SOLUTE AND GAS GEOTHERMOMETERS

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ABSTRACT

In this paper are presented comparisons of temperatures between twelve geothermometers and aquifer temperatures, from three different high-temperature geothermal areas, Krafla in Iceland, Olkaria in Kenya and Mutnovka on the Kamchatka peninsula, Far East Russia. Solute and gas geothermometers based on the various component concentrations and products or ratios of component concentrations are used. Geothermometer temperatures were calculated from the base aquifer water composition using the WATCH chemical speciation program. For some areas, the geothermometers showed some systematic difference. The average value of all geothermometers is considered to yield the most reliable result.

1. INTRODUCTION

1.1 Objectives

The main aim of this project was to interpret chemical data from high-temperature geothermal fields; to predict subsurface temperatures by calculating solute and gas geothermometer temperatures from well data, and to compare those with measurements of temperatures downhole at the level of permeable horizons.

1.2 Use of geothermometers

For the past several decades, water chemistry and gas composition of geothermal fluids have proved useful in assessing the characteristics of geothermal reservoirs, both to estimate temperatures (D'Amore and Panichi, 1980; Arnórsson and Gunnlaugsson, 1983; 1985; Nehring and D'Amore, 1984; D'Amore and Truesdell, 1980; 1985;) and to estimate initial steam fractions in the reservoir fluid (Giggenbach, 1980; D'Amore and Celati, 1983; D'Amore and Truesdell, 1985; Arnórsson et al., 1990). The following geothermometers are most common:

Solute:	*Quartz*	- Fournier (1977);
		- Arnórsson et al. (1998);
	Na - K	- Truesdell (1976);
		- Fournier (1977);
		- Arnórsson et al. (1998);
	Na - Ka - Ca	- Fournier and Truesdell (1973);

Gas:	CO_2 - H_2 and CO_2 - H_2S	Nehring and D'Amore (1984)
	CO_2, H_2S, H_2, CO_2/H_2,H_2S/H_2	Arnórsson and Gunnlaugsson (1985)
	CH_4/CO_2	Giggenbach (1991)

1.3 Assumptions

The composition of aquifer fluids in high-temperature geothermal systems is derived from data on the composition of water and steam samples, collected at the wellhead, and a particular model, which relates the wellhead sample and aquifer fluid compositions. Many studies indicate that geothermal water compositions are controlled by a close approach to mineral-solution equilibria with respect to various elements (Arnórsson et al., 1983a; 1983b; Giggenbach, 1980; 1981; 1988; Michard, 1991; Tole et al., 1993; Gunnarsson and Arnórsson, 2000; Gökgöz, 1998; Arnórsson, 2000a; 2000b; Stefánsson and Arnórsson, 2000; Stefánsson et al., 2000; Karingithi, 2000; Gudmundsson and Arnórsson, 2002; Palandri and Reed, 2001). Changes, which occur in temperature and water composition during boiling between aquifer and wellhead, generally lead to changes in mineral saturation. Such changes may result in mineral precipitation or mineral dissolution. Together with physical processes in the depressurization zone around wells, these changes may cause well discharge compositions to differ from the chemical composition of the aquifer fluid. In this report, chemical analysis of geothermal fluids from the Krafla and Olkaria high-temperature geothermal fields and Mutnovka in Kamchatka were used to estimate subsurface temperatures in respective geothermal systems.

1.4 Approximation

The subsurface temperatures predicted by various geothermometers are evaluated and compared with measured downhole temperatures. Most calculations were performed with the WATCH program (Arnórsson et al., 1982; Bjarnason, 1994). For the present study, five chemical constituents were specifically studied, together with Na/K ratios and Na/K/Ca relationships (the Na-K-Ca geothermometer of (Fournier and Truesdell, 1973). The constituents are SiO_2 in water and CO_2, H_2S, H_2 and CH_4 in steam. These constituents are geoindicators.

2. STUDY AREAS

In this paper, data from three different areas are used to study the relationship between geothermometer temperatures and compare them with aquifer temperatures. The systems considered include Krafla in Iceland, Olkaria in Kenya and Mutnovka in Kamchatka. All these systems occur in volcanic rocks, ranging from basaltic to silicic in composition except for the Mutnovsky area, which is hosted by andesite-dacite, andesite and andesite-basalt. Table 1 gives the chemical composition of the well discharges for the selected wells from Kamchatka. Karingithi (2002) and Gudmundsson and Arnórsson (2002) report the data from Olkaria and Krafla, respectively. All the waters are relatively dilute. The aquifer temperatures range from 195 to 355°C.

TABLE 1: Primary data from Mutnovka

No.	Well	Date of Sampling	Wellhead pressure (bar)	Water (mg/l)																Steam (mmoles/kg)								mg gases/ kg conden.
				CO_2	NH_3	B	SiO_2	Na	K	Mg	Ca	F	Cl	SO_4	Al	Fe	Li	As	pH	CO_2	H_2S	H_2	CH_4	N_2	CO	Ar	He	
1	4A	5.11.1998	7.5	44.3	0.30	19.4	772	273	54.0	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.42	3.3	9.06	6.84	0.83	0.05	0.011	0.57	-	0.013	0.00013	0.015
2	4A	7.11.1998	8.8	43.4	0.30	19.1	805	275	54.5	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.43	4.07	9.09	3.42	0.78	0.04	0.007	0.72	-	0.015	0.00009	0.009
3	4A	9.11.1998	11.2	42.0	0.30	19.4	842	271	53.5	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.43	4.9	9.14	8.62	0.98	0.09	0.023	0.81	-	0.023	0.00020	0.019
4	4A	12.11.1998	11.8	42.3	0.55	19.1	822	272	54.5	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.42	4.2	9.15	5.68	1.12	0.06	0.014	0.88	-	0.017	0.00016	0.014
5	4A	13.11.1998	4.3	45.0	0.55	19.1	821	277	56.0	<0.24	4.2	4.24	244.9	250	<0.27	<0.3	1.43	4.25	9.08	3.35	0.57	0.06	0.014	0.98	-	0.018	0.00017	0.009
6	4A	14.11.1998	6.3	44.6	0.55	19.1	851	277	56.0	<0.24	4.8	4.24	244.9	250	<0.27	<0.3	1.43	4.65	9.15	4.65	1.72	0.11	0.028	1.80	-	0.032	0.00037	0.015
7	016	3.1.1999	4.9	77.9	1.00	27.8	640	256	40.8	<0.24	9.6	1.08	53.9	423	<0.27	<0.3	0.18	1.75	9.16	55.18	7.11	1.93	0.126	1.65	0	0.033	0.00013	0.119
8	016	4.1.1999	7.5	57.3	1.00	19.1	477	181	25.7	<0.24	8.8	0.75	36.2	298	<0.27	<0.3	0.1	1.25	9.2	32.36	5.16	1.74	0.126	1.09	0	0.028	0.00020	0.073
9	016	6.1.1999	9.8	46.9	1.00	18.9	406	138	21.8	<0.24	8.0	0.59	29.4	231	<0.27	<0.3	0.08	1.02	9.05	44.13	5.61	1.75	0.116	1.11	0	0.026	0.00000	0.095
10	016	7.1.1999	11.7	53.2	1.00	20.5	443	153	24.8	<0.24	8.8	0.56	32.6	259	<0.27	<0.3	0.08	1.02	9.04	44.16	6.32	1.78	0.124	1.40	0	0.032	0.00000	0.097
11	016	8.1.1999	13.7	54.6	0.90	20.1	477	153	25.0	<0.24	8.8	0.63	29.4	259	<0.27	<0.3	0.08	1.3	9.1	70.04	6.26	2.11	0.178	2.43	0	0.041	0.00000	0.146
12	016	9.1.1999	15.7	44.3	0.90	13.5	350	115	19.2	<0.24	8.0	0.49	24.5	192	<0.27	<0.3	0.05	1.13	9.04	44.44	5.23	2.28	0.156	1.72	0	0.032	0.00000	0.097

