

## GEOCHEMICAL STUDY OF THE ALID HYDROTHERMAL SYSTEM, DANAKIL DEPRESSION, ERITREA

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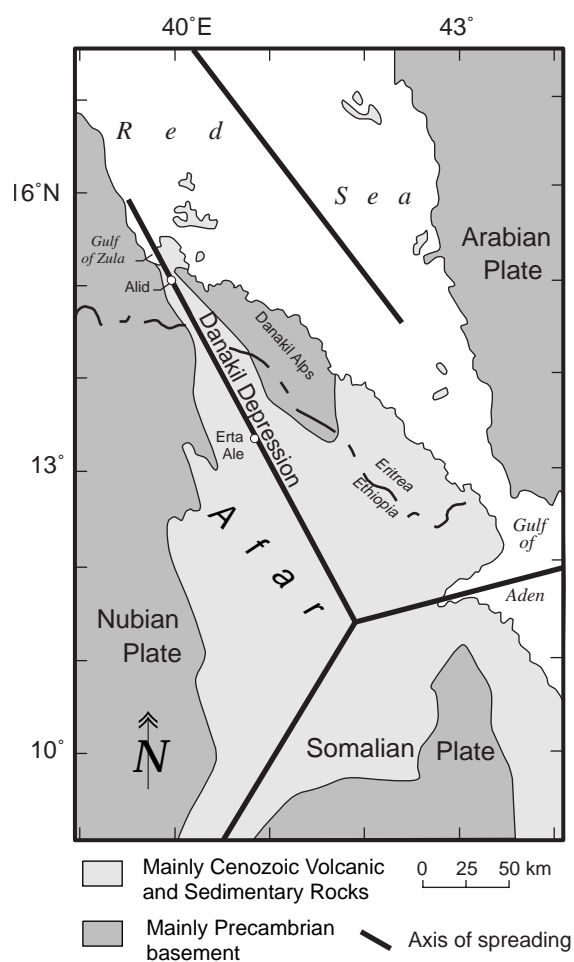
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### ABSTRACT

Detailed geological studies indicate that a relatively young, large, shallow, and still hot magmatic heat source is probably present beneath the Alid volcanic center in the northern Danakil Depression of Eritrea. Fumaroles and boiling pools are distributed widely on the north half of Alid, suggesting that an active hydrothermal system underlies much of that part of the mountain. The area of high convective heat flow covers at least 10 square kilometers. Gas geothermometers indicate likely reservoir temperatures in the range 250°C - 325°C. The isotopic composition of condensed fumarolic steam is consistent with 220-300°C boiling of groundwaters that may have come from various sources, including local lowland rain, fossil Red Sea water, or conceivably, highland rain water that evaporated significantly before percolating underground. Some gases in the reservoir fluid, particularly CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>S may be derived, directly or indirectly, from a silicic intrusion that very likely exists beneath Alid.

### INTRODUCTION

There is an urgent need to develop new domestic sources of energy to foster expansion of the Eritrean economy while minimizing the importation of costly fossil fuels. To help address this need, the USGS was funded by USAID to undertake the first phase of a study of the geothermal energy potential in the eastern lowland region of Eritrea. The Alid volcanic center was selected for detailed study because (1) it is the focus of geologically young rhyolitic volcanism within a background of spreading-related basaltic volcanism and (2) it is the site of many fumaroles (U.N.D.P., 1973; Beyth, 1994). The collection of waters and gases for chemical and isotopic analyses was carried out in February 1996. Standard sampling and analytical procedures were used for water and fumarolic gas samples (Trujillo et al., 1987; Giggenbach and Goguel, 1989; Fahlquist and Janik, 1992).



**Figure 1.** Simplified plate-tectonic map of the Afar Triangle region. Modified from figures in Barberi and Varet (1977).

