

Some Energetic Properties of Mineral Assemblages

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The energetic aspects of redistribution of chemical bonds of lithospheric material during metamorphism, metasomatism, and hydrothermal activity attract interest in connection with the behavior of chemical elements (concentration and dispersion) in PT -gradient fields and the individual properties of atoms. The main function (isobaric–isothermal potential) used to study the phase relations in heterogeneous systems does not make it possible to analyze the transformation of chemical bonds during the change of mineral assemblages in rocks initiated by variation of intense parameters. The atomization energy [7] determined through thermodynamic constants of individual substances can be used to study the energetics of a substance at a given level of its organization.

Until now, this value was largely applied to the description of properties of minerals. In the energetic analysis of rocks on the basis of this value [2, 9], the calculations were performed by summation of atomization energies of individual minerals under normal conditions. The average specific mass atomization energy (E_m , kJ/g) of metamorphic mineral assemblages is estimated in this communication. In contrast to other studies in this field, the E_m values of coexisting equilibrium minerals were calculated at temperatures and pressures corresponding to the formation conditions of these assemblages. The main result of the study is the conclusion of the invariability of the total energy of chemical bonds in metamorphic rocks during their transformation within a wide PT range.

The calculations were based on equilibrium assemblages determined by computer modeling with the application of various software at several stages: (1) construction of PT projections of general phase diagrams of model systems with the Thermocalc v3.23 software package [13] based on the principles of the

solution of nonlinear equation systems with the application of the internally consistent thermodynamic dataset HP98 [10]; (2) calculation of equilibrium mineral assemblages in divariant fields of the obtained projections by the Gibbs energy minimization method with application of the Selector-Windows software package [3] (thermodynamics of minerals and aqueous solutions based on HP98 and SUPCRT92 databases (1998) [9], respectively); (3) calculation of thermodynamic function increments of minerals for PT conditions of their equilibrium assemblages with the tabulation function of the Selector-Windows software package; (4) calculation of the T -increments of formation enthalpy of monatomic gases of chemical elements with the Thermo Build software [12] and the NASA Glenn thermodynamic database (P -increments were omitted in this study); (5) calculation of average E_m values for equilibrium assemblages at various T and P through the data obtained at the preceding calculation stages according to the technique proposed in [1]. In calculations at the second stage, a pure water fluid and rock/water (R/W) ratio equal to 10 were accepted.

We analyzed the simplified thermodynamic models of phase relations in metapelites based on KMASH and KFASH subsystems of the KFMASH pelitic system (Figs. 1a, 1b), metabasites based on the CMASH system (Fig. 1c), and metamorphosed ultrabasic rocks based on the MASH system (Fig. 1d). Since the determination of E_m is applicable only to the pure stoichiometric phases, the solid solutions were excluded from the model. The input data for determining mineral compositions of the assemblages were represented by the following real chemical compositions of metapelites [4], basalts [6], and harzburgites [5] (wt %): K_2O 2.89, MgO 5.84, Al_2O_3 19.24, and SiO_2 72.03 (KMASH); K_2O 2.81, FeO 8.24, Al_2O_3 18.76, and SiO_2 70.19 (KFASH); CaO 11.21, MgO 7.72, Al_2O_3 19.65, and SiO_2 61.42 (CMASH); and MgO 51.03, Al_2O_3 0.90, and SiO_2 48.07 (MASH). The points of E_m measurements are indicated in each of the presented phase diagrams. The respective E_m values with qualitative and

