Journal of South American Earth Sciences 69 (2016) 259–261

Contents lists available at ScienceDirect

Journal of South American Earth Sciences

journal homepage: www.elsevier.com/locate/jsames

Comments

A note on “Origin of components in Chilean thermal waters” by Risacher et al. (2011)

M.A. Alam*, M.A. Parada

Departamento de Geología y Centro de Excelencia en Geotermia de los Andes (CEGA), Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Plaza Ercilla 803, Santiago, Chile

ARTICLE INFO

Article history:
Received 30 January 2013
Accepted 29 September 2013

Keywords:
Geothermal
Chile
Andes
Chloride–Bromide (Cl/Br) ratio
Data handling
Systematics

ABSTRACT

Risacher et al. (2011) have presented voluminous data on thermal waters of Chile that is quite appreciable; however, their work still falls short on several counts. The most notable shortcoming of the work is the presentation and treatment of data. The interpretations are based on questionable premises (viz., extent of seawater intrusion) and considerations (viz., using average chemical composition of rock types for geochemical modeling, considering volcanic rocks as the only rock type in contact with the geothermal fluids) and assumptions not always substantiated by facts (with proper references) could have been corroborated. Use of Cl/Br ratio for discrimination purpose is unconvincing, considering the uncertainty in the measurement of low (<1 mg/L) Br concentration.

1. Introduction

Chilean geothermal systems are one of the least studied and understood ones, despite having immense potential as economical and local source of energy with potential estimated as high as 16,000 MW (Lahsen, 1988). Any contribution towards understanding the Chilean geothermal systems is more than welcome in order to develop Chilean geothermal resources. Nevertheless, any ambiguity or misinterpretation on account of questionable premises or considerations that are more of generalization or speculation and not substantiated can be counterproductive. Scientific knowledge plays a key role in reducing the risk in developing geothermal resources by providing the basis for conceptual models of geothermal systems. Conceptual models are inherently interpretative; therefore the challenge is the best possible interpretation of the available data.

Risacher et al. (2011) provided a review of geothermal waters from Chile and proposed an interpretation on the origin of their chemical components. For this purpose, they have classified the geothermal systems into two groups – arid (northern Chile) and humid (southern Chile). In this paper, we comment on use of non-standard terms, data presentation and interpretations presented by Risacher et al. (2011).

2. Use of non-standard terms

It is inconsequential to comment on the language at this stage; however, use of non-standard terms cannot be overlooked. Coining and using of new terms to describe a new phenomenon or even renaming something in the light of improved understanding is appreciable in scientific literature. However, indiscriminate use of non-standard terms is uncalled for and worth criticism.

Any new term appropriate for qualifying as standard term thenceforth should be properly defined. Such instances of using non-standard terms are likely in the absence of standardization of geothermal terms, but are avoidable with due diligence. In this section, we highlight the use of some non-standard terms used by Risacher et al. (2011).

The term “alteration water” has been used for describing the solution formed as a result of water–rock interaction. These authors have used this term several times, beginning from the abstract and introduction sections; however, the only clue to what this term standards for is in the subsection “6.2 Testing the model”. In this subsection, the main control of the composition of “alteration water” is described as the nature of rock minerals, not their proportion in the rock. If it is so, then this so called “alteration water” is better known as hydrothermal water/fluid/solution, the term used since the inception of geothermal studies. So the use of new term “alteration water” is unwarranted.

Another ambiguous term used by these authors, albeit with some description, is “fumarole spring”, to describe two springs with

---

* Corresponding author. Present address: Energy Development Corporation (EDC) Chile Limitada, Presidente Riesco 5561, Oficina 1003, Las Condes, Santiago, Chile.

E-mail addresses: ayaz@ing.uchile.cl, ayaz.alam@gmail.com, ayaz@edcltd.cl (M. A. Alam).

0895-9811/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jsames.2013.09.013

very low Cl and Br, resulting possibly from interaction of hot fumaroles with the water seeping from a nearby stream, in a fumarolic field. Although use of this term to describe a particular manifestation is fine for explanatory purpose, it does not qualify as a new type of geothermal discharge. These authors have plotted these two discharges as belonging to a different group in (Figures 3, 5–10, 13; Risacher et al., 2011). However, they have neither identified them in the table nor in the text, making it difficult for the readers to appreciate.

