

Various equivalents of the basalts and equivalents of the andesitic rocks of the Goentoer in a broader sense were found among the homoeogeneous inclusions of the youngest eruptive products of the Goentoer properly speaking.

The quartz-containing inclusions of the basalts of Krakatau illustrate the presence of virtual quartz in the groundmass of the hypersthene andesites of the first period, and would as well, be the only traces of differentiation in the mother-magma before the basaltic eruptions, if not, not only the greater part, but all traces of the former basic eruptions had disappeared by a fall-down.

The occurrence of augitefree plagioclase-hypersthene-amphibole-olivine rocks as homoeogeneous inclusions in the products of the Goentoer teaches us that such combinations of minerals may at a greater depth crystallize out of the basaltic magma.

It appears from the calculation of the norm that also the quartz-containing inclusions of Krakatau belong to the rare combinations of minerals because, according to the analyses calculated by WASHINGTON no other rock belongs to the sub-class (II. 3, 4, 3).

Chemistry. — “*On the pyrophoric phenomenon in metals*”. By Prof. A. SMITS, A. KETTNER, and A. L. W. DE GEE (A preliminary communication). (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of February 28, 1914.)

In a previous communication ¹⁾ it was pointed out that the pyrophoric phenomenon would possibly have to be explained by this that the metals obtained in the reduction of certain compounds are comparatively far from the state of internal equilibrium and show an abnormally great power of reaction in consequence of an abnormally large content of the simpler kind of molecule.

The explanation for this phenomenon prevalent up to now, which is of more frequent occurrence than is perhaps supposed (we found it with Cu, Bi, Pb, Ni, Fe) attributed the great reactive power to the very finely divided state; so an explanation which is perfectly analogous to that of the so called “chemical flag” for phosphorus.

Now the possibility might also be considered that in the liberation of the metal a pyrophoric admixture is formed, or that the hydrogen

¹⁾ These Proc. XVI, p. 699.

dissolves somewhat in the metal or becomes denser on the surface and exercises a catalytic influence.

It has, however, appeared that pyrophoric iron may be obtained when different iron compounds are heated for a short time in a hydrogen current at $\pm 350^\circ$. This succeeds with ferro oxalate, ferro tartrate, ferro chloride, and with the oxides of iron, from which follows that no common admixture except hydrogen can be pointed out here, to which the pyrophoric property could be ascribed. Now it appeared, however, that also pyrophoric iron can be obtained when ferro oxalate is heated *without* contact with hydrogen, which proves that the hydrogen certainly does not cause the pyrophoric phenomenon.¹⁾

To test the supposition expressed by one of us, it was examined in the first place what the influence is of the temperature on the pyrophoric phenomenon. Sealed to glass tubes with pyrophoric iron were placed in a thermostat, which was regulated at different temperatures between 250° and 340° . After a certain time the tubes were taken from the bath and opened to find out if the iron was still pyrophoric. The result is given in the following table:

Duration of the heating	Temperature	Result
a week	250°	still pyrophoric
" "	290°	no longer pyrophoric
48 hours	310°	hardly pyrophoric
24. "	340°	no longer pyrophoric

The pyrophoric property of iron, therefore, vanishes with heating to higher temperature. The rapidity with which this happens, increases greatly with the temperature. 310° is about the temperature at which the conversion has taken place almost completely in **48** hours.

That at this temperature a massing together of the powder should have taken place, and that in consequence of this the pyrophoric phenomenon would have disappeared, is pretty well out of the question, and it was therefore of importance to make an attempt to examine whether the transition *pyrophoric iron* \rightarrow *non-pyrophoric*

¹⁾ THIEBAULT [Bull. Soc. Ch. de Paris (3) 31, 135] found that when Bi-mellate is heated in vacuo, pyrophoric Bi is formed; in the same way we obtained pyrophoric Bi from the citrate.

iron is attended with a variation of volume, as in this way an important support might be given to the supposition of an internal transformation.

In a dilatometer constructed specially for the purpose Fe_2O_3 was reduced with hydrogen under such circumstances (temp. and time) that on the ground of experiments, previously taken, the iron could certainly be assumed to be pyrophoric. Then the apparatus was exhausted and filled with mercury, which had been boiled at the airpump¹⁾.

In connection with the experiments in sealed to glass tubes it was to be expected that in case of one or two days' heating nothing could be observed until the neighbourhood of 300° is reached. In agreement with this the following was found:

Temperature	Duration of heating	Change of position of the mercury meniscus
212°	54 hours	0 cm.
284°	22 "	0,2 "
320°	48 "	+14 " On continued heating no change of volume took place any longer ²⁾ .

Accordingly it appeared most convincingly from the dilatometric investigation that a considerable increase of volume takes place exactly in the temperature region where the pyrophoric property of the iron vanishes with such rapidity that it can no longer be demonstrated after ± 48 hours. In virtue of these preliminary experiments it may, therefore, be considered as certain that the transition of pyrophoric iron to ordinary iron is accompanied with an increase of volume. The supposition that pyrophoric iron is iron that is not in internal equilibrium, has thereby greatly gained in probability. In a subsequent communication it will be demonstrated why pyrophoric iron must not be considered as a new modification of iron.

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¹⁾ Iron and mercury were examined after the experiment was over, when the mercury appeared to contain only exceedingly small traces of iron, and the iron to be perfectly free from mercury.

²⁾ At the end of the experiment the iron appeared to be no longer pyrophoric.