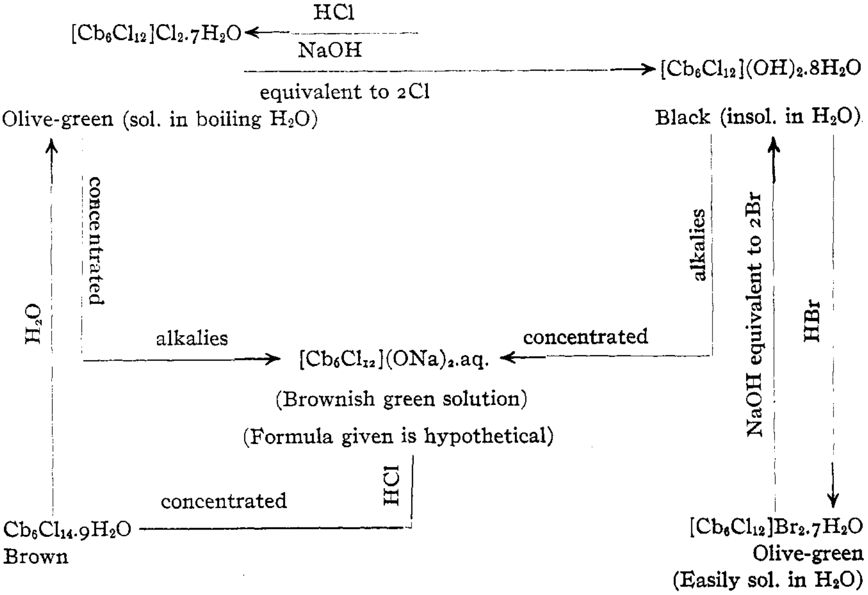
forded additional evidence that there was a constitutional difference between the brown and the green chlorides.

The present investigation had to end at this point because the material had been exhausted and lack of time prevented the preparation of more.

Summary.

1. Columbium furnishes the compound represented by the formula $(Cb_6Cl_{12})Cl_2.7H_2O$, exactly analogous to the bromide of tantalum prepared by Chapin.

2. The following table gives the most important characteristics and relations of the members of this group of derivatives:



UNIVERSITY OF PENNSYLVANIA.

THE HYDROTHERMAL FORMATION OF SILICATES, A REVIEW.

By GEORGE W. MOREY AND PAUL NIGGLI.

Received July 23, 1913.

The study of the conditions of mineral formation and stability has been carried on principally by two different methods, the fusion method and the hydrothermal method. By far the greater number of syntheses have been made by the fusion method, in open vessels at high temperatures, the minerals obtained being those which will separate from dry melts. In the hydrothermal method the components are subjected to the action of water, at temperatures generally near, though often considerably above, the critical temperature of water (ca. 370°), in closed bombs, and therefore under the corresponding high pressures developed by such solutions. In recent years the application of physico-chemical methods to the fusion method of mineral production has resulted in great progress in the elucidation of many problems of petrology and mineralogy. On the other hand, very little really quantitative investigation of hydrothermal reactions has yet been published.

Almost all the experiments in this field were made by the older workers, who were interested merely in the preparation of compounds similar to natural minerals; the conditions under which they worked were never carefully controlled, and the systems with which they operated were in general far too complex to permit of any important general deductions. Nevertheless their work is worthy of attention from all interested in hydrothermal synthesis, as it serves at least as a starting point, and provides us with a number of more or less isolated facts. For this reason compilation of the data was undertaken.

In the following pages the authors have endeavored to assemble all of the work appertaining to hydrothermal reactions, in the hope that it will not only serve as a basis for the necessary quantitative researches, but also point out—at least indirectly—the most promising mode of attack. In the bibliography the aim has been to include all papers, and to give in abstract all data which relate to the actual identification of certain minerals, or are important because of the conditions under which the products were obtained. While it is believed that all the important papers have been included, yet no attempt has been made to search technical journals devoted to industries such as pottery or cement manufacture; it is also possible that some work has been overlooked because it appeared in papers dealing with topics apparently unrelated to the subject in hand. It formed no part of the authors' purpose to include papers dealing with mineral syntheses by means of superheated steam in open vessels (*e. g.*, the work of Meunier[1]), or papers, such as those of Zambonini,[2] on the loss of water by minerals at temperatures above 100°. The references given have all been examined in the original.

It is evident that the term hydrothermal silicates refers merely to the mode of preparation, and that the minerals thus connoted belong not necessarily to any one chemical type, but to many widely separated mineralogical classes. The term has included many of the commonest minerals, such as quartz, feldspars, mica, leucite, nephelite, epidote, hornblendes. Moreover, while many of the minerals prepared hydrothermally—for instance, analcite and chabazite—cannot be obtained from dry melts, yet a large number of the so-called hydrothermal silicates have also been prepared in the dry way—*e. g.*, leucite and anorthite. Several

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[1] Meunier, "Les Méthodes de Synthese en Minéralogie," Paris, 1891.

[2] F. Zambonini, *Accad. Lincei Rome*, 1905, 1–32; 1906, 1–29; *Atti accad. Napoli*, 14, No. 1, 1–127 (1908).

non-silicious minerals, such as corundum (Al_2O_3), diaspore ($Al_2O_3.H_2O$), brucite ($Mg(OH)_2$), have been included in the bibliography, because they are end members of series under consideration and are frequently concomitants of the silicates proper.

The Experimental Methods.

The study of hydrothermal processes is, therefore, merely the study of certain aqueous systems at high temperatures, usually near to and often above the critical temperature of pure water, and therefore under the considerable pressures developed at these temperatures by water or aqueous solutions. The experimental difficulties of such a study are many but are largely connected with the choice of suitable containing vessels and the exact control of the conditions of working.

The high pressures developed and the solvent action of water at high temperatures preclude the use of glass vessels. Daubrée(5),[1] to be sure, used glass tubes, eliminating the effect of pressure by placing the glass tubes inside closed steel tubes with water in the annular space between. Chroustschoff(48)[1] also used glass tubes at temperatures up to 550°, but does not mention taking the above precaution. Both Daubrée and Chroustschoff found that the glass was much attacked; this was not of any great moment to them, as they were concerned only with obtaining a product corresponding to some known mineral. But this solvent action completely precludes the use of glass vessels by present-day investigators who are attempting to obtain definit knowledge of the conditions of formation of particular mineral species.

Most of the investigators have used vessels of steel, made tight in an appropriate manner. Perhaps the simplest form is that used by Sénarmont(3) and later by Doelter(43), namely, a gun-barrel closed by a screw-cap and copper washer. With this apparatus, however, as with many of the older forms, experimental uncertainties were introduced by the lack of a perfectly tight closure, the leak allowing a part, or even all, of the water to escape and thereby causing variations of the pressure (and hence of the concentration) of the water in the course of the experiment.

Friedel and Sarasin(19, 23) used in much of their work a steel tube closed at each end by a cap held tight by bolts, the joint being made tight by means of an iron disc bearing on a copper washer. Doelter, however, who also used a similar tube, states[2] that it is serviceable only when very carefully bolted together, and even then only up to about 450°; further, that it ceases to be serviceable after being used a few times.

Baur(78) used a bomb, typical of those used by recent workers in this field, by means of which an absolutely tight closure can be secured. It

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[1] These numbers refer to the number of the paper in the bibliographical list (p. 1117).

[2] Handbuch Mineralchemie, I, 616.

consists of a steel cylinder, bored out to receive the charge and cover, the latter being a steel plug screwed into the enlarged top of the bore and made tight by means of a copper washer.

An interesting addition to the ordinary type of apparatus was made by Königsberger and Müller(75), who introduced a filtering apparatus of platinum, enabling one to separate the solid from the solution at any temperature.

On account of the action of many solutions on the iron of the bombs, many experimenters have used linings of more resistant metals, such as silver, gold or platinum. Baur, however (78, p. 1125), considers a lining unnecessary, stating that the action on the iron is negligible by reason of the formation of a protective coating of ferrous-ferric oxide. It is undoubtedly true that with neutral solutions the action is slight, but when acid or strongly alkalin solutions are used their solvent action is no longer negligible, and the products obtained are often contaminated by considerable quantities of iron. Indeed, when the iron is corroded to any great extent, the mineral associations may be greatly altered, in which case the products obtained will probably be essentially different from those obtained when the charge is kept free from this component, which often exercises such a profound effect on the final character of the system. While, in the opinion of the authors, lining the bomb with a noble metal is not necessary, still it is advisable that the charge should be placed in a separate container made of gold or platinum. Our experience under such conditions has shown that although the bomb itself may be quite strongly attacked, the contents of the crucible rarely show any appreciable contamination.

Theoretical Principles Underlying Hydrothermal Processes.

Before discussing the general results of the experiments abstracted in the bibliography, we shall consider the basic physico-chemical principles of hydrothermal processes. An exhaustive treatment will not be given, because, on the one hand, the experimental data are too scanty to afford examples of the application of the principles involved, and because, on the other hand, many of these principles have recently been treated in detail by Smits[1] and by Niggli.[2]

Though the mechanisms of the reactions are often complicated, all hydrothermal syntheses are, primarily, crystallizations from aqueous solutions. As such they are comparable with van't Hoff's researches on the oceanic salt deposits, the differences being only in the magnitude of the temperature, pressure and composition (concentration ratios); the differ-

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[1] A. Smits, *Z. Elektrochemie,* **46**, 427 (1903); *Z. physik. Chem.*, **51**, 193 (1905); **52**, 498 (1905); **54**, 498 (1906); **54**, 512 (1906); **67**, 454 (1909); **67**, 464 (1909); **76**, 445 (1911). Also in *Proc. Koninkl. Akad. Wettenschappen Amsterdam.*

[2] P. Niggli, *Z. anorg. Chem.*, **75**, 161 (1912); **77**, 321 (1912); *Centr. Min.*, **1912**, 321–338.

ences in the actual experiment are of course more marked owing to the intervention, at the high temperatures, of certain disturbing factors. The principles involved, however, are not altered by the circumstance that, under the special conditions involved, the concentrations may, by reason of small specific solubilities, be very small, and that the concentration of the solvent itself may be so slight that it has the properties of a gas, since, above the critical temperature, the concentration of the water is dependent upon the pressure prevailing. The parageneses of the minerals obtained are primarily and essentially parageneses in the presence of aqueous solutions, and, as such, are to be differentiated from the paragenetic associations of the same water-free compounds obtained from the dry melt, or in the presence of foreign solvents other than pure water.

The form of the solubility or fusion[1] curves of systems, made up of components whose melting points do not lie far apart, is determined by simple and well-known physico-chemical principles; but in hydrothermal systems the fact that the critical point of one component is at a temperature much lower than the melting point of the other introduces disturbing complications, which render the theoretical treatment of these curves less simple. There is no doubt that silicates are soluble in water, though in many cases only with decomposition, and also that fused silicates may, under appropriate conditions, hold water vapor in solution; in other words, we know the general course of a fractional portion of the solubility curve close to each pure component. What we wish to determin is the general course of the whole curve.

Now, in the T–X projection of the diagram for a binary system, the triple points[2] of the two components are joined by the solubility or fusion curve; the melting points involved are those determined by the prevalent temperature and concentration. It may, of course, happen that part of this curve lies in a metastable region, especially if transformations take place or if the two components are but partially miscible. Just as the triple points are joined by a single continuous solubility or fusion curve (which gives the composition of the liquid coexisting in equilibrium with vapor), so also are the critical points of two substances joined by a critical curve.[3] In this case also a part of the curve may lie outside the stable region, if transformation, decomposition, or limited miscibility occur. The different possible cases which can be logically considered, are two:

I. The solubility curve does not intersect the critical curve.

II. The solubility curve intersects the critical curve.

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[1] The processes of solution and of fusion are in principle identical.

[2] The triple point is the melting point of the substance under its own vapor pressure at that temperature; it is practically the same as the ordinary melting point (at a pressure of 1 atm.) since the variation of melting point with pressure is very small.

[3] That is, the plait curve which represents the locus of all points where the critical phenomena occur with mixtures intermediate between the pure components.

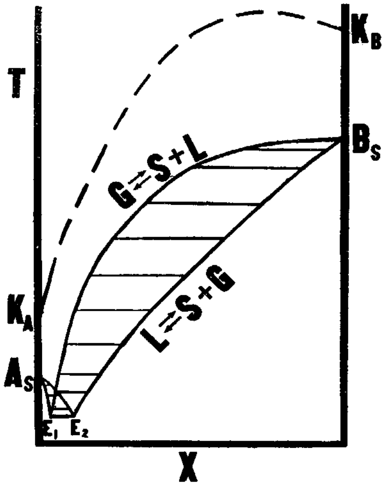

Fig. 1*a*.

Ideal T—X projection of Case I; the critical curve is not intersected by the lines representing two-phase equilibrium in coexistence with solid.

K_A represents the critical point of A (the more volatil component, *e.g.*, H_2O), K_B that of B (the less volatil component, *e. g.*, silicate); the broken line K_AK_B the critical curve.

A_S and B_S represent the melting points of A and B, respectively.

A_S E_1 B_S gives the composition of the vapor in coexistence with liquid and solid; $A_SE_2B_S$ that of the liquid in coexistence with the vapor represented by $A_SE_1B_S$ and with solid.

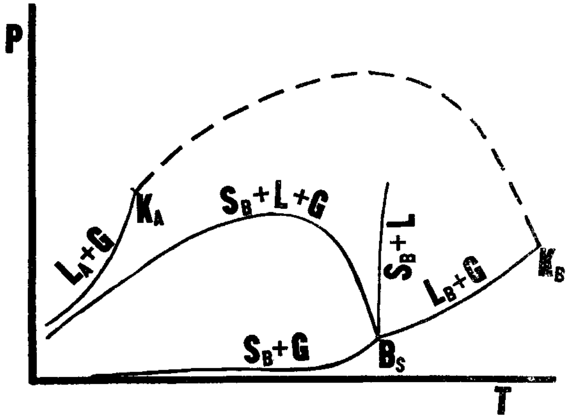

Fig. 1*b*.

Ideal P—T projection of Case I; the critical curve is not intersected by the lines representing two-phase equilibrium in coexistence with solid.

K_A represents the critical point of A, K_B that of B; the broken line K_AK_B the critical curve; B_S the triple point of B (melting point under its own vapor pressure). The eutectic relations at low temperatures are not indicated.

Case I will first be considered. Since the critical points of the components lie at much higher values of temperature and pressure than the corresponding melting points, it follows that, when the solubility and critical curves do not intersect, the solubility curve must be below the corresponding critical curve. Moreover, the two-phase line in coexistence with solid (solid–solution–vapor) must also be below the critical curve. Hence, on the one hand, only unsaturated solutions will show critical phenomena, and, on the other hand, the two-phase line in coexistence with solid phase can be studied without the appearance of critical phenomena. The critical point of the more volatil component is in this case without influence in the solubility relations solid-liquid or solid-vapor. In the system water–silicate we can therefore expect, provided that complications are not introduced by decomposition or limited miscibility, that a continuous two-phase line in coexistence with solid will connect the melting point of ice with the melting point of the silicate. At high pressures, a homogeneous liquid mixture will probably be formed at relatively lower temperatures, since the melting point of the silicate will be lowered throughout the whole concentration range by liquid water. Such a continuous solubility curve has been realized in the system $AgNO_3$–H_2O,[1] and it seems quite probable that the system alkali silicate–water belongs to this type.

Conditions are very different in the second case. Since, in mixtures approaching in composition either one of the pure components, the two-phase line coexisting with solid must be below the critical curve, it follows, that, when the critical curve is intersected in one point by the solubility curve, it must also be intersected in a second point. The two intersections are characterized by the fact that while up to these points the critical phenomena are shown by solutions in contact with solid phase (saturated solutions) between these points the critical phenomena can only take place in supersaturated (metastable) solutions. On both sides of these critical end points the three phases solid–liquid–vapor can coexist, but in the field between them the only stable phases are solid and fluid (gaseous) solutions. While there will be in this case, at high pressures, a continuous solubility curve connecting the two melting points, there will not be a continuous line representing two-phase equilibria in the presence of solid phase. This circumstance has the following consequences, which have a very important bearing on the experimental side of our problem.

In the field below the first critical end point, at a given volume and with a moderate amount of water, the state of the system will be completely determined by the temperature alone. Moreover, variation within certain limits of the amount of water, provided that the tempera-

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[1] Landolt-Börnstein-Meyerhoffer Tabellen, III Aufl., p. 520.

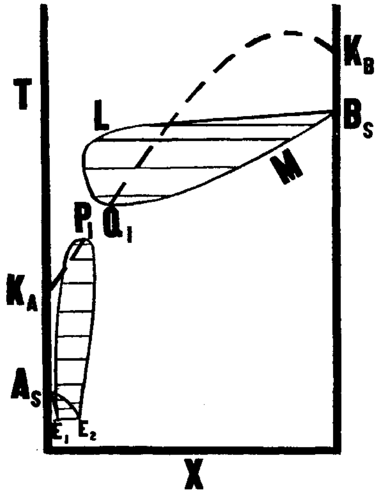

Fig. 2*a*.

Ideal T — X projection of Case II; the critical curve is intersected at P_1 and at Q_1 by both lines of two-phase equilibrium in coexistence with solid.

K_A represents the critical point of A (the more volatil component, *e. g.*, H_2O), K_B that of B (the less volatil component, *e. g.*, silicate); the broken line $K_A P_1$ — $Q_1 K_B$ the critical curve; P_1 and Q_1 the critical end points.

A_S represents the melting point of A, B_S that of B; the curves $A_S E_1 P_1$ and $Q_1 L B_S$ give the composition of the vapor in coexistence with liquid and solid; $A_S E_2 P_1$ and $Q_1 M B_S$ that of liquid in coexistence with the above vapor and with solid.

