MODELLING OF P–T PARAMETERS OF PHASE EQUILIBRIA

V.K.Karzhavin, Z.M.Voloshina
Geological Institute, Kola Science Centre RAS, Apatity

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Thermodynamic investigation is being paid a great attention to in the analysis of the processes accompanied with chemical and phase transformations in a wide interval of temperatures and pressure. For the equiponerous or locally equiponderous processes the calculation of the state parameters allows one to model real conditions with relatively high accuracy and to present information that is difficult to receive by experiments. It is commonly supposed that the composition and thermodynamic features of the equiponderous products unequally depend on elementary composition, temperature and pressure (1). To evaluate the present parameters is the main target in solution of the inverse task of the chemical equilibrium. And it allows using the thermodynamic study methods in a wide range for the solution some geological problems. Temperature and surrounding pressure evaluation (thermo-barometric calculation) in which the minerals were formed is the important task to forecast the developing postmagmatic (metamorphic) processes in natural conditions. In this case the chemical composition of minerals combined in a natural sample is investigated and the calculation of the equilibrium constants of the chemical reactions is made. To evaluate the dependence of the equilibrium constant on temperature at the invariable pressure the following equation is used: $dLnK/dT = \Delta H/RT^2$. To evaluate the dependence of the equilibrium constant on pressure for the isothermal conditions: $dLnK/dP = \Delta V/RT$.

The reliable results of investigation could be achieved in using the wide enough data on thermodynamic conditions of the natural system formation. But in a traditional investigation only some of the chemical compounds that take part in the reactions are taking into account. The quantity correctness of the chosen components in a system should provide the possibility to find out all the reactions in order to receive the objective information. It's good to use TWQ method for evaluation of the equilibrium state in the investigated system. The calculation of temperature and pressure values on the data on chemical compositions of all present phases could be done with the TWQ method (2). The inner compatible base of thermodynamic data on chemical compounds helps to make automatically the calculation with the use of the following equations:

$$T = [\Delta H^o + \Delta V^o (P-1)] / (\Delta S^o - R \, Ln \, K) \text{ and } P = (- RT \, Ln \, K - \Delta H^o + T \Delta S^o) / \Delta V^o.$$

The calculation of the equilibrium constants of chemical reactions is made as the function of temperature and pressure. The calculating curves of the equilibrium constants should cross in one point on P-T plane if the equilibrium exist in the studied system. The equilibrium medium is determined by phase and chemical compositions. And the equations to determine the P, T, and compositions of the equilibrium phases in the cross point are made from the condition of equilibrium of chemical potentials of the system components in all phases. If the studied system is not equilibrium then on P - T plane on account of the displacement of the curves of equilibrium constants an area is formed. The size of this area is in proportion to the deviation rate of the system from equilibrium state. The method gives the opportunity to solve the inverse task also. It means to determine the existence of equilibrium in a studied system on account of the known values of temperature and pressure. The presented work is aimed at evaluation of the possibilities of the TWQ method.

The base of our investigation is the petrographical and microprobe study of the chemical compositions of the mineral phases. The process of model investigations provides the possibilities to evaluate conditions for solving the determination task of P – T parameters of transformation of the studied natural system into the secondary (metamorphic) minerals at the existence of volatile components at the condition of possible equilibrium. Metamorphic system as a compound natural system is determined as a result of evolutive complex of all possible processes in some definite relations. As an example for investigation we took a sample (Panskaya intrusion, Kola Peninsula) with the following mineral association: plagioclase, amphibole, serpentine, chlorite, clynozoisite. The chemical composition of the mineral phases is presented in the table:

	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O
Amphibole 1	53.40	5.36	11.00	15.61	12.51	0.74	0.18
Amphibole 2	52.85	6.45	10.86	15.01	11.95	0.90	0.20
Clynozoisite	40.37	24.72	10.26	0.15	22.76	0.27	0.00
Plagioclase	55.58	28.30	0.00	0.00	10.38	5.74	0.00

The data show the studied mineral system with the following elementary composition: Si, Al, Fe, Ca, Mg, Na, K, H, O. According to the described petrographic composition of the natural sample the following chemical compounds were included into the studied system on the initial stage: $NaAlSi_3O_8$ (albite), $CaAl_2Si_2O_8$ (anorthite), $Ca_2Fe_5Si_8O_{22}(OH)_2$ (actinolite), $Ca_2Mg_5Si_8O_{22}(OH)_2$ (tremolite), $Ca_2Al_3Si_3O_{12}(OH)$ (clynozoisite), $Ca_2FeAl_2Si_3O_{12}(OH)$ (epidotite), Fe_3O_4 (magnetite) and SiO_2 (α-quartz). The combined database of the TWQ method is the source of thermodynamic values of compounds. The reference material

(3) is used in the database. At the initial stage of investigation the variant of "dry" mineral system was studied but chemical relations between the mentioned compounds hadn't been determined. With the successive introduction to the studied mineral system of the volatile components: water, hydrogen, and oxygen some chemical reactions were determined but the evaluation of P-T parameters was impossible. At the result of calculation of System 1, in which all the volatile components are present, we determine the existence of 11 chemical reactions and the lack of equilibrium in such a complex system (Fig.1).

