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THE STRUCTURE AND PROPERTIES OF HYDROUS GRANITIC MELTS

(Figs. 8)

A b s t r a c t : The present paper indicates that consideration of melts approaching magmas in composition as a solution of chemical compounds rather than oxide mixtures enables one to give an accurate description of their properties. The water-melt interaction is thought to involve: a) the formation of a chemical compound on water dissolution in the albitic melt; b) preferential chemical interaction with water of structural units which contain Al^{3+} ion; c) the presence of molecular water and hydroxyl groups at any total water contents. All this evidence is at variance with the popular B u r n h a m model.

Р е з ю м е: В работе показано, что рассмотрение близких по составу к магмам расплавов не как смеси окислов, а как раствора химических соединений позволяет удачно описать их свойства. Относительно взаимодействия расплава с водой утверждается: а) формирование химических соединений при растворении воды в расплаве альбита; б) химическое взаимодействие с водой в первую очередь элементов структуры, содержащих ион Al^{3+}; в) наличие воды в расплавах в двух формах, гидроксильной и молекулярной, практически при любых ее суммарных концентрациях. Все это противоречит широко распространенной модели Б е р н е м а.

A number of hypotheses that have been proposed on the structure of melts are known to fail to give a comprehensive evaluation of the structure and normally bear on some particular property. It is not as yet possible to develop some common basis to account for the whole bulk of available evidence obtained by different methods. Therefore, it seems reasonable to develop such hypothesis which while conforming to the specific task will be based on the sound physico-chemical basis.

The more critical problem in the petrology of magmatic rocks is related with the crystallization process. Consequently, the preference should be given to hypotheses based on the analyses of composition properties of melt patterns in the near-liquidus region and also taking into consideration the available evidence on the changes in T of the liquidus.

As early as 1916, L e v i n s o n - L e s s i n g (L e v i n s o n - L e s s i n g, 1950) wrote that all oxides in the molten magma are grouped into compounds according to their degree of affinity. This conclusion was drawn at a time when information on the properties of silicate melts was extremely scant. However, in the last 70 years the validity and relevance of this approach has been confirmed. The more convincing proof was obtained by comparing formation energies of compounds from oxides with melt crystallization heats (the former is by far larger than the latter). In our view, the phase relations in magmatic systems and changes in melt properties with composition are best

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described with the melt considered in terms of a solution of chemical compounds (minals) which normally make up phases crystallized from the melt.

The occurrence of chemical compounds in the melt has been observed in many studies, where the inflections in the property — composition curves correspond to definite stoichiometric compounds. This was inferred, in particular, from our generalization of data on the density and refraction indeces for glasses and the melt densities in the system R_2O—SiO_2 and RO—SiO_2 (E p e l'b a u m, 19980). The inflections in the composition — property curves correspond to stoichiometric compounds. In Fig. 1 this is shown for the volumetric properties. Inflections were also observed on compositions curves for glasses in ternary systems, in particular, on the joins SiO_2—$NaAlO_2$; $SiO_2Ca(AlO_2)_2$ (L i s e n e n-k o v — V a s i l y e v, 1979) and others, which correspond to albite and anorthite. Electrochemical studies also confirmed the occurrence of compounds in the melts Na_2O—SiO_2 (S h a k h m a t-k i n — S c h u l z, 1980; L e p i n s k y — M a n a k o v, 1977).
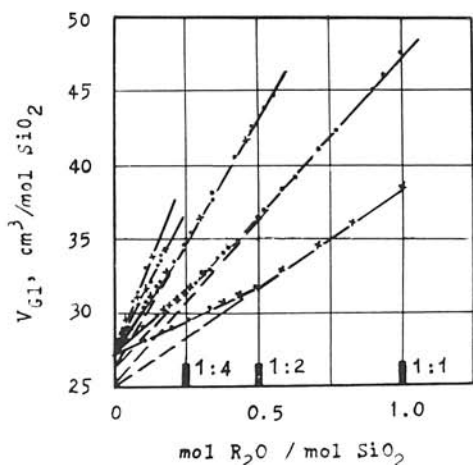

Fig. 1. Correlation between the inflections on the curves molar volume — composition in binary R_2O-SiO_2 system and stoichiometric compounds.