## **GEOLOGIC SETTING**

The Alid silicic volcanic center is located along the axis of the Danakil Depression, the graben trace of a crustal spreading center that radiates NNW from a plate-tectonic triple junction situated within a complexly rifted and faulted basaltic lowland called the Afar Triangle (Figure 1). The Danakil Depression is an off-set subaerial segment of the spreading system that is opening to form the Red Sea (Barberi and Varet, 1977). The northern Danakil Depression lies near or below sea level for much of its extent. It is a graben bounded by the Danakil Alps to the east, which in this area rise to elevations of 400 to 650 masl and the Eritrean plateau or highland to the west, which rises to elevations of 2000-3000 masl. Alid volcanic center is an elliptical structural dome located at the center of the graben. The summit of Alid sits roughly 700 meters above a field of Quaternary basaltic lava that laps unconformably against the north and south flanks of the mountain. The major axis of the mountain is 7 kilometers, elongate in an ENE-WSW direction, perpendicular to the trend of the graben (Figure 2). The minor axis is about 5 kilometers long, parallel to the graben. The dome apparently formed as a result of shallow intrusion of rhyolitic magma, some of which was erupted (Clynne et al. 1996a, 1996b). The doming uplifted Precambrian mica and kyanite schists and deformed an overlying sequence of initially flat-lying Pliocene or Pleistocene sediments capped by lava flows of basalt, basaltic andesite, and rhyolite composition. These sediments and lavas now dip steeply and radially away from the center of uplift (Clynne et al., 1996a, 1996b). Subsequent to structural doming, there were eruptions of pyroxene rhyolite lavas on the flanks of the mountain. Still later, rhyolite was erupted as pumice and a pyroclastic flow from a graben-like summit depression.

## **REGIONAL HYDROLOGY**

The meteorological characteristics of northeastern Africa, including Eritrea and the Danakil region, have been described in various publications and reports, including Food and Agricultural Organization (1983), Michael (1986), Eklundh and Pilesjå (1990) and Beltrando and Camberlin (1993). The annual rainfall on the central highlands is generally 500-700 mm and comes from storms propelled by monsoonal winds blowing from the southwest toward the northeast. This rain occurs mostly in July and August. Little, if any, rain falls on the central highlands from December through February. In contrast, the eastern lowlands receive most of their rain in December and January from storms propelled by monsoonal winds blowing across the Red Sea from the northeast toward the southwest. Here less than 300 mm per year of rain generally falls, but it may be very spotty with no rain falling for a year or more on parts of the lowland

region while other parts are subjected to brief, torrential down-pours. Rivers and streams flowing to the eastern lowlands from the high plateau disappear into alluvial fan deposits, or pond in closed-basin lakes where the water evaporates to form playas. There is also the potential for lenses of relatively fresh and non-evaporated water to pond in the subsurface over deeper bodies of denser brine.

