Review

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Ensuring Accuracy: Critical Validation Techniques in Geochemical Analysis for Sustainable Geothermal Energy Development

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Abstract

Geochemical analysis is a critical tool in geothermal exploration, providing valuable insights into reservoir characteristics. However, obtaining accurate and reliable geochemical data requires rigorous validation techniques. This review examines key factors affecting the accuracy of geochemical data and discusses best practices for ensuring quality. Proper sampling methods, including selection of representative locations, use of appropriate equipment, and adherence to robust protocols for sample collection, filtration, preservation, and storage, are essential for maintaining integrity. Analytical techniques must be carefully selected, with regular calibration and standardization of instruments using certified reference materials. Implementing comprehensive quality assurance and quality control procedures, such as analyzing blanks, duplicates, and spike samples, helps monitor precision and accuracy. Data interpretation should consider the complexities of the geological and hydrological settings, integrating multiple lines of evidence. By following established guidelines and continuously updating methods based on emerging technologies and inter-laboratory comparisons, geothermal teams can optimize the reliability of their geochemical data. Accurate and precise geochemical information, when combined with geological, geophysical, and hydrological data, enables informed decision-making and enhances the success of geothermal projects. As geothermal energy gains importance in the transition to sustainable resources, ensuring the accuracy of geochemical analysis will be crucial for effective exploration and development.

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1. Introduction

Geochemical analysis plays a crucial role in geothermal prospecting by providing valuable insights into the characteristics and potential of geothermal resources and in assessing the environmental implications of geothermal development [1]. Geochemical analysis of geothermal fluids, such as hot springs, fumaroles, and well samples, helps determine the chemical composition of the fluids [2], including the concentrations of various elements and compounds, such as sodium, potassium, calcium, magnesium, chloride, sulfate, and bicarbonate [3] including potentially harmful elements and compounds, geochemical analysis helps identify potential environmental risks associated with geothermal operations. Geochemical techniques, such as geothermometry, use the chemical composition of geothermal fluids to estimate the temperature of the geothermal reservoir at depth. This is based on the principle that the solubility of certain minerals and the equilibrium between different chemical species in the fluid are temperature-dependent. By applying geothermometers, such as the Na-K-Ca geothermometer, the reservoir temperature can be estimated, which is crucial for assessing the geothermal potential of an area [4]. Moreover, geochemical monitoring of geothermal systems over time can detect changes in fluid chemistry that may indicate environmental impacts, such as contamination of groundwater or surface water resources [5]. By providing a comprehensive understanding of the geochemical characteristics of geothermal systems, geochemical analysis contributes to the responsible development of geothermal energy while minimizing negative environmental consequences. This information is essential for developing appropriate mitigation strategies and ensuring the sustainable utilization of geothermal resources [6].

The source of the geothermal fluids, whether they are of meteoric (rainwater), magmatic, or mixed origin, can also be determined by geochemical analysis. This information is obtained by analyzing stable isotopes, such as oxygen and hydrogen isotopes, in the fluids. The isotopic composition can provide insights into the recharge area, fluid circulation paths, and the extent of mixing between different fluid sources [7]. Additionally, geochemical analysis of geothermal fluids and the associated alteration minerals in the host rocks can provide information about the interaction between the fluids and the rocks. This includes the dissolution and precipitation of minerals, which can affect the permeability and porosity of the reservoir rocks [8].

The potential for scaling and corrosion in geothermal wells and surface facilities can be assessed by geochemical analysis. By analyzing the concentrations of dissolved solids, noncondensable gases, and pH of the fluids, the likelihood of mineral precipitation (scaling) and corrosion can be evaluated. This information is crucial for designing and maintaining geothermal infrastructure and ensuring the long-term sustainability of geothermal operations [9–11]. Geothermal potential, when combined with geochemical, geological, and geophysical analysis, can provide a comprehensive understanding of the geothermal system [12]. This includes the heat source, fluid circulation pathways, reservoir properties, and the overall geothermal potential of an area. Geochemical analysis can help identify the most promising locations for geothermal development and guide further exploration and drilling activities [13].

Accuracy and precision are two crucial concepts in geochemical analysis. Accuracy refers to the closeness of a measured value to the true value, while precision refers to the agreement among repeated measurements. Both are essential for reliable data interpretation and decision-making in fields such as geothermal exploration, environmental monitoring, and mineral resource assessment. Accurate and precise data allows for meaningful comparisons between datasets and laboratories, and is particularly important when integrating data from various sources or monitoring changes over time. Although related, accuracy and precision are distinct concepts. A measurement can be precise but inaccurate, or accurate but imprecise. Ideal geochemical analysis should strive for both high accuracy and precision to ensure data reproducibility, which is critical for validating scientific findings, maintaining consistency and ultimately affecting the success and economic viability of geothermal projects [14–19].

