УДК 550.89:553.21/.24:552.4

NUMERICAL MODELLING OF THE METAMORPHIC MINERAL SOLUBILITY IN HYDROTHERMAL SOLUTIONS AT 400-800°C, 1-5 KBAR AND VARIOUS FLUID ACIDITY

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This paper discusses the character of dissolution in aqueous fluid for the 56 usual minerals of metamorphic rocks depending on the *PT*-conditions and fluid composition. Computer modelling of mineral-fluid equilibria carries out the study of solubility. The calculations are accomplished for both pure water and solutions, containing acid (HCl) and alkali (NaOH). We distinguish the seven basic types of the solubility diagrams in dependence of peculiarities of mineral behaviour in acid and alkaline solutions. For most minerals, excepting Qtz, Mi, Ab and Jd, the solubility value is determined mainly by fluid acidity (pH) and weakly by *P*-*T*.

Analysis of the mineral solubility allows to characterize the element mobility depending on the fluid acidity. The most mobility is manifested by Si, K and Na independent of fluid acidity. Ca and Mg are most mobile in acid solutions whereas Fe(II) is mobile in both acid and alkaline fluids. Al is rather immobile element and is transferred mainly in alkaline or strongly acid solutions. The most immobile is Fe(III) - i.e. iron is transferred mainly as Fe(II). Therefore, change of fluid acidity results in dissolution of some components and precipitation of other ones. Minerals of different types could be indicators of the fluid acidity at metasomatism.

Since high solubility of quartz most metamorphic fluids should be silica-saturated. They should also contain significant amount of alkalis. The decrease of P and T can leads to origin of supersaturated silica-alkaline fluids producing metasomatism in country rocks. The solubility of Fe-, Mg- and Ca-bearing minerals is low in alkaline fluids in comparison with acid ones. Hence only primarily acid fluids can produce solutions, enriched in these elements, at their leaching from country metamorphic rocks. Fluids, enriched only in Fe, could have initially both acid and alkaline character.

Key words: minerals solubility, fluid, metamorphism, thermodynamic modelling, fluid acidity, element mobility.

The study of the mineral solubility in hydrothermal solutions in the wide range of temperatures and pressures is the basement necessary for the following analysis of metamorphic, metasomatic and ore forming processes. The mineral solubility, composition of rocks, interacting with fluid, and primary fluid composition determine the equilibrium fluid composition [12–14]. At the same time, fluids can alter the rock composition during metasomatism.

There are two ways to determine mineral solubility. The first way is the direct experimental investigation of the saturated solution. It is the most reliable. However, the experimental determination of the mineral solubility in the wide range of state variables is

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a difficult technical problem, so the data of this sort are limited and do not spread over the whole P-T area of metamorphic conditions. Experimental modelling is also limited by the difficulty in obtaining the equilibrium during mineral dissolution.

The second way permits to investigate a wide *P*-*T* area of mineral formation including conditions unavailable for direct experimental modelling. This way consists in thermodynamic computer modelling basing on methods of chemical thermodynamics. Theoretical prognosis of mineral solubility can be the main method of investigations in the areas of high temperatures, pressures and fluid compositions where experimental studies are limited or impossible. More over, modern analytical techniques do not allow to evaluate the solution acidity and ion composition under high pressures and temperatures without disturbing the obtained equilibrium.

Minerals with complicated composition (containing three and more elements) are usually incongruently dissolved. Incongruent dissolution consists in dissolution of mineral unstable under the given conditions with the presence of fluid and simultaneous crystallization of one or more stable minerals. So, incongruent dissolution can be described as a superposition of simple congruent processes. Moreover, the character of mineral dissolution (congruent or incongruent) depends upon various conditions including mineral association and fluid composition. So, the present paper is devoted to analysis of the behaviour of separate minerals, and we shall discuss only congruent dissolution. The congruent dissolution is possible also in the utmost case of the wholly open system, where all dissolved components are removed from the area of mineral dissolution.

Framework for thermodynamic calculations. In the present paper we analyse solubility for 56 minerals within the system Na₂O–K₂O–CaO–FeO–MgO–MnO–Al₂O₃–Fe₂O₃–SiO₂–H₂O (table). These minerals are oxides and silicates forming metamorphic and metasomatic rocks. The solubility and behaviour of carbonates, ore and accessory minerals are not discussed in the present work. The study of solubility is carried out by mean of computer modelling of the equilibrium between minerals and aqueous fluid using programs FLUID [8, 21] and GBFLOW [4] for 400–800°C and 1 and 5 kbar. Haar–Gallagher–Kell model [15] was used to calculate the properties of aqueous fluid.

The thermodynamic of aqueous species were determined with modified HKF model [22, 23]. This model can be used only for dense aqueous fluid (> 0.35 g/cm³), so the calculations for 1 kbar were done only up to 600°C. The solubility calculations done for pure water and for solutions containing acid (HCl) and alkali (NaOH). Substance concentrations in solutions and the results of solubility calculations are presented in moles of dissolved substance per 1 kg of water and are written in units of the solution molality (e.g., "0.1M HCl" means 0.1 mole HCl per kg H₂O).

The thermodynamic properties of minerals are taken from Holland-Powell dataset [16]. For aqueous species (H⁺, OH⁻, Cl⁻, SiO₂⁰, HSiO₃⁻, Fe³⁺, FeOH²⁺, FeO⁺, HFeO₂⁰, FeO₂⁻, Fe²⁺, FeOH⁺, FeO⁰, HFeO₂⁻, FeCl²⁺, FeCl₂⁰, FeCl⁺, Mg²⁺, MgOH⁺, Mg(HSiO₃)⁺, MgCl⁺, Ca²⁺, CaOH⁺, Ca(HSiO₃)⁺, CaCl₂⁰, CaCl⁺, Na⁺, NaHSiO₃⁰, NaCl⁰, K⁺) we used the data of GEOPIG group (file "slop98.dat", November 30, 1998).

For Al-bearing species $(Al^{3+}, AlOH^{2+}, Al(OH)_2^+, HAlO_2^0, AlO_2^-, NaAlO_2^0, KAlO_2^0)$, NaOH⁰ and KOH⁰ the data by [18] were used. Other species used are AlH₃(SiO₄)²⁺ [20], HCl⁰ [17], KCl⁰ [19].

