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# ZEOLITES. CHEMICAL PROPERTIES AND ORIGIN Zeolity. Cechy chemiczne i pochodzenie

#### ABSTRACT

Introduction. Zeolites as feldspars and feldspatoides derivatives. Chemical character. Mutual coalescences, associates, pseudomorphosies. Nephelite derivatives: natrolite, scolecite, mesolite, thomsonite, comptonite, gismondine, zeagonite, muscovite, cancrinite, phillipsite, marburgite, herschelite, wellsite, curzite. Sodalite derivatives: epinatrolite, episcolecite, epithomsonite, yellow-cancrinite. Leucite derivatives: analcite, laumonite. Plagioclase derivatives: chabazite, gmelinite, acadiolites, levyne. Aluminopentasilicates: lubanite, fojasite. Feldspar derivatives: harmotome, desmine, epidesmine, heulandite, epistilbite, erionite, brewsterite. Aluminoheptasilicate: stellerite. Aluminonona and dekasilicates: mordenite, ptilolite.

Among the products of decomposition of feldspars and feldspatoides the zeolites bear a conspicuous part. Containing calcium and sodiumaluminosilicates with a small admixture of potassium, barium or strontium, they originated with participation of thermic and surface waters, mainly in igneous rocks, less frequently in sediments or rockveins. Easily soluble in mineral acids they leave gelatinous or slimy silica. Distilled water dissolves them weakly. The hydrous solution shows a feeble alcalic character. C. Doelter (1) using closed, internally silvered iron tubes, succeeded in dissolving and recrystallizing in water at 160° C the best part of zeolites. Upon the solubility of zeolites in water there bear witness the observations made in nature, where its wanderings from the primary to the secondary bed are a common phenomenon. Nevertheless these are not true solutions but strongly dispersed suspensions, ready to accept in favourable conditions the primordial crystalline shape. A large mass of water destroys the zeolites, especially at a higher temperature. Triturated in an agate mortar they attract the air moisture. Afterwards, put in an exsicator, they give it back. When heated they deliver their water continuously without leaps. The loss of water begins sometimes already below 100° C. Therefore the foregoing drying of zeolites which precedes the analysis is not to be recommended. Some zeolites instead of the lost water absorb the ammonia, the bromine, the iodine and other bodies.

The zeolites are in all good conductors of electricity. According to B. Gross (2) this happens owing to the great mobility of alcalic ions. The increasing wetness is favourable for its conductibility; whereas the high temperature augments their resistance. Ohm's law has reference only to the shortly constant course of current.

Reiterated twins are common, selfdependant types appear seldom. The mutual coalescences and intergrowings of various zeolites render their examination more difficult.

Considerations of a general character inclined the investigators to accept a common structure for all zeolites having the character of a space net, built up of tetrahedra (SiO<sub>4</sub>) with oxygen ions in the corners and silicon and aluminum ions in the middle. The dimensions of  $(AlO_4)$  tetrahedra differ from  $(SiO_4)$  tetrahedra so little that in certain types they can be mutually exchanged without hurting the structure itself. The separate tetrahedra are joined together by the oxygen atoms. Upon other groupings of atoms the x - ray method gave no answer. Therefore enlarged chemical investigations are much desired. The exchange reactions furnish certain indications concerning above all the strong bases. In this manner the existence of metameric minerals was stated as having identical composition beside different chemical and physical properties.

The quantity of water in zeolites depends closely on the nature of the basis. Therefore the calcium zeolites include more water than the corresponding sodic types.

In connection with the methods of determination of zeolites beside crystallographic and x - ray methods, attention must also be paid to the colouring proceedings applied for the first time in 1872 by J. Lemberg (3), continued and improved afterwards by St. J. Thugutt (4) with a minute observance of time and degree of dehydration. This method consists in an exchange of alcalic ions into silver ions with a following action of potassium chromate. Hereby each zeolite becomes differently coloured. In such a manner the rhombic epinatrolite was discovered as deriving from sodalite (5). Among others the inhomogeneity of hydronephelite was confirmed which had been obstinately treated as a chemical individuum (6). Analogical observations have been made concerning the cancrinite, ittnerite, scolopsite, lintonite, faröelite, galactite. The near relationship between zeagonite and phillipsite was proved as well as the existence of three different types of the latter. It is of interest that for such a subtile inquiry only a few milligram portions of the specimen are sufficient.

The order of crystallization of different zeolites depends strictly on the nature of the parental mineral. The most sensitive among the feldspatoides is the leucite. The next is the sodalite with congenetic nosean and haüyn. On the third place appears nephelite and then follow the feldspars. Analcite deriving from leucite belongs therefore to the earliest products of crystallization. Upon it settles the epinnatrolite deriving from the sodalite. The youngest one is natrolite, deriving from nephelite. All other assumptions in this matter, as the hypothesis of Cornu concerning the connection between the succession of zeolites and their hydration or acidity, have nothing in common with the real state of things.

The pseudomorphosies can in many cases, reveal the nature of the parental mineral, but the main work must be fulfilled by means of minute chemical investigations. The most successful synthesies concerning the genetical problems play only a limited part especially when it appears impossible to reproduce all the conditions given in nature. As the source of zeolites different rocks are known: effusive, deep, metamorphic types, contactproducts, metallic veins, thermic waters. Sometimes conditions seemingly little advantageous can be nevertheless favourable to its origin <sup>1</sup>).

# NEPHELITE DERIVATIVES

Genetical considerations, the existing pseudomorphosies spoke for nephelite as parental mineral of natrolite. In order to be aware of the way in which the above mentioned transmutation could be accomplished it was above all necessary to know the inward structure of the nephelite. Its empirical formula  $K_2Na_8Al_{10}Si_{11}O_{42}$  is composed of 73 atoms being at the same time, according to F. A. Bannister and M. H. Hey (7), unit cell of nephelite. Sometimes calcium replacing the sodium diminishes this number of atoms. St. J. Thugutt (8) pointed out that nephelite heated at 200° C with potassium carbonate solution or with water alone breakes into natrium-aluminotrisilicate, potassiumaluminotrisilicate and natriumaluminate, hence its constitution formula:

8 
$$Na_2Al_2Si_3O_{10} \cdot 3 K_2Al_2Si_3O_{10} \cdot 4 Na_2Al_2O_4$$

at the same time its smallest molecular weight. In comparison with the above cited empirical formula this one includes 219 that is three times as many atoms. This result was fully confirmed by the processes occurring in nature.

Each nephelite component serves as a source of various minerals. The separate components can be joined together in pairs in different manners, and can annex also some alien units and produce a new row of minerals. To begin with the sodium link 8  $Na_2Al_2Si_3O_{10}$  which joined with 16  $H_2O$  gives natrolite: 8  $Na_2Al_2Si_3O_{10} \cdot 16$  H<sub>2</sub>O, including 424 atoms. It should be noted that the same number of atoms was found by M. H. Hey (9) in the space group of natrolite, starting from his own x - ray investigations. Owing to the transuding of the rocks of calcium - bearing waters the natrolite delivers natrium producing the scolecite enriched in its water:  $8 \text{ CaAl}_2 \text{Si}_3 \text{O}_{10} \cdot 24 \text{ H}_2 \text{O}$ . This joined with natrolite gives mesolite:  $8(Ca_2Al_4Si_6O_{20} \cdot 6H_2O + Na_2Al_2Si_3O_{10} \cdot 2H_2O)$ . Identical number of atoms of the space group of both latter minerals was stated by the same author M. H. Hey. Edingtonite is a corresponding aluminotrisilicate of barium.

From natriumaluminate  $Na_2Al_2O_4$  by means of water and carbonic acid there derives the hydrargillite  $Al_2O_3 \cdot 3H_2O$  resp. diaspore  $Al_2O_3H_2O$ . The mechanical mixture of both the

above mentioned minerals with natrolite was for a long time treated as a self dependant mineral under the name of «hydronephelite» or «bergmannite» (10).

The natriumferrate traces accompanying the nephelite become transformed mightily in hematite. Hence the red colour of its primary decomposing products. After passing to the second layer they appear just now colourless.