## **GEOHERMAL MANIFESTATIONS**

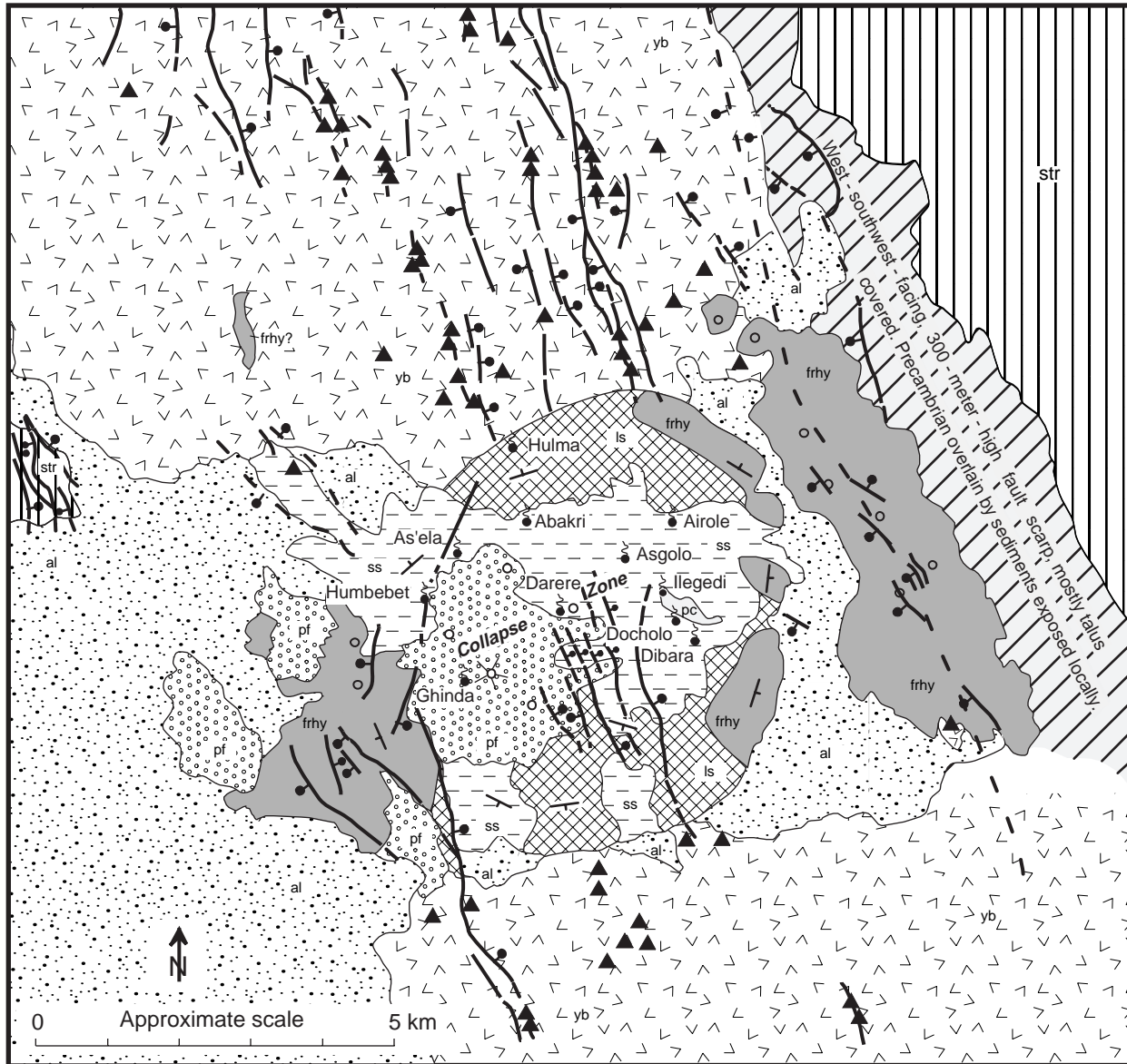
Fumaroles and boiling pools are distributed widely on the north half of Alid, suggesting that a hydrothermal system underlies much of the volcanic center (Figure 2). The presently identified area of this high heat flow is at least 10 square kilometers. We visited nine fumarole areas and selected six as being suitable for sampling of gas and water emanations (Table 1). All vent areas contain fumaroles at temperatures near the boiling point for their elevation. The physical nature and geochemical environment of the hot springs and pools at these sites strongly suggest that the waters consist of mixtures of condensate of fumarolic steam mixed with cooler, shallow groundwater.

















**Table 1.** Selected geothermal features of Alid volcanic center

<b>Sample #</b>	<b>Name</b>	<b>Elev m</b>	<b>Temp °C</b>	<b><math>\delta D</math> ‰</b>	<b><math>\delta^{18}O</math> ‰</b>
<b>Thermal Pools</b>					
ELW96-5	Ilegedi #1	515	50	50	9.69
ELW96-6	Ilegedi #2	515	36	30	3.85
ELW96-7	As'ela #1	480	54	33	3.18
ELW96-8	As'ela #2	480	57	35	3.61
ELW96-9	Ilegedi #3	515	66	24	4.44
ELW96-10	Humbebet	480	<60	12	-0.93
<b>Fumaroles</b>					
ELG96-1	Hulma	225	77	n.a.	n.a.
ELG96-2	Darere	580	95	10	-3.98
ELG96-3	Ilegedi #1	515	95	5	-0.88
ELG96-4	As'ela	480	95	5	-1.69
ELG96-5	Ilegedi #3	515	84	n.a.	n.a.
ELG96-6	Abakri	485	94	-1	-2.81

n.a. not analyzed

Fumaroles vent through rhyolite breccia (Abakri, As'ela, Darere), siltstones (Humbebet), and Precambrian basement rocks (Ilegedi). Therefore, location of the thermal features does not appear to be controlled by lithologic type or contacts of different lithologic units. Most of the thermal manifestations are located at elevations between about 460 and 600 meters, though hot rock and steaming vents also are present as low as 225 meters (Hulma) and slightly higher than 760 meters (Airole). Some fumaroles are



