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Evaluation and Development of Gas Geothermometry for Geothermal Exploration in the East African Rift System

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SUMMARY

The relative lack of surface thermal waters in the East African Rift System means that information about geothermal systems must often be gained from a consideration of fumarolic gas contents rather than water chemistry. This report attempts to evaluate the usefulness of gas geothermometry in defining reservoir temperatures in Rift geothermal systems.

The assessment has been approached in three ways: (i) application of existing published geothermometric equations, (ii) correction for the effects of subsurface modification of gas concentrations, by stable isotopic techniques, and (iii) development of a new geothermometer based on hydrocarbon measurements on samples collected during the present investigations. These took place in wellfields and other geothermal areas in Kenya, Ethiopia and Djibouti during the period 1987-1991. Data collected by previous workers were also used for parts (i) and (ii) above.

The main conclusions of the assessment are as follows. Application of conventional geothermometry during exploration is an uncertain process because of inconsistent results. This is undoubtedly due in part to the often rather weak surface manifestations typical in the Rift, but also in some cases perhaps to unforeseen mineral controls on gas concentrations. Stable isotopic correction of condensation effects on geothermometer results works to a certain extent, but requires a good knowledge of local hydrology for fully effective use. The new methane/ethane geothermometer developed during the course of this work appears to offer a simple way of obtaining a reasonable estimate of subsurface temperatures during exploration in most high-temperature geothermal environments of the Rift System.

RÉSUMÉ

Le manque relatif d'eaux thermales de surface dans la vallée d'effondrement d'Afrique de l'est signifie que l'information sur les systèmes géothermiques doit souvent prendre en compte le contenue des gaz de fumerolles plutôt que la chimie des eaux. Ce rapport tente d'évaluer l'utilité de la géothermomètrie des gaz en déterminant les températures du réservoir dans les systèmes géothermiques de la vallée d'effondrement.

L'évaluation fut cernée de trois façons: (i) mise en application d'équations géothermiques déjà existantes et publiées, (ii) correction des effects de modifications des concentrations souterraines des gaz par des techniques d'isotopes stables, et (iii) le développement d'un nouveau géothermomètre basé sur la quantité d'hydrocarbure des échantillons collectés lors des présentes investigations. Ceci fut appliqué dans des champs de forage et autres zones géothermique du Kenya, de l'Ethiopie et de Djibouti entre 1987 et 1991. Des données collectées par de précédents chercheurs furent aussi utilisées en (i) et (ii) cidessus.

La conclusion principale des évaluations est la suivante: Il est difficile d'appliquer la géothermométrie conventionnelle des gaz à cause de l'inconsistence des résultats. Ceci est sans aucun doute due, en partie, aux manifestations de surface, qui sont typiquement souvent assez faibles dans la vallée d'effondrement, mais aussi, peut-être dans certains cas, à d'inattendus contrôles de la concentration des gaz par les minéraux. Les corrections des effets de condensation par isotopes stables, sur les résultats des géothermomètres sont fiables jusqu' à un certain point, mais nécessitent une connaissance approfondie de l'hydrologie locale pour une utilisation totalement efficace. Le nouveau méthane/éthane géothermomètre développé dans le courant de ce projet parait offir un moyen simple d'obtenir une estimation raisonnable des températures souterraines pendant l'exploration, pour la plus-part des milieux géothermiques de hautes-températures de la vallée d'effondrement.

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This research would have been impossible without the generous cooperation of the Kenya Power and Light Company, the Geothermal Energy Project of the Ethiopian Institute of Geological Surveys and the Institut Superieur d'Etudes et de Recherches Scientifiques et Techniques of Djibouti. Particular thanks are due to Mr Zach Muna, Chief Geochemist, and Mr Musa Arusei (KPLC), Dr Abebaw Endeshaw, Project Manager, and Ato Berhanu Gizaw (EIGS), and M. Anis Abdallah, le Directeur, and M. Jama Khabar and M. Xavier Houdart (ISERST), plus their colleagues who provided such vital assistance.

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late 2	Sampling gases in the field (see also Fig. 2). The collecting funnel (bottom left) is sealed into the hot ground with clay produced by hydrothermal alteration.
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CONTENTS

1. INTRODUCTION

The East African Rift System (Fig. 1) contains many areas of geothermal activity, usually found in association with late-Quaternary volcanic centres. The generally rather arid nature of Rift climates has resulted in groundwater levels often a considerable distance below surface, and consequently few areas of natural discharge. The use of conventional (and elsewhere highly successful) cation and silica geothermometry is therefore seldom possible. Fumarolic discharges of steam and gas are however fairly common, and in most areas offer the only key to temperature conditions in the subsurface. Various gas geothermometers have been proposed, but their application to the comparatively weak fumaroles of the Rift is frequently inappropriate because the more reactive gases tend to disappear while traversing the often large distance from reservoir boil-off to the surface, and because subsurface condensation of steam changes the gas/water ratio.

The object of the investigations reported here was to assess the results of conventional gas geothermometry, to see if corrections based on local conditions could be applied to these geothermometers, and finally to develop any other apparently temperature-dependent gas phenomena for the purposes of geothermometry.

In order to gain reliable information on subsurface temperatures for control purposes, investigations were centred on areas where geothermal wells had already been drilled. These were Olkaria-Eburru (Kenya), Langano (Ethiopia) and Asal-Hanle (Djibouti).

2. BACKGROUND TO THE PRESENT RESEARCH

2.1 Exploration in the Rift

Although two geothermal wells (X1 and X2) were drilled at Olkaria in the 1950s, methodical geothermal exploration of the Rift really began in the early 1970s. With the assistance of specialists, often supported by the UNDP, systematic surface geochemical reconnaissance studies were commenced in each of the three countries. By 1991 initial exploration in both Kenya and Djibouti had been completed, though in Ethiopia (a much larger country) exploration had been largely confined to the Lakes area and the Tendaho graben.

In parallel with these exploration efforts, deep well drilling was taking place at a few specific localities: Olkaria (starting 1973), Eburru (1989), Langano (1981), Asal (1974) and Hanle (1987). Therefore in each of these areas there was at least some information about subsurface conditions, and cation and silica geothermometers applied to the deep fluids usually agreed well with measured temperatures. Away from the drilled areas, however, it was becoming apparent that conventional gas geothermometry used on fumaroles was giving widely varying and often unlikely results when it could be applied at all (Armannsson, 1987). The present project uses both existing and new gas data from all three countries to attempt a thorough review of gas geothermometry in the Rift.

2.2 Geological Setting

Broadly speaking the rift system in East Africa can be split into eastern and western parts. Although the western part possesses some active volcanoes in the Virunga Mountains, it is on the whole a non-volcanic rift. By contrast, the eastern part from Tanzania northwards to Ethiopia has fairly regularly-spaced late-Quaternary volcanoes, generally situated on the rift axis, over a distance of nearly 2000 km. Heat from the magma chambers beneath these volcanoes is the main driving force behind the numerous geothermal systems of the eastern rift (though not all hot water systems are clearly associated with

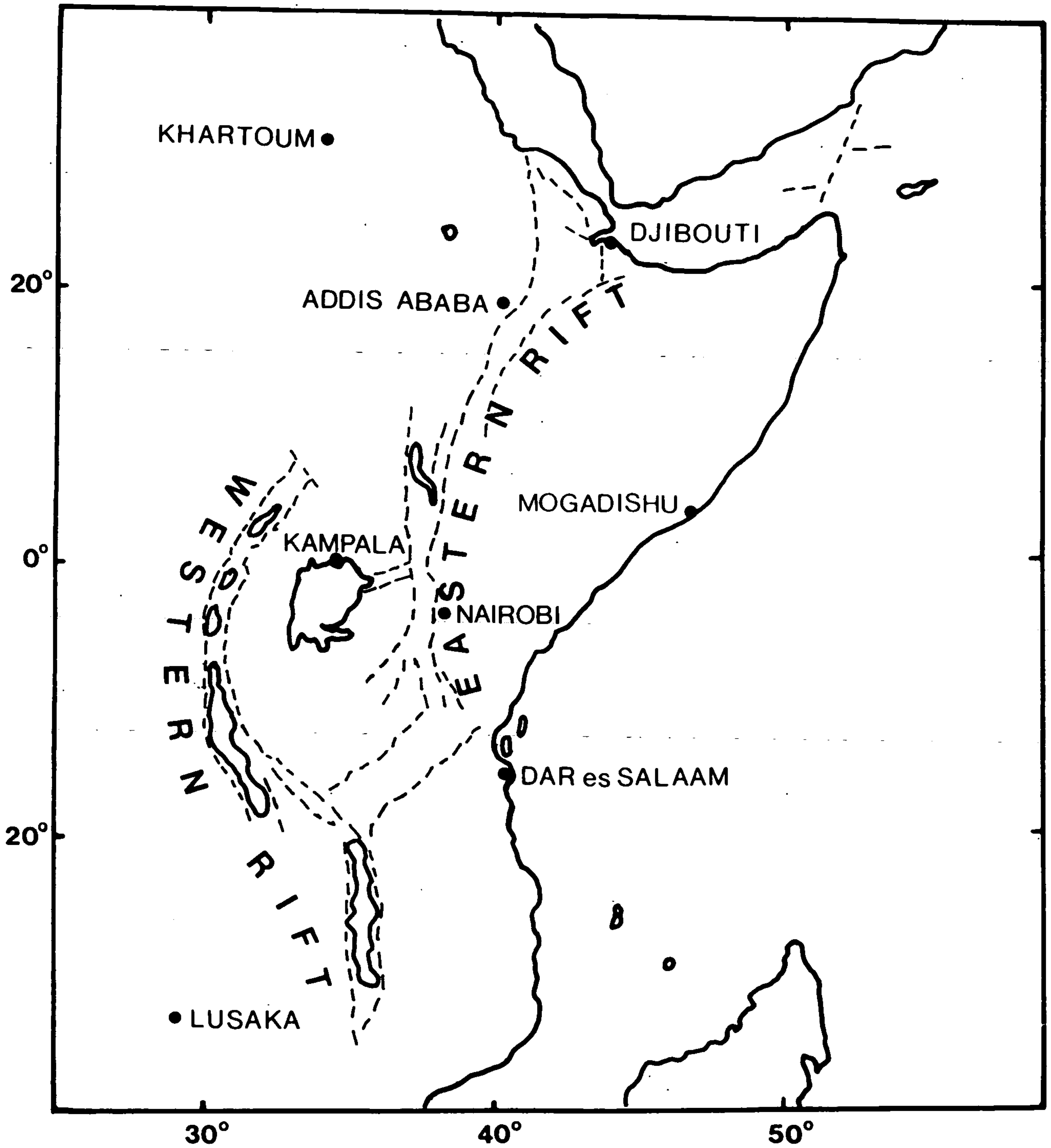

Fig. 1. The East African Rift System.

a late-Quaternary centre). The eastern rift is not however a single structure and consists of several, sometimes en echelon rifts. The most important of these for the purposes of this study are the Gregory Rift of southern-central Kenya, the South Turkana Rift of central-northern Kenya, and the Main Ethiopian Rift of southern Ethiopia. One sample locality in the branching Kavirondo Rift was also visited.

For the purposes of this report, the term ‘Rift’ will be used to represent the eastern rift system. The Rift appears to derive principally from uplift above mantle plumes and shows little sign of extension at the present day. At its northern end, the Rift dies out in the Afar triangle of eastern-central Ethiopia. This area forms a triple junction between the Rift and the actively extensional, oceanic rifts of the Red Sea and Gulf of Aden. The western end of the Aden rift emerges onto land in Djibouti, and it is on this rift that the Asal geothermal area lies. In this structural respect it has more in common with other ocean ridge-type geothermal systems such as those in Iceland than with the Rift *sensu stricto*.

However, while structural differences may have an effect on parameters such as helium isotope ratios, they probably have little effect on the main geothermal gases. Composition and amounts of these gases are much more likely to be controlled by the nature of the rocks and of the water passing through them. In both the Rift and Djibouti, igneous (mainly eruptive) rocks predominate and the few sediments present are associated with lakes (though there have been marine incursions in Djibouti). Thick sedimentary sequences are therefore missing, and the geochemical system is accordingly relatively simple compared to for example Cerro Prieto (Mexico), where sediments can contain coals and other ‘contaminants’. In Kenya and Ethiopia the water feeding geothermal systems (at least those that have been drilled) is low in total dissolved solids (TDS). Chloride, the dominant anion at depth, lies in the range 200-800 mg/kg. In contrast, the working fluid of the Asal geothermal field in Djibouti proved to be basically concentrated seawater (Cl 70000 mg/kg). The corrosive nature of such high-TDS fluids prompted investigations to take place further inland at Hanle in an attempt to find a lower-TDS fluid, but temperatures at depth proved insufficiently high to justify further exploration.

The nature of the drilled sites can be summarised as follows:

(a) All sites have a broadly similar lithology of late-Quaternary eruptive rocks with sparse sediments.

(b) Sites in Kenya and Ethiopia share a similar continental rift structure and have low TDS working fluids.

(c) Djibouti is situated on a spreading ridge with seawater as the main source of the thermal fluid at Asal.

2.3 The Existing Gas Geothermometers

Several gas geothermometers have been proposed over the years, often depending on a knowledge of the gas/steam or steam/water ratios in geothermal systems (Henley et al., 1984) and therefore of comparatively little use to surface exploration. The most comprehensive treatment of gas geothermometry to date has been that of Arnorsson and Gunnlaugsson (1985), who developed geothermometers based on fluid-mineral equilibria which they then calibrated with well temperatures and tested on fumaroles. Their results were convincing, but although the geothermometers were calibrated by reference to geothermal wells in various parts of the world (including Olkaria), they were only field tested on relatively vigorous Icelandic fumaroles. Also, to correct for condensation effects Arnorsson and Gunnlaugsson used evidence from the gas data themselves rather than attempting to use evidence from independent sources, e.g. stable isotopes.

D'Amore and Panichi (1980) proposed an empirical geothermometer based on a combination of various fluid and solid reactions believed to occur in geothermal systems coupled with terms relating temperature to oxygen and carbon dioxide partial pressures. The advantage of this geothermometer is that it requires no gas/steam ratio information, but the disadvantage is that the four gases CO_2, CH_4, H_2 and H_2S are required to use the equation effectively, and these gases cannot always be detected in the Rift fumaroles. Nevertheless it appears to be one of the few geothermometers designed for exploration work rather than for use on geothermal wells to give further information on reservoir conditions (e.g. Arnorsson et al., 1990).

Although Arnorsson and Gunnlaugsson (1985) argued against the use of methane as a gas for geothermometry (because of departures from the apparent controlling reactions), researchers other than D'Amore and Panichi have proposed geothermometers using CH_4. Glover (1972) used a simple calibration curve based on the ratio of CO_2 to CH_4 developed by Ellis and Giggenbach. The invocation of the Fischer-Tropsch synthesis reaction as a control on CH_4 concentrations has also be used to justify the only isotopic geothermometer which has been widely applied in geothermal systems, (Panichi et al., 1975).

For this study it was decided to use only geothermometers in equation form, and therefore the CO_2/CH_4 version has not been used. Equations are listed in Table 1. Solute geothermometers were used when required for temperature information on deep geothermal or hot spring waters (Table 2).

2.4 Existing and New Gas Data for the Rift

Any consideration of gases in the Rift owes much to the efforts in Kenya and Ethiopia of Glover (1972, 1976). He analysed for the usual geothermal gases (H_2, CO_2, CH_4, H_2S, N_2) and also for stable isotopes, including $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$ at Olkaria and Eburru. Unfortunately, from the point of view of possible condensation correction, although he could determine $\delta^{18}O$ he was unable to measure deuterium in fumarole condensates.

Later geochemists collected gases while working on exploration in the Rift and Djibouti, and apart from the state organisations included the BRGM (1983), UNDP (Armannsson, 1987), Geotermica Italiana Srl. (1987a,b) and the British Geological Survey (Allen et al., 1989; Allen and Darling, in press). In most cases gases as above were analysed, together with O and H stable isotope data for the fumarole condensates. In addition, Geotermica Italiana tended to analyse for carbon monoxide, and the British Geological Survey for C_{2+} hydrocarbon gases. While these two teams carried out some $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$ work in Kenya, most gas isotope work in Ethiopia was performed by Craig et al. (1977).

In all cases from Glover onwards, supporting evidence as appropriate was obtained from chemical and isotopic analysis of hot and ambient ground and surface waters. Table 3 attempts to list the areas in which various teams have worked and give details about which gases and isotopes have been analysed.

The new data from the drilled localities presented in this report are often the result of resampling wells and fumaroles for which data already exist. However, a full isotopic and C_{2+} hydrocarbon analysis was not usually available for these sites so the opportunity was taken to collect for these analyses.

