

Chapter 9

Conclusions and Way Forwards



Abstract In this chapter, the main characteristics of the theoretical, activity-based Na–K, K–Ca and Na–Ca geoinicators and the suggested procedure for their use are summarized. Possible improvements related to the choice of the thermodynamic database, the implementation of further theoretical, activity-based K–Ca and Na–Ca geoinicators, and the prediction of the ordering parameter of adularia on the basis of water chemistry are briefly discussed.

The main results of our research are the theoretical, activity-based Na–K, K–Ca and Na–Ca geoinicators, which can be used to compute aquifer temperature and CO₂ fugacity through the procedure summarized in Sect. 9.3. These geoinicators express the temperature dependence of the thermodynamic equilibrium constant of the exchange reactions involving pertinent hydrothermal minerals and take into account the average activities of relevant endmembers in solid solutions as well as Al–Si order-disorder on the tetrahedral sites of adularia if needed.

The same approach was applied also to derive K–Mg and Na–Mg geoinicators, but the usefulness of these geoinicators is limited by the extremely variable activity of clinocllore in chlorites. At best, the K–Mg and Na–Mg geoinicators can be used to assess the minimum concentrations of excess (non-equilibrium) Mg and, consequently, to identify and quantify related cooling and/or mixing processes, which may lead to Mg-silicate (e.g., smectite) scaling, as shown in Chap. 7.

9.1 The Theoretical, Activity-Based Na–K Geoinicators

The theoretical Na–K geoinicators were implemented building on previous findings of Bird and Norton (1981), who showed that Na–K geothermometry is complicated by the different structural state of alkali feldspars and Al–Si order-disorder on their tetrahedral sites. Consequently, a single Na–K geothermometer valid everywhere does not exist. Quite surprisingly, these important findings of Bird and Norton (1981)

have received little attention in the scientific community and several geochemists have continued to propose different calibrations for the Na–K geothermometer.

Further evidence of interest for the elaboration of theoretical Na–K geothermometers is provided by the data available for both the authigenic alkali feldspars present in sedimentary rocks (e.g., Kastner and Waldbaum 1968; Morad 1978; Kastner and Siever 1979; Fishman et al. 1995) and the highly pure K-feldspars and albites synthesized at low temperatures by using hydroxide gels (Flehmig 1977). These data consistently indicate that K-feldspar crystals have various degrees of Al–Si ordering, whereas albite crystals are well-ordered. Assuming that hydrothermal alkali feldspars present in active geothermal systems have order-disorder characteristics similar to those of authigenic alkali feldspars present in sedimentary rocks and synthesized at low temperatures by means of hydroxide gels, the Na/K activity ratio of reservoir liquids is expected to be a function of both temperature and the ordering parameter of hydrothermal adularia, Z , which is equal to 1 for maximum-microcline, the proxy of totally ordered adularia, and assumes the value of 0 for high-sanidine, the proxy of completely disordered adularia.

In agreement with these expectations, 950 of the 1013 selected geothermal liquids (corresponding to 93.8% of the total) have Na/K activity ratio intermediate between the values fixed by low-albite/maximum microcline and low-albite/high-sanidine equilibrium coexistence, providing a strong support to our hypothesis. Interestingly and not surprisingly, also the Na–K geothermometers calibrated by different authors are limited by low-albite/maximum microcline and low-albite/high-sanidine equilibrium co-occurrence.

The two limiting theoretical Na–K geothermometers derived in this work, involving low-albite and either high-sanidine or maximum-microcline have little usefulness because they give equilibrium temperatures differing by 125 ± 3 °C on average, in the range 100–350 °C. Therefore, it is advisable to use the Na/K log activity ratio for computing the ordering parameter Z of hydrothermal adularia in hypothetical equilibrium with the aqueous solution of interest and to use this information in the theoretical K–Ca and Na–Ca geothermometers implemented in this work, representing the subject of the next section.

9.2 The Theoretical, Activity-Based K–Ca and Na–Ca Geothermometers

The theoretical, activity-based K–Ca and Na–Ca geothermometers implemented in this work are controlled by the exchange reactions involving different Ca–Al silicates, namely laumontite, clinozoisite, prehnite, and wairakite, whereas the K–Ca and Na–Ca theoretical, activity-based f_{CO_2} -indicators obtained here are governed by reactions comprising calcite. In addition to Ca–Al silicates or calcite, adularia is also included in the exchange reactions controlling all the theoretical K–Ca geothermometers and some Na–Ca geothermometers. Consequently, these relations are function of the ordering

parameter of hydrothermal adularia which, in turn, depends on the Na–K activity-ratio and aquifer temperature, as recalled in previous section.

