textures. Some of the textures indicate partial melting at depth. In addition to transition textures the rocks also display features that provide new evidence of the crystallization mechanisms of chromite and olivine. This study records micrographically myrmekitic and emulsion textures observed for the first time in Yugoslavian rocks. As far as the author can verify this study also reports the first occurrence of sideronitic textures in any chromite deposit. In some rocks enriched on titanium ilmenite and rutile exsolutions were observed in chromite. Awaruite, maucherite and heazlewoodite were identified for the first time from Yugoslavian localities. The chromite grains often display interior areas containing magnetite and "ferritchromit" which is harder and brighter than regular chromite. Chromite often has been replaced hydrothermally by uvarovite, kaemmererite and Cr-diopside. Because of their positions, mineral associations and textures displayed by ores and rocks these Yugoslavian deposits are morphologically and genetically classified as podiform.



THE OPAQUE MINERALS OF SOME PELITIC METAMORPHIC ROCKS OF  
SCOTLAND AND THE RELATIONSHIP TO METAMORPHISM AND GEOCHEMISTRY

Peter J. Hill, Hershham, U.K.

The opaque minerals described are from the Lower Psammitic Group and the Pelitic and Upper Psammitic Groups of the Lower and Upper Dalradian of Scotland. They include pyrite, pyrrhotite, chalcopyrite, pentlandite, magnetite, hematite, ilmenite and rutile. The rocks come from the chlorite, biotite and garnet zones of Barrovian metamorphism. The most common assemblages are:

ilmenite ± rutile ± pyrrhotite,  
rutile ± pyrrhotite,  
pyrite + chalcopyrite,  
ilmenite + magnetite ± pyrite,  
ilmeno-hematite + magnetite.

Chalcopyrite is a common accessory mineral in sulphide bearing assemblages and pentlandite is found as exsolution inclusions in pyrrhotite. The Lower Psammitic Group contains rutile ± pyrrhotite in chlorite and lower biotite zones and ilmenite ± rutile ± pyrrhotite in the upper biotite and garnet zones. The Pelitic and Upper Psammitic Groups of the chlorite and biotite zones contain all of the assemblages mentioned. The magnetite bearing rocks (with ilmenite or ilmeno-hematite) are albite schists, a rock type which is not found in the garnet zone. The stratigraphic equivalents in the garnet zone contain ilmenite + rutile ± pyrrhotite. The geochemistry reflects the variation in opaque mineral assemblages between the two stratigraphic divisions. The oxidation ratio ( $2\text{Fe}_2\text{O}_3 \times 100 / 2\text{Fe}_2\text{O}_3 + \text{FeO}$  molar) is used to compare the two divisions. The Lower Psammitic Group is relatively reduced and homogeneous whereas the Pelitic and Upper Psammitic Groups are heterogeneous. Also the garnet zone rocks of the Lower Psammitic Group are significantly more reduced than the rocks of chlorite and biotite zones. Several explanations are presented to account for this observation.

ROCKS AND ROCK FORMATION IN AN EXAMPLE OF FRICTIONAL  
FUSION ON A THRUST PLANE IN THE LANGTANG HIMAL, NEPAL

Ludwig Masch and E. Preuss, München, Germany (FRG)

A hyalomylonite in the Langtang Himal, north of Kathmandu, Nepal, was described by Scott and Drever (1953) as an example of fusion on a thrust plane.

The authors of this paper recently revisited this locality, collected new sample material and obtained more detailed information on field relations.

The hyalomylonite is developed as a sheet-like body of a uniform thickness of one to three centimeters on a thrust plane extending over several hundred meters. Of all the conjugate fault planes associated with the thrust, only one was seen to contain hyalomylonite. Diapyre-like pockets rise up to sixty centimeters above the main hyalomylonite sheet. These pockets are created by an upward movement of the melt, and are filled with a hyalomylonite which in some instances becomes pumice like.

