The geothermal potential of continental Yemen: new geochemical and isotopic insights from thermal water and gas discharges.

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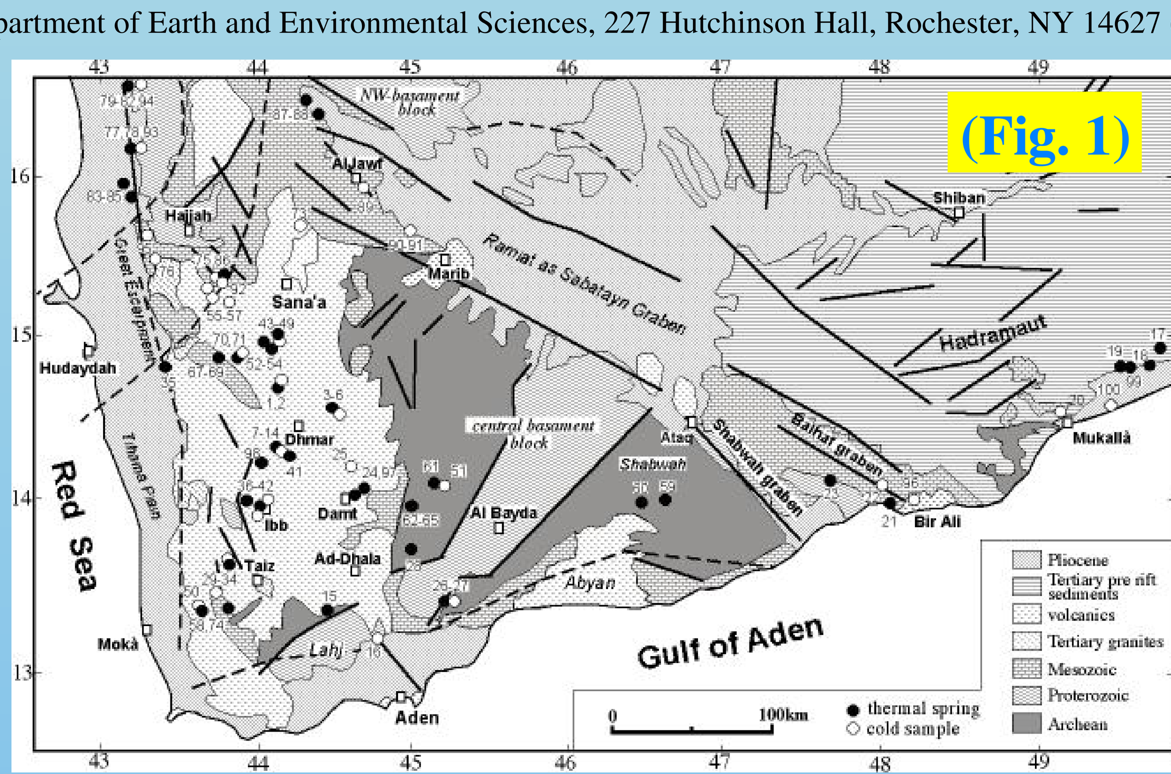
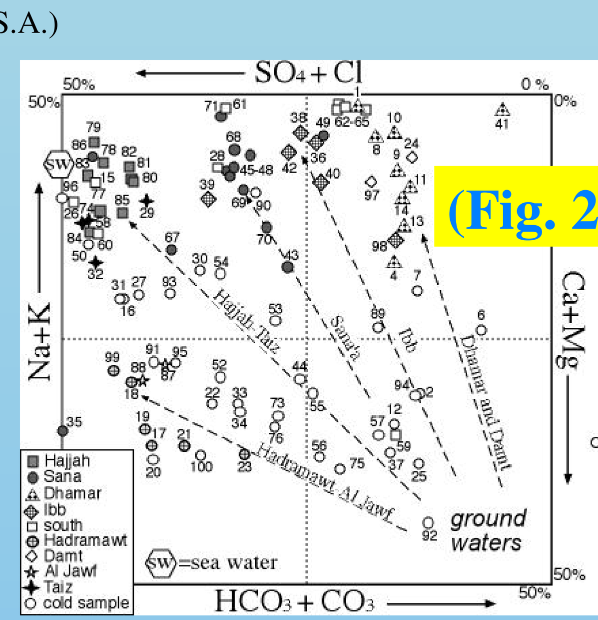
ABSTRACT - Most thermal springs of continental Yemen, fumaroles and boiling water pools (Fig. 1) have been sampled and analyzed for chemical and isotopic compositions in liquid and associated free-gas phases. All the water discharges have an isotopic signature of meteoric origin. Springs discharging in the central volcanic plateau show a prevalent Na-HCO_3-composition, clearly affected by an anomalous flux of CO_2 likely related to active hydrothermal systems located in the Jurassic Amran Group limestone sequence that underlies the 2000-3000 m thick volcanic suite and/or the Cretaceous Tawilah Group sandstone. Although organic CO_2 contribution from meteoric recharge waters cannot be ruled out, all the CO_2-rich gas samples have a $\delta^{13}C$-CO_2 signature that falls in the range of mantle CO_2 ($-3<\delta^{13}C<-7$ ‰ V-PDB). The relatively high $^3He/^4He$ ($1<R/Ra<3.2$) ratios measured in all the CO_2-rich springs and also some mixed N_2-CO_2 gas vents in the far east Hadramaut region suggest significant contribution from mantle to hydrothermal systems residing at the crust level in several areas of Yemen. Yemen thermal springs are only used as spa, bathing and irrigation. Nevertheless, liquid- and gas-geothermometry and geological considerations suggest that there are at least three areas (Al Lisi, Al Makhaya and Damt) inside the Yemen volcanic plateau (around Dhamar) that may have promising perspectives for the future development of geothermal energy in Yemen. Alternatively, they could be used as a source of energy for small-to-medium scale agriculture and/or industrial purposes.