A total of about one thousand reservoir liquids were utilized to test the theoretical, activity-based K–Ca and Na–Ca geoindicators. The temperature given by the K–Ca geothermometers deviates from aquifer temperature by 3.8 °C on average, and the absolute value of the difference between K–Ca temperature and aquifer temperature is lower than 10 °C in 97.3% of the cases. The temperature calculated by means of the Na–Ca geothermometers differs from aquifer temperature by 6.9 °C on average and the absolute value of the difference between Na–Ca temperature and aquifer temperature is lower than 15 °C in 93.5% of the cases.

The K–Ca and Na–Ca f_{CO_2} -indicators give CO_2 fugacities showing absolute deviation of 0.78 log-units, on average, from the CO_2 fugacities calculated by means of speciation calculations. However, the CO_2 fugacities computed by means of the K–Ca and Na–Ca f_{CO_2} -indicators are in satisfactory agreement with the CO_2 fugacities given by the K–Ca f_{CO_2} -indicator of Giggenbach (1984) having an absolute deviation of 0.33 log-units on average.

The good performance of the theoretical, activity-based K–Ca and Na–Ca geothermometers, and to a lower extent of the f_{CO_2} -indicators as well, are not surprising because the controlling exchange reactions involve well-behaved hydrothermal minerals. In fact, the activities of the Ca-bearing endmembers (i.e., laumontite, clinozoisite, prehnite, wairakite, and calcite) in relevant hydrothermal minerals from active geothermal systems (i.e., the solid solutions made up of laumontite/alkali-laumontite, clinozoisite/epidote, prehnite/ferri-prehnite, wairakite/analcime, and trigonal carbonate) exhibit limited variations from the average values and these average activities are not too different from unity.¹

Moreover, the Ca-bearing mineral in equilibrium with each reservoir liquid, either a Ca–Al-silicate (laumontite or clinozoisite or prehnite or wairakite) or calcite can be identified by using the K–Ca and Na–Ca theoretical geothermometers and f_{CO_2} -indicators. This indication is a considerable improvement with respect to the outcomes of the traditional K–Ca and Na–Ca geoindicators, and is probably more reliable than the results of multicomponent chemical geothermometry (see Sect. 5.9), being slightly influenced by pH and Al concentration. Finally, the identification of the Ca–Al-silicate in equilibrium with each reservoir liquid may give a qualitative indication on well permeability. In fact, wairakite is an indicator of high permeability, whereas prehnite and laumontite (if abundant) are indicators of poor permeability (Reyes 1990).

¹Incidentally, the exchange reactions involving grossular were disregarded because grossular activity in 190 garnet solid solutions from active geothermal systems spans a very large range, from less than 2.27×10^{-7} (for 22 cases) to 0.674, with an average of 0.127 and a standard deviation of 0.179.

9.3 Suggested Procedure for the Use of the Theoretical, Activity-Based Na–K, K–Ca and Na–Ca Ge indicators

The suggested procedure for using the theoretical, activity-based Na–K, K–Ca and Na–Ca ge indicators includes a series of steps as outlined below and schematically presented in the workflow of Fig. 9.1.

