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AN ASSESSMENT OF THE RESULTS OF THE IAEA INTERLABORATORY COMPARISONS FOR GEOTHERMAL WATER CHEMISTRY

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ABSTRACT

Since 1985 the International Atomic Energy Agency, Vienna (IAEA) has conducted four interlaboratory calibrations for geothermal water chemistry. Two water samples in each calibration (i.e. eight samples in total) were analyzed in the geochemistry laboratories involved in geothermal developments all over the world. The parameters, pH, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- and SiO_2 were analyzed in all samples together with some analyses of electrical conductivity, B, As and F^-. A statistical evaluation suggests that the analytical error increases with decreasing concentration for all the chemical parameters except for SiO_2 and is of same order of magnitude for concentration less than 1 ppm. The overall error in the analytical data for geothermal waters is ±13%.

There are systematic errors in the data from some laboratories, which is one of the reasons for higher analytical errors in the results of interlaboratory calibrations. Thus to improve the analytical quality of the participating laboratories it is necessary to run some common commercial standards in all the laboratories together with the geothermal water samples, as has been established in case of stable isotope mass spectrometry by the IAEA.

A brief discussion is also presented on the uncertainty in the geochemical interpretation of these data due to the analytical errors to understanding the deep reservoir processes in the hydrothermal systems.

INTRODUCTION

Quality of analytical data of separated water and vapor is of fundamental importance in geochemical modeling of hydrothermal systems. To insure the analytical quality of geochemistry laboratories involved in such activities, Ellis (1976) conducted the first interlaboratory chemical analysis of geothermal waters involving many countries. The scatter in the results during this study revealed serious deficiencies in analytical accuracy and the need for general improvement and standardization of analytical procedures (Giggenbach et al, 1992). Consequently, the International Atomic Energy Agency, Vienna (IAEA) initiated interlaboratory calibrations for geothermal waters within the framework of the project, "*Coordinated Research Program on the Application of Isotope and Geochemical Techniques in Geothermal Exploration*" in 1985. Giggenbach (1992) reported the results of first chemical analysis of geothermal water under this program. The program was re-undertaken by Gerardo-Abaya et al. (1998) and is presently a regular practice to compare the analysis of geothermal waters every year (Alvis-Isidro et al., 1999, 2000).

The objectives of this work are to analyze systematically the chemical data generated under the IAEA interlaboratory calibration program and discuss a plan of action to provide some guidance for future interlaboratory calibrations in order to improve the analytical quality of the participating laboratories.

RESULTS AND DISCUSSION

Table 1 presents the characteristics of samples distributed under the interlaboratory calibration programs. Giggenbach et al. (1992) presented the calibration of three samples, but the third sample was associated with natural organic gas discharge. Therefore the first two samples are only included here. The samples are renamed as SAMP1 and SAMP2 from Giggenbach et al. (1992), SAMP3 and SAMP4 from Gerardo-Abaya et al. (1998), SAMP5 and SAMP6 from Alvis-Isidro et al. (1999) and SAMP7 and SAMP8 from Alvis-Isidro et al. (2000).

Different laboratories used different types of analytical methods. For example, SiO_2 was analyzed with Colorimetry (CO), Atomic Absorption Spectrometry (AA), Inductively Coupled Plasma with Atomic Emission (ICP-AE) and Inductively Coupled Plasma with Mass Spectrometry (ICP-MS). In this study we will consider all the results equally probable.

Statistical data evaluation

There are two types of errors in every measurement: *determinate (systematic) and indeterminate (random) errors* (Bevington, 1969; Box et al., 1978). The determinate errors are due to instrumental defects, reagent impurities, personal errors, method errors, etc. The commercial standards for any chemical parameter were not distributed during the interlaboratory calibrations, so it was assumed that every laboratory had appropriate and standardize techniques to measure each parameter. Thus we will be emphasizing mainly on the random errors, which accompany every measurement and are due to non-permanent causes and include noise present in the measurement. It has been well established for stable isotope interlaboratory calibrations that common calibration or repeating same standards with samples produces quite consistent results (Parr and Clements, 1991).

