Geothermometry and the Principal Types of Geothermometers Used in Petrology

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Abstract

Geothermometry is a practical application of thermodynamics in petrology which follows the estimation of the temperatures at which certain geological processes took place. The geothermometry was and is used mostly in petrology of metamorphic rocks to estimate the temperatures at which the mineral assemblages have reached the thermodynamic equilibrium. This paper presents the notion of geothermometer, presents and comments on the characteristics of the mostly used types of geothermometers. As the experimental petrology makes progress, the geothermomethry will improve and in this way it will offer more and more precise data, which are so useful in petrogenetic interpretations and generally in geological ones.

Key words: *geothermometer, equilibrium, thermodynamics*

Introduction

Geothermometry is a practical application of thermodynamics in petrology through which the temperatures at which certain processes took place, especially those temperatures at which certain mineral assemblages from the metamorphic rocks have attained equilibrium. The main assumption which is made in the frame of this kind of applications is that those minerals from the assemblage that have attained equilibrium at a particular temperature T, that is to be estimated, have been preserved up to now with those compositional characteristics which they had at this temperature T. In other words, although the metamorphic rocks have passed from the high temperature conditions at which their paragenetic mineral association has attained equilibrium to much lower temperature conditions, the retromorphic reactions have not significantly altered the information recorded at that equilibration temperature.

A geothermometer is a mineral reaction that has in the PT diagram a monovariant equilibrium curve with a steep slope (fig. 1.) *i.e.* with a very large dP/dT ratio. This corresponds to a very large reaction entropy $\Delta_r S$ compared to the reaction volume $\Delta_r V$.

In case of geothermometers which imply mixed solid mineral phases, the concentrations of the end members in those solid solutions must be very much dependent on the temperature (in other words, the equilibrium constant K of these reactions is very much dependent on the temperature). In order to use such a reaction as a geothermometer it is necessary to make some calibrations i.e. to determine the variation of the equilibrium constant K with the temperature and if required with the pressure.
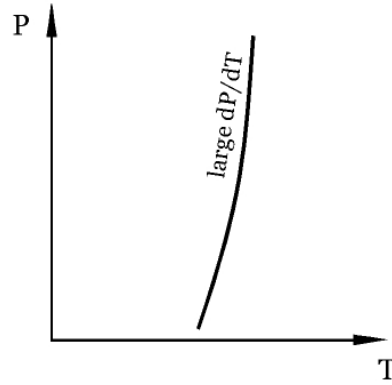
Fig. 1. The aspect of an equilibrium curve in the PT diagram for a reaction
that can be used as a geothermometer

The equilibrium constant of a reaction is given by:

$$\ln K = \frac{-\Delta_r G^0}{RT} \tag{1}$$

where: $\Delta_r G^0$ is the reaction free energy, R is the gas constant, and T is the temperature.

The calibrations can be experimental or empirical. The experimental calibrations are the most accurate and they are performed in laboratories both on artificial or natural mineral assemblage, by modifying in a controlled way the PT conditions. The empirical calibrations implies the finding of the equilibrium constant for the geothermometer reaction in natural mineral assemblage whose equilibration temperatures are determined or estimated using other geothermometers (e.g. by the equilibrium of net transfer reactions that implies relatively pure mineral phases).

To determine the equilibrium temperature of a mineral transformation reaction at constant pressure P, one can start with the relation defining the Gibbs free energy,

$$G = H - T S \tag{2}$$

where H is the enthalpy, S is the entropy and G is the free energy. From eq. (2) results that for a reaction which is at equilibrium at temperature T_e, this relation can be rewritten:

$$\left(\Delta_r G\right)_{T_e} = \left(\Delta_r H\right)_{T_e} - T\left(\Delta_r S\right)_{T_e} = 0 \tag{3}$$

where $\left(\Delta_r G\right)_{T_e}$ is the reaction free energy at the equilibrium temperature (so its value is zero), $\left(\Delta_r H\right)_{T_e}$ is the reaction enthalpy at the equilibrium temperature and $\left(\Delta_r S\right)_{T_e}$ is the reaction entropy at the equilibrium temperature.