(Fig. 1)



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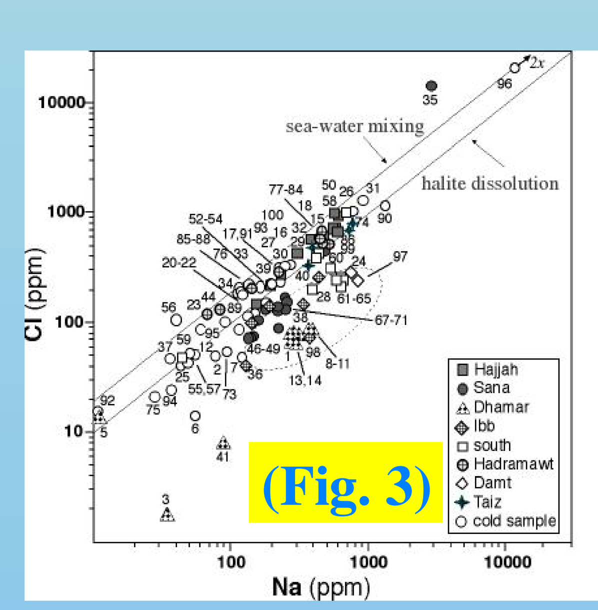

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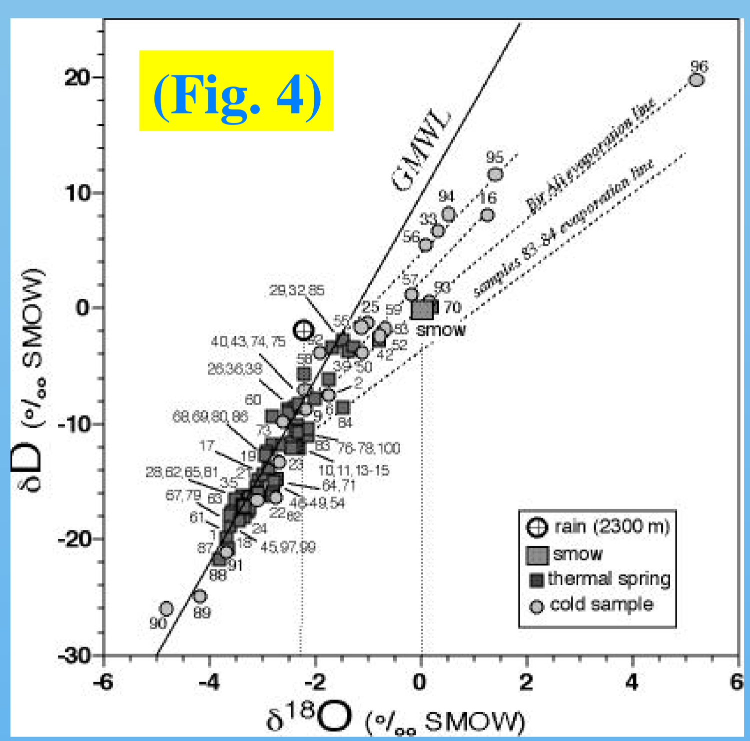