Between P_1 and Q_1 the only phase which can coexist with solid is a fluid (gaseous) solution.

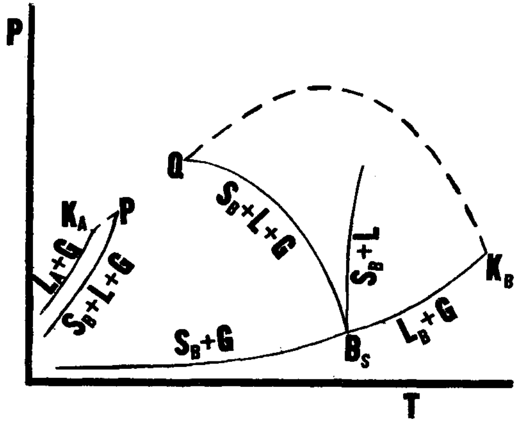

Fig. 2*b*.

Ideal P — T projection of Case II; the critical curve is intersected at P and Q by the two-phase lines in coexistence with solid.

K_A represents the critical point of A, K_B that of B; the broken line $K_A P$ — $Q K_B$ the critical curve; P and Q the two critical end points; B_S the triple point of B.

Between P and Q only fluid (gaseous) solutions are stable in coexistence with solid; the eutectic relations at low temperatures are not indicated.

ture is constant and that stable equilibrium is attained, is without effect on the final vapor pressure or on the concentration of either the saturated vapor or saturated solution; the only effect of such variation (the total volume remaining always the same) is to change the relative amounts of vapor and liquid solution. In the field between the two critical end points the conditions are very different. Here we have a two-component system, and only two phases, solid and fluid solution. The system is therefore divariant; at given temperature and volume a small change in the amount of water will result in a change of pressure, hence of concentration of the vapor phase. It is evident that in this region the possibility of obtaining various minerals is greater, and, conversely, that within this region it is a more difficult matter to reproduce exactly a set of experimental conditions.

The occurrence of cases of the second type is evidently dependent of the following conditions: First, the volatility of the two components must be very different; second, the solubility of the less volatil component in the more volatil component must be small near the critical point of the latter. The critical temperature and pressure of a substance are raised by a dissolved substance; this elevation of the critical temperature is analogous to the elevation of boiling point, and is, according to Centnerszwer, in dilute solutions, proportional to the mol fraction of the solute.

If, at the critical point of water (ca. 370° and 200 atm.), the solubility of a silicate is very small, the saturated solution will show critical phenomena[1] at a temperature and pressure very little above the values for pure water. It follows, as we have seen above, that above this point there is a field in which the stable phases are two—fluid (gaseous) solution and solid. The stable coexistence of liquid and vapor is in this region impossible; but, on the other hand, the fluid phase is just as much a solution as the ordinary aqueous solutions in contact with vapor. The lack of outstanding distinction between liquid and fluid (gaseous) solutions can be shown indeed by an actual example; for at constant pressure the solubility curve for the system ether-anthraquinone, studied by Smits,[2] exhibits no discontinuity at the critical point of the more volatil component.

Hence we may say that, for cases of the second type also, the critical point is without direct influence on the solubility phenomena; this statement is, however, subject to some qualification in its quantitative aspect, the basis of which is the relatively rapid change of solubility which must occur in the immediate neighborhood of the critical point. At temperatures considerably below the critical point, the solubility of the less volatil component in liquid water is much greater than it is in the coexisting vapor phase; but as we approach the critical point the two solubilities

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[1] Provided, of course, that the volume of the system has the appropriate value.

[2] A. Smits, *Proc. Akad. Wettenschappen Amsterdam*, 1911, 191. See Fig. 3.

approach one another, since at the critical point they are identical. In general, therefore, in the region shortly before the critical end point, the solubility in the vapor phase must increase, while that in the liquid phase must decrease.[1] This qualification, then, depends upon a purely local, continuous and thermodynamically determinate phenomenon.

The solubility curve goes from the melting point of one component to that of the other; from what has been said above it follows that the solubility (of the involatil component) in the fluid or (above the second critical end point) subsequent liquid phase will increase with increasing temperature, provided that the components are always completely miscible and that no exothermal reactions occur. In this connection we may remark that the concentration of the liquid is diminishing very rapidly as its critical point is approached, while the concentration of the vapor is rapidly increasing; and that the solubility, if it is reckoned as the concentration of solute in the total amount of solvent present in both liquid and vapor phases, need not diminish in the critical region in all cases, although we shall always have a retrogressive solubility curve if the liquid phase alone is considered.

The critical point, as such, has thus nothing to do with the solubility phenomena, nor with the nature of the solid phase, and Doelter[2] is in error in ascribing to the critical point of water a significant role in hydrothermal synthesis. That the formation of zeolites, or, more generally speaking, of minerals containing water, will be less common at high temperatures is evident, but this circumstance is caused by the increase of the dissociation pressure of such compounds with increasing temperature. The critical temperature of water is not only theoretically without effect on the phenomena in question, but, as a matter of fact, several hydrated minerals have been obtained under conditions such that we are led to conclude that they formed in presence of solutions which were fluid (not liquid).

As an illustration of some of these relations we reproduce the diagram (Fig. 3) given by Smits to exhibit the melting (solubility) lines at various pressures for the system ether–anthraquinone. This system has 2 critical end points; the first (P in Fig. 3) at 203° and 39.7 atm., the second (Q) at 247° and 62 atm. From the diagram we see how the retrogressive character of the solubility lines—an irregularity which is produced by the first critical end point and appears up to a pressure of 61 atm.—disappears at higher pressures. Similar phenomena, differing only in their quantitative relations, may be expected in those silicate-water systems which have two critical end points. The difference caused by the number of phases (the occurrence of a fluid phase only instead of liquid + vapor) is not

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[1] The thermodynamic necessity of this has been proved by A. Smits, *Proc. Acad. Wettenschappen*, **1911**, 120.

[2] *Handbuch Mineralchemie*, 1, 603 (1912); *Phys. Chem. Mineralogie*, p. 216 (1905).

fundamental, but only of purely experimental, importance. If a system solid–liquid–vapor is heated in a closed vessel, the temperature at which either the liquid or the vapor phase disappears is dependent upon the degree of filling, that is, upon the ratio of the amount of water to the volume of the containing vessel. The true critical point is reached only when, at this temperature, the amounts of liquid and vapor are the same (*i. e.*, at the critical volume). In all other cases the last drop of liquid or the last bubble of vapor will disappear at a temperature different from, and in general lower than, the true critical temperature, though the latter does not necessarily coincide with the maximum temperature. Curves showing the transition of the the three-phase system solid–liquid–vapor to the two-phase system solid–fluid in its dependence upon the degree of filling have been discussed by Centnerzwer[1] and by Niggli.[2]

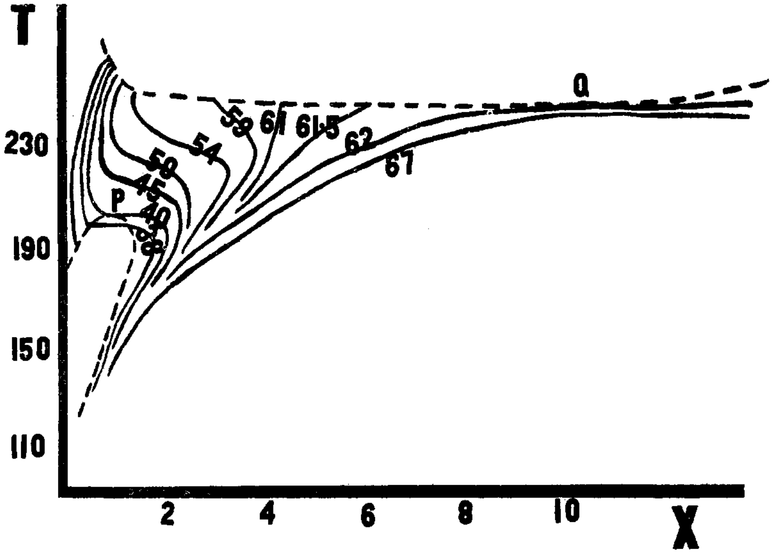

Fig. 3.
(After A. Smits.)

Fusion or solubility lines under given constant pressure in the system ether-anthraquinone.

T—X figure. P represents the first critical end point, Q the second critical end point.

The influence of pressure in such systems may well be enlarged upon. So long as both liquid and vapor phases are present, the pressure developed is independent of the degree of filling, if the solutions are saturated; for a saturated solution has, at a definit temperature, a definit vapor pressure,

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[1] M. Centnerszwer, *Z. physik. Chem.*, **46**, 427 (1903); **54**, 303 (1906); **60**, 441 (1907); **61**, 356 (1908); **69**, 81 (1909); **72**, 72 (1910).

[2] P. Niggli, *Z. anorg. Chem.*, **75**, 179 (1912).

and the only effect of varying the amount of solvent present will be to vary the relative amounts of the liquid and vapor phases. This is no longer true, however, when we pass from the three-phase system to the two-phase system fluid–solid. At a given total volume a change in the degree of filling now causes a change in concentration—that is, pressure—of the fluid phase; hence, as a direct consequence of Henry's law, the amount of the solid in solution in the fluid phase varies with the degree of filling.

From this the possibility is evident that in such systems, at temperatures above the critical temperature, different syntheses may be effected merely by varying the degree of filling. In all experiments at temperatures near or above 400°, therefore, the degree of filling, or at least the exact amount of water present, should be expressly stated. When the amount of water at ordinary temperatures is very different from one-third of the volume of the container, the transition into the two-phase systems may take place at a much lower temperature, as stated above; and this circumstance must always be taken into account.

One condition for the occurrence of the second type (appearance of two critical end points) is that the solubility of the involatil component in the volatil component should be small near the critical point of the latter. Now it is established, as the result of many experiments, especially by Koenigsberger(**75**), that the solubility of many silicates in water about 370° is very small; so that there is every reason to believe that many systems silicate–water belong to this second category.

In most cases, indeed, the solubility is so very small that the first critical end point will be close to the critical point of water itself; the difference will, in general, probably be only of the order of magnitude of degrees. The second critical end point, which also must exist, if neither unmixing nor decomposition occurs, will, in all probability, lie at very high pressures; no case in which it has been reached is known to us. A few silicates, which are relatively soluble in water, give with water systems belonging presumably to the first category; such a system is alkali silicate–water, which is at present being investigated by Morey.

From the above it is evident that there is no essential difference between ordinary aqueous solutions at room temperature and systems silicate–water, even at temperatures near, or above, the critical point of water. From ordinary aqueous solutions a substance begins to separate as soon as its saturation concentration (under the particular conditions) is reached. In precisely the same way the crystallization of stable minerals from aqueous systems containing several relatively involatil components will be determined by the relative insolubility of the possible forms. In this respect these hydrothermal syntheses are similar to the parageneses obtained by van't Hoff in his researches on the oceanic salt deposits, the main difference being that van't Hoff approached his saturation limits by evaporation of the solvent at constant temperature, while in hydrothermal work separation of material from solution would be effected by successive lowerings of temperature. The solubilities of minerals are, however, so very slight that one cannot obtain in this way products even in quantity sufficient for their certain identification; for instance Königsberger in his experiments(75), was able, in general, to identify only quartz.

But we can consider the problem from another point of view, namely, that the reactions take place largely in the solid phase. Many examples of such reactions are known; as an illustration, we may take the well-known fact of the growth of crystals at temperatures below their melting point.[1] In hydrothermal work, we introduce as solid phase a mixture of substances which is believed to be unstable in the presence of solution under the conditions of the experiment. Under such circumstances reactions will take place in the mass of the solid tending to produce the solid phase which is stable under the particular conditions; and when the diminution of free energy accompanying these reactions is a maximum, the parageneses obtained will be identical with those obtained by actual crystallization from saturated solutions under the same conditions. But the solid phase is such a complex system that we cannot, *a priori*, assume that the material actually produced is the stable phase, and, as a matter of fact, many crystals have been obtained which, as we know, are metastable under the conditions given.[2] An excellent example is tridymite, which has been obtained in the hydrothermal way, though its range of stability at ordinary pressures is from 870°–1470°.[3]

As original solid phase, either natural minerals or the amorphous components are used, together with aqueous solutions. With the same original gross composition, the final products, if stable, must be the same in both systems; but this is not true if metastable products appear. The constitutional relations of the silicates would lead one to expect the appearance of the first alteration product of any natural mineral which was present originally; hence the product is in general not identical with that obtained when other materials of the same gross composition are used. For this reason it seems preferable to us to make up the original solid phase from the component oxides, preferably freshly precipitated, even though exact duplication of the state of the original solid phase is rendered somewhat difficult if such more or less colloidal material is made use of.

[1] Cf. the "Sammelkristallisation" of Rinne and Boeke, *Tschermak's Petr. Mitt.*, **27**, 293 (1908).

[2] There appears to be some hope of coördinating the apparently arbitrary appearance of metastable or stable forms by means of Smit's theory of allotropy. A. Smits, *Z. physik. Chem.*, **76**, 421 (1911), and later papers in 1912 and 1913, especially *Ibid.*, **82**, 657 (1913).

[3] See the preliminary paper by C. N. Fenner(81), and especially the complete paper, about to be published in the *American Journal of Science.*

While the stable end product is of necessity independent of the nature of the original materials used, when the total composition and other conditions are the same, still the actual product obtained may not be independent of the nature of the original materials.[1]

Since the products actually obtained in hydrothermal syntheses have not in general crystallized out of cooling supersaturated solutions, but are the result of reactions taking place in the mass of the solid phase, it is to be expected that many of the products obtained will be metastable.[2] It is not justifiable, however, to assume that all products of reactions in the solid phase are metastable; the tendency is always towards the formation of the stable product. Many circumstances, such as the reproducibility of the experimental results and also data from other sources, make it at least highly probable that in a large number of mineral syntheses the stable product has been obtained. Yet it seems to us altogether premature to draw a diagram representing what purports to be the stability fields for these complicated systems, when the facts are so insufficiently ascertained; such diagrams may be altogether misleading, especially to those who are unable to distinguish for themselves between experimentally ascertained facts and inferential assumptions.

The interpretation of the results of hydrothermal syntheses is hampered, moreover, by the fact that we do not know the exact temperature of formation of the products, since some relatively permanent crystals may separate while the temperature is actually being raised initially, or during the final cooling. This factor, however, seems to us to have been overrated, since the cooling may be made very rapid; moreover, minerals formed while the temperature is being raised, but metastable at the temperature of experiment, will be transformed into the stable form when held at constant temperature, unless the rate of transformation of such metastable products is very small.

The circumstance, that the temperature and pressure have not been determined at all accurately in most of the syntheses hitherto made, naturally makes it difficult to obtain a comprehensive view of the present status of the problem. Such difficulties, however, are purely experimental, and can be obviated by the use of suitable technique, *e. g.*, temperatures can be measured with sufficient accuracy by placing the thermoelement in a small hole drilled longitudinally in the wall of the bomb. Neither does the measurement of the pressure appear to be an experimental impossibility. It is often, at least for preliminary work, sufficient to know

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[1] The reactions in the solid phase take place through the medium of the solution, presumably through layers of supersaturated solution in the immediate proximity of the particles constituting the solid phase.

[2] It is of course also possible for metastable products to crystallize out of saturated solutions.

the temperature within about 10 degrees; it is more important to know accurately the degree of filling.

Hitherto we have considered only systems composed of silicates and water only, systems in which special mineralizers such as carbon dioxide, hydrofluoric or hydrochloric acid, either as such or in the form of their salts, are absent. The addition of such mineralizers increases the number of volatil components, since carbon dioxide, hydrochloric and hydrofluoric acids, are all relatively volatil, and introduces a further complication caused by the specific effect of these additions on the dissociation equilibrium of the silicate.

In all cases the chief influence of the addition of mineralizers will be to change the solubility relations involved. For example, from an experiment of Müller and Königsberger(79) it appears that sodium carbonate precipitates orthoclase from solution. That addition of hydrochloric or hydrofluoric acid will have a marked effect on the solubility relations is self-evident, for such additions alter the nature of the solvent.

In general, very little is known in regard to the ionization relations in aqueous solutions at temperatures above about 300°. All experiments hitherto recorded show that increasing temperature is accompanied by a decrease in the degree of ionization, which for different salts of the same ionic type tends to approach the same value.[1] Practically nothing is known in regard to the hydrolytic dissociation of silicates at such temperatures.

General Discussion of the Experimental Work on Hydrothermal Syntheses.

When we consider the various hydrothermal syntheses which have been made as a whole, we must bear in mind the principles outlined in the introduction and in the theoretical discussion. With the possible exception of some work of Baur and of Königsberger, there has been little systematic investigation of this field. We can compare the present condition of the subject to the preliminary surveys for a topographic map of a newly described land; several prominent points and easily accessible routes are known, which afford us some knowledge of the general configuration of the field, but little, or none, of the details. Moreover, the exactness of the data is dependent on the accuracy of the instruments used by the observers.

The study of the paragenetic relations of silicates in aqueous solutions at high temperatures is of such great petrological importance that it is worth while to review briefly the main conclusions which may be drawn from the experimental work recorded in the literature and here brought together for the first time. As we have already pointed out, practically

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[1] A. A. Noyes, Publications Carnegie Institution, No. 63; *Z. physik. Chem.*, **70**, 335 (1910).

nothing is known about the actual stability relations of the minerals obtained.

Examination of the data assembled in the bibliography makes it evident that the results of the various experimenters are in substantial agreement with regard to the "phanerostability"[1] of a number of minerals under hydrothermal conditions; on the other hand, there are a number of discrepancies which are hard to account for.

