Chapter 1
Introduction

Abstract The reasons for moving from the traditional geothermometers and f_{CO_2}-indicators to our theoretical, activity based tools are briefly discussed and the main advantages of the theoretical, activity based geothermometers and f_{CO_2}-indicators presented in this book are underscored.

It might seem that there is something mysterious, almost magical, in the capability of geothermometers to estimate the temperature of geothermal aquifers where hot water comes from. The same applies to the potential of f_{CO_2}-indicators to evaluate the CO_2 fugacity of waters hosted in geothermal reservoirs. Actually, there is no mystery and no magic, because geothermometers and f_{CO_2}-indicators are based on two simple and reasonable hypotheses. The first is the occurrence of thermo-chemical equilibrium between the aqueous solution and the hydrothermal minerals in the geothermal aquifer. The second is the lack of disturbing processes, such as mixing with shallow cold waters or re-equilibration upon cooling, during the ascent of the geothermal fluid to the surface.

Quite surprisingly, most "traditional" geothermometers and f_{CO_2}-indicators call for total (analytical) concentrations. On the one hand, the involvement of analytical data together with the mathematical simplicity of most "traditional" geothermometers explains why they are used so frequently. In fact, most people like simple things. On the other hand, this fact contrasts with the rather complicate speciation of several dissolved components, sometimes determining considerable differences between the total concentration of relevant solutes (e.g., SiO_2, Na, K, Ca and Mg) and the activity of the species actually involved in the mineral-solution reactions of interest (e.g., undissociated SiO_2 and the free ions Na^+, K^+, Ca^{2+} and Mg^{2+}). Since the formation of ion-pairs and aqueous complexes depends on temperature, CO_2 fugacity, and total ionic salinity,[1] in a work we carried out in the early '90s together with our colleagues Giovanni Chiodini and Massimo Guidi (Chiodini et al. 1991), we derived functions

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[1] Total ionic salinity is defined as $\Sigma_{eq} = \Sigma\ m_i \cdot |z_i|$, where m_i is molality of the ith species and $|z_i|$ is the absolute value of its ionic charge.

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relating the total concentrations of solutes and the ratios between the total concentrations of solutes to the three afore-mentioned controlling variables. However, in retrospect, it is more correct and convenient to compute the activities of the species of interest for each individual sample, maintaining the thermodynamic equilibrium constants as benchmarks, rather than to derive functions involving total concentrations, manipulating the thermodynamic equilibrium constants, as done by Chiodini et al. (1991).

Other complications affecting the geoindicators are related to the hydrothermal minerals occurring in geothermal aquifers, several of which are not pure solid phases and some of which exhibit highly variable compositions. These aspects were never considered or were not properly considered, in the derivation of traditional geothermometers and $f_{\mathrm{CO_2}}$-indicators.

A surprising fact, already mentioned above, is the mathematical simplicity of traditional geothermometers, resulting from the adoption of the van't Hoff equation integrated under the assumption of constant reaction enthalpy (e.g., Langmuir 1997) to express the temperature dependence of pertinent thermodynamic equilibrium constants, in most previous studies. The use of this form of the van't Hoff equation requires that the isobaric heat capacity of the reactions controlling water geothermometers is close to zero. This is usually a reasonable or relatively reasonable approximation for the dissolution reactions of silica minerals and the ion exchange reactions governing ionic solute geothermometers as shown in Sect. 5.1.3. However, as already noted by some authors (e.g., Arnórsson 2000), there is no need to rely on this approximation and to obtain simple linear functions relating the logarithm of the thermodynamic equilibrium constant to the absolute temperature inverse.

Activity coefficients of individual ions, γ_{j}, were neglected in several previous studies of water geothermometers, based on the assumption that γ_{j} ratios are close to unity (e.g., Lindsay 1980). This is true or nearly so for the γ_{j} ratios involving two ions of the same charge (e.g., the Na/K ratio) but the γ_{j} ratios involving cations of difference charge, such as the K^2/Mg, K^2/Ca, Na^2/Mg, and Na^2/Ca ratios deviate significantly from unity. In any case, there is no need to use this approximation.

Starting from these premises, we decided to investigate water geothermometers and $f_{\mathrm{CO_2}}$-indicators from the theoretical point of view, adopting the thermodynamic equilibrium constants of suitable mineral-solution reactions as foundation of geothermometric functions and $f_{\mathrm{CO_2}}$-indicators derived in this work. This implies that water geothermometers and $f_{\mathrm{CO_2}}$-indicators involve activity ratios, which must be computed for each sample using a suitable speciation program. Owing to this theoretical approach, the thermodynamic background is summarized in Chap. 2.

Since the geothermometers and $f_{\mathrm{CO_2}}$-indicators are based on the hypothesis of thermo-chemical equilibrium between the aqueous solution and the hydrothermal minerals presumably occurring in the geothermal aquifer, a large effort was devoted to the characterization of both the reservoir liquids and the hydrothermal minerals from active geothermal systems.

For this reason, we have reconstructed over 1000 chemical analyses of reservoir liquids, presumably representative of mineral-solution thermo-chemical equilibrium at aquifer temperatures of 100–350 °C, combining the chemical analyses of the liquid and vapor phases discharged from drilled wells and collected at known separation temperature and pressure. The relevant chemical characteristics of reservoir liquids are presented in Chap. 3. Moreover these reservoir liquids are used to test the geothermometers and f_{CO_2}-indicators, both those traditional and those derived in this work, in subsequent chapters.

For the same reason, over 2200 chemical analyses of hydrothermal minerals from active geothermal systems were compiled and processed, as discussed in Chap. 4. In this way, it was possible to identify the minerals occurring as pure solid phases or nearly so and those present as solid solutions. For the solid solutions, the average activity of the endmembers of interest and other statistical parameters were computed. Average activities were then used in the implementation of water geothermometers and f_{CO_2}-indicators, in subsequent chapters.

Chapter 5 is devoted to the traditional geothermometers and f_{CO_2}-indicators. Their characteristics, strengths and weaknesses are thoroughly treated. Our focus is mainly on the silica, Na–K, Na–K–Ca, Na–Ca, K–Ca, K–Mg and Na–Mg geothermometers as well as on the K–Ca f_{CO_2}-indicator. Nevertheless, other ionic solute geothermometers (e.g., Na–Li, Mg–Li, Ca–Mg, SO_4–F) are briefly recalled, as well as multicomponent chemical geothermometry and the influence of ion complexing on geothermometers and f_{CO_2}-indicators.

The main outcomes of this work are illustrated in Chaps. 6, 7, and 8, which are centered on the theoretical, activity-based Na–K geoindicators, K–Mg and Na–Mg geoindicators, and Ca–K and Ca–Na geoindicators, respectively.

We are aware that the approach we propose here is much more intricate than the simple formulas of traditional geoindicators and that users must have a background in geochemistry and thermodynamics or must acquire it. However, the precision on the calculated geothermal aquifer temperatures and CO_2 fugacities and the additional information on the hydrothermal minerals presumably present in the geothermal reservoir represent significant improvements with respect to the results given by traditional geoindicators and multicomponent chemical geothermometry. We think it is worth a try.

References

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