2.5 BGS Sample Collection Methods

Gas samples were collected from geothermal wells (photograph, front cover), fumaroles (Plates 1 and 2) and hot springs (where water samples were also collected for complementary solute geothermometry). Usually two gas samples were collected: one as a free gas sample, and one over concentrated NaOH

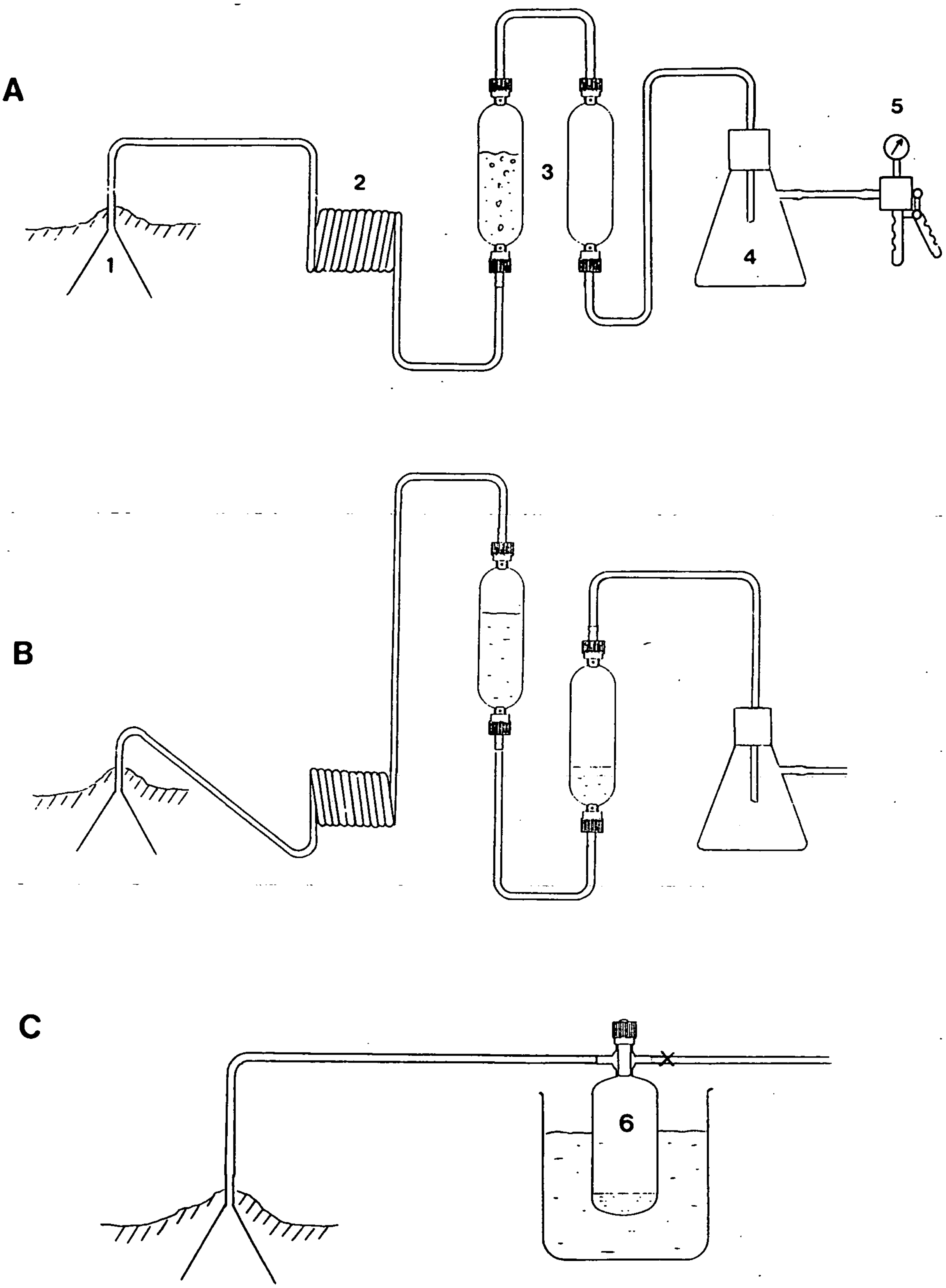

Fig. 2. Collection techniques for geothermal gases. A, steam condensate is collected in first tube by pumping. B, condensate is transferred to second tube by gravity, leaving gas sample in first tube. C, collection of combined steam and gas sample into NaOH solution. (1, collecting funnel 2, condensing coil 3, gas tubes 4, water trap 5, hand pump 6, flask containing 50 ml of 40 per cent NaOH).

solution to absorb CO_2 and H_2S. A free gas sample is considered to give a more accurate percentage analysis, while an absorbed gas sample is necessary for measurement of the gas/water ratio in steam. Free gas samples only were collected from very weak fumaroles and hot springs.

A schematic of the collection process is shown in Fig. 2. Free gases were collected from the steam source in a doubly-terminated glass tube via a condensing coil. The coil was immersed in cooling water or, where transport of cooling water was impractical, was wrapped in lint which was kept moistened (the latent heat required to evaporate water makes a highly effective cooling mechanism). Ideally the coil should be made of stainless steel, though a copper coil was used in Ethiopia and Djibouti. An arrangement of two tubes was generally employed (Fig. 2a), the first being used to trap water before being upended to fill the second (Fig. 2b). This process causes the first tube to fill with gas, and should if possible be carried out under a combination of gravity and gas pressure to minimise the possibility of air contamination. However, weak fumaroles required some assistance from the hand-pump. The water collected during the process was sub-sampled for stable isotope analysis. Plate 2 shows the apparatus in use.

Samples intended for determination of gas/water ratio were collected directly from the steam source into pre-evacuated singly-terminated flasks containing 50 ml of 40% NaOH solution (Fig. 2c).

Gases from warm and hot springs were collected in a variety of ways depending on the nature of individual springs. For very gassy springs, such as Lorusio and particularly Bala (K53), a method similar to Fig. 2b was used. For cooler, less gassy springs a method resembling Fig. 2c was employed, except that NaOH was not used.

In all cases, great care was taken to purge all atmospheric gases from the various tubes and vessels involved in the collection of geothermal gases.

Water samples from all sources intended for isotopic analysis were collected in an unfiltered state and stored in 28 ml glass McCartney bottles. Each water sample for chemical analysis from springs was passed through 0.45μ filters and stored in two 30 ml Sterilin tubes, one acidified with concentrated nitric acid (AnalaR grade). A third tube, diluted 1:10 with distilled water, was usually collected from boiling springs in order to measure silica.

2.6 BGS Analytical Methods

Analysis of gases other than H_2S was carried out by chromatography on free gas samples using Porapak and MS5A columns and TCD and FID detectors. H_2S and CO_2 concentrations in steam were determined by titration of the NaOH condensate.

Isotope analysis of gases was carried out on the free gas sample for $\delta^{13}C_{CO2}$ and (usually) on the condensate sample for $\delta^{13}C_{CH4}$. CO_2 gas was prepared for mass spectrometry by freezing out the water vapour at about -60°C. CH_4 was first converted to CO_2 over CuO at 850°C, then dried as above. Analysis was carried out on a VG 602E mass spectrometer at BGS Wallingford.

Supporting chemical and isotopic analysis of condensates and waters was also carried out at BGS Wallingford. Cations, SO_4 and Si were analysed by ICP, anions by automated colorimetry and HCO_3 by titration. Standard zinc reduction and CO_2 equilibration techniques were used to prepare waters for isotope analysis.

3. EVALUATION OF THE PUBLISHED GAS GEOTHERMOMETERS

3.1 Geothermal Wellfields

The results of gas and isotopic analyses from selected geothermal wells at Olkaria and Eburru (Kenya), Langano (Ethiopia) and Asal (Djibouti) are included in Tables 4 to 9 together with some fumarole and hot spring gas measurements. The geothermometry equations from Table 1 have been applied and the results listed in Table 10.

Clearly, the ultimate test of a gas geothermometer is whether or not it agrees with dependable downhole temperature data. For the purposes of this project it was decided to use solute geothermometry (average of the SiO_2 and Na/K geothermometers, Table 2) as a normally reliable indicator of reservoir temperature, rather than the measured well temperature which can be affected by unpredictable factors.

If the geothermometers are working as designed, the result of a plot versus reservoir solute temperature (T_{res}) should approximate to a 1:1 straight line. However, when plotted in this way (Fig. 3) the scatter of points is sometimes rather large (as for the CO_2 concentration and ratio versions) or, if linear, does not show the expected relationship with temperature (for example the D'Amore-Panichi geothermometer). The remaining geothermometers tend to cluster on the line if they are the high-temperature version, but otherwise to fall beneath the line. The most reliable temperatures are obtained from the H_2S and H_2 >500 mgl^{-1} concentration geothermometers, but for all T_{res} values below 300°C these are inappropriate (except for Asal 3), because chloride values are known to be mostly below 500 mgl^{-1}.

A second test of the published geothermometers is on wellfield (or near-wellfield) fumaroles. At Olkaria (Fig. 4) it is clear that there is seldom agreement between the different calculated temperatures (Table 11) for each site, although it is not necessarily a coincidence that within the spread of values one or two are similar to an adjacent well temperature. No one geothermometer stands out as being consistently closer to reservoir temperatures than another, though on this relatively small sample of sites the H_2 geothermometer gives the most plausible temperatures. Unfortunately not all the fumaroles at Olkaria possess a detectable concentration of hydrogen, and therefore the H_2 temperatures cannot always be calculated. The CO_2 temperatures sometimes appeartoohigh but generally are more likely than would have been predicted from the wellfield results. H_2S temperatures are far too low. The latter are calculated according to the "<300°C and <500 mgl^{-1} Cl" version of the H_2S geothermometer, and would give more plausible temperatures if the alternative version were used. The dual version geothermometers pose the question of whether to follow the rules of use or to choose the more likely temperature. The D'Amore-Panichi geothermometer gives a set of low to medium temperatures for the Olkaria fumaroles. It should be mentioned here that this geothermometer was only used when at least three out of four of the gases in the equation had measurable concentrations. Although detection limit values or a default value of 0.001% are permissible according to D'Amore and Panichi (1980), it was felt that two such values in a calculation might be straining the applicability of this geothermometer. The ^{13}C geothermometer invariably gives high temperatures, sometimes excessively so. The conventional geothermometers can therefore be said to have yielded inconsistent results at Olkaria, both when applied to wells and fumaroles.

At Langano the wellfield area is smaller and there are fewer wells and fumaroles (Fig. 5). However there are some gas analyses for five of the geothermal wells and for seven fumaroles, collected by the UNDP (Glover, 1976), the EIGS (Gizaw, 1989) and the BGS (this report).

In the wellfield, reservoir solute temperatures range from 236 to 309°C except for LA-7 on the western side which indicates 214°C. Hydrogeological

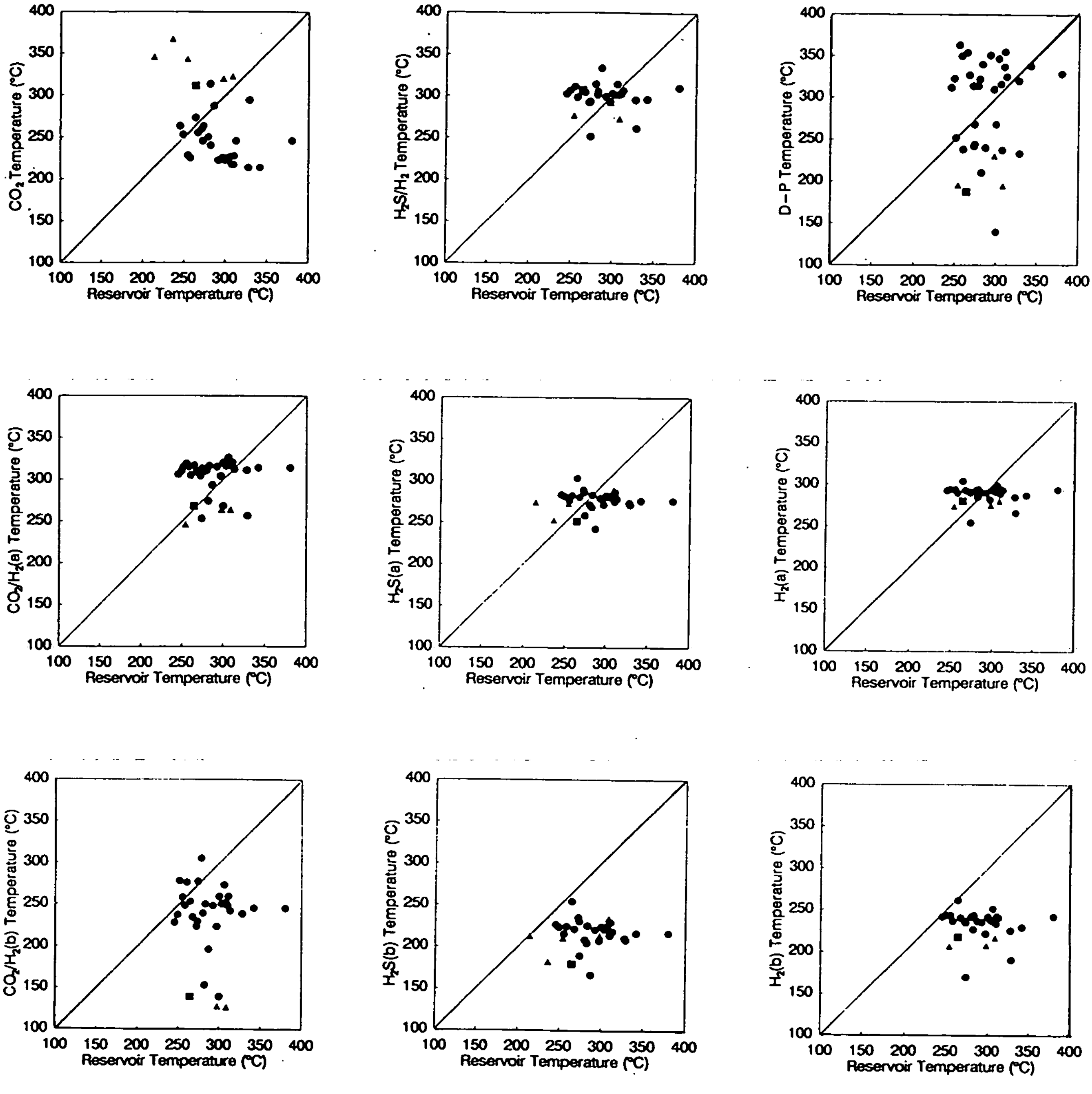

Fig. 3. Gas geothermometry temperatures plotted against reservoir temperatures for geothermal wells in Kenya, Ethiopia and Djibouti (for data refer Table 10). Key: Olkaria - circles, Langano - triangles, Djibouti - square. (a) and (b) refer respectively to the >500 and <500 mgl^{-1} Cl versions of the H_2S, H_2 and CO_2/H_2 geothermometers, D-P refers to the D'Amore-Panichi geothermometer (Table 1).

considerations and the occurrence of hot springs indicate outflow to the south of the Aluto complex, towards Lake Langano. Thus more rapid cooling towards the eastern and western margins of the complex rather than the south would be expected. With reference to Fig. 3 it is apparent that the set of results for the correct salinity (<500 mgl^{-1} Cl) geothermometers falls well short of the solute temperatures. The CO_2 temperatures are rather high and D'Amore-Panichi temperatures too low. The >500 mgl^{-1} Cl geothermometers give the best fit. The use of the gas geothermometers is constrained for most of the fumaroles by a lack of detectable hydrogen, with most of the manifestations being weak and highly contaminated by air. Only at Gebiba (E05) is a full suite possible. Agreement between the CO_2 and 'correct' H_2S geothermometers is in general not good; the gap is never less than 130°C and often much more. Even for the >500 mgl^{-1} Cl version the gap always exceeds 50°C. Some of the CO_2 temperatures are unrealistically high (>300°C) probably owing at least partly to subsurface steam condensation. More reasonable CO_2 temperatures are found to the south of the wellfield along the outflow zone, but still appear rather high. Temperatures given by the 'wrong' H_2S geothermometer seem much more likely, being mostly in the range 200-300°C. The D'Amore-Panichi geothermometer often gives very low temperatures while the ^{13}C geothermometer is much too high.

The conclusions drawn from conventional gas geothermometry applied to the Aluto complex are as follows. Where unmodified gas samples can be obtained as in the wellfield, the 'wrong' >500 mgl^{-1} Cl geothermometers are in fair agreement, and are on average within 25°C of the respective T_{res} values. It is less easy to judge how well the geothermometers function for the fumaroles, but CO_2 temperatures are almost certainly too high. In the absence of hydrogen, H_2S usually gives the only reasonable temperatures, but again only in the 'wrong' version.

Although five wells have been drilled at Asal, only a gas analysis from No. 3 (D01, location Fig. 6) was available for this report. The results of conventional gas geothermometry on this well are given in Table 10. The 'correct' H_2S, H_2 and CO_2/H_2 geothermometers are each within 15°C of the reservoir temperature (264°C), but the CO_2 and H_2S/H_2 are in poor agreement. A fumarole near Asal 5 (D02) gave similar results (Table 11), with comparable temperatures from the H_2S, H_2 and CO_2/H_2 geothermometers, and high temperatures from the CO_2 and H_2S/H_2 versions. The position of the other fumaroles in the wellfield area is not known with certainty, but most are also in the Fiale area (Geotermica Italiana Srl, 1987b) shown in Plate 3 (map in Fig. 6, inset). As if typical for Rift fumaroles, H_2S and H_2 cannot always be detected. However, the available geothermometers, notably CO_2/H_2, give similar temperatures mostly in the 200-300°C range (Table 11). It should be noted that high temperatures were measured at the bottom of the Fiale well A-5 (up to 355°C). The geothermometer temperatures obtained may reflect the influence of an upper, cooler reservoir, or may simply be wrong. The sample from Nord Ghoubet (D03) gives similar temperatures but the fumarole is likely to overlie a somewhat cooler reservoir than the main rift zone and so the CO_2 and H_2S may be the most representative temperatures. At Garrabays (D04) inland in the Hanle area (Fig. 6) the two possible geothermometers (CO_2 and H_2S) give very much lower temperatures averaging 153°C (Table 11), but these are likely to be correct since a nearby exploration well gave a maximum temperature of only 124°C (Zan et al., 1990).

In Djibouti therefore the gas geothermometers (with the exceptions of the D'Amore-Panichi and ^{13}C versions) seem to acquit themselves relatively well, particularly for the fumaroles where H_2-based geothermometers give the most consistent results overall. This is fairly remarkable given the weak output of some of the fumaroles.

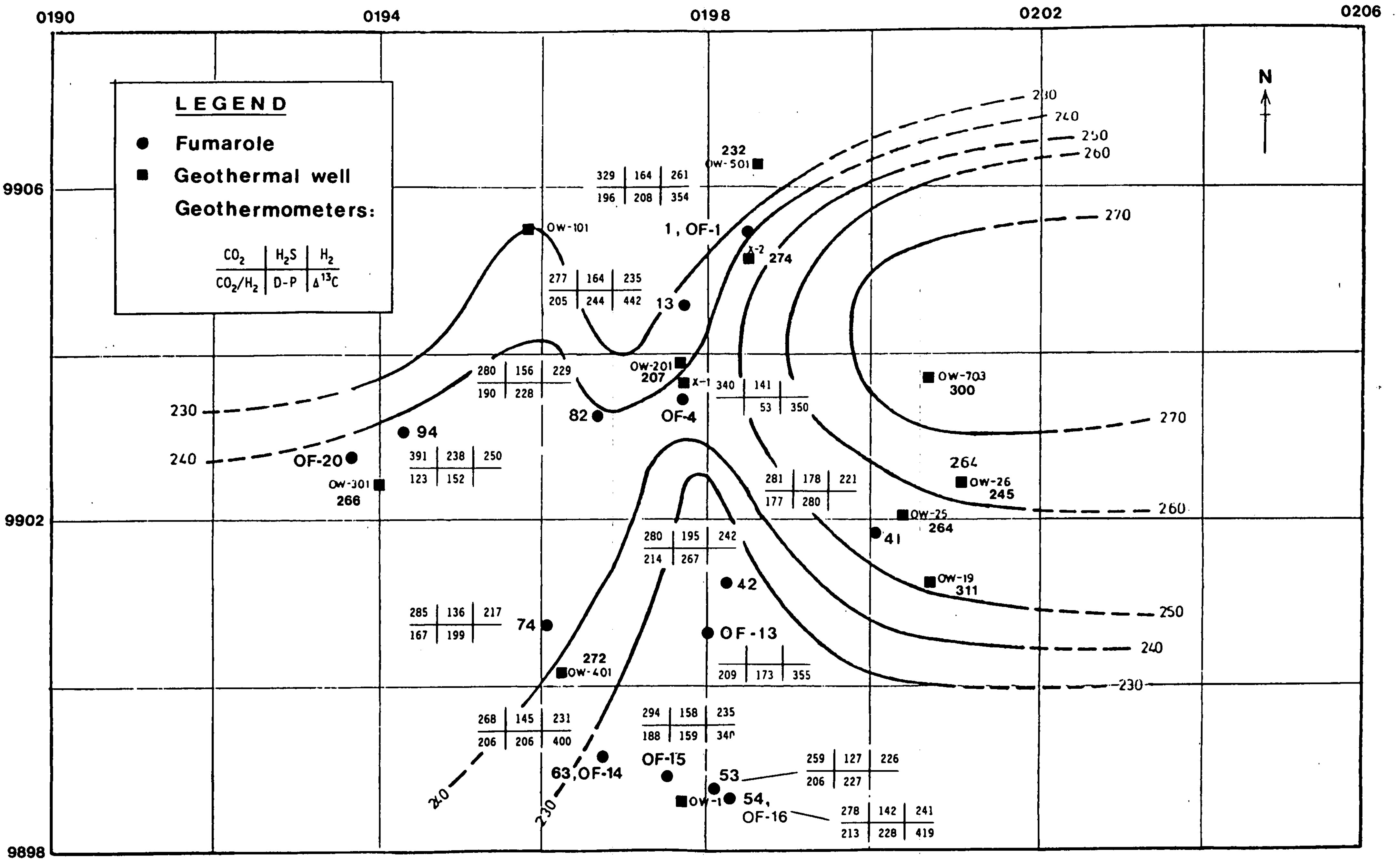

Fig. 4. Olkaria, location of sampled fumaroles with gas geothermometer temperatures. T_{res} values for nearby wells are also shown (refer Table 10 and Muna, 1984). Contours (in °C) are those inferred by KPLC for 1000 m asl. Grid numbers refer to UTM grid. (Map adapted from Haukwa, 1986).

