

CONTRIBUTION

to the Study of the Geochemical Laws of Distribution of Elements, on Base of Metal- lurgical Experiences concerning the Chemical Equilibrium in the Three-Phase-System: Metal : Sulphide : Silicate

BY

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WITH 1 TEXTFIG.

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If metals in metallic state are molten down together with "non-metallic" metalcompounds, f. inst. silicateslags, with which they do not enter into chemical reaction, then the melt will separate in two distinct layers or phases as molten metallic metals have no or extremely little ability to dissolve or to be dissolved in such "non-metallic" molten masses. This characteristic feature of metals in the metallic state is according to experience also possessed by certain chemical compounds of metals with other elements, which should otherwise have been expected to behave as "non-metallic" metalsalts, namely especially certain sulphidic and arsenidic minerals and smelter products, sulphides, selenides, tellurides, arsenides, antimonides, phosphides, carbides, and analogeous compounds, and of these especially those, which in crystalline condition show a "metallic" or "half-metallic" appearance. The latter property, metallic lustre, in combination with a more or less distinct metallic conductivity for electricity is in itself a proof for the metallic nature of these metalcompounds. A further proof is their great solubility in and dissolving-power for pure metals. If we review the whole series of the metal-sulphides and judge their appearance in crystalline condition, then we find, that many have

distinctly metallic appearance, others have "half-metallic" appearance, and a great number "non-metallic" appearance, and if we investigate the matter more closely, then we find, that the other properties of the sulphides correspond very close with their appearance. Thus, the "metallic" sulphides will conduct the electric current like metals by means of freely moveable electrons and behave in molten conditions very nearly as metals in metallic state in that they are very little soluble in "non-metallic", non-sulphidic molten masses, f. inst. silicateslags, but show on the other side great solubility in and dissolving power for metals in metallic state. The "non-metallic" sulphides, on the contrary, show in cold condition practically no conductivity for electricity, but will in molten condition conduct the electric current electrolytically by means of ions under simultaneous transport of substance. Further, they show no solubility in or dissolving power for metals in metallic state, but on the other side a very considerable solubility in and dissolving power for other "non-metallic" molten masses, f. inst. silicateslags of suitable basicity. The "half-metallic" sulphides take in these respects an intermediate position between the "metallic" sulphides and the "non-metallic" sulphides. But even the most "metallic" sulphides show, when compared with metals in metallic state, a certain decrease of the metal nature, appearing f. inst. in their increased although very small solubility in "non-metallic" non-sulphidic molten masses, f. inst. slags, and this solubility increases through the series of the sulphides very much with decreasing metallic properties. Further, even the most distinct "metallic" sulphides show in their behaviour against "non-metallic" sulphides a great difference from metals in metallic state, as in molten condition they show very great, practically unlimited, dissolving power for and solubility in these "non-metallic" sulphides. The result of this solution of "non-metallic" sulphides in "metallic" sulphides is a melt of lower metallic nature than the molten "metallic" sulphide, which fact makes itself noticeable in molten condition by the decreased or wholly disappeared ability of the melt to keep metallic metal in solution, and after cooling, in instances where it solidifies homogeneously, by diminished metallic appearance. Ordinarily, however, on solidification of such melts a very far going differentiation by crystal-

lisation takes place, whereby the melt is again split up in sulphidic components of different nature and hereby side by side crystals of "metallic", "half-metallic" and "non-metallic" appearance may appear.

Many observations tend to proof, that this differentiation by crystallisation is near related to the differentiation, which takes place, when a melt separates in two molten phases and that the causes underlying the two kinds of differentiation are very similar, to each other, as there are many instances of transition from the one kind of differentiation to the other. F. inst. if a molten solution of metallic iron in ironsulphide (FeS) is cooled slowly, then the melt will differentiate by crystallisation in crystals of metallic iron and crystals of FeS, which crystals, if the contents of the melt of metallic iron originally was low, f. inst. under 20 0/0, will appear in a regular cogrowth, the crystals of metallic iron being perfectly included in the considerable bigger cubes of FeS. If the contents of the melt of metallic iron is high and the cooling of the melt slow, then the crystals of metallic iron first formed will sink down and form an "ironsau" at the bottom, but without sharp limit against the sulphidephase, which will also after solidification contain much metallic iron. But, if we take the same solution of metallic iron in FeS at high temperature and then further lower the metallic nature of the ironsulphide by addition of a suiteable amount of "non-metallic" sulphide¹, f. inst. 10 0/0 Na₂S, then the melt will differentiate already in molten condition, as metallic iron will segregate out and form a separate molten phase under the sulphidephase, and the limit between the phases becomes very sharp. If we measure the amount of added "non-metallic" sulphide scanty, then a low percentage of metallic iron is retained in the sulphidephase and differentiates out by crystallisation during the cooling of the sulphidephase, but the crystals are then (i. e. in presence of 10 0/0 Na₂S) not enclosed in the FeS-crystals and may easily be isolated.