From eq. (3) results that:

$$T_e = \frac{\left(\Delta_r H\right)_{T_e}}{\left(\Delta_r S\right)_{T_e}} \tag{4}$$

The reaction enthalpy ($\Delta_r H$) at equilibrium temperature T_e is given by:

$$\left(\Delta_r H\right)_{T_e} = \Delta_r H^0 + \int_{T_0}^{T_e} \frac{d\Delta_r H}{dT} dT = \Delta_r H^0 + \int_{T_0}^{T_e} \Delta_r c_p dT =$$
$$= \Delta_r H^0 + \Delta_r a\left(T_e - T_0\right) + \frac{\Delta_r b}{2}\left(T_e^2 - T_0^2\right) + \Delta_r c_p\left(\frac{1}{T_e} - \frac{1}{T_0}\right) \tag{5}$$

and the reaction entropy ($\Delta_r S$) at the equilibrium temperature T_e is given by:

$$\left(\Delta S_r\right)_{T_e} = \Delta S_T^0 + \int_{T_0}^{T} \frac{\Delta_r c_p dT}{T} = \Delta_r S^0 + \Delta_r a \ln\left(\frac{T_e}{T_0}\right) + \Delta_r b\left(T_e - T_0\right) \tag{6}$$

where: c_p is the specific heat, T_0 is the temperature in the standard condition, and a, b are empirical constants specific to each mineral phase involved in reaction.

It is obvious that finding the equilibrium temperatures of the mineral reaction means to know the thermodynamic data of the minerals involved, including those data for the end members of the solid solutions, given that the mixed mineral phases are frequently involved in these reactions. Moreover in the calculations where solid solutions are involved it is necessary to determine the concentration of the components in these solutions and to quantify the activity for each component. For this purpose there have been developed activity models for the non-ideal solid solutions, because in the most cases the mixing enthalpies ΔH_m and the mixing volumes ΔV_m differ from zero. At present the thermodynamic data needed for the geothermometric studies have been grouped in thermodynamic data bases. The relevance of the determinations obviously depends on the quality of the used data bases. The most well known published thermodynamic databases: Helgeson et al. (1978), Robie et. al. (1979), Robinson et al. (1982), Powell & Holland (1985), Berman et al. (1986), Berman (1988), Holland & Powell (1990), Gerya & Perchuk (1994), Robie & Hemingway (1995). Among these the most frequently quoted and used were Berman (1988) and Holland & Powell (1990).

According to the nature of the reactions, geothermometres are classified in different types. Among these frequently used are the following a) solvus geothermometres ; b) cationic exchange equilibriums geotermomethers ; c) solid-solid net transfer reactions geothermometers; d) solid $\rightleftharpoons$ solid+fluid net transfer reactions geothermometers.

Solvus Geothermometers

Solvus geothermometers are those geothermometers based on temperature dependent miscibility of end members of solid solutions. The notion of "solvus geothermometers" is used in the present not only for systems where the mineral phases are isostructural but also for systems where the involved phases have different internal structures. For a given temperature the equilibration among the mixed phases is also achieved by cationic exchange just as in the case of cationic exchange equilibriums geotermomethers. For this reason, these geothermometers are in fact particular cases of cationic exchange geotermomethers. Solvus geothermometer in feldspar system and solvus geothermometers for ortopyroxene-clinopyroxene system were chosen as examples.

The solvus geothermometer in the felsdpar system: potasic, sodic and calcic

In the potassium feldspar (Kfs) - albite (Ab) - anorthite (An) ternary system, at high temperatures, there is a total miscibility only among Kfs – Ab and Ab – An components. An component is very little miscible with Kfs, this miscibility may be neglected in the range of small temperatures. The first geothermometers used were based on the Ab component distribution in plagioclase and the coexistent potash feldspar (e.g. Whitney & Stromer, 1977 [16]). This geothermometer doesn't give very sure indications not even in the range of the low temperatures because here the equilibrium is very difficult to achieve. In the range of high temperatures ternary solutions must be taken into account, namely you must consider the presence of Kfs in plagioclase and of An in potash feldspar. The first geothermometers which are based on models of the ternary solutions were developed by Ghiorso (1984)[7] and Green & Usdansky (1986)[9]. They use a unique thermodynamic state equation for feldspars even if some of them are monoclinic and other are triclinic. That is why these authors do not estimate the excess volumes of the ternary feldspar and take into consideration the experimental data given by Seck (1971)[14] which had a series of analytical difficulties. These geothermometers admit solubilities between the three components which are smaller than those existent in nature and these geothermometers are not in accordance with a series of equilibria temperatures experimentally obtained. In addition, the temperature predicted by using these thermometers is obviously unrealistic for much equilibrium from natural petrographic systems.