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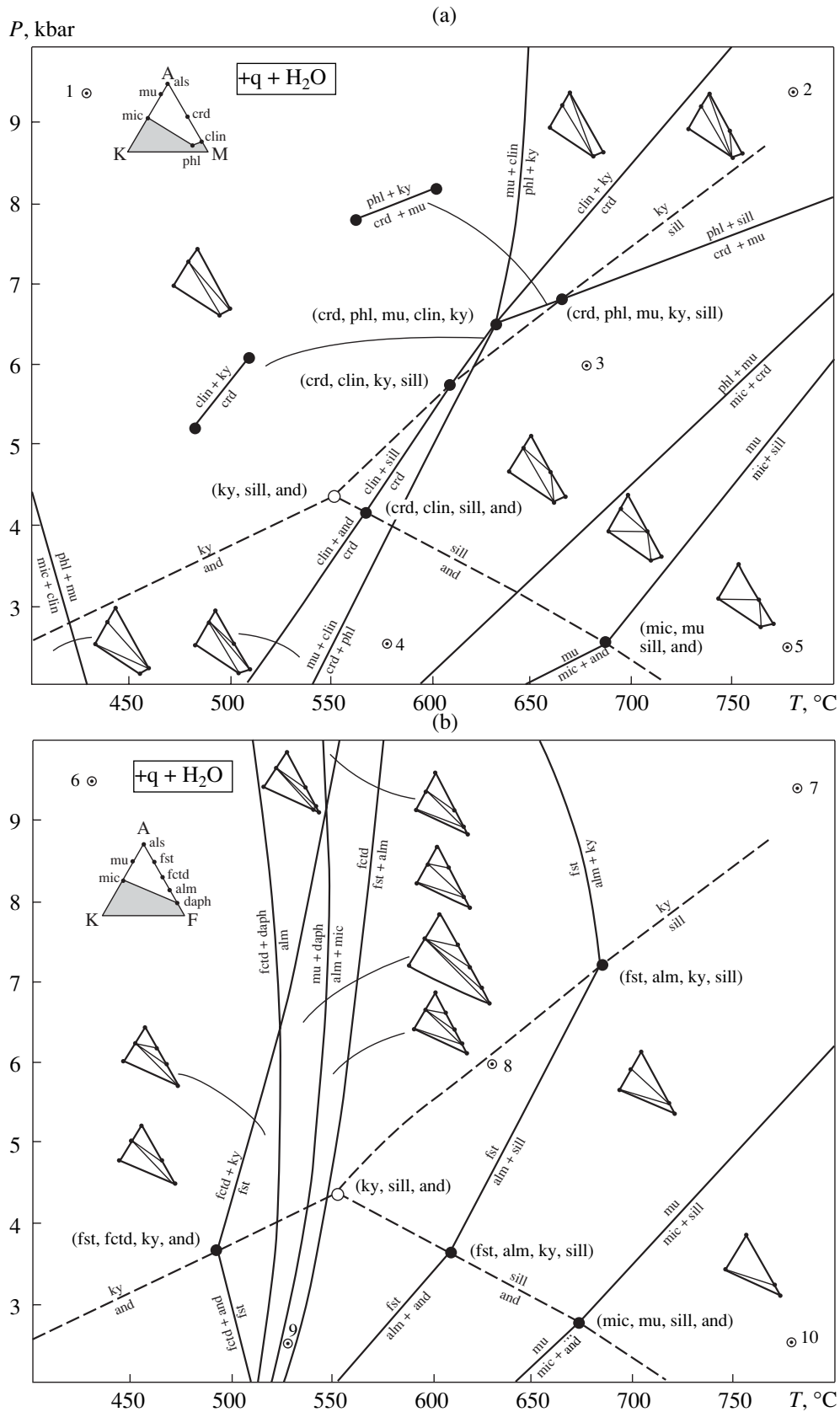


Fig. 1. *PT* projections of the general phase diagram. (a) KFMASH: (and) andalusite, (als) minerals of Al_2SiO_5 composition; (b) KFASH: (fst) Fe-staurolite, (fctd) Fe-chloritoid; (c) CMASH: (pre) prehnite, (di) diopside; and (d) MASH: (anth) antophyllite.