According to the analysis, the lack of the equilibrium in the system is caused by the reactions with hydrogen. The subsequent thermodynamic calculation of the system, at the lack of hydrogen, established that the rest chemical compounds could be in an equilibrium state between each other at T = 404^0C and P = 215 MPa. Under these conditions 7 reactions were determined. The equilibrium constants of them on P-T plane crossed in one point:

$$26\ CaAl_2Si_2O_8 + 10\ Ca_2FeAl_2Si_3O_{12}(OH) + Ca_2Fe_5Si_8O_{22}(OH)_2 + 6\ H_2O =$$
$$=24\ Ca_2Al_3Si_3O_{12}(OH) + 5\ Fe_3O_4 + 18\ SiO_2 \quad (1)$$
$$24\ Ca_2Al_3Si_3O_{12}(OH) + 4\ Fe_3O_4 + 12\ SiO_2 + O_2 =$$
$$=24\ CaAl_2Si_2O_8 + 12\ Ca_2FeAl_2Si_3O_{12}(OH) + 6\ H_2O \quad (2)$$
$$2\ CaAl_2Si_2O_8 + Ca_2Fe_5Si_8O_{22}(OH)_2 + O_2 = 2\ Ca_2FeAl_2Si_3O_{12}(OH) + Fe_3O_4 + 6\ SiO_2 \quad (3)$$
$$2\ Ca_2Fe_5Si_8O_{22}(OH)_2 + 24\ Ca_2Al_3Si_3O_{12}(OH) + 2\ Fe_3O_4 + 3\ O_2 =$$
$$=20\ CaAl_2Si_2O_8 + 16\ Ca_2FeAl_2Si_3O_{12}(OH) + 6\ H_2O \quad (4)$$
$$12\ Ca_2Fe_5Si_8O_{22}(OH)_2 + 24\ Ca_2Al_3Si_3O_{12}(OH) + 13\ O_2 =$$
$$=36\ Ca_2FeAl_2Si_3O_{12}(OH) + 8\ Fe_3O_4 + 60\ SiO_2 + 6\ H_2O \quad (5)$$
$$36\ CaAl_2Si_2O_8 + 6\ Ca_2Fe_5Si_8O_{22}(OH)_2 + 6\ H_2O + 5\ O_2 =$$
$$= 24\ Ca_2Al_3Si_3O_{12}(OH) + 10\ Fe_3O_4 + 48\ SiO_2 \quad (6)$$
$$24\ Ca_2Al_3Si_3O_{12}(OH) + 4\ Ca_2Fe_5Si_8O_{22}(OH)_2 + 5\ O_2 =$$
$$=16\ CaAl_2Si_2O_8 + 20\ Ca_2FeAl_2Si_3O_{12}(OH) + 12\ SiO_2 + 6\ H_2O \quad (7)$$

On the analysis data of chemical reactions (1-7) the lack of compounds bearing sodium and magnesium in their composition is observed. This is the result of non-correct selection of the chemical compounds to the studied system that could take part in the reactions. In spite of this fact we determine that the established by the chemical reactions equilibrium presents in the system with the mentioned composition of minerals but with absence of albite and tremolite. Some affords were taken to indemnify sodium and magnesium by some chemical compounds bearing them. The following minerals bearing sodium and magnesium were introduced into the system separately and in pairs: pargasite, magnesiuoribekite, edenite, glaucophane. At the result of numerous variants of additionally investigations it was established that any complication of the system destroyed the equilibrium state of the system. The equilibrium state in the system composed of all mentioned minerals was established by substitution of actinolite (active agent in reactions 1, 3-7) by pargasite [$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$]. According to thermodynamic calculations the equilibrium in System 2 is described by the following chemical reactions:

