



GEOCHEMICAL METHODS IN GEOTHERMAL SURFACE EXPLORATION

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ABSTRACT

Geothermal water is mostly meteoric and oceanic water in origin, but has been altered by interaction with rock and in some cases magmatic fluids. Geothermal waters have been classified with respect to their anion and cation contents into alkali-chloride water, acid sulphate water, acid sulphate-chloride water and bicarbonate water. Acid waters are generally unsuitable for elucidation of subsurface properties. Conservative constituents are used for tracing origin and flow of geothermal fluids, stable isotopes (especially ^2H and ^{18}O) along with B and Cl being most important, whereas rock-forming constituents (e.g. SiO_2 , Na, K, Ca, Mg, CO_2 , H_2) are used to predict subsurface temperatures. Measurements of soil gas concentrations and flux can be useful for delineating fractures or other permeable structures relevant to flow paths in geothermal systems.

1. INTRODUCTION

Geochemistry plays a major role in exploration for geothermal resources, both during surface exploration and after exploration wells have been drilled and discharged. The main tasks of the geochemist during surface exploration are the selection of sampling locations, sample collection, chemical analysis of the samples and interpretation of the analytical results. In this article, the focus will be on the latter task, but the other three will be addressed in a separate article (Ármannsson et al. 2015).

Interpretation of geochemical data aims at estimating the composition of the subsurface geothermal fluids and to extract from that composition information on the reservoir temperature, fluid origin and recharge, physical processes such as boiling or condensation, and production properties of the fluid such as its scaling potential, gas content and concentration of environmentally sensitive elements. In recent years, soil gas methods have become more commonly employed during geothermal exploration, in particular for the detection and delineation of permeable structures (Fridriksson et al. 2016).

2. CLASSIFICATION OF GEOTHERMAL FLUIDS

It has proved difficult to obtain a genetic classification of subsurface waters. The waters that have been studied in detail are mostly those that are of economic interest as potable water. Water also tends to flow away from its point of origin and undergo water-rock interaction during its travels making it increasingly difficult to decipher its origins. White (1986) attempted a classification which is reproduced here:

- *Meteoric water* circulates in the atmosphere, co-existing with near-surface, uncemented sediments, can circulate in subsurface rocks and dissolve constituents, e.g. evaporates;
- *Ocean water* is partly evaporated products of meteoric water;
- *Evolved connate water* forms in young marine sediments. It is initially 10-50% oceanic or pore water mixed with combined water. Upon increased burial depth more interaction takes place at modest temperatures, and compaction leads to lower pressure environments. Variable salinity is observed and may be due to filtration, evaporation or dissolution of evaporites;
- *Metamorphic water* is contained in or driven from rocks undergoing metamorphic dehydration reactions. Being over-pressured at depth, it may escape in response to lithostatic load;
- *Magmatic water* is derived from oceanic and evolved connate waters subducted along with oceanic crust into the mantle. At deep crustal level it is mostly due to rocks undergoing metamorphism; and
- *Juvenile water* is classified as water that has never circulated in the atmosphere. If it exists, it must be extremely rare. Juvenile ^3He and CO_2 of mantle origin exist and thus suggest that juvenile H_2O may exist too but it has not yet been identified conclusively.

Ellis and Mahon (1977) classified geothermal waters into four categories based on major anions. Their classification is as follows:

- *Alkali-chloride water*: pH 4-11, least common in young rocks, e.g. Iceland. These are mostly sodium and potassium chloride waters although in brines Ca concentration is often significant;
- *Acid-sulphate water*: These waters arise from the oxidation of H_2S to form SO_4 near the surface and most of its constituents are dissolved from surface rock. Thus such water is generally not useful for prediction of subsurface properties;
- *Acid-sulphate-chloride water*: Such water may be a mixture of alkali-chloride water and acid-sulphate water, or it can arise from the oxidation of H_2S to SO_4 in alkali-chloride water or dissolution of sulphur from rock followed by oxidation. Sulphate-chloride waters need not be very acidic and may then reflect subsurface equilibria and be used for prediction of subsurface properties; and
- *Bicarbonate water*: Bicarbonate water may derive from CO_2 rich steam condensing or mixing with water, it is quite common in old geothermal waters or on the peripheries of geothermal areas in outflows. They are commonly at equilibrium and may be used to predict subsurface properties.

Geothermal fluids that are found at the deepest levels of a geothermal system were termed *primary geothermal fluids* by Arnórsson et al. (2007). Such fluids are generally a mixture of up to three fluid components: meteoric water, seawater and magmatic volatiles. When primary fluids rise towards the surface they may undergo various processes to form *secondary geothermal fluids* (Figure 1), including:

- *Depressurisation boiling*, which leads to the formation of a vapour phase and boiled liquid;
- *Vapour condensation* in shallow ground water or surface water, which will produce steam-heated water rich in sulphate or bicarbonate;
- *Mixing of CO_2 gas* from a deeper source with thermal ground water; and
- *Mixing of geothermal water* with shallower and cooler water.