Distribution of the metamorphic minerals by types of their solubility diagrams

Type IQuartzQtzSiO2JadeiteJdNaAl(Si;O_6)AlbiteAbNaAl(Si;O_6)MiscoviteMiKAl(Si;O_8)ParagonitePgNaAl(Si;O_6)ParagonitePgNaAl(Si;O_10)(OH)2ParagonitePgNaAl(Si;O_10)(OH)2ParagonitePgNaAl(Si;O_10)(OH)2ParagonitePgNaAl2(Si;O_10)(OH)2ParagonitePgNaAl2(Si;O_10)(OH)2ParagoniteNaAlpSiO3AndalusiteAndAlpSiO3KyaniteSilAlpSiO3SillimaniteSilAlpSiO3CorundumCorAlpSiO3PeesaAnmadineFepA14(SiO4)3StauroliteStFepA14(SiO4)3,014StauroliteStFepA14(SiO4)3,014StauroliteStFepA14(SiSO4)3,014CordieritefCdFepA14(AlSiO4)3CharonsiteChaFepA14(AlSiO4)3CharonsiteChaFeqA15(AlSiO4)ChloritoidCldFeA14(SiSO4)ChloritoidCldFeA15(SiO4)0(OH)2FerrosiliteFsFe2(Si2O4)GapehtineSplMgA12O4SapphirineSpr422Mage FeFe2O4SapphirineSpr793Mg2A14(SiSO4)(Si2O-)0OHAnniteAnCaA12Si2O4AnorthiteAnCaA12Si2O4LawsoniteZoCa2A12Fe(SiO4)(Si2O-)0OHEpidoteEpCa2A12Fe(SiO4)3RhodoniteRdnMsiO3 <th>Mineral</th> <th>Abbreviation</th> <th>Composition</th>	Mineral	Abbreviation	Composition		
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JadeiteJdNaÅl(Si,O_6)AlbiteAbNaÅl(Si,O_6)MicroclineMiKAl(Si,O_6)Type 2MuscoviteMsKAl(AlSi,O_10)(OH)2ParagonitePgNaÅl2(AlSi,O_10)(OH)2Type 3AndulusiteKyAl ₂ SiO ₅ KyaniteSilAl ₂ SiO ₅ SillimaniteSilAl ₂ SiO ₅ CorundumCorAl ₂ SiO ₅ CorundumCorAl ₂ SiO ₅ AndmineAlmFe ₃ Al ₂ (SiO ₄) ₃ SpessarineSpsMn ₄ Al ₂ (SiO ₄) ₃ SpesarineSpsMn ₄ Al ₄ (SiO ₄) ₇ , SO ₄₄ (OH)4Mg-staurolitemStMg ₂ Al ₄ (AlSi ₅ O ₁₈)CordicriteCrdHg ₂ Al ₄ (AlSi ₅ O ₁₉)Fe-cordicritefCdFe ₂ Al ₃ (SiO ₄) ₇ , SO ₄₄ (OH)4CharositeChaFe ₄ Al ₁₈ (SiO ₄) ₇ , SO ₄₄ (OH)4ChorioidCldFe ₂ Al ₃ (AlSi ₅ O ₁₈)FerrosiliteFsFe ₂ (Si ₂ O ₄)GruneriteGruFe ₅ (Al(AlSi ₅ O ₁₀)(OH)2FerrosiliteFsFe ₂ (Al ₂ (Si ₂ O ₄)SpinelSplMg ₂ Al ₄ (Si ₅ Al ₄ O ₂₀)MagnetiteMagFeFe ₂ O ₄ SaphirineSpr793Mg ₃ SAl ₄ (Si ₅ Al ₄ O ₂₀)(OH)2AnmiteAnCal ₂ Si ₀ O ₃ AnmiteAnCal ₂ Si ₀ O ₃ (Si ₂ O ₇)OOHActinoliteActCa ₂ Al ₅ (SiO ₄) ₃ O(OH)8RhodoniteRdnMg ₂ Al ₄ (SiO ₄) ₃ O(OH)8RhodoniteArdCa ₂ Al ₅	Ouartz	Otz	SiO ₂		
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KyaniteKy A_2SiO_5 SillmaniteSil A_2SiO_5 CorundumCor A_2O_3 HematiteHem Fe_2O_3 Type 4AlmandineAlm $Fe_3A_1(SiO_4)_3$ SpessartineSps $Mn_3A_1(SiO_4)_7SO_14(OH)_4$ Mg-stauroliteSt $Fe_4A_{18}(SiO_4)_7SO_{14}(OH)_4$ Mg-staurolitemSt $Mg_4A_{18}(SiO_4)_7SO_{14}(OH)_4$ CordieriteCrd $Mg_2A_{15}(AISi_5O_{18})$ Fe-cordieritefCd $Fe_2A_{13}(AISi_5O_{18})$ CharositeChaFee_4(AISi_5O_{10})(OH)_8ChloritoidCld $FeA_{12}(SiO_4)O(OH)_2$ FerrosiliteFs $Fe_2(Si_2O_4)$ GruneriteGru $Fe7(Si_8O_2)(OH)_2$ HercyniteHc $FeA_{15}O_4$ SpinelSpl $Mg_{21}O_4$ MganetiteMag $FeFe_5O_4$ SaphirineSpr442 $Mg_{41}A_{15}O_{15}A_{14}SO_{20}$ AnniteAnn $KFe_3(AISi_3O_{10})(OH)_2$ LawsoniteZo $Ca_2A1_5Si_2O_8$ LawsoniteZo $Ca_2A1_5Si_2O_1(OH)_2$ ZoisteZo $Ca_2A1_5Si_2O_1(OH)_2$ AngetiteAnn $KFe_3(Si_2O_1)(OH)_2$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ AnticeFe $Ca_2A1_2(SiO_4)_3$ AntideAdr $Ca_3Fe_2(SiO_4)_3$ AntideAdr $Ca_3Fe_2(SiO_4)_3$ AntideAdr $Ca_3Fe_2(SiO_4)_3$ AntideAdr C	Andalusite	And	Al ₂ SiO ₅		
SillimaniteSil $A_2^2 SiO_5^2$ CorundumCor $A_{2}O_3$ HematiteHemFe ₂ O ₃ Type 4AlmandineAlmFe ₃ Al ₂ (SiO ₄) ₃ SpessartineSpsMn ₃ Al ₂ (SiO ₄) ₇ , O ₁₄ (OH) ₄ StauroliteStFe ₄ Al ₁₈ (SiO ₄) ₇ , O ₁₄ (OH) ₄ Mg-stauroliteStFe ₄ Al ₁₈ (SiO ₄) ₇ , O ₁₄ (OH) ₄ CordieriteCrdMg ₂ Al ₁₈ (SiO ₄) ₇ , O ₁₄ (OH) ₄ CordieriteCrdMg ₂ Al ₁₈ (SiO ₄) ₇ , O ₁₄ (OH) ₄ CordieriteCrdFe ₂ Al ₃ (AlSi ₃ O ₁₈)Fe-cordieritefCdFe ₂ Al ₃ (AlSi ₃ O ₁₈)CharnositeChaFe ₃ Al(AlSi ₃ O ₁₈)CharnositeChaFe ₃ Al(AlSi ₃ O ₁₀)(OH) ₈ ChoritoidCldFeAl ₂ (SiO ₄)0(OH) ₂ FerrosiliteFsFe ₂ (Si ₂ O ₄)GruueriteGruFe ₇ (Si ₈ O ₂₂)(OH) ₂ HercyniteHcFeAl ₂ O ₄ SpinelSplMg ₂ Al ₄ (Si ₂ Al ₄ O ₂₀)MagnetiteMagFeFe ₂ O ₄ SapphirineSpr442Mg ₄ Al ₄ (Si ₂ Al ₄ O ₂₀)AnniteAnnKFe ₃ (AlSi ₃ O ₁₀)(OH) ₂ LawsoniteZoCa ₂ Al ₃ (SiO ₄)(Si ₂ O ₇)(OCH)ZoisiteZoCa ₂ Al ₃ (SiO ₄)(Si ₂ O ₇)OOHEpidoteEpCa ₂ Al ₂ Fe(SiO ₄)(Si ₂ O ₇)OOHAntioliteActCa ₃ Fe ₅ (Si ₆ (Si ₂)(OH) ₂ AnseiteAmsMg ₃ Al ₂ (SiO ₄) ₃ RhodoniteHedCa ¹ ₂ (SiO ₄) ₃ HedenbergiteHed <td>Kvanite</td> <td>Kv</td> <td>Al₂SiO₅</td>	Kvanite	Kv	Al ₂ SiO ₅		
Corundum HematiteCor Hem $A_2^1O_3$ Fe2O3Type 4AlmandineAlmFe3Al2(SiO4)3SpesartineSpsMn3Al2(SiO4)7,5O14(OH)4SpesartineSpsMn3Al2(SiO4)7,5O14(OH)4MgstauroliteStFe4Al18(SiO4)7,5O14(OH)4MgstaurolitemStMg4Al18(SiO4)7,5O14(OH)4CordieriteCrdMg2Al3(AISiO18)Fe-cordieritefCdFe2Al3(AISiO18)ChamositeChaFe3Al4(AISiO4)7,6O14(OH)2CharositeChaFe3Al4(AISiO18)CharositeCldFe42(SiO4)0(OH)2FerrosiliteFsFsFsFe2O4SpinelSplMg4Al2(AISiO4)2MagnetiteMagFeFe2O4SapphirineSpr422Mg4Al4(Si2Al4020)Spr793Mg33Al4_5(Si1,5Al4,5O20)AnniteAnnCaAl2Si2O8LawsoniteLwsCaAl2(Si2O7)(OH)2×H2OZoisiteZoCa2Al3(SiO4)(Si2O7)OOHEpidoteEpCa3Al2Fe(SiO4)(Si2O7)OOHActinoliteActCa3Fe3(Si04)(Si2O7)OOHActinoliteActCa3Fe3(Si04)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa3Al2(SiO4)3HedenbergiteHedCaFe(Si2O6)TschermakiteTsCa2(M3(A1Si04)(Si2O7)3(OH)2VesvavianiteVesCa19Mg3Al2(SiO4)3ChariteActCa3Fe2(SiO4)3GrossularGrsCa3Al2(SiO4)3GrossularGrsCa3Al2(SiO4)3 <td>Sillimanite</td> <td>Sil</td> <td>Al₂SiO₅</td>	Sillimanite	Sil	Al ₂ SiO ₅		
Other $Ia_2 S_3$ HematiteHematiteIdematite $Iype 4$ AlmandineAlm $Fe_2 Al_2(SiO_4)_3$ SpessartineSps $Mn_3Al_2(SiO_4)_3$ StauroliteSt $Fe_4Al_1(sSiO_4)_7, 5O_{14}(OH)_4$ Mg-staurolitemSt $Mg_4Al_1(sSiO_4)_7, 5O_{14}(OH)_4$ CordieriteCrd $Mg_2Al_3(AlSi_5O_{18})$ Fe-cordieritefCd $Fe_2Al_3(AlSi_5O_{18})$ CharnositeCha $Fe_5Al_4(AlSi_5O_{18})$ CharnositeCha $Fe_5Al_2(SiO_4)O(OH)_2$ ChoritoidCld $FeAl_2(SiO_4)O(OH)_2$ FercosiliteFs $Fe_2(Si_2O_6)$ GruneriteGru $Fe_7(Si_8O_{22})(OH)_2$ HercyniteHc $FeAl_2O_4$ SpinelSpl $MgAl_2O_4$ MagnetiteMag $FeFe_2O_4$ SapphirineSpr442 $Mg_4Al_4(Si_2Al_4O_{20})$ AnniteAnn $KFe_3(AlSi_0O_4)(Si_2O_7)O(H)_2 \times H_2O$ ZoisiteZo $Ca_2Al_2(Si_2O_7)(OH)_2 \times H_2O$ ZoisiteZo $Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$ ActicaliteAms $Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$ RhodoniteArct $Ca_3Fe_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ AnsiteArms $Mg_4Al_2(SiO_4)_3$ AnorthiteArm $Ca_2Fe_2(SiO_4)_3$ LawsoniteZo's $Ca_3Fe_2(SiO_4)_3$ ActinoliteAct $Ca_3Fe_2(SiO_4)_3$ AdmasiteArms $Mg_4Al_2(SiO_4)_3$ <td>Corundum</td> <td>Cor</td> <td>$A_{12}O_{2}$</td>	Corundum	Cor	$A_{12}O_{2}$		