2.1 Krafla

The Krafla geothermal area is located in one of the five volcanic systems with fissure swarms in the active volcanic zone of axial rifting in NE-Iceland (Figure 1). These are part of the surface expressions of the Mid-Atlantic Ridge in Iceland. The surface of the Krafla area is mostly covered with basaltic lavas, and a little of hyaloclastites, also of basaltic composition. However intermediate and silicic volcanic units also outcrop in the area. The volcanic activity at Krafla is episodic, occurring every 250-1000 years, each episode lasting 10-20 years. The latest eruptive period started in 1975 and terminated in September 1984. The Krafla central volcano developed a caldera during the last interglacial period, about 100 thousand years ago, which has almost been filled since with volcanic material.

FIGURE 1: Location of the Krafla geothermal area, N-Iceland

Within the Krafla caldera there are numerous fumaroles and hot and altered ground that are mostly connected to tectonic fractures and faults. These geothermal manifestations indicate the existence of a large geothermal system. The exploration of this system began in 1970 (Stefánsson, 1981; Bödvarsson et al., 1984; Ármannsson et al., 1987).

At the beginning of the 1975-1984 volcanic-rifting episode in Krafla (Björnsson et al., 1977), the gas content of the fumarole steam, and in the steam of the only producing well at that time, increased very much, in particular with regard to CO_2. This increase in gas concentration has been attributed to degassing of new magma intruded into the roots of the geothermal system (Ármannsson et al., 1982). The amount of this magmatic gas has since decreased with time. An estimate has been made of the excess fraction of CO_2 in well discharges derived from this source of new magma. The degassing of the new magma upset mineral-CO_2 equilibria in the geothermal reservoir and, therefore, also the CO_2 geothermometer temperature.

Drilling in Krafla started in 1974 with two 1200 m deep exploration wells. Three production wells were drilled in 1975 and by the year 1978, 12 wells had been completed, all of which were in the Leirbotnar field, to the west and south of the Hveragil gully. In 1976 the reservoir fluid at Leirbotnar became contaminated with magmatic gases, causing depositions and corrosion in the wells with simultaneous decline in their productivity. At present 34 wells have been completed in the Krafla area. A 60 MWe power plant is operated in the area and plans to enlarge it to 100 MWe are underway.

2.2 Olkaria

The Olkaria geothermal area, located within the Hell's Gate national park in the eastern branch of the African rift system in Kenya, has been under exploitation for over 20 years. The Olkaria area is situated southwest of Lake Naivasha in the eastern arm of the African Rift Valley in Kenya (Figure 2). The Olkaria geothermal area is associated with the Olkaria volcanic centre which is bound by a northeasterly trending belt of volcanism and substantial normal faulting along the floor of the western Rift Valley. The area is divided into small fields namely East, Northeast, West, Central and Domes. The Olkaria East field is fully developed with a 45 MWe power station in operation. In the Northeast field a 64 MWe power plant is under construction. In Olkaria West a 12 MWe plant is being operated, with plans to expand it to 60 MW.

The area is mostly covered by young Quaternary volcanic material believed to have originated from Longonot and Suswa volcanoes. Altered and warm ground is extensive in this area, with the present manifestations showing a close association with the dominant N-S structures in Olkaria central and ENE-WSW Olkaria fault zone. Volcanic sequences in the Rift Valley overlying the crystalline basement are about 3.5 km thick (Hamilton et al., 1972). According to Healy (1972), basaltic rocks dominate below 1.7 km at Olkaria, whereas acid tuffs and lavas dominate above.

The geological characteristics of Olkaria and the development of the geothermal resource have been described by various authors, e.g. Arnórsson et al. (1990), Omenda (1998), Karingithi (2000).

2.3 Mutnovka

The Mutnovsky geothermal area is located in the Kamchatka peninsula, in the far eastern part of Russia (Figure 3). The Mutnovsky field

FIGURE 2: Map showing the location of the Olkaria geothermal area within the Rift Valley in Kenya

belongs to the Southern Kamchatka volcanic zone and is located about 8 km to the north of the Mutnovsky volcano. The field is connected with the city of Petropavlovsk-Kamchatsky by a 125 km long road where of the last 65 km are unpaved. Access to the field is very difficult during winter time because of heavy snowfall, requiring snow removal for access

The Mutnovsky geothermal area of Kamchatka can be considered as one of the largest areas of heat from the Earth's interior. This region, of about 30 km^2, consists of active thermal manifestations associated with active volcanoes and high-temperature geothermal systems. To the south it is restricted by the composite edifice of Mutnovsky volcano with powerful high-temperature fumaroles, hot springs and steam vents at the crater and northern flank (Kiryukhin and Pruess, 2000).

The Mutnovsky geothermal area is a region with very intense volcanic activity. There are two active volcanoes - Mutnovsky and Gorely, and one extinct and eroded volcano, Zhirovskoy, in the vicinity of the geothermal field. Intense fumarolic activity has been noted in the craters during the entire observation period at Mutnovsky. The last eruption of the Mutnovsky volcano occurred in 2001. This was a phreatic explosion in the young crater, the so-called Active Funnel.
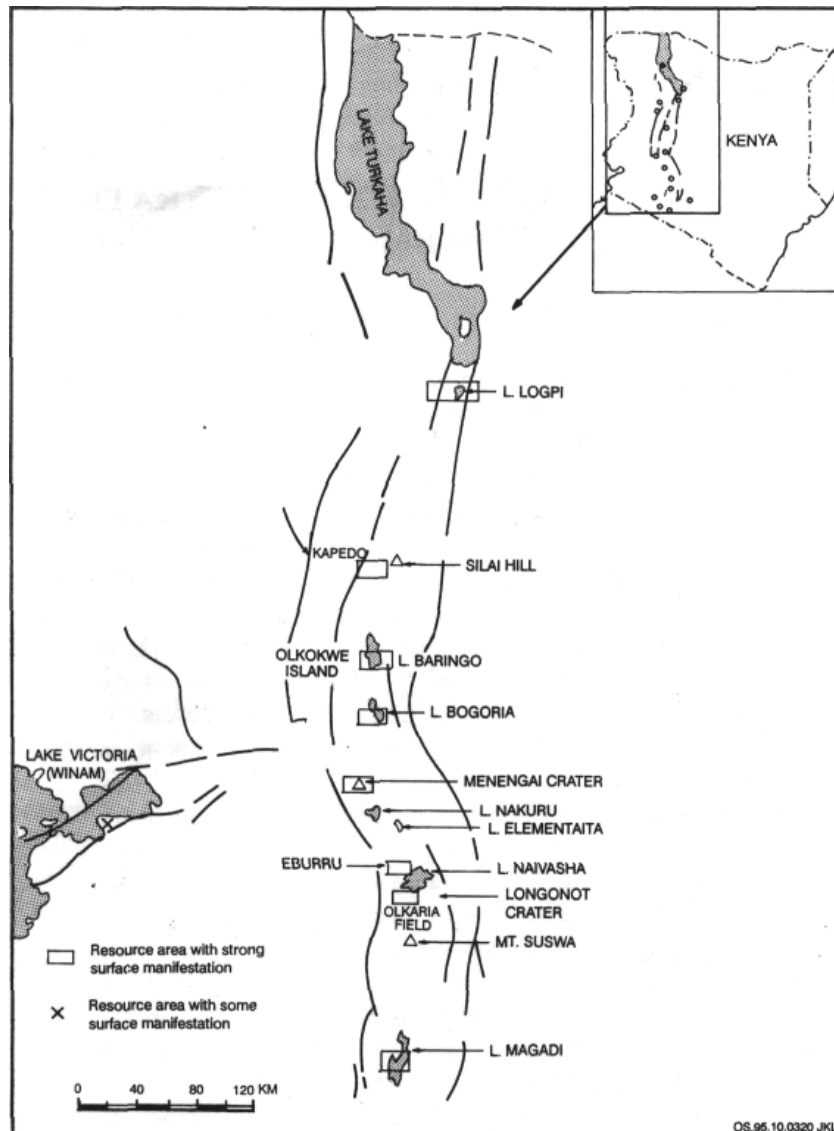
The morphology and some geological characteristics of this mountain were described by Marenina (1956). Several papers on different aspects of the Mutnovsky activity were published after the 1961 eruption (Kirsanov et al., 1964; Polyak, 1965; Serafimova, 1966; Vakin et al., 1976; Sharapov et al., 1979; Polyak et al., 1985; Melekestcev et al., 1987; Taran et al., 1986). These also touch upon the chemical composition of volcanic gases and condensates.