- Step 1. Data organization, including the calculation/assessment of the aquifer temperature for the aqueous solution of interest based on silica geothermometers or other available data, such as measured aquifer temperature and discharge enthalpy for wells.
- Step 2. Speciation calculations to compute the activities of relevant species by means of WATCH, PHREEQC Interactive, EQ3/6, or similar computer programs. If the charge unbalance is lower than 10%, it is possible to proceed to the next step. Otherwise the procedure should be stopped.
- Step 3. Calculation of the pH fixed by mineral-solution equilibrium, pH_{mse} , by means of Eq. (3.10), involving aquifer temperature, total ionic salinity, and the CO_2 fugacity given by speciation-saturation calculations. If the difference between pH_{mse} and the pH given by speciation calculations is less than 1 pH unit, it is possible to proceed to the next step. Otherwise, it is advisable to change the reconstruction of reservoir fluids, adopting a different approach, as discussed in Sect. 3.1.
- Step 4. Calculation of the ordering parameter Z of hydrothermal adularia in hypothetical equilibrium with the aqueous solution of interest on the basis of aquifer temperature and the Na/K activity ratio.
- Step 5. Calculation of CO_2 fugacity by means of the K–Ca and Na–Ca calcite f_{CO_2} -indicators, that is Eqs. (8.45)–(8.48) and the f_{CO_2} —temperature functions controlled by equilibrium coexistence of a Ca–Al-silicate and calcite, that is Eqs. (8.49)–(8.56), based on aquifer temperature and the ordering parameter Z of adularia. If the CO_2 fugacity given by the K–Ca and Na–Ca calcite f_{CO_2} -indicators is higher than the maximum CO_2 fugacity of Ca–Al-silicate/calcite coexistence, then the aqueous solution of interest is in equilibrium with calcite, and the computed CO_2 fugacity is representative of the geothermal aquifer. Otherwise, the K–Ca and Na–Ca geothermometers should be used (see next step) instead of the K–Ca and Na–Ca calcite f_{CO_2} -indicators.
- Step 6. Calculation of the K–Ca and Na–Ca temperatures using the different theoretical, activity-based K–Ca and Na–Ca geothermometers, that is Eqs. (8.29)–(8.44), considering the ordering parameter Z of adularia where needed.
- Step 7. Comparison of the different K–Ca and Na–Ca temperatures with the aquifer temperature established in step 1, selection of the K–Ca and Na–Ca temperatures closest to the aquifer temperature, and identification of the Ca–Al silicate(s) in equilibrium with the aqueous solution of interest or close to this condition.

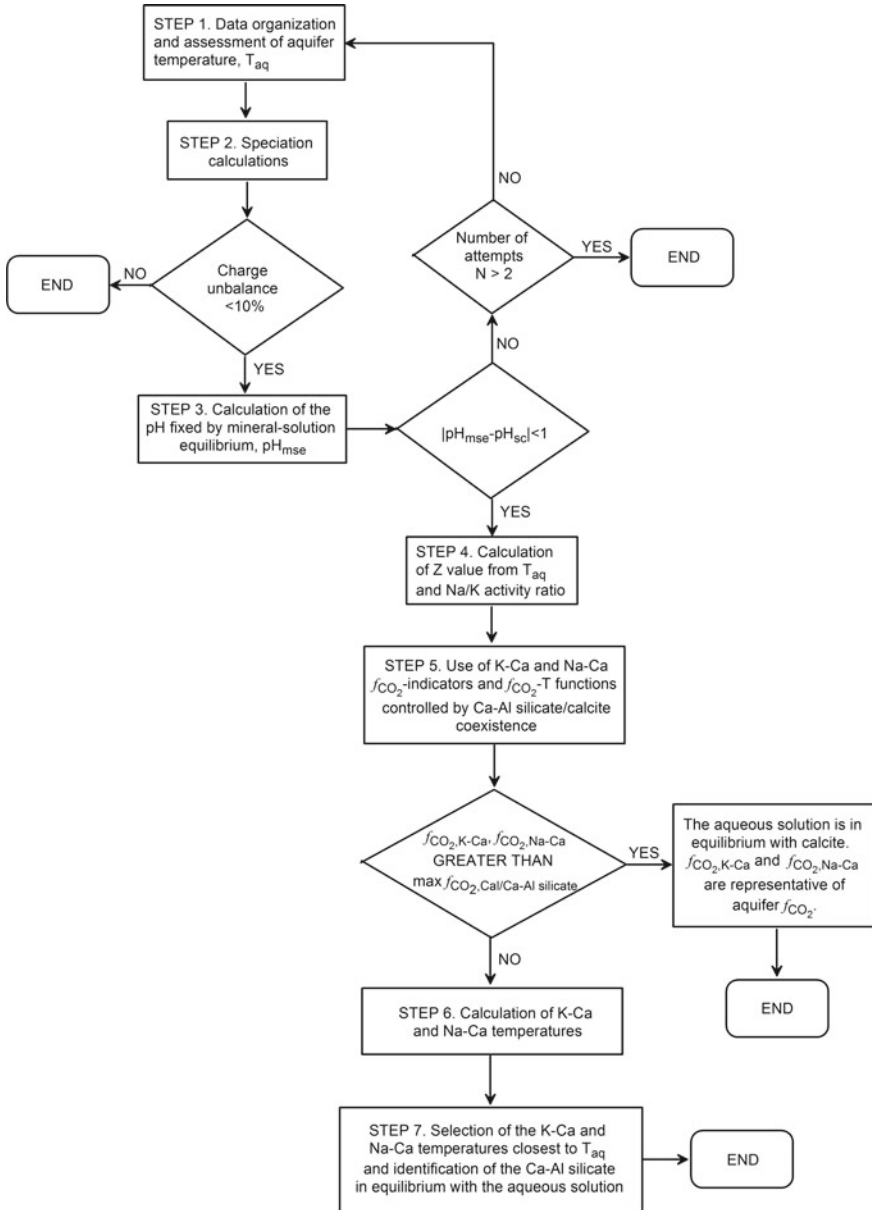


Fig. 9.1 Workflow of the suggested procedure for the use of the theoretical, activity-based Na–K, K–Ca and Na–Ca geoindicators

