THE "ART" OF IN SITU FLUID SAMPLING AND THE REMARKABLE COMPOSITIONAL VARIATIONS IN THE WELLBORE FLUID OF VC-2B, VALLES CALDERA, NEW MEXICO

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ABSTRACT

In situ fluid sampling operations were conducted at VC-2B in January 1990 using two flow-through tools of different designs. Of eight attempts, no runs obtained samples from their intended depth of collection or, if they did, the tools gained additional fluid by inward leakage during their trips back to the surface. Interpretation of the salinity and mass of the fluid samples indicates that they were collected from apparent depths of about 204 to 1045 m, at collection temperatures of about 125° to 240°C. The data show a remarkable two-fold increase in fluid salinity (>9000 versus about 4000 mg/kg Cl) near the top of the well and a relatively thin, dilute "cap" of condensed steam at the top of the water column. Various criteria suggest that these salinity gradients are caused by boiling and condensation of steam in the wellbore during a seven month period of logging, stimulation, flow testing, and other in-hole experiments.

INTRODUCTION

VC-2B, the third Continental Scientific Drilling Program core hole in the Valles caldera, was completed in October 1988 to a depth of 1762 m (5780 ft) and BHT of 295°C (563°F). Project objectives, casing schedule, and preliminary results have been reported by Gardner et al. (1989) and Hulen et al. (1989). One of the primary objectives during the last year has been to try to characterize hydrothermal fluids entering the open-hole section of the bore between 1697 and 1762 m. This interval lies in fractured, hydrothermally-altered Precambrian quartz monzonite beneath the caldera. Although producible quantities of geothermal fluids are known to exist locally in caldera-fill tuffs, the relation of these fluids to deeper fluids in the Precambrian is poorly known. A more general objective of VC-2B is to serve as a test hole for development of high-temperature slim-hole tools. This paper summarizes some results of in situ sampling operations that took place January 17 to 19, 1990.

WHY OBTAIN IN SITU SAMPLES?

There are many reasons why it is necessary to obtain in situ samples of fluids from subsurface aquifers. Some of these reasons were recently stated at the Wellbore Sampling Workshop held in Houston, Texas, in May 1987 (Shevenell et al., 1987). In most cases, samples of fluids collected at the wellhead are sufficient, but in some cases such samples are not sufficient. In general, in situ samples are collected in four types of situations:

1. The well does not flow or is not allowed to flow;
2. Separate aquifers or production horizons must be sampled;
3. Unflashed samples of fluid must be obtained; or
4. Samples of fluid uncontaminated by casing or near-surface aquifers must be obtained.

BACKGROUND TO JANUARY OPERATIONS

VC-2B is lined with CHD-101 coring rods (inside diameter 7.85 cm) from 1697 m to the surface. The bottom 150 m of the rods are cemented. Presently, all fluids entering the bore originate from the Precambrian horizon. In June 1989, VC-2B was stimulated with a nitrogen lift to purge the hole of dilute water and residual drilling fluids and to try to induce self-sustained flow. Purging of the hole was successful, but sustained flow was barely maintained for a period of about 30 hours, after which time the hole was shut-in. Several attempts to turn VC-2B on without LN_2 in June through August 1989 were unsuccessful. In October 1989, initial attempts at in situ sampling were extremely frustrating but one of two runs by the Lawrence Berkeley Laboratory (LBL) tool obtained fluid from about 793 m depth having a chloride content of 6990 mg/kg (ppm). Interpretation of this information suggests that hydrothermal fluids have entered the wellbore from the Precambrian horizon.

In December 1989, a temperature log (Fig. 1) was obtained by Sandia National Laboratories (SNL) using a relatively new temperature probe connected to a dewared data-acquisition system. The day after this log was completed, a quartz crystal experiment of P. M. Bethke (USGS, Reston, VA) was suspended in the hole for four weeks at 1710 m in an attempt to grow synthetic fluid inclusions.

On January 17, 1990, when in situ operations next began, the water level of VC-2B was 204 ± 7 m and the wellhead pressure was about 6.45 atm (95 psia). Operations occurred over a three-day period during a major snow storm. During this period, wellhead pressure dropped to atmospheric conditions and the water level rose to roughly 137 m. Of eight runs, seven produced apparently full bottles and the operations were considered to be highly successful.

