PROCEEDINGS, Sixteenth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 23-25, 1991
SGP-TR-134

QUALITY CONTROL OF CHEMICAL AND ISOTOPIC ANALYSES OF GEOTHERMAL WATER SAMPLES

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ABSTRACT

Chemical and isotopic analyses of geothermal water samples must meet certain levels of accuracy and reliability to be useful for identifying geochemical processes in hydrothermal systems. Quality control is largely a concern for the analytical laboratory, but the geochemist or reservoir engineer using the chemical data must also be concerned with analytical quality. To test accuracy and reliability of analyses available from laboratories, splits of seven water samples were sent to four stable-isotope laboratories, and splits of five water samples were sent to four chemical laboratories. The analyses of each sample were compared among laboratories, and the differences in analyses were evaluated using criteria developed for this comparison. Isotopic compositions were considered reliable if they deviated from mean values by less than 2‰ for hydrogen and by less than 0.15‰ for oxygen. Concentrations of each chemical component were considered reliable if they differed from mean values by less than 10%. Chemical analyses were examined for internal consistency by calculating the error in ionic charge balance and the error between ionic charge and electrical conductivity. To be considered internally consistent, chemical analyses must have less than 5% error in charge balance and less than 10% error in conductivity balance. Three isotope laboratories gave consistent compositions of all samples. No chemical laboratory gave consistent analyses of all samples. Recommendations are made that provide the user of isotopic and chemical data with the ability to better evaluate the quality of analyses.

INTRODUCTION

The examination and interpretation of geochemical data can provide powerful tools for characterizing newly discovered geothermal systems and for monitoring the production and injection of developed geothermal reservoirs. Chemical analyses have long been used to estimate subsurface temperatures, and computer simulations of multiple geochemical equilibria provide the means for predicting scaling and corrosion, for estimating loss of reservoir permeability from mineral precipitation, and for detecting breakthrough of injected water. Isotopic analyses may provide qualitative indications of source areas and volumes for recharge to hydrothermal systems and are used to calculate additional estimates of reservoir temperatures. Isotopic analyses have also been used to determine the contribution of injected water to the total fluid produced from developed geothermal fields. Increasing sophistication of geochemical modeling programs now possible on larger computers makes it imperative to question the quality of isotopic and chemical data. More complex geochemical calculations are not meaningful if the accuracy and precision of the analytical data used in those calculations are questionable.

It is common in studies of aqueous geochemistry to assume that chemical analyses report concentrations that are within ±10% of the actual concentration of any constituent. It is worth noting the limitations that a 10% error places on the most common geochemical calculations, the chemical geothermometers. For a reservoir temperature of 275°C, a 10% error in silica or sodium concentration will change the calculated temperature by about 10°C; and, for a reservoir temperature of 85°C, a 10% error in silica or sodium will change the temperature by 3 to 4°C. In order to evaluate the validity of this often-assumed error limit and to determine the reliability of isotopic data, a test was conducted to compare analyses from several laboratories which analyze geothermal water samples on a routine basis.

Many inter-laboratory comparisons have been conducted in the past, and two recent comparisons dealt with hydrothermal waters. Ellis (1976) sent seven waters to 48 laboratories in 18 countries, and he concluded "the standard of water analysis for many common constituents still leaves much to be desired." Giggenbach and others (1986) sent three waters to 22 laboratories in 19 countries, and they concluded "that there is ample room for improvement." Due to the large number of laboratories used in both of these previous studies, extensive statistical analysis of reported concentrations was possible. In both reports, concentrations of several chemical constituents varied by more than 10% from the mean value.

Many geothermal researchers performing geochemical calculations depend on analyses of samples collected and analyzed by others. This report first discusses methods used to evaluate reported analyses, and then makes suggestions for collection and analysis of new samples. As more geothermal researchers develop and apply geochemical tools to interpret reservoir conditions, it is expected that many will want more control over the collection and analyses of samples.

