VI.—SATURATION OF MINERALS.

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IN a recent paper¹ Professor Shand put forward a plea for the more careful consideration, in rock classification, of the saturated or unsaturated state of the constituent minerals. The criterion of saturation which is assumed is the capability of co-existence with some form of free silica, as shown by the "observed facts of distribution". By means of this criterion, the rock-forming minerals are divided into two groups—the saturated minerals and the unsaturated ones. The former group includes the feldspars, amphiboles, pyroxenes, micas, and most of the so-called accessory minerals, as well as those of pneumatolytic origin; while the latter group comprises the feldspathoids, olivine, the spinels, corundum, and the garnets (except spessartite, which is put into the first class). Rocks are divided into three classes, according as they are made up wholly of saturated minerals, partly of saturated and partly of unsaturated ones, or wholly of unsaturated ones.

The criterion is so obvious that it has been implicitly used, at least in part, in most of the classifications proposed since Zirkel's² in 1866. In the American Quantitative Classification, for example, the ratio of feldspar to leucite (feldspathoid) takes second place only to the ratio of silicic to femic minerals in determining the position of a rock.³ The 'class' is determined by the latter ratio and the 'order' by the former. In practically all cases, however, the application of this idea has not extended beyond the discrimination of the feldspar and feldspathoid-bearing rocks, and what Professor Shand advocates is the extension of the principle to the other minerals of igneous rocks. There are, however, certain inherent difficulties in such a general application, and it is now proposed to consider, very shortly, some of these difficulties.

The first question which arises is whether the method of determining which minerals are saturated and which are not, is sufficiently exact. The distribution of minerals in igneous rocks, apart from all consideration of the history of the rocks, seems to be rather too empirical to be used as a satisfactory criterion. For example, olivine must be included in the list of unsaturated minerals, and yet it occurs along with quartz in a number of rocks. In addition to those mentioned by Professor Shand, several rhyolites in America⁴ and elsewhere⁵ contain olivine and tridymite, while the author has described pitchstone-porphyrries from Arran⁶ containing phenocrysts of olivine and quartz. In the former case the minerals occur in lithophyses and may have had a hydrothermal origin after the consolidation of the rock, while in the latter the olivine is probably xenocrystic. Quartz-dolerites are usually supposed to have caught up

¹ "On Saturated and Unsaturated Rocks": *GEOL. MAG.*, Dec. V, Vol. X, pp. 508-14, 1913.

² *Lehrbuch der Petrographie*, Bd. i, p. 450, 1866.

³ *Quant. Class. of Igneous Rocks*, 1903, p. 123 et seq.

⁴ e.g. Iddings, *Amer. Journ. Sci.*, ser. III, vol. xxx, pp. 58-60, 1885.

⁵ Iddings & Penfield, *ibid.*, ser. III, vol. xl, pp. 75-8, 1890.

⁶ "Pitchstones of South Arran": *Trans. Geol. Soc. Glasgow*, vol. xv, pp. 19-37, 1913.

siliceous material which remains partly undissolved, while the quartz basalts of California¹ have been explained as due to the intratelluric mixing of a dacite and basalt. This explanation has not been fully accepted,² although the presence of a reaction-rim round the quartz crystals indicates their probable xenocrystic origin.

There are two possible ways, however, in which primary quartz (or other silica mineral) may be formed in unsaturated rocks in small quantities. If water be present in a magma consisting mainly of metasilicates, the hydrolitic action of the water vapour or its dissociated constituents at high temperature may cause the metasilicates to partly break up into orthosilicate and free silica, and the latter may finally crystallize as quartz or tridymite.

The other possibility is that the reaction

may be appreciably reversible. It is most probable that all chemical reactions are theoretically reversible, though, in many cases, under suitable conditions a reaction can proceed so far in one direction that the reverse reaction cannot be detected. Since practically all chemical reactions involve an absorption or evolution of heat, it follows that one of the actions in a reversible reaction is, in general, endothermic and the other exothermic, and we can deduce, thermodynamically, that a rise in temperature displaces the equilibrium position in such a way that the endothermic reaction receives the greater acceleration. The formation of a metasilicate by the interaction of silica and an orthosilicate is exothermic, and the reverse reaction is therefore endothermic and will proceed to a greater extent the higher the temperature. Thus the possibility of silica minerals separating from a part-saturated rock will be greater when the crystallization takes place at a high temperature than when it occurs at a lower one.³

