METALLIC SULPHIDE MELTS AS IGNEOUS DIFFERENTIATES

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ABSTRACT

Liquidus data on the system FeS-FeO-SiO_2 is used to derive approximate relationships for the liquidus of the system pyrrhotite-magnetite-gabbroic silicates. Separation of a metallic sulphide liquid from the residual silicate liquid during crystallization of silicates is possible if the oxidation potential of the magma is below some critical value.

INTODUCTION

Deposits of massive pyrrhotite, with an indicated genetic relationship with igneous rocks, are frequently postulated to have formed by some process of segregation of a pyrrhotite-rich melt from a magma. This has been an attractive hypothesis for a considerable time, perhaps because of the easy analogy with slag–matte equilibria of metallurgical systems. In common with most geological processes, which are discussed after the event, many competing hypotheses have arisen. It is not the present purpose to review all of these, but to state what is reasonably well established about relevant metallic sulphide–silicate systems and to extrapolate to magmatic compositions for semi-quantitative, physicochemical testing of the magmatic segregation hypothesis.

The discussion is simplified if only basic magmas such as gabbro are considered and the sulphide component is pyrrhotite. Preliminary study, however, showed that projection to the two-component plane leads to ambiguity, and that the simplest representational system is of three components: gabbro silicates-pyrrhotite-magnetite. This system as such has not been investigated, but the system Fe_2SiO_4-FeS-FeO, which has been studied in some detail, is a model from which semi-quantitative extrapolation is possible.

THE SYSTEM FeS-FeO-SiO_2

The system FeS-FeO-SiO_2 is not strictly ternary in the melting range due to variability of valence of iron in the liquid and crystalline phases. This can be reduced to a dependent variable by ensuring that all phases are at equilibrium with elemental iron. Thus the following phase relations are within the four-component system, projected a small amount to the three-component plane.

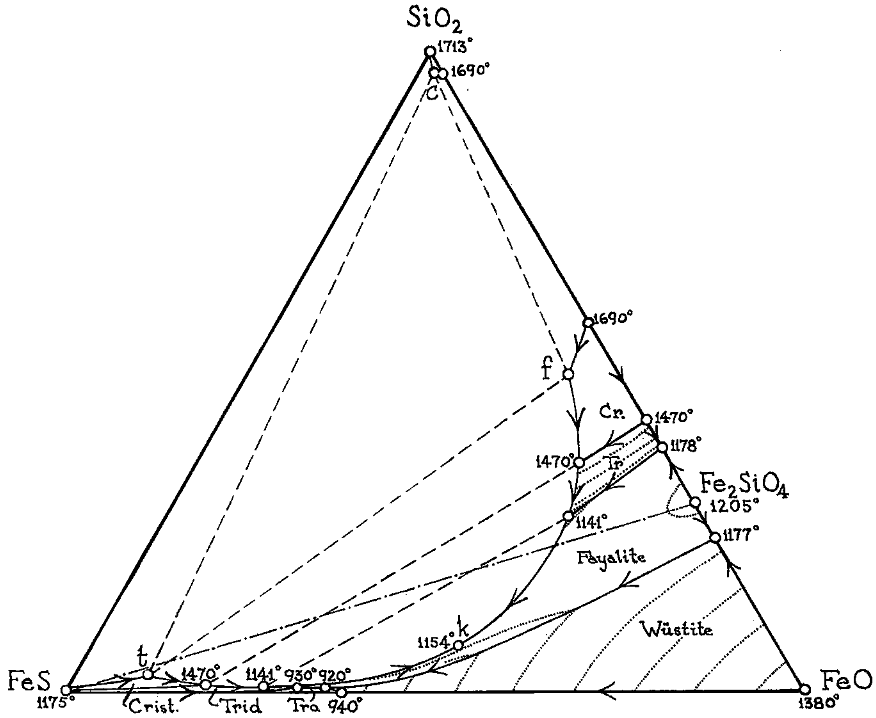

FIG. 1.