Geothermal exploration of the field was carried out during 1978-1990. More than 80 wells have been drilled covering an area of about 25 km^2. Well depth ranges from 1000 to 2500 m. The drilling identified prospect sites in the Mutnovsky area. At present there are plans to construct a 120 MW power plant in the central site. The Mutnovsky reservoir is liquid-dominated.

FIGURE 3: The location of Kamchatka Peninsula and the Mutnovsky geothermal area

3. METHODOLOGY

The data selected from the study areas at Krafla, Olkaria and Mutnovka were collected and presented in different forms. In the case of Krafla, water and steam samples were collected at the same pressure. However, for Olkaria and Mutnovka water samples were collected from the weirbox at atmospheric pressure but steam samples at elevated pressure. Additionally, the Mutnovka data included information on alkalinity but not on total carbonate carbon. The bicarbonate retrieved from the alkalinity measurement was taken to represent total carbonate carbon.

The WATCH chemical speciation program (Arnórsson et al., 1982), version 2.1A (Bjarnason, 1994) was used to calculate aquifer water compositions from the analytical data on water and steam samples collected at the wellhead. To make these data compatible for the WATCH input file, the primary Olkaria and Mutnovka data were modified. The concentrations of gases in steam were changed by adding to the steam samples the steam fraction that is discharged from the atmospheric silencers, formed by depressurization of the separated water from the steam sampling pressure to atmospheric pressure, taking the secondary steam fraction to be free of gas. This modification implies atmospheric sampling pressure for both water and steam samples.

Many of the wells included in the present study have excess enthalpy. For the WATCH calculations of aquifer water compositions, it was assumed that the cause of the excess enthalpy was phase segregation in the producing aquifer (Arnórsson, 2000c; Gudmundsson and Arnórsson, 2002). For Krafla and Olkaria, the aquifer temperature was taken to be that evaluated by Gudmundsson and Arnórsson (2002) and Karingithi (2002), respectively. Temperature logging data for evaluating aquifer temperature were not available for Mutnovka. For that reason the quartz equilibrium temperature was taken to represent the aquifer temperature for the Mutnovka wells. Having obtained the aquifer water concentrations for
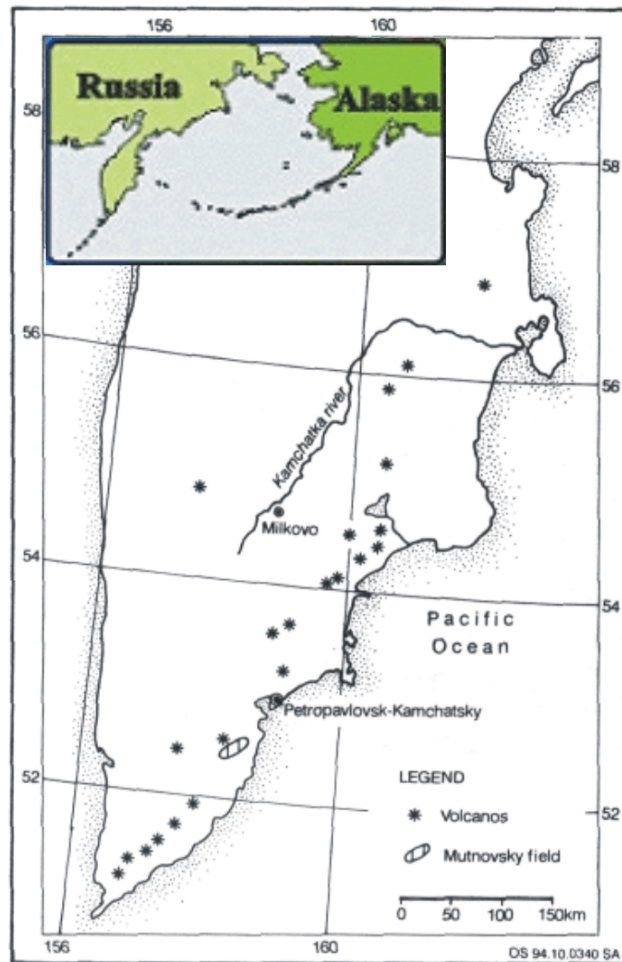
unionized silica, the quartz equilibrium temperatures were calculated from those temperatures. Na-K-temperatures were calculated from Na and K concentrations. This is a good approximation as Na/K concentration ratios are very similar to Na^+/K^+ activity ratios.

The gas geothermometer equations used for the present study are, in most cases, based on gas concentrations or gas concentration products in steam at atmospheric pressure where this steam is assumed to have formed by adiabatic boiling of the parent aquifer water. Gas concentrations in such atmospheric steam were obtained for the gas concentrations in the aquifer, as calculated by the WATCH program, by dividing the steam fraction formed by adiabatic boiling from the aquifer temperature to atmospheric pressure into the calculated gas concentration in the aquifer water. This procedure assumes that all the gas present in the aquifer water is transferred into the steam phase upon boiling. Having obtained the gas concentration in atmospheric steam, temperatures for the respective gas geothermometers were calculated.

4. RESULTS

Geothermometer temperatures have been calculated for three solute geothermometers (quartz, Na/K and Na/K/Ca) and a total of nine gas geothermometers. One of the gas geothermometers is empirical but the rest correspond to an equilibrium constant for specific mineral buffers, or certain gas-gas equilibria. The results are shown in Table 2 and Figure 4. Three calibrations have been used for the quartz geothermometer, those of Fournier (1977), Fournier and Potter (1982) and Arnórsson et al. (1998) and also three for the Na-K geothermometer (Truesdell, 1976; Fournier, 1979; Arnórsson 2000a).