It has been found that many minerals may be formed by a proper choice of conditions, and that under such conditions they are apparently stable; such minerals we shall denote by the term "phanerostable," leaving open the question as to whether they are really stable or only metastable under the given conditions. A distinction must be drawn between minerals which are always reproducible and those whose appearance is more accidental or dependent upon special peculiar conditions. Great weight cannot, in general, be attached to the chemical analyses of the products, as it is extremely difficult to separate the small crystals completely from extraneous material. It must be noted, however, that several of the French experimenters have been able to substantiate the chemical analysis of their product by the optical identification of the mineral in question. On the other hand, formulas such as $6Na_2O.8Al_2O_3.8SiO_2$, deduced solely from chemical analysis of such products, must be accepted with caution. Moreover, the names ascribed to many minerals are subject to a similar reservation, as the relation of the minerals obtained to those found in nature is altogether unknown; for example, sodium thomsonite and potassium nephelite hydrate may or may not be analogous to thomsonite or nephelite.

From the experiments of Lemberg (10, 26, 31, 40, 41), Doelter (43), and Thugutt (54, 56) it is evident that zeolites or zeolite-like substances, as well as hydrated nephelites, are easily prepared at temperatures ranging from 100°–200°. Such zeolite-like substances may also be obtained at these temperatures from the higher anhydrous aluminosilicates, especially in presence of alkalin solutions. The large number of experiments described by Lemberg and Thugutt, which we could treat in very condensed form only, show further that the alkali present in many minerals is easily replaced by the alkali of the solution used. The members of the sodalite-cancrinite-nosean group obtained by such replacement are often more highly hydrated than the natural minerals, and differ from them also in optical properties. The number of hydrated compounds obtained naturally diminishes with increasing temperature; but this circumstance has no connection with the critical point of water. As a matter of fact, many hydrated silicates have been obtained under conditions which point to

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[1] See next paragraph.

their formation from solutions at temperatures above 400°, and therefore presumably from fluid (and not liquid) solutions.

It appears that the parageneses—the nature of the minerals obtained—are but little altered by change of pressure and of temperature within the approximate limits 300° and 550°. For example, C. and G. Friedel (47 and 50), working at a temperature of about 500°, obtained always a "nosean hydrate" when the bomb did not leak—*i. e.*, under high pressure—but ordinary nosean when some of the water escaped—*i. e.*, at lower pressure (smaller concentration of the water). In this region are formed the minerals most commonly obtained from such experiments—quartz, albite, orthoclase, analcite—substances which have been so often prepared that there can be no doubt that they may be formed in nature under similar conditions. There is less frequent record of the synthetic formation of many of the common natural associates of the above four substances; *e. g.*, of hornblende, diopside, aegerite-augite, wollastonite, muscovite, biotite(?), pyrophyllite, andalusite(?), chlorite, pectolite, brucite, magnetite, hematite, corundum, diaspore, etc. The experiments of Friedel(59) and of Baur(71) on the dependence of the formation of feldspars, quartz, analcite and hydrous potassium nephelite on the original composition of the system are in general agreement, although there are some striking discrepancies.

With regard to the phanerostability of the feldspathoids little is known. Leucite was obtained by Meunier(16) at red heat in presence of water vapor at atmospheric pressure and also by Friedel(59) in closed bombs by the action of water on muscovite. The separation of nephelite from systems containing little silica has often been observed; it can always be brought about by starting with muscovite. Apart from the special circumstance that the use of minerals as initial solid phase is apt to result in the appearance of their first decomposition products, the separation of feldspathoids occurs only under special conditions—for instance, in systems rich in alkali, or under relatively low pressure (therefore small concentration of water). The formation of sodalite, nosean and cancrinite at high temperatures (around 500°) is of special interest, because under these experimental conditions the pure alkali minerals can be obtained, while the natural minerals often contain lime.

From the standpoint of stability the numerous syntheses of chalcedony, tridymite and cristobalite are of interest, especially since Fenner(81) has shown that under hydrothermal conditions all of these forms of silica are changed in time to quartz. The system SiO_2 is such a complicated one, however, and the rationale of metastable relations is still so little understood that the occurrence of such accidental syntheses is not to be wondered at.

It seems altogether probable that conditions similar to those which characterize hydrothermal syntheses occurred in nature during the following processes: cooling of igneous rocks with subsequent pneumatolytic action, formation of mineral crevices and veins, and processes of hydrothermal metamorphism. Between these natural parageneses and those produced artificially there is, on the whole, substantial agreement. It must be remarked, however, that most syntheses have been made from mixtures rich in alkali, and that the minerals of the epidote-zoisite group have never been produced artificially in presence of water. The formation of analcite, the zeolites and members of the cancrinite group from eruptive rocks rich in alkali often corresponds, at least in part, to a hydrothermal transformation. In pneumatolytic vein formation, as well as in mineral crevices, the commonest minerals are quartz, albite, orthoclase, mica, chlorite, hematite, etc., those namely which appear oftenest in the course of hydrothermal work; the fact that the members of the sodalite–nosean–cancrinite group, as well as leucite, nephelite and analcite, are rarely found is probably due to the high silica content of most natural solutions, a circumstance which is shown by the formation of quartz. The significance of hydrothermal work for metamorphic processes lies in the fact that it has been demonstrated in this way that feldspars can be formed in the presence of aqueous solutions at temperatures ranging from 300°–500°. This is important because, since many metamorphic rocks are known in which the feldspars have been altered into hydrated minerals, it gives ground for believing that the temperature at which many metamorphic processes occurred may be considerably lower than is generally supposed. All of these deductions are of course merely qualitative; the quantitative study of such systems has barely begun, and is attended by such difficulties that it will, at best, be a slow process. At the same time the qualitative agreement is quite good and of considerable petrologic importance.

The effect of the presence of carbon dioxide in the water is of interest in connection with the formation of veins and crevices. Experiments in this direction were made by Königsberger and Müller (**75**, **79**); their conclusions are not unexceptionable, and conflict with some of their own experimental results. In particular, their deduction with regard to the rapid increase in acidity of silicic acid with increase of temperature—while it may be true—does not, of necessity, follow from any facts yet ascertained. That the silicates are hydrolyzed, there is no doubt; but nothing definit is known with regard to the extent of this hydrolysis, even at ordinary temperature. At ordinary temperature the metasilicates are apparently almost completely hydrolyzed, the silica formed by the process separating in colloidal form; but it must be emphasized that from this fact no certain conclusion as to the strength of metasilicic acid can be drawn. Moreover, it does not necessarily follow that the salts of other silicic or aluminosilicic acids, or even metasilicates at higher temperatures, will be hydrolyzed to the same extent, especially if the silica does not separate in colloidal form. The real dissociation constant—the magnitude of which is at present altogether unknown[1]—can be determined from hydrolysis experiments only if the silica does not separate in colloidal form. From these considerations it is evident that an apparent rapid increase in the acidity of silicic acid does not necessarily imply the reality of this increase. Königsberger and Müller also ascribed the precipitation of quartz on cooling to the displacement of the hydrolytic equilibrium of carbonic acid, but from the data given such a conclusion is hardly justifiable; for of the experiments made in which carbonic acid was present, some gave considerable quartz while others gave none. The effect of the basic ion of $NaHCO_3$ seems much more significant.

The preceding brief summary has intentionally been made somewhat briefer that the data might have warranted. The few quantitative observations hitherto made have in part been discussed by their authors, but this most important side of the problem requires much more thorough investigation than has yet been accorded to it. It must again be emphasized that quantitative research in this field—in special, the ascertainment of the real stability relations—is a matter of considerable difficulty, owing to the special solubility relations and to the complications consequent on the restriction of a large part of the reaction practically to the solid phase; apart altogether from the purely technical troubles associated with the high temperatures and considerable pressures involved. The knowledge of hydrothermal relationships is, however, of such importance to petrology that these difficulties will, in time, doubtless be surmounted; as a starting point for further and better investigation, and as an indication of the limitations of present knowledge of this field, the bibliography which we give will, it is hoped, prove useful.

Conclusion.

In this paper we have assembled all of the available data relating to hydrothermal syntheses, data which unfortunately afford us practically no reliable quantitative information. Moreover, qualitatively even, the data leave much to be desired; for many minerals have been obtained but once by a given investigator, in a manner which was not reproducible and under conditions which were not specified. The minerals which have been most commonly obtained are chiefly those which are stable—or, at any rate, phanerostable—over a wide range of conditions; for example, quartz and the feldspars. In all cases the crystals obtained are very small, so that accurate chemical analysis is usually out of the question; their identification by optical methods may even be doubtful. In the preceding pages we have given and used the mineral names assigned by

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[1] There are reasons for supposing it to be considerably greater than it has in general been assumed to be.

the investigator to the various products, but in doing so we accept no responsibility for their correctness; in certain cases where the identification seemed doubtful we have placed a question mark beside the name in question.

Hydrothermal syntheses, like the paragenetic relationships investigated by van't Hoff, are determined by the solubility relations of all the possible solid phases which may be formed from the components present in the solution, even although the concentration of these components in the solution is vanishingly small. Many of the reactions are, without doubt, practically restricted to the solid phase, although they take place through the medium of the solution. These solubility relationships are thus not simple; but study of the question is further complicated by the frequent appearance of metastable phases, which again is coördinated with the rates of the various possible reactions. Now, as is well known, rates of reaction are often affected very greatly by factors which, in other respects, are of altogether minor importance; hence slight differences—*e. g.*, in the composition, or even in the texture or fineness of grain, of the initial solid phase—may exert considerable influence on the result. These considerations enable us to see that there may in certain cases be difficulties in the way of always being able to reproduce a given result; in order to do this in any case, it is necessary to control carefully the amount of water relative to the volume of the containing vessel (the degree of filling), the temperature, and, if possible, the pressure also. The critical point of water is only a secondary factor in determining the nature of the product, its influence being effected principally through the change in concentration of the solvent (liquid or fluid) in the neighborhood of the critical point.

The thorough investigation of hydrothermal syntheses is thus beset with many difficulties, apart from the technical problems inherent in operating on heterogeneous systems within closed bombs at high temperatures. Nevertheless, our knowledge of the real relationships of these minerals can be advanced materially if care is taken to control the factors involved, the most important of which are the initial composition of the system (including therein the relation between the amount of water and the volume of the bomb) and the temperature.

The Bibliography.

The papers are arranged in chronological order; at the end of the bibliography, a table of the minerals obtained will be found.[1] It is to be understood that all experiments above 100° were made in closed bombs, unless otherwise stated; we may remark that Lemberg and Thugutt used ordinary digesters for temperatures from 150° to 300°.

[1] Doelter's Handbuch Mineralchemie, in discussing the separate minerals, gives some of these references, but not always correctly.

1845 1 SCHAFHAUTLE. *Münchener gelehrte Anzeigen,* **1845,** p. 575. (Cited by L. BOURGEOIS, *Reproduction artificielle des minérals,* Paris, **1884,** p. 80.) Prepd. quartz by heating gel SiO_2 with H_2O in an autoclave.

1848 2 WÖHLER. Cited by BUNSEN. *Ann.,* **65,** 80. Apophyllite heated with H_2O at 180°–190° under a pressure of 10–12 atm. was recrystallized.

1851 3 SÉNARMONT, H. DE. *Ann. chim. phys.,* [3] **32,** 142–5. Used glass tubes, generally enclosed in steel tubes, gel. SiO_2, and H_2O containing HCl or CO_2, heated at 200°–300°; product quartz in six-sided striated prisms with pyramidal terminations. When the soln. contained $NaHCO_3$, CO_2, and some realgar, very little quartz was obtained.

1855 4 MASCHKE, O. *Z. deut. geol. Ges.,* **7,** 438–42. In previous expts. (*Erdmann and Werther's J. prakt. Chem.,* **61,** Heft 1) in which solns. were heated on the water bath in closed glass tubes, hard pyramidal quartz crystals were obtained, insol. in acids and alkalies. In this paper are described expts. in which evapn. of solns. containing SiO_2 gave opal.

1857 5 DAUBRÉE. *Ann. Mines.,* [5] **12,** 289–326. Substances were heated with H_2O in a glass tube, which was placed in a steel tube, and the space between filled with H_2O. Glass with but little H_2O at 400° gave a white, porous mass containing quartz and wollastonite (?). The soln. contained SiO_2, 37%; Na_2O, 63%; K_2O, trace; corresponding approx. to $3Na_2O.2SiO_2$. Feldspar contained in an obsidian was not noticeably attacked. Pyroxene or muscovite, heated alone with H_2O, was unchanged except for a coating of quartz. When the water from the hot springs at Plombiéres, which contains much K silicate, was heated for 2 days, much quartz was deposited, most of which was stated to have come from the alkali silicate. Kaolin, treated with the Plombiéres water, gave crystals of feldspar with a little quartz. When the same water was concentrated and heated in a glass tube, the latter was attacked, giving in part greenish crystals, having a prism angle like augite, compn.: SiO_2, 51%; CaO, 26%; FeO, 22%; MgO, trace. Similarly treated, wood gave a mass resembling anthracite. Daubrée, in his "*Études Synth. Géol. Expt.,*" Paris, **1879,** pp. 154–179, describes the same expts., with crystallographic figures of the minerals obtained. He also speaks of a third mineral found in the white decomp. mass of the glass tube, having the compn. of pectolite; and a fourth mineral, called chalcedony. No crystallographic details.

1857 6 DEVILLE, ST. CLAIRE. *Ann. chim. phys.,* [3] **61,** 309–14. Evapn. expts. with bauxite and NaOH. The results were not very definit, but the product contained, among other things, corundum.

1862 7 DEVILLE, ST. CLAIRE. *Compt. rend.,* **54,** 324–7. Solns. of K silicate and Na aluminate in glass tubes at 170° gave hexagonal tablets of levynite, optically uniaxial, compn.: SiO_2, 44.7%; Al_2O_3, 21.5%; CaO, 0.9%; Na_2O, 5.5%; K_2O, 8.6%; H_2O, 19.7%. The soln. remaining contained neither Al_2O_3 nor SiO_2 in noticeable amts. A similar mixture at higher temp. gave little levynite, but much quartz(?), and the soln. contained Na and K aluminates. Mixtures of K silicate and K aluminate at 200° gave K ittnerite, compn.: SiO_2, 34.1%; Al_2O_3, 28.9%; K_2O, 24.8%; H_2O, 11.5%. A mixture of K silicate and Ba aluminate gave, under similar conditions, a cryst. product, compn.: SiO_2, 35.3%; Al_2O_3, 10.2%; BaO, 30.0%; K_2O, 5.8%; H_2O, 18.9%.

1872 **8** Maschke, O. *Ann. Physik Chem. (Poggendorf)*, [5] **25**, 549–78. Using an aqueous soln. of $Na_2O.4SiO_2$ in a sealed glass tube at 175°–185°, obtained an alkalin soln. and a finely grained ppt. containing (1) needles of a cryst. hydrated silica, (2) aggregates of hydrated silica. On the walls of the glass tube were concretions, the nuclei of which were cryst. anhydrous silica, the outside a cryst. hydrated silica different from the above. The nuclei were stated to contain both tridymite and quartz; at 175°–185° more tridymite, at 195°–205° more quartz. M. states that these concretions were formed during the cooling.

1873 **9** Chroustschoff, K. von. *Am. Chemist*, **3**, 281–6. Used a dialyzed coll. SiO_2 soln., heated at 250° in a glass tube for 14 days, obtained a cryst. powder, d. 2.66–2.80, small hexagonal prisms, probably tridymite. At 350° for 14 days in a gold-lined steel tube, using the same colloidal SiO_2 soln., hexagonal plates of probably tridymite were obtained, d. 2.25–2.51.

1876 **10** Lemberg, J. *Z. deut. geol. Ges.*, **28**, 519–621. Many expts. were made with kaolin and zeolites at 100° (in glass tubes) and at 180°–195°, in aqueous salt solns., to study the replacements of the alkali of the mineral by that of the salt used, or the transformation of the kaolin. Most of the products were amorph. Leucite in 18 hours at 180°–190° with NaCl soln. gave a product of the compn. of analcite, which, when treated with K_2CO_3 soln., regenerated leucite. The replacement was more difficult when the leucite had first been ignited. The Mg of $MgCl_2$ and the Ca of $CaCl_2$ replaced K or Na only partially at 100°; nephelite was more resistant to replacement. Kaolin and $Al(OH)_3$ with alkalin silicate solns. at 100° and 180° gave amorph. "compounds." From many expts. with zeolites and salt solns., L. concluded that natrolite, scolecite, and mesolite can each be transformed into the other in this manner.

1879 **11** Friedel, Charles, and Sarasin, Edmond *Bull. soc. min.*, **2**, 113–17. Two expts. were made, in which a mixture of KOH, pptd. $Al(OH)_3$, and a large excess of gel. SiO_2 were heated with H_2O at a temp. below dark red heat. The first expt., heated for 18 hours, gave hexagonal crystals of quartz, with parallel extinction, and faces $(10\bar{1}0)$, $(10\bar{1}1)$, (0111). The 2nd expt., heated for 38 hours, gave much larger crystals (0.5 mm. long and 0.1 mm. broad); six prism angles could be measured on the goniometer. Prisms hexagonal, striations horizontal, unequally developed $(10\bar{1}1)$ and $(01\bar{1}1)$; some crystals showed sharp rhombohedra, $(10\bar{1}1)$, also with rarer faces. Photomicrographs are given.