The binary system $FeO-SiO_2$ is well known from studies by Bowen & Schairer (1932). The liquidus curves in the binary systems FeS-FeO and $FeS-SiO_2$ were established by Vogel & Fülling (1948) and Ol'shanskii (1948, 1950, 1951 *a*, *b*). The liquidus relations on the $FeS-Fe_2SiO_4$ join are fairly well established by the work of Selivanov, Ginzberg, & Nikolskii (1931), Ginzberg (1933), Ol'shanskii (1948), Runnalls (1949), Curlook (1951), and Yazawa & Kameda (1953). It is now reasonably certain that there is a liquid miscibility gap along this join (*cf.* Andrew & Maddocks, 1932). Within the ternary system, there is still some uncertainty about the phase relations, but a synthesis of data from the above sources, is shown in Fig. 1.

In the ternary system, $FeS-FeO-SiO_2$, three kinds of liquid are stable with each other and with cristobalite (SiO_2). The first is near FeS in composition, low in SiO_2 but containing appreciable FeO, and has a low viscosity. The second is on the SiO_2 side of the Fe_2SiO_4 composition, and low in FeS. The third is very near SiO_2 in composition, and has a high viscosity. Iron oxide, soluble in both iron sulphide and iron silicate liquids, reduces the miscibility gap between them, as shown in Fig. 1.

The critical solution point on this miscibility gap is near 1154°, on the liquidus of fayalite. It will be noticed that the compositional tie lines across this miscibility gap cut across the FeS-$FeSiO_4$ join so that it cannot be treated as a binary system. For example, a 1/1 mixture of FeS and Fe_2SiO_4 would be completely melted at about 1200° to two liquids, the sulphide-rich liquid having appreciable FeO in solution, but little SiO_2, and the silicate liquid having a SiO_2/FeO ratio greater than in fayalite.

THE SYSTEM PYRRHOTITE-MAGNETITE-GABBRO SILICATES

In "magmatic segregation deposits" of iron sulphide and/or oxide, typical minerals are pyrrhotite ($Fe_{1-x}S$) and not troilite (FeS), magnetite (Fe_3O_4) and not wüstite (FeO). This indicates a magmatic oxidation potential greater than that which would exist in the presence of metallic iron. This must change the quantitative relations of the more reduced system, but the qualitative relations appear to be substantially the same.

The system Fe_3O_4-Fe_2SiO_4-SiO_2 is fairly well established from work by Bowen & Schairer (1932), Greig (1927), Schuhmann *et al.* (1935), and Muan (1955). The magnetite-fayalite eutectic is near 1150° and 20% magnetite, whereas the wüstite-fayalite eutectic is at 1177° and 19% wüstite. Ol'shanskii (1950) determined that the pyrrhotite-magnetite-fayalite eutectic is about 80° higher in temperature than the troilite-wüstite-fayalite eutectic, but close to the same composition. Magnetite has a higher melting temperature than wüstite (1591° and 1380° respectively). Therefore the principal effect on the iron oxide liquidus surface in moving from the system with wüstite to the system with magnetite is a steepening of the slope in temperature. Pyrrhotite has a melting point up to about 20° higher than that of troilite, depending on the Fe/S ratio (Chipman, 1948, p. 1215), so that the iron sulphide liquidus varies only slightly with oxidation potential.

When we try to derive the position of the silicate liquidus in the system pyrrhotite-magnetite-gabbro silicates, from analogies with details in the system pyrrhotite-magnetite-fayalite, there is much more uncertainty. The melting temperature of gabbro depends on its normative olivine content in large part, but water content and many other variables are quantitatively significant. A temperature range ±50° from the melting temperature of fayalite (1205°) would enclose most of the measured and calculated temperatures of complete melting of gabbro. Therefore there may be little difference between the positions of the silicate liquidus surface in the pyrrhotite-magnetite-fayalite and pyrrho-

