



## **GEOHERMAL GEOCHEMISTRY HISTORICAL OVERVIEW, PRESENT STATUS, FUTURE OUTLOOK**

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### **ABSTRACT**

Geochemistry is very important for the exploration, development and use of geothermal resources. Success in geothermal geochemistry studies rests largely on the application of the principles of physical chemistry to interpret geothermal fluid chemistry and hydrothermal alteration.

### **1. INTRODUCTION**

Geochemistry is one of the four major geoscientific disciplines involved in the exploration, development and exploitation of geothermal resources. The other disciplines are geology, geophysics and hydrology. Modern geothermal geochemistry rests largely upon the principles of physical chemistry, mostly on chemical thermodynamics but also on kinetics. In future quantum mechanics, the third major discipline of physical chemistry may prove to become useful in predicting the thermodynamic properties of minerals and even of aqueous species. Success in geothermal geochemistry studies, thus, rests largely on the application of the principles of physical chemistry.

### **2. EARLY APPLICATION OF CHEMICAL THERMODYNAMICS TO QUANTIFY GEOLOGICAL PROCESSES**

The first time chemical thermodynamics was applied to understand and quantify geological processes was in 1905 when the Dutch physical chemist v'ant Hoff, who was studying marine evaporites, used thermodynamics to assess the relative stabilities of the calcium sulphate minerals, anhydrite and gypsum, and to predict under which geological conditions they were stable (van't Hoff, 1905). Few years later Victor Moritz Goldschmidt, who has been named the father of modern geochemistry, used chemical thermodynamics for interpreting the mineralogical composition of metamorphic rocks in the Oslo region as a part of his doctoral studies (Goldschmidt, 1911). Thus, the first extensive application of chemical thermodynamics to geological problems was linked to metamorphism. It did not move to any significant extent into other areas of geology and geochemistry for the next 40 to 50 years. Goldschmidt's father was a professor of chemistry at Oslo University at the time his son was studying geology there and he was a good friend of his colleague v'ant Hoff in Holland. That has little doubt influenced the approach the young Goldschmidt took to interpret the field data on the metamorphic rocks around Oslo.

Not long before Goldschmidt's death in 1947 he had a visit from a young geochemist from New

Zealand, Brian Mason. Mason influenced younger New Zealand geochemists, including A. J. Ellis and W. S. Fyfe. Ellis brought physical chemistry into geothermal studies in the late fifties (see e.g. Ellis and Mahon, 1977) and Fyfe was a co-author of the first book, as far as I know, where chemical thermodynamics was extensively used as a tool in the study of metamorphic rocks (Fyfe, Turner and Verhoogen, 1958). This was expanded into a textbook a two years later including also igneous rocks (Turner and Verhoogen, 1960). The first textbook that brought together minerals, aqueous solutions and thermodynamics was written by Garrels and published in 1960 (Garrels, 1960) and later extensively revised (Garrels and Christ, 1965).

### 3. THE BIRTH OF QUANTITATIVE GEOTHERMAL HYDROGEOCHEMISTRY

In the 1960's geothermal geochemistry expanded much through attempts to quantitatively interpret the composition of geothermal fluids by studying the extent to which mineral-solution equilibria prevailed in geothermal reservoirs. These studies led to the development of chemical geothermometers. The pioneering work in this field involved linking experimental data on quartz solubility and field data from Wairakei and Yellowstone National Park (Morey et al., 1962; Fournier and Rowe, 1966; Mahon, 1966). The experimental work revealed that quartz-solution equilibration is attained rapidly - within hours - at temperatures in excess of about 150°C. By contrast, the reaction is very sluggish at room temperature and it is still debated whether equilibration has ever been attained in experiments at such low temperatures. In 1997 results on quartz solubility in the range 21-90°C were published. The duration of the experiment at room temperature was fourteen and a half years.