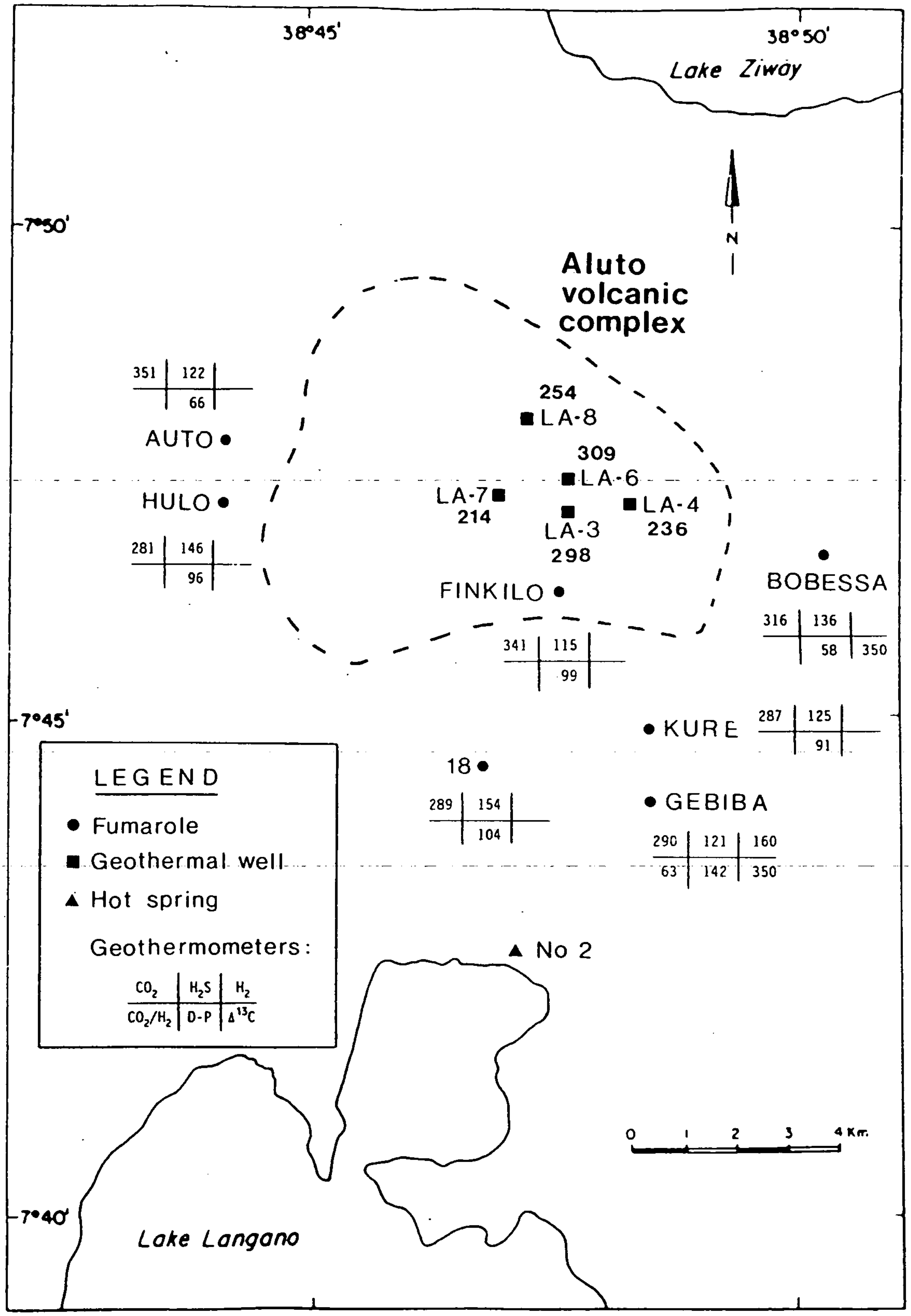

Fig. 5. Langano, location of sampled fumaroles with geothermometer temperatures. T_{res} values for wells are also shown (refer Table 10). (Map adapted from Endeshaw, 1988).

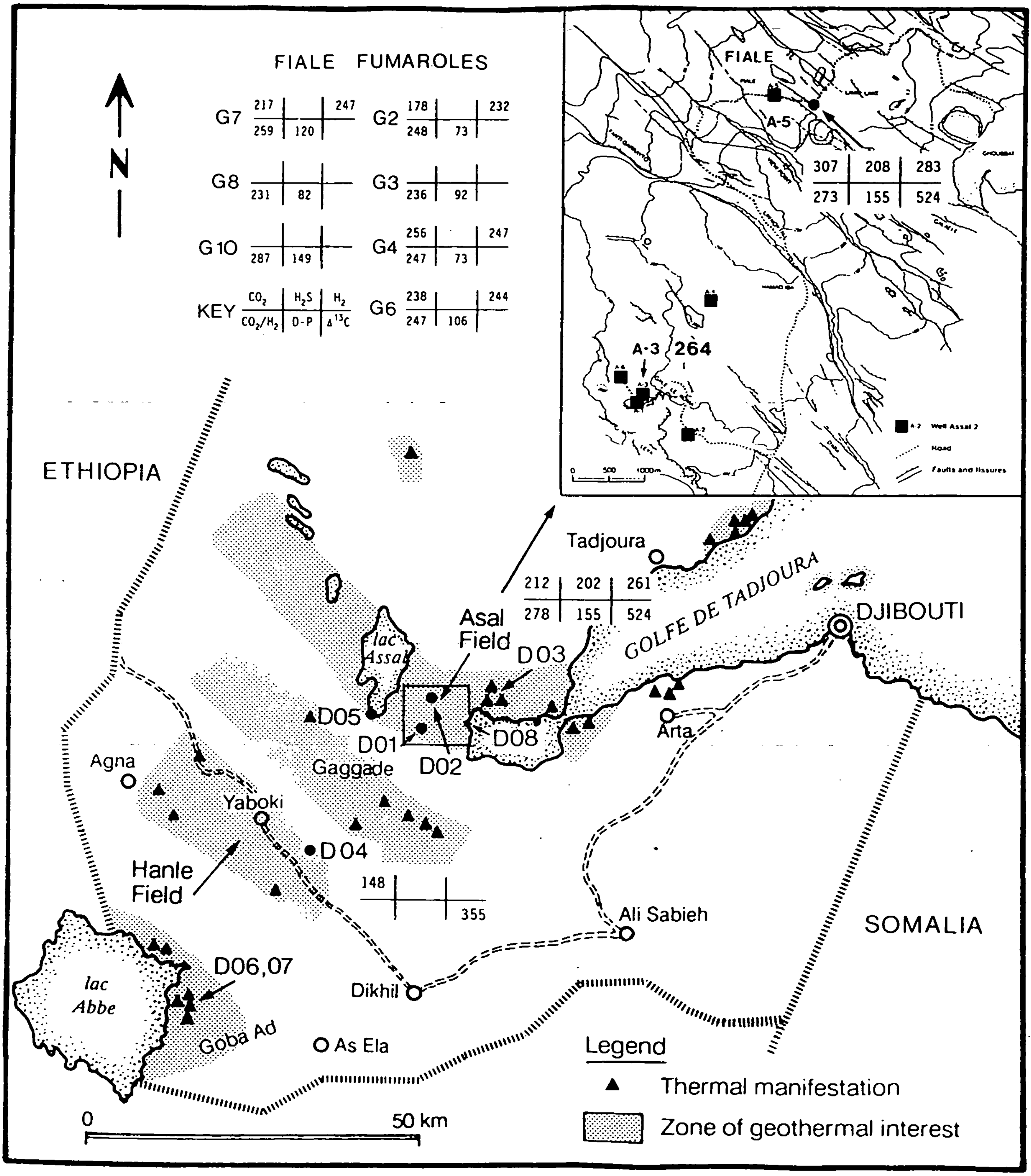

Fig. 6. Djibouti, location of sampled fumaroles with geothermometer temperatures. T_{res} value for well A also shown (refer Table 10). Inset: the Asal geothermal field. (Map adapted from Khaireh, 1989).

3.2 Undrilled Geothermal Areas

Many fumarolic areas exist away from the drilled areas of the Rift and these are now examined, though in less detail than the wellfield areas because of the lack of good control samples. Nevertheless supporting geological and geochemical evidence is available to permit some qualitative judgement about the effectiveness of the conventional gas geothermometers.

South and east of Olkaria, Armannsson (1987) applied the conventional geothermometers to the Suswa, Longonot and Domes areas. He found that CO_2 temperatures in general seemed too high, while the H_2 and H_2S geothermometers often could not be used because concentrations were below detection. The best results appeared to come from the appropriate (<500 mgl^{-1} Cl) H_2 geothermometer in the relatively few cases where it could be applied.

In the Menengai-Bogoria area steam and gases from fumaroles were collected by Glover (1972) and Geotermica Italiana Srl (1987a). The geothermometry equations were used with their results to produce the relevant data in Table 12. The composition of hot spring waters at Bogoria suggests that once again the <500 mgl^{-1} Cl geothermometers are the most appropriate; the most consistent results are obtained from H_2S (average 162°C) and H_2 (average 182°C). Solute geothermometry on the Bogoria springs indicates temperatures of 150°C, but according to the mixing models of Geotermica Italiana temperatures at depth might be 190°C. This range of temperatures is consistent with the H_2S and H_2 results, and also the D'Amore-Panichi temperatures. On the other hand, three-quarters of the CO_2 geothermometer results are above 300°C and are therefore probably inaccurate.

To the north of Lake Bogoria virtually all geothermal survey work in the Kenya Rift has been carried out by the BGS. Fumarolic activity is associated with the volcanic centres of Ol Kokwe, Korosi, Paka, Silali, Emuruan Gogolak and the Barrier (Fig. 7). This work is reported in Allen and Darling (in press) and the gas geothermometry results are reproduced in Table 12.

There are considerable differences between the four centres studied in detail (Korosi, Paka, Silali and Emuruan Gogolak). The amount of surface geothermal activity and differences in geochemical parameters such as presence or absence of detectable H_2 and relative amounts of ^{3}He point to a ranking of prospects in declining order of Paka-Silali-Emuruan Gogolak-Korosi, with the last by some way the poorest. To what extent do the geothermometry results reflect this ranking? If the geothermal reservoir(s) responsible for steam production are similar to others in the Rift as a whole, then Cl concentrations are likely to be <500 mgl^{-1} and therefore the second set of geothermometry equations would apply. Of these the H_2S and H_2 give consistent results, though H_2 is not always detectable (especially at Korosi). Agreement between averages of each particular geothermometer is not consistent: at Korosi 7°, Paka 55°, Silali 25°, Emuruan Gogolak 89°C. However for some of the centres these geothermometers accord with other evidence: for example a temperature around 200°C seems appropriate for Korosi. On the other hand temperatures for Paka and Silali averaging less than 225°C appear to be too low. The >500 mgl^{-1} Cl geothermometers give significantly higher temperatures but again fail to agree consistently with other indicators. The CO_2 geothermometer once again gives temperatures which are implausibly high, especially for Korosi. Notwithstanding this, if all the geothermometers are averaged for each centre, the expected overall ranking proposed above still applies. The technique of averaging temperatures for each centre may be crude, but provides the only rapid means of comparison. The D'Amore-Panichi geothermometer often gives temperatures which are far too low, unlike the Menengai-Bogoria area but similar to the southern part of the Kenya Rift and parts of Ethiopia (see below). The ^{13}C geothermometer gives the usual high and very high temperatures.

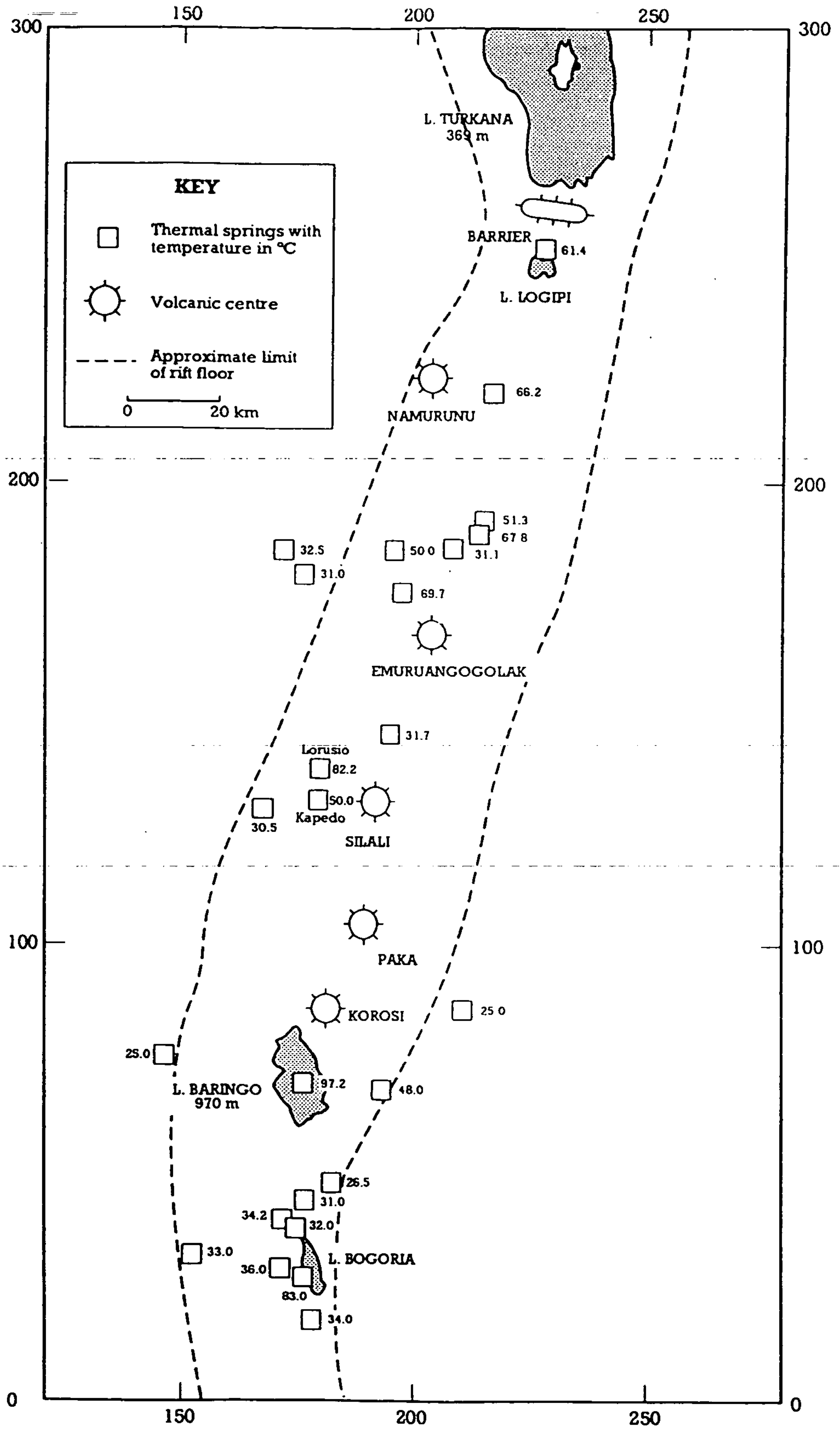

Fig. 7. The Northern Kenya Rift showing the location of the late-Quaternary volcanic centres between Lake Baringo and Lake Turkana. UTM grid points shown.

Apart from the volcanic islands in Lake Turkana, the next fumarolic area to the north is that of the Lakes area of the Main Ethiopian Rift (MER). This area was investigated by Glover (1976) and Craig et al. (1977) who concentrated on gases and isotopes respectively. As in the Kenya Rift, fumarolic activity is mainly associated with late-Quaternary volcanic centres, the principal ones of the Lakes area being Corbetti and Aluto (Fig. 8). To the north, before the MER widens to merge with the Afar triple junction, are other centres some of which, particularly Fantale, most resemble the volcanoes of the northern Kenya Rift. These are less well-explored than the centres of the Lakes area.

The northernmost major centre of the Lakes area, Aluto, has already been considered in relation to the Langano geothermal field situated within the caldera area. The Corbetti complex appears to be basically a caldera structure with two main volcanoes, Chebbi and Urji. Fumarolic areas are relatively common (Fig. 8, inset), though gas concentrations are often low with large amounts of air being present. In many cases H_2S and H_2 were below detection and most of the geothermometers could not be used (Table 13). The remaining CO_2 geothermometer invariably gives temperatures in excess of 300°C which are unlikely to be correct especially for sites towards the edge of or outside the caldera, such as Koka (E09). Only at this site were all gases detectable. The site is likely to be situated above any outflow from the caldera, which would presumably on hydrogeological grounds be directed towards Lake Shalla. However, the probably appropriate (<500 mgl^{-1} Cl) set of geothermometers gives temperatures of 103°C or less, except for H_2 which gives an average of 160°C. The higher Cl geothermometers give temperatures averaging from 196°C to 296°C. The springs sampled by Craig et al. (1977) to the north on the edge of Lake Shalla gave silica temperatures of ~120°C. If these represent cooled outflow from Corbetti then the Koka temperature might be of the order of 160°C. However the Shalla basin may itself be a major caldera structure (very high $^3He/^4He$ ratios were found in the area by Craig et al., 1977), and there may be a complex connection with the Corbetti area (Mohr, 1963). Insufficient is yet known about the hydrogeology of the area to draw further conclusions about Koka.