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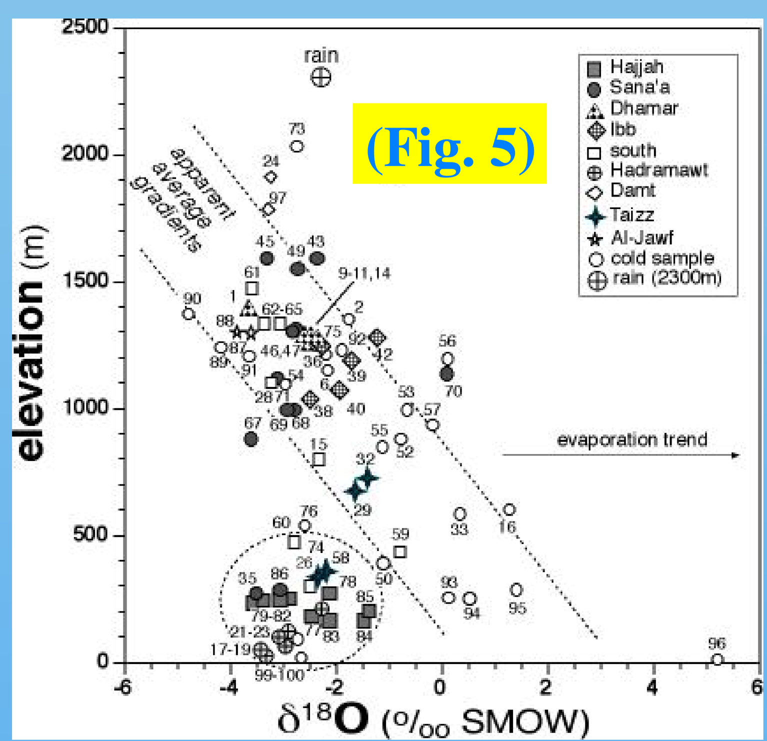
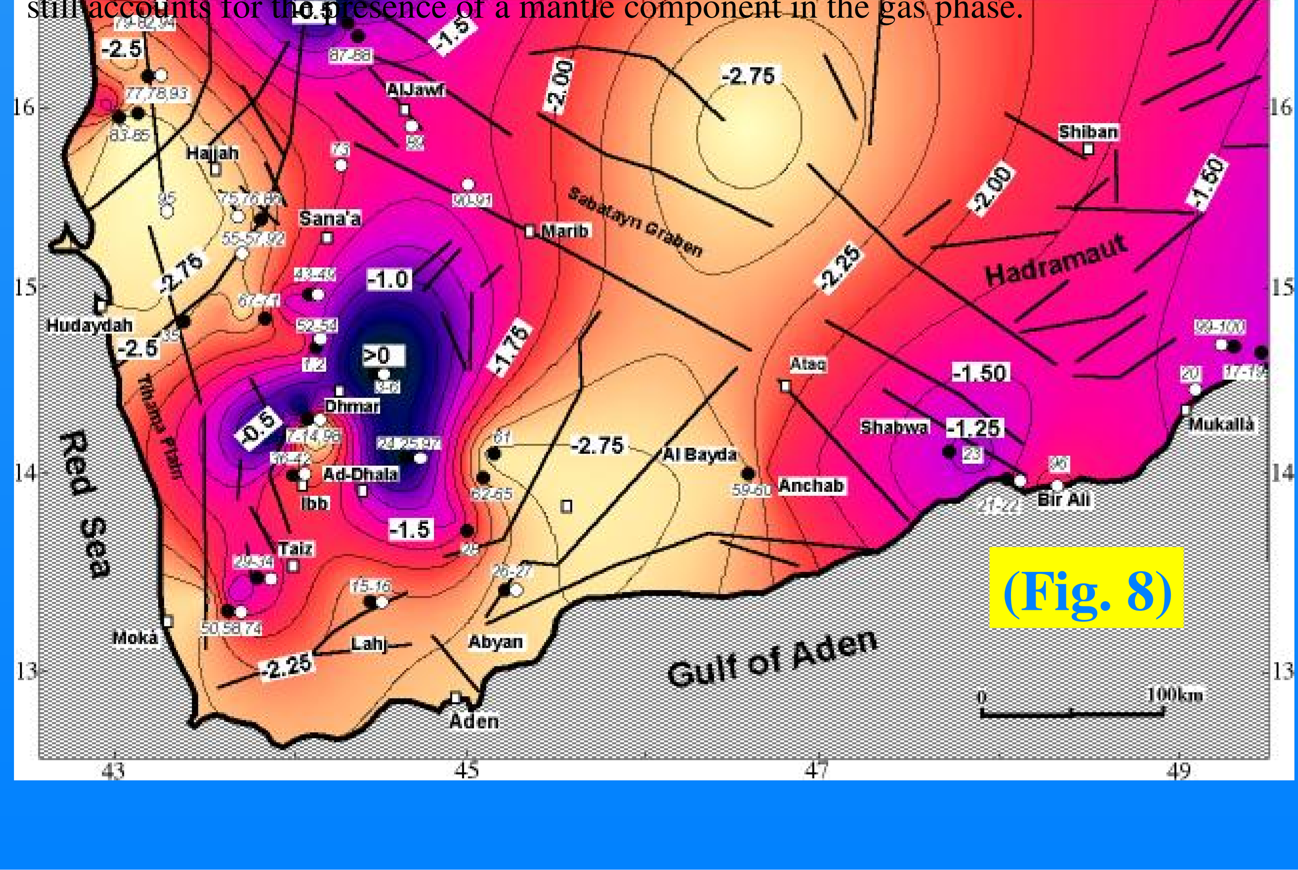