From this definition it is apparent that most of the geothermal fluids collected at surface are secondary, with the exception of primary fluid from low-temperature systems, which may reach the surface without boiling in hot springs or wells with artesian discharge.

From the different origin of geothermal fluids, it follows that some fluids hold more information about the underlying geothermal system than others. The most useful fluid types are unperturbed primary steam and boiled, unmixed geothermal solutions, as they are formed directly from the primary fluid by phase separation. Fluids formed by mixing of a geothermal water and surface water may also be useful

if a mixing trend can be defined and used to infer the composition of the geothermal end-member, but steam-heated surface waters give very limited information about the underlying geothermal system.

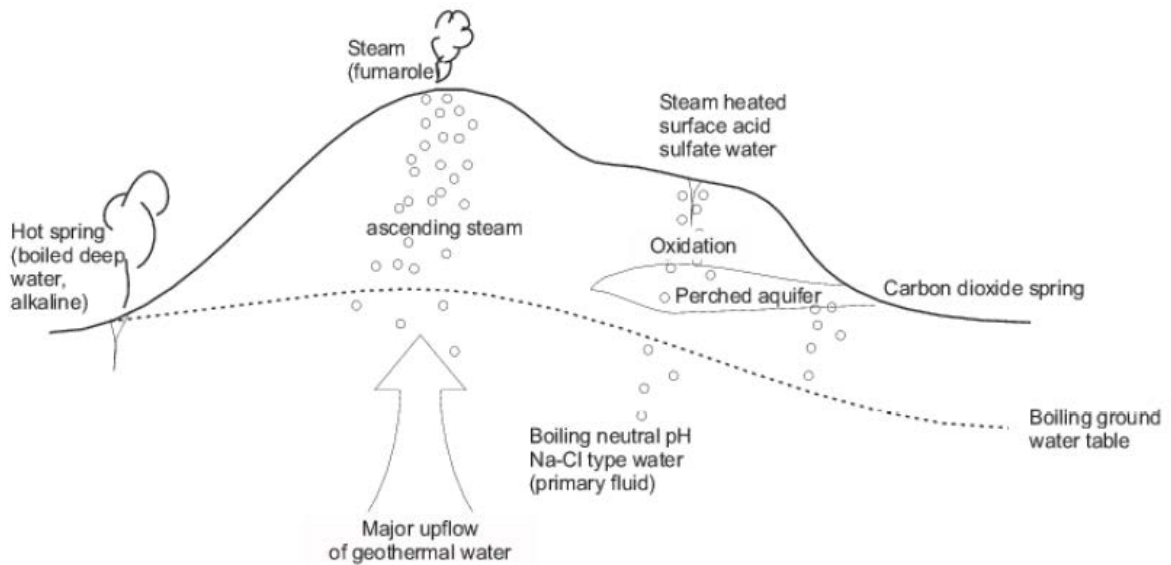


FIGURE 1: Schematic cross-section through the uppermost part of a high-temperature geothermal system depicting the formation of various secondary geothermal fluids. From Arnórsson et al. (2007)

A convenient way of distinguishing between the different types of geothermal water is the use of the chloride-sulphate-bicarbonate ternary diagramme described by Giggenbach (1991). An example of such classification is given in Figure 2. The samples in the diagramme are from wells and hot springs in seven high- and low-temperature geothermal areas around the world. The samples which fall near the chloride and bicarbonate apices of the triangle are likely to give information about the underlying geothermal reservoir; the samples which fall near the sulphate apex are not.