An improvement of the Ghiorso model was achieved by Fuhrman & Lindsley (1988)[6]. They developed a geothermometer involving the simultaneous calculation of three equilibrium temperatures: T_{Ab}, T_{An} and T_{Kfs}. The three temperatures should be identical or very close, these is in fact the checking test.

Elkins and Grove (1990)[4] have elaborated a new geothermometer based on the data obtained as a result of more experiments made in the ternary system, in the following range: T=700-900°C and P_{H20}=1-3 Kbar. They are the first ones to have considered the modification of the expansion for the miscibility gap according to pressure. This relation cannot be neglected, as, in case of feldspars, it was noticed of increase of the gap according to pressure.

By the slow cooling of the high temperature rocks which contain mixed feldspar crystals, the well known exsolutions of albite in potash feldspar and of alkali-feldspar in plagioclase come into being. In these cases the reintegration of the exsolutions, by means of calculations in view of determining the initial composition is absolutely necessary. To solve this problem, some authors (Kroll, 1993 [11]) proposed the use of large fields for the microprobe beams, the moment the analyses of these kinds of feldspar crystals are made.

The solvus geothermometer in the orthopyroxene – clinopyroxene system

The orthopyroxene - clinopyroxene geothermometer is based on the enstatite - diopside solvus. At temperatures higher than 800°C, the slope of the solvus curve towards diopside is considerably changing with the temperature as can be seen from fig. 2. This geothermometer is useful only in the case of some ultramafic rocks in which the pyroxene composition is near to a diopside + enstatite mixture. In many other rocks the pyroxenes have a more complex composition, the performing of some corrections for the others components being necessary.

Lindsley (1983)[12] has determined the phase equilibrium for the system enstatite-ferosilite-diopside-hedenbergite for the thermobaric range: T=800-1200°C and P=1 bar – 15 Kbar. He plots in the three-dimensional graph of this system the solvus isotherms for the orthopyroxenes and the clinopyroxenes that coexists for different pressures (the maximum one is 15 Kbar).

As in the case of feldspars some of the mixed pyroxene crystals that have cooled slowly have exsolutions. The exsolved phase must be reintegrated to obtain the initial composition.
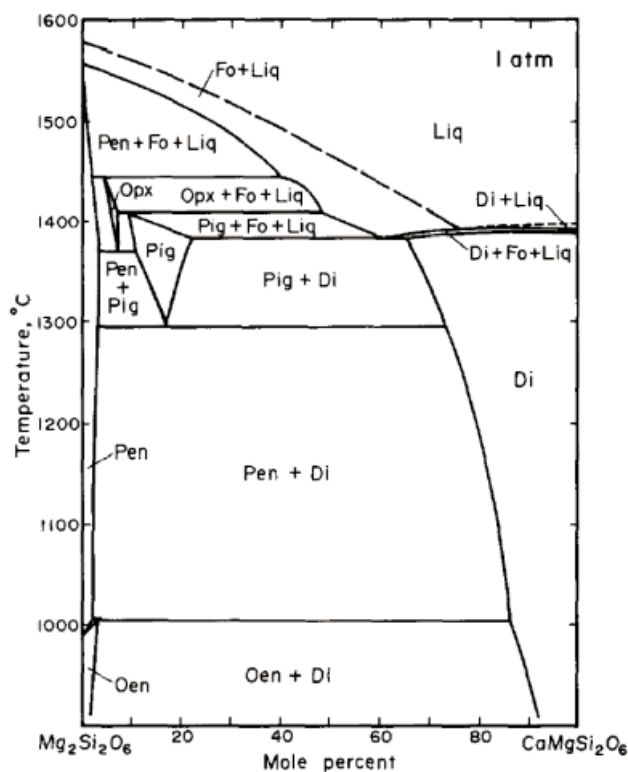

Fig. 2. T-X diagram for the enstatite-diopside system at P=1 atm.
Fo=forsterite; Pen=protoenstatite; Opx=ortopyroxene;
Pig=pigeonite; Pen=protoenstatite; Oen=orthoenstatite;
Di=diopside, Liq=liquid (melt)
(after W. Carlson, 1988[3])