The presence of chemical compounds in melts has been firmly confirmed in studies on mineral dissolution in melts (E p e l'b a u m, 1980). In some cases, the species travel in the melt as a complex (with the mineral's stoichiometry), as if contrary to the inherent diffusion coefficients of different oxides they consist of. In our experiments they were anorthite and nepheline. Finally, usibility curves drawn for carefully chosen components (minals) provide for a good agreement between the experimental liquidus lines and those calculated by S c h r ö d e r' s equation. Consideration of various possible minals, determination of melting enthalpy for the crystallizing phase from the fusibility curves and comparison with independent thermochemical measurements help in turn to those the more likely composition of the minal (E p e l' b a u m, 1983).

It will be noted that treating in the melt as a solution of compounds is a simple way to explain the petrologically relevant patterns of cotectic shifts occurring in complex system when a new component is added. The formation of compounds in the melt is responsible for the eutectic changes in the systems and forms the structural — chemical basis for the acid-base interaction effect. We have shown this earlier (E p e l'b a u m — K u s n e t s o v, 1980) discussing K u s h i r o' s work. It is seen from Fig. 2 that both the character and extent of the shifts are related in the most general way to the type of the compound being formed (the ratio of components' melting enthalpies, the degree of dissociation of the new compound are by all means important, but still, the general relationship mentioned above does exist).

The problem of compounds in melts was studied by M y s e n and co-workers (S h a r m a — V i r g o — M y s e n, 1978 and others) who determined the structures of a variety of glasses and melts of different composition from Raman spectroscopy and identified in them a set of definite anionic groupings (within the certain range of NBO/T). The most essential result derived from these works in the presence of discrete structural anionic units such as SiO_4^{4-}, SiO_3^{2-},
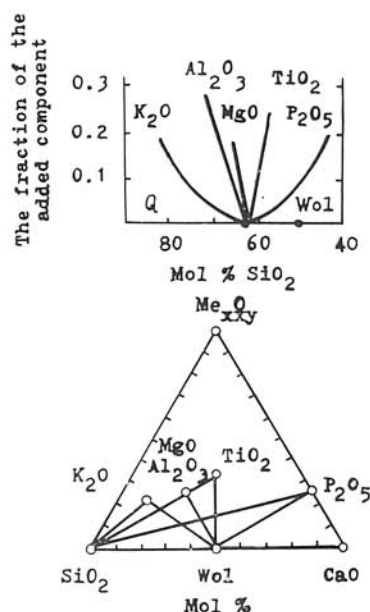

Fig. 2. A shift in the eutectics on addition of the third species is due to the formation of new compounds in the system.
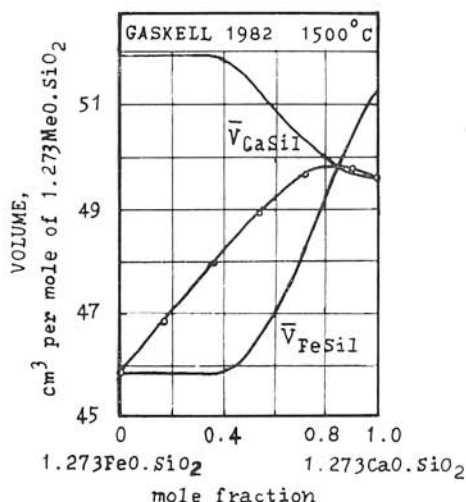
Fig. 3. Changes in the molar volume of the melts 1.273 FeO · SiO$_2$ — 1.273 CaO · SiO$_2$ after G a s k e l l.

$Si_2O_7^{2-}$ and others. Our findings are consistent with M y s e n's in this respect. However, none the less important in the mode in which anions combine with cations compensating for their charges — the fact often neglected on the assumption of sufficiently complete electrolytic dissociation. The type of groups, i. e. type and concentration of particular minals in the melt define the way in which its properties change. To illustrate this idea as well as advantages of the proposed hypothesis in the interpretation of data on melt properties, let us consider our treatment of L e e and G a s k e l l's results on the volumetric properties of melt in the system CaO—FeO—SiO$_2$. Fig. 3 shows the molar volume curve for the melts 1.273 FeO · SiO$_2$ — 1.273 CaO · SiO$_2$ from G a s k e l l's work (G a s k e l l, 1982). Consideration of molar volume variations in this binary system using traditional method reveals entirely unaccountable changes in component's partial molar volumes at calcium silicate contents above