The statistical approach used in this study is first removal of values that are out of trend. These values are generally associated with errors like misprint, some blander, etc. Then the arithmetic mean and standard deviation (S.D.) are computed of the remaining values. The values, which are outliers for the mean ±2 S.D., were rejected. After the removal of outliers, the mean and S.D. of remaining data are again computed.

In general, we don't know the actual errors in the determinations of any parameter. What we may know is some characteristic of the uncertainty or estimated error of each parameter, such as the standard deviation (S.D.) of the distribution describing the probability of determining various values for that parameter (Box et al., 1978; Bevington, 1969). Therefore, the true (expected) value is considered as the mean with an error of ±1 S.D.

Table 2 presents the results of this error analysis for all the samples. The quality of analysis for some elements like Na^+ and K^+ is acceptable; however there are some elements like SiO_2 and HCO_3^- need a revision on their sampling, storage, analytical procedure, etc.

Figure 1 shows a relation between concentration and percentage error for all the parameters except F^-. The experimental data for F^- are few and it is not used generally in the geochemistry of hydrothermal systems. It can be observed in Figure 1 that the error increases with decreasing concentration for all the parameters except for SiO_2 and the error is of the same order of magnitude for concentration lower than 1 ppm.

In order to understand the progress in the quality of analysis of geothermal water in successive interlaboratory calibrations a procedure of dot diagram is used as described by Box et al. (1978). Since the analysis of all parameters for concentration less than 1 ppm are not very reliable, we eliminated first all the data having average concentration less than 1 ppm. The mean and S.D. of percentage errors in all the remaining parameters for each sample are calculated together the normal error distributions. The grand average is the average percentage error in all the parameters for all the samples.

Table 1: Characteristics of samples distributed during the interlaboratory calibration program.

Code	Characteristics
SAMP1	Sample 001 from Giggenbach et al. (1992). A clear colorless boiling (97.5ºC) spring at Waikite. The sample was collected on 31-12-1985.
SAMP2	Sample 002 from Giggenbach et al. (1992). Separated water from the weirbox of well WK66 at Wairakei collected on 30-12-1985.
SAMP3	Sample RASINT 1 from Gerardo-Abaya et al. (1998). A cold neutral pH bicarbonate, low Cl^- spring from China. The sample collected by the East China Geological Institute.
SAMP4	Sample RASINT 2 from Gerardo-Abaya et al. (1998). A high temperature neutral pH, Cl^- geothermal well water from Palinpinon geothermal field, Philippines collected by PNOC-EDC.
SAMP5	Sample WILC-01 from Alvis-Isidro et al. (1999). High salinity water from a boiling spring (94ºC) at Suoh, Lampung in South Sumatera, Indonesia collected by CAIR-BATAN.
SAMP6	Sample WILC-02 from Alvis-Isidro et al. (1999). Water from a low salinity warm spring in San Kamphaeng, Thailand collected by the Department of Geological Sciences, Chiang Mai University and the Electricity Generating Authority of Thailand.
SAMP7	Sample IGWC-01 from Alvis-Isidro et al. (2000). Low salinity water from a cold spring (26ºC) situated in a geothermal area in Southern Luzon, Philippines collected by PNOC-EDC.
SAMP8	Sample IGWC-02 from Alvis-Isidro et al. (2000). High salinity geothermal water from a high-temperature production well at Leyte, Philippines collected by PNOC-EDC.

Table 2: A summary of error analysis for the analytical results of interlaboratory calibrations