EVALUATION CRITERIA

Isotopic compositions for hydrogen and oxygen are reported as the difference (δ) between the ratio of isotopes in a sample and the ratio in the standard (equation 1):

$$[1] \quad \delta = \frac{R(\text{sample}) - R(\text{standard})}{R(\text{standard})} \, 10^3$$

$$\text{where } R = \frac{^{18}O}{^{16}O} \text{ or } R = \frac{D}{H}$$

All ratios (R) are of the heavier isotope to the lighter isotope. This small difference in ratios is reported in per mil (‰) relative to V-SMOW (Vienna standard mean ocean water, Gonfiantini, 1978). Isotopic compositions of geothermal fluids vary widely, and individual analyses contain little intrinsic information that can be used to check their validity. To evaluate the isotopic analysis of an aqueous fluid sample (water or steam), both hydrogen and oxygen isotopic ratios must be determined. Isotopic compositions for water samples can easily be plotted against the global meteoric water line (Craig, 1961) to rapidly identify unusual analyses. The meteoric water line, derived from values for precipitation (rain and snow), rivers, and lakes world wide, is represented by the following expression (2):

$$[2] \quad \delta D = 8\,(\delta^{18}O) + 10$$

where δD and $\delta^{18}O$ are the differences calculated from equation 1. Geothermal water samples usually plot at some distance to the right of the meteoric water line, depending on the amount of oxygen-isotope exchange that has occurred at high temperature between the water and rocks (which typically have more ^{18}O). There is limited possibility for hydrogen-isotope exchange in hydrothermal systems, and the hydrogen isotopic composition of a fluid sample is usually very close to that of the meteoric water which recharges the system. Fluid samples plotting to the left of the meteoric water line are rare and may be suspect.

The evaluation of a chemical analysis depends on the degree to which the analysis reflects the complete composition of the water sample. Many reports include only partial analyses used for a specific purpose, and the quality of partial analyses can rarely be evaluated. Chemical analyses can best be evaluated if they include the field measurement of pH, a complete suite of the major ions (Li, Na, K, Ca, Mg, F, Cl, SO_4, and HCO_3), and the laboratory measurements of pH and conductivity. The chemical species of considerable geothermal interest (SiO_2, B, and Fe) should be added to the basic analyses. From the concentrations of the major ions, it is possible to calculate charge balance and conductivity balance of the sample.

Some general relations are common in geothermal water samples. The concentrations of the cations usually follow a trend with Na > K > Li and Ca > Mg. Among samples from a single system, SiO_2 increases with increasing temperature. The occurrence of other major ions in the analysis, such as phosphate or nitrate, is normally an indication of contamination from surface water.

A few simple calculations were used to determine the reliability of the chemical analyses performed for this inter-laboratory comparison. The ionic species were expressed as equivalent concentrations from the following calculation (equation 3):

$$[3] \quad \text{Equiv. Conc.} = \frac{(\text{concentration})\,(\text{ionic charge})}{\text{molecular weight}}$$

where molecular weight is in grams/mole, concentration is in milligrams per liter (mg/L), and equivalent concentration is in milliequivalents per liter (meq/L). Using equivalent concentrations of the ions, the error in charge balance was calculated from the absolute difference between the sums of cations and of anions divided by the average of the total cations and anions (equation 4):

$$[4] \quad \text{Error } (\%) = \frac{200\,|\Sigma\text{Cations} - \Sigma\text{Anions}|}{(\Sigma\text{Cations} + \Sigma\text{Anions})}$$

The water can have no net electrical charge, so an error greater than 5% in the ionic charge balance is indicative of a problem and the analysis should be repeated. This limit is based on the experience of the authors, and there must be a compromise between a restrictive limit that few samples would pass and a permissive limit that would ignore a significant error in a major ion.

If the electrical conductivity of a water is measured, a comparison can be made between the ionic charge and the electrical conductivity (referred to here as the conductivity balance). The calculation of error is based on an empirical relation for the conductivity of sodium chloride solutions at 25°C. Different ions in solution act to increase or decrease the conductivity from that of sodium chloride, but the relation holds well for many natural waters (Hem, 1970, p. 235). The error in conductivity balance was calculated using the following expression (5):

$$[5] \quad \text{Error } (\%) = \frac{100\,|\text{conductivity} - (100\,\Sigma\text{Cations})|}{\text{conductivity}}$$

where the conductivity is in standard units of microsiemens per centimeter (µS/cm), and the sum of equivalent concentrations of cations (or anions) is first multiplied by 100. The error in electrical conductivity balance should be less than 10% for either anions or cations.