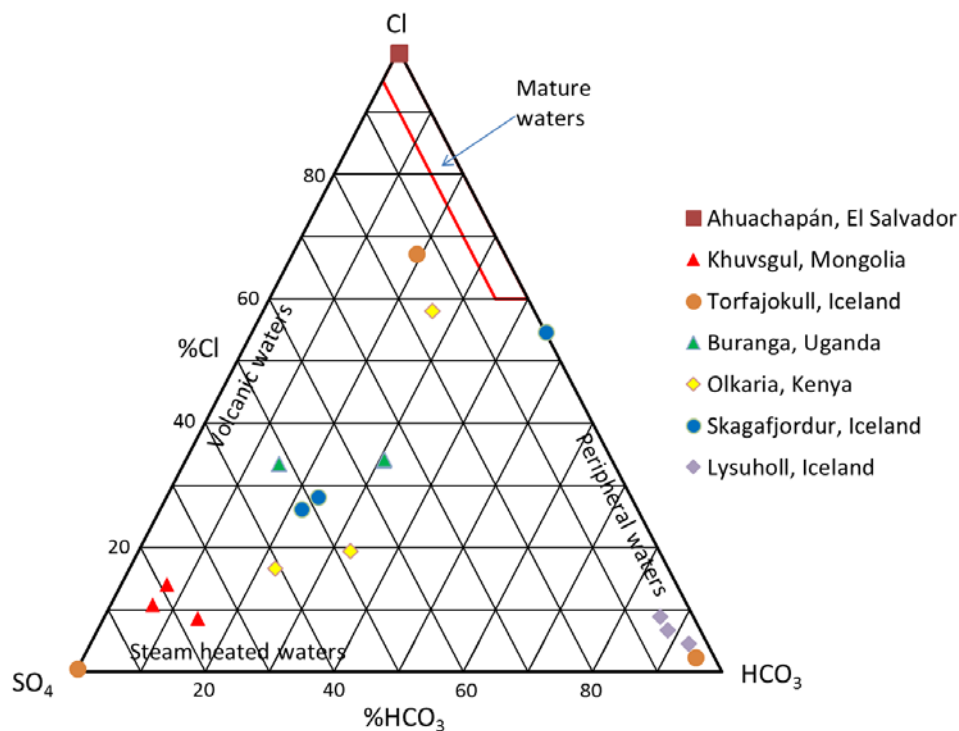


FIGURE 2: Classification of geothermal fluid samples by dominant anions using the ternary diagramme described by Giggenbach (1991)

3. CHEMICAL GEOTHERMOMETRY

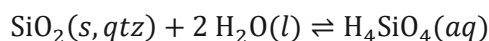
Interpretation of chemical composition of geothermal fluids, liquid or steam, with respect to reservoir temperature is referred to as chemical geothermometry. This is probably the most important application of geochemistry in geothermal exploration, as no other surface method gives information about the reservoir temperature. Chemical geothermometry is based on the following assumptions:

1. The fluids have reached a local equilibrium with secondary minerals in the geothermal reservoir at the reservoir temperature. The chemical equilibria in question need to be sensitive to temperature, i.e. the concentrations (or activities) of aqueous species or concentration (or activity) ratios in the water phase in equilibrium with the minerals need to change systematically with temperature.
2. The composition of the fluids does not change during the ascent from the reservoir, i.e. re-equilibration or dilution has not affected the fluid composition.

While geothermometers are widely used in geothermal studies the above assumptions may not always hold and it is the role of the geochemist to assess whether that is the case or not. The most common types of geothermometers involve the concentrations or activities of dissolved solutes or gases in geothermal fluids, but geothermometers based on isotope ratios have also been formulated. A few of the more common geothermometers are introduced below, but for a more comprehensive discussion on geothermometry the reader is referred to D'Amore and Arnórsson (2000).

3.1 Solute geothermometry

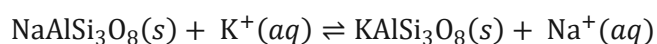
The most commonly used geothermometers for aqueous solutions are the so called silica (SiO_2) geothermometers that are based on the solubility of silica minerals, such as quartz or chalcedony. Quartz is the most stable form of solid SiO_2 in the near surface environment such as in geothermal systems. If an equilibrium has been reached between quartz and dissolved silicic acid in the geothermal solution, the so called quartz geothermometer is the appropriate geothermometer to use.



The quartz geothermometer is generally applicable at temperatures above 180°C and at even at lower temperatures in systems where quartz is present in the host rock. In some cases, e.g. in low temperature systems where the rocks are reactive (i.e. contain relatively soluble minerals) the rock dissolution may be too fast for the quartz precipitation to keep up with the input of dissolved silica and in such systems the solution will reach metastable equilibrium with chalcedony. In such cases the chalcedony geothermometer applies but the quartz geothermometer will yield too high temperatures. Also, if the solutions are unusually reactive, as can be the case when CO_2 concentrations are high, the rock dissolution may be too fast for quartz precipitation to keep up. In such cases the quartz geothermometer will, again, yield too high temperatures.

Several authors have published geothermometer formulae connecting the concentration of dissolved silicic acid and reservoir temperature. Three examples of such formulae are given in Table 1; the chalcedony geothermometer of Fournier (1977), and the quartz geothermometers for boiled and unboiled solutions, published by Fournier and Potter (1982).

Another commonly used geothermometer for thermal waters uses the concentration (or activity) ratio of Na to K in solution. If the aqueous solutions are in equilibrium with Na- and K-bearing aluminosilicates the ratio of Na^+ and K^+ is fixed at a given temperature.



The Na/K ratio decreases with increasing temperature. The precipitation kinetics of these mineral is relatively slow and as a result solutions have generally not reached an equilibrium with the aluminosilicates in low temperature systems. In such cases the Na/K ratio of the aqueous solution may either be inherited from the water recharging the system or derived from the dissolution of the rocks. In the latter case Na/K geothermometers will yield very high reservoir temperatures for K-rich rocks.

Again, several authors have published geothermometry formulae employing the Na/K ratio and other cation ratios in geothermal solutions. Four of those are given in Table 1; the Na-K geothermometers of Arnórsson et al. (1998a) and Giggenbach (1988), the K-Mg geothermometer of Giggenbach (1988) and the Na-Ca geothermometer of Tonani (1980).