The early experimental work on quartz solubility led to the development of the quartz geothermometer. Two kinds of results formed the basis for this chemical geothermometer. One was based on combination of drillhole and experimental data demonstrating that equilibrium between quartz and aqueous solution was closely approached in geothermal reservoirs. The other was that the silica concentrations in well discharges and in nearby thermal springs were quite similar demonstrating that the silica content of hot spring waters was a reflection of temperatures at depth.

The basic publications on the quartz geothermometer appeared in 1966 (Fournier and Rowe, 1966; Mahon, 1966). Several years before it had been observed that a correlation existed between measured temperatures in the drillholes and the silica content of geothermal well and hot spring waters. On the basis of this observation Bødvarsson proposed in 1960 that the silica content of hot springs could be used to predict subsurface temperatures (Bødvarsson and Pálmason, 1961). In 1970 it was demonstrated that chalcedony rather than quartz controlled aqueous silica concentrations in geothermal reservoirs in Iceland having temperatures of less than about 180°C (Arnórsson, 1970).

The 1960's and the 1970's also saw much expansion in the development of isotope geothermometers and at the same time, and a little later, many cation and gas geothermometers were established. The latter have proved useful in estimating subsurface temperatures in areas where surface manifestations consist of fumaroles only. In most cases the cation and gas geothermometers were geochemically rather than thermodynamically calibrated. The reason was that theoretical or thermodynamic calibration failed to yield satisfactory temperature equations for these geothermometers whereas observation showed good correlation between many cation and gas ratios or gas concentrations and aquifer temperatures in wells allowing an empirical correlation to be made between temperature and a specific cation or gas ratio and gas concentration. The reason for failure of theoretical calibration was considered to be imprecise thermodynamic data on the minerals involved in the equilibrium. For some of the cation and gas geothermometers many calibrations have been proposed, particularly for the Na/K geothermometer. It was in fashion that every geochemist studied the relationship between aquifer temperature and aqueous Na/K ratios in "his" wells and, as a product, came up with a new calibration. Careful assessment of experimental data has just recently resulted in a theoretical calibration of this geothermometer so all the empirical calibrations can now be forgotten (Arnórsson et al., 1998).

#### 4. ORIGIN OF GEOTHERMAL FLUIDS

Extensive studies of the isotopic composition of natural waters were initiated in the late 1950's. They revealed that geothermal fluids were largely meteoric by origin (Craig et al., 1956). This revolutionized some earlier ideas that considered geothermal fluids to be largely magmatic. Although it is not questioned today that geothermal fluids are dominantly meteoric by origin, evidence has been provided indicating that there may be a significant magmatic component to some geothermal waters associated with andesitic volcanism (Giggenbach, 1992).

One of the products of chemical and isotopic studies on geothermal fluids has led to the division of their components into two groups, reactive components and unreactive or incompatible components. The former reflect the physical state of geothermal systems. The latter are useful in assessing the origin of the geothermal fluid.

#### 5. AQUEOUS SPECIATION

An important part of quantitative interpretation of geothermal fluid compositions has been the writing of aqueous speciation programs. There are tens if not hundreds of such programs today. However, most of them are not suitable for handling primary chemical data on two-phase geothermal fluids. At least two of these programs have permitted evaluation of how boiling and changes in the temperature of geothermal waters affect mineral saturation and scaling tendencies (Arnórsson et al. 1982; Reed and Spycher, 1984).

The use of these programs, together with basic chemical thermodynamic considerations, have changed the angle somewhat at which one looks at chemical geothermometry. Reed and Spycher (1984) presented so-called mineral saturation diagrams which permit evaluation of the temperatures at which selected minerals are at equilibrium with a particular water. If many minerals indicate equilibrium at about the same temperature, this temperature can be regarded as the best estimate of the chemical geothermometry temperature for that water.