1879 **12** Friedel, C. and Sarasin, E. *Bull. soc. min.*, **2**, 158–61. Expts. were made at temps. below dark red, the heating being continued for 36 hours. Using K silicate, a small amt. of KOH, and a ppt. obtained by adding $AlCl_3$ to K silicate, obtained a product considered to be a mixture of orthoclase and quartz. (It is stated in this paper that orthoclase was obtained in the previous expt.) Orthoclase, determinable faces perpendicular to the plane of symmetry (010), outline imperfectly hexagonal, or a parallelogram, biref, small, angle corresponding to $(\bar{1}01) \wedge (100) = 140°$ (probably typographical error, for orthoclase should be 114°). Faces present, (010), (100), $(\bar{1}01)$. An analysis of the product is given; the results do not correspond to orthoclase, but as the sample analyzed was contaminated to an unknown degree, the analysis is meaningless. D., detd. with Thoulet's soln., sensibly that of orthoclase. Quartz was obtained in the ordinary forms; when the temp. was higher hexagonal crystals of tridymite were found.

1880 13 Friedel, C. and Sarasin, E. *Bull. soc. min.*, **3**, 25–6. Using a mixture of pptd. K-Al silicate, K silicate and H_2O, under conditions similar to those in the preceding expts., obtained orthoclase and quartz, the former with crystal faces parallelograms, extinction with the larger dimension = 3–4°, terminal faces formed angle corresponding to $(001) \wedge (\bar{2}01)$ of orthoclase, (110) missing. Quartz in short bipyramids without prism faces.

1880 14 Meunier, Stan. *Compt. rend.*, **90**, 349–51. Mg was placed in a porcelain tube, one end of which was connected to a source of steam, the other with a source of $SiCl_4$ vapor. When both gases were passed over the Mg at a low red heat, at atmospheric pressure, the reaction was $Mg + SiCl_4 + 3H_2O = MgO.2SiO_2 + 4HCl + H_2$. The crystals obtained were called by Meunier enstatite, but Fouqué and Lèvy, "*Synth. des Min. et des Roches,*" Paris, **1882**, p. 111, showed that it was a monoclinic Mg pyroxene.

1880 15 Meunier, Stan. *Compt. rend.*, **90**, 701–2. H_2O vapor was passed over $AlCl_3$ and Mg contained in an open tube, heated to a low red heat; product mainly spinel, in hard colorless isotropic cubes and octahedra, without action on polarized light, unalterable by boiling HNO_3. In other parts of the tubes were crystals of periclase and corundum. No crystallographic details.

1880 16 Meunier, Stan. *Compt. rend.*, **90**, 1009–12. Exptl. conditions same as (**14**), but Al instead of Mg. When the $SiCl_4$ was in excess, lamellae and needles of metallic Si were obtained; when the H_2O was in excess, amorph. compds. containing Si and Al; and when both vapors were present in equal amts., small needles of the compn. Al_2SiO_5 (SiO_2, 40.91%; Al_2O_3, 58.02%) were obtained, which polarized slightly. When KOH was also added to the charge, brown, regular optically perfectly isotropic trapezoids of leucite were obtained, size 0.003–0.012 mm., compn.: SiO_2, 55.83%; Al_2O_3, 23.54%; K_2O (by diff.), 20.63%. At a slightly different temp. prisms showing orthoclase twinning were obtained but in quantities too small for analysis.

1880 17 Schulten, A. de. *Bull. soc. min.*, **3**, 150–3; *Compt. rend.*, **90**, 1493–5. Heated Na silicate soln., NaOH and an aluminous glass for 18 hours at 180°–190°, product analcite, in crystals 0.1 mm. long, imbedded in gel. SiO_2. The crystals were separated from the impurities by successive treatments with NaOH and dil. HCl solns., though the crystals were somewhat sol. in the latter; an analysis of the product so treated gave: SiO_2, 54.6%; Al_2O_3, 21.8%; Na_2O (by diff.), 15.0%; CaO, trace; H_2O, 8.6%. Crystals were trapezoids of the regular system (211), optically abnormal like the natural mineral, apparently a complex twin composed of 4 pyramidal individuals, with base on the supposed octahedral faces, and apexes meeting in the center. Individual crystals optically uniaxial and positive, α on the supposed octahedral face, γ perpendicular to this face.

1881 18 Friedel, C. and Sarasin, E. *Bull. soc. min.*, **4**, 171–5. Orthoclase and quartz were obtained by heating a mixture similar to that used in (**13**), but containing more $Al(OH)_3$. Analysis of the product gave: SiO_2 (by diff.), 70.03%; Al_2O_3, 15.59%; K_2O, 14.38%; corresponding to orthoclase plus about 5.4% quartz. The orthoclase showed the following forms: (1) orthoclase as in granite, (010) bounded by (100) or (110) and (001), and $(\bar{2}01)$ or $(\bar{1}01)$, extinction on (010) with trace of (100) = 22°, and with trace of (100) = 4°–5°; (2) orthoclase as in trachyte, faces (001) and (010) (dominating) and (110); (3) adular orthoclase, (110), (001) or with $(\bar{1}01)$, angles (measured microscopically) $(001) \wedge (100)$ = 116°–117°, $(001) \wedge (\bar{1}01)$ = 129°–130°, angle on base about 113°, angle on (110), 104°, twinning parallel to (001), extinction with (001), 7°–8°, also Baveno twinning. In some expts. in which there was much K silicate, obtained a hydrated K silicate, in crystals 2–3 mm. long, difficultly attacked by HCl, fusible at pale white heat with intumescence, orthorhombic, with (010), (dominating), (001), (110), prism angle = 105° 8′, plane of optic axes parallel to (010), bisectrix perpendicular to (100), ρ greater than υ.

1881 **19** Friedel, C. and Sarasin, E. *Compt. rend.*, **92**, 1374–8. Used a steel bomb 0.01 m. thick, lined with Cu and Pt, at temp. near dull red heat. Data same as (**12**), (**13**), and (**18**).

1882 **20** Schulten, A. de. *Bull. soc. min.*, **5**, 7–9. With less detail in *Compt. rend.*, **94**, 96–7. Obtained analcite by heating for 18 hours at 180° in a Cu bomb a mixture of Na silicate and Na aluminate in such proportions that the $Al_2O_3 : SiO_2$ ratio was the same as in analcite, together with a "convenient quantity" of lime water. The latter was merely to aid crystallization, as without it good crystals were rarely obtained. The crystals were similar to those obtained in (**17**), in trapezoids and hexahedra, in most cases perfectly isotropic, but optically abnormal crystals were found in one expt. Schulten believed that the trapezoids were formed in very conc. and alkalin solns., the hexahedra under the other conditions.

1882 **21** Schulten, A. de. *Compt. rend.*, **94**, 992–3. A mixture of K silicate and $Ca(OH)_2$ solns. was heated to 180° in a glass tube; product crystals which fused with intumescence, slowly decomp. by HCl, parallel extinction, high double refraction, elongation α, compn.: SiO_2, 64.2%; Al_2O_3, 0.7%; CaO, 14.7%; Na_2O, 3.3%; K_2O, 2.2%; H_2O, 14.5%; corresponding to $(K_2Na_2Ca)O.3SiO_2.2H_2O$.

1882 **22** Ramsay, W. and Hunter. *Rept. Brit. Assn.*, **1882**, 239–40. Used a cast iron bomb, which remained tight at 300°–400°. Finely powdered quartz heated at 300° with H_2O showed no action; powdered chalcedony similarly treated was but little attacked; amorph. SiO_2 was caked into a hard, white opaque glassy mass.

1883 **23** Friedel, C. and Sarasin, E. *Compt. rend.*, **97**, 290–94. Describes a steel bomb which kept tight. When SiO_2, NaOH soln. and Al_2O_3 in the proportions of albite were heated at 400° no albite was formed, but analcite, in icositetrahedra, optically normal, together with globulites and undeterminable needles. When Na silicate corresponding to the amt. found in soln. in the preceding expt. was added to the same mixture as before, heated at 505°–517°–432° (3 measurements) the product consisted of needles or tablets of albite, flattened parallel (010), 0.1–0.2 mm. long, half as broad, most crystals elongated parallel to the intersection between (001) and (010), with extinction angle = 15°–19°, some elongated parallel to the intersection between $(1\bar{1}0)$ and (110), with extinction angle = 4°, angle $(1\bar{1}0) \wedge (010)$ = 116°–118°, other determinable angles 127°–130° and 116°; reentrant angle indicated albite twinning, extinction = 16°–17° between the twinning; compn.: SiO_2, 68.93%; Al_2O_3, 19.23%; Na_2O, 11.61%. Quartz was never found. When KCl in increasing amts. was added to the charge without changing the alkalinity, first quartz with unknown cubic crystals, then large albite crystals, together with small undeterminable crystals similar to orthoclase, were obtained. Analysis of the small crystals mixed with some albite gave: Al_2O_3, 18.89%; Na_2O, 8.53%; K_2O, 3.94%, corresponding to $^1/_3$ orthoclase; and the crystals seemed to be of 2 kinds. Albite was still obtained when the $K_2O : Na_2O$ ratio was 4 : 1; the presence of NaCl did not affect the crystallization.

1883 **24** GORGEU, ALEX. *Compt. rend.*, **97**, 320–23. H or CO_2 satd. with H_2O was passed over a mixture of 1 part of pptd. SiO_2 and 10 parts $MnCl_2$ at a red heat; product varied with length of heating. The first product obtained was red crystals of rhodonite, $MnO.SiO_2$, which on longer heating were transformed into gray crystals of tephroite, $2MnO.SiO_2$. Gorgeu states that the H and CO_2 only served to prevent oxidation, but were themselves without action. Large amts. of alkali chlorides hindered the process, but the result was the same. In the presence of $CaCl_2$, $MgCl_2$ and $FeCl_2$ the product had the general compn: $2RO.SiO_2$, the RO being 1% CaO, 3% FeO, 9% MgO. The silicate prepd. in the presence of $ZnCl_2$ never contained Zn. The rhodonite had a glassy luster, d. 3.68, triclinic prisms; the tephroite had an adamantine luster, d. 4.08, orthorhombic prisms. The salts were hardly oxidized in dry air, difficultly fusible at red heat, and could be recrystallized from molten $MgCl_2$. Rhodonite dissolved in molten $MgCl_2$ in the presence of H_2O vapor gave tephroite; tephroite with SiO_2 in $MgCl_2$ gave rhodonite when protected from the action of air and H_2O.

1883 **25** GORGEU, ALEX. *Compt. rend.*, **97**, 1303–5. H and steam were passed over a mixture of 20–25 g. $MnCl_2$ and 1.5 g. pipe clay in a Pt crucible at cherry red heat for $^1/_2$ hour; product a reddish fused cake containing $MnCl_2$ and spessartite, the latter in yellowish icositetrahedra, 0.03–0.5 mm. long, insol. in HCl, fusible at a strong red heat, $d_{11°} = 4.05$, hardness = 6–7, compn.: SiO_2, 36.10%; Al_2O_3, 21.25%; MnO, 42.70%; CaO, MgO, trace. When $CaCl_2$ was used, crystals were obtained which possibly were grossularite.

1883 **26** LEMBERG, J. *Z. deut. geol. Ges.*, **35**, 557–618. The influence of H_2O on glasses at 100° was studied by heating in open Pt or Ag tubes, covered with a layer of paraffin to prevent evapn.; the heating was continued 10 hours every day at the same temp. A basalt heated for 6 mo. with distilled H_2O took up 2.43% H_2O, which was not removed over H_2SO_4 in 2 weeks; the soln. remaining in the tube had a slightly alkalin reaction. The same basalt heated with K_2CO_3 soln. for 9 mo. gave a glass rich in H_2O, and $CaCO_3$ crystals. A glass made from palagonit from Vidoe heated for 3 mo. with distilled H_2O was but little attacked, but the product contained 8.61% H_2O. The same glass heated with Na_2CO_3 soln. for 2 mo. gave a very strongly hydrated glass and calcite crystals. A contact sintered sandstone heated with Na_2CO_3 soln. gave a glass containing much H_2O, and considerable SiO_2 went into soln. When a glass obtained by heating elaeolite was heated with K_2CO_3 soln. all the Na was replaced by K, and the glass contained 10.89% H_2O. The ignited H_2O-rich glass gave off considerable heat when moistened, and took up 9.8% H_2O. Melted labradorite heated for 13 mo. with K_2CO_3 soln. gave a glass rich in K and the Ca replaced had formed $CaCO_3$. Melted adular and orthoclase heated with Na_2CO_3 soln. gave a strongly hydrated glass containing Na, and much SiO_2 went into soln. Similarly treated, albite glass took up H_2O, and when

K_2CO_3 was used the Na of the mineral was replaced. Augite with K_2CO_3 soln. for 1 year at 100° gave $CaCO_3$, the MgO remained combined with the SiO_2. Concluded that Na compds. take up more H_2O than K compds., but when the glasses are ignited the K glasses take up much H_2O and show a large heat effect, while the Na glasses do not show the latter effects to the same extent. Expts. were made to study the replacements and transformations between solns. and various silicates, working with a Cu digester heated 10 hours daily for the given time Kaolin with an 8% $Na_2O.4SiO_2$ soln. at 180°–190° for 33 hours gave an amorph. H_2O-rich powder similar in compn. to natrolite. (Lemberg(**40**), corrects this, stating that it was a basic analcite.) Allophane at 100° with water glass soln. for 14 days gave an amorph. powder rich in alkali and H_2O. Kaolin with 30% NaOH soln. for 72 hours at 180°–190° gave an amorph. silicate rich in Na_2O and H_2O. Orthoclase for $6^1/_2$ mo. at 100° with 10% NaOH and Na_2SO_4 soln. gave a product 95% crystallized in small columns, compn.: SiO_2, 34.74%; Al_2O_3, 30.04%; CaO, 0.20%; Na_2O, 18.53%; Na_2SO_4, 9.33%; H_2O, 5.88%. Sanidine containing a small amt. BaO had all the Ba eliminated as $BaSO_4$ when similarly treated. Natrolite heated for 3 mo. with 20% NaOH and Na_2SO_4 gave needles of the compn.: SiO_2, 34.03%; Al_2O_3, 30.24%; Na_2O, 17.75%; Na_2SO_4, 13.32%; H_2O, 5.02%. Albite treated 14 days with 30% NaOH gave a product 80% of which was cryst., composed of needles of the compn.: SiO_2, 35.14%; Al_2O_3, 29.66%; Na_2O, 17.39%; Na_2SO_4, 12.63%; H_2O, 4.90%. Similar needles were obtained with labradorite; these needles all had the compn. of a hydrated nosean. Similar expts. with K_2SO_4 and K_2CrO_4 gave amorph. products. Many other expts. were made with solns. of NaOH and KOH and different salts and the products analyzed. All expts. showed that alkalies are easily replaced, and that NaCl, KCl, Na_2CO_3, $NaNO_3$, Na_2S, and Na_2SO_4 are easily added. When solns. of Na_2SiO_3 and salts were heated with $Al(OH)_3$, minerals were obtained resembling those of the cancrinite group; analcite was sometimes obtained; when other salts than Na_2SiO_3 were not added alkalin aluminosilicates, often of simple types, were obtained. When anorthite, with a little augite, was heated for 180 hours at 180°–190° with Na_2CO_3 soln. the product consisted of calcite crystals, amorph. substances, and a columnar mineral similar to cancrinite. Mixtures of $Al(OH)_3$, $CaCl_2$ and Na_2SiO_3 soln. gave a mineral crystallized in bundles and sheaves, which Lemberg considered to be pectolite. Similar minerals were obtained by heating wollastonite, apophyllite, okenite, datolite, and artificial $CaSiO_3$ with Na_2SiO_3 solns. K pectolite was much harder to prepare.

1884 **27** GORGEU, ALEX. *Compt. rend.*, **98**, 920–22. Heated 20 grams of previously dried and fused $FeCl_2$ and 1 gram SiO_2 at a red heat in a stream of H and steam, in an open Pt crucible; product a cake containing excess chloride and crystals of fayalite, 0.5–1.0 mm., compn.: SiO_2, 28.8%; FeO, 71.2%. The product was brown, weakly magnetic, optical properties (detd. by E. Bertrand) gave an acute negative bisectrix. D. 4.23, hardness = 5–5.5. $FeSiO_3$ was never obtained. When Al_2O_3 was used instead of SiO_2, octahedra of spinel were obtained. When MnO was present, a mineral similar to olivine was obtained, compn.: SiO_2, 32%; FeO, 34%; MnO, 34%; probably knebelite. When 50–66% $MnCl_2$ was present, the crystals contained only 19–20% of the total basic oxides as FeO.

1884 **28** GORGEU, ALEX. *Compt. rend.*, **99**, 256–9. When moist air was passed over melted $CaCl_2$ at red heat in an open vessel, the oxychloride $CaCl_2.CaO$

was formed. When pptd. SiO_2 was added, with 1 equiv. $CaCl_2$, $CaO.SiO_2$ was obtained; with 2 equiv., $2CaO.SiO_2$; and with 7 equiv. of chloride a chlorosilicate was obtained. When a mixture of 1 gram SiO_2, 15 grams $CaCl_2$, and 3 grams NaCl were heated at a cherry red, in a current of moist air, a mixture of excess chlorides, the chlorosilicate, round grains of tridymite(?), and long prisms of wollastonite were obtained. Details of the optical exam. are not given, but properties are stated to coincide with those of the natural mineral.

1884 **29** Gorgeu, Alex. *Compt. rend.*, **98**, 1281–2. Mentions the prepn. of fayalite (27). By heating fayalite in air oxidation took place; on treating with HCl, SiO_2 pseudomorphs. of fayalite remained. Expts. with artificial knebelite gave similar results.