Dikelets of tuff-like appearance, composed of comminuted brecciated and glassy material sprout out of these pockets.

The cataclastic rocks on the opposing sides of the thrust plane exhibit different textures. The rocks of the footwall are coherently cataclastic, showing a phyllonitic texture-sand mylonitic banding whereas the rocks of the hanging wall have been strongly fractured and brecciated.

The formation of this rock assemblage and its relation to pseudotachylites and the pumice like rock in the landslide area of Köfels in the Ötztal, Austria, is discussed.

SYNTHESIS OF MANGANESE-BEARING KYANITE AND ANDALUSITE,  
(Al,Mn<sup>3+</sup>)<sub>2</sub>SiO<sub>5</sub>, AND SOME ADDITIONAL RESULTS IN THE SYSTEM  
Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MnO-MnO<sub>2</sub>

Irmgard Abs-Wurmbach and K.Langer, Bochum, Germany (FRG)

High pressure experiments on the join Al<sub>2</sub>SiO<sub>5</sub>-"Mn<sub>2</sub>SiO<sub>5</sub>" of the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MnO-MnO<sub>2</sub> were performed in a piston-cylinder-apparatus using an external MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub>-oxygen buffer. Gem quality andalusite (0.40 wt% Fe<sub>2</sub>O<sub>3</sub>, 0.01 wt% Mn<sub>2</sub>O<sub>3</sub>), Mn<sub>2</sub>O<sub>3</sub>, and high purity SiO<sub>2</sub> served as starting materials in the inner Pd- or Au-capsules. Traces of water were added to promote crystal growth. An excess of 10 % SiO<sub>2</sub> was added to overcome SiO<sub>2</sub>-leaching.

At 20 kb/1000°C, kyanite mixed crystals, (Al<sub>2-x</sub>Mn<sub>x</sub><sup>3+</sup>)SiO<sub>5</sub>, were obtained as slightly yellow-orange crystals with a length of up to 70 nm. The colour is the same as that of natural Mn<sup>3+</sup>-bearing kyanite from Mautia Hill/Tanzania. The range of kyanite solid solubility at 20 kb/1000°C is limited to about 3.5 mole% "Mn<sub>2</sub>SiO<sub>5</sub>" (x=0.07). Within this range, the lattice constants a, b, c, and V increase with Mn<sup>3+</sup>-contents by 0.12 %, 0.11 %, 0.22 %, and 0.44 %, resp., if compared with pure Al<sub>2</sub>SiO<sub>5</sub>-kyanite. The small range of solid solubility in the present system disproves the assumption that higher amounts of Al<sup>[6]</sup> in the kyanite matrix might be substituted by Mn<sup>3+</sup> than by other trivalent 3d-ions of comparable size because of the Jahn-Teller-effect (Langer and Frentrup 1973). In Mn<sup>3+</sup>-rich compositions of the join studied, kyanite<sub>ss</sub> coexists with braunite, Mn<sup>2+</sup>Mn<sup>3+</sup><sub>6</sub>[O<sub>8</sub>|SiO<sub>4</sub>], pyrolusite, MnO<sub>2</sub>, and a SiO<sub>2</sub>-rich liquid. The stable coexistence of pyrolusite with the Mn<sup>2+</sup>-bearing phase braunite at oxygen fugacities of the MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub>-buffer was confirmed by experiments with a mixture 7Mn<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>.

In runs with 25 mole% "Mn<sub>2</sub>SiO<sub>5</sub>" at 15 kb/900°C, i.e. within the stability field of kyanite in the pure Al<sub>2</sub>SiO<sub>5</sub>-system (Richardson et al. 1969), andalusite<sub>ss</sub> was formed as deep green, strongly pleochroitic crystals (viridine) containing up to 19 mole% "Mn<sub>2</sub>SiO<sub>5</sub>". In long runs (30 and 63 hrs), besides andalusite<sub>ss</sub> minor amounts of braunite, corundum<sub>ss</sub> and glass and also traces of kyanite<sub>ss</sub> were found. These results may indicate, that Mn<sup>3+</sup>-substitutions stabilize the andalusite structure type appreciably towards higher pressures and temperatures, and may be of importance for estimations of p-T-f<sub>O<sub>2</sub></sub>-conditions in nature.

