ISSN 1028-334X, Doklady Earth Sciences, 2007, Vol. 413, No. 2, pp. 262–264. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © P.Ya. Azimov, S.A. Bushmin, S.N. L'vov, D.V. Dolivo-Dobrovol'skii, 2007, published in Doklady Akademii Nauk, 2007, Vol. 413, No. 1, pp. 75–77.

GEOCHEMISTRY

Behavior of Minerals of Metamorphic and Metasomatic Rocks in Supercritical Aqueous and Aqueous–Salt Solutions

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Presented by Academician A.A. Marakushev, April 3, 2006

Received April 7, 2006

DOI: 10.1134/S1028334X07020298

Examination of the interaction between minerals and aqueous fluids is important to solve a wide spectrum of petrological, mineralogical, and geochemical problems of metamorphic and postmagmatic processes. Aqueous fluid is the transporting medium for metamorphic reactions, as well as for metasomatic and hydrothermal crystallization [1]. One of the ways to study the equilibrium between minerals and aqueous fluids is numerical modeling [1], which allows study of the interaction between minerals and fluids if experimental data are insufficient or experiments are difficult to perform.

To examine this interaction in postmagmatic and metamorphic processes, we considered the congruent (model) solubility of major minerals of metamorphic and metasomatic rocks in aqueous and aqueous–salt (1 mol NaCl per 1 kg H_2O) solutions of different acidity within the temperature range of 400–600°C (P = 1 kbar) and 400–800°C (P = 5 kbar). Some of the minerals considered below are unstable under these conditions (for example, pyrope or jadeite), but we are interested in the dissolution of minerals formed within the entire range of metamorphic conditions. Congruent solubility was chosen to study the behavior of individual minerals, because incongruent dissolution invokes subsequent dissolution and crystallization. The congruent or incongruent character of dissolution, in turn, depends on the general composition of the system. In particular, kyanite dissolves congruently (incongruently) in the presence (absence) of quartz to form corundum. However, incongruent melting must be considered to examine the behavior of the rock as a whole. Such an analysis is suggested in the course of further investigations.

The solubility was simulated for 57 minerals using the programs FLUID 2.0 [3] and GBFLOW 3.1 [4]. The thermodynamic properties for calculations were taken from [5], and those for the minerals came from the database slop98.dat (version Oct. 30, 1998) [6] for aqueous species. The pH value of the fluid was specified by the HCl/NaOH concentrations within a range of 0 to 1 mol/kg H_2O. The limit concentrations were determined by the constraints of the HKF model [7], which can be applied only for diluted solutions. The applicability of this model for low-density fluids is constrained by $T = 600°C$ at $P = 1$ kbar.

Features of the Solubility Diagrams. Depending on the behavior of minerals in acid and alkaline solutions, six major types of solubility diagrams can be distinguished. Depending on the diagram topology (Fig. 1), the studied minerals dissolved in aqueous solutions can be grouped as follows[1]:

I. Qtz, Mc, Ab, Jd;

II. Ms, Pg, And, Sil, Ky, Cor, Hem;

III. St, Mst. Crd, Fcd, Cld, Spr4, Spr7, Spl, Hc, Mag, Alm, Sps, Ann, Chm, Fs, Cru;

IV. An, Lws, Zo, Ep, Act, Ams, Rdn;

V. Prp, Adr, Rgs, Clc, Ged, Hd, Ts, Ves, Prh, Rbk;

VI. Phl, Prg, Gln, Aeg, Tlc, Ctl, Ath, Cum, Chu, En, Tr, Di, Wo.

For most minerals, the solubility is defined mainly by the acidity (pH) of the fluid and, to a lesser extent, by temperature and pressure. However, minerals with *type I* solubility diagrams show practically no change in solubility with variations of acidity and *PT* conditions. These minerals are characterized by the maximum solubility in fluids of different compositions. The solubility of minerals with *type II* diagrams is maximum in alkaline fluids, significantly decreases in neutral and weakly acid fluids, and increases at high acidity. Minerals of *type III* have amphoteric properties. Their solubility is minimum in neutral areas and significantly higher in acid and alkaline environments. The solubility

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[1] Mineral abbreviations: (Aeg) aegirine, (Ams) amesite, (Chm) chamosite, (Clc) clinochlore, (Cor) corundum, (Fcd) ferrocordierite, (Mst) magnesiostaurolite, (Spr4) sapphirine 4:4:2, (Spr7) sapphirine 7:9:3. Other symbols are as in [8].