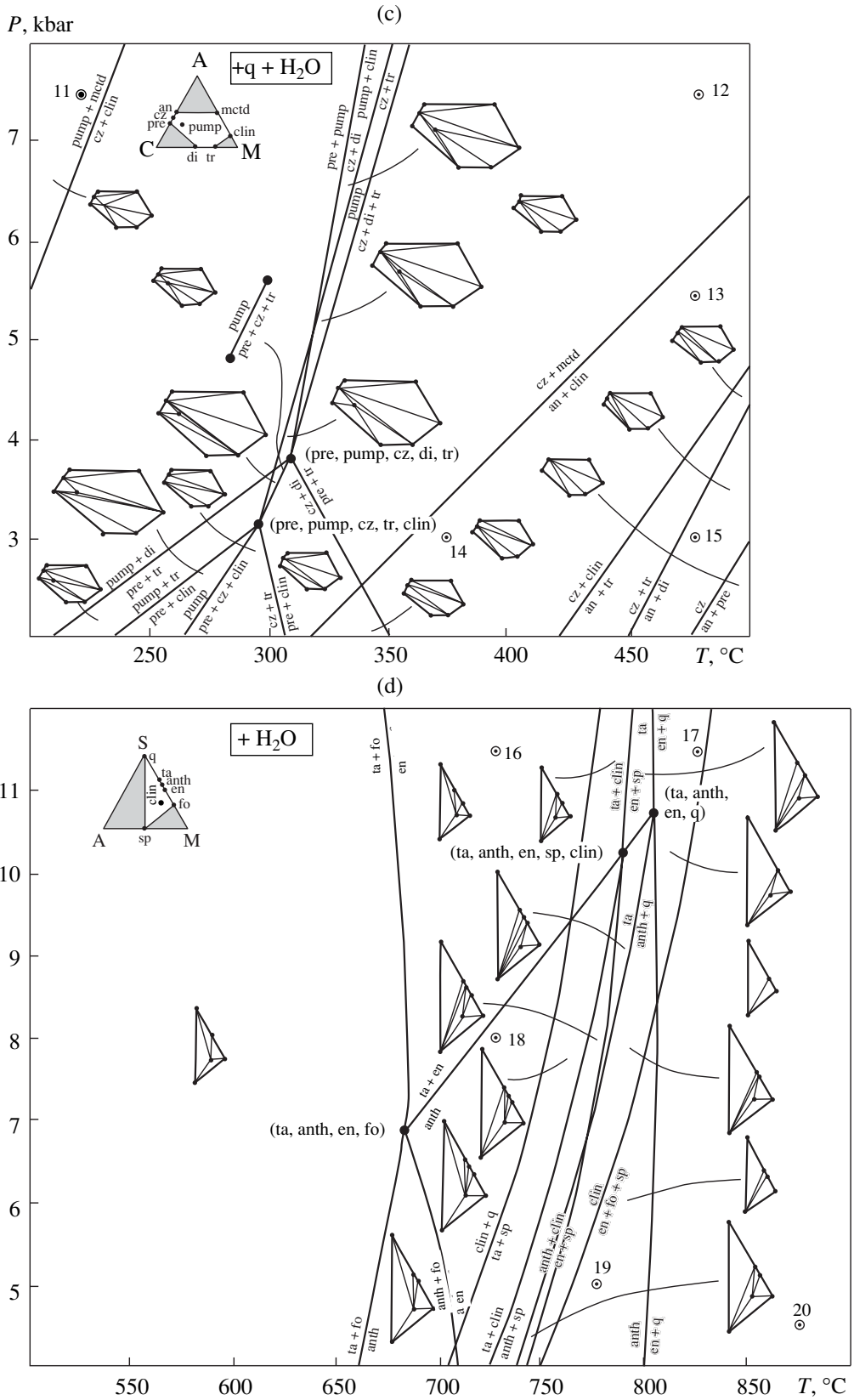


Fig. 1. (Contd.)

Average values of specific mass atomization energy of metamorphic mineral assemblages

Point	T , °C	P , bar	Content of minerals in assemblage, wt %	E_m , kJ/g
1	427	9500	clin 15.61; ky 10.64; mu 23.71; q 50.04	30.49
2	777	9500	phl 20.07; ky 23.50; mu 5.16; q 51.36	29.94
3	677	6000	phl 4.98; crd 31.53; mu 19.47; q 44.02	30.02
4	577	2500	phl 4.98; crd 31.47; mu 19.44; q 44.11	30.04
5	777	2500	crd 42.46; mic 17.10; q 38.31; sill 2.13	29.87
6	427	9500	daph 15.95; ky 11.30; mu 23.16; q 49.59	29.35
7	777	9500	alm 18.96; ky 9.10; mu 23.65; q 48.29	28.78
8	627	6000	alm 13.99; mu 23.49; q 50.24; st 12.28	29.00
9	527	2500	alm 13.98; mu 23.46; q 50.30; st 12.26	29.15
10	777	2500	alm 19.06; mic 16.64; q 45.48; sill 18.82	28.75
11	227	7500	clin 9.73; mctd 10.31; pump 44.74; q 35.22	30.48
12	477	7500	clin 19.95; mctd 1.19; cz 43.84; q 35.02	30.01
13	477	5500	clin 20.57; cz 39.92; an 4.82; q 34.69	30.05
14	377	3000	clin 20.56; cz 39.91; an 4.82; q 34.71	30.14
15	477	3000	tr 12.08; clin 12.72; an 46.30; q 28.99	29.72
16	727	11 500	clin 4.89; en 31.65; fo 63.46	27.91
17	827	11 500	en 33.08; fo 65.66; sp 1.26	27.72
18	727	8000	clin 4.88; fo 31.93; ta 63.19	29.43
19	777	5000	en 33.95; fo 64.80; sp 1.25	27.95
20	877	4500	en 33.74; fo 65.01; sp 1.25	27.93