Further south is situated the Kiraka centre, and south of this the large boiling springs of Abaya, situated to the north of the eponymous lake (Fig. 8). The springs when not drowned fumaroles (frying pans) have Cl in excess of 500 mgl^{-1}, and this set of geothermometers gives temperatures of 199-264°C (Table 13) for Abaya and Duguna. However the <200°C geothermometers give temperatures in the range 130-198°C, which are in agreement with the adiabatic quartz geothermometer result of 197°C for Abaya #6 (E12). Although CO_2 temperatures are again over 300°C, the D'Amore-Panichi geothermometer for both this area and Corbetti gives temperatures usually considerably less than surface boiling point, while in both areas the ^{13}C geothermometry temperatures appear implausibly high.

In the Tendaho graben area of Afar (Fig. 8), Glover (1976) measured over a dozen fumaroles. There were no hot springs available for sampling in the immediate vicinity and therefore little is known about the salinity of fluids at depth, although in this part of the Rift system they are likely to be more saline than further south, and therefore the >500 mgl^{-1} Cl geothermometers may be appropriate. According to the evidence of Glover (1976) and Craig et al. (1977) these are relatively strong fumaroles with detectable H_2S and H_2, and little air contamination. Geothermometer values are given in Table 13, calculated from the data of Glover.

At Loggia the agreement between all the geothermometers except CO_2 is excellent when the crude averages for seven sites are considered. The following averages are obtained: H_2S, 215°C; H_2, 221°C; CO_2/H_2, 231°C; H_2S/H_2, 227°C. Unlike most other fumaroles in the Rift system, CO_2 gives a lower average temperature of 183°C. The results from the three Dubti sites are also consistent (including also CO_2) and rather higher, in the range

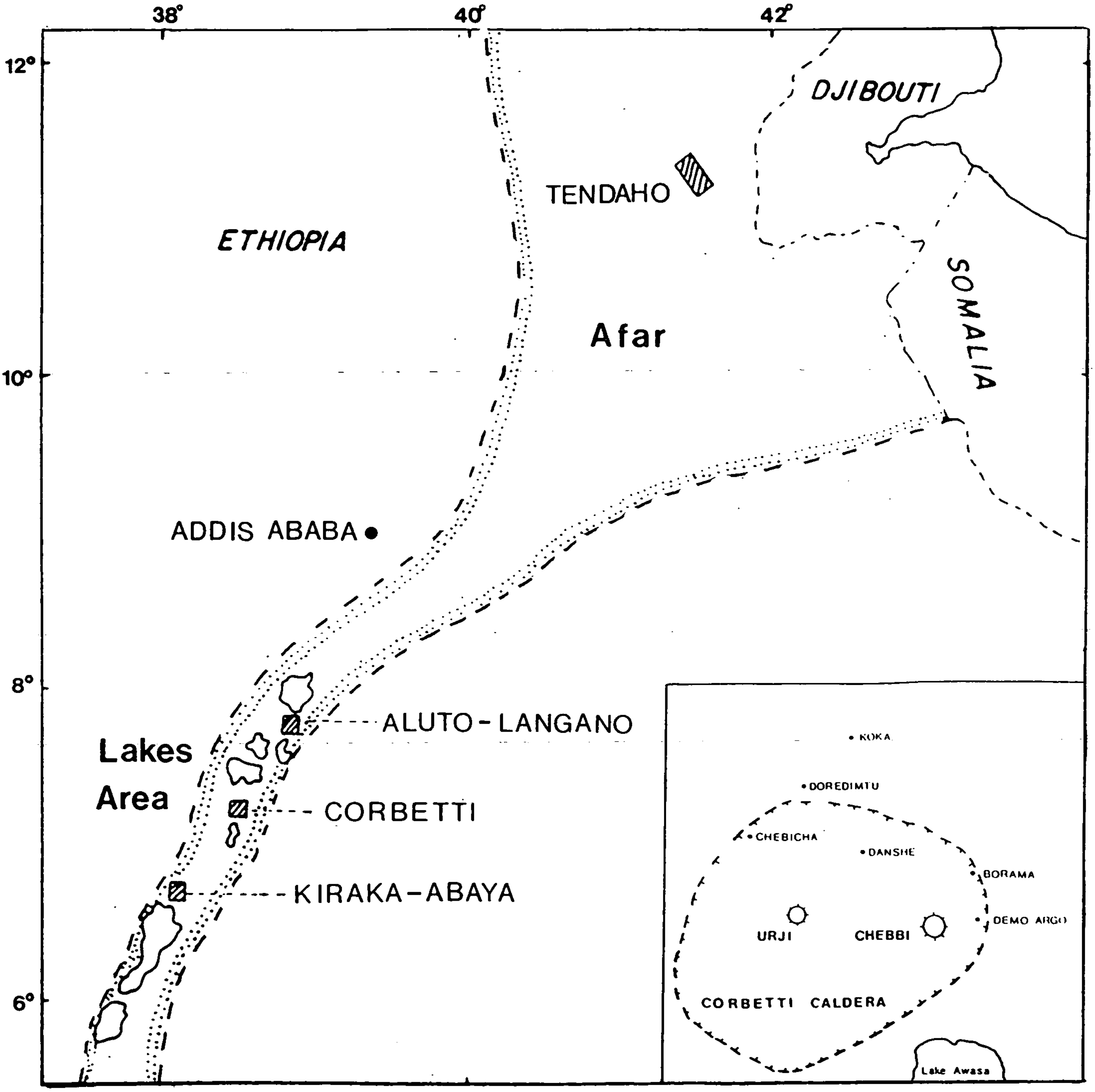

Fig. 8. The Main Ethiopian Rift and Afar, showing the areas where gas geothermometry has been applied. Inset: the Corbetti volcanic complex with fumarole locations. (Map adapted from Endeshaw, 1988).

(based on averages) 263-287°C. The credible CO_2 temperatures suggest that in Afar calcite is genuinely controlling CO_2 concentrations and that underground steam condensation is not an important modifying process locally. This may be particularly the case at Dubti, where the assumption underlying the empirical D'Amore-Panichi geothermometer may also be most closely realised.

3.3 Assessment of the Performance of the Published Gas Geothermometers

The verdict on performance of the conventional geothermometers in the Rift must be one of inconsistency. Locally all the geothermometers can be seen to perform consistently (e.g. in Djibouti, and at Dubti in Afar). This is perhaps because these sites are not in the Rift proper, where the 'wrong' minerals may be controlling gas concentrations (see for example Armannsson, 1987). Apart from these areas, the CO_2 geothermometer very often gives temperatures which are unrealistically high, and the other, salinity-dependent, geothermometers often give unlikely temperatures for likely salinities, and *vice versa*. Often these other geothermometers cannot be applied at all because concentrations of H_2S and H_2 are too low.

The difficulty in using these geothermometers for exploration purposes in the Rift system therefore lies in knowing which of them to use in particular circumstances. However, little indication of what these circumstances might be has emerged from the present study. Corrections to alterations of gas concentrations in steam occurring after boil-off appear to offer the best chance of obtaining more realistic results from the geothermometers, although only subsurface condensation effects appear to be amenable to treatment, and only in certain cases. This is treated in more detail in the next section.

The almost total failure of the $\delta^{13}C_{CO2-CH4}$ geothermometer to agree with any measured or likely subsurface temperature (at least in the upper levels of geothermal reservoirs) casts doubt that C isotopic equilibrium is ever being attained in Rift geothermal systems. From the evidence of C_{2+} alkane measurements it seems likely that CH_4 is being produced from organic sources rather than a CO_2 + H_2 (Fisher-Tropsch) synthesis, and although this does not preclude the eventual attainment of ^{13}C isotopic equilibrium between CO_2 and CH_4 it has been calculated (Giggenbach, 1982) that this may require time periods of the order of 10^7 years at 300°C. The alternative to disequilibrium is the assumption that equilibrium has been obtained, though at a much greater depth and therefore temperature. While this might be possible in some cases, it is unlikely to apply to hot spring systems like Bala (K53, Kavirondo Rift) or to gas produced by dry boreholes like Carbacid at Kerita (K237, on the eastern Rift shoulder in Kenya) which give similarly high ^{13}C temperatures.

It must be emphasised that the published geothermometers have been evaluated here solely in terms of what they can reveal about reservoir temperatures. The various inconsistencies in performance do not necessarily render the geothermometers ineffective for other purposes; the observed differences may well be interpretable in terms of defining reservoir properties and fluid dynamics, although this is outside the scope of the present report.

4. CORRECTION OF GAS GEOTHERMOMETERS USING STABLE ISOTOPES

4.1 The Principle

While subsurface steam condensation is but one of several processes which can affect gas concentrations (see Section 3 above), it appears to be the only one which can in principle be quantified. The use of stable isotopic techniques rather than the internal comparison techniques of Arnorsson and Gunnlaugsson (1985) allows correction to be made to all the geothermometers.

In cases where there is subsurface condensation of steam that is travelling towards a fumarole, apparent concentrations of gas relative to steam will

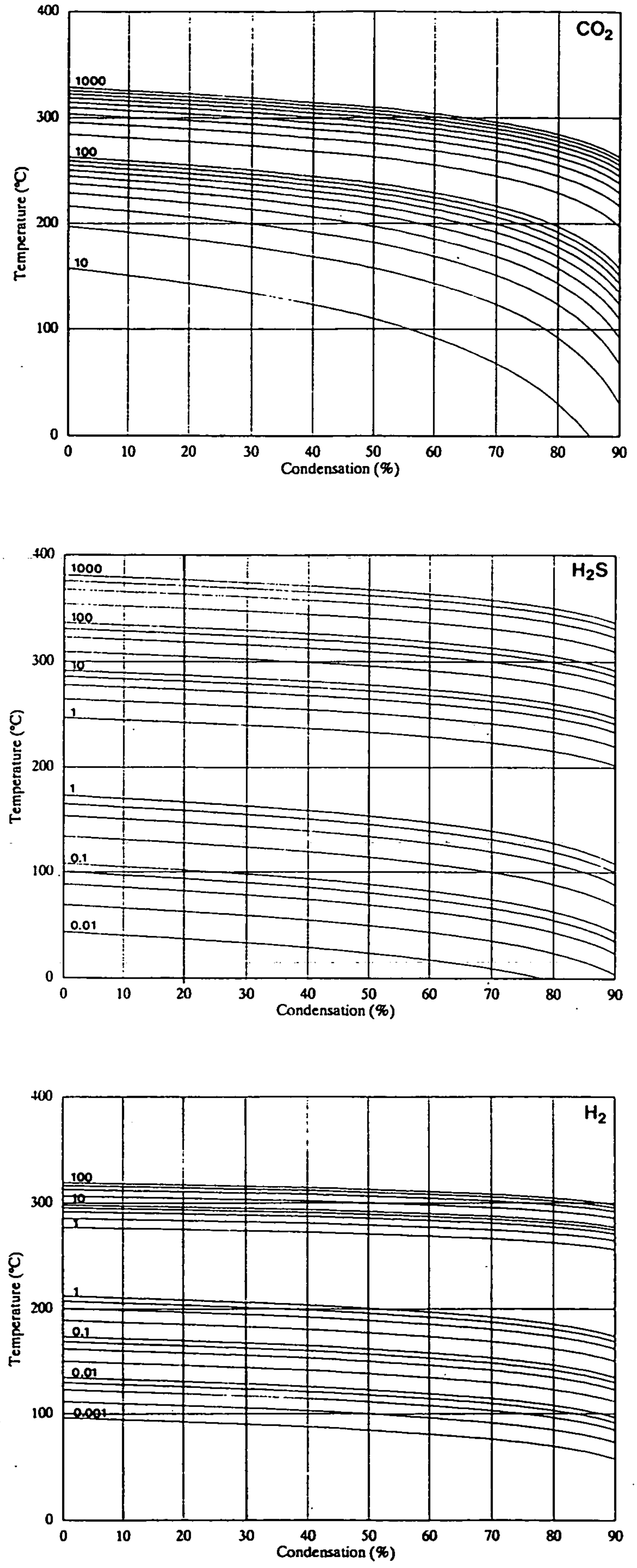

Fig. 9. The effect of steam condensation on calculated temperatures for the CO_2, H_2S and H_2 geothermometers of Arnorsson and Gunnlaugsson (1985). Gas concentrations in mmole per kg steam.

increase and therefore increase geothermometry temperatures. If the isotopic composition of the reservoir before boiling is known or can be inferred, some estimate of the degree of condensation suffered by the steam at each fumarole can be attempted. It is assumed that all fumarole steam is the result of single-stage (maximum-fractionating) separation. In some cases steam isotope composition will fall on or near the single-stage temperature curve, indicating little or no condensation, but in other cases steam may be considerably more depleted in heavy isotopes due to their preferential dropout during condensation. It is assumed for present purposes that such highly-depleted steam can be related to the original water composition by a Rayleigh-type relationship, as proposed in Darling and Armannsson (1989). The equation is

$$(1000 + \delta_r)/(1000 + \delta_i) = f^{\alpha-1}$$

where δ_r = isotopic composition of steam remaining after condensation; δ_i = initial isotopic composition of the steam; f = fraction of steam remaining; α = relevant fractionation factor for a particular temperature.

This relationship can be used to calculate the fraction of steam which has dropped out by condensation. Gas concentrations can then be adjusted and the new geothermometric temperatures calculated. Fig. 9 shows the effects of assuming that a particular gas concentration is the product of varying amounts of steam loss. It can be seen that as more condensation takes place, a given measured concentration could represent a significant temperature range, particularly for CO_2.

One problem in using such a correction is that the isotopic composition of the deep water may not be known with any certainty. However there are often clues from other sources as to what it may be. Another problem is that the processes producing the final steam and gas mixture may be more complicated than the simple condensation-after-single-stage-separation model would suggest. Nevertheless, Fig. 10 shows the basis of attempts to correct apparently condensed fumarole gas samples by use of the isotope technique in different areas of the Rift system where it appears to be feasible. The isotopic composition of steam undergoing progressive condensation is predicted by use of the Rayleigh equation. Radiating lines are temperature-controlled, while the parallel lines represent the fraction of original steam remaining at various stages in the condensation process. Estimated starting compositions for the deep fluid and resulting single stage steam are shown in each case. The position of individual fumaroles on the plot is then translated to an uncondensed steam fraction term. The results are then used to recalculate the conventional gas geothermometers and are given in Table 14. It is clear that only the concentration geothermometers can be modified by these techniques.

4.2 Application to Fumaroles

In the Suswa area CO_2 temperatures generally over 300°C are lowered to the 270-300°C range. To the north, in the Olkaria area, condensation does not appear to be a major factor and no correction has been applied. Not enough is known about deep thermal water in the Menengai-Bogoria area to attempt any isotopic correction. However, north of Lake Baringo the correction has been applied to certain fumaroles on Korosi and Silali. The CO_2 temperatures on Korosi, previously far higher than any supporting evidence would suggest, are reduced, though are still around 300°C. (KR34, the most condensed steam sampled in the Rift so far, has not been corrected because its extremely depleted composition may be the result of special factors). The 'correct' (<500 mgl^{-1} Cl) H_2S geothermometer gives amended results which are rather low.

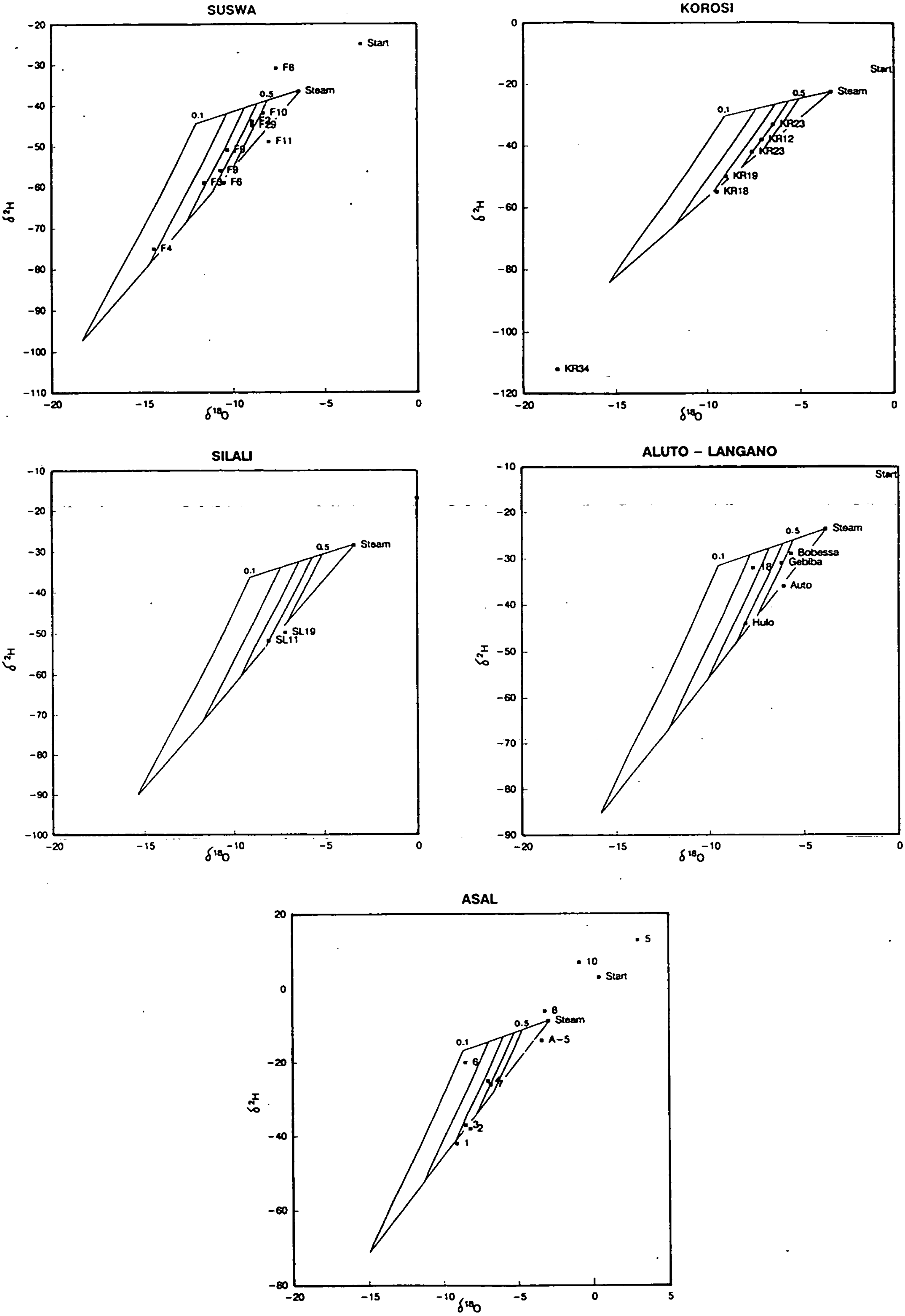

Fig. 10. Stable isotope crossplots with calculated steam condensate fields superimposed on measured fumarole compositions for sites in Kenya, Ethopia, and Djibouti. The parallel lines represent the fraction of original steam remaining after condensation. (Stable isotope values in permil with respect to SMOW)

The results from Silali fumarole SL11 are more convincing, but the already highly varied temperatures from SL19 outside the caldera do not become easier to interpret.