Type 4Type 4AlmandineAlm $Fe_3Al_2(SiO_4)_3$ SpessartineSps $Mn_3Al_2(SiO_4)_3$ StauroliteSt $Fe_4Al_{18}(SiO_4)_7_5O_{14}(OH)_4$ Mg-staurolitemSt $Mg_2Al_{16}(SiO_4)_7_5O_{14}(OH)_4$ CordieriteCrd $Mg_2Al_{16}(SiO_4)_7_5O_{14}(OH)_4$ CordieriteCrd $Mg_2Al_{16}(SiO_4)_7_5O_{14}(OH)_4$ CordieriteCrd $Mg_2Al_{16}(SiO_4)_{75}O_{14}(OH)_4$ CharnositeCha $Fe_5Al(AlSi_5O_{18})$ CharnositeCha $Fe_6(Si_2O_6)$ CharnositeCld $FeAl_2(SiO_4)O(OH)_2$ ChoritoidCld $FeAl_2(SiO_4)O(OH)_2$ FerrosiliteFs $Fe_2(Si_2O_6)$ GruneriteGru $Fer(Si_8O_{22})(OH)_2$ HereyniteHc $FeAl_2O_4$ MagnetiteMag $FeFe_2O_4$ SapphirineSpr442 $Mg_4Al_4(Si_2Al_4O_{20})$ MariteAnn $CaAl_2Si_2O_8$ AnorthiteAn $CaAl_2Si_2O_8$ LawsoniteLws $CaAl_2Fe(SiO_4)(Si_2O_7)OOH$ ZoisiteZo $Ca_3Al_3(SiO_4)(Si_2O_7)OOH$ EpidoteEp $Ca_3Fe_2(SiO_4)_3$ AdmoniteAms $Mg_4Al_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_3)(OH)_2$ VesuvianiteVes $Ca_3Al_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ <td< td=""><td>Hematite</td><td>Hem</td><td>Fe₂O₂</td></td<>	Hematite	Hem	Fe ₂ O ₂		
AlmandineAlmFe3Al2(SiO4)3SpessartineSpsMn3Al2(SiO4)3StauroliteStFe3Al3(SiO4)7,3O14(OH)4Mg-staurolitemStMg4Al18(SiO4)7,3O14(OH)4CordieriteCrdMg2Al3(AlSi5O18)Fe-cordieritefCdFe3Al3(AlSi5O18)ChamositeChaFe3Al(AlSi5O18)CharositeChaFe3Al3(AlSi5O18)CharositeChaFe3Al3(AlSi5O18)CharositeCldFeAJ3(AlSi5O18)GruneriteGruFe7(Si8O22)(OH)2HercyniteHcFeAl2O4SpinelSp1Mg4Al2(Si2Al4O20)MagnetiteMagFeFe2O4SapphrineSpr442Mg4Al3(Si1,5Al4,5O20)AnniteAnnKFe3(AlSi3O10)(OH)2Type 5AnorthiteAnCaAl2Si2O8LawsoniteLwsCaAl2Si2O8ZoisiteZoCa2Al3(SiO4)(Si2O7)OOHEpidoteEpCa2Al3Fe(SiO4)(Si2O7)OOHAttinoliteActCa2Fe3(SiQ22)(OH)2AmesiteAmsMg4Al2(Al2Si2O10)(OH)8RhodoniteRdnMnSiO3Type 6PyropePrpMgaAl2(SiO4)3GrasLa(SiO4)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa3Al2(SiO4)3HedenbergiteHedCaF(Si2O6)StremakiteTsCa2(Mg3Al2)(Al2Si6O22)(OH)2VesvainiteCsCa19Mg2Al1(ISO4)3GrossularGrsCa3H2(SiO4)3Grossular <t< td=""><td></td><td>Туре</td><td>24</td></t<>		Туре	24		
SpesartineSps $M_{13}A_1_2(SiO_4)_3$ StauroliteSt $Fe_4Al_{18}(SiO_4)_{7.5}O_{14}(OH)_4$ Mg-staurolitemSt $Mg_4Al_{18}(SiO_4)_{7.5}O_{14}(OH)_4$ CordieriteCrd $Mg_2Al_3(AlSis_{0.8})$ CordieritefCd $Fe_5Al_5(AlSis_{0.8})$ ChamositeCha $Fe_5Al_5(AlSis_{0.8})$ CharositeCha $Fe_5Al_5(AlSis_{0.8})$ ChloritoidCld $FeAl_2(SiO_4)O(OH)_2$ FerrosiliteFs $Fe_2(SiO_4)O(OH)_2$ GruneriteGru $Fer(Si_8O_{22})(OH)_2$ HercyniteHc $FeAl_2O_4$ SpinelSpl $MgAl_2O_4$ MagnetiteMag $FeFe_2O_4$ SapphirineSpr442 $MgAl_4(Si_2Al_4O_{20})$ AnniteAnn $CaAl_2Si_2O_8$ LawsoniteLws $CaAl_2Si_2O_8$ LawsoniteLws $CaAl_2Si_2O_8(Si_0A)(Si_2O_7)OOH$ ActinoliteAct $Ca_2Al_3Fe(SiO_4)(Si_2O_7)OOH$ ActinoliteAct $Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$ ActinoliteAct $Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$ AdenderiteAms $Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$ RhodoniteRdn $MnSiO_3$ Type 6PyropePrpPyropePrp $Mg_3Al_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ HedenbergiteHed $CaF(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_1(SiO_4)_3(La_2i_2O_{12})(OH)_2$ VessvainiteVes	Almandine	Alm	$Fe_3Al_2(SiO_4)_3$		
StauroliteStFeqAl1[8(SiO4)7,5O14(OH)4Mg-staurolitemStMg4Al18(SiO4)7,5O14(OH)4CordieriteCrdMg2Al3(AlSisO18)Fe-cordieritefCdFeqAl1[8(SiO4)7,5O14(OH)4ChamositeChaFeqAl1[8(SiO4)7,5O14(OH)8ChamositeChaFeqAl1[8(SiO4)7,5O14(OH)8CharoniteCldFeqAl2[SiO4]0(OH)8ChoritoidCldFeqAl2[SiO4]0(OH)2FerrosiliteFsFe2(Si2O6)GruneriteGruFe7(Si8O22)(OH)2HercyniteHcFeAl2[SiO4]0(OH)2SpinelSplMgAl2O4MagnetiteMagFeFe2O4SapphirineSpr422Mg4Al4(Si2Al4O20)AnniteAnnKFe3(AlSi3O10)(OH)2Type 5AnorthiteAnCaAl2Si2O8LawsoniteZoCa2Al3(SiO4)(Si2O7)(OH)2×H2OZoisiteZoCa2Al3[SiO4](Si2O7)(OH)2EpidoteEpCa2Al2Fe(SiO4)(Si2O7)(OH)2AmesiteArmsMg4Al2(Al2Si2O10)(OH)2AndraditeAdrCa3Fe2(Si04)3RhodoniteRdnMmSiO3Type 6PyropePrpMg3Al2(SiO4)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa2(Mg3Al2)(Al2SiO2)(OH)2AndraditeAdrCa3Pl2(SiO4)3HedenbergiteHedCaFe(Si2O6)TschermakiteTsCa2(Mg3Al2)(Al2SiO2)(OH)2VessvianiteVesCa19Mg2Al1(SiO4)12(Si2O7)3(OH)9ClinochloreCclMg	Spessartine	Sps	$Mn_2Al_2(SiO_4)_2$		
SinchicDiscreteMg-staurolitiemStMgAla(SiO)_3)_5O14(OH)_4CordieriteCrdMg2Ala(SiSO4)_5)_5O14(OH)_4CordieritefCdFe2Al3(AlSisO18)Fe-cordieritefCdFe2Al3(AlSisO18)ChamositeChaFesAl(AlSisO10)(OH)8ChloritoidCldFe4L2(SiO4)O(OH)2FerrosiliteFsFe2(Si2O6)GruneriteGruFe7(Si8O22)(OH)2HercyniteHcFeAl2O4SpinelSplMgAl2O4MagnetiteMagFeFe2O4SapphirineSpr442MgAl4(Si2Al4O20)AnniteAnnKFe3(AlSi3O10)(OH)2Type 5AnorthiteAnCaAl2Si2O8LawsoniteLwsCaAl2(Si2O7)(OH)2×H2OZoisiteZoCa2Al3(SiO4)(Si2O7)OOHEpidoteEpCa2Al2Fe(SiO4)(Si2O7)OOHActinoliteActCa2Fe3(Si8O22)(OH)2AmesiteAmsMg4Al2(Al2Si2O10)(OH)8RhodoniteRdnMnSiO3Type 6PrpMg3Al2(SiO4)3PyropePrpMg3Al2(SiO4)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa2(Mg3Al2)(Al2SiO2)(OH)2VesuvianiteYesCa19Mg2Al11(SiO4)12(Si2O7)3(OH)9ClinochloreCclMg2Al2(AlSi3O10)(OH)8	Staurolite	St	$Fe_4Al_{18}(SiO_4)_7 = O_{14}(OH)_4$		
Ing<	Mg-staurolite	mSt	$Mg_{4}Al_{18}(SiO_{4})_{7.5}O_{14}(OH)_{4}$		