4.1 Solute geothermometers

The three different quartz solubility curves, on which the calibration of the quartz geothermometer is based, yield quite similar temperatures. On average, the solubility curve of Fournier (1977) yields 5° and 6°C higher temperatures than the selected aquifer temperature for the Krafla and Olkaria wells, respectively. The corresponding numbers for the calibrations of Fournier and Potter (1982) and Arnórsson (2000b) are 11° and 15°C for these two areas. The selected aquifer temperatures for the Krafla and Olkaria wells, which were taken from Gudmundsson and Arnórsson (2002) and Karingithi (2000), respectively, were evaluated from temperature logging in thermally stabilized wells, the depth level of permeable horizons and geothermometry. Such evaluation is not available for Mutnovka. For Krafla and Olkaria the absolute average deviation is somewhat larger than the average deviation and the standard deviation is even larger (Table 3).

The Na-K geothermometer curve of Truesdell (1976) yields systematically lower temperatures than the quartz geothermometer but higher in the case of the curve of Fournier (1979). The calibration of Arnórsson (2000a) is based on the assumption of equilibrium between solution low-albite/microcline (the stable K-feldspar at low temperatures) and thorough evaluation on thermodynamic data on these minerals yields intermediate values. In the case of Krafla, they are considerably lower than the quartz temperature (23°C on average), but in the case of Olkaria and Mutnovka, the difference is smaller, or 9° and 1°C, respectively. The scatter around the equilibrium curve is considerable as indicated by the results in Table 3 and Figure 4.

For Olkaria and Mutnovka the empirical Na-K-Ca geothermometer yields temperatures quite similar to those of the quartz and Na-K geothermometers, the average differences being 8° and 4°C, respectively. For Olkaria, on the other hand, the difference is much larger, being 37°C on average, the Na-K-Ca geothermometer giving higher values. The high Na-K-Ca temperatures at Olkaria are not considered realistic. They are the consequence of calcium loss from solution between aquifer and wellhead due to much calcite deposition as extensive boiling occurs. Too low calcium concentrations yield high Na-K-Ca temperatures.

TABLE 2:   Geothermometer results

Sample no.	$T_{aquifer}$ (°C)	Solute geothermometers							Gas geothermometers								
		Quartz			Na - K			Na-K-Ca	H_2-CO_2	H_2S-CO_2	CH_4/CO_2		CO_2	H_2S	H_2	CO_2/H_2	H_2S/H_2
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Krafla-3098	245	251	257	261	220	252	228	238	266	263	299	278	214	234	236	256	292
Krafla-3099	245	247	252	254	215	248	224	240	320	291	374	272	279	256	259	245	302
Krafla-3100	280	274	288	306	278	297	276	292	333	307	392	228	313	267	258	208	294
Krafla-3101	275	272	284	300	258	282	260	251	301	291	348	240	280	256	246	220	288
Krafla-3102	230	234	236	235	180	220	196	217	287	277	388	283	250	245	244	244	293
Krafla-3103	210	237	240	240	193	230	206	221	201	220	269	214	174	190	198	212	279
Krafla-3104	265	278	295	317	243	270	247	263	308	296	419	288	271	262	253	242	292
Krafla-3018	250	238	240	240	234	263	240	249	290	273	291	347	195	247	256	302	305
Krafla-3109	260	251	257	261	237	266	242	251	296	279	290	334	211	251	258	295	303
Krafla-3110	240	238	241	241	206	241	216	219	309	284	228	309	223	255	265	300	308
Krafla-3201	245	249	254	258	210	244	220	246	283	274	252	241	247	242	242	243	293
Krafla-3203	280	273	287	304	271	292	270	290	337	304	378	234	310	264	262	218	300
Krafla-3204	275	260	268	277	244	271	248	135	303	281	300	278	251	249	254	261	301
Krafla-3205	200	214	215	210	171	212	188	201	259	249	251	237	220	219	231	243	295
Krafla-3206	240	253	258	263	213	247	223	244	308	279	319	263	265	245	254	250	304
Krafla-3207	225	228	230	227	178	217	193	216	296	276	383	298	248	244	250	257	300
Krafla-3208	200	213	214	209	155	198	175	196	181	248	251	169	212	218	178	157	242
Krafla-3209	250	262	270	279	227	258	234	245	299	272	325	288	245	241	253	264	305
Krafla-3210	210	236	239	238	188	226	202	220	239	230	267	224	209	199	219	229	296
Krafla-3212	215	244	248	250	194	231	207	225	-	228	285	-	159	200	-	-	-
Krafla-3215	240	233	235	234	204	239	215	221	273	-	234	266	171	-	248	301	-
Olkaria-02	255	253	258	263	246	273	250	289	245	230	286	205	235	196	218	210	296
Olkaria-05	240	254	260	266	234	263	240	280	248	239	345	214	245	204	218	203	291
Olkaria-10	235	276	291	311	256	281	258	286	225	229	257	181	233	195	205	189	283
Olkaria-11	250	247	252	255	245	272	249	286	234	238	272	226	207	207	216	225	287
Olkaria-15	245	244	248	250	239	267	243	289	244	228	281	233	209	196	222	236	301
Olkaria-16	230	236	239	238	218	250	226	280	239	215	300	233	202	182	220	235	306
Olkaria-19	210	249	253	256	212	246	222	268	243	230	282	239	204	199	222	239	299
Olkaria-20	265	269	280	294	242	269	246	289	263	252	313	225	247	218	228	219	293
Olkaria-26	255	258	264	272	235	264	240	289	251	243	327	224	238	210	222	214	291
Olkaria-28	230	252	257	262	220	252	228	259	241	231	335	245	210	199	220	230	296
Olkaria-29	240	247	251	254	234	263	240	272	252	238	336	259	213	207	227	241	298
Olkaria-30!	265	262	270	280	252	277	255	295	202	244	-	-	226	212	190	170	258
Olkaria-30ii	260	255	261	266	255	280	257	293	202	237	-	-	207	206	194	187	265
Olkaria-10	245	254	260	266	234	263	240	271	256	230	284	214	236	195	225	222	304
Olkaria-15	250	248	253	256	243	271	247	281	244	227	303	235	212	194	221	232	301
Olkaria-16	245	244	248	250	227	258	234	269	233	221	311	232	203	189	215	227	298
Olkaria-19	255	250	254	258	256	281	258	289	256	244	300	233	231	211	227	228	296
Olkaria-23	245	257	263	270	224	255	231	268	259	236	329	244	227	203	229	235	303
Olkaria-25	255	252	258	262	258	282	260	293	261	235	321	232	236	201	229	229	304
Olkaria-202	220	196	197	190	251	276	253	322	-	179	327	-	266	134	-	-	-
Olkaria-301	270	269	281	295	239	267	244	349	286	257	417	99	370	205	210	70	283
Olkaria-302	260	260	267	275	240	268	244	305	228	215	346	122	294	170	191	112	284
Olkaria-304D	185	217	218	214	159	202	178	241	278	241	430	77	390	185	200	39	285
Olkaria-306	225	242	245	246	198	234	210	282	248	239	359	110	323	192	196	91	276
Olkaria-709	270	241	244	245	313	323	303	351	237	194	290	204	215	158	216	221	318
Olkaria-714	275	256	263	269	271	292	270	310	235	236	304	195	241	202	210	192	284
Olkaria-719	240	246	250	252	232	261	238	280	237	241	314	175	262	205	206	169	279
Olkaria-901	210	240	243	244	196	233	209	268	263	243	326	191	270	205	222	190	295
Olkaria-902	210	230	233	230	175	215	191	239	176	193	300	98	274	149	161	79	266
Olkaria-903	210	225	227	224	179	218	194	255	214	211	319	118	285	167	184	109	279
Mutnovka 1	265	254	260	265	254	279	256	262	135	174	321	191	107	142	161	177	271
Mutnovka 2	268	255	262	268	254	279	256	262	126	164	312	209	49	134	161	197	275
Mutnovka 3	276	260	267	276	251	277	254	262	153	181	307	198	123	149	172	190	277
Mutnovka 4	271	257	264	271	254	279	256	263	138	178	309	205	88	148	165	192	272
Mutnovka 5	270	257	263	270	257	281	258	259	133	157	295	208	50	125	165	205	285
Mutnovka 6	276	260	267	276	255	280	257	257	150	188	282	221	77	160	174	211	273
Mutnovka 7	248	243	247	248	219	252	228	231	254	253	320	230	238	221	218	218	287
Mutnovka 8	221	223	225	221	214	248	224	218	244	239	301	240	213	208	221	231	292
Mutnovka 9	210	213	215	210	232	262	238	220	249	246	316	232	229	215	221	221	289
Mutnovka 10	216	219	220	216	233	262	239	223	249	250	314	233	230	218	222	221	287
Mutnovka 11	222	224	225	222	233	262	239	224	259	253	317	221	248	220	225	212	289
Mutnovka 12	198	204	205	198	241	269	246	219	255	245	307	235	230	213	226	228	294