(Fig. 5)

WATER ISOTOPES - The δD-$\delta^{18}O$ diagram is reported in **Fig. 4** where a quite good alignment of both cold and thermal springs along the GMWL, up to -3 ‰ $\delta^{18}O$ values, is observed. From this value up to the +5.2 ‰ $\delta^{18}O$ of the partially evaporated Bir Ali crater lake, many samples have likely undergone evaporative processes, along more or less parallel lines. Several cold samples from rivers or wadies are isotopically heavier than sea water, and all of them plot in the Ca-SO_4 and/or in the Na-Cl sectors of the diagram **Fig. 2**, possibly in relation to strong evaporation of running waters and salt-bearing soil (halite and gypsum) dissolution. The two isotopically lighter cold springs in **Fig. 4** are located east in the Marib area (**Fig. 1**) at lower elevation with respect to the YTP springs, clearly suggesting a "*continental effect*". In spite of their isotopic lightness, in the $\delta^{18}O$-elevation diagram in **Fig. 5** they are not indeed the more elevated samples, and this clearly excludes that they have only undergone topographic isotopic fractionation. All thermal samples from Hajjah area, Hadramawt, Shabwah and two springs from south of Ta'iz discharge at low altitude (<500 m). They have an isotopic composition of mother rainfalls fed by at elevations higher than 1000-1500 m, with a quite vertical drop underground before the emergence. This well agrees with the fact that the main precipitation areas in Yemen (>800 mm/y) are highly concentrated in the central-southern areas of the YTP, east of Ta'iz and Ibb.

Origin of components and gas-water-rock interaction in Yemen - Values of calculated pCO_2 are reported in the iso-distribution map of **Fig. 8**. A large anomalous area occurs in the YTP, likely due to a strong contribution of deep CO_2 in the volcanic plateau centered at Al Lisi, Al Makhaya and Dam, as also evidenced by the $^3He/^4He$ ratios. Relative high R/R_a ratios were also measured in gas samples outside the YTP, such as the N_2-rich gas phase associated to the thermal springs of Kirsh (R/R_a = 1.21) and at Al Rawdhah (R/R_a = 2.57) in the far east of Yemen (Mukalla area), suggesting the presence of active transpressive deep faults, from where primary mantle ^3He is able to cross, relatively fast, the entire crust. The uprising of deep CO_2 into the thermal aquifer(s) hosted inside the YTP and its consequent acidic solution affects the final pH of thermal aquifers, by contrasting the natural basic evolution of pH during mineral water-rock interaction due to the typical alkaline hydrolysis of silicates. The top left pH-pCO_2 diagram of **Fig. 9** shows this effect. Several thermal discharges are saturated in calcite, being $SI_{calcite}$ inversely proportional to the pCO_2 of the solution (top right of **Fig. 9**), but mostly directly related to the pH of the solution (bottom left of **Fig. 9**). The HCO_3^- and CO_3^{2-} concentration depends on the pH and, therefore, $SI_{calcite}$ is proportional to pH and pCO_2 if the concentration of HCO_3^- ions is due to high pCO_2 in solution. The correlation between HCO_3^- and pCO_2 values (bottom right of **Fig. 9)** suggests that few samples from the central metamorphic basement block have HCO_3^- likely deriving from other sources than CO_2. A pCO_2-temperature correlation diagram is shown in **Fig. 10** where all thermal springs from Yemen lie inside a triangle. where, on the left side, relatively low temperature springs are located, though affected by progressive CO_2 inflow. They have undergone cooling during rising to the surface by: *i)* conduction with the formations hosting the relative aquifers and/or *ii)* because of mixing with colder shallower aquifers perching into the thermal rising ducts. On the top right-hand side of the diagram are positioned the two steam condensates from Al Lisi and the boiling CO_2-bubbling springs emerging at Al Makhaya. These areas are the less affected by both shallow thermal re-equilibration in liquid phase and mixing processes. The helium isotopic ratio at Al Makhaya (R/Ra=0.93) still accounts for the presence of a mantle component in the gas phase.