A combination of calciumaluminotrisilic link with natriumaluminate produces the thomsonite:

 $8\,CaAl_2Si_3O_{10}\cdot 4\,Na_2Al_2O_4\cdot 24\,H_2O$ 

With the increase of calcium there arises the comptonite:

$$8 \operatorname{CaAl}_2 Si_3 O_{10} + 2 \operatorname{Na}_2 Al_2 O_4 + 2 \operatorname{CaAl}_2 O_4 + 28 \operatorname{H}_2 O_4$$

When we remove the rest of natrium we receive the gismondine:  $8 \operatorname{CaAl}_2\operatorname{Si}_3\operatorname{O}_{10} \cdot 4 \operatorname{CaAl}_2\operatorname{O}_4 \cdot 32 \operatorname{H}_2\operatorname{O}$ 

With calcium increasing the included water grows parallelly.

Calciumaluminotrisilicate, joining the potassiumaluminotrisilicate link, transforms itself into zeagonite:

$$8 \text{ CaAl}_{2} \text{Si}_{3} \text{O}_{10} \cdot 3 \text{ K}_{2} \text{Al}_{2} \text{Si}_{3} \text{O}_{10} \cdot 55 \text{ H}_{2} \text{O}$$
(11).

Eight molecules natriumaluminotrisilicate with three molecules natriumaluminate, six molecules calcium - natriumcarbonates and nine molecules of water produce the cancrinite:

 $8 \ CaAl_2Si_3O_{10} + 3 \ Na_2Al_2O_4 + 5 \ CaCO_3 + Na_2CO_3 + 9 \ H_2O$ 

The fourth  $Na_2Al_2O_4$  link, combined with the hydrolized potassiumaluminotrisilicate, produces muscovite:

 $3 [(K,H)Al_2Si_3O_{10}]Na_2Al_2O_4$ 

Attention must be paid to the fact that pseudomorphosies of cancrinite with muscovite after nephelite belong to the wellknown phenomena. Such a combination occurs for example in nephelitesyenite from Ditró and in several other localities of the world.

The aluminotrisilicic links of nephelite are able to join also other alien elements forming the seemingly impenetrable phillipsitic group. However, having in view the internal structure of the parental nephelite, all these problems could be also unraveled. From the three kinds of phillipsite types each distinguishes itself by its own chemical composition; different chromatophilic and peculiar optical properties. Two of them are richer in silica, but differ by the basic ions. The third, containing less silica, is most widely spread in nature under the old name «phillipsite». To the sodic type the once used name «herschelite» was confered, to the calcium type — the name «marburgite», reminding of the place of its origin. From the three nephelite links only two enter into the phillipsite molecule:  $8 Na_2Al_2Si_3O_{10}$ <sup>-1</sup>) and  $3 K_2Al_2Si_3O_{10}$ . Thet third constituent draws out its substance from a foreign source. For phillipsite is leucite transformed into analcite. As suggested by the author, by substracting from all phillipsite contents (Nr. II) both aluminotrisilic links, there remains the investigated analcite. Hence the phillipsite formula:

 $8 \ CaAl_2Si_3O_{10} + 3 \ K_2Al_2Si_3O_{10} + 4 \ (Na_2Al_2Si_4O_{12} + 2 \ H_2O) + 51 \ H_2O$ 

Containing Nr I:

 $SiO_2$   $Al_2O_3$   $Fe_2O_3$  CaO  $K_2O$   $Na_2O$   $H_2O$ S 45.17 23.50 Nr I 6.88 4.33 3.81 16.31 100.00 \_\_\_\_\_ Nr II 45.48 23.68 6.27 3.49 101.34 0.04 5.98 16.40

Nr II — phillipsite from Hohentwiel, according to St. J. Thugutt and T. Woyno.  $Al_2O_3: SiO_2: H_2O$  ratio is in both cases identic = 15:49:59. The microchemically confirmed presence of a little herschelite admixed and of some leucite rests explains a certain difference existing in the strong bases content. The mutual ratio of three phillipsite links = 8:3:4 coincides strictly with that of nephelite. Herein four analcite molecules take the place of four  $Na_2Al_2O_4$  molecules.

The herefore analyzed herschelite from Aci Castello, Etna, (12) represents the calcic type of the phillipsite group. After removing from herschelite Nr III both aluminotrisilicic links:  $8 Na_2Al_2Si_3O_{10}$  and  $3 K_2Al_2Si_3O_{10}$  there remains a desmine - like natrium - calcium - aluminohexasilicate as the third searched link. The herschelite becomes finally expressed as

 $\frac{8 N a_2 A l_2 S i_3 O_{10} + 3 K_2 A l_2 S i_3 O_{10} + 4 \left[ \left(\frac{3}{4} C a_4^{1} N a_2\right) A l_2 S i_6 O_{10} + 6 H_2 O \right] + 42 H_2 O$ 

<sup>&</sup>lt;sup>1</sup>) resp. 8 Ca Al<sub>2</sub> Si<sub>3</sub> O<sub>10</sub>.

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containing Nr IV:

	${ m SiO}_2$	$Al_2O_3$	CaO	$K_2O$	$Na_2O$	$H_2O$	S
Nr IV	47.86	21.41	2.35	3.95	7.81	16.62	100.00
Nr III	47.91	22.40	2.69	3.93	7.99	16.63	101.55
Nr V	3.86	1.73	0.19	0.32	0.63	1.34	8.07

The mutual ratio of the three nephelite constituents = = 8:3:4 recurs here with perfect accuracy.

Desmine is a derivative of sanidine. According to E.Zaniewska-Chlipalska (13) the sanidines contain about 1.25% barium. Esper S. Larsen and F. B. Benett (14) established in the sanidine from Highwood Mountains of Montana up to 5% BaO. Hence the barium presence in desmine and in herschelite. The most advantageous conditions for similar combinations as the building of herschelite appear evidently when the zeolitisation of both parental minerals becomes simultaneously accomplished.

Herschelite occurs besides Sicily, the Giant Island etc. in great quantity in the slimes and muds of the 5 km deep Indian Ocean and of the Pacific. The analysed mud body contains 8.07% herschelite (Nr. V). Notwithstanding the gigantic preponderance of sodium ions in sea water the herschelite totally kept its potassium. The durability of the herschelite space net becomes visible also in its passing from the primary to the secondary bed in the form of ultramicrons. There appears herein the spheroidal radiated, either growing out from the underground in isolated acicular crystals, or suspended freely in mud, partly twined and crossed diversely.

The herschelite treated successively with  ${\rm AgNO}_3$  and  ${\rm K}_2{\rm CrO}_4$  solutions acquires an equal, strong orange hue.

Except the strong bases the formerly analysed marburgite Nr VI differs but little from the above discussed herschelite. The mutual ratio of the three marburgite constituents = 8:3:4 remains unaltered. In connection with the nature of the introduced calcium the quantity of water increases. Hence the formula:

$$\begin{aligned} 8 \, CaAl_2Si_3O_{10} \cdot 3 \, K_2Al_2Si_3O_{10} \cdot 4 \, [(\frac{1}{t}\,Ca\,\frac{1}{2}\,K_2\,\frac{1}{4}\,Na_2)O \cdot \\ Al_2Si_6O_{10} \cdot 6 \, H_2O] \cdot 46^*H_2O. \end{aligned}$$

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Nr VII marburgite calculated according to the above formula.