ContentFreeFe-cordieritefCd $Fe_2Al_3(AlSi_5O_{18})$ ChamositeCha $Fe_5Al(AlSi_5O_{18})$ ChornositeCha $Fe_5Al(AlSi_5O_{18})$ ChloritoidCld $FeAl_2(SiO_4)O(OH)_2$ FerrosiliteFs $Fe_2(Si_2O_6)$ GruneriteGru $Fe_7(Si_8O_{22})(OH)_2$ HercyniteHc $FeAl_2O_4$ SpinelSplMgAl_2O_4MagnetiteMag $FeFe_2O_4$ SapphirineSpr442MgAl_4(Si_2Al_4O_{20})MarrieAnnKFe_3(AlSi_3O_{10})(OH)_2Type 5AnorthiteAnnCaAl_2Si_2O_8LawsoniteLwsCaAl_2(Si_2O_7)(OH)_2×H_2OZoisiteZoCa_2Al_3(SiO_4)(Si_2O_7)OOHEpidoteEpCa_2Al_2Fe_3(Si_8O_{22})(OH)_2AttionativeArtCa_2Fe_3(Si_8O_{22})(OH)_2AmesiteArmsMg_Al_2(Al_2Si_2O_1)MadaditeAddrMasio_3Type 6PyropePrpMg_3Al_2(SiO_4)_3AndraditeAddrCa_3Fe_2(SiO_4)_3GrossularGrsCa_2(Mg_3Al_2(SiO_4)_3HedenbergiteHedCaFe(Si_2O_6)TschermakiteTsCa_2(Mg_3Al_2(SiO_4)_3)HedenbergiteHedCaFe(Si_2O_6)ClinochloreCclMg_2Al_1(AlSi_5O_{10})(OH)_8	Cordierite	Crd	$Mg_{a}Al_{a}(AlSi_{a}O_{a}O_{a})$		
$\begin{tabular}{ c c c c c } \hline Product Produ$	Fe-cordierite	fCd	$Fe_2 Al_2 (AlSi_2 O_{12})$		
ChambaicChambaicFig. R(FB)(0(CH))gChloritoidCldFeAl2(SiO4)O(CH))2FerrosiliteFsFe2(Si2O6)GruneriteGruFe7(Si8O22)(OH)2HercyniteHcFeAl2(O4SpinelSplMgAl2O4MagnetiteMagFeFe2O4SapphirineSpr442MgA4l4(Si2Al4O20)MarnetAnnKFe3(AlSi3O10)(OH)2AnniteAnnKFe3(AlSi3O10)(OH)2Type 5AnorthiteAnCaAl2Si2O8LawsoniteLwsCaAl2(Si2O7)(OH)2×H2OZoisiteZoCa2Al3(SiO4)(Si2O7)OOHEpidoteEpCa2Al2Fe(SiO4)(Si2O7)OOHActinoliteActCa2Fe3(Si8O22)(OH)2AmesiteAmsMg4Al2(Al2Si2O10)(OH)8RhodoniteRdnMnSiO3Type 6PyropePrpMg3Al2(SiO4)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa3Al2(SiO4)3HedenbergiteHedCaFe(Si2O6)TschermakiteTsCa2(Mg3Al2(SiO4)3)CharlesCaFe3(Si2O1)CharlesCaFe3(Si2O1)SpropePrpMg3Al2(SiO4)3GrossularGrsCa3Al2(SiO4)3GrossularTsCa2(Mg3Al2)(Al2Si6O22)(OH)2VesuvianiteVesCa3Al2(SiO4)3GrossularGrsCa3Al2(SiO4)3GrossularGrsCa3Al2(SiO4)3GrossularGrsCa3Al2(SiO4)3	Chamosite	Cha	$Fe_{1} \Delta I (\Delta I Si_{10} \Omega_{10}) (OH)_{0}$		
ChinoldFerFerrosiliteFs $Fe_2(Si_2O_6)$ GruneriteGru $Fe_7(Si_8O_{22})(OH)_2$ HercyniteHc $FeAl_2O_4$ SpinelSplMgAl_2O_4MagnetiteMag $FeFe_2O_4$ SapphirineSpr442Mg_4Al_4(Si_2Al_4O_{20})AnniteAnnKFe_3(AlSi_3O_{10})(OH)_2Type 5AnorthiteAnCaAl_2Si_2O_8LawsoniteLwsCaAl_2(Si_2O_7)(OH)_2×H_2OZoisiteZoCa_2Al_3(SiO_4)(Si_2O_7)OOHEpidoteEpCa_2Al_3(SiO_4)(Si_2O_7)OOHAnesiteAmsMg_4Al_2(Al_2Si_2O_{10})(OH)_8RhodoniteActCa_2Fe_5(Si_8O_{22})(OH)_2Type 6PyropePyropePrpMg_3Al_2(SiO_4)_3AndraditeAdrCa_3Fe_2(SiO_4)_3GrossularGrsCa_3Al_2(SiO_4)_3HedenbergiteHedCaFe(Si_2O_6)TschermakiteTsCa_2(Mg_3Al_2)(Al_2Si_0O_2)(OH)_2VesuvianiteVesCa_19Mg2Al_1(SiO_4)_12(Si_2O_7)_3(OH)_9ClinochloreCclMg_3Al_2(AlSi_3O_{10})(OH)_8	Chloritoid	Cld	$F_{eAl}(SiO_{10})(OH)_{8}$		
InformerItsIt2(S12G) Fer(Si8O22)(OH)2GruneriteGruFer(Si8O22)(OH)2HercyniteHcFeAl2O4SpinelSplMgAl2O4MagnetiteMagFeFe2O4SapphirineSpr442Mg4Al4(Si2Al4O20)Spr793Mg3.sAl4.s(Si_1.sAl4.sO20)AnniteAnnKFe3(AlSi3O10)(OH)2Type 5AnorthiteAnCaAl2Si2O8LawsoniteLwsCaAl2(Si2O7)(OH)2×H2OZoisiteZoCa2Al3(SiO4)(Si2O7)OOHEpidoteEpCa2Al2Fe(SiO4)(Si2O7)OOHAmesiteArmsMg4Al2(Al2Si2O10)(OH)2MesiteArmsMg3Al2(SiO4)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa3Al2(SiO4)3HedenbergiteHedCaFe(Si2O6)TschermakiteTsCa2(Mg3Al2)(Al2Si6O22)(OH)2VesuvianiteVesCa19Mg2Al1(SiO4)3ClinochloreCclMg3Al2(SiO4)3	Ferrosilite	Fe	$Fe_{1}(Si_{1}O_{1})$		
OrtuenteFey($3_180_{22}(G11)_2$ HercyniteHcFeAl ₂ O ₄ SpinelSplMgAl ₂ O ₄ MagnetiteMagFeFe ₂ O ₄ SapphirineSpr42Mg ₄ Al ₄ (Si ₂ Al ₄ O ₂₀)Spr793Mg _{3.5} Al _{4.5} (Si _{1.5} Al _{4.5} O ₂₀)AnniteAnnKFe ₃ (AlSi ₃ O ₁₀)(OH) ₂ Type 5AnorthiteAnCaAl ₂ Si ₂ O ₈ LawsoniteZoCa ₂ Al ₃ (SiO ₄)(Si ₂ O ₇)(OH) ₂ ×H ₂ OZoisiteZoCa ₂ Al ₃ Fe(SiO ₄)(Si ₂ O ₇)OOHEpidoteEpCa ₂ Al ₂ Fe(SiO ₄)(Si ₂ O ₇)OOHAmesiteAmsMg ₄ Al ₂ (Al ₂ Si ₂ O ₁₀)(OH) ₈ RhodoniteRdnMnSiO ₃ Type 6PyropePrpMg ₃ Al ₂ (SiO ₄) ₃ AndraditeAdrCa ₃ Fe ₂ (SiO ₄) ₃ GrossularGrsCa ₃ Al ₂ (SiO ₄) ₃ HedenbergiteHedCaFe(Si ₂ O ₆)TschermakiteTsCa ₂ (Mg ₃ Al ₂)(Al ₂ Si ₆ O ₂₂)(OH) ₂ VesuvianiteVesCa ₁ Mg ₂ Al ₁₁ (SiO ₄) ₁₂ (Si ₂ O ₇) ₃ (OH) ₉ ClinochloreCclMg ₅ Al(AlSi ₃ O ₁₀)(OH) ₈	Gruperite	Gru	$F_2(S_1 O_6)$ Fe (Si O)(OH)		
IncFerago4SpinelSplMgAl2O4MagnetiteMagFeFe2O4SapphirineSpr442Mg4Al4(Si2Al4O20)Spr793Mg3,SAl4,S(Si1,SAl4,SO20)AnniteAnnKFe3(AlSi3O10)(OH)2Type 5AnorthiteAnCaAl2Si2O8LawsoniteLwsCaAl2(Si2O7)(OH)2×H2OZoisiteZoCa2Al3(SiO4)(Si2O7)OOHEpidoteEpCa2Al2Fe5(SiQ02)(OH)2AmesiteAmsMg4Al2(Al2Si2O10)(OH)8RhodoniteRdnMnSiO3Type 6PyropePrpMg3Al2(SiO4)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa3Al2(SiO4)3HedenbergiteHedCaFe(Si2O6)TsCa2(Mg3Al2)(Al2Si6O22)(OH)2VesuvianiteVesCa19Mg2Al1(SiO4)12(Si2O7)3(OH)9ClinochloreCclMg5Al(AlSi3O10)(OH)8	Harownita	He	$F_{7}(51_{8}O_{22})(011)_{2}$		
SpinelSpinMgA2O4MagnetiteMagFeFe2O4SapphirineSpr442Mg4A14(Si2A14O20)Spr793Mg3.5A14.5(Si1.5A14.5O20)AnniteAnnKFe3(AISi3O10)(OH)2Type 5AnorthiteLawsoniteLwsCaA12(Si2O8LawsoniteZoCa2A13(SiO4)(Si2O7)(OH)2×H2OZoisiteZoCa2A13(SiO4)(Si2O7)OOHEpidoteEpCa2A12Fe(SiO4)(Si2O7)OOHAnesiteAmsMg4A12(A12Si2O10)(OH)2AmesiteAmsMg3A12(SiO4)(Si2O7)OOHRhodoniteRdnMnSiO3Type 6PyropePrpMg3A12(SiO4)3AndraditeAdrCa3Fe2(SiO4)3GrossularGrsCa3A12(SiO4)3HedenbergiteHedCaFe(Si2O6)TschermakiteTsCa2(Mg3A12)(A12Si6O22)(OH)2VesuvianiteVesCa19Mg2A11(SiO4)12(Si2O7)3(OH)9ClinochloreCclMg5A1(AISi3O10)(OH)8	Spinal	Enc Sml			
Magnetite Mag Fere204 Sapphirine Spr442 $Mg_4Al_4(Si_2Al_4O_{20})$ Spr793 $Mg_{3.5}Al_{4.5}(Si_{1.5}Al_{4.5}O_{20})$ Annite Ann KFe ₃ (AlSi ₃ O ₁₀)(OH) ₂ Type 5 Anorthite An CaAl ₂ Si ₂ O ₈ Lawsonite Lws CaAl ₂ (Si ₂ O ₇)(OH) ₂ ×H ₂ O Zoisite Zo Ca ₂ Al ₃ (SiO ₄)(Si ₂ O ₇)OOH Epidote Ep Ca ₂ Al ₂ Fe(SiO ₄)(Si ₂ O ₇)OOH Actinolite Act Ca ₂ Fe ₅ (Si ₈ O ₂₂)(OH) ₂ Amesite Ams Mg ₄ Al ₂ (Al ₂ Si ₂ O ₁₀)(OH) ₈ Rhodonite Rdn MnSiO ₃ Type 6 Pyrope Prp Mg ₃ Al ₂ (SiO ₄) ₃ Andradite Addr Ca ₃ Fe ₂ (SiO ₄) ₃ Grossular Grs Ca ₃ Al ₂ (SiO ₄) ₃ Hedenbergite Hed CaFe(Si ₂ O ₆) Tschermakite Ts Ca ₂ (Mg ₃ Al ₂)(Al ₂ Si ₆ O ₂₂)(OH) ₂ Vesuvianite Ves Ca ₁₉ Mg ₂ Al ₁ (SiO ₄) ₁₂ (Si ₂ O ₇) ₃ (OH) ₉	Spiller	Spi	MgAI ₂ O ₄		