Joint Session IMA - DMG:  
TECHNICAL MINERALOGY AND APPLIED CRYSTALLOGRAPHY

SILICON NITRIDE CERAMIC, A POTENTIAL MATERIAL FOR HIGH TEMPERATURE APPLICATION

E.Gugel, Rödental, Germany (FRG)

The majority of ceramic materials such as earthenware, stoneware, porcelain is still based on natural clay or kaolin. Natural or synthetic oxide-powders are the basis of refractory bricks, electro-ceramic products and the pure oxide ceramics.

The group of oxide-free compounds with boron, silicon, carbon and nitrogen is of interest of high temperatures. Some of these are also resistant in oxidizing atmosphere up to high temperatures, because they form a protective silica-layer. For various reasons silicon nitride is particularly promising. Its structure, the chemical and physical characteristics as well as its production methods and the possible use in gas turbines will be discussed.

H.v.Philipsborn, Regensburg, Germany (FRG)

Mineral names such as zinc blende, spinel, perovskite, garnet, scheelite are found these days more often in physical and technical publications than in mineralogical ones. Under discussion are not natural minerals, though, but synthetic single crystals of the same structure type, which display interesting electrical, magnetic, optical, acoustical (in short: electronic) properties.

The use of these crystals relies on crystal chemical knowledge of the relationships between chemical composition and crystal structure on the one hand, and between crystal structure and physical properties on the other hand. Added are successful synthesis of single crystals and insight in the relationships between physical-chemical conditions of crystal growth, the details of crystal structure and defects, and the physical properties mentioned before.

Though a lot of the early research in the field has been done by mineralogists and crystallographers at German universities, the main advances later on were made by chemists, metallurgists, and physicists in American industrial research and development laboratories. Unfortunately there seems to be insufficient communication between these different groups to make full use of the results of one group to the other.

The talk will cover various electronic materials (by crystal structure type), their single crystal synthesis, and physical properties. In all cases reference will be made to corresponding mineral objects, methods, and results. Bridging the gap is of particular importance for the group of silicates, well studied as natural minerals, but hardly tapped as synthetic single crystals for electronic materials.

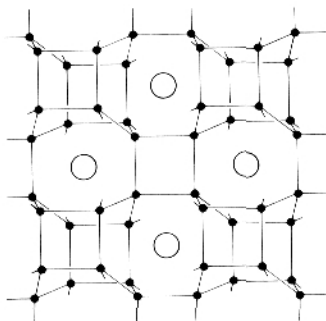
G.Brunner, Zürich, Switzerland

The "behaviour of atoms" is being simulated by means of magnets which float without friction on water or on an air cushion. The structures form themselves, and diffusion, thermal vibrations, ideal structures and defects may be studied.

The magnetisation of the magnets is perpendicular to the plane in which they move. Parallel oriented and similarly magnetised magnets repel each other and form closest packings (resembling Mg and Cu), since the neighbours have largest separations (Acta Cryst. A 27 (1971) 388-390). For structures of two kinds of atoms, by reversing polarity and by mounting each kind at a different height above the plane in which they move, a good approximation to a real force field with an equilibrium position is obtained: at large distances, the difference in height has little influence and the two kinds attract due to the reversed polarity; at short distances they repel due to the neighbourhood of poles of the same sign. Interpenetrations of closest packings with various coordination numbers resemble the structures of NaCl and of ZnS, and also an analogue of CsCl is formed with a transition from the NaCl type to the CsCl type when the "pressure" is increased.