Two in situ samplers of flow-through design were utilized: a MP35N alloy tool made by LBL for the U.S. Department of Energy, Division of Geothermal Technology (similar to the tool described by Solbau et al., 1986) and a titanium tool built for
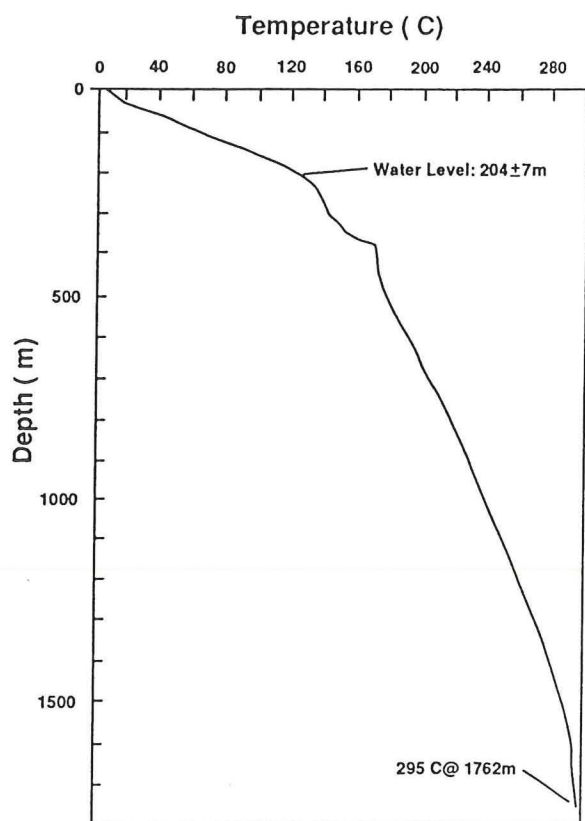
Temperature (C)

Fig. 1. Temperature log of VC-2B obtained on December 12, 1989.

Los Alamos National Laboratory (LANL) by Leutert Instruments, Inc. (R. Charles, LANL, pers. commun.), after extensive redesign of an existing oil field sampler (see footnotes of Table 1). The latter tool was run into VC-2B only once because the mechanical clock became inoperable after returning to the surface. The MP35N tool apparently closed just above and/or at the top of the water column during its first two runs because field tests showed the fluids contained low chloride and relatively low gas pressure. In addition, the first run produced a bottle that was only about half full.

FIELD PROCEDURES

General procedures can be found in Goff et al. (1987). When the in situ sampler is removed from the wellbore, the tool must be cooled to less than 100°C to ensure that all steam is condensed. In January 1990, this was done by covering the tool with snow for 10 to 15 minutes. After cooling, the in situ tool was connected to a gas extraction system (GES) having a known volume (see example in Goff et al., 1987). The GES was pumped down to <0.001 atm with a portable vacuum pump. Because neither tool used in these operations has a temperature well, the exact temperature of gas extraction is unknown but it is estimated to be between 17° and 37°C. Gas is released from the in situ chamber into the GES and the extraction pressure is recorded. Next, gas is released into various collection bottles for analytical work and the pressures in each recorded. Rocking and tapping the in situ chamber helps release more gas from solution but it should be noted that soluble gases such as CO_2 are continuously produced in observable quantities as temperature and pressure drop. For these reasons, pressures must be carefully recorded every time a valve is opened and every container must have a known volume. Bulk gas analyses were performed on the contents of flow-through glass tubes by gas chromatography.

When GES operations are finished, the in situ chamber is opened to the atmosphere and all liquid is drained into a tared 4-l plastic beaker that is then weighed on a portable top-loading balance. After the mass of fluid is measured, an aliquot is removed for field determination of pH, Eh, and chloride. Other field parameters such as alkalinity, sulfate, ammonium, etc. should be measured, but were not during this experiment. We have found that density measurements are more accurately determined in the lab. All remaining fluid was split and preserved in various ways to satisfy the needs of a host of VC-2B collaborators. Splits were analyzed for major and trace element chemistry according to standard procedures (Trujillo et al., 1987).

CALCULATIONS

Depth of Closure

One of the basic assumptions of in situ sampling operations is that in a column of fluid in a wellbore under pressure, the sample chamber will fill completely. This is certainly the case for samplers of flow-through design, which enter the wellbore open but leave the wellbore closed. After the sample chamber is closed, and as the tool is reeled out of the well, continuous temperature drop causes the fluid to cool and the liquid volume to decrease resulting in a head space filled by gas exsolved from the liquid.

In a sense, an in situ sample chamber is analogous to a giant fluid inclusion, thus, the temperature of closure of an in situ chamber is analogous to the trapping temperature of a fluid inclusion. If the density, salinity, and mass of the fluid are known, and if the volume of the in situ chamber is known, the temperature of closure can be calculated. This provides a completely independent check on the depth of closure intended during sampling operations.