A: Fournier (1977);   B: Fournier and Potter (1982);   C: Arnórsson et al. (1998)   D: Truesdell (1976);
E: Fornier (1979);   F: Arnórsson et al. (1998);   G: Fournier and Truesdell (1973);   H: Nehring and D'Amore (1984);
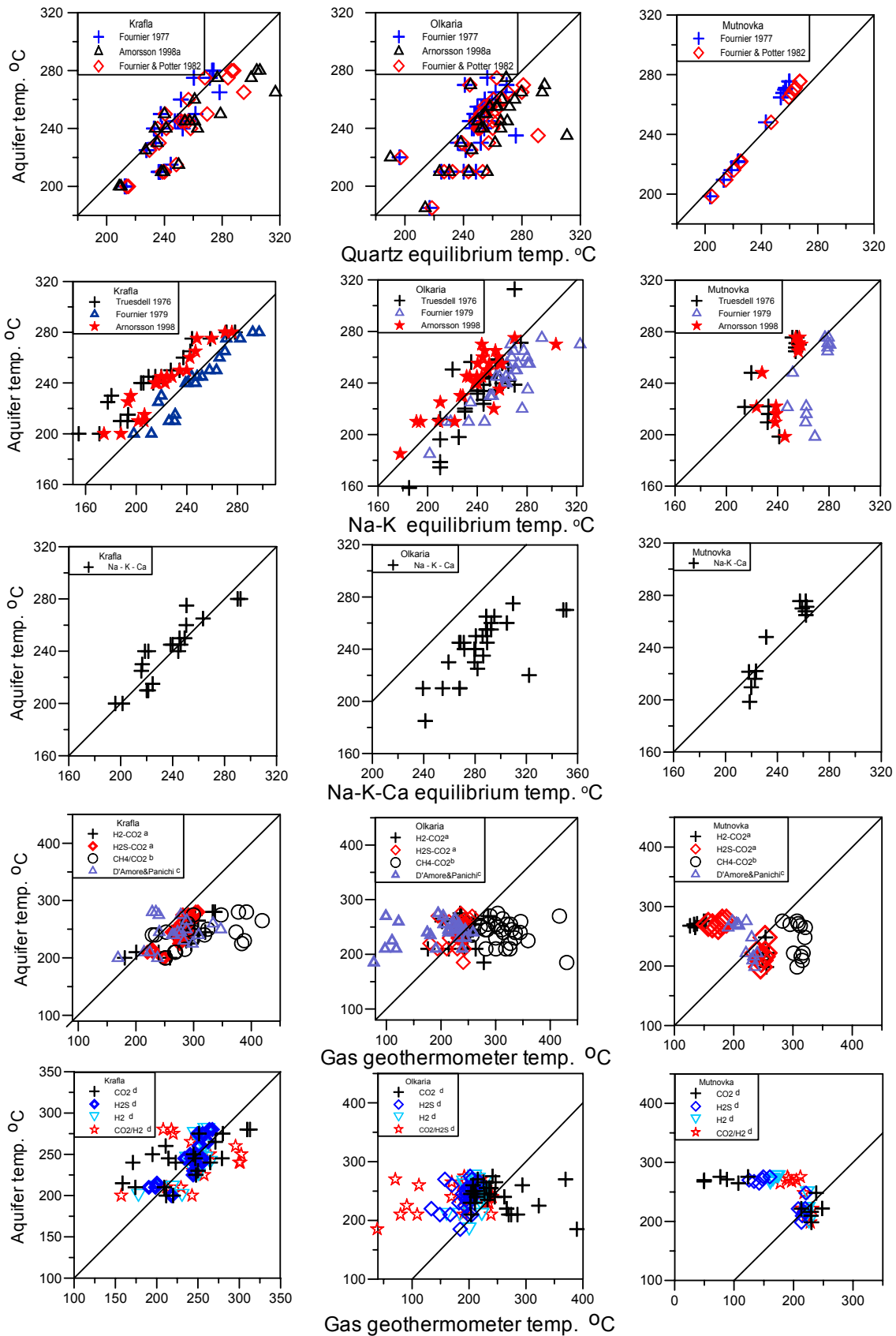I: Nehring and D'Amore (1984);   J: Giggenbach (1991);   K: D'Amore and Panichi (1980);   L-P: Arnórsson and Gunnlaugsson (1985);

(a) Nehring and D'Amore (1984), (b) Giggenbach (1994), (c) D'Amore and Panchini (1980), (d) Arnorsson and Gunnlaugsson (1985)

FIGURE 4:   Temperatures based on geothermometer results;
data from Krafla, N-Iceland in figures on left; data from Olkaria,
Kenya in centre, data from Mutnovsky, Far East Russia on right

TABLE 3: Difference between aquifer and geothermometer temperature (t_{aq}-t_{geoth})
(references for geothermometers see Table 2)