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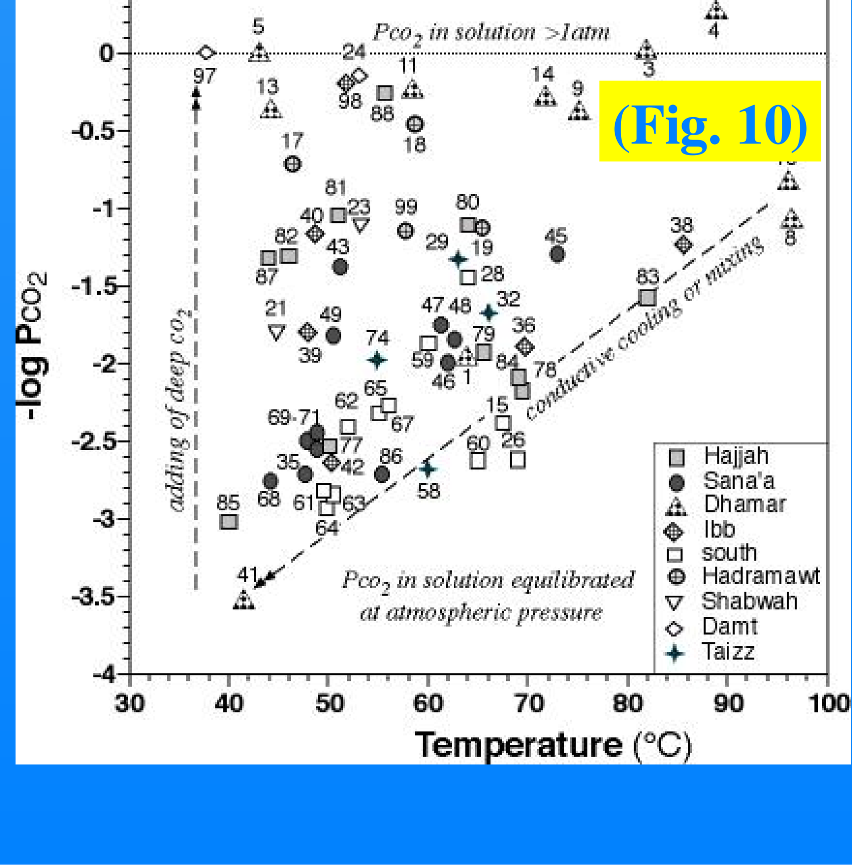

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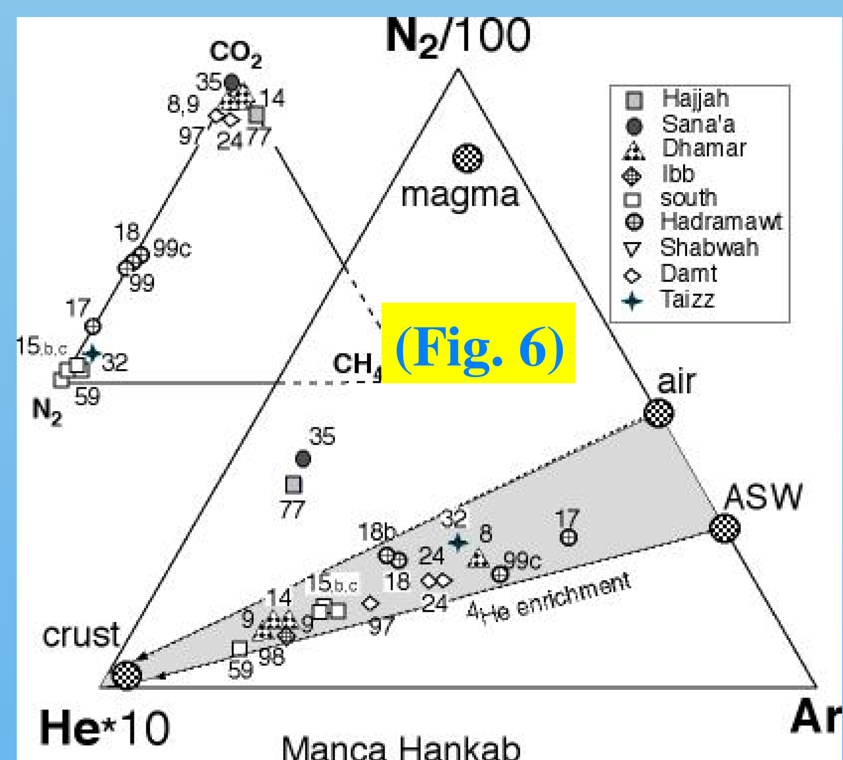