The true in situ density of each fluid sample at (last?) closure of the tool is calculated directly from the measured fluid mass and the tool volume (Table 2, see last four columns). The approximate temperature of closure is estimated from the curves of Fig. 2 (Potter and Brown, 1976) and the analyzed chloride content of the fluid samples. The samples obtained in January are roughly equivalent to 0.6 to 1.5 wt% NaCl solutions. The approximate depth of closure is obtained from the temperature log.

For every run (except runs 1 and 3, which were already known to close higher than intended as discussed above), the calculated depth of (last?) closure is substantially greater than the intended depth of closure. This means that the tools closed higher in the well than intended or that the tools gained excess fluid by in-flow leakage as they were reeled up the wellbore.

Table 1.   Field data for downhole sampling activities, VC-2B, Valles caldera, New Mexico, January 17-19, 1990.

Run	Tool[a]	Date	Time In	Time Out	Intended Depth (m)	Temp. at[b] Int. Depth (°C)	Sample No.	Pressure[c] In GES (psia)	Mass[d] Fluid (g)	Field[e] pH	Field[e] Eh (mV)	Field[f] Cl (ppm)	Comments
1	LBL	1/17/90	9:45A	11:05A	1296	267	VC2B-89	1?	921	7.05	283	90	Low pressure, high pH, low Cl, and low mass indicate tool closed above water column; mostly condensed steam.
2	LANL/INC	1/17/90	12:15A	3:00P	1753	294	VC2B-90	43	823	4.74	-97	>5000	"Deep" fluid
3	LBL	1/17/90	3:00P	4:25P	1296	267	VC2B-91	25	1925[g]	5.06	203	~1000	Low Cl suggests tool closed at top of water column
4	LBL	1/18/90	9:00A	10:30A	1113	249	VC2B-92	44	1932	5.25	198	>5000	"Deep" fluid
5	LBL	1/18/90	11:35A	12:30A	1296	267	VC2B-93	70	1886	5.17	188	>5000	"Deep" fluid
6	LBL	1/18/90	1:30P	2:40P	1247	262	VC2B-94	95	1805	4.99	60	>5000	"Deep" fluid
7	LBL	1/19/90	9:00A	10:20A	1296	267	VC2B-95	90	1850	5.03	73	>5000	"Deep" fluid
8	LBL	1/19/90	11:10A	12:30A	915	229	VC2B-96	110	1811	5.12	62	>5000	"Deep" fluid

[a] LBL tool is 2.140-*l* capacity, 2-1/4" diam., flow-through design, electrical closure, MP35N construction; LANL/INC tool is 0.990-*l* capacity, 1-19/32" diam., flow-through design, clock closure, Ti construction.
[b] Temperatures from temperature log run on December 12, 1989.
[c] Pressure of gas when expanded from tool into gas extraction system (GES).
[d] Mass determined by emptying fluid from tool into tared beaker weighed on top loading balance.
[e] Field pH and Eh determined at temperatures of 7° to 27°C.
[f] Cl determined by Quantabs in field.
[g] Some fluid lost during gas extraction procedures.

Table 2.   Data used to calculate expected mass of fluid at intended depth and depth of tool closure from measured mass of fluid.

Sample No.	Analyzed Chloride (mg/kg)	Measured[a] Density (g/cm³)	Estimated[b] Density (g/cm3)	Intended[c] Temperature (°C)	Estimated[d] Pressure (bars)	Downhole[e] Estimated Density (g/cm³)	Expected[f] Sample Mass (g)	Measured Mass (g)	True[g] Downhole Density (g/cm³)	Temperature[h] Range of Closure (°C)	Depth of[i] Closure (m)
VC2B-89	83	1.0002	---	267	105	---	---	921	---	---	204[j]
VC2B-90	4150	1.0032	1.003	294	145	0.738	730	823	0.831	235-245	1045[k]
VC2B-91	845	1.0006	---	267	104	---	---	1925	---	---	210[j]
VC2B-92	8380	1.0089	1.008	249	90	0.797	1690	1932	0.903	180-190	561[k]
VC2B-93	9440	1.0090	1.011	267	105	0.811	1720	1886	0.881	201-211	719[k]
VC2B-94	5155	1.0042	1.004	262	100	0.795	1685	1805	0.843	223-233	910[k]
VC2B-95	6325	1.0081	1.005	267	105	0.791	1675	1850	0.864	212-222	812[k]
VC2B-96	5446	1.0067	1.004	229	70	0.842	1785	1811	0.846	221-231	891[k]