In geothermal exploration, accurate and precise geochemical data is vital for estimating reservoir temperatures, identifying fluid sources, and characterizing the geothermal system. However, accuracy is more critical than precision in this context. Accurate geochemical data ensures that the measured values are close to the true values, enabling reliable interpretations and decision-making. Inaccuracies in geochemical data can lead to incorrect temperature estimates, misinterpretation of fluid origins, and ultimately, poor decisions regarding the viability and development of geothermal resources. While precision is still important for ensuring consistent and reproducible results, it is secondary to accuracy. High precision with low accuracy can lead to consistently incorrect results, which can be more misleading than imprecise but accurate data. Therefore, geothermal exploration teams should prioritize obtaining accurate geochemical data to support informed decision-making and minimize the risk of costly errors in resource assessment and development planning [20, 21].

Therefore, ensuring high-quality geochemical data through robust Quality Assurance and Quality Control (QA/QC) procedures is crucial for informed decision-making and the successful development of geothermal resources [22–24]. Implementing rigorous

Table 1. Geochemical analysis methods.

No.	Geochemical Analysis Methods	Advantages & Limitations	References
1	*Fluid Sampling and Analysis*		
	• Sampling of geothermal fluids (hot springs, fumaroles, well discharges); • Analysis of major and trace elements using techniques such as: Ion chromatography, gas chromatography, atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS); • Provides information on fluid source, reservoir temperature, and fluid-rock interactions.	Advantages: • Direct sampling of geothermal fluids provides accurate information on fluid chemistry; • Helps identify fluid sources, reservoir temperature, and fluid-rock interactions. • Limitations: • Sampling can be challenging in high-temperature, high-pressure environments; • Sample contamination or alteration may occur during collection and storage.	[25–27]
2	*Geothermometry*		
	• Estimation of geothermal reservoir temperature based on fluid chemistry; • Common geothermometers: Silica (quartz and chalcedony), Cation (Na-K and Na-K-Ca), gas geothermometer and Isotope (oxygen and hydrogen); • Cross-checking temperature estimates using multiple geothermometers.	Advantages: • Provides estimates of reservoir temperature without direct measurements; • Multiple geothermometers can be used for cross-checking results • Limitations: • Assumptions about fluid-rock equilibrium and chemical stability may not always hold true; • Mixing of different fluid sources can lead to erroneous temperature estimates.	[28–30]
3	*Isotope Analysis*		
	• Analysis of stable isotopes (oxygen, hydrogen, carbon) using isotope ratio mass spectrometry (IRMS); • Provides information on water origin, fluid-rock interaction, and fluid mixing; • Radioactive isotopes used for determining fluid age and residence time.	Advantages: • Helps identify the origin and evolution of geothermal fluids; • Provides information on fluid-rock interaction and mixing processes. • Limitations: • Interpretation of isotopic data can be complex and requires a good understanding of the local geology and hydrology; • Some isotopic systems may be affected by secondary processes, such as boiling or degassing.	[2, 31, 32]
4	*Fluid Inclusion Analysis*		
	• Study of fluid inclusions trapped in minerals precipitated from geothermal fluids; • Microthermometry analysis: heating and cooling inclusions to measure temperature and salinity; • Laser ablation ICP-MS for analyzing chemical composition of individual fluid inclusions.	Advantages: • Provides direct information on the temperature, pressure, and composition of paleo-fluids; • Can help reconstruct the history of the geothermal system. • Limitations: • Suitable fluid inclusions may not always be present in the available rock samples; • Interpretation of fluid inclusion data requires careful consideration of post-entrapment modifications.	[33, 34]
5	*Geochemical Modeling*		
	• Simulation of chemical reactions and phase equilibria in geothermal systems using software like PHREEQC, TOUGHREACT, and CHILLER; • Predicts effects of fluid-rock interactions, mineral precipitation/dissolution, and fluid mixing on fluid composition and temperature.	Advantages: • Allows for the simulation of complex geochemical processes in geothermal systems; • Can predict the effects of fluid-rock interactions, mineral precipitation/dissolution, and fluid mixing. • Limitations: • Requires accurate input data and a good understanding of the system's geology and hydrology; • Model results are dependent on the assumptions and simplifications made in the model setup.	[35, 36]

QA/QC procedures is essential for ensuring the accuracy and precision of geochemical data. This includes the use of certified reference materials, replicate analyses, blank samples, and inter-laboratory comparisons [37, 38]. QA/QC practices help identify and correct analytical errors, assess the reliability of the data, and maintain high standards of data quality. To achieve accurate and precise geochemical data, it is essential to use appropriate sampling techniques, follow standard analytical protocols, employ well-calibrated instruments, and adhere to best practices in data processing and reporting. Regular training of personnel, participation in

Table 2. Factors affecting the accuracy of geochemical data.