	$SiO_2$ $Al_2O$	, CaO MgO	K <sub>2</sub> O Na <sub>2</sub> O	$H_2O$	S
Nr VI	47.16 21.70	7.06 0.46	6.74 1.16	17.38	101.66
Nr VII	47.20 21.1	6.96 —	6.49 0.85	17.39	100.00

It is important that from the three nephelite constituents the potassic link  $K_2Al_2Si_3O_{10}$  which occupies the central place of the space net appears the most durable. The waters carry away the surrounding  $Na_2Al_2O_4$  link, the sodium of the aluminotrisilicic link leaves its place to the calcium, from abroad there advance the foreign links which have various character, such as analcite, desmine or erionite, the potassic link persists meanwhile immovable. Depending on the external conditions the zeolitisation of nephelite proceeds with different rapidity and tends in various directions. Certain zeolites belong constantly to the earlier period of transmutations, when others having simple structure appear later. To the first belongs the phillipsite. At Hohentwiel (Baden) it appears in the form of vellow - flesh coloured tablets covered with fibrous natrolite. In the environs of Carlsbad between Satteles and Schömitz the earlier phillipsite intrudes between the phonolite blocks, covers the walls of fissures, but just then upon it there appears natrolite with a little comptonite. In the Bohemian basalts and phonolites of Salesel on the ground of some geodes there appears the fibrous - radiated phillipsite covered with natrolite or epinatrolite. Also on the Hungarian basalts upon Platten Lake the younger natrolite settles about the earlier crystallized phillipsite. (15).

Examining all that occurs on the ground of the transformed nephelite, it is impossible not to remark that there reigns here an uncommon order and harmony. One meets nothing chaotic or arbitrary. During the transformation each atom tends to its place destined beforehand by the parental mineral and preserves at the same time its individuality. Therefore the calcium - bearing marburgite comprises more water than the sodic herschelite. Upon the inward arrangement of the space net of the three above mentioned zeolites we have no information. The chain formula indicates only that there exist certain groupings of atoms able to be removed or exchanged by other units which resembles the radicles known in organic chemistry.

The mutual ratio of the three characteristic links = 8:3:4 must find its distinct reflection in the structure of the space net. With reference to nephelite, its inward skeleton, this pith  $3 K_2 A l_2 S i_3 O_{10}$  is surrounded by a collective electron cover in three directions conditionating the existence of a trigonal axis. The electron sphere of  $4 N a_2 A l_2 O_4$ , surrounded on four sides, diminishes the symmetry. Meanwhile, the electron cover of  $8 N a_2 A l_2 S i_3 O_{10}$  imposed on eight sides, takes seemingly the symmetry up conferring to it the hexagonal type with a sixfold axis, this being however only a screw axis, in accordance with F. A. Bannister and M. H. Hey x-ray research. The symmetry of phillipsite is still more abased, namely owing to the presence of the water of crystallisation and of four links having a more complicated structure than that of sodiumaluminate - bearing nephelite.

Owing to the mutual coalescences and intergrowings of phillipsite, herschelite and marburgite the x - ray searchings of singular types have not given the desired results. For instance it is not known to which of the three types belong the data given by H. Strunz (16) for phillipsite unit cell dimensions:  $a_0 = 10.00$  Å,  $b_0 = 14.23$  Å,  $c_0 = 8.62$  Å. Space group  $C_{2h}^2$  or  $C_{2}^2$ , axes ratio a : b : c = 0.702 : 1 : 0:685.

Phillipsite being sensitive towards thermical action loses already at 93° C 3.06% of water. Heated for half a second at 140° it shows greatest chromatophily. With AgNO<sub>3</sub> and  $K_2CrO_4$  solutions the brown hue appears momentally. Above this temperature the chromatophilic properties become weaker passing into the colours of strawberry and orange. With a growing dehydration it appears turbid, alternately strengthening and weakening. With methylenblue (1 : 1000 H<sub>2</sub>O) natural phillipsite remains indifferent.

Wellsite externally resembles harmotome and phillipsite twins. It seemingly represents a combination of zeagonite with edingtonite, in which a part of barium has been supplied by strontium, calcium, natrium and magnesium. To the formula:

$$8 CaAl_2Si_3O_{10} \cdot 3 K_2Al_2Si_3O_{10} \cdot 4 BaAl_2Si_3O_{10} \cdot 52 H_4O$$

belong the following numbers (Nr VIII):

Al<sub>2</sub>O<sub>3</sub> BaO SiO<sub>3</sub> CaO K<sub>2</sub>O H<sub>0</sub>O S Nr VIII 41.48 23.50 9.43 6.88 4.33 14.38 100.00 According to J. H. Pratt and H. W. Foote (17) the wellsite from Clay Co. Buck Creek in N. Carolina includes: SiO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub> BaO SrO CaO MgO Na<sub>2</sub>O H<sub>2</sub>O S

Nr IX 43.86 24.96 5.07 1.15 5.80 0.62 1.80 13.35 100.01 G. Tschermak (18) denied the selfexistence of wellsite supposing herein a mixture of several aluminotrisilicates : scolecite, natrolite etc. It is not difficult to verify this assumption applying for zeolites the very characteristic microchemical reactions (19). The mutual ratio of three wellsite links corresponds strictly to that of the parental nephelite. The present barium could be furnished by barium-bearing potassiumfeldspar.

In a village Courzy, on the way leading to Symferopol on the Crimea, there occurs an altered porphyrite rock containing besides prehnite, chlorite, calcite, quartz and some zeolites, among them: heulandite, gmelinite, phillipsite, analcite and leonhardite. A. Fersmann (20) met another new zeolite, which seemed to him to be wellsite though the alleged chemical analysis (Nr X) showed a totally different composition in comparison with wellsite:

 $SiO_2 Al_2O_3 BaO SrO CaO K_2O Na_2O H_2O S$ Nr X 49.40 19.02 4.75 0.68 5.70 3.50 0.10 16.68 100.03 turning our attention above all to the overplus of silica. In wellsite the mutual ratio of  $Al_2O_3 : SiO_2 = 1 : 3$ , in the new species = 1 : 4.37. Therefore the very name courzite lent from the locality of its origin. Taking K<sub>2</sub>O as a unity, after repartition of singular links, the corresponding courzite formula is:  $8 CaAl_2Si_3O_{10} \cdot 3 K_2Al_2Si_6O_{16}$ 

4 [
$$(BaSrCaK_2Na_2H_2)OAl_2Si_{16}$$
] · 75 H<sub>2</sub>O

The central potassic link is here a hexasilicate instead of a trisilicate. The mutual ratio between three courzite links is in analogy to nephelite, phillipsite, herschelite, marburgite, wellsite = 8:3:4. Hence their resembling forms of crystals.

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Nephelite is the parental mineral of all these zeolites. Moreover, the presence of some basic water may be also mentioned. Certainly it is the water escaping above 300° C. Courzite belongs to the earlier decomposition products. Upon it there settles natrolite and leonhardite, both having simple structure.

As to the chemical properties of the discussed nephelite derivatives one must emphasize—their ready solubility in diluted acids. Natrolite becomes dissolved already in distilled water. This colloidal solution crystallizes again preserving totally the inward structure of primary natrolite. With a superfluity of water the natrolite becomes decomposed (21), losing a part of soda and silica. According to J. Lemberg (22) the natrolite, heated about 200° C with KCl or other alcalic solutions exchanges only its basic ion as salt of a durable  $H_2Al_2Si_3O_{10}$   $H_2O$  acid.

At 800° C dehydrated natrolite gains with  $AgNO_3$  and  $K_2CrO_4$  solutions a red-orange colour. With methylenblue (1:1000 H<sub>2</sub>O) the hue is strongly sapphirine. Natural n at rolite remains indifferent with the same reactives.

Scolecite treated with natrium, kalium, silver resp. thallium salts in water solutions exchanges readily its calcium for sodium, potassium, silver or thallium. Dehydrated for 2 seconds at  $800^{\circ}$  C it becomes rosy coloured with Ag<sub>2</sub>CrO<sub>4</sub>.

Mesolite shows in the same conditions a pale rosy hue.

Zeagonite appears rosy-orange, but even prolonged dehydration does not weaken its chromatophyllic properties.

Selfdependant thomsonite is a great rarity. Its coalescences and intergrows with various zeolites are not easily discernable, hence the flood of names given to mixtures in the conviction that we have to deal with individual bodies. There may be cited here the «lintonite», the «faröelite» and among others the thomsonite coalescences pointed out by M. H. Hey (23) during his well - known x - ray investigations. For instance winchelite, gibsonite, harringtonite, scoulerite, mesolitine, ozarkite. It is unusual that M. H. Hey did not remark the inhomogeneity of faröelite erroneously regarded as a selfexisting mineral, able to produce with thomsonite some isomorphic mixtures.