In addition to this procedure, it is advisable, not to say it is mandatory, to use the diagrams of K^2/Ca log-activity ratio vs. the absolute temperature reciprocal, Na^2/Ca log-activity ratio vs. the absolute temperature inverse and CO_2 fugacity vs. the absolute temperature reciprocal, allowing an eyeball comparison of all the aqueous solutions of interest with the theoretical geoindicators.

9.4 The Way Forward

The approach to water geothermometry and f_{CO_2} evaluation proposed in this book was thoroughly tested with over one thousand reservoir liquids coming from different geothermal fields worldwide. Therefore, we are confident that it can be applied elsewhere with a high probability of success. Nevertheless, we are aware that the work we did is far from complete for at least two reasons.

The first reason relates to our choice of the thermodynamic database, that will certainly make many people turn up their noses. As long as a standard, internationally accepted thermodynamic database does not exist, it could be interesting to use different thermodynamic databases for calculating the thermodynamic equilibrium constants of the Na–K, K–Ca, Na–Ca, K–Mg, and Na–Mg exchange reactions of interest. This is a fairly simple exercise, which we have deliberately chosen not to perform, apart from the test of alkali feldspars transition temperatures in Sects. 4.2.4 and 6.1, because we trust the thermodynamic database implemented by Helgeson and coworkers and we did not want to complicate too much this book.

A second reason is the limited number of Ca–Al silicates taken into account in this work to implement the theoretical, activity–based K–Ca and Na–Ca geoindicators. In addition to the Ca–Al silicates considered here, that is laumontite, clinzoisite, prehnite, and wairakite, other Ca–Al silicates and Ca-silicates occur as hydrothermal minerals in active geothermal systems and, therefore, are of interest for the elaboration of water geothermometers and f_{CO_2} -indicators. It is worth recalling the Ca-bearing zeolites (e.g., heulandite, stilbite, chabazite, thomsonite, scolecite, mordenite, yugawaralite, levyne, gismondine, and gmelinite), which are stable at low temperatures, usually below 200 °C, as well as actinolitic amphibole, Ca clinopyroxene, andradite-grossular garnet, and wollastonite, which are stable at high temperatures, generally ≥ 300 °C (e.g., Bird et al. 1984). Some of these minerals, however, exhibit large ranges of compositions that might complicate their use for the derivation of suitable geoindicators, similar to what we noted for garnet. Titanite (sphene) might be another Ca-bearing mineral of interest, together with other Ti-bearing solid phases, for the elaboration of geoindicators. The main problem, however, is the lack of reliable thermodynamic data as discussed in Sect. 9.4 and, again, we return to the previous issue.

Furthermore, there is room for improvement related to the ordering parameter Z of adularia, which is a subject of major importance. In fact, in the suggested procedure, Z is computed as a function of the Na/K activity ratio and aquifer temperature, but this approach introduces a sort of vicious circle in geothermometric calculations. Since

previous researches (Martin 1969; Flehmig 1977) have shown that the structural state and the degree of ordering of alkali feldspars depends on pH and Na and K concentrations, it should be possible to predict Z on the basis of water chemistry. We have tried to investigate this possibility but our attempts were unsuccessful. Experiments of alkali feldspar synthesis using hydroxide gels might provide further evidence on the parameters possibly controlling their degree of ordering. Other indications might results from the chemistry of hydrothermal alkali feldspars in geothermal aquifers hosting reservoir liquids rich in boron and ammonium, such as Ngawha and Monte Amiata, because both B^{3+} and NH_4^+ ions are incorporated in the alkali feldspars lattice.

Moreover, other activity ratios might be of interest for geothermometry, e.g., the $SO_4/(F)^2$ ratio, and for the implementation of f_{CO_2} -indicators, e.g. the HCO_3/F and $(HCO_3)^2/SO_4$ ratios, as pointed out by Chiodini et al. (1991). We intentionally avoided to consider these potential geo-indicators in order to conclude this book (or perhaps its first edition) and submit our results, albeit partial, to the attention of the scientific community.

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