Sappnirine Spr442 Mg ₄ Al ₄ (Sl ₂ Al ₄ O ₂₀) Spr793 Mg _{3.5} Al _{4.5} (Si _{1.5} Al _{4.5} O ₂₀) Annite Ann KFe ₃ (AlSi ₃ O ₁₀)(OH) ₂ Type 5 Anorthite An CaAl ₂ Si ₂ O ₈ Lawsonite Lws CaAl ₂ (Si ₂ O ₇)(OH) ₂ ×H ₂ O Zoisite Zo Ca ₂ Al ₃ (SiO ₄)(Si ₂ O ₇)OOH Epidote Ep Ca ₂ Al ₂ Fe(SiO ₄)(Si ₂ O ₇)OOH Actinolite Act Ca ₂ Fe ₅ (Si ₈ O ₂₂)(OH) ₂ Amesite Ams Mg ₄ Al ₂ (Al ₂ Si ₂ O ₁₀)(OH) ₈ Rhodonite Rdn MnSiO ₃ Type 6 Pyrope Prp Mg ₃ Al ₂ (SiO ₄) ₃ Andradite Adr Ca ₃ Fe ₂ (SiO ₄) ₃ Grossular Grs Ca ₃ Al ₂ (SiO ₄) ₃ Hedenbergite Hed CaFe(Si ₂ O ₆) Tschermakite Ts Ca ₂ (Mg ₃ Al ₂)(Al ₂ Si ₆ O ₂₂)(OH) ₂ Vesuvianite Ves Ca ₁₉ Mg ₂ Al ₁ (SiO ₄) ₁₂ (Si ₂ O ₇) ₃ (OH) ₉	Samphining	Mag	$FeFe_2O_4$		
$\begin{array}{ c c c c c } & Spr /93 & Mg_{3.5}Al_{4.5}(Si_{1.5}Al_{4.5}O_{20}) \\ \hline & Ann & KFe_3(AlSi_3O_{10})(OH)_2 \\ \hline & & \\ \hline \hline & & \\ \hline & & \\ \hline & & \\ \hline $	Sapphirine	Spr442	$Mg_4AI_4(SI_2AI_4O_{20})$		
AnniteAnn $KFe_3(AISI_3O_{10})(OH)_2$ Type 5AnorthiteAn $CaAl_2Si_2O_8$ LawsoniteLws $CaAl_2(Si_2O_7)(OH)_2 \times H_2O$ ZoisiteZo $Ca_2Al_3(SiO_4)(Si_2O_7)OOH$ EpidoteEp $Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$ ActinoliteAct $Ca_2Fe_5(Si_8O_{22})(OH)_2$ AmesiteAms $Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$ RhodoniteRdnMnSiO_3Type 6PyropePrp $Mg_3Al_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_1_9Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)(OH)_9$	A	Spr/93	$Mg_{3.5}AI_{4.5}(S1_{1.5}AI_{4.5}O_{20})$		
Iype 3AnorthiteAn $CaAl_2Si_2O_8$ LawsoniteLws $CaAl_2(Si_2O_7)(OH)_2 \times H_2O$ ZoisiteZo $Ca_2Al_3(SiO_4)(Si_2O_7)OOH$ EpidoteEp $Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$ ActinoliteAct $Ca_2Fe_5(Si_8O_{22})(OH)_2$ AmesiteAms $Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$ RhodoniteRdnMnSiO_3Type 6PyropePrp $Mg_3Al_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_1_9Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Annite	Ann	$KFe_3(AIS1_3O_{10})(OH)_2$		
AnorthiteAnCaAl_2Sl_2Q_8LawsoniteLwsCaAl_2(Si_2O_7)(OH)_2×H_2OZoisiteZoCa_2Al_3(SiO_4)(Si_2O_7)OOHEpidoteEpCa_2Al_2Fe(SiO_4)(Si_2O_7)OOHActinoliteActCa_2Fe_5(Si_8O_{22})(OH)_2AmesiteAmsMg_4Al_2(Al_2Si_2O_{10})(OH)_8RhodoniteRdnMnSiO_3Type 6PyropePrpMg_3Al_2(SiO_4)_3GrossularGrsCa_3Al_2(SiO_4)_3HedenbergiteHedCaFe(Si_2O_6)TschermakiteTsCa_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2VesuvianiteVesCa_19Mg_2Al_1(SiO_4)_12(Si_2O_7)(OH)_9ClinochloreCclMg_5Al(AlSi_3O_{10})(OH)_8	Type 5				
LawsoniteLwsCaAl ₂ (Sl ₂ O ₇)(OH) ₂ ×H ₂ OZoisiteZo $Ca_2Al_3(SiO_4)(Si_2O_7)OOH$ EpidoteEp $Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$ ActinoliteAct $Ca_2Fe_5(Si_8O_{22})(OH)_2$ AmesiteAmsMg ₄ Al ₂ (Al ₂ Si ₂ O ₁₀)(OH) ₈ RhodoniteRdnMnSiO ₃ Type 6PyropePrpMg ₃ Al ₂ (SiO ₄) ₃ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCclMg ₅ Al(AlSi_3O_{10})(OH)_8	Anorthite	An	$C_{a}A_{1_2}S_{1_2}O_8$		
ZoisiteZo $Ca_2AI_3(SIO_4)(Si_2O_7)OOH$ EpidoteEp $Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$ ActinoliteAct $Ca_2Fe_5(Si_8O_{22})(OH)_2$ AmesiteAms $Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$ RhodoniteRdnMnSiO_3Type 6PyropePrp $Mg_3Al_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Lawsonite	LWS	$CaAl_2(Sl_2O_7)(OH)_2 \times H_2O$		
EpidoteEp $Ca_2Al_2Fe(StO_4)(St_2O_7)OOH$ ActinoliteAct $Ca_2Fe_5(St_8O_{22})(OH)_2$ AmesiteAms $Mg_4Al_2(Al_2St_2O_{10})(OH)_8$ RhodoniteRdnMnSiO_3Type 6PyropePyropePrp $Mg_3Al_2(StO_4)_3$ GrossularGrs $Ca_3Fe_2(StO_4)_3$ HedenbergiteHed $CaFe(St_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2St_6O_{22})(OH)_2$ VesuvianiteVes $Ca_1_9Mg_2Al_{11}(StO_4)_{12}(St_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSt_3O_{10})(OH)_8$	Zoisite	Zo	$Ca_2AI_3(SIO_4)(SI_2O_7)OOH$		
ActinoliteAct $Ca_2Fe_5(Si_8O_{22})(OH)_2$ AmesiteAms $Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$ RhodoniteRdnMnSiO_3Type 6PyropePrp $Mg_3Al_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Epidote	Ep	$Ca_2Al_2Fe(SiO_4)(Si_2O_7)OOH$		
AmesiteAms $Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$ RhodoniteRdnMnSiO_3Type 6PyropePrpMg_3Al_2(SiO_4)_3AndraditeAdrCa_3Fe_2(SiO_4)_3GrossularGrsCa_3Al_2(SiO_4)_3HedenbergiteHedCaFe(Si_2O_6)TschermakiteTsCa_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2VesuvianiteVesCa1_9Mg_2Al_1(SiO_4)_12(Si_2O_7)_3(OH)_9ClinochloreCclMg_5Al(AlSi_3O_{10})(OH)_8	Actinolite	Act	$Ca_2Fe_5(S1_8O_{22})(OH)_2$		
RhodoniteRdnMnSiO3Type 6PyropePrpMg_3Al_2(SiO_4)_3AndraditeAdrCa_3Fe_2(SiO_4)_3GrossularGrsCa_3Al_2(SiO_4)_3HedenbergiteHedCaFe(Si_2O_6)TschermakiteTsCa_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2VesuvianiteVesCa_19Mg_2Al_1(SiO_4)_12(Si_2O_7)_3(OH)_9ClinochloreCclMg_5Al(AlSi_3O_{10})(OH)_8	Amesite	Ams	$Mg_4Al_2(Al_2Si_2O_{10})(OH)_8$		
Type 6PyropePrp $Mg_3Al_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Rhodonite	Rdn	MnSiO ₃		
PyropePrp $Mg_3Al_2(SiO_4)_3$ AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_1_9Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Туре б				
AndraditeAdr $Ca_3Fe_2(SiO_4)_3$ GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_1_9Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Pyrope	Prp	$Mg_3Al_2(SiO_4)_3$		
GrossularGrs $Ca_3Al_2(SiO_4)_3$ HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Andradite	Adr	$Ca_3Fe_2(SiO_4)_3$		
HedenbergiteHed $CaFe(Si_2O_6)$ TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Grossular	Grs	$Ca_3Al_2(SiO_4)_3$		
TschermakiteTs $Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$ VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Hedenbergite	Hed	$CaFe(Si_2O_6)$		
VesuvianiteVes $Ca_{19}Mg_2Al_{11}(SiO_4)_{12}(Si_2O_7)_3(OH)_9$ ClinochloreCcl $Mg_5Al(AlSi_3O_{10})(OH)_8$	Tschermakite	Ts	$Ca_2(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2$		
Clinochlore Ccl Mg ₅ Al(AlSi ₃ O ₁₀)(OH) ₈	Vesuvianite	Ves	Ca ₁₉ Mg ₂ Al ₁₁ (SiO ₄) ₁₂ (Si ₂ O ₇) ₃ (OH) ₉		
	Clinochlore	Ccl	$Mg_5Al(AlSi_3O_{10})(OH)_8$		