# SODALITE DERIVATIVES

According to St. J. Thugutt (24) sodalite heated above 200 C with weak potassiumcarbonate solution breaks into aluminotrisilicate, sodiumaluminate and sodiumchloride, changing at the same time sodium into potassium.

 $12 \text{ Na}_2 \text{Al}_2 \text{Si}_2 \text{O}_8 \cdot 8 \text{ NaCl} + 8 \text{ K}_2 \text{CO}_3 + 24 \text{ H}_2 \text{O} = \\8 (\text{K}_2 \text{Al}_2 \text{Si}_3 \text{O}_{10} \cdot 3 \text{ H}_2 \text{O}) + 8 \text{ NaCl} + 8 \text{ Na}_2 \text{CO}_3 + 4 \text{ Na}_2 \text{Al}_2 \text{O}_4$ 

From these decomposition products the primary sodalite becomes readily regenerated.

$$8 \operatorname{Na}_2 \operatorname{Al}_2 \operatorname{Si}_3 \operatorname{O}_{10} \cdot 4 \operatorname{Na}_2 \operatorname{Al}_2 \operatorname{O}_4 \cdot 8 \operatorname{NaCl}$$

Boiling water removes already the natriumchloride. After it there retreats natriumaluminate — a source of hydrargillite and diaspore. The remaining aluminotrisilicate  $8 Na_2Al_2Si_3O_{10}$  joins 16 H<sub>2</sub>O producing epinatrolite.

Epinatrolite crystallizes in rhombic prisms, obscurs the light straightly, its double refraction is weaker than that of natrolite. Parallel coalescences of rhombic epinatrolite with monoclinic natrolite are frequent.  $\gamma - \alpha$  of natrolite = 0.0132, that of epinatrolite = 0.0124. With  $\rho < \gamma$ . Epinatrolite undergoes dehydration four times more quickly than natrolite and shows remarkably weaker chromatophillic properties towards silver-chromate and methylenblue. Heated for 7 seconds epinatrolite loses already its capacity to react with silvernitrate. A mixture of epinatrolite, hydrargillite and diaspore was for a long time regarded as a self - existing mineral under the name hydronephelite. This misunderstanding was elucidated by microchemical and exact chemical reactions.

Episcolecite. The supposition that among the decomposition products of sodalite there may exist other metameric bodies besides epinatrolite was entirely confirmed. H. Michel published in 1920 (25) that near Eulau, in phonolite accompanying the marlmud there occurs a new rhombic mineral, namely episcolecite, having the same composition as scolecite:

but other physical properties : G = 2.244,  $n_{\alpha} = 1.512$ ,  $n_{\gamma} = 1.515$ , double refraction weaker than with scolecite.

According to M. H. Hey (26) there exist also two varietes of thomsonite, differing by their shape and by the curve of vapour tension. It is only unknown which of the two modifications concerns the sodalite and which belongs to nephelite. Judging by the epinatrolite the lack of constancy indicates the sodalite as the parental mineral of metameric thomsonite. Such varieties are characterised by an easier solubility, greater vapour tension and lower melting point.

Metameric comptonite:

 $8 \operatorname{CaAl}_2 Si_3 O_{10} + 2 \operatorname{CaAl}_2 O_4 + 2 \operatorname{Na}_2 Al_2 O_4 + 28 \operatorname{H}_2 O_4$ 

and metameric gismondine

$$8 \operatorname{CaAl}_{2}\operatorname{Si}_{3}\operatorname{O}_{10} \cdot 4 \operatorname{CaAl}_{2}\operatorname{O}_{4} \cdot 32 \operatorname{H}_{2}\operatorname{O}_{5}$$

are till now unknown. Only the genetical connection between gismondine and haüyne is confirmed.

The most characteristic are also both varieties of cancrinite. Rosy - coloured, containing a little iron and potassium, it belongs to the parental nephelite (eleolite). The yellow cancrinite, derived from sodalite, is free of such an admixture. The decomposed sodalite loses at first natrium chloride and the fourth part of natriumaluminate. Their place is taken by calciumcarbonate and water.

$$\begin{split} &8 \operatorname{Na_2Al_2Si_3O_{10}} \cdot 4 \operatorname{Na_2Al_2O_4} \cdot 8 \operatorname{NaCl} + 5 \operatorname{CaCO_3} + \operatorname{Na_2CO_3} + \\ &9 \operatorname{H_2O} - \operatorname{Na_2Al_2O_4} - 8 \operatorname{NaCl} = 8 \operatorname{Na_2Al_2Si_3O_{10}} \cdot 3 \operatorname{Na_2Al_2O_4} \cdot \\ &5 \operatorname{CaCO_3} \cdot \operatorname{Na_2CO_3} \cdot 9 \operatorname{H_2O} \end{split}$$

The mutual ratio of sodalite and cancrinite molecular weights = 3876 and 4014 corresponds to that of their specific gravities: 2.29 and 2.37. The yellow colour may proceed from dispersed cerium, lanthanum and didymium. Having in view the above mentioned constitution formula other sodalite derivatives are not expected.

Summing up the obtained results it must be said that in spite of the great similarity of the inward constitution of sodalite and nephelite the alteration products of both minerals are not identic. The disparity concerns not only the chemical but also the physical properties.

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# LEUCITE DERIVATIVES

Analcite. No one of the zeolites evoked as many contradictions concerning their origin as did analcite. When after a certain hesitation the hydrous origin was accepted the analcite was continually treated as an immediate magma product. And when the hydrous origin itself seemed to suggest no more doubts there appeared new difficulties connected with the choice of the parental mineral. Some allowed the priority to sodalite, others preferred nephelite, the leucite having least aspects. The knowledge of the inner structure of the parental mineral proved to be indispensable. It appeared uncommonly clear that among the decomposition products of nephelite and sodalite there is no place for analcite. Taking into consideration the chemical character of analcite as a hydrated aluminotetrasilicate of sodium the leucite represents an anhydrous aluminotetrasilicate of potassium. The unit cell of analcite contains 8 molecules  $Na_2Al_2Si_4O_{12} \cdot 2H_2O$ . The near relationship of both minerals has been also confirmed by the experiments of J. Lemberg (27). Leucite, treated with natrium salts in hydrous solution changes into analcite and vice versa: acting upon analcite with potassium salts regains leucite. St. J. Thugutt obtained the same results (28), applying weak solutions. The analogy between leucite and analcite was also confirmed by J. W. Clarke and G. Steiger (29) by means of ammonia chloride: both minerals gave indentical substitution products.

The extraordinary sensitivness of leucite towards outer acting appears in many observations made in nature. According to A. Lacroix (30) the conversion of leucite into analcite in the lavas of Trebisonda was effected exclusively by surface waters penetrating the rocks.

It is remarkable that H. S. Washington (31) perceiving the presence of characteristic inclusions of leucite from Ghisen's basaltic rocks did not point out the genetical connection between both these minerals.

An important argument speaking for the near relationship between analcite and leucite is the discovery of potassic analcite in the N. A. Montana St., containing 4.48% K<sub>2</sub>O. Lastly, the small residues of potassium in analcite belong to the phenomena often met with. Analcite deriving from secondary layers are ordinarily free of alien admixtures.

The above discussed matters concern the hydrothermal analcite. However, there are adherents of pyrogenic analcite, with Bunsen at their head. For instance G. Tschermak, Evans, Lindgren, Pirsson and Corda, A. Pelikan, E. S. Larsen<sup>1</sup>), Robert Michel<sup>2</sup>) and many others. They consider the analcite, as an exceptional rockforming zeolite which crystallizes immediately from igneous magma.

It is worth attention that H. Rosenbusch (32) was a stern adversary of a magmatic origin of analcite. According to him any one who wishes to impute the stamp of a primary magma secretion to analcime should find it first in the present lavas. That, however, was till now impossible.