- |  |  |
|--|--|
|  Alluvium (al)  |  Strike and dip of beds and lava flows  |
|  Young basalt (yb)  |  Fault, bar and ball on downthrown side |
|  Pyroxene rhyolite: lava (frhy) and pumice (pf)   |  Fault, covered                         |
|  Lava shell (ls): includes basalt, andesite and amphibole rhyolite  |  Fault, approximately located           |
|  Sedimentary sequence (ss): includes basalt lava flows and sills, fine-grained clastic sediments, rhyolite breccia and evaporites |  Vent for post-dome rhyolite pumice     |
|  Stratoid basalt (str)  |  Vent for other rhyolite                |
|  Precambrian basement (pc)  |  Mafic vent                             |
|  |  Fumarole                               |
|  |  Contact                                |

**Figure 2.** Generalized geologic map of Alid volcanic center. Because map was traced from lines on air photograph, the scale is approximate and varies somewhat across the area.

aligned, suggestive of fault control. For example, several areas of alteration, including the one at Hulma, lie in a N50E zone parallel to the north base of Alid. Abakri, As'ela and Humbebet are present in adjacent drainages on the north flank of Alid along a roughly N45E trend.

#### **Chemical Compositions of Thermal Waters**

The thermal pools at Alid all are acid-sulfate in composition and contain little chloride (Clynne et al., 1996a). They are highly evaporated and have relatively high total dissolved solids ranging from about 1500 to 2500 mg/kg. Their compositions are mainly controlled by dissolution of the surrounding host rock by sulfuric acid, resulting in the formation of clay minerals after feldspars, and release of cations to solution. These pools provide relatively little information about deep fluids and cannot be used to infer conditions in any deep reservoir beneath Alid.

#### **Chemical Compositions of Alid Fumaroles**

Complete analyses of gas samples from Alid

fumaroles are listed in Table 2. The samples generally contained more than 95% steam, with the exception of the bubbling pool of Ilegedi #3 where some of the steam condensed in the pool and consequently could not be collected. However, because the fumaroles were not superheated with respect to boiling temperatures at their vent elevations (all about 97°C or less), some steam may have condensed as it rose through the mountain, causing the remaining steam to become enriched in non-condensable gas. Gas/steam ratios shown in Table 2 therefore do not necessarily reflect the compositions of deeper, hotter parent fluids.

With the exception of Hulma, most of the Alid fumaroles have roughly similar gas compositions (Table 2) and insignificant air contamination, shown by oxygen concentrations generally being near or below the detection limit. In contrast, Hulma's high Ar, O<sub>2</sub> and N<sub>2</sub> indicated that 97% of the sample was moist air discharged from a relatively cool (77°C) vent. As'ela was air-free, but was also slightly unusual in its low NH<sub>3</sub> and CH<sub>4</sub> concentrations.