We may therefore with great probability presume that greater differences in the nature of the substances are necessary to cause division of a melt in two or more molten phases, than

¹ The practical execution of the experiment requires some experience, which can not yet be published.

to cause a differentiation by crystallisation during the cooling, and from this latter kind of differentiation we may find all transitions to the most simple case, namely differentiation in fluid and solid by the crystallisation of a sharply defined chemical compound out of its own melt. In the latter case it is known that the difference between the phases is caused by the escape of a certain amount of energy, the latent heat of fusion. Similar causes also seem to prevail with regard to the more complicated processes of differentiation, f. inst. differentiation of a melt into two molten phases, and also in this latter case the separation of the phases seems to be founded more on the difference in the energyconditions of the two substances, measured from a certain common standard, than in the chemical composition of the substances. While metals of very different chemical nature, as f. inst. silver and aluminium, in molten metallic state are unlimited soluble in each other, metallic aluminium is in molten condition perfectly insoluble in its molten sulphide Al_2S_3 , but silver on the contrary in molten condition perfectly soluble in its sulphide Ag_2S . Thus obviously there exists a greater differentiating difference between aluminium and its sulphide than between silver and its sulphide or between metallic silver and metallic aluminium. If we investigate the difference between a metal (M) and its sulphide (MS), which is formed out of the components according to the reaction:



wherein (x) represents the heat of formation of the sulphide, then we find by comparison between the different metalsulphides that the heat of formation (x) plays a very important part for the nature of the metalsulphides, as the "metallic" qualities of the metalsulphides with great regularity diminish with increasing heat of formation, so that sulphides with a heat of formation of less than f. inst. 25 kg-calories per grammatom chemically bound sulphur are "metallic" of appearance and properties, while metalsulphides with a heat of formation exceeding f. ins. 40 Kg-calories per grammatom sulphur are distinctly "non-metallic" of appearance and properties. Practical experience has taught me, that we may draw the conclusions yet further.

If we have a metalsulphide of typical metallic nature and then alloy it in molten condition with a metalsulphide of high heat of formation (= a non-metallic sulphide) in such quantity, that the average heat of formation per gramatom sulphur of the melt is abt. 40 kg-calories then the whole melt will behave as a "non-metallic" sulphide, f. inst. will have extremely little ability to keep metallic metal in solution and will be electrolytically dissociated. The fact that a "non-metallic" sulphide is able to dissolve, or be dissolved in metallic sulphides, indicates, that between the two kinds of sulphides there exists a certain chemical affinity, whereby compounds analogous the sulphosalts are formed, and further that the solution of the one sulphide in the other is accompanied by liberation of a certain amount of energy, on base of which, f. inst. in the before mentioned case, metallic metal is driven out of its solution in the "metallic" sulphide by addition of a "non-metallic" sulphide. It is my personal view, that, when substances very different from each other with regard to their metalnature or non-metallic nature f. inst. measured in the difference of energy from a standard metallic condition, assimilate each other in molten or solid condition, then it is always accompanied by a certain display of energy with corresponding changes in the inner structure of the substances. This applies also to isomorpheous mixtures between substances of different metallic or non-metallic nature, f. inst. between FeS, which is metallic, and ZnS, which has perfectly non-metallic appearance, while isomorpheous mixtures of the two have different degrees of half-metallic appearance, partly just as different from the two components as many chemical compounds from their composing elements. — Otherwise the sulphides of very different nature should not mix in molten condition. An instance of the latter case is the wellknown Orfordprocess, which is based on the fact the that the distinctly "metallic" nickelsulphide is insoluble or only very little soluble in the "half-metallic" or "non-metallic" melt, which results, when coppersulphyr combines with natriumsulphide. The nickel-sulphide in this case behaves as a metal, in metallic state.

The method for separating metallic metal from sulphide in molten state, which is described in the preceeding, may in

geochemical respect attain a certain importance for explaining the sharp limit in the interior of our globe between the kernel, which is supposed to consist of metal in metallic state with iron as chief constituent, and the thereover following zone, which is presumed to consist of molten sulphides with iron sulphide as chief constituent. Over the sulphidezone follows, sharply limited against it, a zone of silicates extending up to the surface of the earth. Prof. V. M. Goldschmidt¹ who has been one of the first to presume approximately the above given upbuilding of the interior of the earth, does in his treatise on the subject not give any satisfactory explanation of, why in the interior of the earth there is a sharp limit, definitively proved by seismic measurements, between the metalkernel and the sulphidezone, when from metallurgy it is known that metallic iron and ironsulphide at high temperatures are perfectly soluble in each other and have no tendency to separate in two phases. It is not permissible to compare this case with the formation of "ironsau" in metallurgical furnaces, because the latter phenomenon is in most cases based on crystallisation during cooling, thus founded on lack of sufficient temperature, which condition can not be presumed to exist in the interior of the earth. Prof. Tamman² tries to explain the separation between the ironphase and the sulphidephase in the interior of the earth by presuming, that the sulphidephase holds in solution abt. 10 % FeO and silicate, which according to his experience lowers the ability of the sulphidephase to keep metallic iron in solution. On base of my metallurgical experience I hold it for possible, that a separation of iron from ironsulphide in molten condition may be attained in this way. But a sulphidephase of this kind would be very unstable in contact with silicate and could under such circumstances only