[a] Density measured at 20°C.
[b] Estimated by interpolation of 25°C data on Table 2 of Potter and Brown (1976).
[c] Determined from temperature log and intended sampling depth (Table 1).
[d] Determined from water level, wellhead pressure, and intended sampling depth.
[e] Estimated from interpolation of data on Tables 2 and 15 of Potter and Brown (1976), assuming sample was collected at intended depth.
[f] Calculated from expected downhole density and the volume of *in situ* tool, assuming tool filled completely at depth.
[g] Calculated from the mass of fluid obtained and the volume of *in situ* tool, assuming tool filled completely at depth.
[h] Estimated from Tables 2 and 15 of Potter and Brown (1976).
[i] Determined from temperature of closure and temperature log.
[j] Actual depth of closure.
[k] Depth of last closure if tool leaked additional fluid into sample chamber.
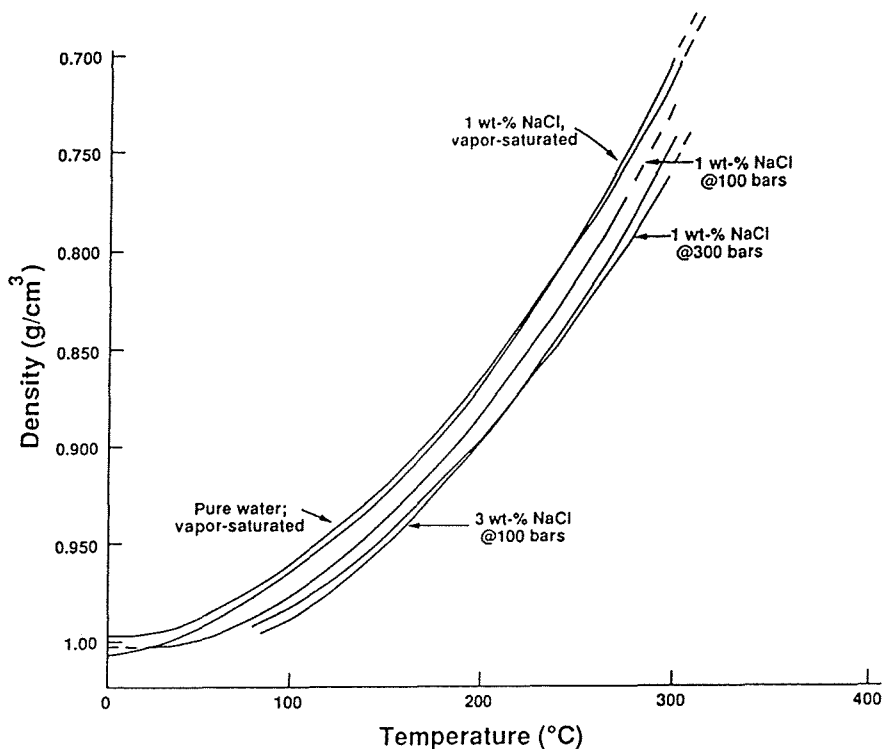
Fig. 2. Plot of fluid density versus temperature for pure NaCl solutions at various conditions bracketing those encountered in VC-2B, January 17 to 19, 1990. Data are from Potter and Brown, 1986.

The first columns in Table 2 demonstrate the calculations that are necessary to determine the mass of fluid the sample chamber should have contained if it closed at the intended depth and did not leak higher in the well. For the six "good" runs, all sample masses are 90 to 240 g greater than expected. Although these calculations are subject to errors in density, pressure, and depth measurements, in all cases the samples are so dilute and the pressures so small that the overall errors are relatively small (± 50 m in the case of run 2).

Moles of Gas Extracted

The moles of gas extracted for each sample (Table 3) are obtained by multiplying the total volume of gas extracted by the extraction pressure and solving the Ideal Gas Law equation,

$$n = \frac{PV}{RT} , \qquad (1)$$

where n = moles of gas, P = pressure of extracted gas (atm), V = volume of extracted gas (l), T = temperature of gas extraction (K), and R = ideal gas constant (8.2059×10^{-2}). The volume of extracted gas in this case is the sum of the head space volume in the *in situ* chamber at 25°C plus the GES volume. An extraction temperature of 25°C (298.15 K) is assumed. The head space pressure (P_2) at 25°C before opening the *in situ* chamber bottle is calculated from

$$P_2 = \frac{P_1 V_1}{V_2} , \qquad (2)$$

where P_1 = GES pressure, V_1 = total gas volume, and V_2 = head space volume.