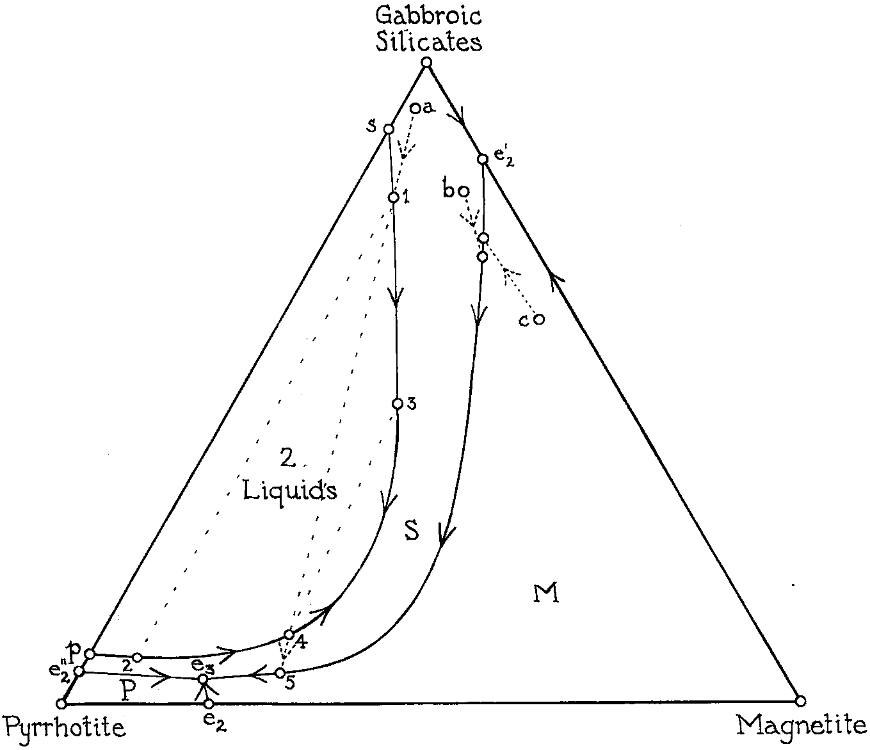

FIG. 2.

tite-magnetite-gabbro silicates. We could expect, however, a significant change in the liquid miscibility limits of the pyrrhotite-silicate join.

Probably the miscibility gap between liquid pyrrhotite and liquid silicates would be decreased by alkalis and hydrogen, which would be expected to be dissolved as sulphides and oxides in both liquids. For example, Na is partitioned equally, as weight per cent Na_2S and Na_2O. between iron sulphide liquid and iron silicate liquid and 1/1.87 between iron sulphide liquid and a calcium iron alumino-silicate liquid (Skappel, 1927). On the other hand, CaO, Al_2O_3, and Cu_2S increase the width of the liquid miscibility gap between iron sulphide and various silicate slags (Yazawa & Kameda, 1953). Commercial soda-lime glasses dissolve only about one per cent FeS (Heinrichs, 1928), and cupola slag (42% SiO_2) at 1300° dissolves 6 per cent FeS (Selivanov *et al.*, 1934). Probably the miscibility gap between liquid iron sulphide and gabbro magma at the silicate liquidus temperature would be wider than in the FeS-FeO-Fe_2SiO_4 system, but the magnitude of the difference is quite uncertain.

An estimate of the position of liquidus surfaces in the system pyrrhotite-magnetite-gabbro silicates, derived as discussed above, is shown in Fig. 2. Three liquid fractionation tracks, starting at compositions (*a*, *b*, and *c*) which have the same pyrrhotite content but different magnetite/silicate ratios, are shown to illustrate three classes of phase sequences of crystallization of compositions near the silicate corner. The projected liquidus tracks during crystallization are shown as straight lines to give qualitative relations: in detail, they are complex curves due to variation of oxidation potential during crystallization (Kennedy, 1948, 1955; Muan, 1955, 1958; Muan & Osborn, 1956; Osborn, 1959).