Mineral	

Abbreviation

End of the table

Composition

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Prehnite	Prh	$Ca_2Al(AlSi_3O_{10})(OH)_2$		
Riebeckite	Rbk	$Na_2Fe_3Fe_2(Si_8O_{22})(OH)_2$		
Gedrite	Ged	$Mg_5Al_2(Al_2Si_6O_{22})(OH)_2$		
Type 7				
Phlogopite	Phl	$KMg_3(AlSi_3O_{10})(OH)_2$		
Pargasite	Pgs	NaCa2Mg4Al(Al2Si6O22)(OH)2		
Glaucophane	Gln	Na ₂ Mg ₃ Al ₂ (Si ₈ O ₂₂)(OH) ₂		
Aegirine	Aeg	$NaFe(Si_2O_6)$		
Anthophyllite	Ath	$Mg_7(Si_8O_{22})(OH)_2$		
Clinohumite	Chu	$Mg_9(SiO_4)_4(OH)_2$		
Cummingtonite	Cum	$Mg_7(Si_8O_{22})(OH)_2$		
Talc	Tlc	$Mg_3(Si_4O_{10})(OH)_2$		
Enstatite	En	$Mg_2(Si_2O_6)$		
Chrysotile	Ctl	$Mg_3(Si_2O_5)(OH)_4$		
Diopside	Di	$CaMg(Si_2O_6)$		
Tremolite	Trm	$Ca_2Mg_5(Si_8O_{22})(OH)_2$		
Wollastonite	Wo	CaSiO ₃		

Results of solubility calculations. To study mineral behaviour in aqueous fluid, we have calculated the mineral solubility at various P-T conditions and fluid acidity. The fluid acidity was presented by concentration of HCl and NaOH in the fluid. The calculations have revealed that for the most of minerals the effect of acidity upon solubility is greater than effect of temperature or pressure. Analysis of solubility dependence on fluid acidity–alkalinity allowed us to distinguish seven main types of solubility diagrams (fig. 1). We characterize below these types and the main features of mineral behaviour in aqueous fluids depending on dissolution conditions.

Types of solubility diagrams.

T y p e 1. The first type of solubility diagrams inheres in quartz and alkalinealuminous silicates: microcline, albite and jadeite. These minerals are well soluble (more than $10^{-2}-10^{-3}$ mole/kg H₂O). Their solubilities are almost independent of the fluid acidity (fig. 1, 2). Solubility of the minerals of this type increases in about half of the order (one order for quartz) with the pressure increasing from 1 to 5 kbar. The increase of temperature from 400 to 800°C causes the rise of solubility in one order. Mineral solubility series in pure water for the first type is presented in fig. 3. With the pressure increase albite becomes slightly more soluble than microcline. In general their solubility is very close. Solubility increases in about 0.3–1.3 orders with the temperature rise and the effect becomes more pronounced with the pressure growth.

T y p e 2. White micas (muscovite and paragonite) are characterized by the second type of solubility diagrams (fig. 1, 4). These minerals are also rather well soluble and have the lowest solubility in pure water, low alkaline and low-middle acid solutions. At low temperatures their solubility increases in 1.0-1.5 orders in alkaline solutions and slightly in strongly acid solutions (0.1-1.0M HCl). Changing of temperature at low pressure (1 kbar) has low influence upon the solubility increases in 0.5-1.0 order in the solutions of different acidity. Solubility of muscovite and paragonite are close (see fig. 3), but at 5 kbar paragonite becomes more soluble than muscovite. Solubility in water increases (in about 0.3-1.0 order), and this effect becomes stronger with the pressure increase.



Fig. 1. Types of the mineral solubility diagrams depending on the metamorphic fluid acidity.

T y p e 3. The third type of solubility diagrams inheres in such minerals as corundum, hematite and alumina silicates (andalusite, kyanite and sillimanite). These minerals have the lowest solubility in pure water and acid solutions with HCl. Alumina silicates are the most soluble in this group (fig.1, 5). Their solubility increases considerably (in 2.0–3.5 orders) in alkaline solutions with NaOH and weakly in acid solutions (0.1–1.0M HCl) at low temperatures. Corundum solubility increases in about 4.0–4.5 orders in alkaline solutions with NaOH and at low temperatures in 1–3 orders in strongly acid solutions (0.1–1.0M HCl). Hematite is the least soluble mineral in this group (fig. 6). Its solubility increases in alkaline solutions and (at low temperatures) considerably in 2.5–5.5 orders in acid solutions.



Fig. 2. Dependence of microcline solubility on the fluid acidity at 400 (l), 500 (2), 600 (3), 700 (4), 800°C (5) and 1 (a) and 5 (b) kbar: the first solubility type.

Temperature change at 1 kbar has no strong influence upon solubility of corundum and alumina silicates in solutions with different acidity. At 5 kbar their solubility can increase together with temperature increase in pure water and acid solutions. But temperature dependence of the hematite solubility has opposite character and is very pronounced. Temperature increase at low pressure can reduce considerably hematite solubility in solutions of various acidity and particularly in strongly acid and strongly alkaline solutions (in about 2.0-3.5 orders). At 5 kbar, temperature increase reduces considerably hematite solubility only in acid solutions (in 1.5-6.5 orders) and this effect reinforces with the rise of acidity. At pressure increase the solubility of minerals belonging to this group, except hematite, can increase within one order. For hematite pressure dependence connected with the increasing of solubility is more obvious (in 1.5–4.0 orders) and this effect is reinforced together with the increase of acidity and alkalinity in comparison with pure water solutions. Solubility series in pure water (see fig. 3) demonstrates that temperature increase at P = 1 kbar does not cause the changing of corundum and alumina silicates solubility and reduces hematite solubility (in about 0.9 order). At P = 5 kbar temperature increase causes the increase of corundum and alumina silicates solubility in water (about in 1.2 order) and, vice versa, reduces hematite solubility in about 0.4 order.



Fig. 3. Mineral solubility series in pure water for 1st-3rd types at 400-800°C and 1 and 5 kbar.