#### 6. PRESENT STATUS

It is not surprising that early developments in geothermal geochemistry focused on the use of geothermometry for the exploration for geothermal resources. Reservoir temperatures constitute the most important parameter with respect to the potential use of the resource. The geothermometry development has, however, not been followed up in accordance with needs for later stages in geothermal development and exploitation. My general impression is that geothermal studies, certainly as far as geochemistry goes, have been taken to a large extent away from the theoretical environment to the practical environment with the result that the geothermal industry has been separated from research and the progress it usually leads to. Basically we have only had more power stations installed. We have neither seen much improvement in the use of geothermal resources nor in the versatility of the utilization. The few who have been engaged in geochemical research on geothermal resources have also tended to sink more and more into the details of geothermometry rather than embarking on new research fields that are of obvious economic and environmental importance to geothermal utilization, such as scaling and the removal of gases from geothermal steam. I know of very few publications that deal with the basic chemistry of scale formation. Scale formation is at times rather looked upon as a process in a random world rather than behaving according to the well established laws of physical chemistry and that, in order to understand scale formation, one needs to understand physical chemistry. Of course, much progress has been made with respect to inhibiting scaling in production and injection wells. Yet, the general approach to avoid

silica scaling from spent waste fluid today is the same as in 1970. The advice is that one should not allow the water to cool below amorphous silica saturation. This means poor exploitation of the thermal energy brought with water and steam to the surface through drillholes.

## 7. FUNDAMENTAL RESEARCH

Most of the studies that I have become acquainted with in the field of scale formation from geothermal fluids is to a considerable extent empirical rather than theoretical. Research allows room for fundamental questions that generally lead to improved knowledge which is followed by progress. Electricity was not the product of practical and economic projects aiming at furthering the use of the candle. It was the product of permitting some researchers to ask and answer fundamental questions. I believe it is the same with scaling problems in the geothermal industry. We will not make a real progress without some fundamental research that will allow us to quantify scaling processes in terms of the laws of physical chemistry.

In 1996-98 a graduate student of mine, Ingvi Gunnarsson, studied magnesium silicate scale formation from geothermal fluids (Gunnarsson and Arnórsson, 1999). The project was financed by three Icelandic energy companies, Hitaveita Reykjavíkur, Hitaveita Sudurnesja and Landsvirkjun. Ingvi demonstrated that a magnesium silicate with a definite stoichiometry, which is amorphous with respect to X-rays, precipitates readily from supersaturated solution. From laboratory experiments he obtained numbers for the solubility product of this magnesium silicate valid in the range 25-250°C. With this information it is now possible to predict for water of a given composition whether or not this magnesium silicate will form scales and under which temperature conditions. And what is most important with the laboratory experimental results is that they have general rather than specific application. The laboratory experiments were not expensive and much less costly than pilot plant studies had been aiming at delineating empirically the conditions that would lead to magnesium silicate formation. The laboratory experiments were laid out on the basis of the principles of chemical thermodynamics. Pilot plant studies are generally not. This is a good example that application of a theory gives the most practical result at the lowest cost.

Inspection of data on the chemical composition of geothermal waters from springs and drillholes indicates that these waters, when below about 100°C, are very close to saturation with the amorphous magnesium silicate just discussed. Waters of higher temperature are undersaturated. This suggests that the solubility of this amorphous magnesium silicate controls the magnesium levels in <100°C geothermal waters. Thus, the experimental work on the amorphous magnesium silicate solubility, has also provided a quantitative explanation of the control of magnesium levels in many natural waters.

## 8. FUTURE OUTLOOK

The possibility of being able to control silica scale formation or eliminate it by removing silica from geothermal waters opens up the possibility of exploiting high-temperature geothermal fluids to low temperatures, thus effectively enlarging any high-temperature geothermal resource and making its exploitation, therefore, environmentally more feasible. My vision of a future geothermal plant lies in maximum extraction of heat from the produced geothermal fluid and injection of any waste brine and condensate. This is only possible if one can prevent scaling at all temperatures. I also envisage that the gases should be extracted from the condensed steam. Success with gas extraction and scale prevention would lead to maximizing the use of the resource and that any geothermal installation would be like a closed system - no discharge of gaseous steam into the atmosphere and no surface disposal of used geothermal fluid. I also think that we should have architects to design geothermal power plants

Much progress has been made at many universities worldwide in the field of aquatic chemistry and mineral-solution reactions during the last two decades as witnessed by very many publications in international journals. It is my impression that the geothermal industry has not benefitted from this as it could have. There are probably two main reasons for this. One is that the geothermal community has put major emphasis on geothermal investigations and development but not much on basic research. The other is lack of employing young people into this industry for part time research with education from first class universities, young people who will bring with them new ideas and ambitious spirit.