¹ Prof. V. M. Goldschmidt: "Geochemische Verteilungsgesetze der Elemente" 1, 2, 3, 4, 5, 6 and 7 in "Videnskapselskapets skrifter 1923, 1924, 1925 og 1926". Prof. Goldschmidt seems as Prof. Tamman to believe the sulphidephase oxidcontaining, while the author stands for a purely sulphidic alkali-sulphidecontaining sulphide-phase covered by a strongly reduced silicate-phase poor in FeO.

² Prof. Tamman: "Zur Analyse des Erdinneren" Z.f.anorg.Chem.1923, p.96.

exist, if there was a very gradual transition from sulphidephase to silicatephase. If it stood in contact with a sharply limited silicatephase, then the latter would extract from the sulphidephase all of its contents of FeO and silicate, so that the reason for the separation of ironphase and sulphidephase would be removed. In metallurgical mattesmelting there has often been operated with silicateslags with up to 50 % FeO, which have stood in contact with ironsulphidemattes at high temperatures, and yet the mattes have contained only insignificant amounts of FeO or silicate. Personally I have during my metallurgical experiments several times had opportunity to observe, that the limit between an ironsulphidephase and a silicatephase has disappeared, the sulphidephase being devoured by the silicatephase. But the conditions for the appearance of this phenomenon has then always been an alcalicontaining very basic silicatephase, the basicity of which was built up of oxides of light metals, standing in contact with an ironsulphidephase containing alkalisulphide, i. e. a sulphidephase whose metallic qualities had been much lowered. Prof. Tamman says in his treatise of the interior of the earth, that if we have a three-phasesystem in perfect chemical equilibrium, wherein we must presume that also each two of the phases are in equilibrium with each other, and if we know the composition of one of the phases, then it should be possible thereof to deduct the composition of the other two phases. Theoretically this may be right, but it requires at all events a much more intimate knowledge of the distribution of the different elements in the three-phasesystem, than we are up to now in possession of. Based on my experience with the three-phasesystem, metal : sulphide : silicate, from numerous metallurgical experiments I can at all events with great certainty say, that if there is a sharp limit between the sulphidephase and the silicatephase of the composition, which Prof. Tamman himself presumes, in the interior of the earth, then a sulphidephase of the composition presumed by Prof. Tamman himself is perfectly impossible. On the other side if we presume, that the silicatephase of the earth has a composition somewhat the same as the assay of the earths crust as given by Prof. V. M. Goldschmidt namely:

SiO ₂	59,09	0/0
Al ₂ O ₃	15,35	„
(Fe ₂ O ₃ + FeO)	6,88	„
CaO	5,08	„
MgO	3,49	„
Na ₂ O	3,84	„
K ₂ O	3,13	„
H ₂ O	1,14	„
TiO ₂	1,05	„
P ₂ O ₅	0,3	„

then I am able to prove, that the sulphidephase of the earth will contain several percent alkalisulphide, at least 4⁰/₀, most probable between 5⁰/₀ and 12⁰/₀ (Na₂S + K₂S). My metallurgical experiments have taught me, that the chalkophile¹ tendency of sodium and potassium in the threephasesystem lie very near that of iron, and in a threephasesystem, where the amount of oxygen is so limited, that the lithophile¹ tendency of iron is reduced to 6,88⁰/₀ (Fe₂O₃ + FeO) in the silicatephase, we are not only within the sphere, wherein sodium and potassium show strong tendency to be transferred to sulphide and as such wander into the sulphidephase, but we have reached a *degree of reduction* of the threephasesystem, where also calcium and even magnesium begin to show considerable chalkophile tendency. This statement stands in opposition to the treatise on this subject by Prof. V. M. Goldschmidt, who classify the alkalimetals as distinctly lithophile elements. Direct experiments have taught me, that this is not correct. In the twophasesystem, silicate

¹ The expressions "chalkophile" and "lithophile" are taken after Prof. V. M. Goldschmidt, who in his before cited treatise on this subject classifies all elements according to their distribution in our globe in in four classes, namely:

- a) "siderophile elements" = elements, which preferably accumulate in the iron-kernel of the earth,
- b) "chalkophile elements" = elements, which preferably accumulate in the sulphidephase of the earth,
- c) "lithophile elements" = elements, which preferably accumulate in the silicate-phase of the earth, and
- d) "athmophile elements" = elements, which preferably accumulate in the atmosphere of the earth.