No	Factors Affecting the Accuracy of Geochemical Data	References
1	*Sample Contamination*	
	• Contamination during sample collection, storage, or transportation can alter the chemical composition of geothermal fluids; • Proper sampling protocols, clean sampling equipment, and appropriate sample preservation techniques are essential to minimize contamination.	[39, 40]
2	*Sampling Representativeness*	
	• Geothermal fluids may have spatial and temporal variations in composition; • Ensuring that the collected samples are representative of the geothermal system is crucial for accurate data interpretation; • Multiple samples from different locations and times may be necessary to capture the system's variability.	[41, 42]
3	*Analytical Techniques and Calibration*	
	• The choice of analytical techniques and their proper calibration can affect the accuracy of geochemical data; • Using appropriate analytical methods with suitable detection limits and precision is important for reliable results; • Regular calibration of analytical instruments and the use of certified reference materials can help ensure data accuracy.	[43, 44]
4	*Sample Preservation and Storage*	
	• Improper sample preservation or storage can lead to chemical changes in geothermal fluids; • Using appropriate containers, filtration, and acidification techniques can help preserve the sample integrity; • Minimizing the time between sample collection and analysis can reduce the risk of sample alteration.	[40, 45, 46]
5	*Data Quality Control and Assurance*	
	• Implementing robust quality control and assurance procedures is essential for ensuring data accuracy; • This includes the use of field and laboratory blanks, duplicates, and spike samples to monitor potential contamination and analytical precision; • Interlaboratory comparisons and proficiency testing can help validate the accuracy of analytical results.	[47, 48]
6	*Interpretation and Modeling Assumptions*	
	• The accuracy of geochemical data interpretation depends on the validity of the assumptions made during data analysis and modeling; • Assumptions about fluid-rock equilibrium, chemical speciation, and thermodynamic properties can affect the accuracy of geothermometry and geochemical modeling results; • Sensitivity analyses and the use of multiple modeling approaches can help assess the robustness of the interpretations.	[49–51]
7	*Geological and Hydrological Complexity*	
	• The complexity of the geological and hydrological settings can affect the accuracy of geochemical data interpretation; • Factors such as fluid mixing, boiling, degassing, and mineral precipitation/dissolution can alter the chemical composition of geothermal fluids; • A good understanding of the local geology and hydrology is essential for accurate data interpretation.	[52–54]

proficiency testing programs, and continuous improvement of analytical methods further contribute to the production of high-quality geochemical data [55–57].

The main objective of this review is to provide a comprehensive overview of the critical role that geochemical analysis plays in geothermal exploration, with a particular emphasis on the importance of accuracy and precision in geochemical data for informed decision-making. By discussing the various applications of geochemical analysis, highlighting the significance of quality assurance and quality control (QA/QC) procedures, and underscoring the importance of best practices in sampling, analysis, and data management, the article aims to synthesize information that emphasizes the crucial role of accurate and reliable geochemical data in understanding geothermal systems and guiding exploration and development decisions.

2. Overview of Common Geochemical Analysis Methods

Geochemical analysis plays a vital role in geothermal exploration, providing essential insights into the characteristics and potential of geothermal resources. By studying the chemical composition and properties of geothermal systems, experts can better understand the underlying processes and optimize resource utilization. Geochemical analysis is crucial not only for evaluating the viability of geothermal projects but also for ensuring their sustainable development and minimizing environmental impacts. Table 1 outlines the different geochemical analysis techniques frequently used in this field, along with their advantages and limitations.

These methods, combined with geological, geophysical, and hydrological data, provide a comprehensive

Table 3. Sampling methods for geothermal resources.