50 mol. %. However, the composition of the melt can be represented as a mixtu-
re of orthosilicate and metasilicate. According to the maximum polarity rule,
the addition of calcium silicate to the iron silicate should lead to the recombi-
nation of cations and anions to yield calcium metasilicate and iron orthosili-
cate, as shown in Fig. 4. Up to point "k" (57 % calcium silicate) only wollastonite
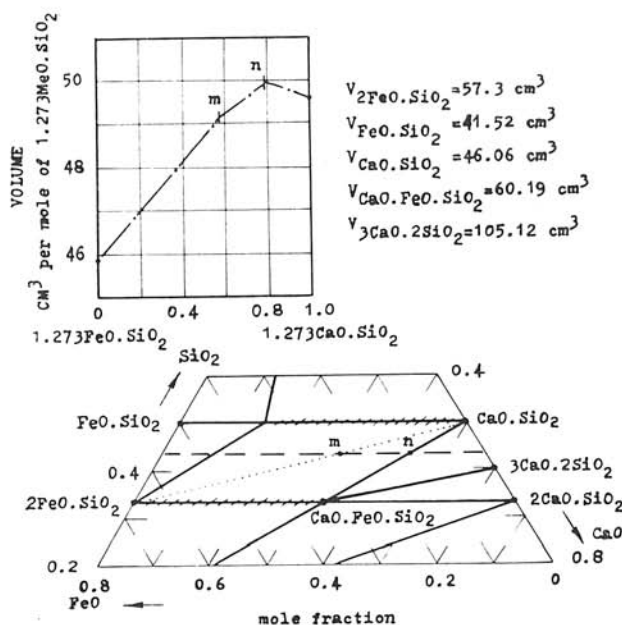molecules are formed in the melt.

$$V_{2FeO.SiO_2} = 57.3 \ cm^3$$
$$V_{FeO.SiO_2} = 41.52 \ cm^3$$
$$V_{CaO.SiO_2} = 46.06 \ cm^3$$
$$V_{CaO.FeO.SiO_2} = 60.19 \ cm^3$$
$$V_{3CaO.2SiO_2} = 105.12 \ cm^3$$

Fig. 4. The melt density — composition relations in the system 1.273 FeO · SiO$_2$ —
1.273 CaO · SiO$_2$ are allowed for accurately if the melt is considered as a solution
several compounds (the partial volumes of the compounds are assumed constant).

However, further increasing of the calcium silicate fraction from 57 to
79 mol. % will change the picture. The fayalite minal is replaced by the ferrous
montichellite. Then at a concentration above 79 mol. % the molecules of ranki-
nite should appear. Accordingly, straight lines are drawn across the marginal
areas in the graph towards the respective ordinated. The line which connects
the points k and m on the ordinates passes through the experimental point
unfortunately the only one, as it is. Consequently, there is a good agreement
between the experiment and hypothesis, and the system considered as solutions
of minals, are described additively, i. e. they are virtually ideal. The determined
partial volumes of the species-minals are constant and given in Fig. 5.
Now consider problems bearing on interaction between water and melt.
It is interesting to determine the effect water has on the liquidus relations in
the system albite-water (E p e l'b a u m, 1983), see Fig. 5. The enthalpy of mel-
ting turns out to be very close to the experimental value obtained by other

methods assuming the formation of Ab · 2H$_2$O (analcime minal). This assumption makes it possible to explain the position of the Q—Ab cotectic in the system involving H$_2$O. The calculated data are in good agreement with the experimentally determined cotectic line on the assumption that Ab 2H$_2$O is formed in the melt. Consequently, dissolution of water, at least in these systems, can be considered in terms of formation of compounds.