: ironsulphide, I have numerous times observed, that a slag containing much FeO is able to stand in contact with a matte containing considerable amounts of Na₂S, f. inst.:

Example No. 1. A slag containing 55,68 % SiO₂, 13,5 % FeO, 15,1 % Al₂O₃, 5,7 % CaO, 8,5 % Na₂O stood in chemical equilibrium with a matte containing abt. 2,5 % Na₂S.

Example No. 2. A slag containing 43,1 % SiO₂, 24,4 % FeO, 3,9 % Na₂O stood in contact with a matte containing 3,97 % Na₂S.

Example No. 3. A slag containing 60,43 % SiO₂, 14,9 % Al₂O₃, 16,3 % CaO, 6,84 % FeO, 3,74 % Na₂O stood in contact with a sulphidephase containing abt. 2 % Na₂S.

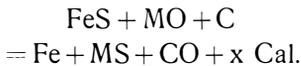
These examples give a picture of the chalkophile tendency of sodium in the twophasesystem, silicate : sulphide, under presumption of a sulphidephase consisting chiefly of ironsulphide saturated with sulphur at a temperature of 1100 to 1200 degrees celsius. Experience has taught me, that the conditions change much by varying the ratio between metal and sulphur in the sulphidephase, the chalkophile tendency of sodium decreasing with increasing sulphurcontents of the sulphidephase. The competition about sulphur seems to be an important connecting link between "metallic" and "non-metallic" sulphides. I have during experiments with practical metallurgical ends often had opportunity to observe the division of sodium between silicate and ironsulphide, when the latter has been in the sulphidationstage corresponding to pyrrhotite, Fe_xS_(x+1), which in a sulphuratmosphere is stable in the interwall of temperature between 565 and abt. 900 degrees celsius. I have many observations pointing to the fact, that the chalkophile tendency of sodium is lower in the pyrrhotitestage than in the FeS-stage, and that it further deminishes by transition from the pyrrhotitestage to the pyritestage (FeS₂).

In the threephasesystem the sulphidephase stands in contact with metallic metal and has consequently a very low stage of sulphidation, f. inst. in the case of FeS and Fe the sulphidephase has a little lower sulphurcontents than corresponding to FeS. In surveying the distribution of elements in a threephasesystem, metal : sulphide : silicate, similar to that

of the interior of the earth, we have to keep in mind, that, when the chemical equilibrium is attained, each two of the phases must also be in equilibrium with each other. In coarse features the chemical equilibrium in the three-phasesystem represents the result of a competition between all elements present about a too scanty amount of sulphur and oxygen. If in such a system we increase the amount of sulphur by further addition of it, then the equivalent amount of metal will be transferred from the metalphase to the sulphidephase. If on the other side we increase the amount of oxygen present, the equivalent amount of metal will be transferred from the metalphase to the sulphidephase and simultaneously the corresponding amount of metal wander out from the sulphidephase to the silicatephase. If, on the contrary, we deminish the amount of oxygen in the silicatephase, then the equivalent amount of elements will wander from the silicatephase into the sulphidephase and force the latter to give off an equivalent amount of metal to the metalphase. Hereby the invasion of elements from the silicatephase as well as the simultaneously on going emigration of elements from the sulphidephase to the metalphase take place in a certain sequence, yet so, that mostly simultaneously several different elements are transferred but in different amounts all according to their place in the sequence of transfer and their concentration in the phases.

I have myself for practical metallurgical ends worked out and patented a process, which makes it possible in a three-phasesystem, metal : sulphide : silicate, to diminish the amount of oxygen and sulphur in the system, and I have, while experimenting with this process, had opportunity to observe different chemical equilibriums, which result under such circumstances. The process consists in using the silicatephase as electrolyte in a meltelectrolysis with the metalphase and sulphidephase connected as cathode, while as anode is used a carbonelectrode dipping into the silicatephase from through the roof of the furnace. The arrangement is shown in fig. 1, wherein (*a*) is the carbonanode, (*e*) the silicateelectrolyte, (*s*) the sulphidephase, and (*m*) the metal-phase. During the electrolysis the cations of the silicatephase will wander against the surface

of the sulphidephase, which is connected as cathode, and here preferentially in a certain sequence under formation of sulphide wander into the sulphidephase, while simultaneously the equivalent amount of metal is given off from the sulphidephase to the metalphase. The anions of the silicatephase, chiefly SiO_3 , simultaneously wander against the carbonanode, where they are neutralized under evolution of oxygen, which combines with the anodematerial and escapes as CO . As long as the electrolysis has the above mentioned run, it may be expressed approximately by the chemical reaction:



and if we put up this reaction with regard to the chief constituents of the silicatephase, then by comparison we get an approximate overlook over in which sequence or in which amounts the different components of the silicatephase will wander into the sulphide-