Cationic Exchange Equilibriums Geotermomethers

The exchange equilibrium consist of cations substitutions at an intra-crystalline level or at an inter-crystalline level. The intra-crystalline exchange equilibrium mean the redistribution of the cations as a function of temperature in the interior of the same crystal between certain positions of the lattice. The inter-crystalline exchange equilibrium mean the cation exchange between coexistent crystals as a function of temperature.
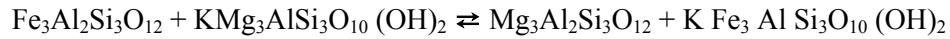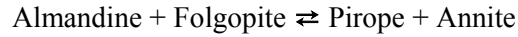
The exchange equilibriums are transformations generally characterized by medium values of $\Delta_r S$ and $\Delta_r H$ and by small values of $\Delta_r V$. Instead of the equilibrium constant K, for these transformations one can more easily operate with the so called distribution coefficient. This distribution coefficient represents the ratio between the exchange cations concentrations in the mineral phases involved in the equilibration process.

Most of the forwarded exchange geothermometres implies the $Fe^{2+} - Mg$ exchange between the ferromagnesian silicates. It is better that these geothermometers to be based not only on thermodynamic calculations but also on experimental calibrations. Because of the fact that in

most silicates there are many substitution possibilities for one and the same position of the crystalline lattice, the presence of other cations different from the ones considered by the geothermometer may lead to objectionable results. In such cases recalibrations and recalculations are needed. The garnet-biotite exchange geothermometer and the garnet-cordierite exchange geotherometer were chosen here as examples.

The garnet-biotite exchange geothermometer

The reaction of this gerothermometer is:

$$Almandine + Folgopite \rightleftarrows Pirope + Annite$$

$$Fe_3Al_2Si_3O_{12} + KMg_3AlSi_3O_{10}(OH)_2 \rightleftarrows Mg_3Al_2Si_3O_{12} + K\,Fe_3\,Al\,Si_3O_{10}\,(OH)_2$$

This is the most frequently used geothermometer, the biotite and garnet being frequently associated minerals in many metamorphic rocks. For this geothermometer many calibrations have been made. Most of these calibrations are empirical or are based on thermodynamic calculations and only few are experimental calibrations. Experimental calibrations are: Ferry & Spear (1978)[5] and Perchuck & Lavrent'eva (1983)[13].

For example the Perchuck & Lavrent'eva (1983) calibration relation is:

$$T(K) = \frac{7843,7 - 0,0246\big(P(bar) - 6000\big)}{5,699 + R\ln K_D},$$

where: $$K_D = \frac{\left(Mg\big/Fe\right)_{Grt}}{\left(Mg\big/Fe\right)_{Bi}}$$ and R=1,98 cal / grad mol.

Holdaway et al. (1997)[10] made improvements to this geothermometer, considering the experimental calibrations, taking into account the iron oxidation states in the two minerals, using the Margules parameters for garnet and calculating by statistical methods the Margules parameters for biotite. The relation they have obtained is:

$$T(K) = \frac{41952 + 0,311P(bar) + G + B}{10,35 - 3R\ln K_D}$$

where: $$G = 3RT\ln\left(\frac{\gamma_{Mg}}{\gamma_{Fe}}\right)_{Grt}, \quad B = 3RT\ln\left(\frac{\gamma_{Mg}}{\gamma_{Fe}}\right)_{Bi}$$ and R=8,3144 J/mol K.
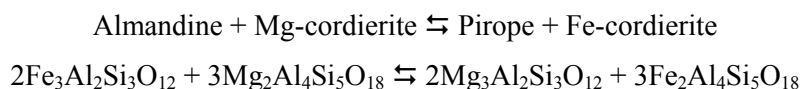
Even if from the theoretical point of view the effects given by the presence of Fe^{3+} in the two minerals on the geothermometer are evaluated, practically the Fe^{3+} content of the biotite is hard to estimate because the oxidation state cannot be determined. As a function of this oxidation state the $Fe^{2+} + (OH)^- \leftrightarrows Fe^{3+} + O^-$ substitution takes place.