$$4\ Ca_2Mg_5Si_8O_{22}(OH)_2 + 14\ CaAl_2Si_2O_8 + 5\ NaAlSi_3O_8 + 4\ H_2O=$$
$$=6\ Ca_2Al_3Si_3O_{12}(OH) + 5\ NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 27\ SiO_2 \quad (8)$$
$$24\ Ca_2Al_3Si_3O_{12}(OH) + 4\ Fe_3O_4 + 12\ SiO_2 + O_2 =$$
$$=12\ Ca_2FeAl_2Si_3O_{12}(OH) + 24\ CaAl_2Si_2O_8 + 6\ H_2O \quad (9)$$
$$12\ Ca_2Mg_5Si_8O_{22}(OH)_2 + 30\ Ca_2Al_3Si_3O_{12}(OH) + 15\ NaAlSi_3O_8 + 8\ Fe_3O_4 + 2\ O_2 =$$
$$=6\ CaAl_2Si_2O_8 + 24\ Ca_2FeAl_2Si_3O_{12}(OH) + 15\ NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 57\ SiO_2 \quad (10)$$
$$6\ Ca_2Mg_5Si_8O_{22}(OH)_2 + 192\ Ca_2Al_3Si_3O_{12}(OH) + 20\ NaAlSi_3O_8 + 36\ Fe_3O_4 + 9\ O_2 =$$
$$=160\ CaAl_2Si_2O_8 + 108\ Ca_2FeAl_2Si_3O_{12}(OH) + 20\ NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 38\ H_2O \quad (11)$$
$$48\ Ca_2Mg_5Si_8O_{22}(OH)_2 + 96\ Ca_2Al_3Si_3O_{12}(OH) + 60\ NaAlSi_3O_8 + 28\ Fe_3O_4 + 6\ H_2O + 7\ O_2 =$$
$$=84\ Ca_2FeAl_2Si_3O_{12}(OH) + 60\ NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 240\ SiO_2 \quad (12)$$
$$Ca_2Mg_5Si_8O_{22}(OH)_2 + 32\ CaAl_2Si_2O_8 + 20\ NaAlSi_3O_8 + 4\ Fe_3O_4 + 10\ H_2O + O_2 =$$
$$12\ Ca_2FeAl_2Si_3O_{12}(OH) + 20\ NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 96\ SiO_2 \quad (13)$$

As pargasite is a high-temperatureer mineral, its appearance in the system transformed the previous established parameters into the interval of higher temperature. The equilibrium constant curves of the chemical reactions data crossed on P-T plane at T = 443^oC and P = 259 MPa

The described material shows the possibilities for thermodynamic calculation to determine equilibrium parameters on results of chemical analysis and chemical reactions in the studied system. It is noted that the positive solution for determination of pressure and temperature values is in condition of correct task.

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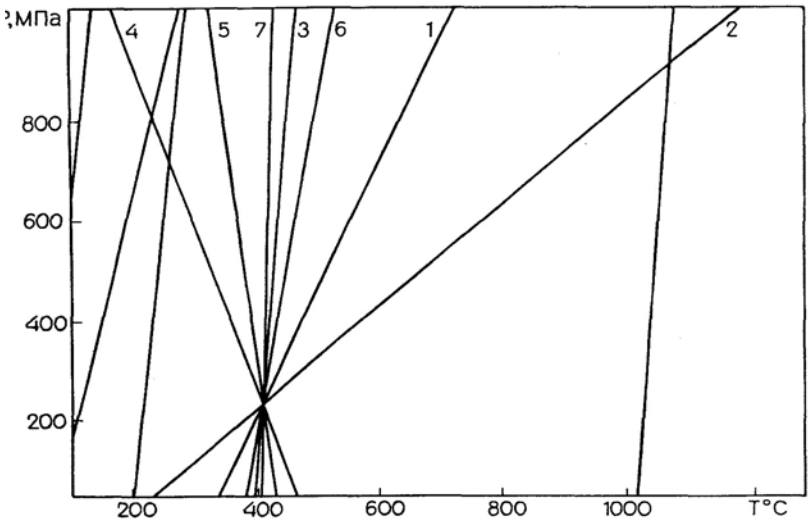

Fig. 1. P-T diagramm (see text)

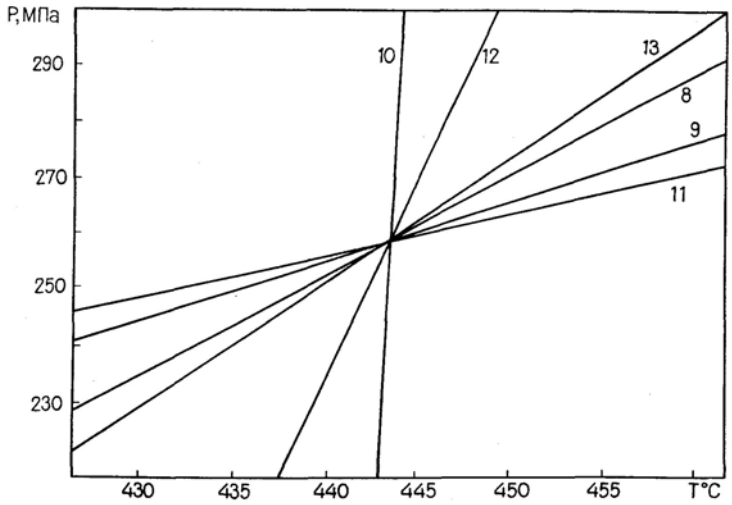

Fig. 2. Estimated P-T parameters of natural sample according to equilibrium system 2