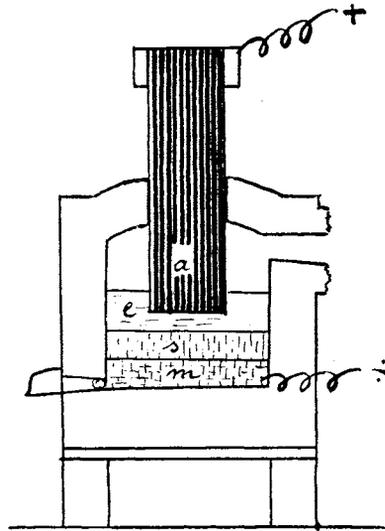


Fig. 1.

phase. The chief reactions are given in the table (pag. 250).

It is to be noted that these and similar reactions also may be made to run clean thermally without electrolysis, but the electrolytic run does not require so high temperature, is easier to regulate and leads to safer equilibriums. The reactions 1) to 8) give expression for the conditions, when the silicatephase is very basic, while the reactions 12) to 19) give a picture of the conditions, when the silicatephase is neutral or acid. The difference between basic and acid silicatephase is especially great in the case of lithium (reactions 6) and 16)). As the silicatephase of the earth is acid especially the reactions 9) to 19) come into consideration. Of the reactions 12), 13), 14) it may be deduced, that the chalkophile tendency of sodium and

		Per Gr.-atom S Kg-Calories
1)	$\text{FeS} + \text{K}_2\text{O} + \text{C} = \text{Fe} + \text{K}_2\text{S} + \text{CO} + 10,4 \text{ Cal.}$	+ 10,4
2)	$\text{FeS} + \text{Na}_2\text{O} + \text{C} = \text{Fe} + \text{Na}_2\text{S} + \text{CO} + 2,5 \text{ ,,}$	+ 2,5
3)	$\text{FeS} + \text{BaO} + \text{C} = \text{Fe} + \text{BaS} + \text{CO} - 25,4 \text{ ,,}$	- 25,4
4)	$\text{FeS} + \text{FeO} + \text{C} = \text{Fe} + \text{FeS} + \text{CO} - 36,5 \text{ ,,}$	- 36,5
5)	$\text{FeS} + \text{CaO} + \text{C} = \text{Fe} + \text{CaS} + \text{CO} - 32,1 \text{ ,,}$	- 32,1
6)	$\text{FeS} + \text{Li}_2\text{O} + \text{C} = \text{Fe} + \text{Li}_2\text{S} + \text{CO} - 46,6 \text{ ,,}$	- 46,5
7)	$\text{FeS} + \text{MgO} + \text{C} = \text{Fe} + \text{MgS} + \text{CO} - 58,9 \text{ ,,}$	- 58,9
8)	$3 \text{ FeS} + \text{Al}_2\text{O}_3 + 3 \text{ C} = 3 \text{ Fe} + \text{Al}_2\text{S}_3 + 3 \text{ CO} - 250,7 \text{ ,,}$	- 83,5
9)	$2 \text{ FeS} + \text{SiO}_2 + 2 \text{ C} = 2 \text{ Fe} + \text{SiS}_2 + 2 \text{ CO} - 129,8 \text{ ,,}$	- 84,9
10)	$3 \text{ FeS} + \text{B}_2\text{O}_3 + 3 \text{ C} = 3 \text{ Fe} + \text{B}_2\text{S}_3 + 3 \text{ CO} - 157,5 \text{ ,,}$	- 52,-
11)	$2 \text{ FeS} + \text{TiO}_2 + 2 \text{ C} = 2 \text{ Fe} + \text{TiS}_2 + 2 \text{ CO} - ? \text{ ,,}$	- high
12)	$\text{FeS} + \text{BaSiO}_3 + \text{C} = \text{Fe} + \text{BaS} + \text{SiO}_2 + \text{CO} - 40,1 \text{ Cal.}$	- 40,1
13)	$\text{FeS} + \text{Na}_2\text{SiO}_2 + \text{C} = \text{Fe} + \text{Na}_2\text{S} + \text{SiO}_2 + \text{CO} - 42,7 \text{ ,,}$	- 41,7
14)	$\text{FeS} + \text{FeSiO}_3 + \text{C} = \text{Fe} + \text{FeS} + \text{SiO}_2 + \text{CO} - 45,- \text{ ,,}$	- 45,-
15)	$\text{FeS} + \text{CaSiO}_3 + \text{C} = \text{Fe} + \text{CaS} + \text{SiO}_2 + \text{CO} - 49,9 \text{ ,,}$	- 49,9
16)	$\text{FeS} + \text{Li}_2\text{SiO}_3 + \text{C} = \text{Fe} + \text{Li}_2\text{S} + \text{SiO}_2 + \text{CO} - 111,6 \text{ ,,}$	- 111,6
17)	$2 \text{ FeS} + \text{Li}_2\text{SiO}_3 + 2 \text{ C} = 2 \text{ Fe} + \text{SiS}_2 + \text{Li}_2\text{O} + 2 \text{ CO} - 194,9 \text{ ,,}$	- 97,5
18)	$3 \text{ FeS} + \text{Al}_2\text{Si}_3\text{O}_7 + 3 \text{ C} = 3 \text{ Fe} + \text{Al}_2\text{S}_3 + 2 \text{ SiO}_2 + 3 \text{ CO} - 256,6 \text{ ,,}$	- 88,5
19)	$4 \text{ FeS} + \text{Al}_2\text{Si}_2\text{O}_7 + 4 \text{ C} = 4 \text{ Fe} + 2 \text{ SiS}_2 + \text{Al}_2\text{O}_3 + 4 \text{ CO} - 274,3 \text{ ,,}$	- 68,5