1885 **30** Gorgeu, Alex. *Ann. chim. phys.*, [6] 4, 515–61. A collected account of the work recorded in (24), (25), (27), (28), (29), and the following additional expts.: Heated 20 grams $MnCl_2$, 1 gram SiO_2 at a red heat at atm. pressure in an atmosphere of H and H_2O; product a Mn chlorosilicate, $2MnO.SiO_2.2MnCl_2$, in regular red crystals. Using $FeCl_2$, in 2 expts. only, an isotropic Fe chlorosilicate was prepd. Expts. on the prepn. of alkalin earth and Pb sulfates are also given.

1885 **31** Lemberg, J. *Z. deut. geol. Ges.*, **37**, 959–1010. About 30 grams of $Na_2SiO_3.8H_2O$ crystals were melted in their crystal H_2O, to the melt was added 2–3 grams of either datolite, wollastonite, gypsum, or $CaCO_3$, and the mixture heated at 190°–200° for 78–100 hours. Product in each case, besides indeterminate grains, was bundles or sheaves of a pectolite-like mineral. Kaolin heated for 78 hours with 37% KOH gave an amorph. substance of the compn.: $K_2O.Al_2O_3.2SiO_2$, which, when added to molten Na_2SiO_3 and treated the same as before, gave an amorph. mass. Poorly formed crystals were obtained by treating kaolin with 56% NaOH soln. Nephelite with 56% NaOH gave regular crystals. Elaeolite, anorthite, haüynite, sodalite, and ittnerite with very strong KOH or K salt solns. gave amorph. or poorly formed biref. columns of compn.: $K_2O.Al_2O_3.2SiO_3$; KCl gave a different result. While ordinary analcite with K_2CO_3 soln. was converted to leucite, fused analcite gave a silicate rich in H_2O. Adular, sanidine and albite treated with Na_2SiO_3 soln. at 200° gave regular(?) crystals, and others similar to pectolite. Chabazite could be transformed into analcite. Spodumene similarly treated with Na_2CO_3 soln. showed alteration. Many other similar expts. were made, and also many replacement expts., in which the product was usually amorph. From many expts. it was found that Na-K silicates by heating at 200° with Na salt solns. gave compds. with a H_2O content between 8–9%, this reaction going easier in alkalin than in acid solns.

1885 **32** Friedel, C. and Sarasin, E. *Bull. soc. min.*, **8**, 304–5. Small calcite crystals were obtained by heating $CaCl_2$, pptd. $CaCO_3$, and 60–70 cc. H_2O for 10 hours at 500°; with 20 grams $CaCl_2$ and a few grams $CaCO_3$ the crystals were large enough for goniometric measurement. Crystals were simple rhombohedra, normal angle (goniometer) $= 74° 54', -55', -52'$. Growth similar to crystal skeleton. No aragonite.

1886 **33** Doelter, C. *Neues Jahrb. Min. Geol.*, **1886**, I, 124. Steam was passed over fused $CaCl_2$ at atm. pressure, temp. not stated; product rectangular tablets, with parallel extinction, biaxial, cleavage parallel to one direction of the rectangle, little sol. in cold dil. HCl, sol. in hot conc. HCl, low hardness.

1887 **34** CHROUSTSCHOFF, K. VON. *Bull. soc. min.*, **10**, 31–6; *Neues Jahrb. Min. Geol.*, **1887**, I, 205–8. Quartz was obtained by heating a coll. soln. of SiO_2 to 250° "almost every day for 6 months." Started with 4 tubes, 3 of which burst soon, the other in 6 mo. Some crystals as large as 8 mm. long and 3 wide, of type of vein quartz, with (10$\bar{1}$0), (10$\bar{1}$1), (01$\bar{1}$1) and twice (11$\bar{2}$1), and (51$\bar{6}$1), striated parallel to intersection (10$\bar{1}$0), (51$\bar{6}$1); (11$\bar{2}$1) also present. Tridymite was also formed in fusion expts.

1887 **35** CHROUSTSCHOFF, K. VON. *Bull. soc. min.*, **10**, 137–40. Description of a new form of app. which was used for heating glass containers up to 500°.

1887 **36** CHROUSTSCHOFF, K. VON. *Compt. rend.*, **104**, 602–3. Used a glass tube, heated at 250°–300°, and a 10% colloidal soln. of SiO_2; product quartz, with prism (10$\bar{1}$0) and rhombohedron predominating, rhombohedron (01$\bar{1}$1) little developed, (51$\bar{6}$1) rare. Also heated at 300° SiO_2 soln., dialyzed colloidal Al_2O_3 soln. and KOH; product small quartz crystals and rhombic lamellae corresponding to the adular orthoclase of Friedel and Sarasin.

1887 **37** GORGEU, ALEX. *Bull. soc. min.*, **10**, 278–84, in more detail in *Ann. chim. phys.*, [6] **10**, 145–69. By acting on kaolin mixed with 10 parts NaCl at red heat in the presence of H_2O vapor or HCl, an amorph. silicate insol. in H_2O was obtained, compn.: SiO_2, 41.20%; Al_2O_3, 35.70%; Na_2O, 20.40%; CaO, 0.55%; MgO, 0.65%; NaCl, 1.50%; corresponding to $Na_2O.Al_2O_3.2SiO_2$ + chloride. With 20 parts KI, KBr or KCl, a cryst. compd. attacked by H_2O, compn.: $K_2O.Al_2O_3.2SiO_2$ + halide, was produced. With K_2CO_3 and kaolin at cherry red heat an amorph. compd., compn.: $K_2O.Al_2O_3.2SiO_2$ was produced, and a similar result was obtained with Na_2CO_3, the product in this case being biref. At a strong, red heat octahedral crystals of the compn. $K_2O.Al_2O_3.SiO_2$ were obtained, together with other compds. of unknown compn. Analyses are given in the 2nd reference; no crystallographic details.

1887 **38** FRIEDEL, G. AND SARASIN, E. *Bull. soc. min.*, **10**, 169. An announcement that the authors had prepd. topaz by the action of H_2SiF_6 soln. on a mixture of SiO_2 and Al_2O_3 at 500°. No details.

1887 **39** GORGEU, ALEX. *Bull. soc. min.*, **10**, 271–8. Worked at a red heat and ordinary pressure, passing air and steam over an intimate mixture of SiO_2 and $CaCl_2$; product obtained varied with the length of heating and the compn. of the mixture. With 1 gram SiO_2 and 15–20 grams $CaCl_2$, besides the normal Ca silicate, a deliquescent chlorosilicate, $2CaO.SiO_2.CaCl_2$, rhombic, high biref., axial angle about 25°; and the chlorosilicate, $CaO.SiO_2.CaCl_2$, hexagonal, optically positive, were obtained. (G. gives the formulae $2CaO.SiO_2.CaCl$ and $CaO.SiO_2.CaCl$.) Identification and compn. doubtful. With a gram SiO_2, 15 grams $CaCl_2$, and 3 grams NaCl the chlorosilicate, round grains of tridymite(?), and long prisms of wollastonite(?) were obtained. Product treated with dil. AcOH (1 : 20) and analyzed gave, after deducting 12.7% tridymite, SiO_2, 52.1%; CaO, 47.9%. Wollastonite had high biref., plane of optic axes horizontal, positive, one axis strongly inclined, d = 2.8–2.9, hardness = 3.5. The formation of wollastonite was doubted by Doelter (43, p. 120, footnote). An orthosilicate was also obtained, identification doubtful. When some $MgCl_2$ was present, transparent crystals of a pyroxene were obtained, extinction angle = 39°.

White clay with $CaCl_2$, fused in a current of moist air, gave a tetrahedral silicate whose compn. was probably $6CaO.3Al_2O_3.3SiO_2.2CaCl_2$. The same melt pulverized and heated a short time with sugar soln. gave an insol. residue of monoref. crystals, in trapezoids and octahedra, probably grossular(?).

1887 **40** LEMBERG, J. *Z. deut. geol. Ges.*, **39**, 559–600. Kaolin treated with strong $Na_2O.nSiO_2$ solns., *n* ranging from 1–4, gave chiefly columnar and roundish kernels of a mineral similar to analcite, which, when treated with KCl, gave leucite. Using $K_2O.SiO_2$ soln., indeterminable bundles or sheaves were obtained, which, on treating with NaCl soln., gave regular crystals of analcite. Kaolin with NaOH soln. gave approx. the compn.: $4(Na_2O.Al_2O_3.2SiO_2) + 5H_2O$, in which the Na_2O could with difficulty be replaced by K_2O. Kaolin treated with K_2CO_3 gave hexagonal tablets of K nephelite; with Na_2CO_3 a cancrinite powder. By the action of Na_2CO_3 soln. at 200°, feldspars were changed into analcite, the action being more rapid the higher the SiO_2 content. Anorthite gave a cancrinite-like product. Fused feldspars with K_2CO_3 soln. at 100° gave products resembling chabazite, etc.; at 200° the products contained more Na_2O and H_2O, similar to those obtained with phillipsite, leonhardite, and fused analcite. Scapolites treated similarly gave products similar to zeolites, poorly crystallized. Prehnite with K_2CO_3 gave columns of a zeolite-like product; Na_2CO_3 gave a cancrinite containing CaO and Na_2O. Scolecite with NaCl gave a natrolite, which was reconverted into scolecite by $CaCl_2$ soln. Fused scolecite with K_2CO_3 gave an unknown product, which, with Na_2CO_3, gave cancrinite, with Na_2SO_4 or NaCl, analcite. Fused natrolite gave similar products. In addition to the above a large number of expts. were made in which thomsonite, spodumene, jadeite, andesine, labradorite, and albite were heated with various salt solns., and the products, which were chiefly amorph., were carefully analyzed. All these minerals were more or less transformed, generally with addition of H_2O; the compn. of the product was often similar to analcite, and often the salt used was taken up, producing a compd. similar in compn. to the members of the cancrinite-sodalite group. An interesting point was that fused minerals often gave products different in compn. from those obtained with the natural mineral.

1888 **41** LEMBERG, J. *Z. deut. geol. Ges.*, **40**, 625–56. Haüynite and sodalite treated with $MgSO_4$ or $CaCl_2$ gave only amorph. products; both were easily decomp. by $MgSO_4$, while the haüynite was much more easily decomp. by the $CaCl_2$ than the sodalite. A large number of glasses made by fusing oligoclase, andesine, labradorite, natrolite, elaeolite, stilbite, leonhardite, prehnite, tremolite and wollastonite were heated with H_2O at about 200°; the amorph. products contained amts. of H_2O from 2.2–30%, mostly about 8–9%. Kaolin, serpentine and pitchstone were ignited and then heated with H_2O; the products contained considerable H_2O. In addition a number of minerals were heated with K_2CO_3, Na_2CO_3 or K_2SiO_3 solns., and the products, which were mostly amorph., analyzed. Topaz heated 174 hours at 200°–210° with Na_2SiO_3 soln. was converted into a zeolite-like alkali aluminosilicate.

1889 **42** BRUHNS, W. *Neues Jahrb. Min. Geol.*, **1889**, II, 62–5. Apparatus a steel bomb, lined with Pt, with cover held down by bolts, and made tight by means of a Cu washer, which was protected from the action of the soln. by Pt. Freshly pptd. $Fe(OH)_3$ heated for 10 hours with H_2O at 250° gave merely anhydrous amorph. Fe_2O_3. When a trace of NH_4F was added to the same charge, hexagonal plates of hematite, 0.03–0.08 mm. long, were obtained, angle about 120°. With Al_2O_3 under similar conditions, at 300°, corundum, in pale blue prisms with pyramidal terminations, 0.1 mm. long, were produced, but at 250° the product was amorph. Crystals of quartz, 0.5–0.8 mm. long, were easily made in a similar manner from SiO_2, but when glass was used a higher temp. was necessary. At 300°, 50 hours were necessary to get quartz from K water glass, with Na water glass quartz was easily obtained in 10 hours. Using microcline, compn.: SiO_2, 64.33%; Al_2O_3, 18.61%; K_2O, 13.49%; Na_2O, 3.56%; and heating for 56 hours at 300° with H_2O containing a little HF, on the walls of the tube were found crystals of tridymite, 0.05–0.1 mm. long, in imbricated hexagonal plates. Crystals gave no residue when heated with HF, and gave the reactions of $SiO_2(Na_2SiF_6$, silica skeleton). On the Pt cover was a crust of large (0.5 mm.) crystals, isotropic, of form of K_2SiF_6, octahedra with cubes predominating, but insol. H_2O, qual. examination gave SiO_2, K, F, Al_2O_3. The other end of the tube contained unchanged feldspar. Attempts to crystallize TiO_2 and SnO_2 failed, but ilmenite and magnetite were obtained.

1890 **43** DOELTER, C. *Neues Jahrb. Min. Geol.*, **1890**, I, 118–39. Worked either in a closed nickeled gun-barrel or in a Ag-lined steel tube. Apophyllite was recrystallized by heating the powdered mineral for 3 weeks at 150°–160° with H_2O charged with CO_2; product in small transparent columns showing a prism with pyramids and base, or the more tabular forms with parallel extinction. This mineral was also prepd. by heating okenite with K_2SiO_3 soln. containing CO_2 for about 30 days at 200°. The okenite dissolved completely, and formed several new minerals, apophyllite predominating. Crystal forms base, prism, pyramid, distinct, though microscopic. Some okenite was also recrystallized, in small radiating bundles of needles, parallel extinction, little effect on polarized light. Okenite heated with H_2O containing CO_2 was recryst. in fine needles; heated for a long time with $AlCl_3$ and Na_2CO_3 solns. containing CO_2 gave analcite in icositetrahedra with sharp outlines, and apophyllite in small crystals (prism and pyramid), and chabazite in rhombohedra. Chabazite was recryst. from H_2O containing CO_2 at 150°, product fairly large rhombohedral crystals, angle 93°–95°, extremely weak biref., extinction angle 20°. The same mineral was also recryst. from liquid CO_2(?). Heulandite was recryst. from H_2O containing CO_2, heated 11 days at 170°, the large crystals obtained appearing mostly as 6-sided (clinopinacoid) or rectangular (orthopinacoid) with dome and base, the first having extinction angle = 0°–20°, cleavage along symmetry plane, weak biref. Figure obtained on the clinopinacoid showed angle of axis = 40°–50°, character positive, compn.: SiO_2, 58.90%; Al_2O_3, 14.02%; CaO, 8.53%; H_2O, 15.19% (by diff.) (analysis made on 0.3 gram). Heulandite was also synthesized by heating anorthite with freshly pptd. SiO_2 gel. in H_2O and CO_2 for 14 days. The product contained, besides unchanged anorthite, heulandite, showing both rectangular and 6-sided tablets, the first with parallel, the 2nd with inclined extinction (less than 20°), low biref., axial angle measured approx. in one case was 50°, cleavage parallel to plane of symmetry. Chabazite(?) was also obtained in this expt. Analcite was easily synthesized in characteristic icositetrahedra from SiO_2, Al_2O_3 and Na_2O in H_2O at 100°–200°. Natrolite was recryst. from H_2O containing CO_2 at 160° in bundles of prisms with pyramidal termination, cross section showed parallel extinction, medium biref. Also recryst.

from $NaHCO_3$ soln. Attempts to prepare it from nephelite and SiO_2 at 300° and from nephelite and alkali carbonate at 200° failed; analcite was obtained in the latter case. Scolecite could be recryst. as above, as unsatisfactory prisms or bundles of needles similar to the natural mineral. Scolecite was but slightly decomp. by H_2O at 80°, with 10% Na_2CO_3 it was 43.9% decomp. with enrichment of the soln. in SiO_2.

1890 **44** FRIEDEL, C. AND G. *Bull. soc. min.*, **13,** 129–39. By heating at 500° muscovite from Moos, Norway, with $^1/_4$–$^2/_3$ parts KOH and at least 20 parts of H_2O, obtained, besides unchanged muscovite, hexagonal crystals of nephelite, optically uniaxial, compn. corresponding to $^1/_3$ K nephelite and $^2/_3$ Na nephelite. Using NaOH better crystals were found, 0.5–0.8 mm., d = 2.65, uniaxial, compn. corresponding to $^1/_4$ K and $^3/_4$ Na nephelite. Using mica with the amt. KOH and K_2SiO_3 necessary to form leucite got orthoclase, tabular parallel to (010), faces (010), (001), (110), present, Karlsbad twinning, angle (001) ∧ (100) = about 116°, extinction on the intersection between (001) and (010) = 4°–5°. With a mixture of 1 part mica, 1 part calcined SiO_2, and 0.7 parts KOH obtained, besides orthoclase and nephelite, a few crystals of leucite, 1 mm. long, quadratic prisms and pyramids, angles (measured on the goniometer) pyramid ∧ prism = 43° 25′. Double refraction negative. In complicated forms, (100), (110), (001) and two pyramids (simple and double pyramids). Various modes of twinning, the simplest parallel (112). Striated on (101) parallel to intersection with pyramid. D = 2.5. HCl gave pulverent SiO_2.

1890 **45** FRIEDEL, C. AND GEORGES. *Compt. rend.*, **110,** 1170–8. A summarized account of expts. described in (44), (46), (47), and in addition the following: CaO with mica gave the octahedral crystals of an unknown hydrated $CaO\text{-}Al_2O_3$ silicate previously obtained. When $CaCl_2$ was used, besides unchanged mica, anorthite was formed, extinction angle = 37°, twinning parallel to (001) bounded by (010) and $(\bar{2}01)$, also by (110) and (130). Angles measured on goniometer: (001) ∧ (110) = 114°–115°; (001) ∧ $(\bar{1}30)$ = 98°. Twinning parallel (010) and $(\bar{2}01)$. D = 2.77; compn.: SiO_2, 42.67%; Al_2O_3, 36.44%; CaO, 21.47%.