Total Fluid Composition

Gas compositions (in mol%) for each sample are listed in Table 4. Major and trace element chemistry of the fluid (in mg/kg) for each sample is listed in Table 5. Because the fluid has not flashed, no corrections are applied to the analyses. The equation to convert gas compositions in Table 4 to chemical values shown at the bottom of Table 5 is

$$G_i = \frac{n(MW_i)(X_i)10^3}{m} , \qquad (3)$$

where G_i = gas component i (mg/kg), MW_i = molecular weight of component i, X_i = mole-fraction of component i, and m = mass of fluid (kg).

Table 3. Data used to calculate moles of gas extracted from VC-2B *in situ* samples.

Sample No.	Tool Volume (cm³)	Fluid Mass (g)	Fluid[a] Volume (cm³)	Tool Head Space Vol. (cm³)	GES Volume (cm³)	Total[b] Gas Vol. (cm³)	GES Pressure (atm)	Tool Head Space Pres. (atm)	Gas Extracted (*l*-atm)	Gas[c] Extracted (moles)
VC2B-89	2140	921	921	1219	42.6	1262	0.068?	---	---	---
VC2B-90	990	823	821	169	80.5	250	2.93	4.32	0.731	0.0299
VC2B-91[d]	2140	1925	1925	215	42.6	258	1.70	2.04	0.438	0.0179
VC2B-92	2140	1932	1917	223	42.6	266	2.99	3.57	0.795	0.0325
VC2B-93	2140	1886	1865	275	42.6	318	4.76	5.50	1.512	0.0618
VC2B-94	2140	1805	1798	342	42.6	385	6.46	7.27	2.486	0.1016
VC2B-95	2140	1850	1841	299	42.6	342	6.12	6.99	2.091	0.0855
VC2B-96	2140	1811	1804	336	42.6	379	7.48	8.43	2.833	0.1158

[a] Fluid mass divided by estimated fluid density (Table 2) except samples VC2B-89 and VC2B-91 (density assumed to be 1.0000).

[b] Sum of head space volume and GES volume.

[c] Calculated from ideal gas law assuming extraction temperature to be 25°C. True extraction temperatures are 17° to 37°C.

[d] Calculations for sample VC2B-91 are approximate because some water was lost during gas extraction procedures.

Table 4. Gas analyses of *in situ* samples collected from core hole VC-2B, Valles caldera, New Mexico. Values in mol%.[a]

	VC2B-89	VC2B-90A	VC2B-91A	VC2B-92A	VC2B-93A	VC2B-94A	VC2B-95A	VC2B-96A
He	<0.01	0.002	<0.001	<0.001	0.002	<0.001	<0.01	0.0006
H_2	~0.6	1.83	0.348	20.91	9.52	9.48	8.81	9.81
N_2	~77	0.186	59.55	1.02	0.818	0.763	0.68	0.543
O_2	~20	0.0338	12.70	0.0544	0.090	0.171	<0.05	0.126
Ar	<0.05	0.002	0.758	0.018	0.010	0.012	<0.05	0.0084
CO	---	0.008	<0.005	0.017	0.017	0.039	---	0.040
CH_4	<0.5	0.148	0.338	1.12	1.31	0.592	1.14	0.660
CO_2	<0.5	97.78	23.31	79.65	88.12	89.53	90.20	87.38
C_2H_4	---	<0.0005	0.001	0.012	0.0042	0.002	---	0.002
C_2H_6	<0.5	0.0057	0.001	0.0299	0.0299	0.013	<0.05	0.015
H_2S	<0.5	0.284	<0.001	0.002	<0.0004	0.0033	<0.05	0.0065
C_3H_6	---	0.0007	<0.001	0.0022	0.0010	0.0006	---	0.0009
C_3H_8	---	0.0044	<0.001	0.0241	0.0242	0.012	---	0.0126
C_4H_8	---	0.0025	<0.003	0.0197	0.0236	0.009	---	0.010
C_4H_{10}	---	0.0012	<0.003	0.0086	0.0073	0.005	---	0.004
Total	~98	100.29	97.01	102.89	99.98	100.63	100.83	98.62

[a] Analyses by W. C. Evans (USGS) except VC2B-89 and VC2B-95A, which were analyzed by P. E. Trujillo, Jr. (LANL).

Improving the Results

Besides measuring the volumes of all sample chambers, the GES, gas containers, and their connecting tubes to ± 1 cm^3, if possible, we have found that use of highly accurate pressure gauges reading absolute pressure are worth their extra expense and larger size. Knowing the exact temperature of gas extraction improves the value of T used in Eq. 1 and refines the calculation of fluid density and, therefore, the calculation of V used in in Eq. 1.