T y p e 4. The fourth type of solubility diagrams inheres in the minerals rich in amphoteric elements Al and Fe: Fe- and Mg-staurolites, cordierite and Fe-cordierite, chloritoid, sapphirines, almandine, spessartine, chamosite (Fe-chlorite), spinelids (spinel, her-cynite and magnetite), ferrosilite (Fe-orthopyroxene), grunerite, annite. These minerals are less soluble than the minerals of the previous groups and have the lowest solubility in pure water (fig. 1, 7, 8). In acid solutions their solubility increases in 1.5-7.0 orders and in alkaline solutions – in 1.0-4.5 orders.

Temperature increase at pressure of 1 kbar reduces the solubility of alumina minerals (chloritoid, staurolite, spinel, sapphirine, cordierite) in 0.5–1.0 order in acid and alkaline solutions. For ferrous minerals (magnetite, annite, almandine, grunerite, chamosite, ferrosilite) some influence of temperature on the solubility is observed only in alkaline solutions. At 5 kbar, temperature change has little influence on the solubility of minerals belonging to this group, excepting staurolite. The solubility series in pure water is presented in fig. 9. At low pressure solubility of minerals of the fourth group in water is constant or weakly reduces as the temperature increases. E.g., Mg-spinel solubility reduces in 0.6 order and magnetite solubility – in 0.8 order. At P = 5 kbar chloritoid, ferrosilite, spinel and chamosite change their place in the solubility series: chloritoid can become more soluble than ferrosilite, and spinel – more soluble than chamosite. With temperature increase at 5 kbar the water solubility changes weakly. For example, solubility



ity of chamosite and chloritoid increases in 0.7–0.9 order. Magnetite makes an exception: its solubility decreases with temperature increase as at low pressure.

Fig. 4. Dependence of muscovite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the second solubility type. Conventional signs here and further same, as in a fig. 2.

T y p e 5. This type inheres in silicates rich in Ca or Mg and Al or Fe^{3+} : anorthite, lawsonite, Mg-chlorite (amesite), epidote and zoisite, actinolite and, also, rhodonite. These minerals have the lowest solubility in pure water, low acid, low- and middle alkaline solutions (fig. 1, 10, 11). Their solubility increases in about 2.0–3.5 orders in acid solutions and not considerably in strongly alkaline ones (~0.1–1.0M NaOH). Temperature increase at 1 kbar can reduce solubility of epidotes and anorthite in ~0.5–2.0 orders both in acid and alkaline solutions, whereas amesite – only in alkaline solutions. At 5 kbar, temperature changing has even less influence upon the solubility of these minerals. But for amesite in alkaline solutions the weak temperature dependence of solubility can change into the opposite one. Mineral solubility series in pure water is shown in fig. 12. With temperature increase at low pressure water solubility of these minerals is almost



constant or slightly decreases (in $\sim 0.2-0.4$ order). With temperature increase at high pressure the solubility in water slightly increases (in $\sim 0.2-0.6$ order).

Fig. 5. Dependence of andalusite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the third solubility type.

T y p e 6. This type of solubility diagrams inheres in Al- and Fe-bearing silicates rich in Ca and Mg – garnets (pyrope, grossular, andradite), hedenbergite, some amphiboles (tschermakite, gedrite, riebeckite), vesuvianite, prehnite, clinochlore (Mg-chlorite). These minerals have the lowest solubility in pure water and alkaline solutions (fig.1, 13). In acid solutions their solubility increases in $\sim 2.0-3.5$ orders in comparison with water. Temperature increase at low pressure can reduce the solubility in $\sim 0.5-2.0$ orders in acid solutions and in ~ 0.5 order in the alkaline ones. With temperature increase at 5 kbar the solubility reduces weakly (andradite) or does not change in solutions with various acidity.



Fig. 6. Dependence of hematite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the third solubility type.

Exclusions are clinochlore, prehnite, and riebeckite. Their temperature solubility dependence changes to the opposite one in alkaline solutions: it slightly increases (in ~0.5 order) as temperature grows. Mineral solubility series in pure water is presented in fig. 12. Temperature increase at low pressure causes some decreasing of mineral solubility in water (in ~0.2–0.3 order). At temperature increase and high pressure the mineral solubility in water is almost constant or slightly increases (in ~0.2–0.3 order), excepting andradite. Its solubility slightly decreases (in ~0.3 order) at temperature increase, as it is at low pressure.

T y p e 7. This type of solubility diagrams inheres in Mg- and Ca-silicates without Al and Fe: Mg- and Mg-Ca-amphiboles and pyroxenes (anthophyllite, cummingtonite, tremolite; enstatite, diopside), wollastonite, clinohumite, talk, serpentine (chrysotile), and also Ca- and Mg-silicates rich in alkaline elements: K-Mg mica (phlogopite), Na-bearing



amphiboles (pargasite, glaucophane) and Na-bearing pyroxene (aegirine). These minerals have the lowest solubility in alkaline solutions (fig.1, 14–16).

Fig. 7. Dependence of almandine solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the fourth solubility type.

Solubility of minerals belonging to the seventh type increases considerably in acid solutions (in ~1.5–4.5 orders) and weakly decreases in alkaline solutions (in ~0.5–2.0 orders). Temperature growth at low pressure decreases the solubility in ~0.5–1.5 orders in acid solutions, wollastonite solubility decreases in ~0.5 order in alkaline solutions. Temperature increase at high pressure does not change the solubility of most of minerals in the solutions with different acidity. So, glaucophane solubility increases in ~0.3 order only in alkaline solutions, whereas wollastonite and clinohumite solubility decreases in ~0.5 order in alkaline solutions. Aegirine solubility increases in ~0.3 order in alkaline solutions and decreases in ~0.5–1.0 order in the acid ones. Mineral solubility series in pure water solution is presented in fig. 16. Mineral solubility changes a little or decreases a bit (in ~0.2–0.4 order) at temperature increase and P = 1 kbar.



Fig. 8. Dependence of cordierite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the fourth solubility type.

Mineral solubility in water changes not considerably at temperature increase and P = 5 kbar, but for minerals containing alkaline elements it can increase a little (in ~0.2–0.4 order) and in minerals without alkaline elements it decreases a little (in ~0.2–0.3 order).

Effect of fluid acidity/alkalinity on mineral solubility. For all mineral groups, except the first type, the value of mineral solubility is mostly determined by fluid acidity-alkalinity and at a lesser degree – by P-T conditions. The solubility depends on changing of P-T conditions only for the minerals of the first type and does not depend for them on the solutions acidity.

Effect of temperature and pressure on mineral solubility. In neutral aqueous solutions the t e m p e r a t u r e effect is more pronounced (within \sim 1 order and more) for minerals from 1–4 types. Mineral solubility increases with temperature and pressure increase for the 1st and 2nd types. Changing of solubility is almost constant or slightly decreases with temperature increase at low pressure, and, vice versa, it increases at high pressure for minerals of the 3–6th types and alkaline-bearing minerals of the 7th type. There are exclusions for different types, such as hematite, magnetite and andradite: their solubility decreases with temperature increasing at any pressures. The same behaviour is

observed for the alkali-free minerals of the 7th type: their solubility decreases with temperature increasing at any pressures. In acid or alkaline solutions the solubility dependence on temperature is even more complicated: it can become stronger, weaker, disappear or change onto the opposite one.



Fig. 9. Mineral solubility series in pure water for the 4th type at 400–800°C and 1 and 5 kbar.

In neutral solutions p r e s s u r e enlarges the solubility of all considered minerals (~1 order). The role of pressure increases together with temperature rise. In acid and alkaline solutions pressure does not enlarge the solubility value, but this dependence becomes more differentiated. For minerals of the second and third types pressure dependence of solubility is more pronounced in acid solutions (it increases in ~0.3–2.0 orders) than in alkaline (in 0.2–0.5 order). The exclusion is hematite: its solubility can increase in ~4 orders in acid solutions and in ~3 orders in alkaline conditions. Higher temperature corresponds to stronger pressure dependence in acid solutions. Solubility of the most minerals of the other types increases both in acid and alkaline solutions in about 0.3–2.0 orders.

Elements mobility in fluids. Dependence of the mineral solubility on mineral composition and comparison of mineral behaviour in different fluids allows to characterize element mobility making up these minerals according to fluid acidity. The presented above description demonstrates that the most soluble minerals are quartz and silicates of alkalis and alumina. The solubility decreases with the decrease of alkali and silica content and increase of alumina content (see feldspars and micas). Solubility of alkali-free alumina silicates (Al_2SiO_5) is pronouncedly lower, and pure alumina (corundum) is even less soluble. Hence, we can make the following conclusions.



Fig. 10. Dependence of anorthite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the fifth solubility type.

Silica mobility does not depend really on the fluid acidity and is determined by P-T conditions. Si concentration in solution can reach 0.7 mole/kg H₂O (in equilibrium with quartz at 800°C and 5 kbar). Mobility of alkaline elements is also high in solutions with any acidity and is more dependent on P-T conditions. Concentration of alkalis in equilibrium solution can reach 0.05–0.10 mole/kg H₂O.

Iron (II), calcium and magnesium are mobile in acid solutions. Acidity increasing causes considerable increasing of their mobility. In equilibrium with minerals Fe(II) and Mg concentrations can reach in acid solutions 0.1-0.3 mole/kg H₂O and Ca – 0.5 mole/kg H₂O. Fe(II) is mobile also in strong alkaline solutions (up to 0.3 mole Fe²⁺/kg H₂O) but less than in acid solutions. Mg and Ca mobility is rather low (not higher than $2\cdot10^{-4}$ mole Ca/kg H₂O and $3\cdot10^{-5}$ mole Mg/kg H₂O).



