

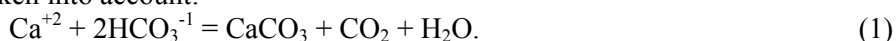
AT THE MECHANISM OF ALLOCATION OF MINERALS: MAGMATIC AND METAMORPHIC ROCKS

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The mechanism of formation of mineral (MF) is meant as the chemical reaction bringing in its allocation (Макаров, 2001). Frequently the decision of a problem leans on results of experiments which speak about possible, instead of valid processes MF. So for garnets it is offered not less than 37 equations of formation reactions which choice for the decision of genetic tasks is not unequivocal. In the scientific practice task comes nearer to the named task about forms of a presence of substance in a solution (Щербина, 1956; Dialects etc., 1966; Диман etc., 1966; Дурасова, 1971; Badgers, 1974; Дадзе, 1981; Некрасов, 1984; etc.). Apparent continuation of the decision of a similar task is «thermodynamic modelling». It is based on calculation of forms of a substance presence on the thermodynamic data in real natural solutions.

At the decision of the declared task (Макаров, 1993, 1997, 2001) it is determined T formations ($T_f = T_{is}$) minerals (M) on the isotope data as concentration of isotopes does not depend on pressure (P). This temperature (T_{is}) is compared to independent reference definitions T_s (homogenization and melt inclusions). As agreed T_{is} and T_s the composition of connection (C), taking place in thermodynamic, including isotope (ITB), balance with investigated M comes to light. It is supposed, that the mineral M and connection C are formed at disintegration of initial substance (IS) as then there is clear an existence of this balance. This position is illustrated by the analysis not absolutely exact equation (1): in it water of solvent (H_2O)_s is not taken into account:



Entering it in (1), we receive true variant:



The last shows, that components in brackets are formed at decomposition associate of HCO_3^{-1} (hydrated CO_2), i.e. $2[HCO_3^{-1}] \rightarrow 2[CO_2-OH] \rightarrow [CO_3^{-2}-CO_2-H_2O]$. The similar mechanism of an explanation of isotope balance (IB) is probable in reactions, for example, $Si(OH)_4 \rightarrow SiO_2 + 2H_2O$ (Ганеев, 1975; Rimstidt, Barnes, 1980), conducting to sedimentation of quartz, cassiterite and etc. minerals. The aforesaid indirectly proves to be true formation IB minerals in experiences with graphite (Банникова etc., 1987), sheelite (Устинов etc., 1990). Hence, established in (2) IB reflects intermolecular IB, and the chemical compound of M and C allows determining composition of initial substance (IS).

For the decision of the task new types of isotope thermometers (ITM) [1] are created. In a basis of their use with reference to connections with isotopes of two elements (mica, carbonates, sulfates etc.) lay axioms: the same mineral of M which in all samples is formed in one and two times, and at same T is analyzed; M is in a condition the shooting ITM with the same connection C; in isothermal conditions equality $1000 \ln \alpha (M-C) = f(T) = \text{const}$ for all samples, where α is a parameter thermodynamic is carried out fractionation of isotopes between M and C. Then equality $S = (\ln \alpha_2) / (\ln \alpha_1) = f(T)$ takes place.

Classes ITM are allocated:

A. Two-mineral isotope geothermometers

And 1. Monoelement ITM with simultaneously formed minerals. It is unique form ITM used now; it is based on reaction of an exchange of kind $M_1^* + M_2 = M_1 + M_2^*$, where (*) - enrichment of heavy isotope. At its use numerous mistakes are supposed. As a whole, this form ITM has phenomenological and is not intended for definition T.

And 2. Mono- and two-element ITM with minerals in any time and temperature relations, and $T_{о\text{о}p}$ one (standard) from them and its composition $C_{\text{стан}}$ are known beforehand.

B. Monomineral ITM are based on the analysis of different elements isotopes distributions in one mineral (carbonates [O-C], muskovites and biotites - [O-H], sulfates [O-S] and so forth).