Note: (clin) Clinocllore, (ky) kyanite, (mu) muscovite, (q) quartz, (phl) phlogopite, (crd) cordierite, (mic) microcline, (sill) sillimanite, (daph) daphnite, (alm) almandine, (st) staurolite, (mctd) Mg-chloritoid, (pump) pumpellyite, (cz) clinozoisite, (an) anorthite, (tr) tremolite, (en) enstatite, (fo) forsterite, (sp) spinel, (ta) talc. Abbreviations of minerals correspond to the format of the HP98 dataset [10].

quantitative compositions of equilibrium assemblages are given in the table.

The presented data show that the E_m value for the mineral assemblages of systems which simulate the rocks formed in the lithospheric conditions (KMASH, KFASH, and CMASH) ranges from 28.75 to 30.49 kJ/g (average 29.72 kJ/g). If a greater number of points are taken into account, the average E_m approaches 30 kJ/g. Analysis of model systems of various component compositions indicates that Fe-rich systems, such as KFASH, are distinguished by diminished values of energy indexes. The introduction of additional independent components (e.g., Mg) increases the E_m level up to the mean value of ~30 kJ/g, which is typical of the majority of metamorphic mineral assemblages. The MASH system is characterized by a still lower average E_m value due to the specific set of phases included into the model. Its mineral composition corresponds to the ultramafic mantle rocks with predominance of the insular and chain structures. The process of serpentinization, which accompanies the exhumation of these rocks, may be regarded as an adjustment of the energetic state of mantle material to crustal conditions. For a hypothetical complete replacement of this type, the E_m value reaches 31.81 kJ/g under normal conditions.

As follows from the aforesaid, the total energy of chemical bonds of solid substance during the formation and transformation of metamorphic rocks remains constant irrespective of T , P , and chemical and phase compositions. The KMASH and CMASH diagrams (Figs. 1a, 1c) in combination with the table show that the E_m value remains constant during variations in T and P that control the change of mineral assemblages across monovariant equilibria lines and does not depend on the assemblage of minerals involved in the model. This specific property is manifested in any silicate system used for simulation of phase relations in metamorphic rocks located in the Earth's crust (normal chemism zone).

The revealed property of metamorphic mineral assemblages indicates that the mineral substance is transformed at a common energy level (CEL) for all such metamorphic rocks. It is evident that the reactions of mineral formation are governed by the constraint providing a specific distribution of chemical bonds, when solid-phase product of any transformation of the initial assemblage is characterized by $E_m \sim 30$ kJ/g. The correspondence of energy saturation of metamorphic rocks to this value is explained by the following fact: a fixed quantity of energy accounts for a mass unity of solid substance of arbitrary component and phase com-

positions. As a result, the average E_m value remains constant at any transformation of mineral assemblages caused by variations of intensive parameters. We deal here with the part of internal energy that accounts for valence bonds.

The independence of the energetic state of solid substance from external conditions indicates that the CEL should be regarded as a leading factor that controls mineral equilibria. In light of the aforesaid, these equilibria are regulated by an optimal distribution of the fixed quantity of energy (per unit mass) in valence bonds rather than by an abstract energy minimum. The effect of mechanisms holding the chemical bond system within a permissible range under varying external conditions is expressed at different levels of substance organization. At the level of individual phases, the energy of bonds is held within the permissible range by solid solutions that provide the existence of minerals of variable composition. At the level of mineral assemblage, variations in quantitative proportions of minerals serve as a regulator. At the level of metamorphic facies, changes in mineral assemblages fulfill this function.

Since the solid substance lacks excess energy, only a limited number of energetically advantageous combinations of chemical bonds are formed in nature, constraining the number of known mineral species. This constraint, one of the numerous consequences of the existence of CEL, is commonly attributed to other factors [8]. In general, the implications of the revealed property of metamorphic mineral assemblages should be linked with the possibility of establishing interrelations between individual characteristics of chemical elements and specific features of their distribution in rocks, migration ability, and so on depending on the variation of temperature, pressure, and other external parameters. The modeling results presented in this communication are based on the analysis of metamor-

phic mineral assemblages. However, since the study was carried out with methods of equilibrium thermodynamics, the conclusions obtained may be extrapolated to rocks of any origin given that all existing phases have attained thermodynamic equilibrium.

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