**Table 2.** Gas Geochemistry of Alid Fumaroles

Sample Num.	ELG96-1	ELG96-2	ELG96-3	ELG96-4	ELG96-5	ELG96-6
Location	Hulma	Darere	Ilegedi #1	As'ela	Ilegedi #3	Abakri
Temp. (°C)*	77	95	95	95	84(gas from bubbling pool)	94
CO <sub>2</sub> (mol%) <sup>#</sup>	2.50	97.93	95.53	98.20	95.89	98.86
H <sub>2</sub> S	0.112	0.219	0.876	0.749	0.662	0.143
H <sub>2</sub>	0.057	1.093	2.498	0.503	2.624	0.605
CH <sub>4</sub>	0.031	0.225	0.132	0.061	0.144	0.085
NH <sub>3</sub>	0.050	0.128	0.389	0.004	0.005	0.095
N <sub>2</sub>	76.1	0.412	0.598	0.473	0.653	0.209
O <sub>2</sub>	20.3	0.0023	nd	nd	nd	0.0005
Ar	0.908	0.0054	0.0126	0.0116	0.0140	0.0047
He	nd	0.00151	0.00047	0.00046	0.00073	0.00018
N <sub>2</sub> /Ar	83.8	76.3	47.5	40.8	46.6	44.5
Gas/Steam (mol/mol)	–	0.0448	0.0199	0.0259	1.701	0.0565
δ <sup>13</sup> C (‰VPDB) <sup>†</sup>	–	-3.4	-3.4	-4.9	-3.3	-3.3

Gases collected in bottles according to methods of Fahlquist & Janik (1992)

\*ELG96-2,3,4,6 were boiling-temperature fumaroles with no superheat. Temperature readings may be ~2°C lower than actual conditions.

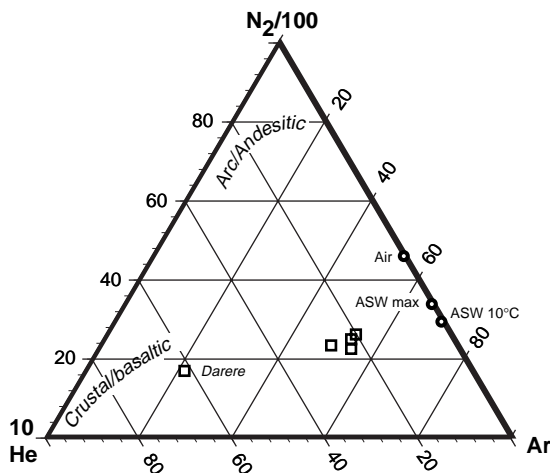
<sup>#</sup>Gas concentrations in mol% of dry gas.

nd not detected; – not determined

<sup>†</sup> δ<sup>13</sup>C in CO<sub>2</sub> from fumarole gas.

The thermal pools at As'ela also contained considerably less  $\text{NH}_3$  than those at Ilegedi (Clynne et al., 1996a). This is puzzling because As'ela is located within the shell unit that contains sedimentary rocks, whereas Ilegedi #1, with higher methane and ammonia concentrations, vents directly from the basement schists. Darere was unique in its higher He concentrations. But, in spite of these variations in minor gas constituent abundances, similarities among the Alid fumaroles were more noticeable than differences. The non-condensable gas compositions of all samples range from 95.5-98.9 mol%  $\text{CO}_2$ , and  $\text{H}_2$  is generally the next most abundant component (0.5-2.6 mol%).

The  $\text{N}_2/\text{Ar}/\text{He}$  relations in the fumarolic gases are strongly indicative of a parent geothermal reservoir water that initially was air-saturated groundwater. All data fall on a trend from air-saturated water to a crustal/mantle basalt endmember (Figure 3). The Darere fumarole is enriched in He, which may come from radioactive breakdown of crustal components or could be provided by mantle input in the form of basaltic magmas underlying Alid. As would be expected, there is little evidence for an arc/andesitic input of nitrogen to the system through crustal recycling at subduction zones (Giggenbach, 1995).



**Figure 3.** Triangular diagram ( $\text{N}_2/100$  vs.  $10\text{He}$  vs.  $\text{Ar}$ ) for gas samples from fumaroles on Alid volcanic center.

Within the geothermal system, the  $\text{O}_2$  in air-saturated groundwater is removed by reaction with rocks at high temperature, whereas  $\text{N}_2$  and  $\text{Ar}$  remain relatively unchanged. The ratio  $\text{N}_2/\text{Ar}$  for fumarole

gases ranges from 41-48, similar to a value of 38 for air-saturated water (Figure 3). This "reacted" groundwater has been enriched in  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{He}$  of crustal or magmatic origin, yielding the present "parent" geothermal reservoir water.