Fig. 11. Dependence of actinolite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the fifth solubility type.

The least mobile elements are aluminium and iron (III). The corundum and hematite solubility points to their low mobility. The low limit of aluminium concentration in fluid in equilibrium with corundum is $1.5 \cdot 10^{-5}$ mole Al/kg H₂O (400°C, 1 kbar, 10^{-3} M HCl), the upper limit – 0.9 mole Al/kg H₂O (800°C, 5 kbar, 1M NaOH). Alumina mobility increases considerably together with alkalinity increase.

Equilibrium Fe(III) concentration in solution is rather low (see fig. 6): in neutral solutions it is not higher than 10^{-8} mole/kg H₂O, but in strong acid solutions at 5 kbar Fe(III)concentration in fluid reaches $10^{-3}-10^{-2}$ mole/kg H₂O. Basing on hematite and magnetite solubility it is obvious that iron should be transported in the solution mostly in the form of Fe(II) and oxidation of iron takes place directly at the crystallization of ferriferous minerals.



Fig. 12. Mineral solubility series in pure water for the 5th and 6th types at 400–800°C and 1 and 5 kbar.

So, changing of acidity should cause transition of some components into solution and deposition of the other ones. Such conclusions coincide with the series of element mobility revealed from study of the natural metasomatic processes [5, 7] and experimental investigation of metasomatism [6].

Analysis of metasomatic columns and mineral behaviour at metasomatism. Minerals belonging to different groups demonstrate different behaviour depending on the solution acidity. As a result, they can be indicators of acidity/alkalinity of the influencing solutions in the process of metasomatism. In the simplest cases it is quite enough to analyse the minerals from the inner zones of the column, which are in equilibrium with the flowing solution.

For example, enrichment of the inner zones of metasomatic column with poor-soluble minerals of the third type indicates, that this column was formed under the influence of acid solutions (acid metasomatism, acid leaching). Accumulation or appearance of minerals of the sixth or seventh types indicates, that this column was formed under the influence of alkaline solutions (alkaline or basic metasomatism).



Fig. 13. Dependence of grossular solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the sixth solubility type.

In more complicated and not obvious cases it is necessary to analyse the minerals not only from the inner zones but also from the middle and outer zones of a metasomatic column. We should consider different diagram types in this case.

At acid metasomatism the changing of mineral composition towards the inner zone should be determined by the differences in mobility of the mineral-forming components. In the inner zones of acidic columns the growth of acidity should result in stability of Fe-Mg minerals, rich in Al and Fe^{3+} (cordierite, staurolite, garnet, magnetite, etc.), and accumulation of minerals, rich in Si and Al. Hence, in inner metasomatic zones we can observe, for example, cordierite-andalusite and staurolite-andalusite metasomatic quart-zites [1–3]. At the further acidity growth Fe- and Mg-bearing minerals are dissolving but alumina minerals (e.g., andalusite) continue to accumulate.

K and Na mobility can be high in solutions of any acidity, so albite-andalusite and muscovite-andalusite quartzites are formed in the inner zones of acidic columns as well as quartz-albite rocks and albitites – in the inner zones of alkaline columns. Solubility of light micas increases in relation to alumina silicates according the increasing of solution

acidity. As a result we should expect their earlier disappearance in the inner zones of acid columns with the simultaneous accumulation of kyanite, and alusite or sillimanite in assemblage with quartz.



Fig. 14. Dependence of phlogopite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the seventh solubility type.

Acid plagioclases are less stable in neutral solutions at low pressure than calcareous ones. The stability of acid plagioclases should increase at the fluid acidity growth. Therefore acid plagioclases can accumulate in the inner zones of metasomatic columns.

Chemical specialisation of solutions. Study of the solution composition in equilibrium with metamorphic rocks is one of the most effective ways to determine the composition of metamorphic fluids [13, 14]. Since quartz has the largest solubility and occurs in most types of metamorphic rocks, metamorphic fluids should be, as a rule, rich in silica. Considerable amounts of SiO₂ and alkalis proceeds into aqueous fluid at dissolution of the minerals belonging to the fist and second types. These elements also prevail in neutral and acid solutions at the decomposition of the minerals belonging to the other types.



Fig. 15. Dependence of enstatite solubility on the fluid acidity at 400–800°C and 1 and 5 kbar: the seventh solubility type.

At the decrease of temperature and pressure solutions become supersaturated with these elements. This can explain the appearance of aggressive silica-alkaline fluids, producing metasomatism in metamorphic complexes.

In general, solubility of Fe-, Mg- and Ca-containing minerals in alkaline solutions is lower than in the acid ones. So, only initially acid solutions (possible reasons for their origin are discussed in [10, 11] can result in the formation of basic metamorphic fluids rich in these elements. However, fluids, enriched only in Fe, could have originally both acid and alkaline reaction.

Fluid acidity affects also composition of solid solutions and, hence, character of the intracrystalline growth zoning. The influence of fluid acidity on the element distribution between metamorphic garnet and aqueous fluids is considered in [9].

Conclusions.

- 1. The obtained numerical data can be used for numerical modelling, petrological and experimental investigations.
- 2. For all minerals, except for the first types (Qtz, Jd, Mi, Ab), the solubility value is determined mainly by the fluid acidity/alkalinity (pH) and, less, by *P*-*T* conditions.

Only the mineral solubility of the first type is determined by the P-T conditions and is almost independent from the fluid acidity.

3. Minerals of different types can be indicators of acidity or alkalinity of the initial solutions at study of the metasomatic processes. Analysis of the solubility diagrams for minerals from different metasomatic zones allows to estimate chemical composition and acidity of parent fluid and to reveal the influence of fluid composition over the changing of the mineral composition of metasomatites.



Fig. 16. Mineral solubility series in pure water for the 7th type at 400–800°C and 1 and 5 kbar.

- 4. Dependence of the mineral solubility on mineral composition and comparison of behaviour in various fluids permits to characterize the element mobility under different the fluid acidity and to estimate element concentrations in the solution.
- 5. Since quartz has the largest solubility and occurs in many metamorphic rocks, metamorphic fluids should be enriched in silica. Appearance of aggressive silica-alkaline fluids, producing metasomatism in metamorphic complexes, can be explained by the dissolution of considerable amounts of silica and alkalis at high *PT*-parameters and any acidity. At the same time, only primarily acid solutions can originate metamorphic fluids rich in Fe, Mg, Ca, owing to leaching of these elements from metamorphic rocks.

The work is supported by grants RFBR#01-05-65174 and RFBR#02-05-64803, HIII-615.2003.5 and MK-999-2003-05, BRHE program (grant Y1-G-15-04) and Russian Science Support Foundation.

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ЧИСЛОВЕ МОДЕЛЮВАННЯ РОЗЧИННОСТІ МЕТАМОРФІЧНИХ МІНЕРАЛІВ У ГІДРОТЕРМАЛЬНИХ РОЗЧИНАХ ЗА 400–800°С, 1–5 КБАР ТА РІЗНОЇ КИСЛОТНОСТІ ФЛЮЇДІВ

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Розглянуто характер розчинення у рідкому флюїді 56 звичайних мінералів метаморфічних порід залежно від *PT*-умов і складу флюїдів. Виконано комп'ютерне моделювання рівноваги мінерал-флюїд. Обчислення виконані як для чистої води, так і для розчинів, що містять кислоту (HCl) і луг (NaOH). Виділено сім головних типів діаграм розчинності залежно від особливостей поведінки мінералів у кислих і лужних розчинах. Для більшості мінералів, за винятком кварцу, мікрокліну, альбіту й жадеїту, розчинність визначена, голово, кислотністю флюїдів (pH), менше – *PT*умовами.

Аналіз розчинності мінералів дав змогу схарактеризувати рухливість елемента залежно від кислотності флюїдів. Наймобільніші елементи – Si, K i Na, незалежно від кислотності флюїдів. Са і Mg найрухливіші в кислих розчинах, тоді як Fe²⁺ мобільне й у кислих, і в лужних розчинах. Al – слабко рухливий елемент і переноситься, переважно, у лужних або сильно кислих розчинах. Найбільш нерухомим є Fe³⁺, тобто залізо переноситься, головно, у вигляді Fe²⁺. Тому зміна кислотності флюїдів приводить до розчинення одних компонентів і осадження інших. Мінерали різних типів можуть бути індикаторами кислотності флюїдів під час метасоматозу.

Завдяки високій розчинності кварцу більшість метаморфічних флюїдів повинна бути насичена SiO₂. Вони також повинні містити значну кількість лугів. Падіння тиску й температури може приводити до виникнення пересичених кварц-лужних флюїдів, які метасоматично змінюють вмісні породи. Розчинність Fe-, Mg- і Савмісних мінералів нижча в лужних флюїдах, порівняно з кислими. Отже, тільки первинно кислі флюїди можуть продукувати розчини, збагачені цими елементами, під час їхнього вилуговування із вмісних метаморфічних порід. Флюїди, збагачені тільки залізом, спочатку могли бути і кислими, і лужними.

Ключові слова: розчинність мінералів, флюїд, метаморфізм, термодинамічне моделювання, кислотність флюїдів, рухливість елемента.

Стаття надійшла до редколегії 02.09.2004 Прийнята до друку 15.11.2004