In Ethiopia the corrections can be applied to some of the fumaroles of the Aluto complex, where there is evidence from the geothermal wells for the deep water isotopic composition. Maximum effects are seen at the No. 18 fumarole (Glover, 1976) where CO_2 temperature is reduced by 47°C. At Corbetti and Tendaho there are insufficient data to define a starting composition and corrections have not been attempted.

In the rift zone of Djibouti some of the fumaroles at Asal show evidence of condensation. However the CO_2 geothermometer did not even before correction give the usual high values, and the recalculated temperatures now appear to be too low in some cases. Corrections to the H_2 geothermometer are considerably smaller and more in line with what is known about geothermal reservoir temperatures at Asal.

4.3 Assessment of the Isotopic Correction Process

Although condensation corrections based on stable isotope evidence can be applied in several rift localities, they are not usually sufficient in scale to correct the apparently most wayward of the geothermometers (usually the CO_2 version). In a sense this is not unexpected; it has already been demonstrated that the CO_2 geothermometer does not work well in the Rift proper, even when sampled in geothermal wells where condensation cannot be playing a major role. Also, condensation must usually be indicative of long and tortuous paths for steam and gas before they reach the surface, thus giving time for the unquantifiable effects of diffusion and reaction to occur.

The use of condensation corrections for geothermometry therefore seems to be of marginal importance to exploration in the Rift system. Their application has not led to a fundamental re-interpretation of geothermal potential in any area and their use is probably best restricted to particular local circumstances.

5. A NEW GAS GEOTHERMOMETER BASED ON HYDROCARBON RATIOS

5.1 Ideal Geothermometer Characteristics

The comparative failure of the conventional geothermometers to give a consistent picture of subsurface temperatures in the Rift can be attributed to various factors. The **minerals** controlling gas equilibria may not be the same in the Rift as elsewhere; at Olkaria, for example, calcite is somewhat below saturation and may not be the only carbonate phase controlling CO_2 concentration (Armannsson, 1987), thus rendering the CO_2 geothermometer inapplicable. Considerable depths to water table promote the occurrence of three phenomena: **subsurface steam condensation**, which will affect the concentration of all gases; **diffusion** of the lighter gases, which will tend to affect H_2 the most; **reaction** of gases with wallrock, which may explain why H_2S concentrations are low or beneath detection. These problems will affect concentration and ratio geothermometers alike.

The effects of subsurface condensation can be corrected to some extent by the application of stable isotopic techniques as described in the previous section. The application of this method is however often circumscribed by scarcity of information on the isotopic composition of the deep thermal waters. The other factors are not amenable to any straightforward correction.

The ideal gas geothermometer would therefore have the following characteristics:

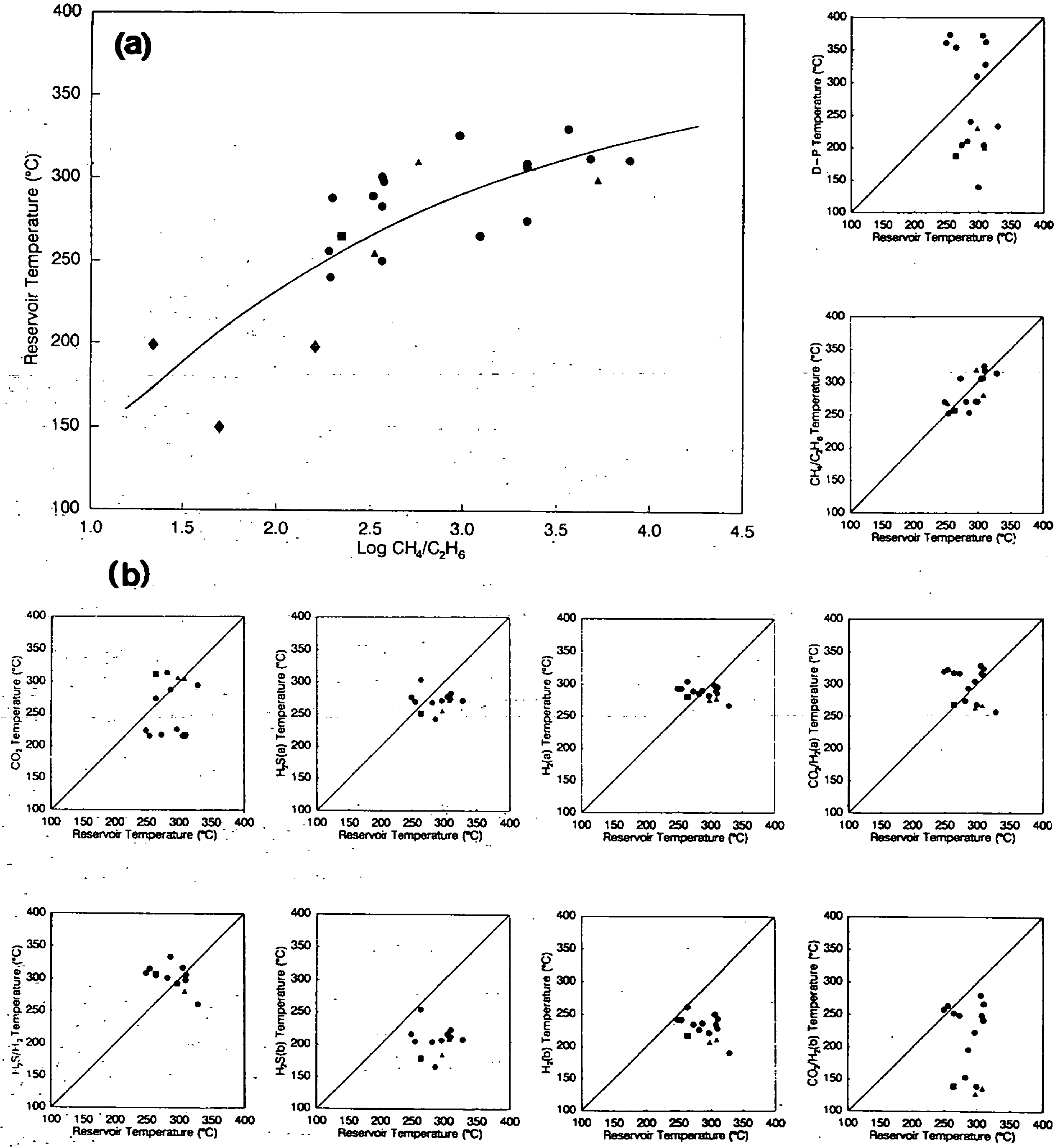

Fig. 11. (a) Plot of T_{res} versus log CH_4/C_2H_6 for geothermal wells at Olkaria, Langano and Asal, (b) Performance of all the gas geothermometers for the same data set. Symbols as for Fig. 3, plus diamonds to represent gases associated with springs.

(a) based on a ratio, which would be much less affected by problems of condensation than a concentration geothermometer,

(b) using similar gases, which would be relatively immune to differentiation by diffusion,

(c) using comparatively unreactive gases, which would not be consumed during passage to the surface, and

(d) using gases which can be detected down to low concentrations, and which could be measured even in weak or air-contaminated fumaroles.

During the BGS survey work in the Kenya Rift, it became apparent that the ratio between methane and ethane might provide a basis for geothermometry. The hydrocarbons are not particularly reactive or diffusive gases, and also have the advantage that they can be determined down to very low concentrations using a gas chromatograph with a simple flame ionisation detector.

The methane/ethane relationship with temperature seems unlikely to be mineral-controlled. The results of $\delta^{13}C_{CH4}$ analyses (mainly in the range -20 to -30‰) suggest that the source of hydrocarbons is primarily thermogenic, presumably from dissolved organic matter and perhaps sedimentary material. There is abundant evidence from the literature of the petroleum industry that hydrocarbon generation can start at temperatures of less than 100°C, probably producing significant amounts of C_{2+} gases in addition to methane. When these gases enter the hotter parts of hydrothermal plumes, breakdown of the C_{2+} gases to CH_4 appears to occur almost logarithmically with increased temperature.

5.2 Calibration of the Methane/Ethane Geothermometer

In an attempt to calibrate this putative geothermometer (generally referred to below as the C_1/C_2 geothermometer), the samples collected from geothermal wells were measured for CH_4 to C_4H_{10} in addition to the conventional gases whose geothermometry has been treated earlier in this report (Section 3). As before the samples chosen were all from wells at Olkaria, Langano and Asal, plus two localities where fumaroles could be sampled close to related boiling springs, at Ol Kokwe Island in Lake Baringo (Kenya), and at the Abaya spring at the northern end of Lake Abaya (E12, Ethiopia). Once again, aquifer temperatures are represented by the average of Na/K and quartz geothermometers except for Abaya where the quartz maximum steam loss version is used (Table 2).

The results of a plot of log CH_4/C_2H_6 versus reservoir temperature are shown in Fig. 11 together with a series of plots for the published geothermometers on the same data set. By comparison with plots for the conventional geothermometers, a better correlation with temperature is observed and a curve with a correlation coefficient of $r^2 = 0.64$ can be fitted to the data according to the following equation where R represents log CH_4/C_2H_6:

$$t^{\circ}C = 454.8 - (586.4/R) + (281.4/R^2)$$

The plotted points fit the curve with a standard deviation of 27°C. Since most of the data points for the curve come from geothermal wells the curve is adequately constrained in the 200-300°C range. Few wholly satisfactory sites for lower temperatures seem to be available and a degassing spring at Kageinya was included to provide an extra data point in the lower temperature range. The geothermometer is suitable for CH_4/C_2H_6 ratios from 10^1 to 10^5 (the maximum usually measurable) corresponding to temperatures of 150-350°C. The results of applying the new geothermometer to fumarolic gases are given in Table 15.

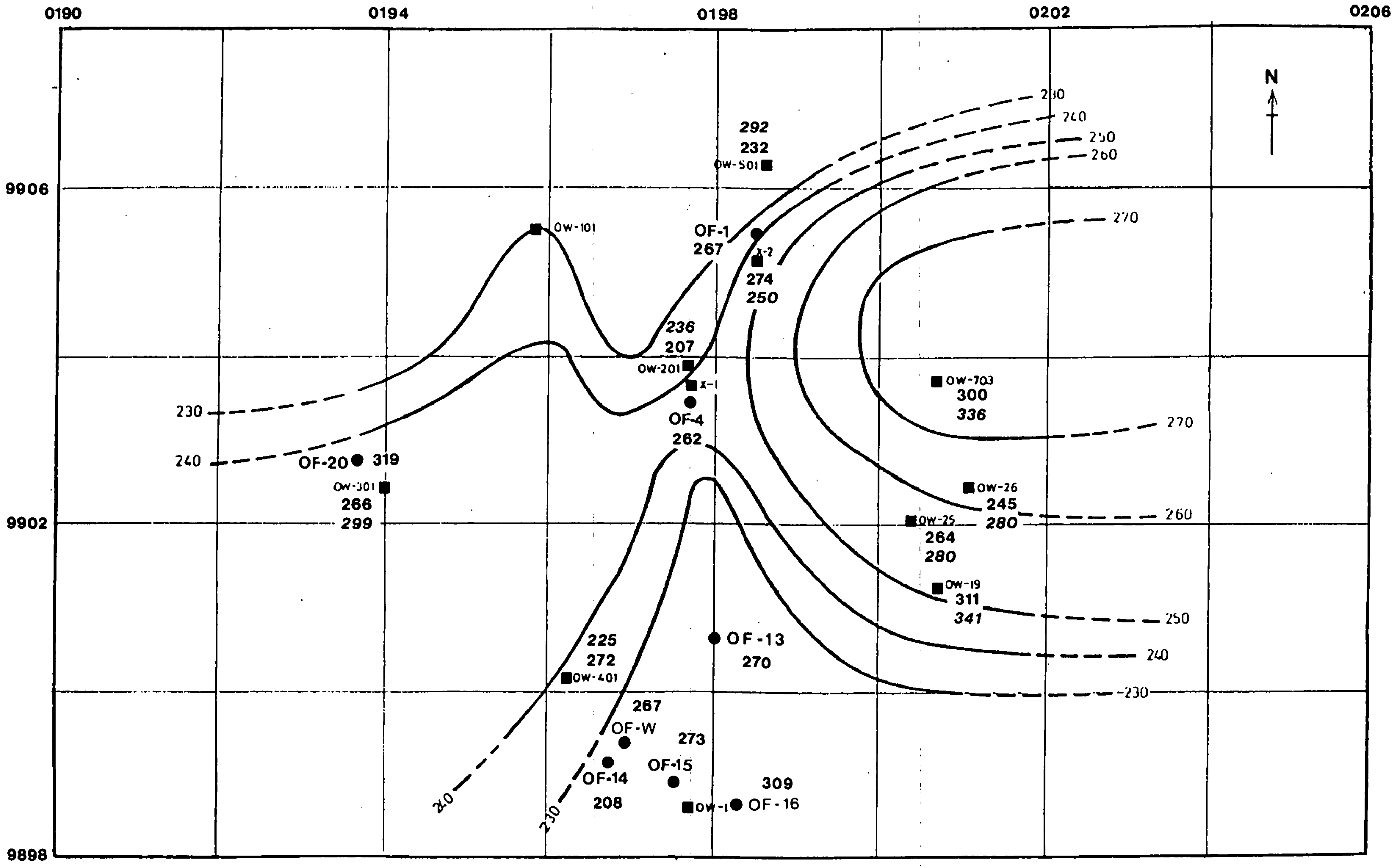

Fig. 12. Olkaria, location of sampled fumaroles with log C_1/C_2 geothermometer temperatures. T_{res} values for nearby wells are also shown (refer Table 10 and Muna, 1984) together with measured maximum temperatures (in italics). Contours (in °C) are those inferred by KPLC for 1000 m asl. Grid numbers refer to UTM grid. (Map adapted from Haukwa, 1986).

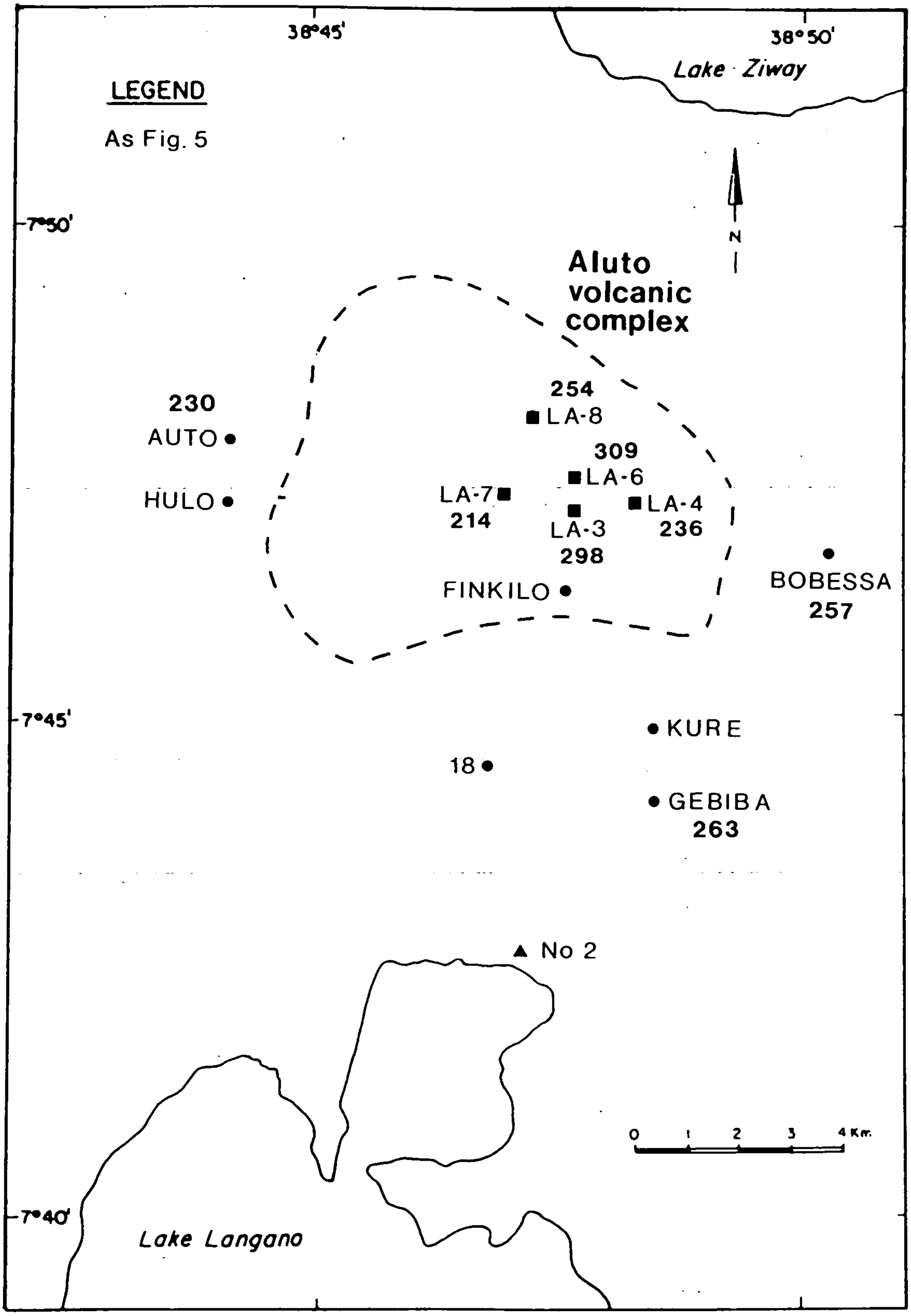

Fig. 13. Langano, location of sampled fumaroles with log C_1/C_2 geothermometer temperatures. T_{res} values for wells are also shown (refer Table 10). (Map adapted from Endeshaw, 1988).