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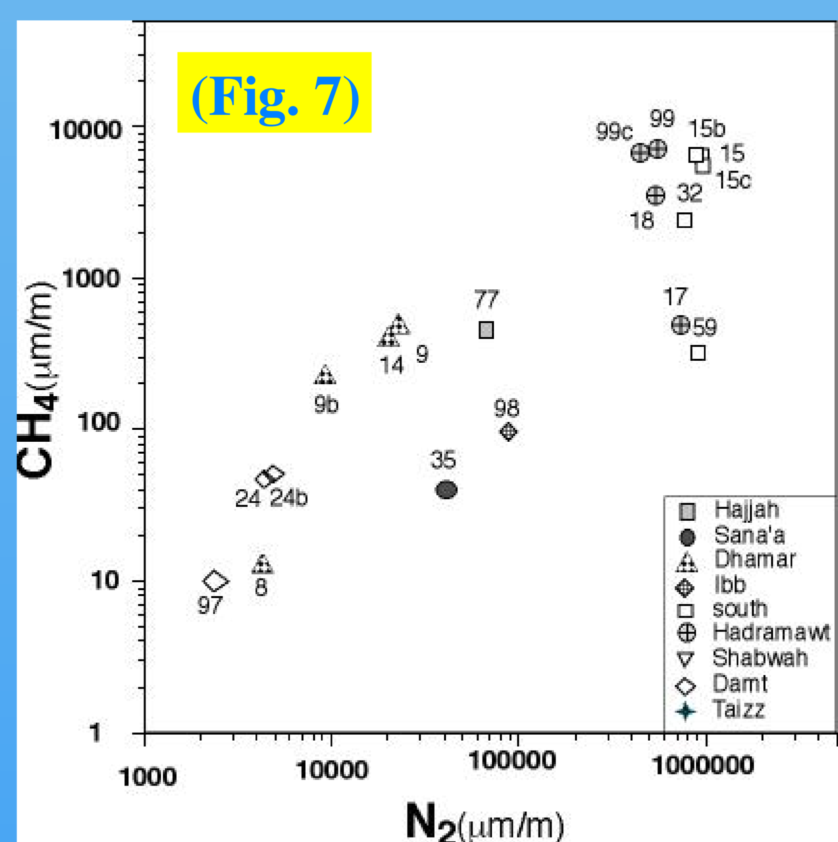

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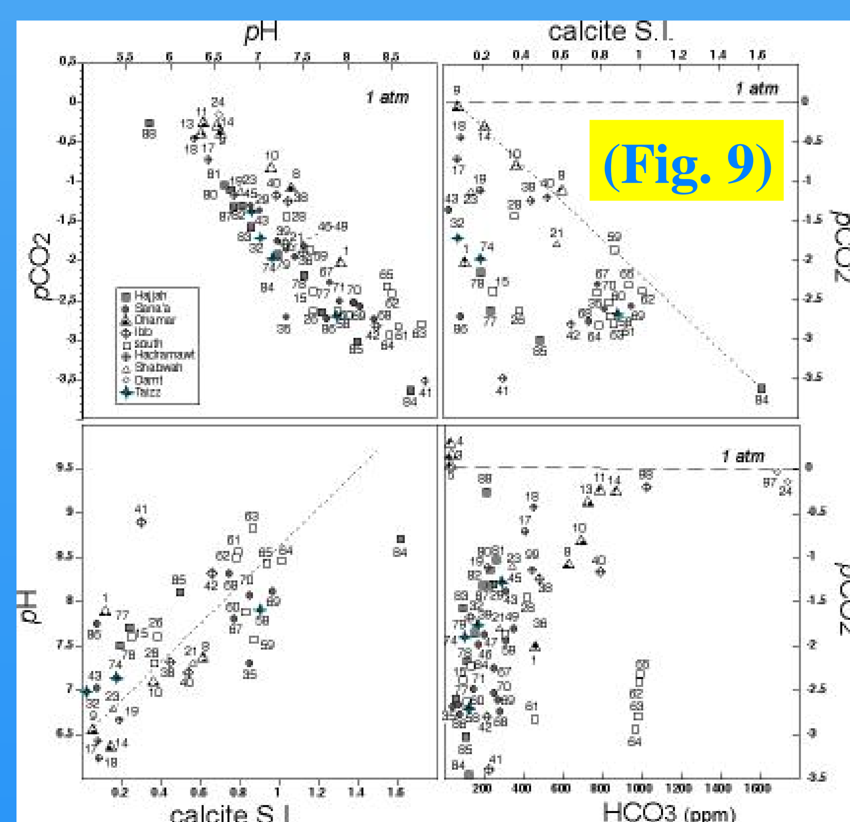
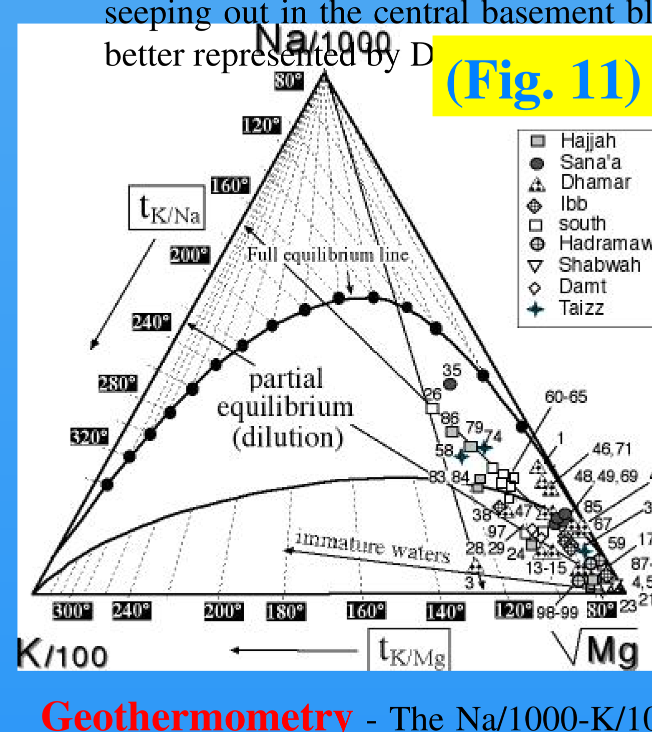