Sample no.	$T_{aquifer}$ (°C)	Solute geothermometers							Gas geothermometers								
		Quartz			Na - K			Na-K-Ca	H_2-CO_2	H_2 S-CO_2	CH_2/CO_2		CO_2	H_2	H_2	CO_2/H_2	H_2S/H_2
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Krafla-3098	245	-6	-12	-16	25	-7	17	7	-21	-18	-54	-33	31	11	9	-11	-47
Krafla-3099	245	-2	-7	-9	30	-3	21	5	-75	-46	-129	-27	-34	-11	-14	0	-57
Krafla-3100	280	6	-8	-26	2	-17	4	-12	-53	-27	-112	52	-33	13	22	72	-14
Krafla-3101	275	3	-9	-25	17	-7	15	24	-26	-16	-73	35	-5	19	29	55	-13
Krafla-3102	230	-4	-6	-5	50	10	34	13	-57	-47	-158	-53	-20	-15	-14	-14	-63
Krafla-3103	210	-27	-30	-30	17	-20	4	-11	9	-10	-59	-4	36	20	12	-2	-69
Krafla-3104	265	-13	-30	-52	22	-5	18	2	-43	-31	-154	-23	-6	3	12	23	-27
Krafla-3018	250	12	10	10	16	-13	10	1	-40	-23	-41	-97	55	3	-6	-52	-55
Krafla-3109	260	9	3	-1	23	-6	18	9	-36	-19	-30	-74	49	9	2	-35	-43
Krafla-3110	240	2	-1	-1	34	-1	24	21	-69	-44	12	-69	17	-15	-25	-60	-68
Krafla-3201	245	-4	-9	-13	35	1	25	-1	-38	-29	-7	4	-2	3	3	2	-48
Krafla-3203	280	7	-7	-24	9	-12	10	-10	-57	-24	-98	46	-30	16	18	62	-20
Krafla-3204	275	15	7	-2	31	4	27	140	-28	-6	-25	-3	24	26	21	14	-26
Krafla-3205	200	-14	-15	-10	29	-12	12	-1	-59	-49	-51	-37	-20	-19	-31	-43	-95
Krafla-3206	240	-13	-18	-23	27	-7	17	-4	-68	-39	-79	-23	-25	-5	-14	-10	-64
Krafla-3207	225	-3	-5	-2	47	8	32	9	-71	-51	-158	-73	-23	-19	-25	-32	-75
Krafla-3208	200	-13	-14	-9	45	2	25	4	19	-48	-51	31	-12	-18	22	43	-42
Krafla-3209	250	-12	-20	-29	23	-8	16	5	-49	-22	-75	-38	5	9	-3	-14	-55
Krafla-3210	210	-26	-29	-28	22	-16	8	-10	-29	-20	-57	-14	1	11	-9	-19	-86
Krafla-3212	215	-29	-33	-35	21	-16	8	-10	-	-13	-70	-	56	15	-	-	-
Krafla-3215	240	7	5	6	36	1	25	19	-33	-	6	-26	69	-	-8	-61	-
Olkaria-02	255	2	-3	-8	9	-18	5	-34	10	25	-31	50	20	59	37	45	-41
Olkaria-05	240	-14	-20	-26	6	-23	0	-40	-8	1	-105	26	-5	36	22	37	-51
Olkaria-10	235	-41	-56	-76	-21	-46	-23	-51	10	6	-22	54	2	40	30	46	-48
Olkaria-11	250	3	-2	-5	5	-22	1	-36	16	12	-22	24	43	43	34	25	-37
Olkaria-15	245	1	-3	-5	6	-22	2	-44	1	17	-36	12	36	49	23	9	-56
Olkaria-16	230	-6	-9	-8	12	-20	4	-50	-9	15	-70	-3	28	48	10	-5	-76
Olkaria-19	210	-39	-43	-46	-2	-36	-12	-58	-33	-20	-72	-29	6	11	-12	-29	-89
Olkaria-20	265	-4	-15	-29	23	-4	19	-24	2	13	-48	40	18	47	37	46	-28
Olkaria-26	255	-3	-9	-17	20	-9	15	-34	4	12	-72	31	17	45	33	41	-36
Olkaria-28	230	-22	-27	-32	10	-22	2	-29	-11	-1	-105	-15	20	31	10	0	-66
Olkaria-29	240	-7	-11	-14	6	-23	0	-32	-12	2	-96	-19	27	33	13	-1	-58
Olkaria-30!	265	3	-5	-15	13	-12	10	-30	63	21	-	-	39	53	75	95	7
Olkaria-30ii	260	5	-1	-6	5	-20	3	-33	58	23	-	-	53	54	66	73	-5
Olkaria-10	245	-9	-15	-21	11	-18	5	-26	-11	15	-39	31	9	50	20	23	-59
Olkaria-15	250	2	-3	-6	7	-21	3	-31	6	23	-53	15	38	56	29	18	-51
Olkaria-16	245	1	-3	-5	18	-13	11	-24	12	24	-66	13	42	56	30	18	-53
Olkaria-19	255	5	1	-3	-1	-26	-3	-34	-1	11	-45	22	24	44	28	27	-41
Olkaria-23	245	-12	-18	-25	21	-10	14	-23	-14	9	-84	1	18	42	16	10	-58
Olkaria-25	255	3	-3	-7	-3	-27	-5	-38	-6	20	-66	23	19	54	26	26	-49
Olkaria-202	220	24	23	30	-31	-56	-33	-102	0	41	-107	-	-46	86	-	-	-
Olkaria-301	270	1	-11	-25	31	3	26	-79	-16	13	-147	171	-100	65	60	200	-13
Olkaria-302	260	0	-7	-15	20	-8	16	-45	32	45	-86	138	-34	90	69	148	-24
Olkaria-304D	185	-32	-33	-29	26	-17	7	-56	-93	-56	-245	108	-205	0	-15	146	-100
Olkaria-306	225	-17	-20	-21	27	-9	15	-57	-23	-14	-134	115	-98	33	29	134	-51
Olkaria-709	270	29	26	25	-43	-53	-33	-81	33	76	-20	66	55	112	54	49	-48
Olkaria-714	275	19	12	6	4	-17	5	-35	40	39	-29	80	34	73	65	83	-9
Olkaria-719	240	-6	-10	-12	8	-21	2	-40	3	-1	-74	65	-22	35	34	71	-39
Olkaria-901	210	-30	-33	-34	14	-23	1	-58	-53	-33	-116	19	-60	5	-12	20	-85
Olkaria-902	210	-20	-23	-20	35	-5	19	-29	34	17	-90	112	-64	61	49	131	-56
Olkaria-903	210	-15	-17	-14	31	-8	16	-45	-4	-1	-109	92	-75	43	26	101	-69
Mutnovka 1	265				11	-14	9	3	130	91	-56	74	158	123	104	87	-6
Mutnovka 2	268				14	-11	12	6	141	104	-45	59	218	134	107	71	-8
Mutnovka 3	276				24	-1	22	14	122	95	-31	78	152	127	104	86	-2
Mutnovka 4	271				17	-8	15	9	133	93	-38	66	183	123	106	79	0
Mutnovka 5	270				13	-11	12	11	137	113	-25	62	220	145	105	65	-15
Mutnovka 6	276				21	-4	19	18	126	88	-7	54	199	116	101	64	2
Mutnovka 7	248				29	-4	20	17	-6	-5	-72	18	10	27	25	31	-39
Mutnovka 8	221				7	-26	-2	3	-23	-17	-80	-18	8	14	0	-10	-71
Mutnovka 9	210				-23	-52	-29	-10	-39	-37	-106	-22	-20	-5	-12	-11	-79
Mutnovka 10	216				-17	-46	-23	-7	-33	-34	-98	-17	-14	-2	-6	-5	-71
Mutnovka 11	222				-11	-40	-17	-2	-37	-31	-95	1	-26	2	-3	10	-67
Mutnovka 12	198				-43	-70	-47	-20	-57	-47	-108	-37	-32	-15	-28	-30	-96
Numerical Average	Krafla	-5.0	-10.9	-15.3	26.7	-6.0	17.7	9.5	-41.1	-29.0	-69.6	-21.3	6.4	2.8	0.0	-4.2	-50.9
	Olkaria	-6.0	-11.3	-15.4	9.0	-20.2	3.1	-43.2	0.9	11.8	-78.2	46.1	-5.3	48.5	30.5	54.7	-48.0
	Mutnovka				3.5	-24.0	-0.8	3.5	49.5	34.4	-63.3	26.4	88.1	65.7	50.2	36.4	-37.6
	ALL	-5.6	-11.1	-15.4	13.9	-16.2	7.2	-16.8	-3.3	3.0	-72.3	19.3	16.4	37.1	24.4	31.8	-46.8
Absolute Average	Krafla	10.8	13.2	16.9	26.7	8.4	17.7	15.2	44.0	29.0	71.3	38.1	26.2	12.9	15.0	31.3	50.9
	Olkaria	12.4	15.4	19.4	15.7	20.4	10.3	43.2	21.3	20.2	78.2	49.2	41.8	48.5	33.3	57.1	48.5
	Mutnovka				19.0	24.0	18.8	9.9	81.9	62.9	63.3	42.3	103.3	69.3	58.3	45.7	37.9
	ALL	11.7	14.5	18.4	20.0	17.1	14.4	27.5	40.7	31.3	72.9	44.8	48.4	41.0	32.2	46.4	47.1
Standard deviation	Krafla	12.7	12.4	15.4	12.1	8.4	8.6	31.9	25.0	14.3	50.4	41.2	32.3	14.4	17.7	39.4	23.4
	Olkaria	16.4	17.1	19.4	17.3	13.4	13.9	18.5	30.5	23.9	47.8	50.2	57.7	23.2	23.3	54.9	24.6
	Mutnovka				21.8	22.9	22.6	11.5	86.5	66.8	34.5	43.2	107.2	66.0	57.7	43.6	36.7
	ALL	14.9	15.2	17.7	19.0	15.9	16.2	34.1	54.9	41.3	46.1	54.3	72.1	41.4	36.3	54.2	27.0

