NOTES AND NEWS

THE STRUCTURAL NATURE OF THE MINERALIZER ACTION OF FLUORINE AND HYDROXYL

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INTRODUCTION

Students of pegmatites and ore deposits have been impressed with the importance of certain elements, notably H, F, Cl, C, and S, whose presence has apparently aided the formation of the minerals in the suite. Such elements are known as *mineralizers*. Mineralizers aid in the formation of minerals in two ways. In the first place, they enter into the compositions of certain of the minerals of the suite and thus are the cause of the appearance of certain minerals uncommon to the igneous rocks. It is chiefly in this way that the mineralizers reveal their presence during mineral deposition. But their presence is also attended by an increase in the sizes of the crystals deposited. From this it is deduced that the presence of mineralizers increases the fluidity of the mineralizing solutions. Fluidity is often correlated with the volatility of the mineralizers, since the common occurrence of the elements H, F, Cl, C, and S under ordinary conditions is as the gasses H_2O, F_2, Cl_2, CO_2, and SO_2. The reduction of viscosity by mineralizers may be regarded as well established by field evidence. What is the explanation of the action?

In this note it is pointed out that the mineralizing action of hydrogen and the halogens can be explained, and even put on a semi-quantitative basis.

THE NATURE OF VISCOSITY IN SILICATE MELTS

Consider a siliceous magma. Each silicon atom is surrounded by four oxygen atoms. According to the electrostatic valency principle,[1] each silicon extends a bond of strength 1 to these oxygens; each oxygen should also receive bonds totaling its valence, namely 2. If the silicon: oxygen ratio of the melt is high, many oxygen atoms may satisfy their charge of -2 by receiving bonds of strength 1 from each of two silicon atoms. Whenever this sharing of oxygen atoms occurs, it causes the silicon and oxygen atoms to become part of an irregular but extended space network in the melt.

Now, the viscosity of a liquid pervaded by these network fragments is directly related to the average number of these Si-O-Si bridges per silicon atom. In pure melted SiO_2, there is an average of 2 bridges per Si

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[1] Pauling, Linus, The principles determining the structure of complex ionic crystals: *Jour. Am. Chem. Soc.*, **51**, 1010–1026, especially 1017–1018 (1929).

atom; in melted $MgSiO_3$ there is an average of 1 bridge per Si atom; while in melted Mg_2SiO_4 there are no bridges per silicon atom. (In the magnesium silicates, the Mg-O bridges make an inferior contribution to the viscosity.) It is for this reason that increasingly siliceous "dry" magmas are increasingly viscous. In pure molten SiO_2, the viscosity of the glass is crudely comparable with the viscosity of a cristobalite crystal, which it resembles in structure, particularly with regards to nearest neighbors and number of bridges per Si atom.

This bridge relation can easily be generalized and put into quantitative form. Let,

O = the total number of oxygen atoms in the magma;
Si = the total number of silicon atoms in the magma;
S = the total number of shared oxygen atoms in the magma;
b = the total number of bridges in the magma.

Then, the total number of oxygen atoms per silicon atom is equal to the maximum 4, reduced by the number of half-oxygens belonging to other silicon atoms due to sharing, or

$$\frac{O}{Si} = 4 - \frac{\frac{1}{2}S}{Si}. \tag{1}$$

Therefore,

$$\frac{\frac{1}{2}S}{Si} = 4 - \frac{O}{Si}. \tag{2}$$

Now, where a bridge occurs, it is shared between two silicon atoms, so the bridge-per-silicon ratio is

$$\frac{b}{Si} = \frac{S}{2Si}. \tag{3}$$

Comparing this with (2), it is evident that

$$\frac{b}{Si} = 4 - \frac{O}{Si}. \tag{4}$$

In other words, the bridge density, per silicon, is 4 reduced by the oxygen: silicon ratio.

THE RÔLE OF FLUORINE AND HYDROXYL

In case an OH^- or an F^- (or other halogen) ion is substituted for an oxygen atom at the corner of a silicon tetrahedron, the substitution removes a possible network bridge. This is because the sum of electrostatic valence bonds which can be received by a univalent ion is limited to 1. Thus, a single silicon atom saturates an OH^- or F^- ion. Of course, each oxygen bridge must be replaced by two OH^- or F^- ions in order to satisfy the two silicons on opposite ends of the substituted bridge.