Because most fluids collected during *in situ* operations are unflashed, their pH is surprisingly acid, yet they still contain CO_2 in solution as bicarbonate. These solutions are metastable. Filtering of the fluid during sample preparation generally causes effervescence of CO_2. On-site titration of metastable species on unfiltered aliquots will improve the fluid analysis at atmospheric conditions.

Another loss of CO_2 and other gases occurs when the pressure in the *in situ* chamber drops from the gas extraction pressure to atmospheric pressure. To calculate the concentration of gas species in solution in equilibrium with gas at the separation pressure requires application of Henry's Law constants for solutions of appropriate salinity at conditions of separation.

CHEMICAL VARIATIONS IN VC-2B WELLBORE FLUID

Some very interesting variations can be observed in the chemistry of the fluid presently residing in the VC-2B wellbore. For example, if the chloride contents of the samples are plotted against the calculated depth of closure (Fig. 3), a concentration bulge occurs at a depth of about 700 m, which is more than twice as concentrated as the deepest sample collected (1045 m). Sample VC2B-88, collected at a depth of about 743 m in October 1989, falls on the same trend as the January 1990 samples. Similar concentration profiles are seen when plotting other relatively conservative species with depth (Na, K, Li, Br, B, etc.) Samples VC2B-89 and VC2B-91 are extremely dilute compared to other samples suggesting they primarily represent condensed steam.

Such variations indicate that the fluid in the upper part of the water column has extensively boiled (flashed) and that condensed steam sits at the very top of the water column. Because the sample chamber of VC2B-89 was less than half full, it is possible that the bottle closed in a zone where vigorous boiling and splashing occurs just above the "static" water level. Other facts that support this conclusion are the gas composition (air), low gas pressure, high pH, and high Eh of the fluid. Sample VC2B-91 also contains gas dominated by air, thus, even though the sample chamber for this run was nearly full, VC2B-91 can only have been collected at the approximate top of the water column.

The effect of boiling can be further investigated by plotting the ratio of total CO_2 to chloride (mg/kg basis). Above 850 m, VC-2B wellbore fluid shows an extreme depletion of CO_2 relative to chloride that must be caused by boiling. The sharp concentration spike at 890 m is possibly an artifact, since alkalinity was not determined on the fluids in the field and Henry's Law constants were not applied to the data to correct for CO_2 lost after the sample chambers were opened. On the other
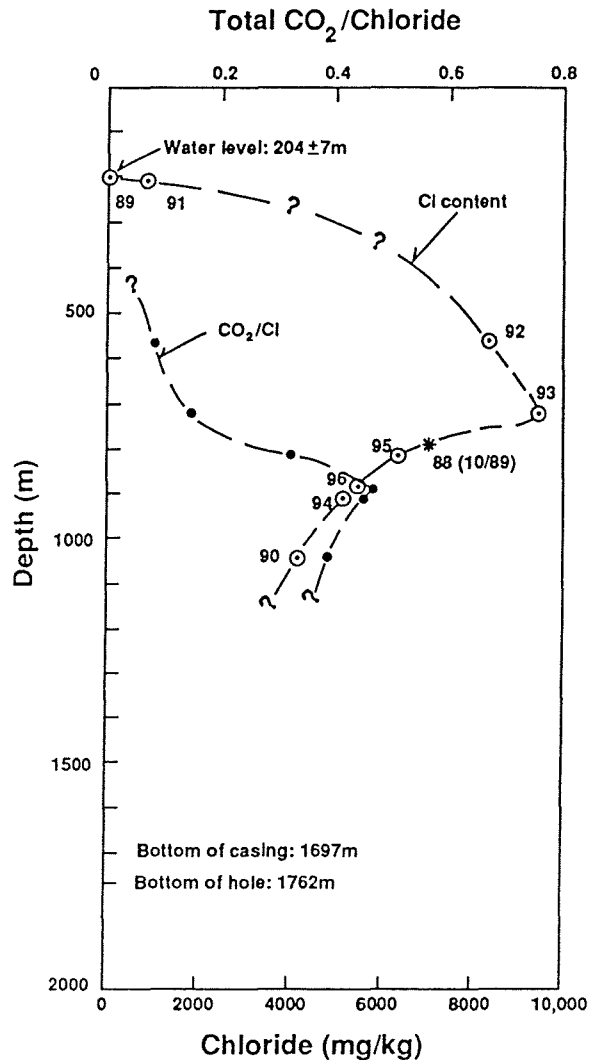

Fig. 3. Plots of depth versus chloride content and depth versus total CO_2/chloride (mg/kg basis) for *in situ* wellbore samples, VC-2B.

hand, the concentration spike may represent proof that, in some runs, additional fluid was added to the sample chambers by leakage higher in the wellbore. In such cases, a small proportion of high chloride, low CO_2 fluid is added to relatively low chloride, high CO_2 fluid, which might produce odd compositions such as samples VC2B-94 and VC2B-96.