The disadvantages of a criterion such as this empirical one of 'saturation', and indeed of all similar empirical ones, become more manifest when the stability relations of the minerals in a rock are considered. So many factors, external and internal, influence the cooling of a rock, that in many cases the resultant solid is not in a condition of maximum stability, and one function of a rational classification should be to indicate in what way, and to what extent, there is deviation from a state of equilibrium. For instance, many rocks show evidence of undercooling, not only with regard to the passage from the liquid to the solid state, but also with regard to transformations in the solid state. Thus glass is not a true solid but merely an undercooled liquid, and, as such, is a metastable phase at ordinary temperatures. Devitrification, i.e. the transformation to the more stable crystalline form, follows, in accordance with the Principle of Maximum Work, the glass having a higher potential than the solid.

¹ Diller, Bull. U.S. Geol. Surv., 1891, No. 79, pp. 21-33.

² Cf. Iddings, Bull. U.S. Geol. Surv., 1890, No. 66, pp. 20-32.

³ Since this was written, Bowen & Andersen (*Am. Journ. Sci.*, ser. IV, xxxvii, pp. 487-500) have described experiments which show that on cooling a melt of the composition MgO-SiO₂, some forsterite separates out first and then the residual liquid crystallizes as a mixture of silica and clinoenstatite.

The comparative rarity of leucite may be explained in a similar way. This mineral seems to form only in a small temperature interval,¹ and if, by undercooling or otherwise, crystallization takes place outside this interval, the final product is a mixture of orthoclase and nepheline. This may also be expressed by saying that the reaction

is reversible, and proceeds towards the formation of leucite only through a certain temperature range.

In this case, the effect of undercooling is not merely physical but chemical also, and is therefore analogous to the phenomena observed in the cadmium-antimony alloys.² A mixture of equal atomic percentages of cadmium and antimony, cooling from the fused state, deposits crystals of a compound Cd Sb , if the melt is inoculated; otherwise, without inoculation, undercooling takes place and a mixture of antimony and a compound $\text{Cd}_3 \text{Sb}_2$ separates. The freezing-point curve of the metastable system therefore differs from that obtained under conditions of stable equilibrium. The system albite-(soda)-nepheline is probably similar, save that the compound, analcite, requires the presence of water before it is formed, in addition to definite conditions of temperature and pressure.

Undercooling, however, may take place in the solid state as well as in the liquid state, and involve the presence of unstable or metastable phases. Instances of this phenomenon are common amongst the rock-forming minerals, silica itself being a good example. According to recent work,³ β -cristobalite is the modification of silica stable above $1,470^\circ$; β -tridymite, between 870° and $1,470^\circ$; β -quartz between 575° and 870° ; and α -quartz below 575° . The occurrence of tridymite in certain effusive rocks, such as the trachyte of Drachenfels, is well known, and it will be obvious from the above that the mineral must be an unstable phase. Its origin may be due to crystallization from the magma at a temperature above the transition-point, and then owing to the rapid cooling, the transformation to quartz may be inhibited. It is possible, however, as Fenner⁴ has pointed out, that crystallization may have occurred below 870° , and that an unstable form has developed in accordance with Ostwald's rule, that the most stable phase may not be attained directly, but that phases of intermediate stability may first form. As in the first case, a rapid fall to ordinary temperatures might greatly reduce the velocity of inversion. There are apparent exceptions to Ostwald's rule, but it is possible that these may be explained by the thermodynamic potential of the liquid at the given temperature being lower than, or nearly equal to, the potential of the modifications which fail to appear. In the case of tridymite, quartz, etc., the change is apparently physical and is confined to a polymorphic transformation.

The hornblendes and pyroxenes may constitute another example of the same type. While there is still some obscurity regarding the

¹ Cf. Washington, *Journ. Geol.*, xv, pp. 257-79, 357-95, 1907.

² Kurnakov & Konstantinov, *Zeit. anorg. Chem.*, lviii, pp. 12-22, 1908.

³ Fenner, "The Stability Relations of the Silica Minerals": *Amer. Journ. Sci.*, ser. IV, xxxvi, pp. 331-84, 1913.