Just about everywhere in the world the geothermal industry is small. This industry should be aware of the advantages of being small. I am convinced that the success of building up know-how in Iceland on geothermal resources and their exploitation was very much linked to attracting young research scientists to Orkustofnun - the National Energy Authority and allowing them to spend some of their time on research but some on specific investigation and development projects. In this way they learned practical work from the development projects but they also identified areas where research and improved knowledge was needed and that influenced more than anything else their choice of research projects. I think that the policy by which Orkustofnun has been operating for the last 10-20 years has not been favorable for furthering know-how. This policy needs to be changed towards more fundamental research. I also think that the attitude in some developing countries, who are exploiting or interested in exploiting their geothermal resources, is too narrow. Geochemical and other work in these countries I sometimes find to be laid out as routine, whether it be exploration, development or exploitation of geothermal resources. Access to literature is a major drawback as well as the time allocated to experts to read, absorb or create new knowledge.

### **8.1 Improved analytical techniques**

The last 10 years have seen huge progress in analytical techniques for many elements in aqueous solution. Instruments are getting more and more expensive, more and more sophisticated and at the same time more difficult to operate but also much faster. A whole new world has been opened for trace element analysis by high resolution inductively coupled plasma mass spectroscopy. This has led to the development of specialized service laboratories in Europe and the United States who carry out very many analyses annually at a very low cost and they only require a small sample. The geothermal industry needs to be aware of this. In future it may prove to be most attractive economically to analyse only gaseous components, pH and may be a few other elements in a small local laboratory but ship samples to commercial laboratories for other analyses, in which case there would be a shift of emphasis in the geochemical work for geothermal projects towards less analytical work but with the main emphasis on sampling and data interpretation.

### **8.2 Linking of geothermal exploitation and research**

Revolutionary progress has been made in the last 10-20 years with the application of physical chemistry, mostly chemical thermodynamics, to water-rock interaction processes and other aspects relevant to the exploitation of geothermal resources. It is said that Albert Einstein once expressed the view that he was not interested in chemical thermodynamics. "It has been well established", he said, "and I don't think there is much to be added to it." Indeed chemical thermodynamics is well established. And it has proved to be a very powerful tool to understand and solve many problems related to the exploitation of geothermal resources but, of course, mostly in the chemical industry. Although Einstein was not interested to work on chemical thermodynamics, many of us, even today, find it fascinating, often hard to understand and without the faintest clue whether or not its basic theory could be improved. I firmly believe myself that the understanding of the principles of chemical thermodynamics, as they stand today, is of fundamental importance for making progress in the field of geothermal geochemistry.

Various new research fields have been developed during the last one to two decades that are linked one way or another to geothermal features. These include the production of enzymes using thermal bacteria and the intriguing question about the origin of life. It has now been demonstrated that simple mixing of seawater and geothermal seawater emerging on the deep ocean floor leads to such chemical activities of carbon dioxide, nitrogen and water that organic compounds, such as amines, are stable, so according to thermodynamic theory they, at least, tend to form where the temperature is right. Life is abundant around some of the submarine geothermal vents. How were little guys like pyrococcus born? They live in small holes in scales which have formed around thermal vents on the deep ocean floor and they like temperatures of about 90°C. Did chemical reactions make them that are predictable by the principles of chemical thermodynamics in just the same way as chemical reactions involving only inorganic compounds are predictable? The geothermal industry should be open to participate in this type of research. That would attract good researchers, stimulate the environment and bring in new knowledge and ideas, no doubt to the benefit of the geothermal sector. A lot of money goes into this research today. Why not keep it close to geothermal companies?

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