The Eh of the fluid changes dramatically with increasing depth (Table 1) becoming very reducing (as it should be) in the lowest, and presumably, least boiled fluid that was sampled. Fluid Eh may also be affected by reaction of fluid with the steel casing because the iron (and manganese) content increases as concentration increases and Eh is partly dependent on the oxidation state of multivalent cations. Other components that have either been affected by boiling and / or reaction with casing

Table 5. Total compositions of VC-2B *in situ* samples compared to VC-2A fluid. All values in mg/kg except where noted. Chemical analyses by P. E. Trujillo, Jr. and D. Counce. Gas analyses by W. C. Evans except VC-2A (C. J. Janik, USGS) and VC2B-95 (P. E. Trujillo, Jr.).

	VC-2B								VC-2A
									[a]
Sample No.	VC2B-89	VC2B-90	VC2B-91	VC2B-92	VC2B-93	VC2B-94	VC2B-95	VC2B-96	
Date	1/17/90	1/17/90	1/17/90	1/18/90	1/18/90	1/18/90	1/19/90	1/19/90	8/27-28/87
Depth of Sample, m	~204	1045	210	500 *461*	854 *779*	904 *910*	822 *812*	872 *891*	490
Collection Temp., °C	~125	242 *140*	~128	178 *185*	197 *206*	227 *218*	207 *217*	224 *226*	210[b]
Equilibration Temp., °C									
(Qtz cond.)[c]	121	371	174	231	294	333	309	326	215
(Na-K-Ca)[c]	217	300	273	321	322	308	313	305	281
Major Elements									
SiO_2	74	882	184	383	651	781	708	760	315
As	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	1.92
Ca	13.9	78.5	25.6	135	152	91.5	112	103	5.9
Mg	0.79	0.76	1.07	1.72	1.37	1.01	1.10	1.07	0.14
Sr	0.18	1.22	0.37	1.89	2.16	1.22	1.51	1.30	0.76
Na	52.6	2350	464	4300	4960	2770	3260	2910	1842
K	13.6	700	142	1450	1645	880	1075	900	308
Li	0.85	32.8	6.04	58.9	65.1	31.2	40.9	35.8	26.5
HCO_3	71	105	104	135	121	109	109	101	273
CO_3	0	0	0	0	0	0	0	0	0
SO_4	10.4	7.8	8.8	26.0	24.1	11.2	15.1	12.0	54.8
F	0.89	5.67	0.94	2.45	4.04	3.92	3.95	4.10	5.68
Cl	83.4	4150	845	8380	9440	5155	6325	5445	2943
Br	0.27	13.6	2.64	26.8	30.0	16.3	18.8	75.1	5.9
B	1.37	29.6	8.06	66.2	71.0	37.4	47.0	39.8	25.6
Trace Elements[d]									
Ba	0.56	0.32	0.56	1.12	1.10	0.68	0.82	0.72	0.11
Co	<0.002	<0.002	0.007	0.020	0.034	0.028	0.030	0.023	<0.001
Cr	<0.002	0.005	0.002	0.004	0.003	0.009	0.008	0.008	<0.002
Cs	0.15	5.45	1.15	8.70	9.15	5.50	7.10	6.15	3.25
Fe	0.14	15.1	11.7	31.2	29.9	21.4	23.6	20.8	0.33
I	<0.01	0.21	0.03	0.35	0.41	0.22	0.26	0.21	0.2
Mn	0.14	3.74	1.14	3.35	3.01	2.12	2.89	2.20	0.01
Mo	0.006	<0.002	0.003	0.005	0.003	<0.002	<0.002	<0.002	0.004
NH_4	2.37	2.49	3.13	2.49	3.22	5.63	5.59	6.83	0.63
Ni	0.007	0.024	0.016	0.034	0.019	0.034	0.046	0.028	<0.002
Pb	<0.002	<0.004	<0.004	0.028	0.041	<0.004	<0.004	<0.004	0.003
Rb	0.16	11.5	2.15	19.3	22.6	12.7	15.3	13.6	4.30
S_2O_3	<0.01	9.12	<0.01	0.10	0.18	<0.01	<0.01	<0.01	2.3
Zn	<0.02	<0.02	0.04	6.5	5.2	0.08	0.12	0.06	0.02
Gas Components[e]									
He	---	0.0035	---	---	0.0026	---	---	0.0015	0.0017
H_2	---	1.33	---	7.03	6.24	10.7	8.14	12.6	0.0467
N_2	---	1.89	---	4.80	7.51	12.0	8.80	9.72	1.95
O_2	---	0.393	---	0.293	0.944	3.08	---	2.58	0.000
Ar	---	0.029	---	0.121	0.131	0.270	---	0.215	0.0625
CO	---	0.081	---	0.080	0.156	0.615	---	0.716	---
CH_4	---	0.860	---	3.01	6.87	5.33	8.43	6.75	0.0284
CO_2	---	1563	---	589.5	1270	2217	1834	2458	885
C_2H_6	---	0.062	---	0.151	0.294	0.220	---	0.288	---
H_2S	---	3.51	---	0.011	---	0.063	---	0.141	5.68
NH_3	---	---	---	---	---	---	---	---	2.10