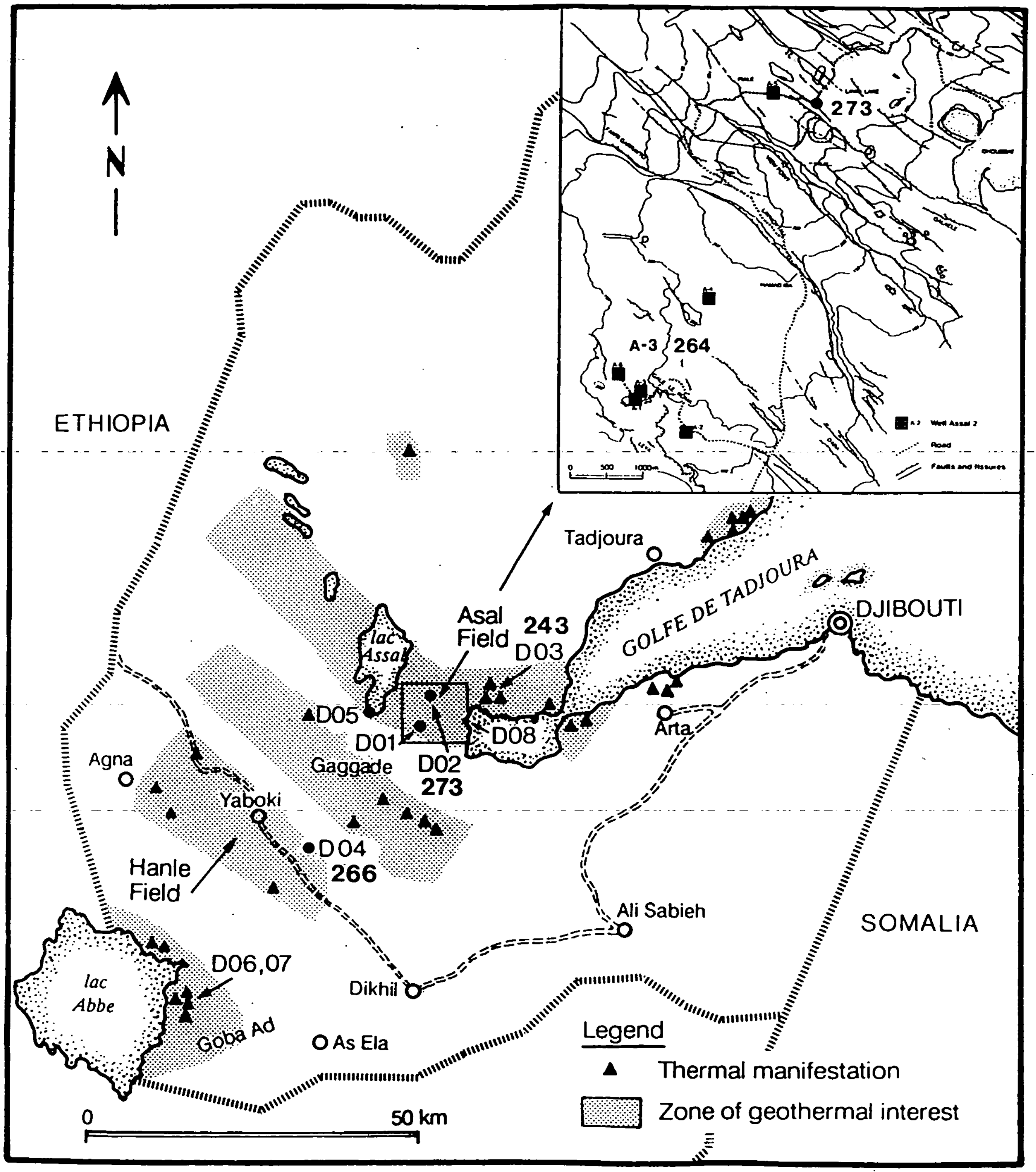

Fig. 14. Djibouti, location of sampled fumaroles with log C_1/C_2 geothermometer temperatures. T_{res} value for well A-3 also shown (refer Table 10). (Map adapted from Khaireh, 1989).

These results can be assessed in two ways: quantitatively for fumaroles in the vicinity of the geothermal wells, and more qualitatively for fumaroles elsewhere.

5.3 Application to Geothermal Wellfield Fumaroles

Maps of the Olkaria, Langano and Asal geothermal fields are given in Figs. 12-14 which also provide details of well and fumarole temperatures.

It is apparent at Olkaria that results for fumaroles are often in reasonable agreement with maximum or solute temperatures in nearby wells (Fig. 12). For example, C_1/C_2 temperatures for fumaroles OF-1, OF-4, OF-W and OF-20 are all within 30°C of the maximum or solute temperature. The fumaroles OF-13, OF-15 and OF-16 do not have nearby wells for comparison, except for the unsuccessful OW-1 well. Judging by the estimated 1000 metres above sea level temperature contours in Fig. 12, it seems unlikely that deep temperatures could fall off so quickly towards OW-1, and therefore the 273°C temperature for OF-15 is not inconceivable. The 309°C temperature for OF-16 seems less likely in this part of the geothermal field, which lies along the Ololbutot fault. The best-explored areas of Olkaria are the eastern (presently producing) and northeastern wellfields, but these areas have little or no fumarolic activity. If the geothermometer temperature data are considered on an averaged basis across the wellfield the following figures are obtained: average fumarolic C_1/C_2 temperature 271°C, average solute temperature 291°C. These figures can be compared with an average measured stable temperature of 270°C for the same wells (totalling 33 in all). At Eburru (Table 15) the two fumaroles measured gave temperatures of 325 and 347°C, compared to a measured temperature in well EW-1 of 280°C but a solute T_{res} value of 329°C.

There are fewer data for the Langano field (Fig. 13) and the fumaroles are much less close to wells. However the methane/ethane temperatures are in reasonable agreement with what is known about the system. The nearest fumarole to the wellfield has a temperature of 257°C compared to the nearest well with a solute temperature of 236°C. Outflow from the system proceeds to the south of the Aluto complex where it is ultimately manifested by hot springs with a quartz temperature of 180°C at E11 near the North Bay of Lake Langano. The Gebiba fumarole is situated on this outflow and gives a C_1/C_2 temperature of 263°C. To the west of the complex where temperatures appear to be declining according to the evidence of well LA-7, the Auto fumarole gives a cooler temperature of 230°C. While these C_1/C_2 temperatures may seem a little high for marginal areas of the complex it should be remembered that both solute and measured temperatures for the centre of the complex are over 300°C.

The small number of samples collected in Djibouti give less unequivocal results. It can be seen in Fig. 14 that the result for the fumarole near well Asal-5 gives a C_1/C_2 temperature of 273°C, which lies midway between the upper and lower reservoir temperatures of 190°C and 355°C measured in the Asal-5 well (Zan et al, 1990). At Nord Ghoubet subsurface temperatures are likely to be lower than in the centre of the rift zone so a C_1/C_2 temperature of 243°C seems plausible. Inland in the Hanle area, the Garrabays fumarole gives a temperature of 266°C. The nearby H2 well, however, only measured a temperature of 120°C at a depth of 2000 m (solute composition unknown). Either the C_1/C_2 temperature in the fumarole is incorrect or conditions change rapidly between the fumarole and borehole. Possibly there is faulting, or by some other means the gases are arriving from a greater depth than that achieved by the well.

5.4 Application to Fumaroles in Undrilled Geothermal Areas

Methane/ethane geothermometer temperatures for fumaroles outside drilled geothermal fields are included in Table 15. Because ethane has not been routinely measured on geothermal gases by previous researchers the amount of

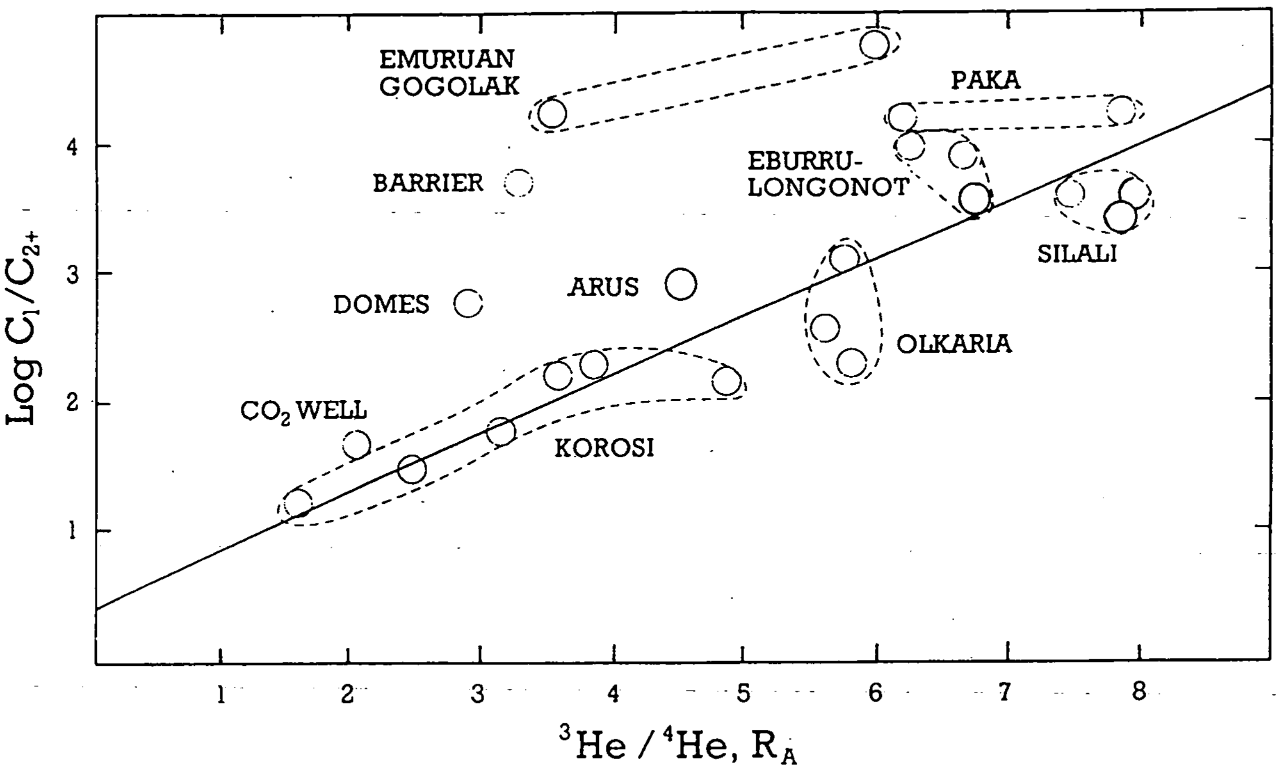

Fig. 15. Plot of log C_1/C_{2+} versus $^3He/^4He$ for gases in the Kenya Rift Valley.

data is smaller than for the conventional geothermometers. Nevertheless some assessment of performance is possible.

In the southern Kenya Rift there are some results from the Suswa, Longonot, Domes (the probable eastward continuation of the gross Olkaria structure), and Eburru areas. Apart from a rather unlikely high temperature (302°C) for Mount Margaret, an outlying geothermal manifestation to the southeast of Longonot, most other C_1/C_2 temperatures are plausible. Akira (actually a steam-yielding 'dry' borehole) is situated on the probable outflow from Olkaria and yields a temperature of 261°C. The Domes fumarole F-15 has a rather higher temperature of 279°C, similar to temperatures in the Olkaria field on the opposite side of the Ol Njorowa (Hell's Gate) gorge. Longonot fumarole F-23 situated in the main crater has other indications of having a high-temperature source (Allen et al., 1989) and the average of two samples collected here is 321°C. The Suswa sample from F-7, a fumarole situated on the caldera wall and some km away from the most vigorous hydrothermal activity associated with the ring graben and central 'island' block, gives a high temperature of 324°C but this does not contradict the assessment of Armannsson (1987). The nearest graben fumarole, F-12, indicated a temperature of 287°C while fumarole F-28 on the island gave a temperature of 314°C. Arus, the only fumarole sampled in the Menengai-Bogoria thermal province, gave a temperature of 281°C.

The most comprehensive set of data has been obtained from the volcanic centres of the northern Kenya Rift, principally Korosi, Paka, Silali and Emuruan Gogolak. As stated earlier in this report these are grounds on which the centres can be ranked as geothermal propsects in order of declining vigour Paka, Silali, Emuruan Gogolak and Korosi, with the last the poorest by some margin. The C_1/C_2 geothermometer partially confirms this, with an average temperature of 217°C for Korosi, while Paka and Silali have average temperatures of 303°C and 304°C respectively. However, Emuruan Gogolak (which was the least easy of the four centres to assess) has an average fumarole temperature of 327°C. This is based on only two fumaroles, but two other fumaroles had no detectable ethane, suggesting a very high CH_4/C_2H_6 ratio hence temperature (Allen and Darling, in press). Emuruan Gogolak appears to have been the most recently active of the centres and might therefore on theoretical grounds have been expected to show the highest temperatures. A similar situation obtains for the Kakorinya centre on the Barrier complex at the south end of Lake Turkana, where a C_1/C_2 temperature of 315°C was obtained. In both cases the ratio $^3He/^4He$ does not fall on the presumably temperature-based linear relationship with log C_1/C_{2+} (very similar to C_1/C_2) seen for all Rift centres from Silali southward (Fig. 15), thus raising the possibility of some change in the underlying structure and/or geothermal hydrology of the Rift between Silali and Emuruan Gogolak.

In Ethiopia, the methane/ethane temperatures for the Langano field have already been considered. There are also data from a weak fumarole at Boku (probably associated with the Gedemsa centre near Nazret) which indicate a rather high temperature of 298°C, and data from three fumaroles in the Corbetti area (Fig. 8). Two of these fumaroles were situated within the caldera; both had large amounts of air contamination but gave temperatures of 259°C and 284°C respectively. To the north of the caldera, a highly gaseous fumarole at Koka gave the significantly lower temperature of 153°C; this fumarole may or may not be on the outflow from Corbetti (see section 3.2 for discussion).

No gas samples were collected from north of the Boku-Sodere thermal area, and there are therefore no data from the Tendaho area. The only geothermal manifestation sampled in Djibouti west of the Asal-Hanle area (already considered above) was one of the 'chimney' thermal springs of Lake Abbe. This is briefly considered in the next section.

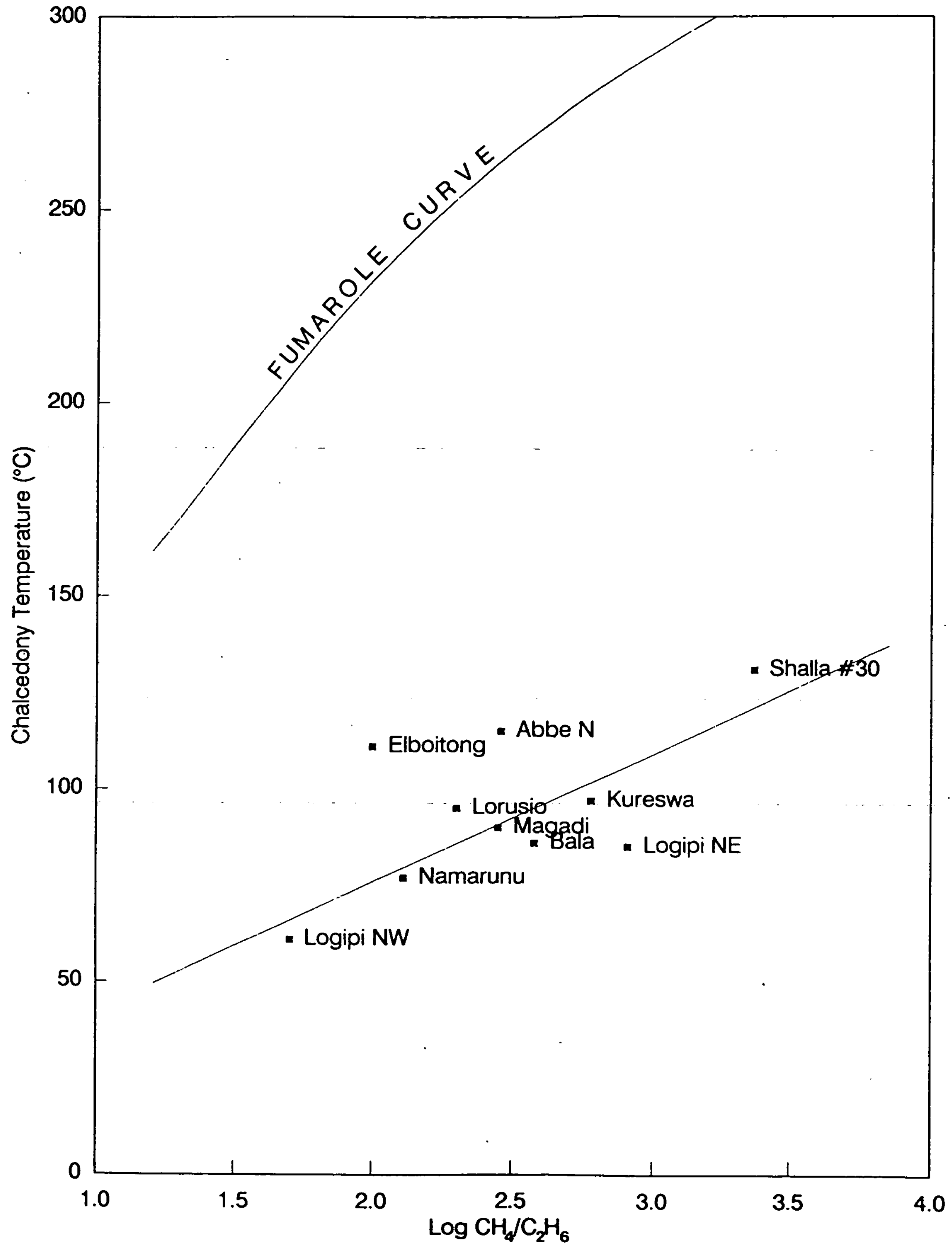

Fig. 16. Plot of solute geothermometer temperature versus log CH_4/C_2H_6 for hot springs in Kenya, Ethiopia and Djibouti. Temperatures based on chalcedony geothermometer (refer Table 2). Regression line for fumarole C_1/C_2 gas geothermometer shown for reference.

5.5 Hydrocarbon Geothermometry of Hot Spring Gases

The C_1/C_2 ratio has also been investigated for hot springs. Fig. 16 shows a plot of log CH_4/C_2H_6 versus chalcedony temperature for hot springs in Kenya, Ethiopia and Djibouti (chemical and isotopic data for some of these sites are reported in Tables 16 and 17). The regression line through the data points is based on all points except Elboitong and is flatter in gradient than the high temperature curve and considerably displaced towards cooler temperatures.