No.	Proper Sampling Methods for Geothermal Resources	References
1	*Sampling Location Selection*	
	• Choose sampling locations that are representative of the geothermal system; • Consider factors such as well depth, temperature, pressure, and flow rate; • Sample from various points within the geothermal system, including wells, springs, and fumaroles.	[21, 58, 59]
2	*Sampling Equipment and Materials*	
	• Use clean, inert, and temperature-resistant sampling equipment and containers; • Avoid using materials that can react with or contaminate the geothermal fluids (e.g., metals, plastics); • Ensure that the sampling equipment is properly calibrated and maintained.	[60, 61]
3	*Sample Collection Procedure*	
	• Flush the sampling point to remove stagnant or contaminated fluids; • Collect samples directly from the geothermal source to minimize air contact and cooling; • Use a sampling method that preserves the fluid's chemical and physical properties (e.g., gas-tight samplers for dissolved gases).	[62–64]
4	*Sample Filtration and Preservation*	
	• Filter samples on-site to remove suspended solids that can alter the fluid chemistry; • Use appropriate filter pore sizes (typically 0.45 μm or 0.2 μm) depending on the analytical requirements; • Preserve samples as needed using techniques such as acidification, refrigeration, or freezing.	[65–67]
5	*Sample Volume and Replication*	
	• Collect sufficient sample volume to accommodate all required analyses and potential replicates; • Consider collecting duplicate or triplicate samples for quality control purposes; • Ensure that the sample volume is compatible with the analytical methods and detection limits.	[68–70]
6	*Sample Documentation and Labeling*	
	• Record detailed information about each sample, including location, date, time, temperature, pH, and any other relevant field parameters; • Label samples clearly and uniquely, using a numbering system and waterproof labels; • Maintain a detailed sampling log and chain of custody records.	[71–73]
7	*Sample Storage and Transportation*	
	• Store samples in appropriate conditions (e.g., cool, dark, and secure) to prevent degradation or contamination; • Transport samples to the analytical laboratory as quickly as possible, following any specific storage and handling requirements; • Ensure that the samples are properly packaged and labeled for transportation.	[74–76]
8	*Quality Assurance and Quality Control (QA/QC)*	
	• Implement a robust QA/QC program that includes field blanks, duplicates, and standard reference materials; • Follow standard operating procedures (SOPs) for sampling, preservation, and analysis; • Regularly review and update sampling protocols based on QA/QC results and new best practices.	[55, 77–79]

understanding of geothermal systems and guide exploration and development. Advancements in analytical techniques and data interpretation continue to improve the accuracy and precision of geochemical data, leading to better-informed decision-making in geothermal exploration and management. Despite the limitations, these geochemical analysis techniques, when used in combination and integrated with other geological, geophysical, and hydrological data, provide valuable insights into the characteristics and dynamics of geothermal systems. Ongoing research and technological advancements aim to address the limitations and improve the accuracy and reliability of these techniques in geothermal exploration and development.

3. Factors Affecting the Accuracy of Geochemical Data

In geothermal exploration, the accuracy and dependability of geochemical data are essential for making well-informed decisions and evaluating geothermal resources effectively. The precision of geochemical data is influenced by numerous factors throughout the entire process, starting from sample collection and extending to the interpretation of the data. To ensure that geochemical analyses produce reliable and useful results, it is crucial to understand these influencing factors. The following points highlight some of the key aspects that affect the accuracy of geochemical data in the context of geothermal exploration (Table 2).

To minimize the impact of these factors on geochemical data accuracy, it is important to follow best practices in sample collection, preservation, analysis, and interpretation. This includes using appropriate sampling protocols, analytical techniques, and quality control measures. Additionally, integrating geochemical data with other geological, geophysical, and hydrological information can help constrain the interpretation and

Table 4. Calibration and standardization of instruments.

No.	Calibration and Standardization of Instruments	References
1	*Calibration Standards*	
	• Prepare or obtain calibration standards with known concentrations of the analytes of interest; • Use certified reference materials (CRMs) or commercially available standard solutions traceable to national or international standards; • Ensure that the calibration standards cover the expected concentration range of the samples and bracket the sample concentrations.	[80–82]
2	*Calibration Curve*	
	• Analyze a series of calibration standards with increasing concentrations of the analytes; • Establish a calibration curve by plotting the instrument's response (e.g., absorbance, peak area, or intensity) against the known concentrations of the standards; • Use an appropriate calibration model that best fits the data and minimizes the residuals.	[83–85]
3	*Blank Correction*	
	• Include appropriate blank samples in the calibration process; • Subtract the blank signal from the sample and standard signals to correct for any background or contamination; • Monitor the blank levels regularly to ensure that they remain below the method detection limits.	[86–88]
4	*Calibration Frequency*	
	• Perform initial calibration before analyzing samples and whenever there are significant changes in the instrument's performance or operating conditions; • Conduct periodic calibration checks using independent calibration verification (ICV) standards to monitor the instrument's stability and accuracy; • Recalibrate the device whenever the results from ICV surpass acceptable limits or indications of instrument drift are observed.	[89–93]
5	*Quality Control Samples*	
	• Analyze quality control (QC) samples, such as method blanks, laboratory control samples (LCS), matrix spikes, and duplicates, along with the calibration standards and samples; • Use QC samples to assess the method's performance, precision, accuracy, and to identify any potential matrix effects or interferences; • Establish acceptance criteria for QC sample results based on the project's data quality objectives and regulatory or method-specific requirements.	[44, 94, 95]
6	*Standardization*	
	• Use standardization techniques to correct for instrumental drift or to normalize the data obtained from different instruments or laboratories; • Employ internal standards, which are compounds added to all samples and standards at a known concentration, to correct for variations in sample introduction or instrument response; • Use external standards, such as CRMs or proficiency testing samples, to assess the accuracy and comparability of the data across different methods or laboratories.	[43, 96–98]
7	*Traceability and Documentation*	
	• Maintain a complete and accurate record of all calibration and standardization activities, including the preparation of standards, calibration curves, and QC sample results; • Ensure that all standards and reagents are traceable to their original sources and have valid expiration dates; • Document any deviations from the standard procedures, along with the corrective actions taken and their justifications.	[55, 99, 100]
8	*Continuous Improvement*	
	• Regularly review and update the calibration and standardization procedures based on the instrument's performance, method requirements, and advances in analytical techniques; • Participate in inter-laboratory comparisons and proficiency testing programs to assess the accuracy and comparability of the data and to identify areas for improvement; • Provide ongoing training and support to the laboratory personnel to ensure consistent and reliable implementation of the calibration and standardization procedures.	[101–103]