### Gas Geothermometry

We employed nine gas geothermometers (Table 3). In our experience, the D'Amore and Panichi (1980) method, which utilizes the relative abundances of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2$ , generally gives the most reliable results. The D'Amore and Panichi (1980) geothermometer indicates reservoir temperatures of  $265^\circ\text{C}$  for Ilegedi, the largest and most active of the Alid geothermal manifestations. The abundance of methane is negatively correlated with the calculated geothermometer temperature, so that addition of organically derived methane in the shallow subsurface would cause the geothermometer to give temperatures that are lower than the actual reservoir temperature.

Another commonly used geothermometer is the  $\text{H}_2/\text{Ar}$  method outlined by Giggenbach and Goguel (1989). As temperature increases, water is progressively dissociated, creating higher partial pressures of hydrogen. Argon is used to normalize the abundance of hydrogen, as it has a low solubility in water, similar to that of hydrogen. The  $\text{H}_2/\text{Ar}$  ratio therefore does not change significantly due to secondary processes such as condensation, mixing and boiling. In general, there are no significant extraneous sources of  $\text{Ar}$  to geothermal systems, making  $\text{Ar}$  a reliable normalizing component. Air contamination of a gas sample, if it were to occur, would result in high  $\text{Ar}$  concentrations and lower temperatures calculated by the  $\text{H}_2/\text{Ar}$  geothermometer. Instead, at Alid the  $\text{H}_2/\text{Ar}$  method yields very high temperatures, ranging from  $290\text{-}336^\circ\text{C}$ .

The  $\text{CH}_4/\text{CO}_2$ , and  $\text{CO}_2/\text{Ar}$  geothermometers (Giggenbach and Goguel, 1989) also yield high temperatures, up to  $340^\circ\text{C}$  for Ilegedi (Table 3). Gases from Darere, As'ela and Abakri also hinted at consistent and high temperatures of at least  $210^\circ\text{C}$ , and generally much higher. Of the nine gas geothermometers used, only one yielded temperatures less than  $200^\circ\text{C}$  for any Alid fumarole (Table 3). As discussed above, contamination of the samples by shallow groundwater and organically derived materials would tend to force underestimations of the original reservoir temperatures. The clear implication of the gas geothermometers is that the subsurface reservoir feeding the fumaroles is quite hot, likely over  $225^\circ\text{C}$  and possibly over  $300^\circ\text{C}$ .

**Table 3.** Results of gas geothermometry in °C

	T-DP	T-HA	T-MC	T-CA	T-FT	T-C	T-HC	T-SC	T-CN	Min	Max
ELG96-2	218°	336°	323°	296°	293°	243°	248°	176°	297°	176°	336°
ELG96-3	266°	336°	340°	278°	324°	241°	268°	210°	286°	210°	340°
ELG96-4	225°	290°	370°	280°	280°	243°	229°	206°	293°	206°	370°
ELG96-5	262°	334°	338°	276°	325°	241°	269°	203°	284°	203°	338°
ELG96-6	206°	323°	358°	299°	283°	243°	234°	166°	315°	166°	358°

DP: D'Amore & Panichi (1980)

HA: Hydrogen-Argon; Giggenbach & Goguel (1989)

MC: Methane-Carbon Dioxide;

Giggenbach & Goguel (1989)

CA: CO<sub>2</sub>-Argon; Giggenbach & Goguel (1989)

FT: Fischer-Tropsch; Arnórsson & Gunnlaugsson (1985)

C: Carbon Dioxide; Arnórsson & Gunnlaugsson (1985)

HC: H<sub>2</sub>+CO<sub>2</sub>; Nehring & D'Amore (1984)

SC: H<sub>2</sub>S+CO<sub>2</sub>; Nehring & D'Amore (1984)

CN: CO<sub>2</sub>/N<sub>2</sub>; Arnórsson (1987)