The composition of the "second component,, in the system Ab-H$_2$O as determined form the Ab-melting data

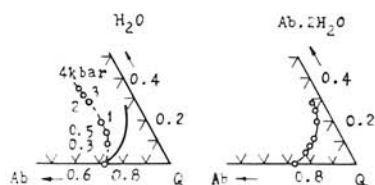| second component	H$_2$O	2H$_2$O	4H$_2$O	Ab.4H$_2$O	Ab.2H$_2$O
H$_{m'}^{Ab}$ kkal/mol Ab	5.76	3.68	2.36	3.31	13.00

Fig. 5. With the suitable choice of components a reasonable agreement can be achieved between Tuttle and Bowen's results and the theoretical cotectic in the system Q-Ab-H$_2$O.
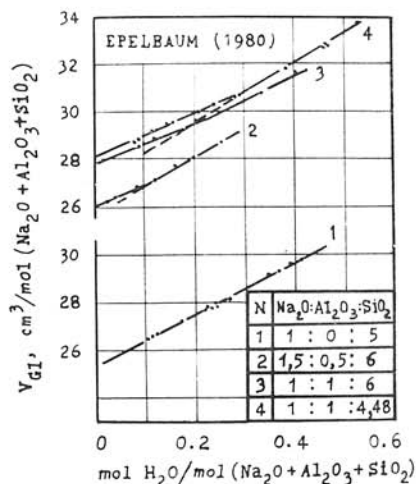

Fig. 6. Positions of the discontinuity points on the plot the molar volume versus water content for the aluminosilicate glasses are defined by their Al$_2$O$_3$ content.

It should be noted that these results are at variance with the well-known Burnham model (Burnham, 1975).

We have found that there is a discrete relationship between the glass properties and water content in the melt (Fig. 6) and that the reaction of water dissolution in the alumosilicate melt involves Al^{3+}, possibly in the form of Si-O-Al. This transpires from both correlation of the inflections in the Fig. 6 with Al$_2$O$_3$ content in melts and also from comparison of the curves showing the changes in the partial properties of silicates with content of different species as indicated in Fig. 7. These observations, too contrast with Burnham scheme.

Burnhams' model which states that the molecular water does not appear in the Ab-H$_2$O melt below 50 mol. % total dissolved water is also at variance with recent data for hydrous glasses in the near-infrared. According to Stolper (Stolper, 1982) virtually all glasses contain both molecular water and hydroxyl groups. Our independent and simultaneous study of the water albite glasses gave similiar results. The sets of data are shown in Fig. 8. The difference is that in our results hydroxyl groups are the dominant species up to 5.3 wt. %

total water. S t o l p e r' s view that the two forms of water are present in the melt at low total dissolved water contents agrees with our spectroscopic data: both molecular water and hydroxyl groups were detected in the spectrum of a glass obtained at 50 bars H_2O. This alone is sufficient to make B u r n h a m' s model invalid. Furthemore, it seems useless to recalculate molecular weights of all melts to the molecule containing eight oxydens as B u r n h a m did. The
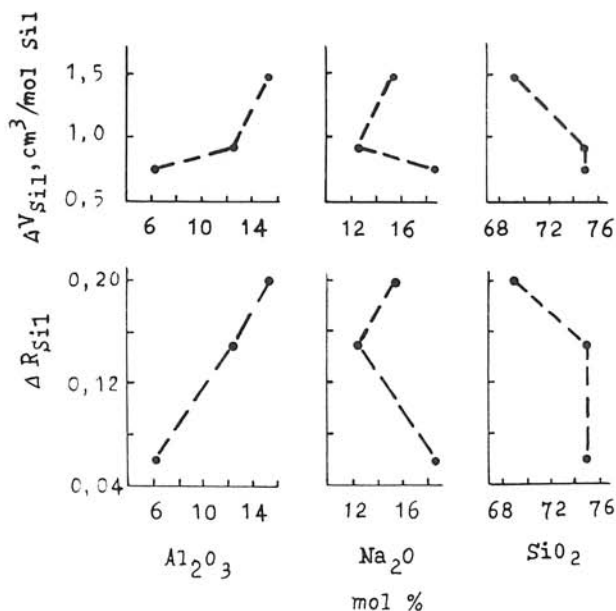

Fig. 7. Correlation between the Al_2O_3 content in glasses and change in the partial properties of anhydrous silicate on transition to higher water contents.

seemingly general pattern of water solubility in different melts breaks down once one takes into account the variations in the temperature dependence of solubility in acidic and basic melts, or significant differences in water solubility between feldspar melts (O x t o b y — H a m i l t o n, 1978). Moreover, we consider such generalizations totally inadequate because they describe the acid — base interaction between the melt and water with no allowances made for the starting acidity of the melt. Rather, it seems more necessary to find such a description of water dissolution which would allow for the dependence of the water solubility on the melt composition.