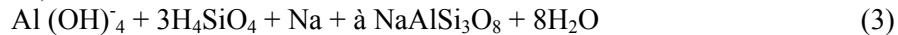
We accept (Галимов, 1973), that in reactions of natural MF the condition the shooting ITM in system of M-C is always kept. Apparent infringement the shooting ITM is caused: а). influence of the imposed processes, in particular, diffusion; б). Methodical mistakes (the most widespread case). в). mistakes of a

choice of a component C. The decision of a task based on construction on several samples of an isotherm with angular factor $S = f(T)$.

Some results of the decision of a task about mechanism of MF are given below.

Analysis $T_{из}$ of granitic minerals which the magmatic nature does not cause doubts in researchers, results in a sequence of crystallization: (Bi, Q) ($\approx 750^\circ\text{C}$) > Il (≈ 650) > Mt (600-650) > Kf (≈ 570) > Mu (450-570) > Al (440-500) > Gr (≈ 300) (Макаров, 1991, 2001, 2002). The same order of allocation of minerals is revealed in metamorphic rocks is not dependent on metamorphism steps. The data for quartz (Q) and garnet (Gr), being coordinated with results of the analysis melt inclusions, do not correspond to the accepted point of view on conditions of their allocation. So Q does not finish process of crystallization of acid magma, and together with biotite (Bi) is an early mineral. Low Gr $T_{оф}$ are established in rocks even high metamorphism steps. As a whole, the order of allocation of minerals in metamorphic rocks and rocks which magmatic nature does not cause in researchers any doubts, reflects them metasomatic transformation.

All silicate minerals isotopically equilibrium to water (Макаров, 1991, 1996, 2002). They are formed at decomposition hydrated complexes under the circuit $(\equiv\text{Si} - \text{O} - \text{Si} \equiv)_{\text{melt}}^{+6} \rightarrow 2(\text{H}-\text{O}-\text{Si} \equiv)_{\text{melt}}^{+3}$ [Анфилов etc., 1985]. In a vicinity of point T_{crs} due to polymerization sybotoxic groups $(\equiv\text{Si} - \text{O} - \text{H})_{\text{melt}}$ it is formed associate of H_4SiO_4 , decomposed under circuit $\text{H}_4\text{SiO}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}$. The received results correspond to formation (education), for example, Albite (Al) on reaction (3) (Reesncon, Keller, 1965; Рыженко etc., 1981; Алексеев etc., 1989).



The close mechanism of sedimentation can be accepted for feldspar (Kf), Bi and muscovite (Mu). Situation with ore minerals is different.

Magnetite (Mt) of magmatic and some metamorphic rocks is allocated in IB with rutile (Ru) on reaction $6\text{Il} + \text{O}^{2-} \rightarrow 6\text{Ru} + 2\text{Mt}$ (Jarosh, 1955; Busek, Kell, 1966; Karnegi Institute, Washington, 1971) at decomposition ilmenite (Il). This concerns also reaction of formation itself Il due to decomposition ulvospinel (Fe-pseudobrukite) $\text{Fe}_2\text{TiO}_5 \rightarrow \text{Il} + \text{Ru}$. In contact rocks IB between Mt- CO_2 it is caused by destruction Fe- containing carbonates $(3\text{FeCO}_3 + \text{O} \rightarrow \text{Mt} + 3\text{CO}_2$ [Mueller, 1973] or $6\text{FeCO}_3 \rightarrow \text{Mt} + 5\text{CO}_2 + \text{C}$ [Miller etc., 1972]).

Studying MF is possible also on the analysis of isotherms of distribution of relations of crystal-chemical factors of characteristic elements (Fe^{+3} , Fe^{+2} , Al, Mg, Ca etc.) and search of minerals M_x , in thermodynamic balance with which researched M is allocated (Макаров, 1991, 1999). It is supposed, that M-form during disintegration of initial substance (IS), keeping a condition of thermodynamic balance between products of disintegration. Use of geochemical geothermometers is based on theory ITM stated above.