H. Kroll, J. Löns, H. Pentinghaus, Münster, Germany (FRG)

During a systematic investigation of substituted feldspars<sup>1)</sup> a new framework structure has been found, an orthorhombic modification of NaAlGe<sub>3</sub>O<sub>8</sub>, which has  $a = 8.428$ ,  $b = 8.907$ ,  $c = 4.955$  Å,  $\alpha = \beta = \gamma = 90^\circ$ , and space group  $Pm\bar{2}_1n$ . The distribution of Al and Ge within the framework is random. Neglecting the slight distortions within the framework, the topologic symmetry is  $I4/mmm$ , as can be seen in the figure.



The prominent feature of the structure is the occurrence of six-membered tetrahedral rings, the apices of which point up, up, down, up, up, down. By virtue of a mirror plane normal to the  $a$  axis cages are formed which are bounded by four six-membered rings. The cages are related by a pseudo-body centering

vector. This structure type was first predicted by Wells (1954) as a topologically possible framework structure.

The orthorhombic NaAlGe<sub>3</sub>O<sub>8</sub> compound is stable below 550°C, 1 Kbar P<sub>H<sub>2</sub>O</sub>. It transforms to the corresponding disordered feldspar when heated at about 800°C under dry conditions. The orthorhombic polymorph of CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> displays cell parameters and a powder diffraction pattern strikingly similar to this new compound.

1) BRUNO and PENTINGHAUS: Research on types of Feldspars. - Proc. of the NATO Advanced Studies Inst. on Feldspars, University of Manchester Press (in press).

W. Dosch and E. Memapuri, Mainz, Germany (FRG)

Highly effective and selective adsorbers were prepared by covering external surfaces of montmorillonites with heavy metals. The specific adsorptive properties of such samples was tested for poisonous or badly odorous substances such as insecticide phosphoric ester, organic sulfur compounds (1) or substances used militarily (2). Possible uses of the new adsorbers are decontamination of gases and liquids, including water purification and carriers for pesticides. The adsorption of phosphoric ester was tested for different adsorbers. Montmorillonites covered with heavy metals, in particular a hectorite covered with 5 wt.% Ag, showed the best properties regarding the amount and the rate of adsorption. The capacity of this adsorber for different esters amounts to 20 to 40 wt.%. The decay of poisonous residues with time in presence of an inert liquid was measured by gas chromatography. In addition adsorption isotherms were determined. X-ray work and scanning electron microscopy reveal the adsorbed substances to be fixed mainly on external surfaces of the adsorber. The internal structural swelling of the clay plays only a minor role. Besides silver, a number of other heavy metals are effective in montmorillonite as carrier, though in a less pronounced way. The adsorbed substances can be washed out with pyridine by displacement adsorption. Solvents influence the adsorption independently of their dielectric constant, polarity or dipole moment. Adsorption proceeds easily in n-hexane, methanol, chlorine carbon hydrogen, less in acetone, and water, little in acetonitrile, toluene, furane, dioxane. No adsorption takes place when pyridine, which is adsorbed preferentially, is present as a solvent. The optimum of heavy metal coverage is about 4-5 weight %. In experiments with water (25 ml) contaminated with phosphoric ester (100 mg), 99 % of the poison was adsorbed by 2 g hectorite (with 4 % Ag).

- (1) W. Dosch, H. Keller, T. Poles: Studies on the absorption of phosphoric esters, sulfur compounds and other poisons, unpublished.
- (2) W. Dosch, H. Keller: Universelle Entgiftungsmittel für chemische Kampfstoffe, Zivilverteidigung 2 (1972) 68-74.

R.Singh Dev, Essen, Germany (FRG)

For pollution control it is of great importance to know the chemical bulk composition of dusty emissions as well as the special form in which harmful elements are present. Gas dusts of a series of home and industrial refuse incinerators were analysed chemically for the elements Be, Sr, Ba, Cu, Ni, Mn, Cd, Zn, Pb, Ti, Cr, Cl, F, and P.