The reasons for the difference between the curves are not fully understood. The different gas solubilities of methane and ethane may play a part; CH_4 has a lower partition coefficient than C_2H_6, which might in certain circumstances favour CH_4 in transfer to the gas phase, thus raising log CH_4/C_2H_6 for a particular temperature. Perhaps more fundamentally, none of the hot springs sampled shows evidence of temperatures greatly in excess of 100°C and they are accordingly unlikely to represent cooled high-temperature outflow waters (which might well have lost virtually all their gases during boil-off anyway). This difference in thermal history may be responsible for the disparity between the two trends. Also, spring waters may be mixtures between cool, near-surface waters and thermal waters, and this would tend to increase the scatter in any correlation between log CH_4/C_2H_6 and temperature.

Nevertheless the good agreement may offer scope for the development of a gas geothermometer for waters, given more data. While solute geothermometers have frequently proved to be reliable in many parts of the world, there are certain circumstances (for example in the highly alkaline waters of the Rift) where their use may be less appropriate. Indeed the chalcedony geothermometer used for plotting versus log CH_4/C_2H_6 may itself need some adjustment in this respect in order to calibrate reliably such a gas geothermometer.

5.6 Assessment of the Performance of the Methane/Ethane Geothermometer

The C_1/C_2 geothermometer is empirical, being based largely on observations from Rift System geothermal wells. However it also seems to work for fumaroles, giving results which in most cases do not contradict other evidence, both geochemical and geological. In particular, independent confirmation seems to be offered by the generally good correlation between $^3He/^4He$ and log CH_4/C_2H_6 (Fig. 15). It is difficult to see any connection between these parameters other than temperature; all things being equal, the highest $^3He/^4He$ values will be found above the hottest parts of hydrothermal plumes. The geothermometer appears to work equally well with gas-rich and highly air-contaminated fumaroles. It requires no knowledge of steam/gas ratio, and the two gases CH_4 and C_2H_6 are easy to measure down to very low concentrations by gas chromatography.

Because there is only one version of the equation, no knowledge or estimation of groundwater chloride content or temperature is necessary before the geothermometer can be used. Although there is comparatively little data from Djibouti, the geothermometer appears to function adequately whether the reservoir is low in chloride, as in the Rift proper, or very high as at Asal.

There is some evidence that hot spring gases also have a relationship between CH_4/C_2H_6 and temperature, but this requires further evaluation.

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TABLES 1-17

TABLE 1. PUBLISHED GAS GEOTHERMOMETRY TEMPERATURE FUNCTIONS

(a) Arnorsson and Gunnlaugsson (1985):

CO_2	: $-44.1 + 269.25Q^2 + 9.52Q^3$	Applicability: universal
H_2S H_2 CO_2/H_2 H_2S/H_2	: $+246.7 + 44.81Q$: $+277.2 + 20.99Q$: $+341.7 - 28.57R$: $+304.1 - 39.48R$	Applicability: all waters above 300°C and waters in the range 200-300°C if chloride > 500 mgl^{-1}
H_2S H_2 CO_2/H_2	: $+173.2 + 65.04Q$: $+212.2 + 38.59Q$: $+311.7 - 66.72R$	Applicability: all waters below 300°C and waters in the range 200-300°C if chloride < 500 mgl^{-1}

where Q = log gas concentration in mmoles per kg of steam, R = log gas ratio

(b) D'Amore and Panichi (1980):

$$t^\circ C = (24775/\alpha + \beta + 36.05) - 273$$

$$\text{where } \alpha = 2\log(CH_4/CO_2) - 6\log(H_2/CO_2) - 3\log(H_2S/CO_2)$$

$$\beta = -7\log PCO_2$$

When H_2, H_2S or CH_4 are absent, a vol % of ≤0.001 should be used

$PCO_2 = 0.1$ if $CO_2 < 75\%$
$PCO_2 = 1.0$ if $CO_2 > 75\%$
$PCO_2 = 10$ if $CO_2 > 75\%$ and $CH_4 > 2H_2$ and $H_2S > 2H_2$

(c) Panichi et al (1975):

$$1000 \ln\alpha = -9.01 + (15.30 \times 10^3 T^{-1}) + (2.361 \times 10^6 T^{-2})$$

$$\text{where } \alpha = (^{13}C/^{12}C)_{CO2}/(^{13}C/^{12}C)_{CH4}$$

$$\text{nb: } 1000 \ln\alpha \approx \delta^{13}C_{CO2} - \delta^{13}C_{CH4}$$

TABLE 2. SOLUTE GEOTHERMOMETER EQUATIONS

a. **Silica (quartz) - no steam loss**

$$t^\circ C = C_1 + C_2S + C_3S^2 + C_4S^3 + C_5 \log S$$

where S = silica concentration, mgl^{-1}
C_1 = -4.220×10^1
C_2 = 2.883×10^{-1}
C_3 = -3.669×10^{-4}
C_4 = 3.167×10^{-7}
C_5 = 7.703×10^1

b. **Silica (quartz) - maximum steam loss at 100°C**

$$t^\circ C = (1522/5.75 - \log S) - 273.15$$

c. **Silica (chalcedony)**

$$t^\circ C = (1032/4.69 - \log S) - 273.15$$

d. **Sodium/Potassium**

$$t^\circ C = (1217/1.483 + \log [Na/K]) - 273.15$$

(All equations from Fournier, 1989)

TABLE 3. INVESTIGATING TEAMS AND SOURCES OF GEOTHERMAL GAS DATA FOR THE RIFT

Country/Locality (State Organisation)	'Normal' gases	C_2-C_5 Hydrocarbons	Carbon monoxide	Carbon isotopes	Helium isotopes	Hydrogeology
KENYA (MERD, KPLC)						
Magadi/Bala	BGS^{14}	BGS^{1}	-	BGS^{14}	BGS^{1,u}	BGS^{1}
Suswa-Longonot-Domes	UNDP^{2} BGS^{1}	BGS^{1}	-	BGS^{1}	BGS^{1} ?SIO	BGS^{1}
Olkaria-Eburru	UNDP^{3} KPLC^{5} BGS^{14}	BGS^{14}	-	UNDP^{3} BGS^{6}	BGS^{1,u}	UNDP^{4} BGS^{1}
Menengai-Bogoria	UNDP^{3} GIS^{6}		GIS^{6}	BGS^{u}	BGS^{u}	GIS^{6}
Baringo-Turkana	BGS^{7,u}	BGS^{7,u}	-	BGS^{7,u}	BGS^{7,u}	BGS^{7,u}
ETHIOPIA (EIGS)						
Abaya-Langano	UNDP^{8} SIO^{9} EIGS^{10} BGS^{14}	BGS^{14}	-	SIO^{9} BGS^{14}	SIO^{9} BGS^{u}	?
Awash-Tendaho	UNDP^{8} SIO^{9} ?ELC^{11}		- ?ELC^{11}	SIO^{9}	SIO^{9}	?
DJIBOUTI (ISERST, EDD)						
Asal-Abbe	BRGM^{12} GIS^{13} BGS^{14}	BGS^{14}	GIS^{13}	?BRGM BGS^{14}	BGS^{u}	?

Key to Table 3:

'Normal' gases: CO_2, CH_4, H_2, H_2S, N_2

BGS - British Geological Survey
BRGM - Bureau de Recherches Geologiques et Minières
EDD - Électricité de Djibouti
EIGS - Ethiopian Institute of Geological Surveys
ELC - ELC Electroconsult
GIS - Geotermica Italiana Srl
ISERST - Institut Superieur d'Etudes et de Recherches Scientifiques·
KPLC - Kenya Power and Light Company
MERD - Ministry of Energy and Regional Development
SIO - Scripps Institute of Oceanography
UNDP - United Nations Development Programme

1. Allen et al (1989)
2. Armannsson (1987)
3. Glover (1972)
4. McCann (1974)
5. Muna (1984)
6. Geotermica Italiana Srl (1987a)
7. Allen and Darling (in press)
8. Glover (1976)
9. Craig et al (1977)
10. Endeshaw (1988)
11. ELC Electroconsult and Geotermica Italiana Srl (1986)
12. B.R.G.M. (1983)
13. Geotermica Italiana Srl (1987b)
14. This report

u. Unpublished or undergoing analysis

TABLE 4. GAS ANALYSES FOR SAMPLES COLLECTED AT OLKARIA, EBURRU AND AREA (KENYA), 1989-90.

Site	Sample Source	Temp °C	pH	CO_2	H_2S	H_2	O_2+Ar	N_2	CO_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
				mmole/kg	mole %								
OF-1	F	92.6	3.95	1913	0.03	1.8	0.38	1.52	95.7	0.61	0.0018	0.0010	0.000067
OF-4	F	94.6	4.85	1494	0.005	<d	16.3	60.1	23.4	0.15	0.00055	<d	<d
OF-13	F	95.1	5.45	-	-	2.4	2.4	12.0	82.7	0.49	0.0013	0.00060	<d
OF-14	F	93.8	4.05	-	-	2.3	2.0	11.1	84.2	0.38	0.0074	0.00011	<d
OF-15	F	90.8	-	282	0.14	0.97	6.3	23.6	68.8	0.24	0.00054	<d	<d
OF-16	F	95.7	4.45	414	0.14	3.3	0.64	4.0	90.3	1.6	0.00055	<d	<d
OF-20	F	78.3	2.75	-	-	<d	1.6	4.3	94.1	0.034	0.000006	<d	<d
EF-1*	F	-	5.75	-	-	<d	20.4	75.7	3.3	0.33	0.000004	<d	<d
OW-10	G	-	-	28.4	10.3	21.0	<d	0.64	65.9	2.20	0.0011	0.000013	<d
OW-11	G	-	-	28.2	11.0	7.1	<d	<d	80.9	1.13	0.00014	0.000004	<d
OW-12	G	-	-	29.8	-	10.1	<d	<d	89.5	0.46	0.00021	0.000002	<d
OW-19	G	-	-	29.5	13.6	14.4	<d	<d	70.2	1.74	0.00037	0.000005	<d
OW-22	G	-	-	33.6	10.0	11.8	<d	0.64	77.8	0.43	0.0013	0.000060	<d
OW-23	G	-	-	28.4	7.98	14.4	<d	0.43	76.9	0.26	0.0014	0.000066	<d
OW-25	G	-	-	134	10.1	10.1	<d	0.35	79.0	0.44	0.00036	0.000006	<d
OW-703	G	-	-	-	-	0.25	<d	0.21	99.5	0.069	0.00019	0.000004	<d
OW-710	G	-	-	536	0.52	0.40	<d	1.21	97.8	0.12	0.00033	0.000015	<d
OW-711	G	-	-	211	0.35	1.76	<d	<d	97.7	0.18	0.00093	0.000076	<d
OW-713	G	-	-	35.2	7.7	3.72	<d	4.62	83.6	0.38	0.0010	0.000071	<d
EW-1	G	-	-	272	1.18	0.09	<d	0.34	97.4	0.99	0.00027	0.000008	<d
K03 L. Magadi	H	82.9	8.80	-	-	<d	3.9	30.2	56.9	9.05	0.032	0.010	<d
K53 Bala	H	72	7.60	-	-	0.21	0.01	9.86	89.6	0.28	0.00053	0.000017	<d
K236 Menengai	H	76	-	-	-	<d	17.2	78.3	4.45	0.033	<d	<d	<d
K237 Carbacid	B	-	-	-	-	0.001	<d	0.35	98.4	1.24	0.019	0.0052	0.0021

B - dry CO_2 borehole; F - fumarole; G - geothermal well; H - hot spring <d - below detection

* probable contamination by air after sampling

All OW and EW samples collected by the Kenya Power and Light Company

TABLE 5. STABLE ISOTOPE ANALYSES FOR STEAM AND GAS SAMPLES COLLECTED AT OLKARIA, EBURRU AND AREA (KENYA), 1989-90.

Site	Sample Source	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C_{CO2}$	$\delta^{13}C_{CH4}$
		% SMOW		‰PDB	
OF-1	F	-2.0	- 4	-3.4	-28.8
OF-4	F	-3.1	- 3	-5.6	-27.2
OF-13	F	-2.6	- 6	-4.0	-26.5
OF-14	F	-4.0	+ 5	-3.2	-26.0
OF-15	F	-4.1	-17	-4.5	-26.7
OF-16	F	-1.9	- 3	-5.0	-26.6
OF-20	F	-10.0	-19	-3.6	-24.5
EF-1	F	-8.0	-31	-	-
OW-10	G	-	-	-	-28.1
OW-11	G	-	-	-	-28.4
OW-12	G	-	-	-	-27.0
OW-19	G	-	-	-	-26.4
OW-22	G	-	-	-	-27.3
OW-23	G	-	-	-	-27.3
OW-25	G	-	-	-	-27.3
OW-703	G	-	-	-	-21.1
OW-710	G	-	-	-	-27.7
OW-711	G	-	-	-	-29.0
OW-713	G	-	-	-	-29.1
EW-1	G	-	-	-	-23.2
K03 L. Magadi	H	-	-	-8.0	-
K53 Bala	H	-	-	-7.3	-26.8
K236 Menengai	H	-10.4	-	-6.9	-
K237 Carbacid	B	- 3.9	-	-2.4	-20.5

B - dry CO_2 borehole
F - fumarole
G - geothermal well
H - hot spring

All OW and EW samples collected by the Kenya Power and Light Company

TABLE 6. GAS ANALYSES FOR SAMPLES COLLECTED AT LANGANO AND LAKES AREA (ETHIOPIA), 1990.

No.	Site	Sample Source	Temp °C	CO_2 mmole/kg	H_2S	H_2	O_2+Ar	N_2	CO_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
					mole %								
E01	LA-3	G	-	425	0.34	0.16	<d	<d	98.3	1.2	0.00023	0.000008	0.000004
E02	LA-6	G	-	384	0.89	0.22	<d	<d	98.7	0.16	0.00035	0.000043	0.000038
E04	Bobessa	F	-	559	0.049	<d	11.4	39.8	48.7	0.14	0.00060	0.000016	<d
E05	Gebiba	F	93	187	0.053	0.011	0.041	0.22	99.4	0.32	0.0011	0.00033	0.00032
E06	Auto	F	90	5802	0.00005	<d	20.9	76.0	3.1	0.017	0.00018	0.000047	<d
E07	Chebicha	F	80	379	<d	<d	22.1	77.4	0.55	0.0065	0.000009	<d	<d
E08	Danshe	F	90	4162	0.00013	<d	20.7	73.0	6.3	0.032	0.00013	0.000011	0.000005
E09	Koka	F	94	491	0.013	0.0030	<d	<d	99.8	0.17	0.014	0.0058	0.0027
E10	Boku	F	73	-	<d	0.0018	21.6	76.1	2.3	0.016	0.000011	<d	<d
E13	Abaya #7	H	88	-	-	0.0007	18.2	64.2	17.6	0.0042	0.00019	0.000007	0.000012
E15	Shalla #30	H	96	-	-	<d	17.9	65.3	14.8	2.0	0.00085	0.00025	0.000071
E16	Sodere	H	65	-	-	<d	3.8	18.2	78.0	<d	<d	<d	<d

F - fumarole; G - geothermal well; H - hot spring

<d - below detection; nm - not measured

TABLE 7. STABLE ISOTOPE ANALYSES FOR STEAM AND GAS SAMPLES COLLECTED AT LANGANO AND AREA (ETHOPIA), 1990.

No.	Site	Sample Source	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C_{CO2}$	$\delta^{13}C_{CH4}$
			% SMOW		%PDB	
E01	LA-3	G	-	-	- 4.7	-28.5
E02	LA-6	G	-	-	- 3.9	-27.0
E04	Bobessa	F	-5.7	-29	- 4.1	-25.7
E05	Gebiba	F	-6.2	-31	- 4.1	-25.7
E06	Auto	F	-6.1	-36	- 7.5	-
E07	Chebicha	F	-4.9	-31	- 8.7	-29.9
E08	Danshe	F	-5.0	-29	- 7.1	-30.7
E09	Koka	F	-2.1	- 9	- 3.5	-28.6
E10	Boku	F	-	-35	-10.7	-24.0
E13	Abaya #7	H	-	-	- 3.2	-18.0
E15	Shalla #30	H	-	-	+ 0.8	-21.9
E16	Sodere	H	-	-	-10.2	-

F - fumarole; G - geothermal well; H - hot spring

TABLE 8. GAS ANALYSES FOR SAMPLES COLLECTED IN DJIBOUTI, 1989-90.

No.	Site	Sample Source	pH	CO_2	H_2S	H_2	O_2+Ar	N_2	CO_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
				mmole/kg	mole %								
D01	Asal - 3*	G	-	510	0.23	0.25	0.04	0.29	99.1	0.16	0.00073	0.00030	0.00019
D02	Asal (5)	F	5.35	454	0.0027	0.037	20.1	70.8	9.1	0.00087	0.000002	<d	<d
D03	N. Ghoubet	F	5.25	27.2	0.061	0.10	18.4	65.0	16.5	0.023	0.00016	0.000014	0.000033
D04	Garrabays	F	5.65	8.6	<d	<d	21.6	78.1	0.33	0.0077	0.000024	0.000002	<d
D07	Abbe N.	H	6.05	-	-	<d	15.3	83.8	0.45	0.48	0.0035	0.0010	0.00031

F - fumarole; G - geothermal well; H - hot spring

<d - below detection

* sample collected by Dr H Armannsson, who also provided CO_2 and H_2S concentrations

TABLE 9. ISOTOPE ANALYSES FOR STEAM AND GAS SAMPLES COLLECTED IN DJIBOUTI, 1989-90.

No.	Site	Sample Source	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C_{CO2}$	$\delta^{13}C_{CH4}$
			% SMOW		%PDB	
D01	Asal - 3	G	-2.4*	-	-3.0	-25.9
D02	Asal (5)	F	-3.4	-14	-5.7	-32.1
D03	N. Ghoubet	F	-3.9	-20	-3.1	-17.0
D04	Garrabays	F	-8.1	-57	-9.8	-31.1
D07	Abbe N.	H	-	-	-	-29.3

F - fumarole; G - geothermal well; H - hot spring

* Analysis provided by Dr H Armannsson

TABLE 10. RESULTS OF PUBLISHED GAS GEOTHERMOMETERS APPLIED TO GEOTHERMAL WELLS IN KENYA, ETHIOPIA AND DJIBOUTI (TEMPERATURES IN °C). RAW DATA SOURCES AS REFERRED TO BELOW.