1890 **46** FRIEDEL, C. AND G. *Bull. soc. min.*, **13,** 182–7. Analysis of the leucite previously obtained (44). Sodalite and nephelite were prepd. at 500° by the action of NaOH and NaCl soln. on mica, the NaCl being present in amts. ranging from $^1/_3$–2 times the wt. of mica used. Sodalite crystals rhombic dodecahedra and hexahedra, twinning parallel to (211), often elongated parallel to an axis of the cube. Optically isotropic, gave gel. SiO_2 with acids, d. = 2.32, color grayish, compn.: SiO_2, 36.75%; Al_2O_3, 32.41%; Na_2O, 25.75%; K_2O, 0.47%; Cl, 6.36%. The same Cl content was obtained with quite different amts. of NaCl; the formula was probably $3(2SiO_2.Al_2O_3.Na_2O).2NaCl$. Expts. with 6 grams SiO_2, 5.15 grams Al_2O_3, 3.6 grams Na_2CO_3 and 1.95 grams NaCl, corresponding to this formula, gave only isotropic globulites. Mica and CaO gave small octahedra of an unknown mineral.

1890 **47** FRIEDEL, C. AND G. *Bull. soc. min.*, **13,** 238–41. A hydrated nosean was obtained by heating for 3 days at 500° 6 grams mica, 3 grams NaOH, and 6 grams $Na_2SO_4.10H_2O$. Product in hexagonal prisms, $(10\bar{1}0)$, $(11\bar{2}0)$ with pyramid $(10\bar{1}1)$, deeply striated parallel to C, measured angles 30, 60, 90°. Optically negative, uniaxial, low biref., normal angle between 2 pyramidal faces = 24° 22.7′. Other angles were calculated and compared. Analysis: SiO_2, 34.81%; Al_2O_3, 29.91%; SO_3, 7.25%; Na_2O, 23.34%; H_2O, 3.95%; formula $3(Na_2O.Al_2O_3.SiO_2) + Na_2SO_4 + 2H_2O$. Besides these crystals, brown hexagonal lamellae, uniaxial, negative, d. that of mica, not appreciably attacked by HCl, were found. Since the original material contained MgO, this was probably biotite. Expts. with added MgO were without result.

1890 **48** Chroustschoff, K. von. *Compt. rend.*, **112**, 677–9; *Neues Jahrb. Min. Geol.*, **1891**, II, 86–90. Worked in thick-walled evacuated glass tubes, vol. 25 cc., heated for 3 mo. at 550°, using a mixture of colloidal SiO_2 soln., colloidal $Fe(OH)_3$, colloidal $Fe(OH)_2$, lime water, freshly pptd. $Mg(OH)_2$, and several drops of a NaOH-KOH soln. Product contained among other things, long, thin dark-colored prismatic crystals of hornblende, 1 mm. long, 0.5 mm. thick, faces (010), (110), (011) visible, angle $(110) \wedge (1\bar{1}0)$ could only be approx. measured, angle $(011) \wedge (0\bar{1}1) = 148° 28'$. Cleavage indistinct, extinction $C : \mathfrak{c}_{Na} = 17° 56'$, optical character negative, pleochroism $\mathfrak{c}$ bluish green, $\mathfrak{b}$ yellowish green, $\mathfrak{a}$ pale yellowish green, dispersion $\rho > \upsilon, \gamma - \alpha = 0.025$, mean index = 1.628, 2V = about 82°, $d_{15°} = 3.2452$, compn.: SiO_2, 42.35%; Al_2O_3, 8.11%; Fe_2O_3, 7.91%; FeO, 10.11%; MgO, 14.33%; CaO, 13.21%; Na_2O, 2.18%; K_2O, 1.87%; ignition (H_2O), 0.91%. Also found light prismatic green crystals, faces (110), (100) visible, rarer (010), and dome terminations, mean index = 1.65, extinction partly parallel, partly at angle = 37°, $\gamma - \alpha = 0.027$, optical character positive, apparently a diopside-like pyroxene. Also found colorless grains and crystals, poorly developed, faces (100) visible, isotropic, possibly analcite(?). Other minerals were quartz, 0.2 mm. crystals, faces $(10\bar{1}1)$, $(01\bar{1}1)$, $(10\bar{1}0)$; and thin flakes resembling adular.

1891 **49** Friedel, G. *Bull. soc. min.*, **14**, 7–10. Corundum and diaspore could not be prepd. by heating a soln. of NaOH satd. with Al_2O_3 at boiling, but were obtained when excess Al_2O_3 was present. The amt. of excess Al_2O_3 was without influence; corundum only was obtained at 530°–535°, both at 450°–500°, and diaspore only at 400°. If SiO_2 was present it crystallized as quartz. The corundum was in short reddish uniaxial negative rhombohedra; with slight Al_2O_3 excess at 530° with $(22\bar{4}3)$. The angle between two faces in this form (normal angle) was 51° 40'. The reddish color was ascribed to the presence of a little Cr_2O_3. The diaspore was in colorless flat prisms, with rectangular outline, often with curved faces, with angle 105° to cleavage plane. Not attacked by acids. Biref. small, biaxial, axial plane parallel to cleavage plane. When CaO was present calcite was found; SiO_2 crystallized as quartz. Hematite was obtained from Fe_2O_3 at from 450°–500° in hexagonal lamellae; below 280° only amorph. powder was found, no göthite.

1891 **50** Friedel, C. and G. *Bull. soc. min.*, **14**, 69–75. By heating mica with NaOH and Na_2SO_4 soln. obtained a nosean containing a small amt. H_2O, rhombic dodecahedra modified by the faces of a cube, isotropic, d. = 2.28, easily attacked by dil. HCl, compn.: SiO_2, 32.43%; Al_2O_3, 31.13%; SO_3, 7.61%; K_2O, 4.24%; Na_2O, 20.13%; H_2O, 2.32% (cf. (**47**); the difference was ascribed to the fact that the bomb leaked during this expt.). A cancrinite-like mineral was obtained with 14 grams mica, 7 grams NaOH, 14 grams Na_2CO_3, and H_2O at 500°, formula $3(2SiO_2.Al_2O_3.Na_2O).Na_2CO_3.2H_2O$, crystals hexagonal, with prism and pyramid, angle of the pyramidal face = 23° 49'—25° 1', d. = 2.35, optically negative, biref. = 0.010.

1891 51 FRIEDEL, G. *Bull. soc. min.*, **14**, 74. Brucite was obtained by the action of NaOH soln. on MgO at 400° as colorless hexagonal micaceous flakes, uniaxial, positive, high biref., optically positive. Additional note G. FRIEDEL. *Ibid.*, **14**, 194–5.

1891 52 GRAMONT, A. DE. *Compt. rend.*, **113**, 83–4. Used apparatus of Friedel, charge an intimate mixture of 25 grams borax and 5 grams pptd. $CaSiO_3$, heated for 36 hours at 400° in the presence of H_2O. Product a mixture of amorph. material, wollastonite, a crystallin powder in crystals too small for optical detn., and datolite, in crystals having the appearance of being monoclinic, with extinction angle very small, strong biref. Fouqué pronounced the crystals optically negative. Compn.: SiO_2, 35.39%; CaO, 35.95%; H_2O, 6.65%; FeO, 1.19%; B_2O_3, 20.82%. The same crystals were also obtained by the action of Na_2SiO_3 soln. on K borax at 300°.

1891 53 FOUQUÉ, F. AND MICHEL-LÈVY, A. *Compt. rend.*, **113**, 283–5. Used 1.5 grams of a glass made by fusing a granite from Vire, with 6 drops H_2O, heated at red heat, product merely sintered together. In the center of the clumps was some white crystallin material, not attacked by acids, containing SiO_2, Al_2O_3, K_2O, Na_2O and CaO, under the microscope showed the habit of orthoclase. Spinel and biotite(?) were also found.

1891 54 THUGUTT, STANISLAUS JOSEPH. *Z. anorg. Chem.*, **2**, 64–107, 113–56. The following expts. were all at about 200°: By the action of 16.8 grams NaOH dissolved in 105 cc. H_2O on 35 grams kaolin, a hydrated Na nephelite, $4(Na_2O.Al_2O_3.2SiO_2).5H_2O$, was obtained in rhombic crystals, low biref., parallel extinction, dominant faces (100), (010), (001), twinnings and fourlings. Fatty acids aided the crystallization. Attempts to prepare substituted members of the sodalite group from the hydrated Na nephelite or from kaolin generally resulted in amorph. products, which were carefully analyzed. In a few cases the above hydrated Na nephelite was obtained; also amorph. Li nephelite; and occasionally a few poorly formed crystals of unknown minerals. Kaolin treated with phenol soln. was partially decomp.; treated with 47% KOH kaolin gave an amorph. product; and treated with 1% NaOH gave clear biref. needles, compn. corresponding closely to $4(Na_2O.Al_2O_3.3SiO_2).15H_2O$. Treated with alkalin silicate solns. of different conc. kaolin gave, besides amorph. products, needles and globulites containing H_2O and more SiO_2 than the kaolin. K nephelite treated with 1% K_2SiO_3 soln. gave needles with parallel extinction, compn.: SiO_2, 46.88%; Al_2O_3, 22.00%; K_2O, 19.87%; H_2O, 11.25%; other similar expts. gave partly amorph., partly cryst., products. Corundum treated with H_2O alone was little altered, 4.5% H_2O was taken up; treated with alkalin solns. after ignition corundum was partly altered to amorph. products. Diaspore was little altered by H_2O alone; with a soln. of K_2SiO_3 it was partly altered to crystals with inclined extinction, combinations of (110), (100), (001), (hkO); samples for analysis could not be isolated. Several natural glasses took up a small amt. H_2O when heated with H_2O.

1892 55 CHROUSTSCHOFF, K. VON. *Bull. acad. Sci. St. Petersburg*, **1892**, I, 148–52. Apparatus was a 3-piece iron bomb lined with Pt and closed by a screw and Cu washer. *Expt. I.* Used mixture of SiO_2, $Al(OH)_3$ and $Zr(OH)_4$, all in gelatinous form, heated for 12 hours, final temp. a red heat. All H_2O was lost in this expt. Product amorph. and in thin flakes, with occasional pyramids and prisms, largest 0.035 mm., average 0.012 mm., low biref., extinction parallel to 2 sides of the hexagon (consequently mineral was not hexagonal), d. = 2.87, compn.: SiO_2, 53.65%; Al_2O_3, 23.76%; ZrO_2, 14.54%; H_2O, 7.86%. *Expt. II.* Bomb remained tight. Used gel. SiO_2 and $Zr(OH)_4$, product contained zircon, faces (111), (221), (311), (101), (110), (100) visible, biref. high, most crystals developed in pyramids (111), a few had long prismatic habit (111), (110), a few short prismatic, (111), (110). Crystals (111), (110), (100), rare, (101) and (221) and ditetragonal pyramids very rare. $D_{12}{}^\circ$ = 4.4537, compn.: SiO_2, 32.84%; ZrO_2, 67.17%.

1894–5 Thugutt, St. J. *Neues Jahrb. Min. Geol., Beil. Bd.*, **9**, 554–624. The
56 rhombic hydrated Na nephelite previously obtained (**54**) was heated with various solns. and the replacements studied. When 5 grams were heated with 500 cc. 2% K_2CO_3 soln. for 95 hours at 186°–191°, and later for 96 hours at 196°–202° with fresh soln., 0.528 gram Al_2O_3 went into soln., while the compn. of the mass, composed of globulites and a few weakly biref. needles, was that of a K natrolite. Hydrated Na nephelite with H_2O gave product similar to nacrite. When Na anorthite, obtained by fusing the hydrated Na nephelite, was heated 98 hours at 174°–177°, then 97 hours at 205°–211°, with 2% K_2CO_3 soln., the soln. contained $^1/_3$ of the Na_2O and Al_2O_3, and needles of K natrolite were obtained. K nephelite when heated with H_2O for a long time at 196°–230° gave a micaceous product and an alkalin soln. A blue chloride-sodalite (from elaeolite-syenite from Ditró) with 2% K_2CO_3 soln. at 192°–195°, then at 211°–214°, gave needles of K natrolite, and a soln. containing NaCl, NaOH and Al_2O_3. Similar expts. were made on various sodalites with similar results. Nephelite with 2% K_2CO_3 soln. gave in part natrolite, with sepn. of iron oxide. Elaeolite with H_2O at 200° gave a product similar to potash mica, and Al_2O_3 in soln. Kaolin (2 grams) at 192°–202° with 190 cc. 2% KOH soln. gave "K natrolite," with Al_2O_3 in soln. Kaolin (3 grams) with 190 cc. 1% NaOH soln. gave needles of the compn. $Na_6Al_6Si_8O_{28}.5H_2O$. At 100° different products were obtained, and much more SiO_2 and Al_2O_3 went into soln. Sanidine (2.8 grams) with 1–2% KOH soln. showed no effect. By the action of dil. K_2CO_3 soln. on members of the sodalite and nephelite group K natrolite was formed, which when heated on the steam bath with 5% Na_2CO_3 soln. gave "a silicate $Na_2Al_2Si_3O_{10}.4H_2O$, a hydrated Na natrolite." More expts. in which analcite and leucite are converted into each other are given. When 15.3 grams $NaAlO_2$ and 7.3 grams NaOH and 3.7 grams Na_2CO_3 were dissolved in H_2O, the clear soln. diluted to 130 cc. and heated 79 hours at 184°–190° with 3.7 grams CO_2, most of the Al_2O_3 separated was amorph., but some diaspore in biref. needles with sharp terminations and parallel extinction was found, as well as a little dawsonite.

1895 Chroustschoff, K. von. *Bull. Acad. Sci. St. Petersburg*, **1895**, 27–33.
57 Using amorph. SiO_2 with HBF_4 and H_2O in a Pt-lined bomb found no change below 180°; from 180°–228° got regular crystals of cristobalite, d. = 2.412, faces (111), (100), (110) visible, isotropic, ref. index = 1.58, sol. HF, 99.78% SiO_2; from 228°–235° got no quartz; 240°–300° quartz; 310°–360° tridymite and quartz.

1895 Spezia, Giorgio. *Atti Accad. Sci. Torino*, **30**, 455–65. H_2O under a pressure
58 of 1750 atm. at ordinary temp. had no action on apophyllite, at 93°–107° and 500 atm. there was no marked action, but H_2O at 190°–211° under the normal pressure for that temp. strongly corroded the mineral in 13 days. Glass behaved in a similar manner.

1896 59 FRIEDEL, G. *Bull. soc. min.*, **19**, 5–14. When muscovite was treated with 10% NaOH soln. at 200° only nephelite was formed and the action was slow. At 500° with 2% NaOH the action was more rapid, and nephelite and a new mineral were formed. With but little SiO_2 present, nephelite only was found; when the Na_2O : SiO_2 ratio was 1 : 1, nephelite and analcite were found; with ratio 1 : 2 or 1 : 3, no nephelite, but analcite and albite; with ratio 1 : 4 and over, only albite and quartz were obtained. The new silicate was best obtained when 4–5 grams muscovite were heated with 40 cc. 8–10% NaOH soln., at 500°–530°. It was easily attacked by HCl, compn.: SiO_2, 40.78%; Al_2O_3, 36.73%; Fe_2O_3, trace; CaO, 0.15%; Na_2O, 15.40%; K_2O, 1.88%; H_2O, 4.93%, crystals rhombic, colorless, $d_{18°}$ = 2.378, crystal form similar to that of olivine, (110), (001), (010), (201) visible, twinning parallel (110), fourlings, angles, measured on goniometer, $(110) \wedge (1\bar{1}0) = 114° 20'$, $(110) \wedge (010) = 122° 50'$, $(010) \wedge (021) = 163° 30'$, $(010) \wedge (021) = 133° 30'$. On (001), (010) weak biref., negative on (010), positive on (001), n_m perpendicular (100), n_g perpendicular (001), n_p perpendicular (010), $n_m — n_p = 0.0018$, $n_g — n_m = 0.0017$, $n_m = 1.52$, axial angle about 88°, acute negative bisectrix n_p. Heating expts. were also made on the new mineral, from which it was concluded that the H_2O was in solid soln. This mineral could not be obtained with a greater SiO_2 content. Na cancrinite was also found, due to Na_2CO_3 in the NaOH.

1896 60 FRIEDEL, G. *Bull. soc. min.*, **19**, 18–22. Describes the etch figures on muscovite remaining after preparation of sodalite, using 5 grams NaOH, 3 grams NaCl and H_2O at 300°.

1896 61 SCHULTEN, A. de. *Bull. soc. min.*, 157–61. Saturated ammoniacal $Al(OH)_3$ solution was heated on a sand bath 15 days, in such a manner that the NH_4OH only slowly escaped, and hydrargyllite was obtained. Hydrargyllite was also obtained better crystallized by slow precipitation from a solution prepared by dissolving 25 grams Al in 75 grams NaOH dissolved in 400 cc. H_2O, by passing CO_2 through the boiling solution. Product contained 64.47% Al_2O_3, 34.76% H_2O, 0.53% SiO_2; $d_{15°}$ = 2.423, slowly attacked by boiling HCl or H_2SO_4, crystals glittering monoclinic prisms, 0.3 mm. long, faces (100), (110), (001) visible, cleavage parallel to (110), angles $(110) \wedge (100)$ and $(110) \wedge (1^{1}0)$ about 120°, monoclinic, angle of extinction with plane of prism = 20°, optically positive, twinning parallel to (100).

1896 62 SPEZIA, GIORGIO. *Atti Accad. Sci. Torino*, **31**, 246–50. Found that plates of quartz kept at 27° for several months with H_2O under a pressure of 1750–1850 atm. did not diminish in weight and showed no etch figures. Pressure alone has no influence on the solubility of quartz.