Min = lowest temp. of all geothermometers

Max = maximum temp. of all geothermometers

### **Isotopic Compositions of Thermal, Surface and Ground Waters**

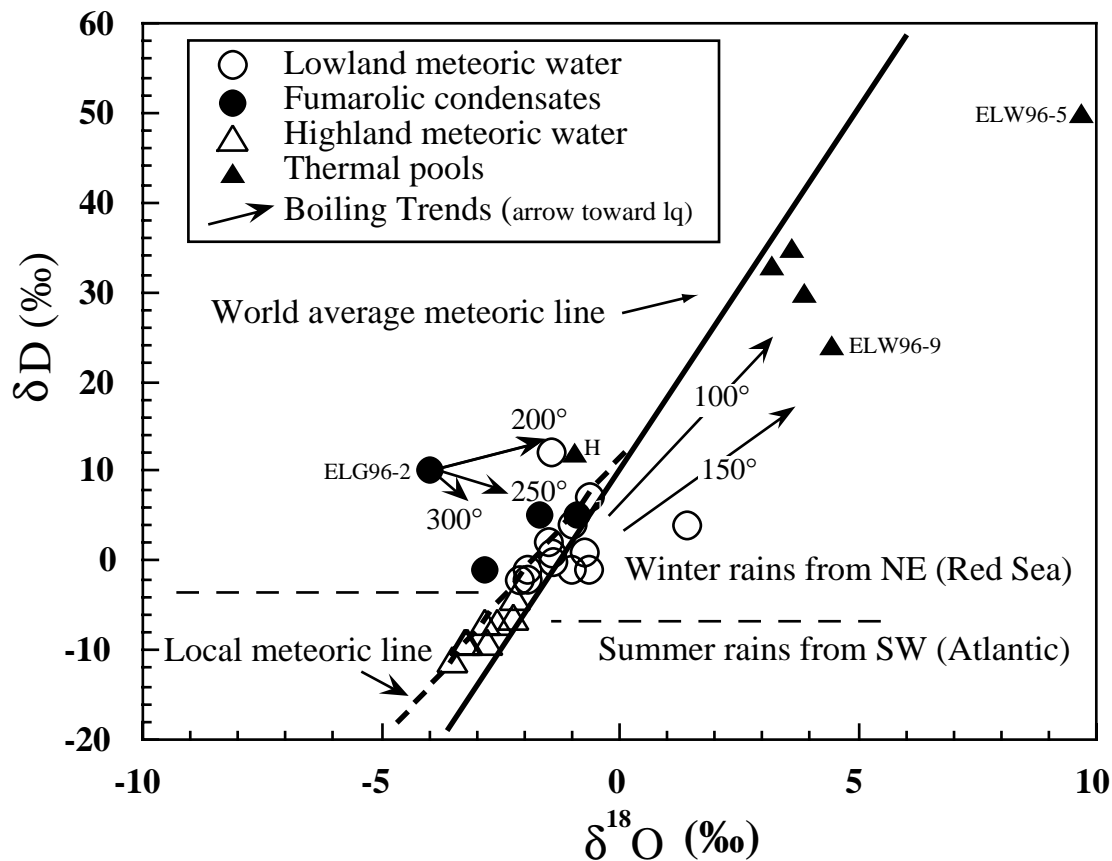
Isotopic compositions of Alid hydrothermal features and of groundwaters from the highland and lowland regions surrounding Alid are plotted in Figure 4, which also shows the trend line for meteoric waters throughout the world (Craig, 1961). In this figure, most of the Eritrean meteoric waters lie along a "local" trend slightly above the world average meteoric line. An important observation is that all of the meteoric waters collected in the central highlands are isotopically lighter (more negative values) than the meteoric waters collected in the eastern lowlands. These results were expected, given the regional rainfall patterns and topography. Lowland rains are produced from clouds coming from the northeast, off the Red Sea. Because the Red Sea itself is partially evaporated, and contains  $\delta D$  values greater than VSMOW and up to +9 ‰ (Craig, 1966), rains derived from the Red Sea should also be high in  $\delta D$ . In contrast, summer rains in the Eritrean highlands are not sourced from the Red Sea, and the high elevation of this area results in rains that are slightly depleted in D.