(Fig. 9)

WATER CHEMISTRY - Thermal samples are divided into 9 groups according to the area of emergence (Hajjah, Sana'a, Dhamar, Ibb, the South, Hadramawt, Damt, Al Jawf and Ta'iz in **Fig. 1**), whereas cold samples, comprising some waters collected in summertime with temperature ≥40 °C, constitute a separate homogeneous group. Only few cold samples have the typical Ca-HCO_3 composition (**Fig. 2**) coinciding with cold wells located at high elevation. Generally speaking, salinity (TDS) values vary from as low as 273 up to more than 83,000 (Bir Ali crater lake) mg/L. In Fig. 2 several evolutionary trends can be recognized: 1) Hadramaut and Al Jawf, Ca(Na)-SO_4(Cl) composition, likely deriving from the dissolution of *sabkha*-related gypsum and/or halite along their hydrological circuits; 2) Hajjah-Ta'iz: thermal springs circulating in crystalline formations and/or geological units characterized by the presence of halite (marine evaporites) or connate marine waters; 3) Sana'a, 4) Ibb and 5) Dhamar and Damt trends have a progressive increase in the Na-HCO_3 component. The Na-HCO_3 increase for 3, 4 and 5 is evidenced in the Na-Cl binary plot of **Fig. 3**. The Hajjah, Ta'iz and Hadramawt areas, as well as many cold samples, fall in the area delimited by the seawater-meteoric water dilution and the halite dissolution lines. The Dhamar, Damt, Ibb and Sana'a discharges and some samples from the Sout lie on the right side of the Cl/Na=1 line.

GAS CHEMISTRY AND ISOTOPES - The CO_2-N_2-CH_4 diagram is in the top left-hand side of **Fig. 6** where three groups are distinguished: *i)* CO_2-dominated gases, from YTP (Yemen Trap Plateau) and one spring from Hajjah; *ii)* N_2-dominated gases, from South Yemen: near Ta'iz, in the Lahj district and at Shabwah; *iii)* N_2-CO_2 gases from Hadramawt area. No gas emissions are dominated by CH_4, the highest content being at Hadramawt (<7000 μmol/mol). In **Fig. 6** the Ar-He(x10)-N_2(/100) diagram also is shown with *i)* pure air (N_2/Ar=83), *ii)* air-saturated water (ASW) (N_2/Ar=38), *iii)* andesitic gases (N_2/Ar=800) and *iv)* gases generated in the crust. With the exception of two samples from Hajjah and Sana'a, all the remaining gases are in the gray "crustal" trend. All the CH_4 contents are related with those of N_2 (**Fig. 7**), suggesting that N_2 (mainly derived from the atmosphere) is also partly related to an organic shallow origin as also supported Similar information can be derived from the light hydrocarbons data (not reported). In spite of this, the $CH_4/(C_2H_6+C_3H_8)$ ratio, coupled with the generally low CH_4 contents, suggests that the feeding fluids at Damt and Al Makhaya are characterized by relative higher temperature (about 150 °C). The $\delta^{13}C$-CO_2 values suggest that those gases seeping inside the YTP have a prevalent mantle-related value (-4.0 to -8.0 ‰), whereas CO_2 from the South and from the Hadramaut has a lighter isotopic signature ($-10<\delta^{13}C<-15$ ‰). The $^3He/^4He$ isotopic ratios are from 0.03 to 3.21 R/Ra (where R is the $^3He/^4He$ ratio measured in the sample and Ra is that of the air, 1.39×10^{-6}) and can be related to a two-member mixing process: a crustal source region, related to the N_2-rich Anchab gas (# 59), seeping out in the central basement block and (R=0.025) and a deep source (mantle) better represented by D[illegible] and Al Rawdhah (R/Ra=2.57) in Hadramaut.