Giggenbach (1988) combined the Na-K and K-Mg geothermometers into a ternary diagramme, which would be useful for determining the extent of equilibrium between the geothermal fluid and host rock. This approach is based on the different rates of the two cation exchange reactions, the K-Mg reaction responding much faster to temperature changes than the Na-K reaction. Using the ternary diagramme, Giggenbach (1988) classified waters into *immature*, *partially equilibrated* or *fully equilibrated*, the latter meaning that the water was fully equilibrated with respect to all three components. On the other hand, immature water is not equilibrated with respect to these components and is therefore not suitable for geothermometry. An example of such a ternary diagramme is given in Figure 3.

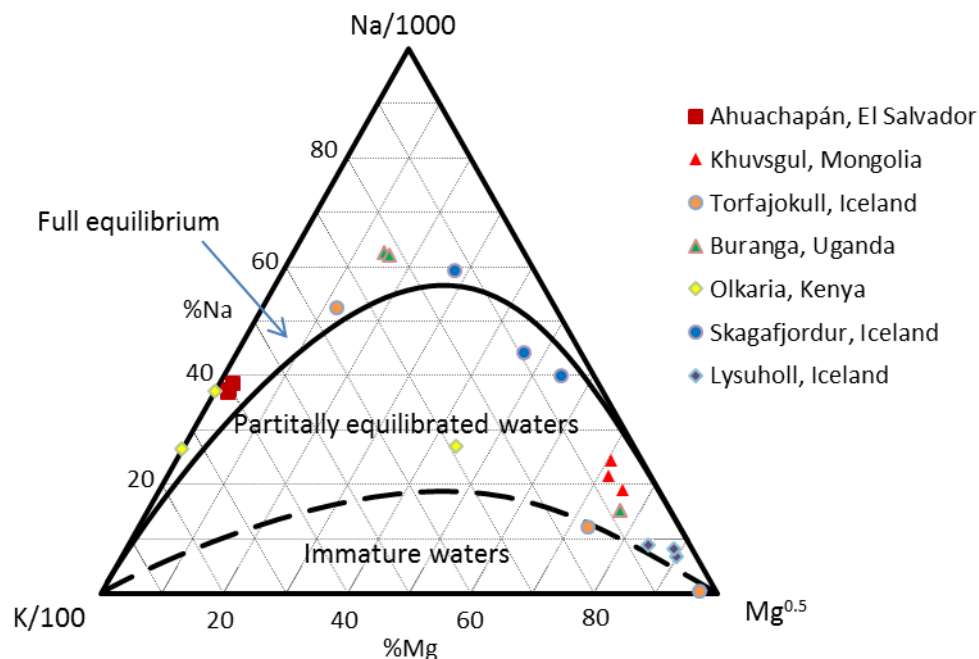


FIGURE 3: The cation ternary diagramme described by Giggenbach (1991), combining the Na-K and K-Mg geothermometers

3.2 Gas geothermometry

In a similiar way as the solute geothermometers, gas geothermometers have been formulated to estimate subsurface temperatures from gas concentrations in steam, assuming that either gas-gas or gas-mineral equilibria exist at depth. These are either empirical or theoretical formulae and their applicability depends on the presence of particular minerals in the host rock (Figure 4). The gases most often employed are the major reactive geothermal gases; CO₂, H₂S, H₂ and CH₄, sometimes in conjunction with inert gases such as N₂ and Ar, which concentrations are expected to be source-controlled rather than controlled by equilibria with minerals. As in the case for the solute geothermometers, formulae exist both for concentrations of single reactive gases and gas ratios – either between two reactive gases or reactive and inert gases.

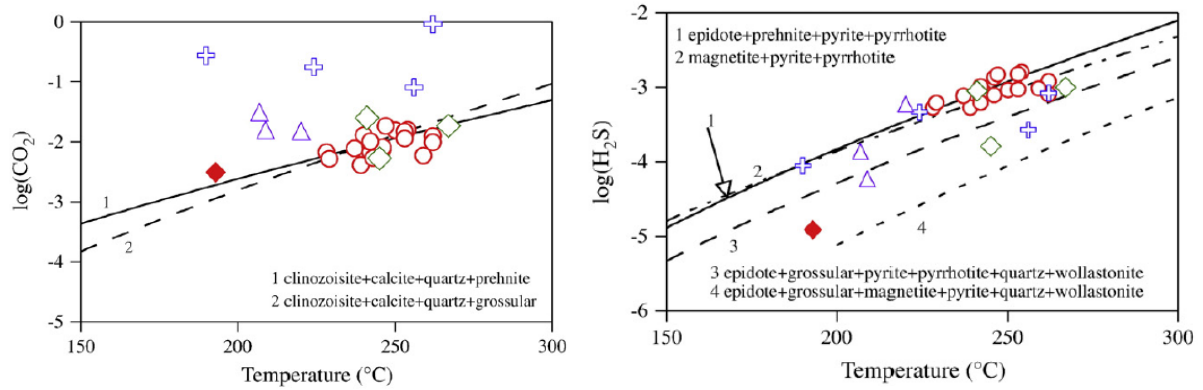


FIGURE 4: Examples of temperature dependent equilibria between gases and different mineral assemblages. The gas samples are from Olkaria, Kenya. From Karingithi et al. (2010)

Yet again, a number of authors have published formulae for gas geothermometry. Arnórsson et al. (1998b) published a set of six geothermometers, for the concentrations of CO_2 , H_2S and H_2 , and the CO_2/N_2 , $\text{H}_2\text{S}/\text{Ar}$ and H_2/Ar ratios. These formulae are given in Table 1 below.