	pH	Elec. Cond.	Li	Na	K	Mg	Ca	Cl	SO4	HCO3	B	SiO2	F
		µS/cm	ppm										
						SAMP1							
Mean	8.03		2.11	193.5	7.4	0.27	8.1	132.6	31.8	295.3	1.3	145.5	
S.D.	0.26		0.21	15.4	1.0	0.22	0.7	7.2	3.3	18.7	0.2	7.7	
No. of Data	22		19	20	19	16	17	18	18	21.0	12	14	
						SAMP2							
Mean	8.41		10.79	1154.8	171.7	0.05	18.4	1962.6	34.8	31.1	26.2	367.6	
S.D.	0.55		0.64	62.4	14.4	0.06	2.8	16.8	2.8	18.5	2.7	247.5	
No. of Data	22		18	19	18	14.0	19	17	18	19	13	19	
						SAMP3							
Mean	7.91	368.9	0.05	10.7	6.8	3.01	55.2	2.7	46.7	154.4		52.5	3.9
S.D.	0.17	31.1	0.02	0.6	0.6	0.19	4.1	1.2	2.1	8.7		4.4	0.2
No. of Data	13	9	6	15	13	14	12	10	12	13		12	11
						SAMP4							
Mean	6.87	27374.4	9.72	5271.1	1097.8	0.06	172.8	9676.2	14.8	72.6		495.5	1.2
S.D.	0.21	598.0	0.33	230.1	47.2	0.03	27.0	156.1	2.4	3.7		294.3	0.3
No. of Data	15	9	6	14	13	14	14	14	12	9		15	11
						SAMP5							
Mean	8.03	4576.8	4.72	849.8	142.4	0.11	13.3	1374.0	97.7	66.3		466.8	5.6
S.D.	0.10	452.2	0.51	97.1	8.7	0.09	2.7	133.5	23.2	26.2		182.3	5.1
No. of Data	25	17	20	25	22	22	20	25	26	25		23	10
						SAMP6							
Mean	8.85	728.1	0.34	166.3	16.3	0.04	2.0	5.7	32.4	318.5		178.1	17.6
S.D.	0.13	21.6	0.06	5.2	1.9	0.03	0.3	2.1	5.5	29.1		13.0	3.5
No. of Data	24	15	21	22	24	19	21	23	21	21		19	10
						SAMP7							
Mean	7.22	158.8	0.02	14.4	1.9	4.76	10.4	11.8	6.0	62.4	0.2	96.8	0.3
S.D.	0.23	5.2	0.01	1.2	0.3	0.46	1.6	4.0	3.0	5.2	0.1	12.0	0.1
No. of Data	34	22	20	30	26	29	29	33	31	30	25	31	18
						SAMP 8							
Mean	7.81	11952.7	6.26	2323.1	409.7	0.04	35.5	3932.0	33.4	44.0	49.4	773.1	1.7
S.D.	0.10	413.9	0.72	158.7	19.5	0.03	5.1	100.3	5.3	14.2	7.1	147.2	0.3
No. of Data	33	22	24	31	30	30	28	32	30	31	26	30	16