1897 63 LUNGE, G. AND MILLBERG, C. *Z. angew. Chem.*, **13**, 393–8, 424–31. A summary of the older work on the solubility of the various forms of SiO_2, and many original experiments on the solubility of quartz, opal and amorphous SiO_2 in boiling alkalin and carbonate solutions.

1898 64 SPEZIA, GIORGIO. *Atti Accad. Sci. Torino*, **33**, 289–308, 876–82. The soly. of quartz in H_2O does not depend on the pressure but only on the temp. By slow evapn. of solns. containing SiO_2 opal was deposited, but when alkali was present the SiO_2 separated as quartz. The rhombohedral faces of quartz were most easily attacked, and on the same faces there was the greatest deposit of SiO_2 from Na_2SiO_3 solns. The more rapid growth of quartz crystals in the direction of the vertical axis explains the common prismatic form of the mineral. These directions of max. and min. rate of growth of quartz, respectively parallel and perpendicular to the vertical axis, were confirmed by expts. on crystals cut in various directions. Opal treated in the same way was changed to an aggregate of quartz crystals.

1898 **65** BARUS, C. *Am. J. Sci.*, [4] **6**, 270. Announces the impregnation of glass with H_2O to such an extent that it melted below 200°, the soln. occurring with a contraction in bulk. Heated in the air the hydrous glass swelled enormously with loss of H_2O, leaving a white, porous pumice resembling pith.

1899 **66** FRIEDEL, C. *Bull. soc. min.*, **22**, 17–18. New analysis of G. Friedel's prepn. in (**59**). Comp: SiO_2, 39.98%; Al_2O_3, 32.95%; Na_2O, 19.09%; K_2O, 3.19%; H_2O, 5.80. Compn., $NaAlSiO_4.0.5H_2O$, resembles thomsonite, but all the CaO is replaced by Na_2O and the H_2O content is different.

1899 **67** FRIEDEL, G. *Bull. soc. min.*, **22**, 20–25. By heating 5 grams muscovite with 40 cc. 9% NaOH soln. for 36 hours at 508°–510° obtained nephelite, the new silicate described (**59**), and another new silicate. The latter was only obtained once, forms colorless cubic crystals; $d_{12.5°}$ = 2.660; forms observed octahedra, rhombic dodecahedra, leucitohedra, and hexahedra. Probably hemihedral-tetrahedral, but optically abnormal. Biref. = 0.0046, extinction = 5°–6°, strongly twinned, single individuals monoclinic, compn.: SiO_2, 41.92%; Al_2O_3, 26.43%; CaO, 0.25%; Na_2O, 31.25%; formula $8SiO_2.3Al_2O_3.6Na_2O$. Crystal figures are given.

1900 **68** SPEZIA, GIORGIO. *Atti Accad. Sci. Torino*, **35**, 750–61. Dil. solns. of Na_2SiO_3 exerted a decided solvent action on quartz at high temp.; at lower temp. the quartz was deposited.

1900 **69** BARUS, C. *Am. J. Sci.*, [4] **9**, 161–75. Cf. (**65**). An ordinary soft glass was heated with H_2O in a steel bomb, using 210 grams of the finely powdered glass and 50 grams H_2O, and heating at 210° for 12 hours. Product hard and opalescent, and homogeneous except for some inclusions of partially converted glass. Heated in the air it swelled enormously with loss of H_2O, forming a white pith-like mass; left in the air it gradually broke up, probably due to the effect of internal stress. When 180 grams of this product was heated to 210° with 50 cc. H_2O more H_2O was taken up, and the glass changed to a friable mass which did not swell up when heated; about 10 cc. of viscous soapy black soln. was left in the bomb. Repetition of this treatment gave a similar result. When the action was observed in a capillary tube under pressure (applied by means of a Hg column) the phenomena were different at different temps. At 185° the glass of the tube absorbed H_2O, swelling enormously, and became white and turbid. At 210°, however, soln. took place rapidly, forming a clear liquid, and while soln. was taking place the compressibility was very large, but fell suddenly at the end. When a soln. of $Co(NO_3)_2$ was used the glass acted as a semi-permeable membrane, only taking up the H_2O.

1901 **70** FRIEDEL, G. *Bull. soc. min.*, **24**, 141–59. Muscovite heated with 5% LiOH soln. in a closed bomb at 500° gave an amorph. product; lepidolite from Rozena similarly treated was but slowly attacked, but (1) large rhombic prisms of a Li silicate, (2) cubes of LiF, and (3) small amts. of unknown crystals, were obtained. Lepidolite was rapidly attacked by NaOH, producing the above Li silicate without admixture of other bases, and Na-K nephelite free from Li. When carbonate was present, Li-free alkali cancrinite was found. Li aluminosilicate cannot be prepd. in this manner. The Li silicate was prepd. by heating at 500° a LiOH soln. with excess amorph. SiO_2; product, water free; compn.: SiO_2, 67.1%; Li_2O, 32.9% = Li_2SiO_3; crystal form similar to phenacite; colorless; rhombohedra of 116° 7′ predominating, also prisms $(11\bar{2}0)$, $(10\bar{1}0)$, and (0001) common, $(12\bar{3}2)$ and $(22\bar{4}3)$ frequent, $(12\bar{3}2)$ hemihedral. $D_{15°} = 2.529$, mineral uniaxial, positive, minimum ref. index = 1.65, biref. = 0.020. On account of the resemblance of the mineral to phenacite, LiOH and NaOH solns. were heated with BeO and SiO_2 at 500°; product both Li_2SiO_3 and phenacite, no isomorphous mixture. The Li orthosilicate could not be prepd., but Li_2SiO_3 took up SiO_2 in solid soln.

1902
71
BAUR, EMIL. *Z. physik. Chem.*, **42**, 567–76. Worked at 520° in a steel cylinder closed by a conical screw cap.

Expt. No.	SiO_2. G.	$KAlO_2$. G.	Product.
1	5	2.0	Quartz and an unknown mineral in radiating clusters, n = 1.65, biref. = 0.015. Optically positive, axial angle small, elong. perpendicular to plan of axes.
2	5	3.3	Quartz and globulites of orthoclase.
3	5	5.0	Quartz, orthoclase, sections of which perpendicular to $\mathfrak{c}$ showed large axial angle, extinction angle = 5°, ref. index lower than Canada balsam, biref. weak, Carlsbad twinning.
4	5	15.0	Orthoclase, in plates with unequal 6-sided border, showing a large axial angle perpendicular to positive bisectrix, elongation $\mathfrak{a}$, formed a very small angle with an edge.
5	5	25.0	Mostly amorph., some few undeterminable needles that $NaAlO_2$ gelatinized with HCl.
6	13	4.5	Quartz.
7	5	2.3	Quartz.
8	5	4.3	Quartz, albite showing twinning, ref. index less than Canada balsam; tridymite in tablets composed of many individuals variously oriented, ref. index lower than Canada balsam, weak biref., small axial angle, optically positive.
9	5	10.0	Albite, with characteristic ref. index and biref., elong. along *a* axis, optical character of chief zone negative, twinning lamellae parallel to chief zone, extinction angle very small, chief face approx. parallel to plane of axis.
10 11	5	15.0	Both expts. gave crystals which gelatinized with HCl, and had most of the characteristics of nephelite, but did not correspond to any known min. Rectangular tablets, ref. index slightly higher than Canada balsam, acute bisectrix perpendicular to observed faces, large axial angle. Elongation $\mathfrak{a}$, biref. at least 0.015, parallel extinction.

1906
72
ALLEN, E. T. (cited by DAY and SHEPHERD). *Am. J. Sci.*, [4] **22**, 297. Very fine quartz crystals were obtained by heating a soln. of $MgCl_2.6NH_4Cl$ and Na_2SiO_3 for 3 days at 400°–450°. Large crystals 2 mm. long, often barrel shaped, with short rhombohedral terminal faces, striations horizontal.

1906
73
DOELTER, C. *Min. petrog. Mitt.*, **25**, 79–112. Used a tube similar to that used by Sarasin, *11 grams of a mixture of* $CaHCO_3$ *and pptd.* SiO_2, *with* 45 cc. H_2O; product wollastonite in strongly biref. biaxial crystals; max. extinction angle = 30°; partly in long flakes, partly in radiating groups;

sol. hot conc. HCl; insol. dil. HCl. Analysis of some crystals having a surface coating of SiO_2 gave: SiO_2, 55.01%; H_2O, 0.91%. D = 2.75, hardness = 4.5. From 4 grams of a mixture of KOH, SiO_2 and $Al(OH)_3$ in proportion of $KAlSi_3O_8$, heated for 8 days at 400°, obtained numerous crystals corresponding to orthoclase. From 2.5 grams analcite and 2.5 grams of a mixture of $NaAlO_2$ and SiO_2 in proportions of analcite, plus 1 gram $NaAlO_2$ and 60 cc. H_2O, heated 11 hours at 430° obtained a few twinned lath-like crystals resembling albite and a few highly refracting crystals resembling corundum. Analcite was also obtained from nephelite, H_2O, alkali carbonate and CO_2. An expt. using 6 grams of the above analcite mixture and 30 cc. H_2O at 400° gave hexagonal flakes of probably nephelite and much analcite in icositetrahedra. Two expts. at 90°, the first with 5 grams of a mixture of Na_2CO_3, Al_2O_3, and SiO_2 in analcite proportions, the 2nd 1 gram of a mixture in natrolite proportions, both plus a little natrolite, gave natrolite in radiating clusters, and a rhombic mineral with higher refraction, probably diaspore. At 190°, 3 grams of a mixture of natrolite with 70 cc. H_2O, seeded with natrolite, gave both natrolite and diaspore; and at 200° a mixture of the compn. of analcite gave analcite crystals. Concluded that in conc. solns. at 90° natrolite is formed from a mixture of the compn. of natrolite; at 190°, analcite from the same mixture; an analcite mixture, seeded with natrolite, at 90° gives natrolite, and at 190°, analcite.

1906 **74** ALLEN, E. T., WRIGHT, F. E., AND CLEMENT, J. K. *Am. J. Sci.*, [4] **22**, 405. Worked in a steel bomb closed by a Cu disc held in place by a screwed-on steel cap, used either $MgCl_2.6NH_4Cl$ soln. or a mixture of $MgCl_2$ soln. with $NaHCO_3$, and either amorph. SiO_2 or Na_2SiO_3. Heated 3–6 days at 375°–475°. Obtained magnetite, in octahedra; a Mg amphibole in aggregates of fibers with parallel elongation, extinction C, ref. index below 1.60, biref. low; fosterite, with extinction parallel to prism edge, ref. index about 1.66, much stronger biref. than either metasilicate or quartz; and quartz (cf. (72)).

1906 **75** KÖNIGSBERGER, JOHN AND WOLF J. MÜLLER. *Centr. Min.*, **1906**, 339–48, 353–72. Worked in a steel bomb lined with Pt-10% Ir alloy, fitted with an apparatus for filtering, and placed in a shaking apparatus. Expts. 1–4 were made with a Thuringian glass, compn.: SiO_2, 69.21%; Al_2O_3, 2.48%; Fe_2O_3, 0.45%; MgO, 0.52%; CaO, 9.84%; K_2O, 1.98%; Na_2O, 14.91%. *Expt. 1.* 8 grams glass in pieces 2–5 mm. were heated with 60 cc. H_2O and 2 grams CO_2 for 60 hours at 360°, filtered, and slowly cooled (the same exptl. conditions were used in 2, 3 and 4). In filter tube found 0.07 gram quartz, in crystals 0.01–0.05 mm., d. = 2.63, completely sol. HF, ratio lengths along *a* (perpendicular to major axis) and *c* was 1 : 2.5, prism faces and one rhombohedral face well formed, other rhombohedral faces rare and small, biref. fairly strong, ref. index higher than Canada balsam, interfacial angles measured corresponded to those calc. for quartz. The solid residue consisted of (1) quartz, 0.05–0.2 mm. long, with prism and rhombohedra, (*a*) : (*c*) = 1 : 3 and 1 : 2, striated perpendicular to the major axis; (2) chalcedony, in radial aggregates; (3) some weakly biref. aggregates which could not be identified; (4) calcite. *Expt. 2.* Used 8 grams glass, 60 cc. H_2O, 10 grams CO_2. No noticeable crystallization in the filter tube; glass covered with a white crust of quartz and chalcedony. The soln. contained 2.5 grams dry substance, 1.4 grams of which was CO_2, no Al_2O_3 or SiO_2. *Expt. 3.* 8 grams glass, 60 cc. H_2O, 15 grams CO_2. No crystals in filter tube; glass but slightly attacked, had thin coating of small biref. particles and quartz(?). *Expt. 4.* 10 grams glass, 50 cc. H_2O. In filter tube 0.2 gram crystals, chiefly quartz, partly in long crystals, (*a*) : (*c*) = 1 : 7, partly short, (*a*) : (*c*) = 1 : 1.5, faces as in Expt. 1; also amorph. SiO_2, with properties corresponding to opal. Glass completely decomp., partly changed into amorph. SiO_2; partly into chalcedony; partly into tridymite, in imbricate hexagonal plates, interfacial angle = 120°, d. = 2.3; ref. index little greater than 1.407, sol. NaOH and HF; partly into a Na anorthoclase, showing plates which scratched glass, without symmetry, consequently triclinic, faces (010), ($\bar{2}$01), (110), (001), (111), extinction angle with one side = 3°–8°, interfacial angles = 80°–81°, and 116°–117°, indistinct cleavage often (010), rarer (001), ref. index $\mathfrak{a}$ = 1.515, $\mathfrak{b}$ greater. In expts. 5–9 an obsidian was used, compn.: SiO_2, 74.3%; Al_2O_3, 13.0%; Fe_2O_3, 2.6%; MgO, 0.3%; CaO, 1.0%; Na_2O, 3.8%; K_2O, 4.6%; H_2O, 0.3%. *Expt. 5.* 10 grams obsidian, 60 cc. H_2O, 48 hours at 320°, filtered, slowly cooled (similar exptl. conditions in 6, 7, 8). Obsidian little attacked, in filter tube were (1) small biref. needles, (2) small, red, transparent plates containing Fe, (3) small isotropic or slightly biref. hexagonal crystals. Glass remaining but slightly attacked, some pieces covered with a gray crust of fine needles and reddish brown concretions. *Expt. 6.* 10 g. obsidian, 50 cc. H_2O, 15 grams CO_2. Obsidian had thin coating of carbonate. *Expt. 7.* 10 grams obsidian, 60 cc. H_2O, 3 grams CO_2, 2 grams $NaHCO_3$. Obsidian but lightly attacked, but more than in Expt. 6. A little quartz in filter tube; a crust on the obsidian composed of same needles and concretions as before, and also poorly formed chalcedony and many small biref. crystals, probably quartz. *Expt. 8.* 10 grams obsidian, 60 cc. H_2O, 4 grams $NaHCO_3$. Much more strongly attacked. About 0.3 gram quartz in filter tube, similar to that in Expt. 1, with +R and —R generally unequally developed, chiefly with face ($6P^6_5$). Photomicrograph given. In the filter tube were also (1) small brownish red kernels of an Fe_2O_3 compd., (2) large thick approx. hexagonal tablets, with small biref., ref. index probably close to that of Canada balsam, (3) regular transparent crystals showing equal development in all directions. The obsidian residue consisted of well-formed quartz crystals, and dark colored amorph. concretions. *Expt. 9.* 10 grams obsidian, 40 cc. of soln. compn.: H_2O, 85%; CO_2, 5%; Na, 2.5%; K, Li, 1.5%; Ca, 0.3%; CO_3, 3.5%; Cl, 1.5%; SO_4, 0.7%; corresponding to the authors' average compn. of the soln. from which crevice minerals crystallize. Heated to 420° for 42 hours, filtered, slowly cooled, product in filter tube a few quartz crystals; residual obsidian covered with a thin, grayish green crust, on which were thin radiating aggregates of a dark green silicate, insol. in conc. HCl, with clear yellowish green plechroism, color in direction of n_p dark green, direction n_g light green, extinction angles with elongation = 38°, biref. strongest in direction of elongation. Needles lying on other faces showed smaller extinction angles and much smaller biref. Hardness greater than the obsidian, d. = 3.36; treated with HF left a residue containing Fe and Na. Mineral probably a pyroxene rich in iron, an aegirite-augite. Quartz and thin reddish transparent plates of probably hematite were also found. *Expts. 10, 11, 12.* The following minerals were heated with 40 cc. H_2O for 24 hours at 350°. *Expt. 10.* Quartz showed corrosion on the rhombohedral faces, but no attack was visible on the prism faces. *Expt. 11.* Muscovite was very strongly attacked, chiefly perpendicular to *c*. *Expt. 12.* Diopside was about $^1/_5$ decomp., the chief effect being parallel to (110), etch figures also obtained on (100) and (010). Part of the diposide was transformed into fine, thin, white threads. *Expt. 13.* Adular was not strongly attacked, the greatest effect being parallel to the chief cleavage (010). *Expt. 14.* (1) quartz, (2) adular, (3) muscovite, (4) granite were heated 24 hours with 50 cc. of 20% Na_2CO_3 soln. at 300° in a Ag tube, which did not hold completely tight. The minerals dissolved completely, remaining in soln. when cold. *Expt. 15.* Muscovite, quartz, adular, spinel, calcite, fluorspar and biotite were heated to 370° for 48 hours with 60 cc. H_2O, 1 gram Na_2CO_3, and 10 grams CO_2, and filtered. Only a small amt. of carbonate was found in the filter tube; the minerals were little attacked, the calcite showing the greatest action, and the muscovite and fluorspar a slight change. Pure 30% NaOH dissolves most silicates at 115°. From the preceding expts., K. and M. draw some conclusions in regard to the acidity of silicic acid, the most important being that the acidity of silicic acid increases more rapidly with increasing temperature than does that of other weak acids found in nature.