The experiments of J. Lemberg (33) and my own ones (34) pointed out that of all feldspatoides leucite appears to be the least resistible, the second place belongs to sodalite, the third is occupied by the nephelite. Therefore analcite is the first to crystallize, then comes epinatrolite and after them the natrolite. Sometimes the traces of leucite perish to the eye, especially when it curdles and finally stiffens filling up the free spaces between the earlier crystallized minerals. Such a mineral adorned in foreign accidental contours is for instance the analcite deriving from leucite and occurring in missourites. It makes the impression of a primary mineral crystallized immediately from igneous magma.

Analcite occurs also in certain sediments although only in a small quantity. In 1946 W. D. Forster and F. L. Feicht (35) described some concretions, weighing about 2 kg, composed chiefly of pyrite beside some dolomite, calcite, kaolinite and a little analcite. To explain the origin of the analcite the authors appealed to certain experiments. S. F. Powell (36) heated some aluminates and silicates with water at  $180 - 430^{\circ}$  C. W. Noll (37) received in 1936 analcite by boiling natriumaluminate solution with silica under the pressure of 87 atm. during 15 - 24 hours at 300° C.

<sup>&</sup>lt;sup>1</sup>) E. S. Larsen, C. R. Soc. géol. de France 3 Décembre 1945.

<sup>&</sup>lt;sup>2</sup>) Robert Michel C. R. Ac. Sc. Paris 226 (1948) 2159.

Laumonite  $CaAl_2Si_4O_{12} \cdot 4H_2O$  contains:

$\mathrm{SiO}_2$	$Al_2O_3$	CaO	$H_2O$	S
51.07	21.70	11.91	15.32	100.00

In comparison with the insensitive analcite the natural laumonite treated with methylenblue or silverchromate becomes blue resp. rosy coloured. If dehydrated it appears turbid and gradually loses its chromatophilic properties. The conditions of its origin are not stated well enough. The inward structure has not been investigated. The experiment of J. Lemberg (38) undertaken in order to convert its calcium into sodium by means of natrium carbonate solution indicates only that there exists a certain relationship between laumonite and analcite. The same was also confirmed by the pseudomorphosies of analcite after laumonite met by Greg and Letts om at Bowling in Scotland. In a basaltic rock at Poonah and in Hartfield Moss (Renfrewshire) laumonite occurs accompanied by analcite.

# PLAGIOCLASE DERIVATIVES

## Chabazite and gmelinite

It is not easy to say what the chabazite twins represent without being sure about their individuality. The data assembled by C. Hintze (39) do not give a satisfactory answer in this regard. Among numerous analyses there reigns an uncommon chaos. The oscillations concern not only the strong bases but also the mutual ratio between alumina and silica, balancing within wide limits — from 3 to more than 5 molecules of silica towards 1 molecule of alumina. The selection of a characteristic type presents great difficulties in such conditions. The above mentioned mutability concerns not only the chabazites of various origin but also certain types growing from a common bulk.

According to Streng (40), W. Fresenius (41) and J. Lemberg (42) the chabazites represent some combinations of calciumaluminobisilicate with natriumaluminohexasilicate, similar to the plagioclases. This hypothesis baffled the expectations for want of any parallelism between the increase of sodium and silica. Rammelsberg (43) adopted the-

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refore another conception combining together three different links: the aluminotri-tetra-and pentasilicates. And when this assumption also proved unsatisfactory the calcium-sodiumaluminotetrasilicate with six molecules of water was acknowledged as the fundamental element of all chabazites. To such a norm there corresponds only the chabazite from Cyprus which has been analysed by Damour (44).

Pure calcium or sodium types are not known. The chabazites from Annerod Nr. XI and from Rübendörfel near Aussig Nr. XII, the gmelinite from Aci Castello Nr. XIII approach only the above mentioned norm.

Nr XI	44 (Ca $Al_2Si_4O_{12} \cdot 6H_2O$ ) $\cdot$ 3 (Na $_2Al_3Si_4O_{12} \cdot 6H_2O$ ) $\cdot$
	$\cdot$ 1 (K <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> $\cdot$ 6 H <sub>2</sub> O)
	_

- Nr XII 44 (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> · 6 H<sub>2</sub>O) · 3 K<sub>2</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> · 6 H<sub>2</sub>O) · (Na<sub>2</sub>Al<sub>3</sub>Si<sub>4</sub>O<sub>12</sub> · 6 H<sub>2</sub>O)

	Nr. XI	theor.	Nr. XII	theor.	Nr. XII	I theor.
$\mathrm{SiO}_2$	47.00	47.33	47.50	47.20	47.46	47.89
$\mathrm{Al}_2\mathrm{O}_3$	19.71	20.11	20.00	20.06	20.18	20.35
$Fe_2O_3$	0.15				<del>-</del>	
CaO	10.63	10.12	10.20	10.10	0.25	0.25
$Na_2O$	0.65	0.76	0.23	0.25	9.35	9.28
$K_2O$	0.33	0.39	1.24	1.15	4.17	4.27
$H_2O$	22.29	21.29	21.40	21.24	17.65	17.96
	100.76	100.00	100.57	100.00	99.06	100.00
$SiO_2$ :	$A1_2O_3$	4.05:1	4.0	04:1	4.01	: 1

As expected, the calcium - bearing chabazites Nr XI and Nr. XII contain more water than the gmelinite Nr. XIII. In other sodiocalcic types, for instance in chabazite Nr. XIV from Cape Blomidon or in chabazite Nr. XV from Cyprus, this difference is no more visible and the quantity of six molecules of water for one aluminosilicate molecule appears normal.

Nr. XV 11 (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> · 6 H<sub>2</sub>O) · 10 (Na<sub>2</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> · 6 H<sub>2</sub>O) · 1 (K<sub>2</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> · 6 H<sub>2</sub>O)

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	Nr. XIV	theor.	Nr. XV	theor.
$SiO_2$	47.19	47.10	46.37	47.01
$Al_2O_3$	20.13	20.02	19.55	19.98
CaO	7.44	7.33	5.26	5.49
$Na_2O$	3.54	3.48	5.51	5.52
$K_2O$	0.91	0.88	0.78	0.84
$H_2O$	20.53	21.19	22.00	21.16
	99.74	100.00	99.47	100.00
$\mathrm{SiO}_2:\mathrm{Al}_2\mathrm{O}_3$		4:1	4.03	: 1

The chabazite from Cyprus Nr. XV may be explained with a little deviation also by the formula:

 $CaAl_2Si_2O_8 \cdot 6 H_2O \cdot Na_2Al_2Si_6O_{16} \cdot 6 H_2O$ 

reminding of the plagioclases.

Independently of the five above cited chabazites the norm in the others is:  $4 \operatorname{SiO}_2 : 1 \operatorname{Al}_2 \operatorname{O}_3$  either transgressed or not attained. To the first there belong the chabazites from Bergen Hill Nr. XVI, from Antrim Nr. XVII, from Pinacle Island Nr. XVIII, from Two Island Nr. XIX.

	Nr		Nr		Nr		Nr	
	XVI	theor.	XVII	theor.	XVIII	theor.	XIX	theor.
$SiO_2$	48.67	48.53	48.56	48.92	50.67	<b>49.88</b>	51.36	51.81
$Al_2O_3$	18.72	19.41	18.05	19.37	18.50	18.86	17.81	18.26
$Fe_2O_3$	0.10		0.11		0.15	<u> </u>	0.15	
CaO	2.60	2.66	6.13	6.74	1.05	1.29	5.68	5.90
$Na_2O$	9.14	8.85	3.85	4.02	9.88	10.02	3.92	4.35
$K_2O$		<b>5</b> .	0.39	0.44	0.16		0.23	0.34
$H_2O$	21.35	20.55	21.66	20.51	20.15	19.95	20.96	19.34
	100.58	100.00	98.75	100.00	100.56	100.00	100.11	100.00
$SiO_2$ : A	$l_2O_3$	4.40 :	1	4.51:	1	4.64:1		4.86:1

Some chabazites called acadiolites contain still more silica. Here belongs the chabazite from Parsboro Nr. XX and from Cape Blomidan Nr. XXI, both approaching the formulas A and B.