The stable isotopic compositions of thermal pools and steam condensates from Alid are listed in Table 1. The waters collected from thermal pools all are isotopically very heavy ( $\delta D$  up to +51 ‰) and plot below the world meteoric line (Figure 4). Their isotopic compositions result from <100°C evaporation of relatively stagnant bodies of water that are mixtures of local groundwater and steam condensate. Reaction of the relatively stagnant, acidic pool water with wallrock will shift the  $\delta^{18}O$  of the water to heavier values relative to the meteoric-water line. This might be a contributing factor in the attainment of the extremely heavy  $\delta^{18}O$  values for samples 5 and 9 (Figure 4).

The sample collected at Humbebet (ELW96-10, Table 1) plots above the average world meteoric line (labeled H in Figure 4) and contains the lowest TDS of any of the pools. Its odd isotopic composition is nearly identical to that of rain water that fell on Alid during the early morning of Feb. 5 ( $\delta D = +12\text{‰}$ ,  $\delta^{18}O = -1.4\text{‰}$ ) which is typical of isotopically enriched precipitation derived from the Red Sea. This is not surprising given that ELW96-10 was collected from a tepid seep rather than a hot evaporating pool, and may have relatively less thermal component.

The isotopic compositions of the condensed fumarolic steam samples all lie above the average world meteoric line (Figure 4). This is expected because boiling solutions always produce steam that has a  $\delta^{18}O$  value less than that of the coexisting liquid water. In contrast, the  $\delta D$  of steam is less than that of the coexisting liquid water only at temperatures <220°C. Above 220°C the  $\delta D$  of steam is greater than that of the coexisting boiling liquid. In Figure 4 arrows radiating from the dot ELG96-2 (Table 1) point in the direction of the composition that a coexisting boiling liquid would have if steam of isotopic composition given by point ELG96-2 physically separated from that liquid at the indicated temperature. Steam separation from a boiling liquid at a temperature lower than about 200°C appears to be unlikely as this would require the reservoir water to be more enriched in deuterium than any groundwater identified in this study.

The relations shown in Figure 4 indicate that the fumarolic steam could have been derived by high-temperature boiling of water that is isotopically similar to meteoric water that falls in the lowland region. The isotopic composition of the steam condensate also is compatible with a deep reservoir



**Figure 4.** Stable isotope compositions of Eritrean meteoric waters and hydrothermal fluids on Alid. See text for discussion. Full analyses and locations are listed in Clynne et al. (1996a).

fluid that is fossil Red Sea water, perhaps left over from a time when the Red Sea filled the Danakil Depression. In contrast, the isotopic data indicate that the fumarolic steam could not have been derived from a boiling reservoir water that is isotopically similar to the highland meteoric water. However, it is possible (though not very likely) that the parent reservoir fluid is highland water that was previously evaporated at a low temperature (atmospheric conditions) before percolating underground where it eventually entered the Alid hydrothermal reservoir. Finally, there is little indication of mixing with connate, metamorphic or mantle-derived water which would be relatively lower in  $\delta D$  and higher in  $\delta^{18}O$ .

The  $\delta^{13}C$  of  $CO_2$  in the Alid fumaroles varies from -3.3 to -4.9 ‰ VPDB, consistent with a magmatic source of  $CO_2$ , possibly mixed with carbon from marine carbonate. Much of the  $H_2S$ , and He emitted from Alid fumaroles may also be derived, directly or indirectly, by magmatic input from the subsurface granitic intrusion that likely exists beneath Alid.

#### **RESOURCE POTENTIAL**

The Alid volcanic center contains about a dozen identified areas with steaming ground or active fumaroles. All of these geothermal emanations have temperatures at or below the boiling temperature of water, but gas geothermometers indicate high subsurface temperatures of 250°C or more. The formation of Alid, a structural dome, by forceful intrusion of silicic magma is likely to have created abundant fractured zones beneath the volcanic center. Young basaltic volcanism on the flanks of Alid indicates that heat flow continues to be high, though it is unknown whether the silicic intrusion still contains any molten material. All of these factors can be interpreted as favorable for the potential of Alid as a viable field for geothermal power production. Future work should focus on identifying any zones of high heat flow and permeability that would serve as ideal sites for geothermal wells.

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