Starting with a liquid at point *a*, and cooling, silicates begin to crystallize when the temperature reaches the value on the liquidus surface at that point. As silicates crystallize, the composition of the residual liquid goes to point 1. It is now saturated with sulphide, and as crystallization of silicates proceeds, a sulphide melt with a composition at point 2 begins to appear. The two liquid phases change in composition, the silicate liquid from point 1 to point 3, and the sulphide liquid from point 2 to point 4, as silicates crystallize. The silicate liquid disappears as the temperature of points 3 and 4 is reached. Further crystallization of silicates is now from the metallic sulphide liquid, the composition of which goes from point 4 to point 5. Below point 5, magnetite crystallizes from the metallic sulphide liquid along with silicates (in small amount) until the liquid reaches the composition of the eutectic, e_3. Pyrrhotite, magnetite, and silicates crystallize together in that order of abundance until the liquid is used up.

Starting with a liquid at point *b*, the phase sequence during cooling does not involve a stage of crystallization in which there are two liquids. The crystallization sequence is silicates, silicates + magnetite, pyrrhotite + magnetite + silicates.

Starting with a liquid at point *c* (which could have a liquidus temperature the same as at point *a*), the crystallization sequence is magnetite, silicates + magnetite, pyrrhotite + magnetite + silicates.

The compositions of points *a*, *b*, and *c* are related in that they have the same concentration of FeS, but different ratio of ferrous to ferric iron. (A selected system containing no ferric iron would be plotted on the FeS-silicates join.) Thus compositions at points *b* or *c* can be derived from that at point *a* by partial oxidation. However, if a composition at point *a* and at the silicate liquidus temperature is oxidized at *constant temperature*, the track of the composition could be through point *b* to point *c*, at which magnetite would begin to crystallize, and from point *a* to point *c* the temperature would be *above* that of the liquidus surfaces and the silicate-magnetite cotectic line. Early crystallization of magnetite in oxidized basaltic lava has been noted in the field and has been demonstrated in the laboratory.

Needless to say, there are many natural variables other than oxidation potential in magmas and consequently there are many complications that must be considered in detailed analyses of possible phase sequences during cooling. It is reasonably certain, however, that we can accommodate physico-chemical data by adopting the working hypothesis that in basic magmas there are two classes of sequences possible, one involving separation of a sulphide melt from the silicate melt during crystallization of silicates, and the other involving no liquid immiscibility during crystallization. Both classes of paragenesis develop a final liquid fraction rich in pyrrhotite, but this terminal liquid, expected in a dry magma, may not be reached in hydrous magmas due to the appearance of a separate aqueous phase.

One of the most important points involved in future testing of the hypothesis is that, if relatively early separation and segregation of a sulphide liquid does in fact take place in some basic magmas, this liquid would have a much larger Ni/Cu ratio than a residual sulphide liquid after crystallization of the bulk silicates and magnetite. Nickel is removed from residual magmatic liquids by crystallization of silicate minerals, especially the ferromagnesian minerals, at a greater rate than copper. Therefore, in comparing the minor element composition of points 2 and e_3 in Fig. 2, both would be expected to contain most of the copper in the system, but the former, a sulphide liquid stable with a silicate melt as well as silicate crystals, would contain a considerable amount of nickel, whereas the latter sulphide liquid would be low in nickel after nearly complete crystallization of silicates and magnetite. Other minor elements, taking into account their chemical affinities, could be treated in analogous ways. If the hypothesis holds, the Ni/Cu ratio of massive sulphide blebs or segregations in basic intrusives would give a measure of the timing of beginning of sulphide melt separation, and indirectly, of the oxidation potential of the magma at the time of separation. The reverse of this relation, which may have some economic importance, is that the greater is the oxidation potential of a basic magma, the greater is the concentration of magnetite in the final rock and the lower is the probability of a nickel-rich pyrrhotite segregation. In other words, if the hypothesis holds, the Ni/Cu ratio in pyrrhotite segregations from any one class of unmetamorphosed basic intrusives would be inversely related to the magnetic susceptibility of the rock.

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