Transmission- and scanning electron microscopy were used to determine the morphology of dusts in view of their effects on the lung. Phase analysis of the special "form" of the elements present was done by small-area diffraction on the transmission electron microscope combined with energy-dispersive chemical analysis.

Chemical analysis of the dusts has shown that the concentrations of harmful materials are below the officially tolerated limits. Phase analysis indicates that the major part of harmful elements is bound in such a way (as compounds slow to dissolve or insoluble under atmospheric conditions) that harmful effects on the environment are not to be expected.

Author Index

(underlined page = speaker)

Abdel-Khalek, M.L.	107	Bosch-Figueroa, J.M.	<u>55, 64, 65, 66</u>
Abs-Wurmbach, I.	<u>194</u>	Bowie, S.H.V.	<u>67</u>
Ackermann, D.	91	Brunner, G.	<u>197</u>
Allmann, R.	<u>89</u>	Bunch, T.E.	111
Alviola, R.	11	Burnham, C.W.	<u>160</u>
Amthauer, G.	<u>57</u>	Bussen, T.V.	7
Anderson, G.M.	<u>9</u>		
Anderson, O.L.	<u>184</u>	Camargo, W.G.R. de	<u>56</u>
Annersten, H.	<u>177</u>	Cerný, P.	<u>5</u>
Arbunies Andreu, M.	<u>55</u>	Cervelle, B.	63
Asakura, M.	137	Cesbron, F.	41
Ashraf, M.	<u>21</u>	Chesterman, Ch.W.	<u>43</u>
Atkin, D.	67	Chukhrov, F.V.	<u>39</u>
Augustithis, S.S.	<u>110</u>	Clark, B.C.	<u>148</u>
Baird, A.K.	148	Deicha, G.	<u>23</u>
Bakun-Czubarow, N.	<u>190</u>	Diessel, C.F.K.	112
Baltzinger, Ch.	<u>134</u>	Donnay, G.	89
Bank, H.	111	Dosch, W.	199
Barabanov, V.F.	<u>58</u>	Drits, V.A.	<u>78, 100</u>
Barlier, J.	26	Dudek, A.	189
Barnes, V.E.	<u>149</u>		
Baro, R.	134	El Goresy, A.	<u>154</u>
Baronnet, A.	<u>136</u>	Endo, Y.	135
Batrakova, Yu.A.	138	Engelhardt, W.von	<u>146</u>
Bayh, W.	<u>130</u>	Eskova, E.M.	7
Berhardt, H.-J.	154	Essene, E.J.	<u>156</u>
Bershov, L.V.	179		
Bettermann, P.	<u>91</u>	Fabbi, B.P.	43
Bettetini, E.	<u>24</u>	Fediukova, E.	<u>189</u>
Berthelon, J.P.	<u>41</u>	Fleet, M.E.	<u>77</u>
Besteiro, J.	<u>65, 66</u>	Fojt, B.	<u>42</u>
Bhaskara Rao, A.	<u>44</u>	Font-Altaba, M.	<u>64, 65, 66</u>
Bird, G.W.	103	Frank-Kamenetsky, V.	<u>87</u>
Bishop, F.C.	90	Fransolet, A.M.	<u>12</u>
Blattner, P.	<u>103</u>	Fukuda, K.	97
Bogolepov, V.G.	<u>37</u>		