barium lie very near that of iron, and this stands in correspondance with metallurgical experience. Further, comparison between the reactions 14) and 15) teaches us, that calcium is less chalcophile than iron. Practical metallurgical experiments have taught me that, if the sulphidephase contains noticeable amounts of CaS, then the silicatephase can not contain over a certain amount of FeO, namely abt. 7 % (FeO + FeS), or less, the contents varying with the basicity. Thus the contents of FeO in the silicatephase may be used as an indicator for pre-telling, if noticeable amounts of CaS, MgS and others may be expected in the sulphidephase. But even a considerable amount of FeO in the silicatephase does not exclude alkalisulphide or bariumsulphide in the sulphidephase. It is hereof evident, that the question if an element is to be classified as "chalcophile" or "lithophile" in a threephasesystem, metal : sulphide : silicate, is dependent upon the *degree of reduction* of the silicatephase or the system as a whole, and this degree of reduction finds its expression not in the relation between oxygen and metal in the silicatephase, but in the chemical composi-

tion of the silicatephase judged in connection with the composition of the sulphidephase, especially the latter's contents of the elements of the silicatephase. In reality practically all the components of the silicatephase may be proved qualitatively to be present in the sulphidephase, but in different quantities all according to their concentration in the system and their position in the sequence of transfer from silicate to sulphide, and the degree of reduction of the silicatephase. Further, the position of the element in question in the sequence of transfer from the sulphidephase to the metalphase plays a certain part, as it decides if the said element is at all able to achieve any concentration in the sulphidephase.

If we have a threephasesystem, iron : ironsulphide : silicate wherein the silicatephase besides the ordinary constituents of slags also contains a certain amount of all heavy metals, then the result will be, that by chemical reaction between the silicatephase and the other phases the chief amount of the heavy metals more precious than iron will be transferred to the sulphidephase or (and) the metalphase, being replaced in the silicatephase by the equivalent amount of FeO. Thus there results a silicatephase somewhat of the composition as the metallurgical mattesmelting slags, high in FeO, and if this slag is used as electrolyte in the before described process of molten electrolysis over a sulphidephase, then, as the oxygen contents in the silicatephase diminishes, in the first line iron will be transferred from the silicatephase to the sulphidephase, and simultaneously with iron the rest of more precious heavy metals and besides considerable amounts of potassium, sodium and barium if present. When the FeO-contents of the silicatephase has gone down far enough, then also calcium, magnesium and other heavily transferrable elements begin to wander into the sulphidephase. Last comes aluminium, silicon, titanium and, in acid silicatephase, lithium. But long before these latter, on progressing reduction of the silicatephase, are the only chief elements left as oxides in the silicatephase, small amounts of them may be stated to be present in the sulphidephase, and with regard to silicon it has, because of the volatility of its sulphide under atmospheric pressure, so great tendency to be