The effect of hydroxyl or fluorine can be incorporated into (4), thus expressing the effect quantitatively. Let F be the total number of F^-

ions, and let OH be the total number of OH⁻ ions in the magma. Then since each one of these ions reduces the number of sharable oxygen atoms, the quantity $(4-F/Si-OH/Si)$ must be substituted for 4, and $(O+OH+F)$ must be substituted for O in (1), (2) and (4). Taking account of these substitutions, there results,

$$\frac{b}{Si} = \left(4 - \frac{F}{Si} - \frac{OH}{Si}\right) - \frac{(O+OH+F)}{Si} \qquad (5)$$

or

$$\frac{b}{Si} = 4 - \frac{O}{Si} - \frac{2OH}{Si} - \frac{2F}{Si}. \qquad (6)$$

We are now in a position to appreciate the "fluxing" nature of fluorine and hydroxyl. When these fluxes are missing, the transition from magma to crystals is essentially that of the freezing of a silicate melt. The crystallization process is slowed down by the structural requirement of relatively slow migration of the atoms enmeshed in the silicated space net to the growing crystal nuclei. Crystallization under these conditions is equivalent to a kind of devitrification of a glass at somewhat elevated temperatures. The introduction of enough of the fluxes OH and F, however, transforms the glass structure into a liquid structure by eliminating oxygen bridges. This action effectively breaks down the continuous silicate network into an aggregate of tiny silicate islands of molecular dimensions.

Both OH and F (as well as other halogens) are independently highly effective in doing this, as can be seen from (6). In this relation, it should be observed that *not* the weight fractions of OH/Si and F/Si are involved, but rather the atomic fractions. Since both OH and F have quite small atomic weights, a small weight percentage of either of these is very effective in eliminating oxygen bridges. Furthermore, the introduction of either of these ions is twice as effective as the corresponding introduction of an additional oxygen into the melt, since the terms OH/Si and F/Si are modified by a coefficient 2 in (6).

Of course, when OH is present in the melt, it may function not only as a terminator of a silicon bond, as outlined above, but, under favorable conditions, it may also contribute to the formation of liquid water. Such conditions occur when the temperature is sufficiently low so that there is a substantial association of OH⁻ and H⁺ to form H_2O. These functions of OH can occur simultaneously and in this way OH can contribute in a dual rôle to the transition of the magma from a glassy melt structure to a liquid structure in which crystallization occurs readily.

Conclusion

This note can be appropriately terminated by stating the conclusion that the univalent negative ions behave as mineralizers chiefly because

their presence is instrumental in causing a magma to undergo a transition from a glassy state to a liquid state.

(Arguments along somewhat similar lines can be advanced for the mineralizing action of C, P, and S, but the arguments are not so straightforward as those given above for the action of the univalent negative ions.)

THE HYDRATES OF SODIUM TETRABORATE

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During an attempt to prepare the x-ray diffraction powder patterns of the products formed during the dehydration of borax, several features were noted which we do not believe have been reported previously.

Samples of borax ($Na_2B_4O_7 \cdot 10H_2O$) were heated to constant weight at atmospheric pressure at temperatures of 80° C., 100° C. and 200 °C. Another portion of borax was dehydrated at room temperature (approximately 25° C.) over calcium chloride desiccant. After five weeks this last sample had not reached constant weight Table 1. The products were examined by the x-ray diffraction powder technique.

The powder data obtained were in good agreement with the published patterns for the deca and penta hydrates (1). The composition of these hydrates was confirmed by chemical analyses of samples prepared under controlled conditions.

TABLE 1. DEHYDRATION OF $Na_2B_4O_7 \cdot 10H_2O$

Temperature	Loss as Moles of Water	Structure
25° C.	5.5	$Na_2B_4O_7 \cdot 10H_2O$
80° C.	6.6	$Na_2B_4O_7 \cdot 5H_2O$
100° C.	8.2	Not crystalline
200° C.	8.9	$Na_2B_4O_7 \cdot 5H_2O$

The loss of water from the decahydrate and pentahydrate of sodium tetraborate without noticeable change in the x-ray diffraction pattern is evidence of the presence of water loosely held in the structure. Similar behaviour is reported in the case of calcium sulphate hemihydrate (2, 5, 7) and the zeolites (3). The fact that no x-ray diffraction pattern was given by the product from heating at 100° C. has an important bearing on the x-ray identification of sodium tetraborate in commercial products.

Sodium tetraborate tetrahydrate is found in nature as the mineral kernite. It has also been synthesized (4, 6). This synthesis was repeated, borax in a sealed tube being permitted to cool slowly from 130° C. to 65° C. The x-ray diffraction pattern of the product was the same as that