improve the overall accuracy of the geothermal system characterization.

4. Proper Sampling Methods for Geothermal Resources

Geochemical data obtained from geothermal resources heavily depends on the methods used for sampling, preserving, and storing the fluids. These processes are crucial to ensure that the original chemical composition of the geothermal fluids remains intact and unaltered, which is essential for accurate data interpretation. Proper sampling, preservation, and storage techniques help minimize the risks of chemical reactions, microbial activity, and physical changes that could affect the quality of the samples. Table 3 provides further information on these important steps, which are necessary to guarantee the precision and trustworthiness of geochemical data derived from geothermal sources.

By following these proper sampling methods, geothermal exploration teams can ensure that the collected samples are representative, uncontaminated, and suitable for accurate geochemical analysis. It is important to tailor the sampling approach to the specific characteristics of the geothermal system and the analytical requirements of the study. Collaboration with experienced geochemists and hydrogeologists can help optimize the sampling strategy and minimize potential sources of error.

By implementing proper sample preservation and storage techniques, geothermal exploration teams can maintain the integrity of the collected samples and ensure the accuracy of the geochemical data. It is important to follow established standard operating procedures (SOPs) and to consult with experienced geochemists and analytical laboratories to determine the most appropriate preservation and storage methods for each specific project and analytical requirement.

5. Calibration and Standardization of Instruments

Calibration and standardization are fundamental to achieving high-quality geochemical data in the exploration and management of geothermal resources. These critical processes ensure that the instruments used in geochemical analysis deliver accurate, precise, and consistent results across various measurements and conditions. By systematically aligning the instruments' responses to known values, these procedures not only correct for any potential drift or bias but also enhance the reliability of the data. Such rigor in calibration and standardization is vital for geothermal professionals to confidently utilize the data in resource assessment, reservoir characterization, and strategic decision-making. The detailed aspects and importance of these processes are further explored in Table 4, highlighting their role in the field of geothermal geochemical analysis.

By implementing rigorous calibration and standardization practices, geochemical laboratories can ensure the accuracy, precision, and comparability of the data generated from geothermal fluid analyses. These practices are critical for the proper interpretation and use of geochemical data in geothermal exploration and reservoir management.

6. Conclusion

This review highlights the critical importance of employing proper validation techniques in geochemical analysis for geothermal exploration. Proper sampling methods are essential to obtain representative and uncontaminated geothermal fluid samples. Calibration and standardization of analytical instruments ensure the accuracy and comparability of measurements. Robust QA/QC programs are crucial for monitoring contamination, assessing precision, and validating accuracy. Data interpretation should consider the geological and hydrological complexity of geothermal systems, as well as the limitations of models and geothermometers. Integrating geochemical data with geological, geophysical, and hydrological information is necessary for a comprehensive understanding of geothermal systems.

Continuous improvement of analytical techniques and adherence to best practices in data management and reporting are essential for maintaining the reliability of geochemical data. By following these validation techniques, geothermal exploration teams can ensure the accuracy and precision of geochemical data, leading to better-informed decision-making and successful geothermal resource development. This review underscores the vital role of rigorous validation in geochemical analysis for geothermal prospects. Employing proper validation techniques is critical for ensuring the reliability of geochemical data and optimizing geothermal exploration efforts.

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