[a] VC-2A values determined by averaging five analyses of samples taken during surface flow tests. Samples are VA-295 to -298 and VA-300.

[b] Formation temperature.

[c] Equations in Fournier (1981).

[d] The following elements are below the detection limits (in parentheses) for all VC-2B samples: Ag (<0.001); Al$_{(tot)}$ (<0.4); Cd (<0.002); Cu (<0.002); Hg (<0.2); Sb (<0.2); Se (<0.2); and U (<0.2).

[e] Gas analyses show samples VC2B-89 and VC2B-91 contain mostly air. Oxygen reported in other samples probably results from small leaks in GES or gas bottles.

are H_2S and arsenic. For comparison, VC-2A reservoir fluid (which was collected during surface flow tests, where water does not reside in static contact with casing) has much lower iron and much higher arsenic and H_2S.

The effect of boiling on the "equilibrium" temperature of the fluid can be seen in Table 5, which lists geothermometer temperatures. The formation temperature between 1697 and 1762 m (where fluid enters the wellbore) is 292° to 295°C. Quartz conductive temperatures from samples below 700 m exceed the formation temperature indicating that wellbore fluids are excessively supersaturated in silica with respect to quartz. This can only be partly explained by boiling because the deepest sample contains the most silica. On the other hand, equilibrium temperatures calculated using the Na-K-Ca geothermometer show slight increases over formation temperature in the boiled horizon. The lowest sample has a calculated temperature (300°C) that is very close to the formation temperature, suggesting the least change due to boiling.

Finally, the effect of the construction metal of the *in situ* chambers on fluid chemistry can be assessed by examination of data in Table 5. High-temperature water in static contact with iron casing produces excess H_2 by the reaction

$$3H_2O + 2Fe \longrightarrow 3H_2 + Fe_2O_3 \ . \qquad (4)$$
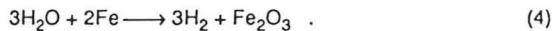
The same type of reaction may take place in *in situ* chambers made of exotic metals as suggested by the high H_2 contents of samples VC2B-90 through VC2B-96. For these six samples, H_2 contents generally increase with depth and collection temperature, whereas fluid concentrations decrease. All *in situ* samples from VC-2B were collected in the cased portion of the bore and all samples contain much more H_2 than formation water from VC-2A collected by surface flow tests. H_2S may also react with tools made of exotic metals. In some cases, these metals may react with the *in situ* fluid to release trace amounts of exotic components, such as cobalt (see Table 5).

CONCLUSIONS

A suite of eight *in situ* samples collected from core hole VC-2B in January 1990, gives the following results:

1. The two *in situ* tools either closed higher in the wellbore than their intended sampling depth or they gained excess fluid by leakage on their trips to the surface. Assuming that the *in situ* chamber is analogous to a gigantic fluid inclusion, the closure temperature can be calculated from the salinity, density, and mass of the fluid and the volume of the chamber.

2. The *in situ* samples display a remarkable zone of increased fluid concentration near the upper part of the wellbore. Interpretation of physical and chemical parameters indicates that this concentrated horizon has been caused by boiling in the wellbore. A relatively thin layer of dilute water that must be primarily condensed steam, overlies the concentrated horizon. A very thin horizon of erupting fluid mixed with air and exsolved gases occurs at the "static" water level during sampling operations.

3. High-temperature geothermal fluid, standing in a wellbore cased with steel, reacts with the steel. With respect to

VC-2B, excess H_2 is produced, iron and manganese are dissolved, arsenic is probably precipitated, and H_2S is consumed. Additional reactions of small but measurable magnitude may occur to the fluid in the *in situ* sample chamber, even if the chamber is made of exotic, corrosion-resistant metals.

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