4.2 Gas geothermometers

In the case of the Krafla wells, the CO_2-H_2 and CO_2-H_2S geothermometers of Nehring and D´Amore (1984) yield somewhat higher temperatures than the selected aquifer temperatures and the solute geothermometer temperatures, the average being 36° and 18°C in the case of the selected aquifer temperature. On the other hand, the difference is negligible for the Olkaria wells. For the two wells at Mutnovka, the CO_2-H_2 and CO_2-H_2S geothermometer temperatures are on average 55° and 35°C lower than the quartz equilibrium temperature. The low geothermometer values are attributed to low gas content of the Mutnovka wells. In some cases the gas concentrations of CO_2 and H_2S in steam are similar to total carbonate carbon and total sulphide concentration in water samples. It seems unlikely that degassing of water has been so incomplete upon boiling. Inadequate sampling is suspected.

At Krafla, the CO_2 geothermometer of Arnórsson and Gunnlaugsson (1985) yields temperatures which are on average 3°C lower than the selected aquifer temperature. The corresponding number for Olkaria is −5°C, i.e. the CO_2 geothermometer temperature is on average 5°C lower. However, at Olkaria the standard deviation of the difference is high, or 58°C. It is observed that wells in Olkaria West yield anomalously high CO_2 temperatures whereas most of the wells in the Olkaria East production field are low. As for the CO_2-H_2 and CO_2-H_2S geothermometers, the CO_2 temperatures are low for the Mutnovka wells.

H_2S temperatures at Krafla, using the curve of Arnórsson and Gunnlaugsson (1985) for "dilute" waters, are on average 6°C lower than the selected aquifer temperatures. The corresponding numbers for Olkaria and Mutnovka are 48° and 64°C, respectively. The standard deviation for the Olkaria wells is 26°C. It is, thus, evident by comparison with the average departure from the selected aquifer temperature values that H_2S temperatures for Olkaria are systematically low. As for geothermometer results described above for other geothermometers, the low H_2S temperatures for the Olkaria wells are considered to be the consequence of inadequate collection of steam samples.

The results for the H_2 geothermometer for the Krafla wells using the curve valid for "dilute" waters are on average just about the same as the selected aquifer temperature. The standard deviation is 18°C. For both Olkaria and Munovka, the H_2 temperatures ("dilute" waters) are on average 41° and 57 °C lower than the selected aquifer temperature. For Mutnovka well 4A, the H_2 temperatures are about 100°C lower than the quartz equilibrium temperature but for well 016 in this area, the two geothermometers yield quite similar temperatures. Had the H_2 geothermometer curve, which is applicable to "saline" waters, been used the H_2 temperatures from all the study areas would be higher than the selected aquifer temperatures, or by 49°, 35° and 22°C, on average, for Krafla, Olkaria and Mutnovka, respectively.

The CO_2/H_2 geothermometer, which is applicable to dilute waters, is on average 6°C higher than the selected aquifer temperature for the Krafla wells, or about the same as that of the quartz geothermometer. By contrast, the same average is lower by 55° and 33°C for Olkaria and Mutnovka. Wells in Olkaria West and two of the three wells in Olkaria Domes possess high CO_2/H_2 temperatures whereas in the Olkaria East production field the CO_2/H_2 temperatures are generally rather similar to the selected aquifer temperature. At Mutnovka, well 4A has CO_2/H_2 temperatures, which are considerably lower than the quartz equilibrium temperature, but for well 016 in this area the opposite is the case.

The CH_4/CO_2 geothermometer of Giggenbach (Giggenbach 1991) shows higher temperature than the selected aquifer and quartz equilibrium temperatures for all the areas by more than 60°C. The average number is 70°, 78°, and 63°C, corresponding to Krafla, Olkaria and Mutnovka, respectively. The Olkaria and Mutnovka numbers are set close together, excluding two points for Olkaria (wells 301 (417°C) and 304D (430°C) - aquifer temperature of well 304D is only 187°C). For Mutnovka well 4A, the CH_4/CO_2 geothermometer temperature is about 56-72°C higher than the quartz equilibrium temperature, but for well 016 the average temperature is 80-108°C higher. For Krafla, calculated CH_4/CO_2 display a wide range from the values shown by other geothermometer to over 400˚C.

The D'Amore and Panichi geothermometer is based on the ratio of pairs for CH_4/CO_2, H_2/CO_2 and H_2S/CO_2. In this case we have three different pictures. Gas geothermometer temperature for Krafla is higher than the aquifer temperature. The numerical average is –21°C, but the absolute average is 38°C. For Olkaria, the results are 46° and 49°C, respectively. In most cases, gas geothermometer temperatures are lower than aquifer temperatures. For the Mutnovka area, the average is 26° and 42°C, respectively. The standard deviation for Krafla is 41, for Olkaria 50 and for Mutnovka 43.

5. DISCUSSION AND CONCLUSIONS

Chemical geothermometers are useful for estimating underground temperature in geothermal systems. They rely on chemical data of water from springs (solute geothermometers) and steam from fumaroles (gas geothermometers). Geothermometers are also useful, together with temperature logging date, in identifying the depth levels of producing horizons in wells.