Galli, E.	<u>82</u>	Jobbins, E.A.	<u>59</u>	Logan, C.T.	<u>19</u>	O'Connell, R.J.	<u>182</u>
Ganeev, I.G.	<u>139</u>	Jones, M.P.	<u>74</u>	Lopez Soler, A.	64,65, <u>66</u>	Offler, R.	112
Gasparrini, E.	172					Okrusch, M.	111
Gebauer, D.	<u>188</u>	Kabesh, M.L.	<u>107</u>	Madureira, J.B. de	56		
Gerasimovsky, V.I.	<u>108</u>	Kallio, P.	<u>11</u>	Marfunin, A.S.	<u>179</u>	Pabst, A.	<u>183</u>
Giardini, A.A.	<u>30</u>	Karup-Moller, S.	66	Margolis, S.V.	149	Pagel	<u>33</u>
Gilbert, M.C.	<u>84</u>	Kashkai, C.M.	<u>93</u>	Martin, R.	<u>25</u>	Pentinghaus, H.	<u>81,198</u>
Gollo, E.	87	Kashkai, M.A.	93	Masaitis, V.L.	<u>144</u>	Perchuk, L.L.	<u>106,166</u>
Goncharov, Yu.I.	78	Kato, A.	<u>96,97</u>	Masch, L.	<u>193</u>	Pertsev, N.N.	<u>104</u>
Gorbatshev, R.	<u>105</u>	Kazitsyn, Yu.V.	<u>120</u>	Matsubara, S.	96	Philipsborn, H.von	<u>196</u>
Grafenauer, S.	<u>191</u>	Keester, K.L.	<u>133</u>	Medenbach, O.	154	Phillips, M.W.	80
Grauert, B.	<u>187</u>	Keil, K.	<u>143,148</u>	Melka, K.	98	Phillips, R.	<u>34</u>
Gritti-Baudracco, C.	<u>35</u>	Kennedy, G.C.	124	Melton, C.E.	30	Pinet, M.	63
Grünenfelder, M.	188	Khalek, C.A.	107	Memapuri, E.	<u>199</u>	Poirot, J.P.	<u>50</u>
Gübelin, E.J.	<u>49</u>	Kholief, M.M.	<u>29</u>	Menshikov, Yu.P.	7	Pokorný, J.	98
Gugel, E.	<u>195</u>	Khomyakov, A.P.	7	Merkov, A.N.	7	Povarennykh, A.S.	<u>47</u>
Gurevich, L.P.	175	Kim, Soo Jin	<u>46</u>	Micheelsen, H.	<u>31</u>	Preuss, E.	193
		Kleppa, O.J.	<u>155</u>	Minato, H.	<u>88</u>	Prewitt, C.T.	<u>129</u>
Haefner, R.	<u>131</u>	Klitzsch, E.	152	Mincheva-Stefanova, J.	<u>114</u>		
Hänny, R.	187	Kolonin, G.P.	<u>176</u>	Mirwald, P.W.	<u>124</u>	Rabe, H.	<u>117</u>
Hafner, S.S.	<u>167,180</u>	Kopp, O.C.	28	Miyamoto, M.	<u>153</u>	Rajamani, V.	129
Han, T.M.	<u>45</u>	Kornetova, V.A.	<u>95</u>	Momoi, H.	97	Ramdohr, P.	154
Harada, K.	99	Koshino, Y.	137	Mones Roberdeau, L.	<u>52</u>	Rapp, G.	14
Harder, H.	<u>53</u>	Koski, R.A.	43	Moore, P.B.	<u>15</u>	Rasumny, J.	<u>27</u>
Hassan, F.	<u>178</u>	Kossovskaya, A.G.	<u>100</u>	Mozgova, N.N.	<u>116</u>	Recker, K.	181
Heikal, M.A.	107	Kostov, I.	<u>121</u>	Mücke, A.	<u>152</u>	Reeve, E.J.	9
Heinrich, E.W.	<u>6,8</u>	Kotov, N.	87	Mukerjee, M.	<u>20</u>	Rimsaite, J.	<u>18</u>
Hill, P.J.	<u>192</u>	Kovalenko, V.I.	10			Rinaldi, R.	<u>101</u>
Hinrichsen, T.	<u>86</u>	Kraut, F.	<u>145</u>	Naganna, C.	<u>122</u>	Roberts, W.L.	<u>14</u>
Hodenberg, R.von	<u>92</u>	Kroll, H.	<u>80,198</u>	Nagashima, K.	<u>99</u>	Robinson, P.	<u>83</u>
Hoefs, M.	<u>32</u>	Kühn, R.	92	Nagesh, N.B.	112	Rodrigues da Silva, R.	<u>13</u>
Honda, M.	99	Kusakabe, H.	88	Nakhla, F.M.	<u>68</u>	Roedder, E.	<u>28</u>
Hooker, M.	<u>72</u>			Naldrett, A.J.	<u>172</u>	Roeder, P.L.	<u>158</u>
Hrušková, J.	<u>94</u>	Langer, K.	194	Navrotsky, A.	<u>163</u>	Rose, H.J.	148
		Lapides, I.L.	10	Neiva, A.M.R.	<u>17</u>	Ross, M.	83
Iino, J.	99	Laptev, Yu.V.	176	Newesely, H.	<u>54</u>	Rost, F.	57
Ito, J.	97	Leckebusch, R.	<u>181</u>	Newton, R.C.	155	Rost, R.	<u>150</u>
Ivanov, I.P.	169, <u>175</u>	Lévy, C.	<u>63</u>	Nishida, T.	135	Ryabchikov, I.D.	<u>162</u>
		Liebau, F.	<u>73</u>	Nogues Carulla, J.	<u>64</u>	Ryakovskaya, S.M.	138
Jaffe, H.W.	83	Löns, J.	<u>198</u>				