⁴ Fenner, *loc. cit.*, p. 342.

relations of these two groups, the evidence both of petrography and of synthetic work¹ is in favour of pyroxene being the high temperature form and hornblende the low temperature one. In the diorites and gabbros, hornblende often appears as a parallel growth on pyroxene, and many cases have been described of the former mineral containing cores of the latter.² Similarly augite is often found pseudomorphed by hornblende. It has been argued against this view that the hornblende, and the pyroxene from which it forms, have different compositions, particularly where the alteration has been aided by pressure, as in the formation of hornblende schist by the alteration of a dolerite.³ This difference, however, is probably due to the fact that these minerals are capable of combining many molecules in solid solution, and that this capability varies with the conditions of crystallization. Thus, at Garabal Hill,⁴ the margin of an intrusion is a hornblende diorite with about 30 per cent of hornblende, and the centre, a few feet distant, is a hornblendite with 85 per cent of hornblende, while the composition of the two rocks is approximately the same. The cases of alteration of hornblende into pyroxene would seem to be explained by reheating due to later intrusions,⁵ or to some similar cause.

Another change which may take place in the solid state is the breaking up of a solid solution on cooling. Vogt⁶ describes the separation of augite from solid solution in enstatite and also ascribes this origin to some perthitic growths.⁷

So far, only the effect of temperature on the formation of stable minerals has been considered. The conditions of pressure, however, also exert a considerable influence, particularly in many plutonic rocks. When an igneous rock contains minerals which are generally of metamorphic origin, it is assumed that these have formed under pressure. For example, garnet is a typical product of metamorphism, and when it does occur in a plutonic rock it has probably crystallized under high pressure. In the case of the Charnockite Series, the garnet seems to have originated in this way, as there is other evidence of the rocks having undergone dynamic action,⁸ while the eclogites in many cases show similar effects.⁹ Fermor¹⁰ postulates for the formation of kodurite, an infra-plutonic zone of garnet-bearing rock.

The evidence of synthetic work is likewise in favour of garnet forming only under particular conditions of pressure and probably

¹ Allen, Wright, & Clement, *Amer. Journ. Sci.*, ser. iv, xxii, pp. 385-438, 1906; Allen & White, *ibid.*, ser. iv, xxvii, pp. 1-47, 1909; Doelter, *Neues Jahrbuch*, 1897, pt. i, pp. 1-26.

² Cf., for example, Allport, *Q.J.G.S.*, xxxv, pp. 637-42, 1879; Wyllie and Scott, *GEOL. MAG.*, Dec. V, Vol. X, pp. 499-508, 536-45, 1913.

³ Teall, *Q.J.G.S.*, xli, pp. 133-44, 1885; see also Harrington, *Rec. of Progress. Geol. Surv. Canada*, 1877-8, p. 21 G.

⁴ Wyllie & Scott, *loc. cit.*

⁵ Cf. Lacroix, *Minéralogie de la France*, i, pp. 668-9, 1895.

⁶ *Q.J.G.S.*, lxx, pp. 100-1, 1909.

⁷ *Tscher. Min. u. Pet. Mitt.*, xxiv, pp. 537-42, 1905.

⁸ Holland, *Mem. Geol. Surv. India*, xxviii, pp. 117-249, 1898.

⁹ Cf. Hezner, *Tscher. Min. u. Pet. Mitt.*, xxii, pp. 437-505, 1903, for origin of eclogites.

¹⁰ *Rec. Geol. Surv. India*, xlii, pp. 208-30, 1912; xliii, pp. 41-7, 1913.

in a narrow temperature range. Numerous observers¹ have reported that garnet, on fusion, breaks up and finally recrystallizes as a mixture of other minerals such as anorthite, monticellite, melilite, etc. Attempts to synthesize garnet have not met with much success, though the formation of the mineral has been reported in a few cases.² Hence we may assume that if a rock containing garnet had crystallized by a normal cooling process, under ordinary pressures, garnet would be entirely replaced by other minerals. In some cases it is probable that some of the minerals did not form under such high pressure as the garnet, and hence the latter would be liable to undergo resorption by the residual liquid magma. The well-known celyphite border which occurs round pyrope crystals in peridotites may arise in this way by the action of a liquid residual magma on the pyrope, under pressures much lower than those at which the latter form and therefore under conditions which would render pyrope an unstable phase.