The present study involves estimation of aquifer temperatures in wells from three high-temperature geothermal fields, namely Krafla in Iceland, Olkaria in Kenya and Mutnovka in Kamchatka, Russia involving the use of three solute geothermometers (quartz, Na-K and Na-K-Ca) and nine steam geothermometers (CO_2-H_2, CO_2-H_2S, CO_2, H_2S, H_2, CH_4/CO_2, CO_2/H_2S, H_2S/H_2 and $CO_2/H_2S/H_2/CH_4$). Two of the solute geothermometers are based on thermodynamic calibration and one on drillhole data. Three of the gas geothermometers are thermodynamically calibrated but four empirically. However, three of the empiric calibrations are considered to rest on equilibration between aqueous CO_2, H_2S and H_2 and specific hydrothermal mineral buffers.

The solute geothermometers yield results that are well consistent internally. However, the Na-K geothermometers tend to indicate lower temperatures than the quartz geothermometer when extensive calcite precipitation has taken place from dilute, low-calcium water. Thus, for wells at Olkaria the Na-K-Ca geothermometer yielded high temperature estimates. Otherwise, it compares well with the Na-K geothermometer results.

Gas geothermometer temperatures show more scatter than those of the solute geothermometers and some of them differ systematically. In particular the CH_4/CO_2 geothermometer of Giggenbach indicates higher temperature than other geothermometers. This geothermometer is based on the Fisher-Tropsch reaction ($CO_2 + 4H_2 = CH_4 + H_2O$). Equilibrium for this reaction is approached very slowly, even at high temperatures. The cause of the higher CH_4/CO_2 temperatures is considered to be significant departure from equilibrium according to the Fisher-Tropsch reaction and not an indication of high temperature at deep levels in the geothermal system considered for the present study.

The mineral buffers likely to control the aqueous concentration of CO_2, H_2S and H_2 in high- temperature geothermal water have compositions that will vary with the composition of the host rock. These minerals include epidote, prehnite and garnet. Traditionally, different mineral buffers may be involved in different areas if the composition of the host rock differs sufficiently. For this reason, empirically calibrated geothermometers may be advantageous over thermodynamically calibrated ones. For the present study, the empirically calibrated CO_2, H_2S, H_2 and CO_2-H_2 geothermometers of Arnórsson and Gunnlaugsson (1985) were selected instead of the same gas geothermometers calibrated thermodynamically by Arnórsson and his coworkers.

Comparisons between the geothermometer results show some systematic differences. Yet, with the exception of the CO_2-H_2 gas geothermometer, they give a reasonable good indication of the aquifer temperatures for the wells in the study areas. On average, all the geothermometers, with the exception of the CH_4/CO_2 geothermometer, give the following temperatures for Krafla, Olkaria and Mutnovka: 250°, 229°, and 211°C, respectively, the standard deviation being 18°, 31° and 27°C. For Krafla the average

geothermometer temperature of 250°C is similar to the selected average aquifer temperature of 242°C. The difference is higher for Olkaria. There, the average aquifer temperature is 242°C, whereas the average geothermometer temperature is 229°C. This difference is largely due to the low temperatures of the H_2S, H_2, CO_2-H_2 and $H_2S/H_2/CH_4$ geothermometers. The cause is most likely due to the empirical calibration of the gas geothermometers not being accurately applicable to the Olkaria geothermal reservoir. At Mutnovka, the gas geothermometers give lower temperatures than solute ones. This is blamed on inadequate sampling of steam, which yielded low gas concentrations. It is concluded when information is lacking in hydrothermal mineral assemblages in a geothermal system and the composition of the minerals constituting these assemblages, it is best to use all available geothermometers to estimate aquifer temperature in wells or underground temperatures when applying the geothermometers to springs and fumaroles. The average value should be taken to be the best. The standard deviation of results from individual geothermometers gives information about the reliability of the average.

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TABLE 1:   Primary data from Mutnovka

No.	Well	Date of Sampling	Wellhead pressure (bar)	Water (mg/l)																Steam (mmoles/kg)								mg gases/ kg conden.
				CO_2	NH_3	B	SiO_2	Na	K	Mg	Ca	F	Cl	SO_4	Al	Fe	Li	As	pH	CO_2	H_2S	H_2	CH_4	N_2	CO	Ar	He	
1	4A	5.11.1998	7.5	44.3	0.30	19.4	772	273	54.0	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.42	3.3	9.06	6.84	0.83	0.05	0.011	0.57	-	0.013	0.00013	0.015
2	4A	7.11.1998	8.8	43.4	0.30	19.1	805	275	54.5	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.43	4.07	9.09	3.42	0.78	0.04	0.007	0.72	-	0.015	0.00009	0.009
3	4A	9.11.1998	11.2	42.0	0.30	19.4	842	271	53.5	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.43	4.9	9.14	8.62	0.98	0.09	0.023	0.81	-	0.023	0.00020	0.019
4	4A	12.11.1998	11.8	42.3	0.55	19.1	822	272	54.5	<0.24	3.0	4.24	244.9	250	<0.27	<0.3	1.42	4.2	9.15	5.68	1.12	0.06	0.014	0.88	-	0.017	0.00016	0.014
5	4A	13.11.1998	4.3	45.0	0.55	19.1	821	277	56.0	<0.24	4.2	4.24	244.9	250	<0.27	<0.3	1.43	4.25	9.08	3.35	0.57	0.06	0.014	0.98	-	0.018	0.00017	0.009
6	4A	14.11.1998	6.3	44.6	0.55	19.1	851	277	56.0	<0.24	4.8	4.24	244.9	250	<0.27	<0.3	1.43	4.65	9.15	4.65	1.72	0.11	0.028	1.80	-	0.032	0.00037	0.015
7	016	3.1.1999	4.9	77.9	1.00	27.8	640	256	40.8	<0.24	9.6	1.08	53.9	423	<0.27	<0.3	0.18	1.75	9.16	55.18	7.11	1.93	0.126	1.65	0	0.033	0.00013	0.119
8	016	4.1.1999	7.5	57.3	1.00	19.1	477	181	25.7	<0.24	8.8	0.75	36.2	298	<0.27	<0.3	0.1	1.25	9.2	32.36	5.16	1.74	0.126	1.09	0	0.028	0.00020	0.073
9	016	6.1.1999	9.8	46.9	1.00	18.9	406	138	21.8	<0.24	8.0	0.59	29.4	231	<0.27	<0.3	0.08	1.02	9.05	44.13	5.61	1.75	0.116	1.11	0	0.026	0.00000	0.095
10	016	7.1.1999	11.7	53.2	1.00	20.5	443	153	24.8	<0.24	8.8	0.56	32.6	259	<0.27	<0.3	0.08	1.02	9.04	44.16	6.32	1.78	0.124	1.40	0	0.032	0.00000	0.097
11	016	8.1.1999	13.7	54.6	0.90	20.1	477	153	25.0	<0.24	8.8	0.63	29.4	259	<0.27	<0.3	0.08	1.3	9.1	70.04	6.26	2.11	0.178	2.43	0	0.041	0.00000	0.146
12	016	9.1.1999	15.7	44.3	0.90	13.5	350	115	19.2	<0.24	8.0	0.49	24.5	192	<0.27	<0.3	0.05	1.13	9.04	44.44	5.23	2.28	0.156	1.72	0	0.032	0.00000	0.097