Risacher et al. (2011) have used the term "accretive margin", while describing the subducted sediments as source of Cl and Br in thermal waters of southern Chile. Although the term "accretive margin" has been used by some other workers as well (e.g., Hampel et al., 2004; Bachmann et al., 2009), accretionary margin (e.g., Karig and Sharman, 1975) is the more widely used and accepted term. The term 'accretive margin' is largely a financial jargon, while the term 'accretionary margin' is almost exclusively used in tectonic context.

3. Data presentation

There are inconsistencies in the presentation of data, which could have been avoided, had due care been taken. For example, different units have been used to describe the same parameter (e.g., concentration) in a single table, viz. alkalinity in milliequivalents per liter (meq/L); total dissolved solids (TDS) in milligram per liter (mg/L) and elemental and ionic concentrations in millimol per liter (mmol/L). Risacher et al. (2011) should have converted and reported all the concentration values in any one unit, using the reported thermal water density values, for better appreciation of the data. Risacher et al. (2011) have reported alkalinity, without mentioning its type, viz., bicarbonate, carbonate or hydroxide alkalinity. We presume it is total alkalinity that has been reported to two decimal digits. However, the accuracy to which it can be measured with prevalent techniques (e.g., METROHM-EP titroprocessor, with detection limit of 0.3 mg/L of CaCO3) is to just one decimal place. Moreover, the geochemical data has been presented by Risacher et al. (2011) without any regard for significant figures. Data on cold springs, lakes, rain and seawater samples (data points shown only in the diagrams) have not been provided in the paper or as Appendix.

The reference ellipsoid (presumably WGS84) is not mentioned while reporting the UTM coordinates of the sampling points. Moreover, geographical latitude and longitude have been used in the location map of the studied area, whereas the sample locations in the table are given in the UTM coordinate system.

4. Using Cl/Br ratio

The Cl/Br ratio has been used as a tracer to determine the origin and evolution of groundwater, surface water and brines in oil and gas exploration (Freeman, 2007). The Cl/Br ratio facilitates distinguishing the atmospheric chloride contribution from other origins in groundwater, viz. brines, seawater intrusion and water–rock interaction. Risacher et al. (2011) have used Br/Cl ratio alone to assess and emphasize on the seawater component in the thermal waters of the area, which are diluted (low TDS, Br, Cl values). However, vast vegetation covers in southern Chile can modify the Cl/Br ratios of local bulk composition of the recharge water, especially during the periods of lesser marine aerosols, associated with the rainfall (Martens et al., 1973). Moreover, the geothermal discharges in the area have a Br/Cl ratio much higher than that of seawater (2×10^{-4}) and are freshwaters with Cl concentrations less than 200 mg/L. The measured Cl concentration, together with hydrogen and oxygen stable isotope ratios, indicates a meteoritic origin of the thermal waters of the area.

Moreover, the difficulty in measuring usually low Br concentrations in natural water has limited the application of Cl/Br ratio. Risacher et al. (2011) have hyphenated the error for all components in the range ±2 to ±5%, although different instruments and techniques have been used. Low concentrations (<1 mg/L) of Br requires techniques better than common spectrometric analytical and neutron activation methods (viz., ion-selective electrode method, colorimetric method) for its determination. High performance liquid chromatography (HPLC) can accurately measure the concentrations less than 5 mg/L, with detection limit of 1 mg/L (Davis et al., 2004). However, the error could be up to ±8% for low Br concentration and Cl/Br ratios over 1500 (e.g., Alcalá and Custodio, 2008). Risacher et al. (2011) have not specified the details of the Br, analysis although Br concentrations are vital for their interpretations. Risacher et al. (2011) have used both ion chromatography (IC) and inductively coupled plasma mass spectroscopy (ICP-MS) for Br analysis; however, they have not identified the used technique in table showing Br concentrations. While Br concentration data using ICP-MS can be used with greater degree of confidence, those with IC cannot.