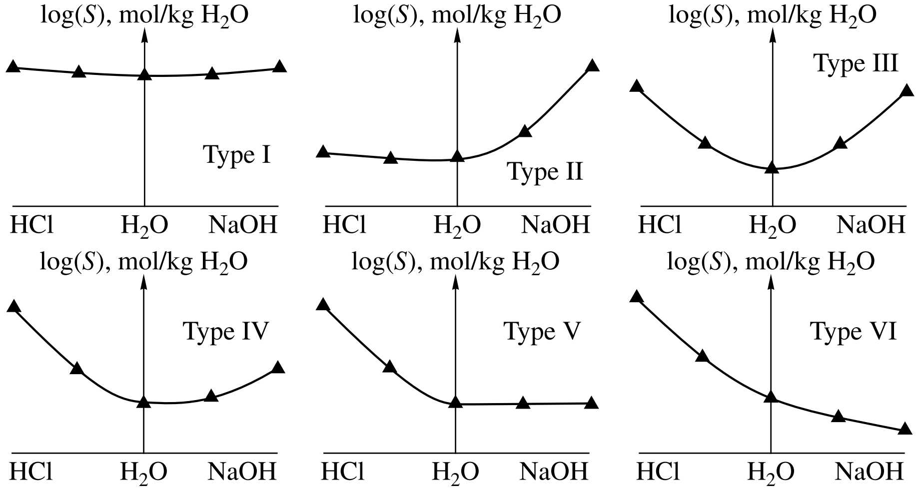

Fig. 1. Types of solubility diagrams for minerals from metamorphic and metasomatic rocks in hydrous fluids versus environmental pH (contents of HCl and NaOH).

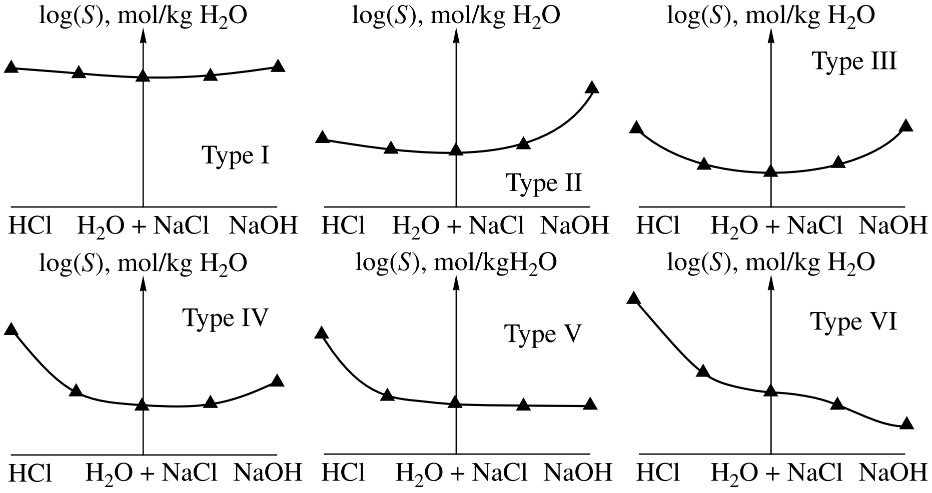

Fig. 2. Types of solubility diagrams for minerals from metamorphic and metasomatic rocks in hydrous–salt fluids (H_2O–1M NaCl) versus environmental pH.

of type IV minerals is maximum in acid solutions, decreases with increasing alkalinity, and again increases in strongly alkaline fluids. The type V diagrams, unlike the type IV, show no increase in solubility in strongly alkaline environments as compared to weakly alkaline and neutral solutions. In minerals of type VI, the solubility is maximum in strongly acid solutions and decreases with an increase in pH.