Ore Mt (Бондарева, 1977, 1978) Odessa-Belocerkov zones (Ukraine) for $T_3 = 500^\circ\text{C}$ and $P=1$ kbar it is equilibrium olivine (Ol) [on (Fe^{+2}) - (Ca-Mg-Mn)] and to corundum (Cor) [Fe^{+3} -Al], forming association Mt-Ol-Cor. Last by analogy to experiments (Михеев, Стулов, 1955) is formed at decomposition rich Fe^{+2} - and Fe^{+3} - chlorite.

Pyrope (Pyr) of eclogite xenolites in Yakutia kimberlite pipes (Харьків etc., 1989) associates with diopside and enstatite (Px), it is rare kyanite. For Pyr $T_f = 1000-1200^\circ\text{C}$, the Px = $980-1400^\circ\text{C}$; $P = 40-75$ kbar (Пономаренко, 1976; Pike, 1976; etc.).

Samples of analyses are described by the equations (Макаров, 2002) which correspond to balance Pyr with Px at $T = 1200^\circ\text{C}$ and $P \sim 25$ кбар, that will be coordinated to geological supervision. Association of Pyr- Px is formed at decomposition IS. The estimation of composition of IS bases on ratio Pyr/Px: more often ≈ 1.0 . Then $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{CaMgSi}_2\text{O}_6 = \text{CaMg}_4\text{Al}_2\text{Si}_5\text{O}_{18}$ is cordierite (Crd), formed, probably, on reaction (Anortite) + (Mg-Ol) = 2 (Mg- Crd) (McLelland, Whitney, 1980)).

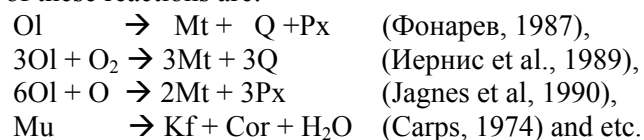
For chromites and Cr- spinels from pipes «Удачная» I and «Мир» (Yakutia) (Ковальский etc., 1979) $T_f \approx 1240^\circ\text{C}$ (Таран etc., 1989), P has no precise values. Parameters of the equation

$\ln [(Cr+\text{Fe}^{+3})/Al] = -1.27 \ln (\text{Mg}/\text{Fe}^{+2}) + 2.65$ at $T = 1200^\circ\text{C}$ and $P = 25-30$ kbar correspond to reactions of exchange: $\text{FeCr}_2\text{O}_4 + \text{Mg} = \text{MgCr}_2\text{O}_4 + \text{Fe}$ and $0.5\text{MgAl}_2\text{O}_4 + \text{Cr} = 0.5\text{MgCr}_2\text{O}_4 + \text{Al}$.

The combination of isotope and thermodynamic (geochemical) methods of definition $T_{оф}$ of minerals creates is basis for construction of reactions MF. One of examples of it (reaction of sedimentation calcite Cc) is described above. On the isotope data in wide interval T ($0-450^\circ\text{C}$) it is established IB in associations

Cc- CO_2 and Cc- H_2O^* . These combinations correspond to sedimentation of a mineral on the equation (1). The second case is considered on an example of reaction (3): on the isotope data the isotope system Al- H_2O is always observed; on the geochemical data isomorphic replacement between ions K^+ and Na^+ is observed, i.e. elements are in the dissolved ionic form in a solution. These data correspond to distribution of all elements only on the equation (3). Absence of the thermodynamic data for $\text{Fe}(\text{OH})_4^-$ confidently more does not allow to prove reaction (3) as instead of $\text{Al}(\text{OH})_4^-$ can be connection $\text{AlO}_2^-(\text{FeO}_2^-)$.

The received results eliminate the reactions, which are not having under self the sufficient basis; they can be examined as false; they do not explain real distribution of isotopes and elements between products of reactions. Examples of these reactions are:



Reference

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(22) 2004
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2004
 URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2004/informbul-1_2004/izotop-2e.pdf
 Published on July, 1, 2004

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