Risacher et al. (2011) have asserted the presence of seawater component in all the geothermal waters of southern Chile based on Cl/Br ratios. However, Br concentrations are close to detection limits, making Cl/Br ratio an unreliable criterion to ascertain the origin of thermal waters.

5. Problem with the use of average

Regional average of total dissolved solid (TDS) contents (Northern Chile: 880 mg/L, Southern Chile: 3770 mg/L) for the geothermal discharges reported by Risacher et al. (2011) that have ranges like 125–8140 and 150–21,750 mg/L for northern and southern Chile respectively, does not make any sense. Moreover, the data is quite skewed, with 62% discharges with TDS values below 500 mg/L in northern Chile and 76% discharges with TDS values above 1000 mg/L in southern Chile. Such statistical values neither represent nor imply anything in chemical terms. Chemical composition can only be presented for individual discharges and can be treated as such. Even in the case of different discharges of the same system, average composition makes no sense. Any variation in the chemistry of the discharges of the same system can be used to quantify the extent of dilution caused by mixing of near surface cold meteoric water or other near surface processes. However, average composition of these discharges neither represents anything nor can be used for any purpose. Moreover, the rock composition used for modeling is an average composition from different volcanic rocks of SVZ, and do not consider the granitic basement at all.

6. Lithological consideration

While evaluating the origin of components in the thermal waters, Risacher et al. (2011) have classified the thermal waters into two main groups, namely, Northern and Southern waters. In this context, Risacher et al. (2011) make a categorical and alarming statement that deep evaporatives below volcanic rocks occur only in the north and they are "completely absent in the south". According to Grunder et al. (1987), who studied hydrothermal system of the Calabozos Caldera in Southern Chile, Mesozoic evaporites are integral part of subsurface stratigraphy of many geothermal areas in Central-Southern Chile.

To evaluate the role of water–rock interaction in establishing the chemical signatures of the discharges they have considered only the volcanic rocks (Table 5,6,7; Risacher et al., 2011), as if the granitic basement rocks have no role to play. Absence of granitic rocks at subsurface seems an unlikely scenario, given the widespread occurrence of granitic rocks in the vicinity of many geothermal areas in Central-Southern Chile (e.g., Sepúlveda et al., 2004).

The anomalous (or slightly abnormal) presence of certain components, viz. fluorine (F) can be explained in terms of interaction of the geothermal water with the granitic rocks for southern Chilean Andes (SCA). In SCA, there is no significant difference in F concentration in the thermal discharges proximal and distal to the regional volcanic centers (e.g., Pérez, 1999). For example, in the case of active degassing Villarrica volcano, no point source of volatile degassing (e.g., fumaroles, mud pools) exits on its flanks. In the absence of detectable diffuse degassing on its flanks, Witter et al. (2004) concluded that the measured volatiles emitted from the summit crater represent the total flux of these volatiles out of the volcano, thus ruling out any subsurface degassing of magma that could contribute volatiles to be absorbed by hot or cold groundwater.

Non-volcanic F could be derived from fluorite present in the granites (fluorite-bearing syenogranite; Welkner et al., 2002) in the area. According to Ellis and Mahon (1964), for fluorite/water system, the ionic balance between Ca and F upholds according to the following relation up to 230 °C, which is well within the expected temperatures of the geothermal systems in SCA:

$$CaF_2 = Ca^{2+} + 2F^-$$

However, stoichiometrically higher amount of F is liberated to the solution above 230 °C due to the insoluble nature of $Ca(OH)_2$.

$$CaF_2 + 2H_2O = Ca(OH)_2 + 2HF$$

Volcanic rocks, considered by Risacher et al. (2011) to model the possible water–rock interaction, form the upper part of the geothermal systems in the area. The interaction of the ascending geothermal waters with these rocks is less likely, largely due to insufficient time for the reactions to take place.

We take a strong exception to “seawater expelled from the subducted lithosphere into the mantle” (Risacher et al., 2011), as the source of Cl and Br from subducted wet sediments in thermal waters of southern Chile. Seawater in the subducted sediments will be expelled even before the breakdown of hydrous metamorphic minerals that triggers partial melting of the asthenospheric wedge. As a result, seawater would not affect the melting region in the asthenosphere. Even if seawater is added to the asthenospheric wedge (melting region); it will either be incorporated into hydrous minerals of the granitic basement or in volcanic glasses. How can H_2O in hydrous magmatic minerals or volcanic glasses be extracted without a pervasive water–rock interaction? Risacher et al. (2011) seem to have not considered this question.