Thus it will be seen that there are grave objections to the garnets being considered as saturated or unsaturated in the way felspar or nepheline might be. If spessartite be considered as saturated merely on account of its co-existence with quartz in certain rocks, and the other garnets as unsaturated on account of the absence of this property, the result would be, not only to divide closely related garnet rocks into two widely different groups but also probably to class each with rocks from which they might differ considerably both in chemical and mineralogical composition. The conclusions of Boeke³ render it very improbable that spessartite differs essentially from the other garnets, as he finds that almandine forms a continuous series of solid solutions, with both spessartite and pyrope, and that grossularite and andradite form a similar series. The two latter, however, form with each of the others systems which conform to Roozeboom's fifth type, as does also the system pyrope-spessartite, two limited series of solid solution being formed. Any differences which do exist, are likely to occur between those minerals which give systems of the latter type, but such differences, if any, would probably be physical. Similar objections exist with regard to the micas, which also seem to form generally under particular conditions of pressure and temperature.

Although the hornblendes and pyroxenes are found along with quartz, it is probable that the members of these groups which contain the sesquioxides—alumina and ferric oxide—can react with free silica under certain conditions. The most generally accepted explanation of the presence of these oxides is that they occur in molecules of the type $R''Al_2SiO_6$ (Tschermak's silicate), where R is ferrous iron or magnesium, which molecules are obviously unsaturated with respect to silica. Harker⁴ explains certain phenomena of differentiation as due to a reaction taking place between diopside and

¹ Bourgeois, *Annales Chim. Phys.*, ser. v, xxix, p. 458, 1883; Vogt, *Mineralbildung in Schmelzmassen*, 1892, pp. 186-8, etc.

² Gorgeu, *Annales Chim. Phys.*, ser. VI, iv, pp. 536-53, 1885.

³ Boeke, *Zeit. Kryst. Min.*, liii, pp. 149-57, 1913.

⁴ *Geol. Small Isles* (Mem. Geol. Surv. Scotland), 1907, p. 91.

Tschermak's silicate with the production of olivine and anorthite. Again, minerals such as tourmaline and topaz are usually the result of pneumatolytic or fumarolic action, and as such it is impossible to deduce from their co-existence with silica in rocks that they would form during the normal cooling of an 'acid' magma.

From what has been said above it is obvious that a classification of igneous rocks can no longer be made dependent on such a factor as saturation with respect to silica, particularly when applied in this empirical fashion. During the period of cooling, rocks are subjected to many vagaries, owing to the impossibility of the external conditions being uniform, and any classification dependent on the final mineralogical composition without reference to the 'cooling-history' is not of much use. Any group of igneous rocks must be subdivided according to the method of development of the particular rocks, and it is impossible to compare directly on a purely modal basis a rock which has formed through a normal cooling process and is therefore in a state of equilibrium and one which is not in equilibrium owing to such causes as undercooling, inhibition of transformation either in the liquid or solid states, or the formation of some or all of the constituent minerals under abnormal conditions of pressure and temperature. In rocks of similar composition, the minerals which develop in the latter case are often widely different from those arising in the former one, and hence such minerals as the garnets, topaz, etc., cannot be said to be 'saturated' or 'unsaturated' in the sense that albite, nepheline, or leucite can be. Similar objections exist with regard to a classification on a basis of the chemical composition or of the 'norm' derived from it, and one of the chief advantages of the American system is that it provides an extremely good method of indexing the increasing volume of rock analyses.

These two factors, however, the chemical and mineralogical composition, are the only ones we have for a basis in classification, but they must be correlated in such a way that as much information as possible is obtained regarding the 'cooling-history' of the rocks. The crystallization of rocks can no longer be considered either as wholly fortuitous, or as wholly the result of a normal cooling process, but as the result of the operations of the laws of physical chemistry. Hence the objects of a rock classification must be to correlate rocks not only of similar chemical composition but also with similar 'cooling-histories'.

The data for this can be derived from (*a*) the determination of chemical composition, (*b*) of mineralogical composition, (*c*) the field relations of the rocks, (*d*) the evidence of synthetic work in mineralogy. The defects of most of the current classifications can be traced to the position of paramount importance given to some one of these bases and to the subordinate positions assigned to the others. The occurrence of minerals in rocks, as shown by the 'observed' facts of distribution, must be correlated with the other evidence—particularly that of field relations and of synthetic work—concerning the conditions of equilibrium both during the cooling process and in the solid phases observed in the rock. It is only in this way that we can acquire a knowledge of the genetic relationships and the general history of igneous rocks.