TABLE 1: Selected formulae for geothermometry. S represents the concentration of SiO_2 in mg/kg; Y represents the logarithm of molal concentration ratio Na/K ; Na , K , Mg and Ca represent the concentrations of these elements in mg/kg; and Q represents the logarithm of the relevant gas concentrations or concentration ratios in mmol/kg. Logarithms are base 10

Component	Temperature equation ($^{\circ}\text{C}$)	Published by:
SiO_2 , chalcedony	$t = \frac{1309}{5.19 - \log S}$	Fournier, 1977
SiO_2 , quartz	$t = -42.2 + 0.28831S - 3.6686 \times 10^{-4}S^2 + 3.1665 \times 10^{-7}S^3 + 77.034 \log S$	Fournier and Potter, 1982
SiO_2 , quartz, boiled	$t = -53.5 + 0.11236S - 0.5559 \times 10^{-4}S^2 + 0.1772 \times 10^{-7}S^3 + 88.390 \log S$	Fournier and Potter, 1982
Na-K	$t = 733.6 - 770.551Y + 378.189Y^2 - 95.753Y^3 + 9.544Y^4$	Arnórsson et al., 1998a
Na-K	$t = \frac{1390}{1.750 + \log\left(\frac{\text{Na}}{\text{K}}\right)} - 273.15$	Giggenbach, 1988
K-Mg	$t = \frac{4410}{14.0 + \log\left(\frac{\text{K}^2}{\text{Mg}}\right)} - 273.15$	Giggenbach, 1988
Na-Ca	$t = \frac{1096.7}{3.08 - \log\left(\frac{\text{Na}}{\sqrt{\text{Ca}}}\right)} - 273.15$	Tonani, 1980
CO_2	$t = 4.724Q^3 - 11.068Q^2 + 72.102Q + 121.8$	Arnórsson et al., 1998b
H_2S	$t = 4.811Q^2 + 66.152Q + 177.6$	Arnórsson et al., 1998b
H_2	$t = 6.630Q^3 + 5.836Q^2 + 56.168Q + 227.1$	Arnórsson et al., 1998b
CO_2/N_2	$t = 1.739Q^3 + 7.599Q^2 + 48.751Q + 173.2$	Arnórsson et al., 1998b
$\text{H}_2\text{S}/\text{Ar}$	$t = 4.108Q^2 + 42.265Q + 137.6$	Arnórsson et al., 1998b
H_2/Ar	$t = 0.640Q^2 + 43.260Q + 170.0$	Arnórsson et al., 1998b

4. TRACING FLUID ORIGIN

Whereas geoindicators or reactive constituents of geothermal fluids play the major roles in geothermometry, the non-reactive or conservative constituents are of most importance when tracing the origin of geothermal fluids. In particular stable isotopes and binary or ternary relations between conservative components such as B, Br and Cl are important tracers of the origin of geothermal fluids.

4.1 The use of stable isotopes

Isotope ratios are commonly used to trace the origin of the geothermal solutions or dissolved components in solution. The most abundant isotope pairs in a water sample are the ratios of the stable isotopes of hydrogen, i.e. ^2H and ^1H , and the stable isotopes of oxygen; ^{18}O and ^{16}O . The ratios are usually reported as *per mille* deviations from Standard Mean Ocean Water (SMOW), denoted δD ($^2\text{H}/^1\text{H}$) and $\delta^{18}\text{O}$ ($^{18}\text{O}/^{16}\text{O}$):

$$\delta_{\text{sample}} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000\text{‰}$$

By definition, ocean water has δ -values close to 0‰, but because lighter water molecules evaporate more easily than the heavier ones, the clouds formed by evaporation are expected to be more depleted in the heavier isotopes than the source fluid, i.e. $\delta < 0$. Contrariwise, the heavier water molecules precipitate faster from the clouds than lighter molecules, so the first precipitation from a cloud is expected to be more enriched in heavy isotopes than the cloud itself. As the clouds move further away from their origin, they become more and more depleted in the heavy isotopes, i.e. the precipitation becomes lighter. Therefore, lighter precipitation is to be expected further inland and at higher altitudes. Seasonal changes are also observed, with lighter precipitation in winter than summer, and long-term climatic changes produce a similar effect.

The reason for the usefulness of stable isotope ratios for tracing water origin is that after precipitation there is little change in the ratios, although the water may travel long distances. Local annual means for precipitation have been established and Craig (1961) showed that a meteoric line describing the relationship between δD and $\delta^{18}\text{O}$ applies all over the world ($\delta\text{D} = 8 \cdot \delta^{18}\text{O} + 10$), although deviations are known and local lines have been described. The stable isotope values in unaltered groundwater are thus expected to satisfy this equation.