Well	$T_{res}^{c,e}$	CO_2	H_2S	H_2	CO_2/H_2	H_2S/H_2	H_2S	H_2	CO_2/H_2	D-P	$\Delta^{13}C$
		Cl > 500 mgl^{-1}					Cl < 500 mgl^{-1}				
KENYA											
OW-2[a]	313	244	277	292	311	305	217	239	241	324	
OW-3[c]	274				312				276	267	
OW-4[c]	260				304				275	237	
OW-5[a]	258	224	281	289	314	297	223	235	247	349	
OW-6[a]	283	239	282	293	315	304	224	242	249	339	
OW-7[a]	303	224	279	290	315	300	220	236	249	346	
OW-8[c]	251				314				277	251	
OW-9[c]	278				309				304	313	
OW-10[a]	306	236	286	298	322	309	230	250	265	258	
OW-10[b]	306	214	276	297	327	316	215	249	279	371	
OW-11[a]	310	218	274	290	317	304	213	236	253	344	
OW-11[b]	310	214	273	285	312	297	211	227	241	327	
OW-12[a]	308	216	278	290	317	300	219	235	253	268	
OW-12[b]	308	216		288	315			233	248	203	
OW-13[a]	272	259	288	290	303	291	234	235	222	313	
OW-14[a]	267	254	279	292	308	303	220	239	233	326	
OW-15[a]	328	212	272	284	310	294	209	224	237	319	
OW-16[a]	342	212	275	286	313	295	215	228	244	337	
OW-17[a]	280	249	270	292	310	313	207	240	238	321	
OW-18[a]	380	244	275	293	313	309	215	241	244	328	
OW-19[a]	311	235	288	292	315	296	234	240	249	346	
OW-19[b]	311	216	281	294	322	305	222	242	266	361	
OW-20[a]	292	221	278	289	314	298	219	234	247	350	
OW-21[a]	273	271	285	289	297	292	229	233	208	279	
OW-21[b]	273	216		288	315			233	248	203	
OW-22[a]	249	282	284	294	300	303	228	243	214	283	
OW-22[b]	249	222	275	292	318	307	215	240	257	360	
OW-23[a]	255	240	282	294	315	305	224	243	250	352	
OW-23[b]	255	214	268	292	321	314	204	240	263	372	
OW-24[a]	300	221	281	292	319	302	223	240	258	267	
OW-25[b]	264	272	302	303	316	304	253	260	252	353	
OW-26[a]	245	262	282	292	305	301	225	240	227	311	
OW-703[b]	300				267				138	138	
OW-710[b]	282	312	267	284	273	300	203	225	152	209	
OW-711[b]	287	286	241	289	292	332	165	235	195	239	
OW-713[b]	297	224	270	281	303	292	206	220	222	309	
X-2[d]	274	262	257	253	252	250	188	168	102	243	431
EW-1[b]	329	293	270	265	255	260	207	189	109	232	
ETHIOPIA											
LA-3[b]	298	305	254	274	262	291	184	206	126	229	315
LA-3[e]	298	331	293				240				
LA-4[e]	236	366	251				180				
LA-6[e]	309	339	305	282	257	261	258	220	115	186	
LA-6[b]	309	303	271	276	266	280	208	210	135	199	326
LA-7[e]	214	344	273				211				
LA-8[e]	254	342	271	273	245	275	209	205	86	194	
DJIBOUTI											
A-3[b]	264	310	250	279	267	306	178	216	138	186	329

T_{res} - Reservoir temp, average of Na/K and SiO_2 geothermometers of Fournier (1989).
OW, X - Olkaria; EW - Eburru; LA - Langano; A - Asal

D-P - D'Amore and Panichi empirical geothermometer; $\Delta^{13}C$ - carbon isotope geothermometer

a - Arnorsson et al (1990); b - this report; c - Muna (1984); d - Glover (1972);
e - Gizaw (1989)

TABLE 11. RESULTS OF PUBLISHED GAS GEOTHERMOMETERS APPLIED TO GEOTHERMAL WELLFIELD FUMAROLES IN KENYA, ETHIOPIA AND DJIBOUTI (TEMPERATURES IN °C). RAW DATA SOURCES AS REFERRED TO BELOW.

Fumarole	CO_2	H_2S	H_2	CO_2/H_2	H_2S/H_2	H_2S	H_2	CO_2/H_2	D-P	$\Delta^{13}C$
	— Cl > 500 mgl^{-1} —					- Cl < 500 mgl^{-1} -				
Kenya										
133/4/1[a] (≡ OF-1)	310	243	297	292	345	168	249	195	218	415
133/4/13[a]	277	240	290	296	333	164	235	205	244	442
133/4/41[a]	281	250	282	284	310	178	221	177	280	
133/4/42[a]	280	262	294	300	322	195	242	214	267	
133/4/53[a]	259	215	285	297	347	127	226	206	227	
133/4/54[a] (≡ OF-16)	250	212	283	298	347	122	224	209	229	487
133/4/63[a] (≡ OF-14)	268	227	287	296	340	145	231	205	238	469
133/4/74[a]	285	221	280	280	332	136	217	167	199	
133/4/82[a]	280	235	286	290	331	156	229	190	228	
133/4/94[a]	391	292	298	261	303	238	250	123	152	
OF-1[b]	348	237	310	292	374	159	272	197	198	293
OF-4[b]	340	224				141			53	350
OF-13[b]				298				209	173	355
OF-14[b]				297				207	173	331
OF-15[b]	294	236	290	289	337	158	235	188	159	340
OF-16[b]	305	238	302	301	358	161	258	216	226	350
OF-20[b]									62	363
133/1/53[a]	264	245	289	301	328	171	234	216	241	
133/2/77[a]	309	246	300	296	347	173	254	205	213	612
133/2/80[a]	295	237	300	303	357	159	255	221	221	635
EF-2[b]				294				201	152	
Ethiopia										
Bobessa[b]	313	236				157			57	350
Bobessa[c]	318	206				114			59	
Gebiba[b]	282	202	342	229	277	108	147	48	157	350
Gebiba[c]	298	219	256	242	292	133	173	78	126	
Finkilo[c]	341	207				115			99	
Kure[c]	287	213				125			91	
No. 18[c]	289	234				154			104	
Aluto 'B'[c]	357	239				162			64	
Auto[b]	388	201				106			63	
Auto[c]	313	222				137			68	
Hulo[c]	281	232				146			96	
Djibouti										
Asal (5)[b]	307	208	283	273	349	117	222	152	140	280
N. Ghoubet[b]	212	202	261	278	313	108	182	164	155	524
Garrabays[b]	148									355
G2[d]	178		232	248			130	92	73	
G3[d]				236				65	92	
G4[d]	256		247	247			158	90	73	
G6[d]	238		244	247			150	91	106	
G7[d]	217		247	259			157	118	120	
G8[d]				231				53	82	
G10[d]				287				184	149	

133/4 prefix - Olkaria; 133/1 and 2 - Eburru OF - Olkaria; EF - Eburru; G - Fiale and area

D-P - D'Amore and Panichi empirical geothermometer; $\Delta^{13}C$ - carbon isotope geothermometer

a - Glover (1972); b - this report; c - Glover (1976); d - Geotermica Italiana Srl. (1987b)

TABLE 12. RESULTS OF PUBLISHED GAS GEOTHERMOMETERS APPLIED TO FUMAROLES IN UNDRILLED GEOTHERMAL AREAS IN KENYA (TEMPERATURES IN °C). RAW DATA SOURCES AS REFERRED TO BELOW (GEOTHERMOMETER TEMPERATURES ALREADY PUBLISHED ELSEWHERE, MAINLY FOR THE SOUTHERN RIFT, ARE NOT INCLUDED).

Fumarole	CO_2	H_2S	H_2	CO_2/H_2	H_2S/H_2	H_2S	H_2	CO_2/H_2	D-P	$\Delta^{13}C$
	—— Cl > 500 mgl^{-1} ——					- Cl < 500 mgl^{-1} -				
Bogoria Area:										
C-25[a]	301	234	293	290	345	155	242	192	190	
D-11[a]	307	245	273	260	298	170	204	122	164	
F-7[a]	320	243	278	261	309	168	214	124	155	
F-17[a]	303	243	279	270	310	168	215	143	171	
F-18[a]	297	243	268	258	291	167	196	117	170	
F-25[a]	310	254	280	269	303	184	218	142	170	
G-10[a]	303	246	282	274	314	172	221	154	176	
G-12[a]	300	239	287	282	329	163	230	172	187	
G-16[a]	295	241	276	270	308	165	211	145	172	
B-14[b]				236				64	82	
B-17[b]	303	240	250	230	259	163	162	51	161	
B-18[b]	307	245	246	224	248	171	156	37	163	
B-20[b]	307	241	256	238	270	165	174	68	179	
B-91[b]				216				18		
B-214[b]	306	237	260	242	280	159	180	79	173	
B-216[b]	285	227	236	219	244	144	136	25	154	
B-217[b]	303	231	252	234	271	151	167	60	159	
B-220[b]	313	238	254	232	269	160	170	55	161	
B-291[b]	286	222	230	211	238	137	126	7	124	
Baringo-Turkana:										
OK1[c]	335	269	299	283	325	206	253	175	210	498
KR12[c]	321	267				202			64	
KR18[c]	333	227				145			103	368
KR19[c]	340	242				167			108	389
KR23	339	210	245	208	276	120	153	0	47	533
KR34[c]	342	243				167			51	323
PK1[c](ave.)	317	281				222			100	354
PK4[c]	286	231	298	303	357	150	250	222	238	307
PK7[c]	318	273	298	288	319	212	250	187	160	389
SL7[c]	299	264	287	283	308	198	230	175	226	395
SL11[c]	299	325				287			83	
SL14[c]	302	263	285	279	305	197	227	166	217	368
SL15[c]	274	243	280	284	312	168	217	177	226	359
SL16[c]	315	295	278	263	262	243	213	127	148	403
SL19[c]	384	301	238	182	183	252	140	-61	100	
SL22[c]	386	283	253	202	227	226	168	-14	53	417
EM9[c]	353	295	254	214	218	243	170	14	65	466
EM20[c]	341	312	250	214	196	268	163	13	76	409
BR1[c]	286	218	256	247	289	132	173	90	98	328

OK - Ol Kokwe Island; KR - Korosi; PK - Paka; SL - Silali; EM - Emuruan Gogolak; BR - Barrier

D-P - D'Amore and Panichi empirical geothermometer; $\Delta^{13}C$ - carbon isotope geothermometer

a - Glover (1972); b - Geotermica Italiana Srl (1987a); c - Allen and Darling (in press)

TABLE 13. RESULTS OF PUBLISHED GAS GEOTHERMOMETERS APPLIED TO FUMAROLES IN UNDRILLED GEOTHERMAL AREAS IN ETHIOPIA (TEMPERATURES IN °C). RAW DATA SOURCES AS REFERRED TO BELOW.

Fumarole	CO_2	H_2S	H_2	CO_2/H_2	H_2S/H_2	H_2S	H_2	CO_2/H_2	D-P	$\Delta^{13}C$
		—— Cl > 500 mgl^{-1} ——				– Cl < 500 mgl^{-1} –				
Lakes Area:										
Koka[a]	333	198	259	229	312	103	178	49	91	
Koka[b]	309	193	239	213	279	96	142	10	57	297
Doredimtu[a]	318									
Chebicha[a]	321									
Chebicha[b]	302									357
Danshe[a]	313									
Danshe[b]	375	199				104			56	318
Borama[a] (ave.)	312									
Demo Argo[a]	315									
Deguna[a]	320		233	199			130	-21	54	
Abaya #7[a]	369	264	257	213	251	198	175	10	136	
Abaya #7[b]				216				18	58	498
Boku[b]				253				104	94	542
Tendaho:										
Loggia 17[a]	156	231	228	247	226	150	122	90	109	
Loggia 21A[a]	246	231	247	250	261	151	157	97	97	
Loggia 25[a]	148	214	220	238	225	126	108	68	97	
Loggia 120[a]	192	199	224	234	246	105	115	60	79	
Loggia 129[a]	178	194	198	201	201	96	66	-17	129	
Loggia 131[a]	175	227	225	239	224	144	116	71	94	
Loggia 172[a]	190	207	207	210	206	116	82	4	142	
Airobera[a]	214	201				107			63	
Ber Bahari[a]	91	219	229	259	238	133	124	119	118	
Dofan[a]	295	321	308	314	297	281	269	247	367	
Dubti 1[a]	267	267	282	290	296	203	222	191	248	
Dubti 2[a]	262	268	275	281	281	204	207	171	231	
Dubti 3[a]	273	255	271	272	285	185	200	149	269	

D-P - D'Amore and Panichi empirical geothermometer;

$\Delta^{13}C$ - carbon isotope geothermometer

a - Glover (1976); b - this report

TABLE 14. RESULTS OF STABLE ISOTOPIC CORRECTION OF CONDENSATION EFFECTS ON GEOTHERMOMETER TEMPERATURES FOR SELECTED FUMAROLES IN KENYA, ETHIOPIA AND DJIBOUTI (TEMPERATURES IN °C). RAW DATA SOURCES AS REFERRED TO BELOW.

Fumarole	CO_2 init	CO_2 corr	H_2S init	H_2S corr	H_2 init	H_2 corr	H_2S init	H_2S corr	H_2 init	H_2 corr
			Cl > 500 mgl^{-1}				Cl < 500 mgl^{-1}			
Kenya										
F-2[a]	312	290								
F-3[a]	324	289								
F-4[a]	335	288								
F-6[a]	292	269								
F-9[a] (ave.)	330	301								
F-10[a]	294	275								
KR12[b]	321	296	267	249			202	176		
KR18[b]	333	302	227	205			145	113		
KR19[b]	340	308	242	219			167	134		
KR23[b]	339	313	210	192	245	237	120	94	153	138
SL11[b]	299	272	325	308			287	262		
SL19[b]	384	358	301	287	238	232	252	232	140	129
Ethiopia										
Bobessa[c]	313	297	236	224			157	140		
Gebiba[c]	282	259	202	188	242	235	108	87	147	135
Auto[c]	388	379	201	196			106	100		
18[d]	289	242	234	206			154	114		
Hulo[d] (ave.)	281	251	232	214			152	126		
Djibouti										
G2[e]	178	116			232	224			130	114
G4[e]	256	215			247	238			158	140
G6[e]	238	129			244	225			150	116
G7[e]	217	170			247	239			157	142

F - Suswa; KR - Korosi; SL - Silali; G - Fiale

init - initial geothermometric temperature; corr - geothermometric temperature after correction of gas concentration by isotopic method.

a - Armannsson (1987); b - Allen and Darling (in press);
c - this report and Gizaw (1989); d - Glover (1976) and Craig et al. (1977);
e - Geotermica Italiana Srl (1987)

TABLE 15. RESULTS OF THE METHANE/ETHANE GEOTHERMOMETER APPLIED TO FUMAROLES IN KENYA, ETHIOPIA AND DJIBOUTI

Fumarole	Log CH_4/C_2H_6	Temp °C
KENYA		
Suswa		
F-7	3.95	324
F-12	2.92	287
F-28	3.61	314
Longonot		
F-23 (average)	3.83	321
Mt Margaret	3.26	302
Olkaria-Domes		
OF-1	2.53	267
OF-4	2.44	262
OF-13	2.58	270
OF-14	1.71	208
OF-15	2.65	273
OF-16	3.46	309
OF-20	3.75	319
OF-W	2.53	267
H-1	2.43	261
F-15 (average)	2.75	279
Eburru		
EF-1	4.92	347
EF-2	3.96	325
Menengai-Bogoria		
Arus	2.79	281
Korosi		
KR12	2.42	261
KR18	1.64	202
KR19	1.65	203
KR23 (average)	1.60	197
KR34	1.90	224
Paka		
PK1 (average)	3.92	323
PK4	4.11	329
PK7	2.34	256
Silali		
SL7	3.55	312
SL11	2.34	261
SL14	3.55	314
SL15	3.34	306
SL16	2.72	288
SL19	4.34	335
SL22	3.39	309
Emuruan Gogolak		
EM9	3.51	310
EM20	4.71	343
Barrier		
BR1	3.64	315
ETHIOPIA		
Aluto		
Bobessa	2.37	257
Gebiba	2.46	263
Auto	1.98	230
Corbetti		
Chebicha	2.84	284
Danshe	2.39	259
Koka	1.08	153
Gedemsa		
Boku	3.16	298
DJIBOUTI		
Asal (5)	2.64	273
N. Ghoubet	2.16	243
Garrabays	2.51	266

TABLE 16. CHEMICAL AND STABLE ISOTOPIC ANALYSES OF WATERS COLLECTED IN THE LAKES AREA (ETHIOPIA), 1990.

No.	Site	Sample Source	Temp °C	pH	Na	K	Ca	Mg	HCO_3	Cl	SO_4	Si	Li	B	F	$\delta^{18}O$	$\delta^{2}H$
										mgl^{-1}						- ‰SMOW -	
E11	Langano #2	H	65	7.9	740	85.6	9.18	2.6	1470	464	21.9	92.2	0.532	2.66	28	-0.2	- 6
E12	Abaya #6	H	96	9.5	1330	186	0.35	<0.1	2480	686	108	154.0	1.39	3.19	66	+0.1	-10
E13	Abaya #7	H	88	6.8	5.7	9.2	1.28	0.3	22	2.2	87.6	48.9	0.007	0.03	0.28	+9.7	+14
E14	Wondo Genet	H	65	7.1	173	44.5	11.1	3.5	600	23.3	<0.05	60.0	0.047	0.08	1.45	-2.1	-11
E15	Shalla #30	H	96	8.8	2190	20.0	0.60	<0.1	3460	1470	30.3	33.4	0.474	5.65	76	+2.8	+12
E16	Sodere	H	65	7.3	550	29.7	14.7	8.3	1340	140	113	52.2	0.232	1.28	7.2	-1.8	+ 5
E17	Lake Langano	S	-	9.4	370	20.6	4.94	1.7	791	155	14.7	33.2	0.007	0.64	14	+7.5	+39
E18	Lake Awasa	S	-	9.2	159	31.1	8.91	5.5	505	28.3	0.9	35.4	0.121	0.14	8.2	+7.8	+47
E19	River Awash at Sodere	S	-	-	-	-	-	-	-	-	-	-	-	-	-	+1.7	+ 9

G - geothermal well; H - hot spring; S - surface water

TABLE 17. CHEMICAL AND STABLE ISOTOPIC ANALYSES OF WATERS COLLECTED IN DJIBOUTI, 1989-90.

No.	Site	Sample Source	Temp	pH	Na	K	Ca	Mg	HCO_3	Cl	SO_4	Si	Li	B	F	$\delta^{18}O$	$\delta^{2}H$
			C		mg l^{-1}											- ‰SMOW -	
D01	Asal - 3*	G	-	-	29200	5030	17035	22.9	335	78425	11	237	15.3	10.1	9.8	+0.9	-
D05	Korilli*	H	36	6.45	10310	464	3040	466	55	22670	253	30.3	2.18	4.2	-	-1.3	-
D06	Abbe C.	H	75	8.70	493	14.6	157	<0.1	26	785	304	41.6	0.136	1.00	0.90	-2.9	-23
D07	Abbe N.	H	90	6.05	901	29.7	213	0.3	18.6	1530	323	47.9	0.290	1.55	1.14	-3.7	-27
D08	Plage de Ghoubet	S	-	-	-	-	-	-	-	-	-	-	-	-	-	+0.4	+ 3

F- fumarole; G - geothermal well; H - hot spring; S - seawater

* Analyses provided by Dr H Armannsson