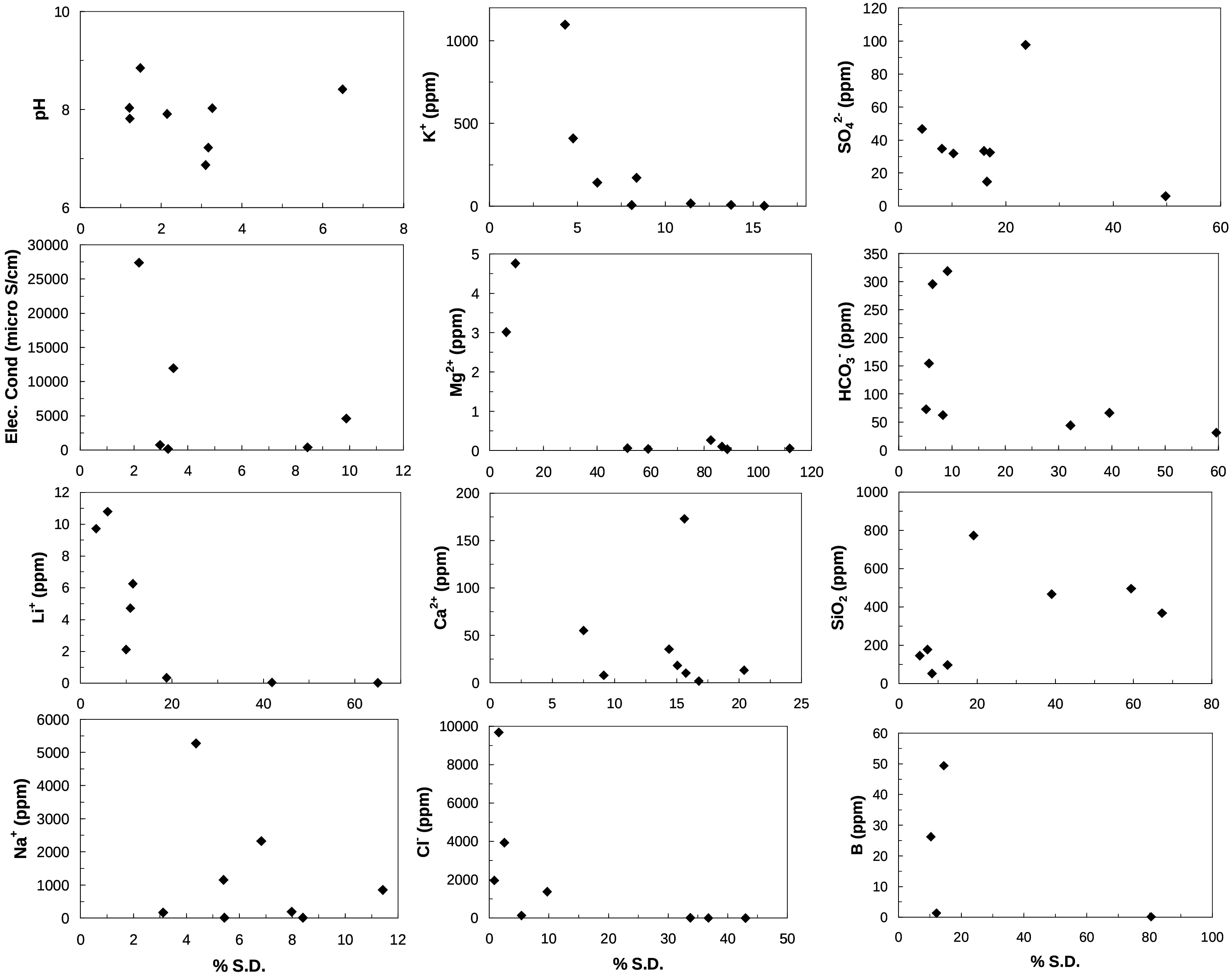

Figure. 1. A relation for the parameter concentration with its percentage error. The error in general is higher for low concentrations except for silica.