Errors in charge balance of more than 5% or in conductivity balance of more than 10% usually result from three main sources: 1) an important ion was not analyzed, 2) a mistake was made in an analysis of a major ion, and 3) a decimal point was misplaced. If the conductivity balance error is low for cations and high for anions, the anion analyses are the likely source of error. Calculations of error in charge balance and in conductivity balance only consider the ionic species. Some waters with high concentrations of unusual ions may repeatedly fail these tests. Friedman and Erdmann (1982) describe the quality assurance program of the USGS National Water Quality Laboratory and give further discussion of ways to identify analytical errors.

If the same water samples were analyzed by several laboratories, the concentrations of each constituent may be compared among laboratories by calculation of the means and deviations from the means. If the concentrations from one laboratory are significantly different (greater than 15%) than those from other laboratories, the anomalous concentrations are suspect. Geochemical calculations made in the examination of a geothermal water are only valid if the constituent concentrations used in the calculations are from one analysis at a time. Many geothermal researchers have averaged concentrations of a constituent (such as silica) from several different samples and suggested that calculations using these averages are more significant in evaluating reservoir conditions. By using averages, these researchers have actually ignored the possible errors in individual analyses and have presented a concentration that is not directly related to the reservoir or to the conditions during sample collection or analysis.

ISOTOPIC ANALYSES

Sample Collection

Based on the discussion above, several procedures are available to judge the reliability of geochemical data received from a laboratory. Evaluation of reported analyses is limited to calculations and comparisons that examine internal consistency. Much greater control of analytical quality is available if new samples are submitted for analysis. In submitting new samples, there is the possibility for interaction between the collector and the analyst that may result in more meaningful analyses. Water samples for isotopic analysis should be collected and shipped in 60-ml glass bottles with air-tight (polyseal) caps, and every effort should be made to prevent evaporation. This volume of sample will allow repeat analyses if necessary. If an error is suspected in sample preparation or in mass spectrometric analysis, the analyst should attempt to measure a duplicate preparation.

Suggestions for Isotopic Analyses

It is not cost effective for most researchers to request isotopic analyses from more than one laboratory, so the laboratory to be used should be chosen carefully. Most stable-isotope laboratories will have a quality control manual, and a copy of the manual should be requested when a laboratory is being considered for analytical work. Requests for isotopic analyses should include differently labeled duplicates of about 10% of the samples to provide an internal check of analytical consistency. It is useful to resubmit a water sample that has been analyzed for isotopic ratios at some previous time and to compare the results. The USGS Water Resources Division isotope laboratory (Reston, VA) routinely divides incoming waters into two samples, and each is analyzed on a different day to identify any instrumental or procedural errors. This procedure of dividing samples is not common to all laboratories, and duplicate samples submitted at different times will provide a check on time dependent errors. It is reasonable to request the isotope values obtained for the standards used to calibrate the analyses of a set of your samples as well as the established values for those standards. This request becomes more important if a laboratory is used repeatedly with the same standards.

Analytical Methods

All isotopic ratios were determined by mass spectrometry, but equipment and analytical methods differed among laboratories. The standard methods used to exchange oxygen isotopes of water with carbon dioxide, to separate and measure the carbon dioxide isotopic composition, and to calculate the composition of the water are described by Epstein and Mayeda (1953). Two different methods were used to prepare hydrogen from water samples for isotopic analysis. The older method involves conversion of water to hydrogen gas through reaction with uranium metal at temperatures from 400 to 700°C (Bigeleisen and others, 1952). More recently, many laboratories have used zinc shot to convert water to hydrogen gas, and Tanweer and others (1988) suggested zinc reaction at temperatures over 460°C and a ten-fold excess of zinc over the stoichiometric amount required. Only the USGS Geologic Division isotope laboratory (Menlo Park, CA) used the older uranium method. The USGS Water Resources Division isotope laboratory (Reston, VA) now uses the Japanese Hokko (trademark) beads (3% platinum) to equilibrate isotopes between water and hydrogen, but this method was not used for analyses in this report.

Test Results

Splits of seven water samples were sent to three isotope laboratories within the USGS and to a laboratory which preforms commercial analyses. Interlaboratory comparison of isotope compositions of hydrogen and oxygen in each sample was limited to calculation of the deviation from the mean of the measurements. The limited number of analyses did not warrant further statistical calculations. Isotope compositions determined by the various laboratories are generally very similar. Significant differences exist in the age of the mass spectrometers and in the methods of sample preparation. Based on the limits of reproducibility, analyses were considered anomalous if the measurements deviated from the mean value by more than 2‰ for hydrogen or by more than 0.15‰ for oxygen. The USGS Geologic Division laboratory (Menlo Park, CA) has the oldest mass spectrometer of the laboratories in this comparison, and analyses slightly exceeded our acceptable error limits on two hydrogen isotope measurements and three oxygen isotope measurements. The remaining analyses were within acceptable limits.