transferred into sulphide, that it is necessary to uphold a certain basicity in the silicatephase, if the electrolysis shall not run under continued volatilisation of SiS_2 . Under the high pressure, which must exist in the interior of the earth, this reaction of course does not come into consideration. The "non-metallic" sulphides: alkalisulphide, alkaline earthsulphides, etc. newformed by the electrolysis are, as explained before, also very considerably soluble in silicate slags of suitable basicity, and divide themselves in a certain relation between the sulphidephase and the silicatephase. Hereby the silicatephase obtains certain contents of sulphurjons, which, if they are present in the neighbourhood of the anode, are anodically precipitated more easy than oxygen. Therefore, when the concentration of sulphurjons in the silicatephase has become great enough, then the electrolysis will no longer run under consumption of the silicatephase, but at the cost of the sulphide-phase, sulphurjons wandering from the surface of the sulphidephase through the silicatephase to the anode, where they are precipitated as sulphur-vapor, while the equivalent amount of metal is transferred from the sulphidephase to the metalphase. If at the beginning we start with a silicatephase of the composition somewhat as nephelite $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$, increasing the basicity by further addition of a little CaO , and a sulphidephase with FeS as chief constituent, then this run of the electrolysis will set in, when the sulphidephase has assimilated 8.0 to 13.0% Na_2S , while the contents of sulphur in the silicatephase simultaneously grow to between 2.0% and 5.0% S. The silicate-phase will then contain between 4.0% and 5.0% FeO , which keeps constant as long as the sulphidephase is present. Of course this equilibrium is very dependent upon the basicity of the silicatephase and its chemical composition, of the temperature, of the electrolysis and further to a certain extent also of the currentdensity. The above datas are taken from electrolysisexperiments at moderate temperatures, between 1200 and 1500 degrees celsius. I will in this connection also give the result of an electrolysis experiment at higher temperatures with a somewhat basic silicatephase, wherein beside aluminiumsilicate also considerable amounts of magnesiumsilicate and calciumsilicate were present. The electro-

lysis did run with a current of between 1000 and 1500 Amp. in 19 hours at a temperature of between 1600 and 1800 degrees celsius. The silicatephase then at the end showed a sulphurcontents of no less than 9,93 % S, corresponding to more than 20 % sulphide in the *silicatephase*. If, on base of the analysis of the phases, I divide this sulphurcontents of the silicatephase between its components as best I understand we arrive at following assays of the phases at the end of the experiment:

<i>Silicatephase:</i>	<i>Sulphidephase:</i>	<i>Ironphase:</i>
SiO ₂ 26,7 %	FeS 75,16 %	Si 1,24 %
Al ₂ O ₃ 14,4 „	Metal. Fe 3 to 4 „	C 0,38 „
MgO 24,7 „	Cu ₂ S 3,38 „	Cu ¹ 0,2 „
MgS 7,4 „	Na ₂ S 8,0 „	S ¹ 0,3 „
CaO 5,3 „	CaS 4,77 „	Rest iron.
CaS 8,0 „	MgS 4,56 „	
FeO 4,0 „		
FeS 2,5 „		
Na ₂ O 1,1 „		
Na ₂ S 3,0 „		

It may hereof be deducted, that with increasing degree of reduction of the silicatephase on the one side the chalkophile tendency of all the components of the silicatephase increase, and on the other side the *lithophile* tendency of sulphur increases. This may under certain conditions be driven so far, that the two phases swallow up each other, forming only one phase.

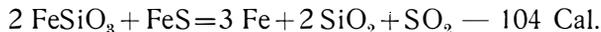
Our globe has once very long ago been a four-phase-system, metalphase : sulphidephase : silicatephase : gasphase, but it is so no longer. At present the chemically inactive surface of the earth, separates the atmosphere from the interior of the earth, and there exists no chemical equilibrium between the two. But it may be assumed, that the interior of the earth does represent a very ideal threephasesystem, metal : sulphide : silicate which on cause of the long period the three phases

¹ The contents of S and Cu in the iron are put in on base of results from other electrolysis-experiments. The carbon-contents may be accidental.

have stood in contact with each other, must have reached complete chemical equilibrium. In this threephasesystem it is only the silicatephase which is somewhat accessible to us, and on base of its composition we must deduct the composition of the other phases. For this purpose according to the previous explanations in the first place we have to examine the degree of reduction of the silicatephase. If, for this end, we go out from the composition of the earths crust as given by Prof. V. M. Goldschmidt (table on page 250), then we find the contents of iron given as 6,88 % ($\text{FeO} + \text{Fe}_2\text{O}_3$). In the threephasesystem, metal : sulphide : silicate, trivalent iron is not able to exist on cause of the great competition about oxygen. Prof. J. H. L. Vogt has also stated, that Fe_3O_4 is never found in mattes which simultaneously contain metallic iron. (J. H. L. Vogt: "Die Sulfid-silikatschmelzlösungen" 1919 p. 30). Thus instead of 6,88 % ($\text{FeO} + \text{Fe}_2\text{O}_3$) in the silicatephase of the threephasesystem we have to reckon with the equivalent amount of ($\text{FeO} + \text{FeS}$). It is of interest to compare these contents with the contents ($\text{FeO} + \text{FeS}$) = 6,5 % of the silicatephase of my experiment cited on page 252, especially, when remembering, that the earths crust is resulted by solidification and oxydation of the surface of the silicatephase of the earth. Thus, the contents of iron in the earths crust indicate, that the silicatephase of the earth has reached a degree of reduction at which not only potassium, sodium and barium show strongly chalkophile tendencies, but at which also calciumsulphide in considerable amount will appear in the sulphidephase. The truth of this statement is very much backed up by the fact, that the mineral oldhamite (CaS) is found in the troilitephase of meteorites. As, by direct metallurgical experiment, it is easy to prove, that potassium and sodium are much easier to transfer from silicate to sulphide than calcium, we can on base of the contents of ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) in the earths crust with certainty pretell, that the sulphidephase in the interior of the earth contains much alkalisulphide. On base of my experiments I estimate, that the sulphidephase in the interior of the earth will contain between 5 % and 12 % ($\text{Na}_2\text{S} + \text{K}_2\text{S}$), most probable between 8 % and 12 %. Besides that about 2 to 5 % CaS .