7. Concluding remarks

While we really appreciate the efforts of Risacher et al. (2011) for the voluminous data on thermal waters of Chile that cannot be repudiated, inconsistency in its presentation, together with their interpretations based on questionable premises and considerations (viz., treating volcanic rocks as the only type of rocks in contact with the geothermal fluids, seawater expelled from the subducted lithosphere into the mantle as source of Cl and Br) and assumptions not always corroborated, make this work fall short of the expected standard.

Acknowledgements

We acknowledge the financial support through PBCT PDA-07 project of CONICYT, Chile. Authors would like to thank the anonymous reviewers for their invaluable comments and suggestions.

References

Alcalá, F.J., Custodio, E., 2008. Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal. J. Hydrol. 359, 189–207.

Bachmann, R., Glodny, J., Oncken, O., Seifert, W., 2009. Abandonment of the South Penninic-Austroalpine palaeosubduction zone, Central Alps, and shift from subduction erosion to accretion: constraints from Rb/Sr geochronology. J. Geol. Soc. Lond. 166, 217–231.

Davis, S.N., Fabryka-Martin, J., Wolfsberg, L.E., 2004. Variations of bromide in potable ground water in the United States. Ground Water 42, 902–909.

Ellis, A.J., Mahon, W.A., 1964. Natural hydrothermal systems and experimental hotwater/rock interaction. Geochim. Cosmochim. Acta 28, 1323–1357.

Freeman, J.T., 2007. The use of bromide and chloride mass rations to differentiate salt-dissolution and formation brines in shallow groundwater of the Western Canadian Sedimentary Basin. Hydrogeol. J. 15, 1377–1385.

Grunder, A.L., Thompson, J.M., Hildreth, W., 1987. The hydrothermal system of the Calabozos Caldera, Central Chilean Andes. J. Volcanol. Geotherm. Res. 32, 287–298.

Hampel, A., Kukowski, N., Bialas, J., Huebscher, C., Heinbockel, R., 2004. Ridge subduction at an erosive margin: the collision zone of the Nazca Ridge in southern Peru. J. Geophys. Res. 109, B02101. http://dx.doi.org/10.1029/2003JB002593.

Karig, D.E., Sharman, G.F., 1975. Subduction and accretion in trenches. Geol. Soc. Am. Bull. 86, 377–389.

Lahsen, A., 1988. Chilean geothermal resources and their possible utilization. Geothermics 17, 401–410.

Martens, C.S., Wesolonsky, J.J., Harns, R.C., Kaifer, R., 1973. Chloride loss from Puerto Rico and San Francisco Bay area marine aerosols. J. Geophys. Res. 82, 8778–8791.

Pérez, Y., 1999. Fuentes de Aguas Termales de la Cordillera Andina del centro – sur de Chile (39–42° Sur). Ser. Nacl. Geol. Min. Santiago Chile Bolet. 54, 65.

Risacher, F., Fritz, B., Hauser, A., 2011. Origin of components in Chilean thermal waters. J. S. Am. Earth Sci. 31, 153–170.

Sepúlveda, F., Dorsch, K., Lahsen, A., Bender, S., Palacios, C., 2004. The chemical and isotopic composition of geothermal discharges from the Puyehue-Cordón Caulle area (40.5°S), Southern Chile. Geothermics 33, 655–673.

Welkner, D., Godoy, E., Bernhardt, H.-J., 2002. Peralkaline rocks in the Late Cretaceous del Salto Pluton, Eastern Patagonian Andes, Aysén, Chile (47°35′S). Rev. Geol. Chile 29, 3–15.

Witter, J.B., Kress, V.C., Delmelle, P., Stix, J., 2004. Volatile degassing, petrology, and magma dynamics of the Villarrica Lava Lake, southern Chile. J. Volcanol. Geotherm. Res. 134, 303–337.