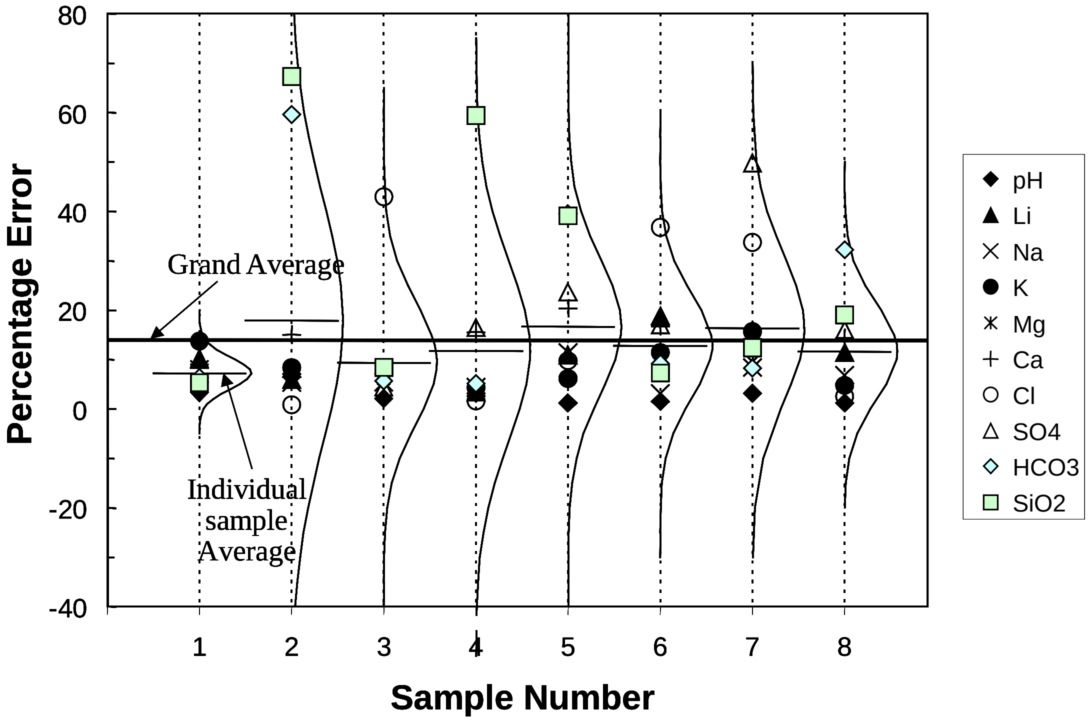

Figure 2: A dot plot for percentage error (Box et al., 1978). The grand average is the average percentage error in all the parameters for all the samples. Similarly, the average error for individual sample with its normal distribution is also shown.

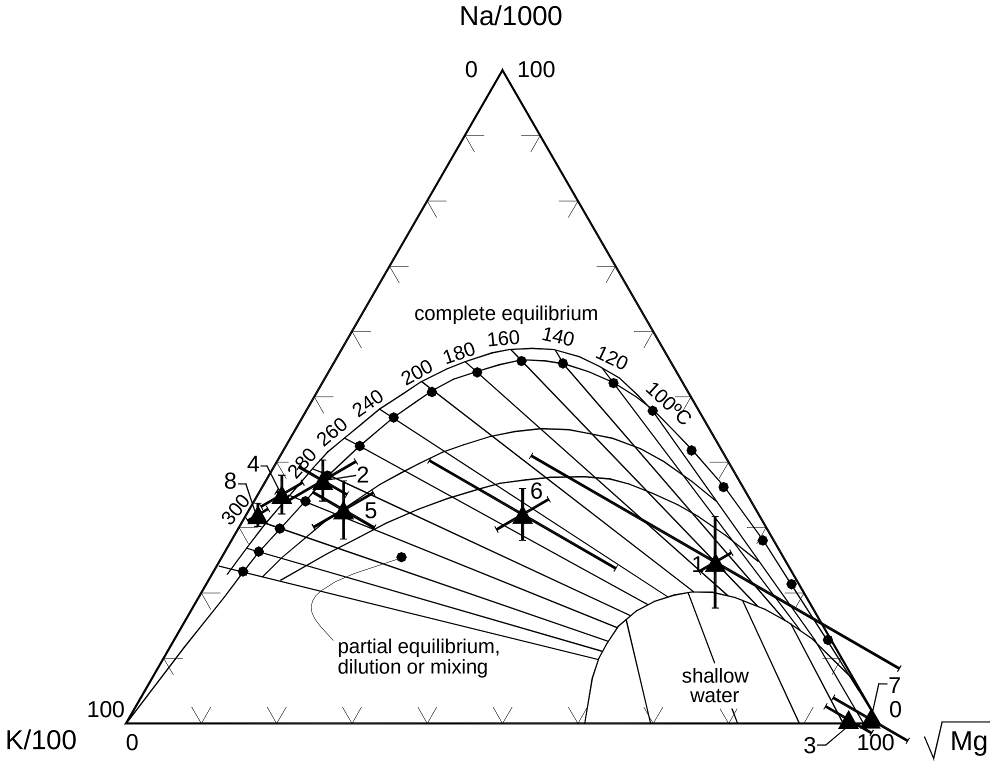

Figure 3: The sample locations in the Na-K-Mg triangular diagram of Giggenbach (1988) to identify the type of waters. The bars on each data point are the average errors (±1 S.D.), calculated through propagation of errors (Bevington, 1969). The concentration of Mg^{2+} in the geothermal water is less than 1 ppm and has the error of same order of magnitude.