In the aqueous–salt solutions, the topology of diagrams (Fig. 2) and distribution of minerals by types differ from purely aqueous solutions:

I. Qtz, Mc, Ab, Jd;

II. Ms, Pg, St, Mst, And, Sil, Ky, Cor, Hem;

III. Crd, Fcd, Cld, Spr4, Spr7, Spl, Hc, Mag;

IV. Alm, Sps, Ann, Chm, Fs, Gru, An, Lws, Zo, Act, Rdn, Rbk;

V. Ams, Prp, Ts, Ep, Hd, Prh, Gln, Aeg;

VI. Phl, Prg, Grs, Adr, Clc, Ged, Ves, Tlc, Ctl, Ath, Cum, Chu, En, Tr, Di, Wo.

The solubility diagrams in a hydrous–salt fluid, unlike those for a hydrous fluid, display significantly weaker pH dependence in the near-neutral field in the presence of NaCl. In particular, the solubility curve in hydrous solutions for type III diagrams approximates a parabola or even has a V-shaped form, flattening near the neutral point to acquire a trough-shaped form in hydrous–salt solutions. The type VI diagrams in the near-neutral field show distinct bending. Such behavior is related to the decreasing acidic properties of HCl in the solutions of alkali metal salts, which is visually expressed in the diagrams a_{H^+}/a_{Me^+}.

Influence of Mineral Composition on the Solubility Diagrams. The distribution of minerals in terms of types show that their solubility is determined by chemical composition rather than structure. Silicates of different structural types but similar compositions behave similarly (e.g., albite and jadeite; anorthite, lawsonite, and zoisite; magnesium silicates; and others). Polymorphic modifications have practically similar solubility. This indicates that solubility is determined by the behavior of mineral-forming elements in the solutions, and this property allows us to determine their mobility. The comparison of minerals with different proportions of elements makes it possible to estimate the contribution of individual elements in the topology of phase diagrams.

Minerals with high silica and alkali contents, quartz and alkali feldspar included, are the most soluble phases regardless of fluid acidity. With the increasing role of bivalent cations (Fe^{2+}, Mg, and Ca) and Al, the solubility in neutral solutions significantly decreases. The least soluble are minerals with high Fe^{3+} content. Calcium minerals are more soluble than magnesium minerals. Aluminous minerals are the most soluble in alkaline environments, while minerals with high Ca or Mg contents are more soluble in acid solutions. Correspondingly, minerals rich in alkali earth minerals, alumina, and silicates of Fe^{2+} and Mn^{2+} exhibit amphoteric properties: their solubility is minimum in neutral solutions and higher in acid and alkaline solutions. An increase in pCl has an inverse correlation with the amphoteric properties of Fe^{2+} and a positive correlation with mafic properties of bivalent cations. An increase in pressure leads to the growth of solubility of all minerals. Temperature has an intricate influence (the solubility of minerals with an increase in temperature can increase, decrease, or remain nearly constant).

The obtained tendencies in the behavior of the mineral solubility in fluids of different compositions allowed us to draw the following conclusions concerning the mobility of elements in the fluid systems. The mobility of Si and alkalis (K and Na) is high in the solutions of any acidity. Al is sufficiently mobile in alkaline solutions and weakly mobile in neutral and acid solutions, especially as compared to other elements. Its mobility increases only in ultra-acid environments. Fe^{3+} shows a similar behavior, but its mobility in all solutions is significantly lower than that of Al. Fe^{2+}, Ca, Mg, and Mn are sufficiently mobile in acid solutions. With decreasing pH and increasing acidity, these solutions are more intensely enriched in Fe^{2+} and Ca and less intensely enriched in Mg. In the alkaline solutions with low salinity, Fe^{2+} and Mn are mobile (amphoteric behavior), whereas Mg and Ca have extremely low mobility. In general, the change in solution acidity must lead to a significant change in fluid composition owing to the transfer of some components to the solution and precipitation of other components. Such conclusions are consistent with empirical series of element mobility, which were deduced from the study of natural metasomatic zoning [9–11] and experimental study of metasomatism [12, 13].

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 05-05-65333 and 05-05-65334), the program BRHE of CRDF and the Ministry of Education and Science of the Russian Federation (joint grant no. Y1-G-15-04), and the Foundation for the Support of Russian Science.

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