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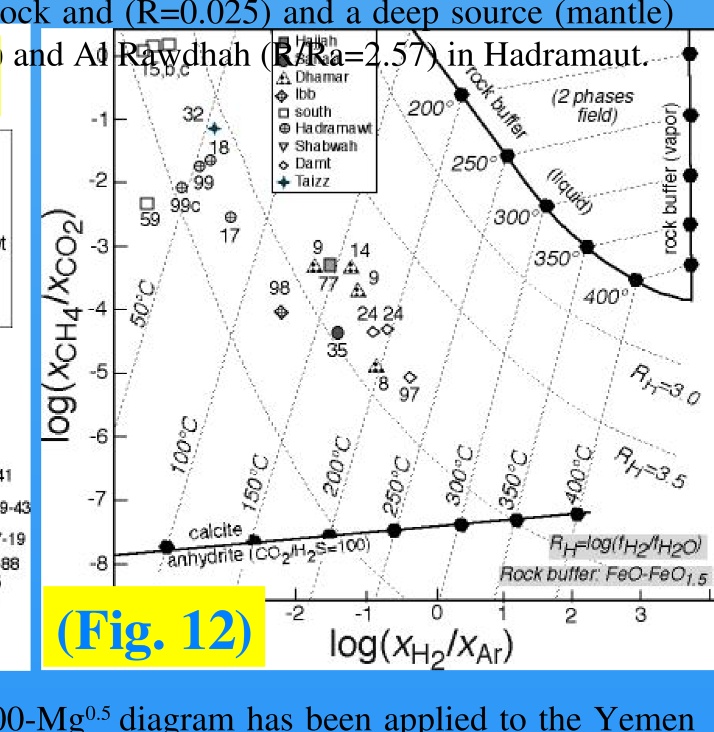

(Fig. 12)

Geothermometry - The Na/1000-K/100-$Mg^{0.5}$ diagram has been applied to the Yemen water samples. In spite of the high deep temperature suggested by the K/Na geothermometer, all samples are clearly positioned far from any certain hydrothermal equilibrium. Samples closer to the right ascending branch of the full equilibration curve suggests that re-equilibration and/or dilution play a relevant role in the final cationic composition of most thermal springs, i.e K/Mg temperature (<130 °C) are more realistic.

In **Fig. 12** all gas samples have been plotted in a $\log(CH_4/CO_2)$-$\log(H_2/Ar)$ diagram, where gas compositions from hydrothermal systems located between the full equilibrium line for liquid-dominated, two phases and vapor-dominated 200-400 °C systems, are completely missing in Yemen. All gas compositions plotted in the diagram seem to be far from any deep equilibrated high-temperature conditions. Nevertheless, two different groups of gases can be recognized. The first one, on the top left side of the diagram, characterized by relative higher CH_4 content and lower H_2, includes samples from the South of Yemen and the eastern Hadramaut region; the second one, with relatively lower CH_4 and higher H_2, pertains to those gases emerging from the YTP (Dhamar, Ibb, Damt). Although quite re-equilibrated at relative lower temperature, the second group suggests relative higher deep temperature of the source in the range 150-200 °C. Being the relative thickness of the volcanic YTP of at least 2000-3000 m and considering that at Al Makhaya and Al Lisi there are boiling mud-pools and fumaroles, respectively, we might consider the base of the volcanic products as the main reservoir source of rising fluids inside the YTP, at likely temperature of 150-200 °C. Considering that mixing and re-equilibration affect the chemical composition of both gas and liquid phases, such a temperature has to be considered as the minimum temperature existing at that depth.

CONCLUSION - The chemical-physical features of the Yemen fluid manifestations suggest an active tectonics that is present not only in the volcanic YTP and surrounding areas, but also spread in other regions, e.g. Hadramaut region. This agrees with the presence of active basaltic volcanism at several places inside the YTP (Dhamar, Al Lisi, Damt, Harra of Arhab, Jabal el-Marha) and along the Aden coast and the occurrences of magmas residing at shallow depth. The areas of Al Lisi, Al Makhaya and Damt can be considered of very high geothermal potentiality. As a further possible economic resource, shallow explorative wells at Damt could be drilled to verify the possibility to produce CO_2 for Yemen industry. Both the relatively high $^3He/^4He$ ratio and almost 40 % by vol. of CO_2 in the gas phase with $\delta^{13}C$-CO_2 values in the mantle range at Ar Rawdhah (Hydramaut) suggest very active tectonics also in the Mukalla area. Alternatively, such high ^3He value could be related to the presence of residing mantle magma in the crust. Finally, as many thermal springs have TDS values < 1000 mg/L they could be used for both agriculture and drinking purposes.