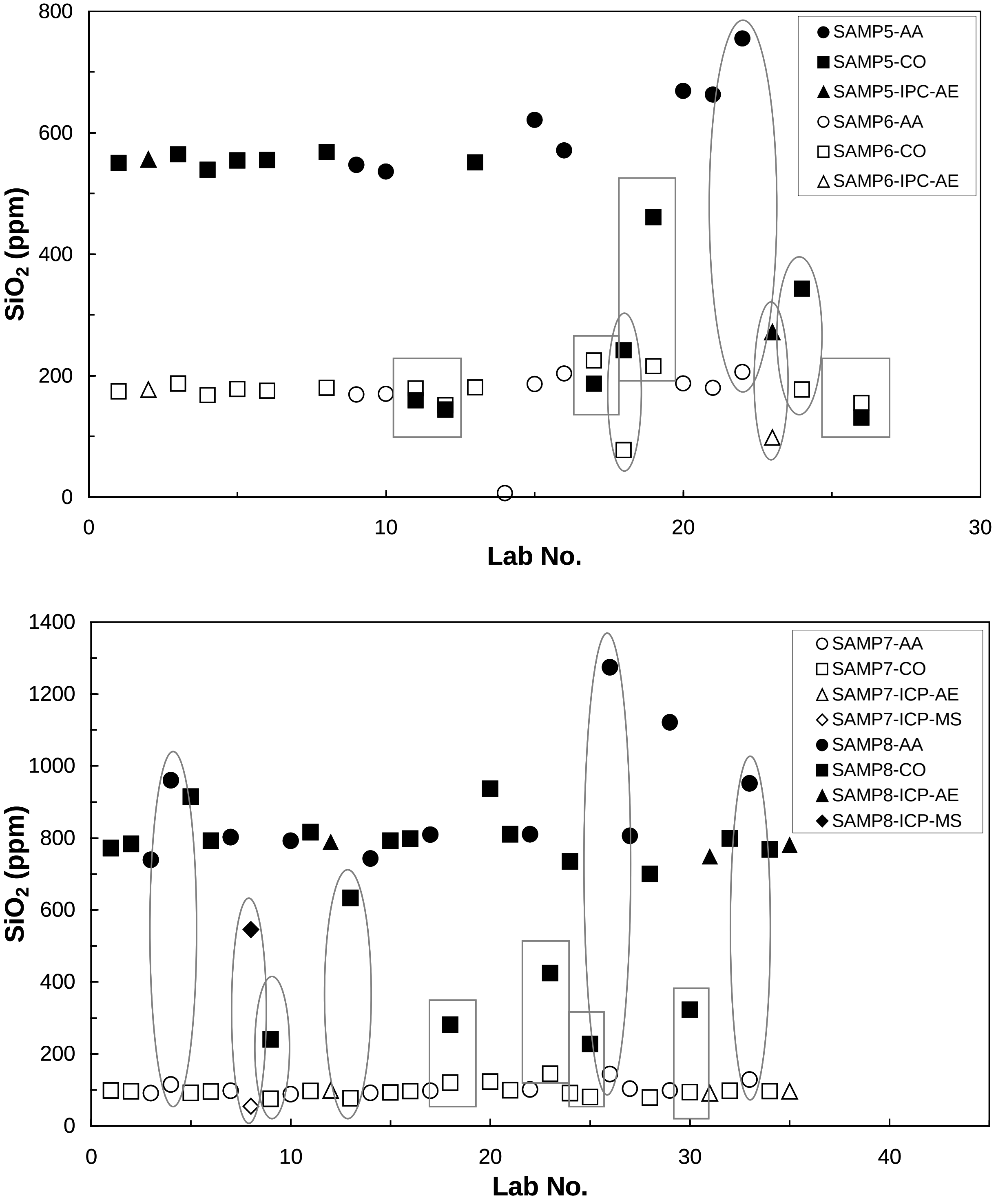

Figure. 4. Comparison of the results of silica analysis for SAMP5 to SAMP8. The sample pairs (SAMP5–SAMP6 and SAMP7–SAMP8) are plotted together in order to compare the data from same laboratory. Ellipse around the points indicates a systematic error in the data. There are some laboratories, which have unclassified errors in their analysis (shown with rectangle). The notation after the samples denotes the method of analysis: AA – Atomic Absorption, CO – Colorimetry, ICP-AE – Inductively Coupled Plasma with Atomic Emission and ICP-MS – Inductively Coupled Plasma with Mass Spectrometry.