CHEMICAL ANALYSES

Sample Collection

At the time of collection, the temperature and pH should be measured, and the total alkalinity of the water determined by titration with 0.05N sulfuric acid to the inflection point of the titration curve (Barnes, 1964). Most chemical species should be preserved during collection to stabilize concentrations for later analysis in the laboratory. Water samples should be prepared for laboratory analysis as follows: 1) for anion analysis, a portion of the water should be filtered through 0.45-µm pore size membrane filter to remove particles and biological material, and 2) a portion of the water should be filtered and acidified to pH 2 with concentrated, high-purity hydrochloric acid to stabilize the cations, particularly magnesium, calcium, and iron, by preventing precipitation of carbonates, sulfates, or hydroxides. Samples should be shipped in 500-ml polypropylene bottles with tightly fitting caps. Blanks of distilled, deionized water, should be treated in the field with the same procedures and preservatives as the samples to test for contamination in sampling and processing.

Suggestions for Chemical Analyses

As suggested for isotopic analyses, sets of samples submitted for chemical analyses should include differently identified (blind) duplicates of some samples to provide an internal check of analytical consistency. It is also useful to resubmit water samples that have been analyzed at some previous time and to compare the results. Duplicates of some water samples can be spiked with known additions of specific ions to test the analytical ability of a laboratory to determine the increase in concentration.

Analytical Methods

The chemical laboratories chosen for this comparison used different methods for preparation and analysis of the samples. Each laboratory used similar methods for chloride (Mohr - argentometric titration), fluoride (ion-selective electrode), alkalinity (acid titration), and conductivity (electrical cell) analysis. The atomic absorption method was used to determine cation concentrations (Na, K, Li, Ca, Mg, Fe) by three laboratories; but one used inductively--coupled argon plasma (ICP) spectrophotometry. Silica concentration was determined by the molybdate-blue method in two laboratories or by ICP in two laboratories. Three laboratories determined boron by ICP (one also checked the boron with vis-UV), but one lab used the dianthrimide method. Sulfate was determined gravimetrically by two laboratories, one used a turbidimetric titration, and one used ion chromatography. Each analytical method has a concentration range for optimum measurement. As the lower limit of detection is approached, the percent error could become very large. To properly evaluate the analyses, laboratories must report their limits of detection for each chemical species.

Test Results

One USGS Laboratory and three commercial laboratories were selected for this analytical comparison because they performed many analyses on geothermal water samples. This inter-laboratory comparison produced some interesting and surprising results. Correspondence among the chemical analyses of the five water samples was worse than expected. None of the four laboratories provided completely acceptable analyses of all samples, and one laboratory reported significantly anomalous concentrations of major solutes in all five samples. We conclude that it would be poor judgment to rely on chemical analyses from only one laboratory without a thorough understanding of the quality assurance procedures of that laboratory. From calculations of charge balance and conductivity balance, many of the worst analyses were easily identified, and repeat analyses could be requested. These calculations should have been performed routinely by the analytical laboratories to avoid reporting obvious errors. The concentrations of lithium, magnesium, iron, fluoride, and sulfate in some samples were below the limits of detection for the analytical methods used. One laboratory did not report an acceptable value for chloride in any of the five samples (three were low and two were high), and, as a result, calculated errors in charge balance and conductivity balance were also unacceptably high. This difficulty with all of the chloride concentrations reported, strongly suggests instrumental or procedural errors. It must be remembered that we are comparing the values reported by individual labs against the average of selected values. With the exception of silica, where ICP gives higher concentrations than molybdate blue, the use of different analytical methods does not seem to be responsible for the inter-laboratory differences.

ACKNOWLEDGEMENTS

The authors greatly appreciate the cooperation and information provided by the analysts about their analytical methods and their routine error checking. Suggested changes by several reviewers have enhanced this report. The review of Cathy Janik (USGS) is especially appreciated. Funding for this project was provided by the Geothermal Division of the U.S. Department of Energy and by the Geothermal Research Program of the U.S. Geological Survey.

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