In the case of polymetamorphic rocks a major problem is finding the stage of metamorphism in which the chemical compositions of the garnet and biotite resulted by equilibration (chemical compositions which can be now determined by analysis). In the most metamorphic rocks that

contain garnet and biotite, the biotite is present in much larger proportions than the garnet. For this reason the Mg/Fe ratio in biotite modifies very little as a function of temperature compared to this ratio modification in garnet. So, it is considered that the maximum of the Mg/Fe ratio in garnet corresponds to the maxim temperature at which the equilibration took place between the two minerals.

Garnet-cordierite exchange geothermometer

The garnet-cordierite exchange equilibria geotermmother is based on the following reaction:

$$Almandine + Mg\text{-}cordierite \leftrightarrows Pirope + Fe\text{-}cordierite$$

$$2Fe_3Al_2Si_3O_{12} + 3Mg_2Al_4Si_5O_{18} \leftrightarrows 2Mg_3Al_2Si_3O_{12} + 3Fe_2Al_4Si_5O_{18}$$

Perchuck & Lavrent'eva [13] have calibrated this geothermometer in a temperature range T=600-1000°C at pressures of 6 Kbar. The calculation formula is:

$$T(K) = \frac{3020 - 0,018P(bar)}{\ln K_D + 1,287},$$

where

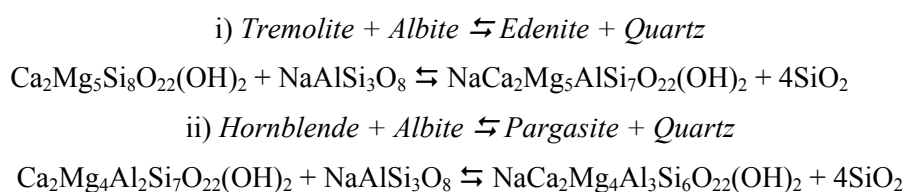$$K_D = \frac{\left(\frac{Mg}{Fe}\right)_{Crd}}{\left(\frac{Mg}{Fe}\right)_{Grt}}.$$

As it can be observed from this calculation formula, the effect of pressure has in this case a very small importance. This geothermometer can be applied only to aluminosilicatic rocks, in which these two minerals coexist. The coexistence of these two minerals is possible only in the low and medium pressure range, the increasing of the metamorphic degree implying a transfer of magnesium from cordierite to garnet.

Solid-Solid Net Transfer Reactions Geothermometers

The net transfer equilibrium geothermomethers are reactions that lead to the integral transfer of the chemical elements from the reactants into the products of those reactions. An example for this type is the hornblende-plagioclase-quartz net transfer geothermometer.

Hornblende-plagioclase-quartz net transfer geothermometer

This geothermometer is based on the next two chemical reactions:

i) *Tremolite + Albite ⇆ Edenite + Quartz*

$$Ca_2Mg_5Si_8O_{22}(OH)_2 + NaAlSi_3O_8 \leftrightarrows NaCa_2Mg_5AlSi_7O_{22}(OH)_2 + 4SiO_2$$

ii) *Hornblende + Albite ⇆ Pargasite + Quartz*

$$Ca_2Mg_4Al_2Si_7O_{22}(OH)_2 + NaAlSi_3O_8 \leftrightarrows NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 4SiO_2$$
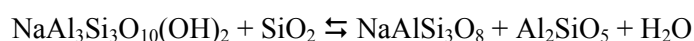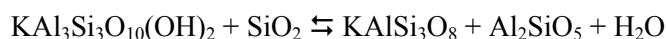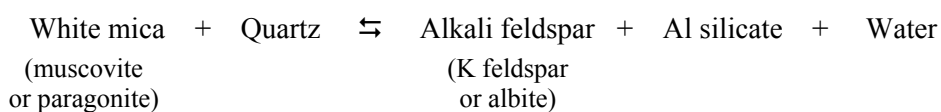
For this geothermometer empirical calibrations were made by Graham & Navrotosky (1986)[8] and Holland & Blundy (1990)[2] and also semi-empirical calibrations by Blundy & Holland (1994). The Blundy & Holland (1994) calibration includes also the tschermakitic amfiboles. These reactions can be used as geothermometers only in the case of the silica saturated rocks.
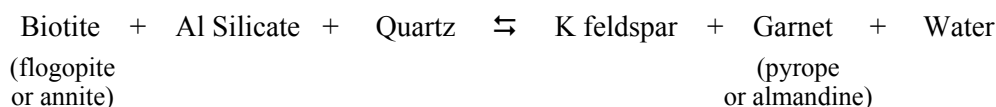
Solid ⇌ Solid+Fluid Net Transfer Reactions Geothermometers

The solid ⇆ solid + fluid net transfer reactions imply large entropy variations. These reactions can be used as geothermometers in those ranges of pressure in which the fluid compressibility is relatively low and constant and only if the fugacity for those fluids is known. In the most cases of natural reactions, the compositions of the fluids are hard to determine and $P_{fluid} \neq P_{total}$.