A 30 
$$(CaAl_2Si_5O_{14} \cdot 6H_2O) \cdot 12 (Na_2Al_2Si_5O_{14} \cdot 6H_2O) \cdot 3 (K_2Al_2Si_5O_{14} \cdot 6H_2O)$$

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В	24 (Ca $Al_2Si_4O_{12}$ ·	6 H <sub>2</sub> O)	· 6	$(CaAl_2Si_6O_{16})$	· 6 H <sub>2</sub> O)	•
	12 (Na <sub>2</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>16</sub> ·	6 H <sub>2</sub> O)	· 2	$(K_2Al_2Si_6O_{16} \cdot$	6 H <sub>2</sub> O)	

	Nr. XX	Nr. XXI	A	В	
$\mathrm{SiO}_2$	52.02	53.71	52.62	52.23	
$Al_2O_3$	17.88	17.63	17.89	18.09	
CaO	4.24	6.52	6.55	6.77	
$Na_2O$	4.07	3.10	2.90	3.00	
$K_2O$	3.03	0.80	1.10	0.76	
$H_2O$	18.30	17.98	18.94	19.15	
	99.54	99.74	100.00	100.00	
$SiO_2:Al_2O_2$	3	4.95:1	5.17:1		

The ratio of six molecules of water to one molecule of aluminosilicate seems to be constant. Whereas the ratio of the strong bases is variable. In chabazites poor in silica there appears an aluminotrisilisic link as a constituent which abates the acidity. Here belongs the chabazite Nr. XXII and XXIII, both from Richmond (Australia).

15 (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>  $\cdot$  6 H<sub>2</sub>O  $\cdot$  11 (Na<sub>2</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>  $\cdot$  3 H<sub>2</sub>O) Nr. XXII Nr. XXIII 12 (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>  $\cdot$  6 H<sub>2</sub>O  $\cdot$  10 (Na<sub>2</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>  $\cdot$  6 H<sub>2</sub>O)  $\cdot$ 2 ( $K_2Al_2Si_3O_{10} \cdot 6H_2O$ )

	Nr. XXII	theor.	Nr. XXIII	theor.	
${ m SiO}_2$	46.26	46.62	43.84	43.60	
$Al_2O_3$	23.04	22.16	20.99	21.18	
CaO	7.02	7.02	5.89	5.82	
$Na_2O$	5.96	5.70	5.78	5.36	
$K_2O$	0.09		1.83	1.63	
$H_2O$	18.52	18.50	21.97	22.41	
	100.89	100.00	100.30	100.00	
$SiO_2$ : $Al_2O_3$	3.41 :	: 1	3.55 : 1		

In Nr. XXII one is surprised at the lack of water with a simultaneous increase of calcium. It proves a certain inhomogeneity of this type. Strictly speaking the problem of chabazite constitution must be delayed to some later time. The proofs undertaken by the author (45) advise a certain caution. Namely dehydrated chabazite from Usti (Bohemia) treated at

800° with  $AgNO_3$  and  $K_2CrO_4$  solutions appears not homogeneously coloured. The bright and dark stripes suggest the presence of two different compounds. The similarly investigated gmelinite from New Scotland did not seem more homogeneous. This may be also the cause of optical failures, as stated by Mallard.

The colouring methods, and among them the silver method which has been quoted many a time, rendered valuable services thanks to their simplicity, facilitating for instance the discernment of parallel coalescences of rhombic epinatrolite with monoclinic natrolite (46), of thomsonite with mesolite (47) and of other seemingly homogeneous bodies. With time this method has been improved by a minute observation of temperature, time and dehydration conditions. X - ray research of M. H. Hey (48) undertaken to the same end greatly reduced the number of «new minerals» erroneously regarded as selfexisting ones.

Returning to the chabazite group it would be necessary to determine its unit cell, its space group and axes ratio. Meanwhile all that has been done till now bears the stamp of uncertainty.

H. Strunz (49) joins all the chabazites in the space group  $D_{3d}^5$ ,  $a_0 = 13.75$  Å,  $c_0 = 14.94$  Å,  $(c_0/a_0) = 1.087$ ,  $\alpha = 94^024'$ , z = 6. To avoid the fractions it would be necessary to magnify this formula four times:

6 (Ca, Na<sub>2</sub>, K<sub>2</sub>) Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>  $\cdot$  6 H<sub>2</sub>O,

representing at the same time the samallest molecular weight. For gmelinite  $(Na_2Ca)Al_2Si_4O_{12} \cdot 6H_2O$  H. Strunz quotes the following data: (c/a) = 1.017,  $\alpha = 105^045'$ , rhomboedric symmetry uncertain.

To the rocks upon which chabazite grows there belong: the granite, gneiss, diorite, granulite, porphyre, melaphyre, dolerite, limburgite, andesite, phonolite, basalte, tephrite,, trachite, pegmatite, quartz veins, crystalline schists. It is evident that there appears a different chabazite on the granitic ground than on basic rocks. For both of them, however, the plagioclases are the chief parental minerals. Their zeolitisation according to A. Lacroix (50) is accomplished in the Pyrenees Mts. relatively quickly. The process of zeolitisation does not cease

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even at  $0^{\circ}$ . The alternate night frost and the insolation during the day break the rock minerals facilitating the access of chemical agents.

It would seem that some analogical chabazite types should correspond to the separate plagioclase types. In fact no such parallelism was observed, except the one Cyprus type.

The chabazites bear various alien constituents. In the acid types there appear the aluminohexasilicates, in the basic types there occur the aluminotrisilicic links derived from nephelite or from sodalite. Traces of orthoclase resp. sanidine are visible in the potassic link, containing barium and strontium rests. The participation of the parental nephelite or so-dalite reveals their decomposition product — natrolite resp. epinatrolite. Hence also the probability of the existence of some metameric basic chabazites.

As to the inner structure neither the experiments of C. Doelter (51) undertaken in order to recrystallize some powdered chabazite samples in water saturated with carbonic acid, nor the efforts of H. Deville (52) to receive chabazites by joining their implied compounds, did not throw any light upon this question. The essays of J. Lemberg (53) reiterated at various times showed only the facility of exchange of strong bases of chabazite. According to J. Lemberg, from the same solution, with barium salts prevailing, there might crystallize the harmotome, and with a surplus of calcium — the chabazite. Meanwhile, much like the harmotome, the chabazites have nothing in common with regard to their inward structure.

## Levyne

Levyne, erroneously regarded by Breithaupt and Hausmann as an alteration product of chabazite bearing less silica, represents a selfexisting mineral. Cleavage parallel (0221) not distinct, differing from chabazite. Levyne is soluble in hydrochloric acid leaving gelatinous silica. The colouring capacity differs from that of chabazite. With AgNO<sub>3</sub> and  $K_2CrO_4$  solutions there appears a pale orange hue. Dehydrated at 500° C it becomes clear orange, darkening in proportion to the increasing dehydration. Levyne from Golden (Colorado) Nr. XXIV contains according to Hildebrand and Cross:

SiO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub> CaO Na<sub>2</sub>O K<sub>2</sub>O  $H_2O$ S Nr. XXIV 46.97 22.39 10.85 0.79 1.17 18.03 100.20 Nr. XXV 22.32 10.94 0.73 1.10 46.90 18.01 100.00

Nr. XXV corresponds to the formula:

 $\begin{array}{l} 32 \; (CaAl_{2}Si_{4}O_{12} + 6\;H_{2}O) + 18 \; (CaAl_{2}Si_{3}O_{10} + 3\;H_{2}O) \\ 3 \; (Na_{2}Al_{2}Si_{3}O_{10} + 2\;H_{2}O) + 3 \; (K_{2}Al_{2}Si_{3}O_{10} + 2\;H_{2}O) \end{array}$ 

The calcium - aluminotetrasilicic link reminds of the chabazite. The adjoined aluminotrisilicic links belong to the minerals of the natrolite type.

Levyne occurs in rocks containing besides various feldspars also the feldspatoides. In Deryfjord there appears chabazite accompanied by natrolite and scolecite — zeolites constituting the levyne.