1908
76 ALLEN, E. T. AND J. K. CLEMENT. *Am. J. Sci.*, [4] **26**, 101–18; *Z. anorg. Chem.*, 68, 317–37.—A study of the loss of H_2O from various hornblendes. Tremolite which had been heated to 923° and had lost 85.1% of its H_2O was soaked in H_2O for 20 hours and dried at 110°; 11.8% of its H_2O was regained. A specimen of tremolite which had been heated to 933° and had lost 47.4% of its H_2O was heated with H_2O in a closed bomb at 400°, dried at 110°, contained 2.15% H_2O while the original mineral contained 2.31%. A beryl from which the H_2O had been removed by heating took up practically no H_2O when similarly treated.

1909
77 FRIEDEL AND GRANDJEAN. *Bull. soc. min.*, **32**, 150–54. Finely pulverized augite from a basalt heated at 450°–460° showed little action; heated at 550°–560° for 40 hours with a soln. containing 4% Al_2O_3 and 5% NaOH gave (1) long feathers of mesotype, grouped in rosettes, identified by optical properties which are not given, (2) a few yellowish isotropic very refringent octahedra, probably spinel, (3) brilliant green micaceous plates, almost hexagonal, outline flattened perpendicular to the axis with smaller index, *i. e.*, the sharp negative bisectrix, negative, angle of optic axes small, variable, distinct plechroism, n_p colorless or pale yellow, n_g and n_n green, crystals easily attacked by boiling HCl, probably a chlorite, (4) numerous small indeterminable crystals. In the 2nd expt. diopside from Zillerthal was treated with a strong NaOH soln., about 25%, heated 40 hours at 550°–570°; the only determinable mineral was a chlorite, in brownish red lamellae. The plates were flexible without elasticity, largest 0.1 mm., and were partly single, partly imbricate, partly irregularly ramified. D. = 2.67–2.70, compn.: SiO_2, 28.4%; MgO, 36.2%; Al_2O_3, 15.2%; Fe_2O_3, 4.4%; CaO, 2.3%; H_2O, 11.5%; alkalies not detd. Outline hexagonal, but angles not 120°, biaxial, positive, larger index perpendicular to cleavage, optic angle small and variable, variations (with D-line) from 10°–35° in the same crystal, $n_g - n_p = 0.0009$, dispersion large, strong plechroism, n_g brown, n_m and n_p green or yellowish green, max. absorption parallel n_g. Similar in most respects to pennine, but direction of max. absorption not the same.

1911
78 BAUR, EMIL. *Z. anorg. Chem.*, **72**, 119–61. Worked in a steel bomb, closed by a steel plug, and made tight by a Cu washer. Preliminary expts. showed that the products obtained were substantially the same at 350° and 450°, and were independent of the amts. of H_2O; the most of the expts. were made at 450°. No analyses were made of the products obtained, but analyses

are given of the materials used. The data are summarized in the following table, the weights being given in grams. The asterisks refer to the crystallographic descriptions by Becke below:

No.	SiO_2.	Al_2O_3.	K_2O.	H_2O.	Misc.	Product.
2, 7, 10	0.7	0.54	0.69	1.7	......	Or, K neph., Fj.
31, 11	0.7	0.54	0.69	4.1	......	*Or, K neph., Fj.
8, 9	0.7	0.29	0.37	1.6	......	Or, Fj.
12	0.7	0.21	0.26	3.0	......	Or, Fj.
32	0.7	0.12	0.16	1.8	......	Qu, Fj.
41	0.7	0.54	0.69	2.1	0.5 CaO	K neph.
44	0.7	0.37	0.48	4.0	0.1 $CaCO_3$	K neph., Pk, Or.
56	0.6	0.29	0.55	6.0	0.21 CaO	*K. neph., Pk.
57	1.44	0.21	0.96	6.0	1.0 $CaCO_3$	Or, calcite.
58	1.44	0.21	0.96	6.0	2.0 $KHCO_3$ 1.0 $CaCO_3$	Calcite, gyrolite.
59	1.44	0.41	1.23	6.0	2.0 $KHCO_3$ 1.0 $CaCO_3$	Or, calcite. ......
60	1.44	0.65	1.55	6.1	2.0 $KHCO_3$ 1.0 $CaCO_3$	Or, K neph., calcite.
65	0.7	0.71	0.26	3.3	......	*Andalusite, Pyr.
66	0.7	0.79	0.37	3.3	......	Fj, Pyr.
67	0.7	0.60	0.37	3.2	......	Or, Fj, Pyr.
68	0.7	0.87	0.48	4.3	......	Pyr.
69	0.7	1.00	0.63	4.3	......	*M, Fj, Pyr.
70	0.7	1.11	0.80	4.4	......	K neph., Fj.
72	0.95	1.14	0.63	4.5	0.17 CaO	Pyr, Fj, K neph.
73	0.95	0.70	0.37	3.9	0.21 CaO	Pyr, Or.
74	0.90	0.40	0.26	3.2	0.17 CaO	Opal, Or.
			Na_2O.			
45	1.94	0.16	0.5	4.5	1.26 CaO	Pk.
46	2.73	0.12	0.8	7.2	0.9 CaO	Pk, Ol.
48	3.0	0.27	0.8	8.6	0.38 CaO	*Pk, Qu.
49	1.8	0.09	0.64	5.5	1.0 $CaCO_3$	Pk, Qu.
50	2.1	0.09	0.64	5.5	0.7 CaO	*Pk, Ol.
51	2.1	0.09	0.64	5.5	1.2 $CaCO_3$	Pk, Qu, gyrolite.
52	2.1	0.22	0.72	5.6	1.2 $CaCO_3$	Pk, Ol.
53	0.75	0.18	0.23	7.1	0.12 CaO	Pk, desmin.
54	1.8	0.27	0.59	5.80	0.35 CaO 2.0 $CaCl_2$	Pk, Ol.
55	1.8	0.3	0.77	5.6	1.1 $CaCl_2$	Pk, Ol.
63	1.8	....	0.59	0.54	1.0 $CaCO_3$	*Pk, Qu.
64	0.3	0.18	0.41	6.2	1.7 $NaHCO_3$	Amorph.
75	0.7	0.13	0.08	3.1	....	Qu, Ab.
77	0.7	0.22	0.14	3.1	....	*Ab.
78	0.7	0.31	0.19	4.2	....	Ab.
79	0.7	0.81	0.19	4.5	....	Anal.
80	0.7	0.53	0.06	3.3	....	Opal, Pyr.
81	0.7	0.62	0.11	3.8	....	Opal, Pyr.
82	0.7	0.35	0.09	3.7	....	Opal.
83	0.7	0.49	0.15	3.8	....	Opal.
84	0.7	0.67	0.25	4.4	....	Amorph.

Abbreviations used in above table: Or, orthoclase; K neph., hydrated K nephelite; Fj, K faujasite; Qu, quartz; Pk, pectolite; M, muscovite; Ol, oligoclase; Ab, albite; Anal., analcite. Optical determinations by Becke.

No. 48. Quartz in pyramids, +R and —R, uniaxial positive, $\gamma - \alpha$ 0.009, ref. index that of quartz (α-quartz).

No. 31. Orthoclase, biaxial, ordinarily with rhombic outline, α in the short, γ in the long diagonal of the rhombus, extinction on the symmetry plane = 4°–5°, n_g = 1.524, n_p = 1.517.

No. 50. Oligoclase, ref. index of Canada balsam, 2 inclination angles = 63 and 72.5°, (100), $(10\bar{2})$, (101), extinction of α with trace of (001) = +11°, α = 1.529, oligoclase-albite.

No. 77. Albite, angle $(010) \wedge (001)$ = about 64°, extinction of α = 20° with trace of (001).

No. 13. K faujasite, octahedra, n = 1.394, optically normal.

No. 6. Hydrated K nephelite, uniaxial, negative, biref. about 0.005, τ = 1.525(6).

No. 65. Andalusite, columns, with parallel extinction, low terminations, angle of edge with verticle axis = 50°, γ or β 1.652.

No. 69. Muscovite, hexagonal tablets, with angles about 60°, extinction parallel to a pair of sides (β), β and γ in plane (001), β 1.630. Pyrophyllite, rosettes and bundles, parallel extinction, γ in long direction, fairly high biref., $\gamma - \alpha$ = 0.002, ref. index = 1.50.

No. 53. Desmin, needles, α in direction of elongation, biref. greater than 0.02, ref. indices larger and smaller than 1.495, α = about 1.488, plane of optic axes parallel to elongation, identification not certain.

No. 49. Gyrolite, hexagonal tablets, high biref., $\omega - \varepsilon$ = 0.06, ω = 1.529(?), identification not certain.

No. 63. Pectolite, needles with parallel extinction, γ in direction of elongation, biref. = about 0.03, γ = 1.620.

No. 56. K pectolite, optically exactly the same as No. 63.

1912 **79** MÜLLER, W. J. AND KÖNIGSBERGER, J. *Z. angew. Chem.*, **25,** 1273–7. A general account of the expts. described in (**75**), together with incomplete accounts of some new expts. $Al(OH)_3$ with K water glass in proportions of $KAlSi_3O_8$ gave K analcite (?) or leucite (?); in the presence of CO_2 orthoclase with Baveno twinning was found. When, by the aid of a special apparatus, Na_2CO_3 was added to the filtered soln. orthoclase was produced. Carbonates, therefore, ppt. orthoclase.

1912 **80** DOELTER, C. AND E. DITTLER. *Sitzungsber. kaiserl. Akad. Wiss. Wein*, **121,** *Abt. I*, Oct., 1912. 2.7 grams of $MgCO_3$ containing $Mg(OH)_2$ and 4.88 grams Na_2SiO_3 were moistened with H_2O and heated in a hard glass tube 100 hours at 200°, and the process several times repeated after washing the ppt. (It is stated in a footnote that some work was done in an iron tube at 350°, but no indication is given as to what expts. or how many were so done.) The product was a mixture containing aggregates of needles, high biref., chief zone positive with extinction parallel to interfacial angles, ref. index = 1.588; the authors say that it was probably a silicate similar to steatite. Magnetite crystals were also present. A mixture of 3.08 g. mol $MgCl_2$ and 2.28 g. mol hydrated SiO_2 were fused at 1200° and H_2O vapor led over the product at 700°–800°, but the product was not crystallin, and only 0.99% H_2O was taken up.

1912 **81** FENNER, C. N. *J. Wash. Acad. Sci.*, **2,** 471–80. Quartz was easily prepd. by heating either SiO_2 glass or pptd. SiO_2 in a steel bomb with Na_2CO_3

soln. for 2–3 days. When either tridymite or cristobalite was treated similarly, quartz was always obtained. "In no case has the presence of tridymite or cristobalite in preparations made in aqueous solns. been detected, but, on the contrary, when the higher forms of SiO_2 have been used they have always recrystallized as quartz."

TABULAR SUMMARY.

Mineral.	Literature.
Silicates:	
Orthoclase,	(12), (13), (16), (18), (23), (?36), (44), (?47), (53), (71), (74), (78), (79).
Anorthoclase,	(75).
Albite,	(23), (59), (71), (?74), (78).
Oligoclase,	(78).
Anorthite,	(45).
Leucite,	(10), (16), (31), (44), (?56), (?79).
Nephelite,	(44), (46), (59), (67), (70), (74).
K-nephelite,	(40), (54).
Hydrous K-nephelite,	(?78).
Hydrous Na-nephelite,	(54), (56).
Li nephelite,	(?54).
(See also miscellaneous.)	
Analcite,	(10), (17), (20), (21), (26), (31), (40), (43), (?47), (?56), (59), (74), (78).
Basic analcite(?)	(?26).
Sodalite,	(46).
Ittnerite,	(7).
Nosean,	(50).
Hydrous nosean(?),	(26), (47).
Cancrinite,	(40).
Na-cancrinite,	(50), (59), (70).
Cancrinite-like mineral,	(26).
Apophyllite,	(2), (43).
Natrolite,	(?10), (?26), (?40), (43), (56), (74), (?77).
K-natrolite,	(56).
Natrolite with large H_2O content,	(56).
Scolecite,	(?10), (?40).
Mesolite,	(?10).
Heulandite,	(43).
Chabazite,	(?40), (43).
Levynite,	(7).
Okenite,	(43).
Gyrolite,	(78).
Na-thomsonite,	(59), (66), (67).
K-faujasite,	(?78).
Pectolite,	(5), (26), (31), (78).
Muscovite,	(?56), (78).
Biotite,	(?47), (?53).
Pyrophyllite,	(78).
Chlorite,	(77).
Steatite(?),	(?80).
Wollastonite,	(?5), (?28), (?39), (52), (74).
$CaSiO_3$,	(28), (?33) ,(39).

TABULAR SUMMARY (*continued*).

Mineral.	Literature.
Diopside,	(5), (47).
Pyroxene,	(39).
Mg pyroxene,	(14).
Aegirine-augite,	(75).
Rhodonite,	(24).
Hornblende,	(47).
Tremolite,	(76).
Mg-amphibole,	(73).
Forsterite,	(73).
Fayalite,	(27).
$CaSiO_4$,	(28), (39).
Knebelite,	(27).
Tephroite,	(24).
Grossular,	(?25), (?39).
Mn garnet,	(25).
Topaz,	(38).
Datolite,	(52).
Phenacite,	(70).
Zircon,	(55).
Hydrous Zr-Al silicate,	(55).
Miscellaneous Silicates:	
Li_2SiO_3,	(78).
Hydrated K-Ba-Al silicate,	(7).
Hydrated K silicate,	(18).
$(K_2Na_2Ca)O.3SiO_2$,	(37).
$K_2O.Al_2O_3.2SiO_2$,	(37).
$K_2O.Al_2O_3.2SiO_2$,	(31), (37)
$Na_2O.Al_2O_3.2SiO_2$,	(37).
Hydrated Ca-Al silicate,	(45).
$6Na_2O.3Al_2O_3.8SiO_2$(?),	(67).
K-F-Al silicate,	(42).
Ca chlorosilicate,	(28), (39).
Mn chlorosilicate,	(30).
Fe chlorosilicate,	(30).
Oxides, Hydroxides, Carbonates, Etc.:	
Quartz,	(1), (3), (4), (5), (?7), (8), (11), (12), (13), (18), (23), (34), (36), (42), (48), (49), (57), (59), (64), (68), (71), (72), (75), (78), (81).
Tridymite,	(8), (9), (?12), (?27), (?39), (42), (57), (75).
Cristobalite,	(57).
Crystallin hydrated silica,	(8).
Chalcedony,	(5), (75).
Opal,	(4), (?8), (64), (75), (78).
Al_2SiO_5,	(16), (78).
Corundum,	(6), (15), (42), (49), (54), (?74).
Diaspore,	(49), (54), (56), (?74).
Hydrargyllite,	(61).
Hematite,	(42), (49).
Ilmenite,	(42).
Periclase,	(15).

TABULAR SUMMARY (*continued*).

Mineral.	Literature.
Brucite,	(59).
Spinel,	(15), (27), (53), (77).
Magnetite,	(42), (73).
Calcite,	(32), (49), (75).
Magnesite,	(?80).
Dawsonite,	(?56).

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.
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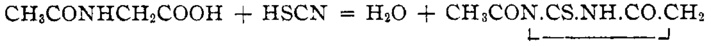
HYDANTOINS: THE SYNTHESIS OF 2-THIOHYDANTOINS FROM ACYL DERIVATIVES OF α-AMINOACIDS.

[TWENTY-THIRD PAPER.]

BY TREAT B. JOHNSON AND WALTER M. SCOTT.

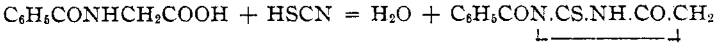
Received June 26, 1913

It has been shown by the writer and his co-workers[1] that an acyl derivative of an α-amino acid can enter into an interesting reaction with ammonium thiocyanate in acetic anhydride solution. These reagents interact in an unique manner, in this anhydrous solvent, with formation of an acylthiolhydantoin. For example, aceturic, I, and hippuric acids, III, combine with the thiocyanate forming 2-thio-3-acetylhydantoin, II, and 2-thio-3-benzoylhydantoin, IV, respectively.[2] This reaction has also been applied successfully with acetyalanine,[3] V, and with the cyclic acylamino acid, namely, pyrrolidonecarboxylic acid,[4] VII. The acyl



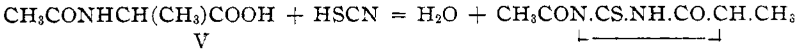
$$CH_3CONHCH_2COOH + HSCN = H_2O + CH_3CON.CS.NH.CO.CH_2$$

I. II.



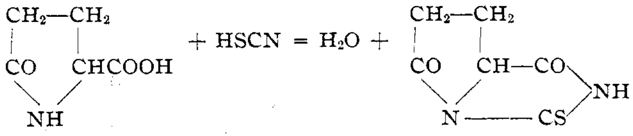
$$C_6H_5CONHCH_2COOH + HSCN = H_2O + C_6H_5CON.CS.NH.CO.CH_2$$

III. IV.



$$CH_3CONHCH(CH_3)COOH + HSCN = H_2O + CH_3CON.CS.NH.CO.CH.CH_3$$

V VI.



VII. VIII.

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[1] See Addenda to this paper.

[2] Johnson and Nicolet, THIS JOURNAL, **33**, 1975.

[3] Johnson, *J. Biol. Chem.*, **11**, 98.

[4] Johnson and Guest, *Am. Chem. J.*, **47**, 242.