With regard to the above data interaction with water, it should be said that they suffer from the same disadvantage I had already mentioned: being obtained by different methods, they often lead to conflicting conclusions: on the one hand, the compound $Ab \cdot 2H_2O$ may be formed, on the other — the interaction of water with the Si-O-Al unit seems to be possible as well; and finally, the presence of both molecular water and hydroxyl groups is established.

Indeed, it does not as yet seem possible to work out a self-consistent quantitative model to account for all these results. On the qualitative side, however, the situation is not as bad as that, because water dissolution in such melt involves interaction with the Si-O-Al unit of the albite molecule. At the same time molecular water is not necessarily to be thought as physically dissolved but it may occur in the same form as that found in zeolites. So, the general formula of the new molecules approaches $Ab \cdot 2H_2O$.

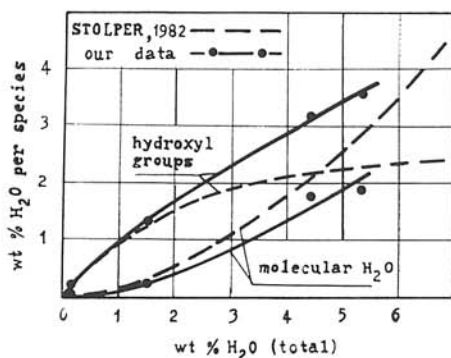Further study is needed to test the validity of the proposed scheme.

Fig. 8. The infrared spectroscopy analysis clearly indicated that both molecular and hydroxyl water is present in the melt.

REFERENCES

BURNHAM, C. W., 1975: Water and magmas: a mixing model. Geochim. cosmochim Acta. (London), 39, 8, pp. 1077—1084.

EPEL'BAUM, M. B., 1980: Silicate melts with volatiles. Nauka (Moscow), 256 pp.

EPEL'BAUM, M. B., 1983: On the choice of minals in silicate melts. Ocherki phisiko-khemicheskoi petrologii. Nauka (Moscow), 11, pp. 214—19.

EPEL'BAUM, M. B. — KUSNETSOV, A. D., 1980: On cotectic relations in a closed ternary system and acid-base interaction effect. Geokhimiya (Moscow), 4, pp. 513—519.

GASKELL, D. R., 1982: The densities and structures of silicate melts. Advances in physical geochemistry. Springer Verlag (New York), 2, pp. 153—172.

LEPINSKY, B. M. — MANAKOV, A. I., 1977: Physical chemistry of oxide and oxifluoride melts. Nauka (Moscow), 190 pp.

LEVINSON-LESSING, F. Yu., 1950: Selected works: Advances in petrography in Russia. Ed. AN SSSR (Moscow), 2, 322 pp.

LISENENKOV, A. A. — VASILYEV, A. I., 1979: Study of interactions on the joins $CaAl_2O_4$-SiO_2 and $CaGe_2O_4$-SiO_2 by physico-chemical methods. Phisika i Khimiya stekla (Leningrad), 5, pp. 537—545.

OXTOBY, S. — HAMILTON, D. L., 1978: Water in plagioclase melts. Natur. Environ. Res. Council Publs. (Manchester), Ser. D., 11, pp. 36—37.

SHAKHMATKIN, B. A. — SCHULZ, M. M., 1980: Thermodynamic properties of glass-forming melts in the system Na_2O-SiO_2 in the temperature range 800—1200 °C. Phisika i Khimiya stekla (Leningrad), 2, pp. 129—135.

SHARMA, S. K. — VIRGO, D. — MYSEN, B., 1978: Structure of glasses and melts of $Na_2O.xSiO_2$ (x = 1, 2, 3) composition from Raman spectroscopy. Carnegie Inst., (Washington), Year b. pp. 649—652.

STOLPER, E., 1982: Water in silicate glasses: an infrared spectroscopic study. Contr. Mineral. Petrology (Berlin — New York), 1, pp. 1—17.

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