Therefore, the sharp limit in the interior of the earth between the metallic kernel and the thereon following sulphide-phase must be presumed to be caused by the contents of the sulphidephase of "non-metallic" sulphides, especially alkali-sulphides and alkalineearthsulphides. By seismic measurements the limit between the sulphidephase and the metalphase in the interior of the earth has been found to lie at a depth of abt. 2900 km under the surface of the earth, while in the same way the limit between the sulphidephase and the silicate-phase has been found at abt. 1200 km under the surface of the earth.

At the time, when our globe was really a fourphasesystem, metal : sulphide : silicate : gas, and the fluid silicatephase stretched up to the surface of the earth, there was to begin with no threevalent iron present in the silicatephase. At the high temperature then prevailing reactions analog 1) to 19) on page 250 would run far from left to right clean thermally, and where no carbon was present chemically bound sulphur would react with chemically bound oxygen, f. inst. analog the reactions:



thus causing an extreme degree of reduction of the system. The gasphase would then chiefly have consisted of N, CO, CO₂, SO₂, H₂O, H₂S, S, and besides that would have been heavily loaded with other volatile oxides, sulphides and halogensalts. By progressing cooling of the earth condensation of different products took place, and the above mentioned reactions would begin to run in the opposite direction, so that the gasphase would begin to have an oxydising and sulphidising effect on the surface of the silicatephase, whereby by and by an oxydised earths crust was formed, wherein minerals containing threevalent iron, as f. inst. magnetite, specularite, pyrrhotite (Fe₇S₈), pyrite (FeS₂), certain silicateminerals, etc., are represented but which are continually not present in the real three-phasesystem of the interior of the earth. By the invasion of oxygen into the surface of the silicatephase, the latter's contents of "non-metallic" sulphides were converted into oxides, giving off their contents of sulphur to the heavymetalsulphides, which

were thereby transformed into higher sulphidized minerals, as pyrite, pyrrhotite, copperpyrite, etc. Further it causes the transformation of part of the iron contents of the silicate phase into magnetite and specularite, which partly segregates out of the silicate phase. In this way there result magmatic differentiations as a result of reaction between the gas phase and the silicate phase by progressing cooling of the surface of the earth.

It has hereto been presumed by most scientists on this field that magmatic differentiations are in most cases the result of fractional crystallisation of the magma. Prof. W. C. Brögger has put up the rule, that "The sequence of differentiation of a rock goes parallel with its sequence of crystallisation". This of course holds good in very many cases and is a very important rule. But experience from experiments with meltelectrolysis in the three phases system has taught me the fact, that a magma also can differentiate without crystallisation. From electrolysis in aqueous solution it is known, that somewhat big difference of concentration inside the electrolyte may be caused by the electrolysis. The same also takes place by meltelectrolysis and is especially remarkable in a tough fluid silicate electrolyte. In my experiments with meltelectrolysis using silicates as electrolytes I have had ample opportunity to observe, that the basicity increases near the cathode and the acidity near the anode. In this connection I will mention a small experiment in graphite crucible. The aim of the experiment was the removal of the last traces of sulphur from molten iron by using it as cathode in a meltelectrolysis with a silicate as electrolyte and a carbonelectrode dipping into the silicate as anode. The electrolysis lasted for 1 1/2 hour with a current of 50 Amp. the crucible containing abt. 2 kg. iron and 2.5 kg. silicate. On ending, the anode was taken out, the crucible lifted out of the furnace and allowed to cool somewhat quick in air. After solidification the chief amount of the silicate proved perfectly homogen glassy of grey black colour, but on the surface of the ironingot (the cathode) there had crystallised out a 3 mm thick layer of a shisty grey green mineral, while at the surface in the neighbourhood of the anode there were white inclusions in the glass. Thus cathodically there appeared a crystallisation perfectly

different from the other part of the electrolyte. In similar way I presume that differentiations at a big scale may have taken place in the silicatephase of the earth under the influence of electrolytic currents, as here the distances are greater and the conditions much more favourable for this kind of differentiation than in a small crucible. It is my conviction, that the electrolytic wandering of ions has played and plays a very important part in the magmatic differentiation of silicates, especially as a means of splitting up a magma in a basic part and an acid part.