The bigger the stoichiometric quantity of the fluids (expressed as moles) in a reaction is the bigger is the uncertainty for the location of the equilibrium curve in the PT diagram for this reaction. The reactions which have among their products or reactants only one mole of fluid are most appropriate for geothermometric applications even if they give only approximate temperature indications. Examples of such mineral reactions are:

> White mica   +   Quartz   ⇆   Alkali feldspar   +   Al silicate   +   Water
> (muscovite   (K feldspar
> or paragonite)   or albite)

$$KAl_3Si_3O_{10}(OH)_2 + SiO_2 \leftrightarrows KAlSi_3O_8 + Al_2SiO_5 + H_2O$$

$$NaAl_3Si_3O_{10}(OH)_2 + SiO_2 \leftrightarrows NaAlSi_3O_8 + Al_2SiO_5 + H_2O$$

and

> Biotite   +   Al Silicate   +   Quartz   ⇆   K feldspar   +   Garnet   +   Water
> (flogopite   (pyrope
> or annite)   or almandine)

$$KMg_3AlSi_3O_{10}(OH)_2 + Al_2SiO_5 + 2SiO_2 \leftrightarrows KAlSi_3O_8 + Mg_3Al_2Si_3O_{12} + H_2O$$

$$KFe_3AlSi_3O_{10}(OH)_2 + Al_2SiO_5 + 2SiO_2 \leftrightarrows KAlSi_3O_8 + Fe_3Al_2Si_3O_{12} + H_2O$$

Discussions and Conclusions

The geothermometry is the most efficient method by which the geologists are able to elucidate the thermal evolution of the Earth's crust and mantle. It is expected that in the future, as the experimental petrology makes progress, the geothermometry will improve and in this way to become one of the most easy to use methods of research in the field of geology. That is why the main aim of this paper is to extend the interest of geologist for the theoretical basis of the method and to prevent its inadequate use, which may generate errors with unpleasant consequences; secondly this paper aims also to present in short the difficulties that this method meets nowadays. The main reasons for which the geothermometrical studies can give erroneous results are:

o   The application of these methods on rocks the mineral associations of which have not attained equilibrium;

o   The errors which may appear during the experimental calibration of the geothermomethers;

o   The choosing of some activity models for the real solid solutions (non-ideal solid solutions) that does not reflect close enough the real thermodynamic transformations;

o The application of geothermomethers to mineral assemblage that were formed and eventually evolved at temperatures and pressures different from those for which the calibrations have been made;

o The impossibility to evaluate the way in which the distribution order/disorder of certain elements such as Si and Al in the crystal lattice of the silicates (feldspars, pyroxenes, cordierite) influences the position of the equilibrium curves in the PT diagrams;

o The unsatisfactory determinations or the determinations by inconsequent methods of the Fe^{2+}/Fe^{3+} ratios in minerals like garnet, biotite, amphiboles etc.

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Geotermometrie şi principalele tipuri de geotermometre folosite în petrologie

Rezumat

Geotermometria este o aplicaţie practică a termodinamicii în petrologie care urmăreşte estimarea temperaturilor la care s-au desfăşurat anumite procese geologice. Geotermometria a fost şi este folosită cel mai mult în petrologia rocilor metamorfice pentru estimarea temperaturilor la care paragenezele minerale au atins echilibrul termodinamic. Această lucrare prezintă notiunea de geotermometru, prezintă şi comentează caracteristicile celor mai utilizate tipuri de geotermometre. Pe masură ce petrologia experimentală va progresa, geotermometria se va perfecţiona şi ea furnizând astfel date din ce în ce mai sigure, atât de utile în interpretările petrogenetice şi în general geologice.