Sacroug, A.	178	Toulmin, P.	148
Sadrzadeh, M.	41	Touray, J.C.	<u>26</u>
Sakharova, M.S.	<u>138</u>	Tresham, A.	59
Schneer, C.J.	<u>71</u>	Troll, G.	84
Schulien, S.	168	Troneva, N.V.	113
Schürmann, K.	<u>85</u>		
Scott, S.D.	<u>128</u> , 172	Ulrichova, D.	98
Seeliger, E.	<u>123</u> , 152	Urusov, V.S.	<u>170</u>
Sellschop, M.	130	Utada, M.	88
Semenov, E.I.	<u>7</u>		
Shadlun, T.N.	<u>113</u>	Vladykin, N.V.	<u>10</u>
Shibuya, G.	<u>115</u>		
Shironosova, G.P.	176	Waldbaum, D.R.	164
Shivakumar, B.S.	112	Warburton, D.L.	<u>180</u>
Shlain, L.B.	79	Watanabe, T.	<u>97</u>
Shmakin, B.M.	<u>16</u>	Waterston, C.D.	72
Silberman, M.L.	43	Williams, S.A.	<u>40</u>
Simmons, W.B.	<u>8</u>	Windley, B.F.	90
Simpson, P.R.	67	Wise, W.S.	<u>173</u>
Singh Dev, R.	<u>200</u>	Woensdregt, C.F.	<u>132</u>
Skippen, G.B.	<u>159</u>	Wood, B.J.	<u>157</u>
Smith, F.W.	34	Woodhead, J.A.	<u>164</u>
Smith, J.V.	<u>90</u> , 101	Wyart, J.	<u>127</u>
Sobolev, N.V.	<u>109</u>		
Soboleva, S.V.	79	Yajima, T.	167
Soptrajanova, G.	187	Yamamoto, T.	137
Speranskii, A.V.	179	Yamanaka, T.	88
Steele, I.M.	90	Yoshimura, T.	97
Stöffler, D.	<u>147</u>	Young, B.R.	59
Stoynov, S.	<u>70</u>		
Strunz, H.	<u>60</u> , <u>69</u> , <u>151</u>	Zakharchenko, A.I.	<u>36</u>
Sunagawa, I.	<u>51</u> , <u>137</u>	Zalutskii, V.V.	<u>38</u>
Sylvester, G.	9	Zemann, J.	<u>119</u>
		Zharikov, V.A.	169
Takano, Y.	<u>135</u> , 153	Zhouchlistov, A.P.	79
Takeda, H.	153	Zvyagin, B.B.	<u>79</u>
Tat Tram, Nguen	87	Zyrianov, V.N.	166
Tomashenko, A.	87		