It can be observed in Figure 2 that the normal error distributions are overlapping. The average error is of the same order for all the samples and is around the grand average. Thus it can be concluded that there is no appreciable improvement in the analytical quality for the geothermal water samples in the successive interlaboratory calibration. There is an overall error of the order of 13%. One of the reasons for it could be the existence of systematic errors in the analytical data from some laboratories.

Geochemical prediction for reservoir processes

Fluid geochemistry is a powerful tool in the geothermal industry in predicting the deep reservoir processes; however very little has been done on the effect of analytical errors in geochemical data to the uncertainty in the results. The analytical errors in the parameters of geothermal fluid affect the estimate of deep reservoir temperature, geothermal fluid classification, chemical speciation, etc. Here we will discuss only the effect of analytical errors on the Na-K-Mg diagram proposed by Giggenbach (1988) to identify the reservoir fluid characteristics and the formation of natural manifestation with mixing of geothermal components and local groundwater. Geothermal fluids have the concentration of Mg^{2+} generally less than 1 ppm. It means that the analytical error is quite high in the determinations of Mg^{2+} in geothermal fluids. In other words the triangular diagram is effectively binary diagram between Na^+ and K^+ for geothermal waters under the circumstances.

Figure 3 shows the location of all the samples in the Na-K-Mg diagram. The bars on the points show the errors, which were calculated using the methodology of propagation of errors described by Bevington (1969). It can be observed in the figure that the mixed waters have higher uncertainties. It is associated with the uncertainty in the analysis of Mg^{2+}. The similar effects will be manifested on the deep reservoir chemical speciation. Thus the quality of analysis is of vital concern in the geochemical modeling of hydrothermal systems.

A critique on silica analysis

It is really strange that there is higher error for higher concentration of silica. Firstly, there could be some problems of silica precipitation during the storage and transportation of samples, but it is not found uniform. To understand more on the silica analysis the samples, SAMP5 to SAMP8 are plotted in Figure 4. The sample pairs (SAMP5-SAMP6 and SAMP7-SAMP8) were plotted together to compare the data for same laboratory. There are systematic errors in the data from some laboratories, which are marked with ellipse around them. There are some laboratories, which have consistent analysis for lower concentration, but the measurement for higher concentration is significantly different. These are marked with square around them. In order to understand the reasons for these inconsistencies, there is need of running some commercial standards together with the interlaboratory calibration samples in all the laboratories.

Table 3: A comparison of the results of silica analysis (ppm) before and after removing the data from the laboratories having systematic errors.

Sample	Before removing data	After removing data
SAMP5	466.8±182.3	574.5±43.7
SAMP6	178.1±13.0	179.6±9.3
SAMP7	96.8±12.0	96.2±7.5
SAMP8	773.1±147.2	806.4±83.7

Table 3 presents the statistical analysis of silica concentrations. The data are compared before and after removing the data from the laboratories, which have the above mentioned errors. There is substantial improvement in the data quality on removing the data, which have systematic errors. Thus the systematic error is one of the factors for high inconsistency in the results of interlaboratory calibrations.

Additionally, the analysis of cations is better than that of anions. Thus there is need to revise the procedure for the anion analysis. There is also high spread in the analysis of HCO_3^-. We are working on them.

CONCLUSIONS

1. The statistical analysis of all the chemical parameters suggests that there is no appreciable improvement in the quality of analysis of geothermal waters in the successive interlaboratory calibration. The overall error in the analysis of geothermal water is of ±13%.
2. The analytical error for concentrations less than 1 ppm is of the same order of magnitude. Therefore, the geochemical interpretation based on these parameters (e.g. Mg^{2+}), which have concentration less than 1 ppm in geothermal waters, is not reliable unless the measurement precision is improved.
3. There are systematic errors in the analysis from many laboratories. Thus it is necessary to run some commercial standards together with the samples in future interlaboratory

calibrations in order to understand the reasons for the inconsistency and reduce the systematic errors.

4. There are some serious problems with sampling and analytical procedures for SiO_2 and HCO_3^-.
5. It is extremely necessary the continuation of the interlaboratory calibration program to obtain acceptable analytical quality for all the participating laboratories.

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