When isotope ratios are used to trace the origin of geothermal water, it is important to realise that although the isotope values suggest the origin, processes such as mixing, water-rock interaction, condensation and age may have to be accounted for. In particular, oxygen isotope exchange with rock at high temperature will lead to enrichment of ^{18}O , i.e. the composition will move from the meteoric line towards higher $\delta^{18}\text{O}$ (Figure 5). The extent of this shift depends on various properties of the water-rock system, such as temperature, host rock composition, water-rock ratio etc. For example, silicate minerals have $\delta^{18}\text{O}$ values of about 8-12‰ whereas carbonate minerals have $\delta^{18}\text{O}$ of about 29‰, resulting in a larger oxygen isotope shift assuming that all other factors are equal.

Other stable isotopes may also be useful for tracing the origin of dissolved constituents. For example, strontium (Sr) isotopes are distinctly different between different rock types and yet another value is found in seawater. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in water may therefore be used to infer the rock type with which the geothermal solutions have reacted.

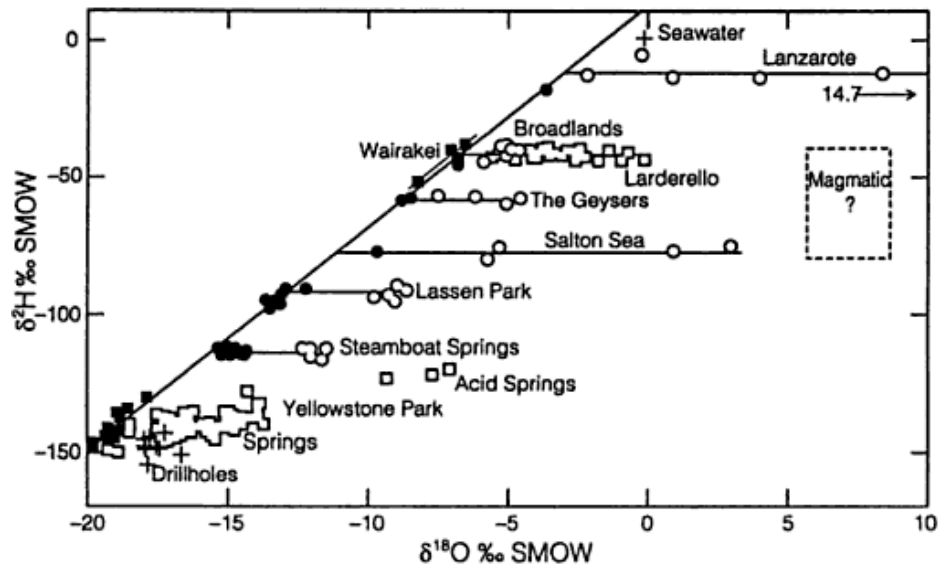


FIGURE 5: Samples of groundwater (filled symbols) and altered geothermal water (empty symbols) from various geothermal areas around the world, along with the global meteoric water line. The shift towards higher $\delta^{18}\text{O}$ is due to isotope exchange with rock. From Truesdell and Hulston (1980)

4.2 The use of conservative constituents

The boron concentration of seawater and thus precipitation is low, but that of rocks and volcanic steam is much higher. Contrariwise, the chloride concentration of seawater is high but low in rocks and volcanic steam. Thus the B/Cl ratio can be used to trace the mixing of sea water or magmatic steam with precipitation (Figure 6).

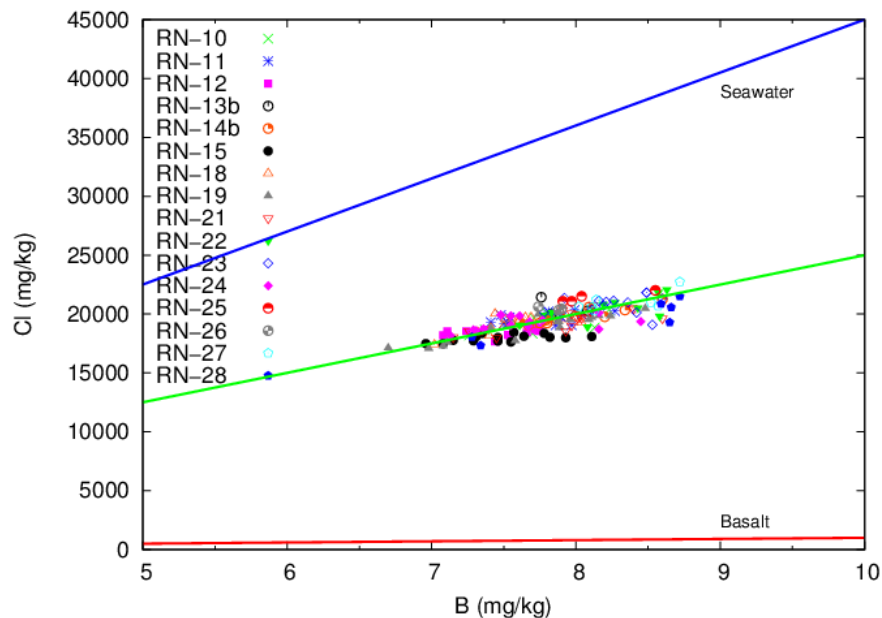


FIGURE 6: The concentrations of B and Cl in geothermal solutions in Reykjanes, Iceland. Also shown are the concentration ratios in seawater and tholeiitic basalt. From Óskarsson et al. (2015).