#### Aluminopentasilicates

Here belongs the monoclinic lubanite known only from Lubań in Silesia, soluble in hydrochloric acid leaving gelatinous silica, containing:

${ m SiO}_2$	$Al_2O_3$	FeO	CaO	MgO	$H_2O$	S
47.84	16.74	0.56	16.17	1.35	17.08	99.74

according to the formula:

$$(Fe,Ca,Mg)_2Al_2Si_5O_{15} \cdot 6H_2O$$

In basaltic rocks there occurs also another pentasilicate, namely fojasite:

$$(CaAl_2Si_5O_{14} \cdot 10 H_2O) \cdot (Na_2Al_2Si_5O_{14} \cdot 10 H_2O)$$

containing:

${ m SiO}_2$	$Al_2O_3$	CaO	$Na_2O$	$H_2O$	S
46.81	15.91	4.36	4.84	28.08	100.00

in hydrochloric acid almost totally soluble.

The structure and origin of both zeolites is unknown at present.

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## POTASSIUM FELDSPAR DERIVATIVES

## Harmotome

The structure of harmotome was interpreted in various ways. Some joined it with phillipsite and desmine, others prefered chabazite or analcite. As to the crystal form there really exists a distinct resemblance between harmotome and phillipsite. Here and there the same monoclinic symmetry and similar twins which delude, repeat and cross themselves many times. Hence the misunderstandings at the statement of their nature.

 $(Ba,K_2)Al_2Si_5O_{14} \cdot 5H_2O$  is the empirical harmotome formula. W. Fresenius (54) supposed herein the existence of two different links: of bariumaluminohexasilicate corresponding to albite, and of an alcalic aluminobisilicate reminding of the anorthite. This interpretation was accepted by L. Langemann (55) and afterwards by J. Lemberg (56) on the basis of certain experiments. Lemberg did not take under consideration the fact that harmotome may be an aluminopentasilicate.

The isomorphy of harmotome and herschelite suggests it necessary to accept the analogical herschelite formula for harmotome:

16 (BaAl $_2$ Si $_6$ O $_{16}$ ) $\cdot$ 6 H $_2$ O)	4	$4 (BaAl_2Si_3O_{10} \cdot 3 H_2O)$
	2	$2 (\mathrm{Na}_{2}\mathrm{Al}_{2}\mathrm{Si}_{3}\mathrm{O}_{10} \cdot 2 \mathrm{H}_{2}\mathrm{O})$
		$I (CaAl_2Si_3O_{10} \cdot 3H_2O)$
		$I (K_2Al_2Si_3O_{10} \cdot 3H_2O)$

corresponding to certain harmotomes from Strontian Nr. XXVI and XXVII analysed by Damour (57), and Nr. XXVIII analysed by Rammelsberg, and to harmotome from Andreasberg Nr. XXIX analysed by J. Lemberg (58).

	Nr.	Nr.	Nr.	Nr.	
	XXVI	XXVII	XXVIII	XXIX	theor.
$\mathrm{SiO}_2$	47.60	47.59	47.52	46.74	47.63
$Al_2O_3$	16.39	16.71	16.94	16.04	16.19
$Fe_2O_3$	0.65	0.56	<u> </u>		
BaO	20.86	20.45	20.25	20.37	20.31
CaO			<u> </u>	0.30	0.37
$K_2O$	0.81		1.00	0.68	0.62

$Na_2O$	0.74		1.09	0.82	0.83
$H_2O$	14.16	14.16	13.45	15.05	14.05
	101.21	99.42	100.25	100.00	100.00

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The ratio between aluminotri — and hexasilicic links which in harmotome = 2:1, differs from that of herschelite which makes 4:11. It is worth while to notice that the three aluminotrisilicic links, reminding of the three nephelite derivatives : edingtonite, natrolite and scolecite, occur in nature accompanying the harmotome.

The space group of phillipsite (resp. herschelite) and of harmotome is in both cases identic  $= C_{2h}^2$ . The unit cell dimensions differ meanwhile:

for harmotome —  $a_0 = 9.80$  Å,  $b_0 = 14.10$  Å,  $c_0 = 8.66$  Å for phillipsite  $a_0 = 10.00$  Å,  $b_0 = 14.25$  Å,  $c_0 = 8.62$  Å

The axes ratio:

of harmotome a:b:c = 0.695:1:0.614,  $\beta = 124^{\circ}50'$ 

of phillipsite a:b:c = 0.702:1:0.685,  $\beta = 125^{0}40'$ 

The salient similarity of both minerals is favourable to various isomorphous mixtures. Hence the well - known discordances of their composition.

In order to confirm the presence of the admixed phillipsite group representatives it is sufficient, according to St. J. Thugutt and T. Woyno (59), to act at 800° C upon dehydrated harmotome with concentrated solution of acid potassium chromate. A sulphur - yellow colour indicates the presence of harmotome. In such a way the presence of harmotome was confirmed in phillipsites from Annerod, Einsiedlerthal, Richmond. One sample from Einsiedlerthal contained nearly 70% harmotome.

It is also possible to distinguish the two minerals by means of  $AgNO_3$  and  $K_2CrO_4$  solutions, by dint of which only phillipsite gains the orange hue, the harmotome remaining unaltered. At 100° C dehydrated, both minerals become coloured but in an unequal degree. Moreover, the harmotome is characterized by parallel bright and dark streaks, crossed sometimes in two directions, which prove their inhomogeneity.

As far as the optical properties are concerned the harmotome shows in convergent light a strong inclination of the negative bisectrix towards the forepost of the crystal. The plain of optical axes is perpendicular to (010). In parts which are parallel to (010) there appears the positive bisectrix. Cleavage parallel (010) is distinct, parallel (001) less distinct. H = 4.5, sp. gr. 2.44 — 2.5.

Harmotome, like the representatives of the phillipsite group, draws its matter from two different sources: the one is the bariumbearing feldspar, the other is nephelite. From the first there proceeds the bariumaluminohexasilicic link, from nephelite — the aluminotrisilicic link.

## Desmine

Pure calcium desmine  $CaAl_2Si_6O_{16} \cdot 6H_2O$  Nr. XXX does not occur frequently. Usually a part of calcium is taken by sodium and a little potassium. The mutual ratio between calcium and sodium is variable. More often there appear the types Nr. XXXI and Nr. XXXII.

Nr. X	XXI 4	4 (Ca $Al_2$	$Si_6O_{16} \cdot 6$	$5 H_2O$ )	$(Na_2Al_2)$	$Si_6O_{16}$ ·	6 H <sub>2</sub> O)
Nr. XX	XII 3	$B (CaAl_2S)$	$\mathrm{Si}_{6}\mathrm{O}_{16}\cdot\mathbf{e}$	$6 H_2O$	$(Na_2Al_2)$	$\mathrm{Si}_{6}\mathrm{O}_{16}$ ·	6 H <sub>2</sub> O)
		$\mathrm{SiO}_2$	$\mathrm{Al}_2\mathrm{O}_3$	CaO	$Na_2O$	$\rm H_2O$	S
Nr. Z	XXX	57.51	16.29	8.94		17.26	100.00
Nr. X	XXI	57.40	16.26	7.14	1.98	17.22	100.00
Nr. XX	XII	57.37	16.26	6.69	2.47	17.21	100.00

The monoclinic desmine is soluble in hydrochloric acid leaving slimy silica. With AgNO<sub>3</sub> and  $K_2CrO_4$  solutions the orange colour appears. At 100° C the hue becomes darker. Dehydrated at 800° C it takes with the above reactives a rosy hue. by a prolonged dehydration it becomes opaque, losing its chromatophylic properties.

## Epidesmine

It was investigated for the first time by V. Rosický and St. J. Thugutt (60). Symmetry orthorhombic: it represents an aluminohexasilicate of calcium with some natrium- and potassium aluminosilicates:

$$18 \operatorname{CaAl}_2 Si_6 O_{16} + 2 \operatorname{Na}_2 Al_2 Si_6 O_{16} + K_2 Al_8 Si_6 O_{16} + 140 \operatorname{H}_2 O_{16} + K_2 Al_8 Si_6 + K$$

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containing:

With 10%  $AgNO_3$  and 20%  $K_2CrO_4$  solutions it takes a bright hue. At 100° the colour becomes dark orange, but inhomogeneous. Dehydrated at 800° C it takes the colour of a strawberry. Readily soluble in hydrochloric acid it leaves slimic sandy silica.

The transparent epidesmine occurring at Żółta Brzoza in Silesia produces together with the yellowish orthoclase a not exceedingly big cover on the calcite scalenoedrons proceeding, as it seems, from potassium feldspar.

## Heulandite

 $CaAl_2Si_6O_{16} \cdot 6H_2O$  contains:

$\mathrm{SiO}_2$	$Al_2O_3$	CaO	$H_2O$	S
57.51	16.29	8.95	17.25	100.000

The pure calcic types occur unfrequently. Its common admixture is the sodiumaluminotrisilisic link:

 $5\,CaAl_2Si_6O_{16}\cdot Na_2Al_2Si_3O_{10}\cdot 33\,H_2O$ 

containing:

$\mathrm{SiO}_2$	$Al_2O_3$	CaO	$Na_2O$	$H_2O$	S
56.12	17.35	7.93	1.76	16.84	100.00

The basic type of heulandite is attached to nephelite-bearing rocks. The sodium and calcium links are joined chemically as a certain whole, which is confirmed by the silver reaction appearing after suitable dehydration of heulandite, the hue being homogeneous though not very intense. Delivering its water above 210° C, the heulandite shrinks suddenly, espacially along the axis b. The chief source of heulandite is the potassic feldspar from which there arises the often admixed potassium, strontium and lithium.

Besides both the above mentioned heulandite types there occur also its mixtures.

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Epistilbite

 $CaAl_2Si_6O_{16} \cdot 5H_2O$  containing:

${ m SiO}_2$	$Al_2O_3$	CaO	$H_2O$	S
59.21	16.78	9.21	14.80	100.00

A part of calcium is supplied by the sodium in the form of aluminotrisilicate.

Monoclinic epistilbite extinguishes the light uprightly, at the same time losing the character of twinship and imitating the orthorhombic symmetry. Hard to dissolve in hydrochloric acid, it leaves sandy silica. After strong boiling the hydrochloric acid acts no more. Towards silver nitrate and potassium chromate epistilbite is anactive.

 $2\,CaAl_2Si_6O_{16}\cdot K_2Al_2Si_6O_{16}\cdot Na_2Al_6Si_6O_{16}\cdot 24\,H_2O$ 

contains:

${ m SiO}_2$	$Al_2O_3$	CaO	$K_2O$	$Na_2O$	$H_2O$	S
56.52	16.01	4.39	3.70	2.43	16.95	100.00

After heating the delivered water shows a strong alcalic reaction. Towards  $AgNO_3$  and  $K_2CrO_4$  solutions erionite is inactive.

Orthorhombic crystals of erionite occur in Silesia near Kłodzko forming a thin cover upon quartz; in a rhyolite tuff of Teigarhorn (Iceland), in Durkan (Oregon) with sanidine, plagioclase, blackish chlorite and much noble opal. It appears also as the component of marburgite.

Brewsterite

 In the limits of 200° C it extinguishes the light straightly. After cooling it retakes its primary symmetry. Endowed with strong pyroelectrical properties it dissolves in acids leaving sandy silica.

## Aluminoheptasilicates

Stellerite  $CaAl_2Si_7O_{18} \cdot 7H_2O$  discovered in the year 1909 by J. Morozewicz (61) in diabasic tuffs of the Copper Island, one of the Commander Isles, contains:

$SiO_2$	$\mathrm{Al}_2\mathrm{O}_3$	CaO	$H_2O$	S
59.66	14.49	7.95	17.90	100.00

Between  $50^{\circ} - 150^{\circ}$  C it is more sensitive than desmine, above 150° C desmine surpasses stellerite in this regard. At 50° a partial dehydration begins (0.18% H<sub>2</sub>O), at 100° stellerite loses a little more than one molecule of water, at 200° it loses already four of them, while analcite remains quite intact. Stellerite does not regain the whole delivered water. After heating to 125° its space net is destroyed. Treated with AqNO<sub>3</sub> and  $K_2CrO_4$  solutions it shows an unequal bright orange hue. At  $100^{\circ}$  this colour becomes stronger. Dehydrated at  $140^{\circ}$  it appears strawberry-streaked, the colour becoming weaker in proportion to the proceeding dehydration. At 1540° its chromatophilic properties perish altogether. The streaked hue proves its inhomogeneity. Treated for two hours with hydrochloric acid it keeps its former shape gradually losing the property of a double refraction. The plain of the optical axes is at the same time changed from (010) into (100).

Stellerite is accompanied by quartz, calcite, some zeolites such as: analcite and desmine. The youngest product is the native copper.

Aluminonona- and dekasilicates

The monoclinic mordenite  $(Ca_1K_2, Na_2) Al_2Si_9O_{22}$ . 6 H<sub>2</sub>O from Seisseralpe contains (62):

 $SiO_2 Al_2O_3 Fe_2O_3 CaO MgO K_2O Na_2O H_2O S$ 66.86 12.13 0.03 3.86 0.17 0.67 2.41 13.87 100.00 according to the formula:

 $(2\frac{1}{4}CaO, \frac{1}{4}K_2O, 1\frac{1}{2}Na_2O) 4 Al_2O_3 + 36 SiO_2 + 24 H_2O$ 

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In order to avoid the fractions the above formula must be magnified four times.

In acids not wholly soluble: with AgNO<sub>3</sub> and K<sub>2</sub>CrO<sub>4</sub> solutions it appears equally rusty - rosa coloured, except the spherolitic silica.

Orthorhombic ptilolite  $(Ca, K_2, Na_2)Al_2Si_{10}O_{24} \cdot 7H_2O$ from Volhynia contains according to St. J. Thugutt (63): Al<sub>2</sub>O<sub>3</sub> Fe<sub>2</sub>O<sub>3</sub> CaO MgO K<sub>2</sub>O Na<sub>2</sub>O H<sub>9</sub>O S SiO<sub>2</sub> 1.01 2.460.02 5.32 0.74 12.95 67.00 10.68 100.18 Hence the formula:

 $(1\frac{1}{2} \text{ CaO}, 2 \text{ K}_2 \text{ O}, \frac{1}{2} \text{ Na}_2 \text{ O}) + 4 \text{ Al}_2 \text{ O}_3 \cdot 40 \text{ SiO}_2 \cdot 26 \text{ H}_2 \text{ O}$ 

To avoid the fractions the above formula should be magnified two times.

It is partially soluble in acids. Triturated in an agate mortar it does not attract the atmospheric humidity, differing by this property from other zeolites. At 1000°C it melts giving uncoloured glass. Chromatophilic properties weak. Treated with  $AgNO_3$  and  $K_2CrO_4$  solutions it becomes rusty - rosa. After dehydration the hue becomes more saturated and passes into rusty - orange without getting turbid.

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# STRESZCZENIE

Zeolity jako pochodne skaleni i skaleniowców. Ich cechy chemiczne. Wędrcwki ze złoża pierwotnego na złoże wtórne. Wzajemne zrosty i przerosty. Zawartość wody w zależności od natury zasady mocnej. Metody kolorystyczne oznaczania zeolitów. Kolejność krystalizacji a minerały macierzyste. Postacie zapożyczone i ich interpretacja.

Typy pochodzące bezpośrednio z nefelinu: natrolit, skolecyt, mezolit, tomsonit, komptonit, gismondyn, zeagonit. Typy mieszane: kankrynit z muskowitem, filipsyt, marburgit, herszelit, welsyt, kurcyt.

Wytwory sodalitu: epinatrolit, metaskolecyt, metatomsonit oraz żółty kankrynit.

Wytwory leucytu: analcym, lomonit.

Wytwory plagioklazowe: chabazyt, gmelinit, akadiolit, lewin.

Glinopięciokrzemiany: lubanit, fożasyt.

Wytwory skaleni alkalicznych: harmotom, desmin, epidesmin, heulandyt, epistylbit, erionit, brewsteryt.

Glinosiedmiokrzemian: stelleryt.

Glinodziewięciokrzemian: mordenit.

Glinodiesięciokrzemian: ptylolit.

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