Other conservative constituents have also been used to similar effect, e.g. Li, Rb, Cs, and N_2 – for example in the Li-Cs-Rb and Li-Cl-B ternary diagrams proposed by Giggenbach (1991).

4.3 Dating

One way of studying the origin of geothermal water is by dating. For this two types of methods have been used, i.e. determination of radioactive materials and chlorinated fluorocarbons (CFCs). Of radioactive substances, ^3H with a half-life of 12.43 years has been extremely useful for relatively young waters. It is measured in tritium units (1 TU = 1.185 Bq/L). The natural cosmogenic level in precipitation is a few TU but rose to ≈ 2000 TU from the 1950s to 1963/1964 but is down to ≈ 10 TU at present. For older waters dating with ^{14}C with a half-life of 5730 years has been used. It is present in atmospheric CO_2 , the living biosphere and hydrosphere after production by cosmic radiation but underground production negligible and therefore it cannot be used for carbon from a magmatic source. The ^{14}C content is often presented as % modern carbon (pMC), grown in in 1950. Fallout ^{14}C (in CO_2) has been used to date water with mean residence time less than 150 years. CFC-dating is based on the detection of man-made organic chlorinated fluorocarbons, which first appeared in 1928.

5. SOIL GAS METHODS

Geothermal gas is transported to the surface with rising steam from boiling high-temperature systems, or is released from low-temperature liquids as they decompress on their way to the surface. Some of the gas escapes through steam vents or other point sources, but some of the gas is released diffusely through soil. The distribution of geothermal gases in soil can elucidate their pathways the surface, thus indicating permeability. For this reason, soil gas methods are becoming more commonly used in recent years for geothermal exploration. These methods can be divided into two main categories, i.e. gas flux methods, in which the flux of gases through soil is quantified, and soil gas concentration methods, in which samples of soil gas are collected for analysis either on site or in the laboratory.

The results of soil gas studies have been used to indicate the presence of a geothermal reservoir and also the shape of the soil gas anomalies may be used to infer the orientation of the structures (fractures) by which gas flows to the surface. However, it is important to keep in mind that the presence of anomalous concentrations of gases in soil are not unambiguous evidence for the geothermal activity, in particular where no other geothermal surface manifestations are present. Elevated flux of cold CO_2 is commonly observed in areas where tectonic activity has resulted in deep and extensive faulting, in which case soil gas anomalies are not necessarily evidence for a geothermal reservoir at depth.

5.1 Diffuse flux of gas through soil

Diffuse gas flux (most commonly CO_2) through soil is most commonly quantified using the closed chamber method, in which a closed container of known volume and transectional surface area is placed face-down on the spot of ground which is to be measured, and the concentration of the gas inside the chamber is measured continuously using a gas detector (Figure 7). If gas is emitted from the soil, its concentration will increase with time, and the accumulation rate may then be used to calculate the flux of gas through the soil in units such as $\text{g/m}^2/\text{day}$.

In order to properly locate the geothermal soil degassing anomalies, the spacing between measuring points must not be too large. A general rule of thumb is that the spacing between measuring points should be about 1/3 or 1/5 of the width of the anomaly. If the points are more widely spaced, the results can be very misleading, both in terms of the location and direction of the anomalies.

When mapping in the field, it is very convenient that the results of soil gas flux measurements are available instantaneously, i.e. no significant processing of the data is needed so the mapping strategy may be adapted in the field as deemed necessary. For that reason, it is common to start soil gas flux mapping by measuring on long profiles perpendicular to the suspected direction of active fractures and measuring with a fairly narrow spacing (e.g. 25 m between points). If all measurements are low the

sampling distance may possibly be increased to save time, but if anomalous gas flux is detected it may be mapped in more detail on a closely spaced grid.

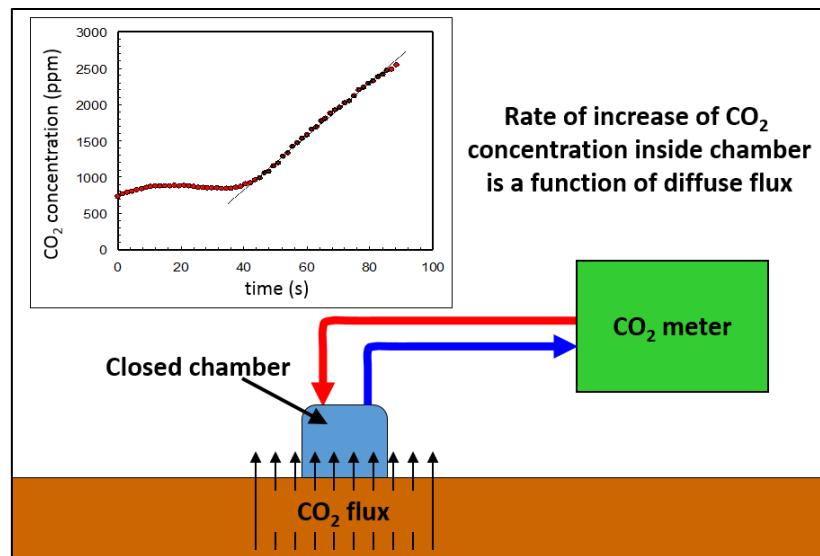


FIGURE 7: Basic principle of soil gas flux measurements using the closed chamber method

By mapping the CO₂ flux through soil in a geothermal prospect, often in conjunction with the measurement of soil temperature at a fixed depth, it may be possible to locate active fractures and other permeable structures which may turn out to be good drilling targets (Fridriksson 2009; Fridriksson et al. 2016). The changes in soil gas flux may also be used to quantify the changes in surface activity upon utilisation of a geothermal resource and to calculate the total gas emissions and heat flow from the field (Óladóttir and Fridriksson, 2015; Figure 8).

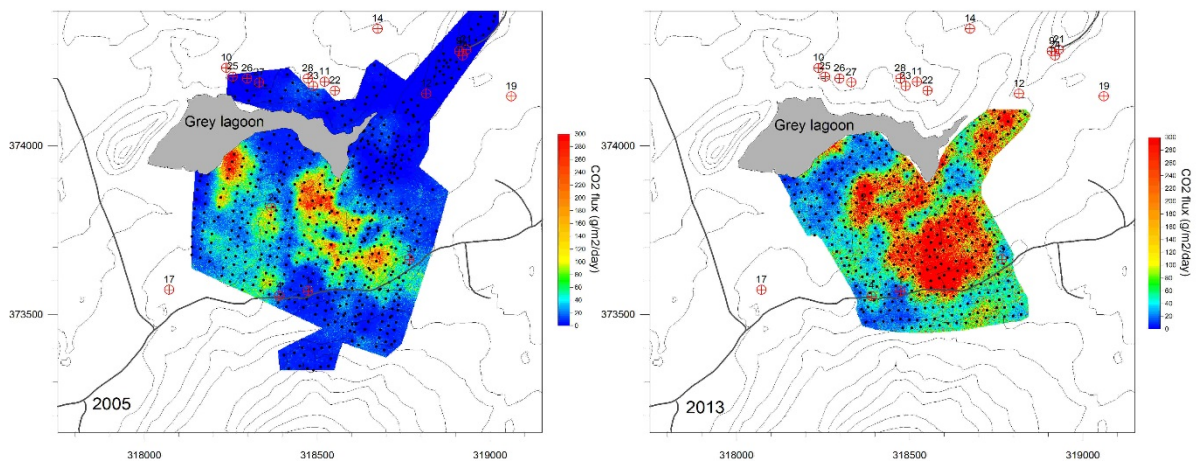


FIGURE 8: CO₂ flux through soil in the Reykjanes geothermal area in 2005 (left) and 2013 (right). From Óladóttir and Fridriksson (2015).

5.2 Soil gas concentrations

The collection of soil gas samples for analysis is typically performed by inserting a probe to a depth of 0.5-1.5 m and pumping a sample either directly into an analytical instrument or a container from which the sample may later be analysed in the laboratory. The most commonly analysed gases for this purpose are CO₂, He, and Rn but H₂S and Hg are also sometimes employed. In some cases, gas isotope ratios are determined in addition to the gas concentrations, as the isotope data may provide additional

information about the source ($^3\text{He}/^4\text{He}$) of the gas or its flow-rate ($^{220}\text{Rn}/^{222}\text{Rn}$) to the surface. As soil gas sample collection is more time-consuming and the analysis more expensive than the measurement of soil gas flux, sample collection is often focussed on the most promising areas as determined by soil gas flux mapping.

6. CONCLUSIONS

Geothermal water is mostly meteoric and oceanic water in origin, but has been altered by interaction with rock and in some cases magmatic fluids. Geothermal waters have been classified with respect to their anion and cation contents into alkali-chloride water, acid sulphate water, acid sulphate-chloride water and bicarbonate water. Acid waters are generally unsuitable for elucidation of subsurface properties. Conservative constituents, in particular stable isotopes, B and Cl, are used for tracing origin and flow of geothermal fluids whereas rock-forming constituents are used to predict subsurface temperatures. Measurements of soil gas concentrations and flux can be useful for delineating fractures or other permeable structures relevant to flow paths in geothermal systems, as well as for quantifying changes in surface activity of the geothermal field, both in the natural state and during utilisation.

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