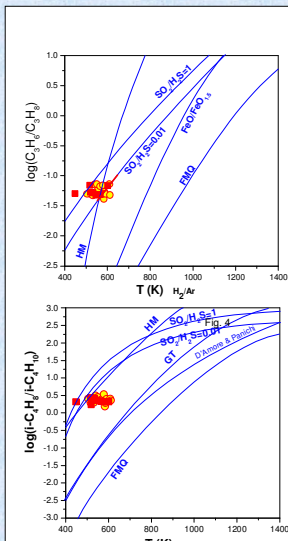
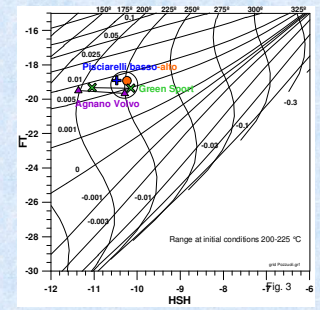
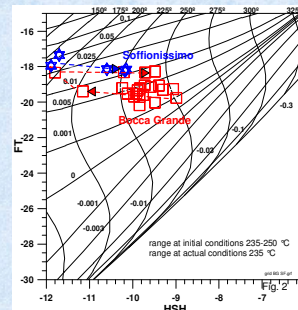
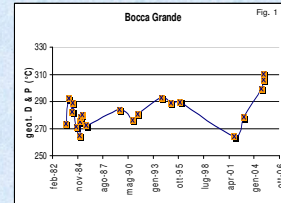


Gas geothermometers

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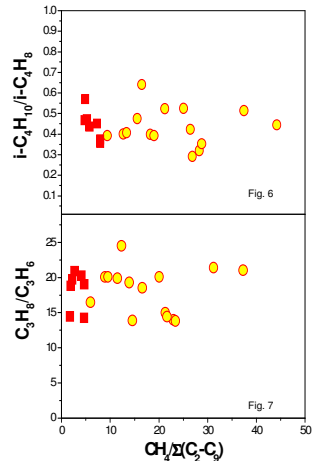
Gas geothermometers are based on equilibrium chemical reactions between gaseous species. For each reaction considered a thermodynamic equilibrium constant may be written, where the concentration of each species is represented by his partial pressure in vapor phase. The gas-gas equilibrium in geothermal fields with two phase-components should not reflect the real gas composition present in the reservoir. It depends from many factors like gas/steam ratio. It is assumed that there is no re-equilibration of the chemical species from the source or sources to wellhead. The fluids analyzed are those collected at the well head. In geothermal fields the concentrations (or ratios) of gases like CO₂, H₂S, H₂, N₂, NH₃, and CH₄ are controlled by temperature. Because of that, data from gas have been used to study a correlation between the relative gas concentrations and the temperature of the reservoir using the D'Amore and Panichi (1980) geothermometer based on partial pressures of CO₂, H₂S, CH₄, H₂, where CO₂ is externally fixed (fig. 1). Hydrocarbon compounds in fumarolic gases result less abundant (up to one order of magnitude) with respect to those measured in gases sampled from the productive wells. This compositional difference is likely to be caused by the partial dissolution into the superficial aquifer of hydrocarbons which fed the fumaroles, since these compounds are characterized by a higher solubility with respect to that of the other inert gases (mainly due to their higher molecular weight). On the contrary, productive-well fluids, directly derived from the geothermal reservoir, are not affected by this "scrubbing" process. Nevertheless, light hydrocarbon compounds, such as methane, ethane, propane, propene, i-butane and i-butene, show very similar solubility, thus the equilibrium reactions among them, depending on their reciprocal ratios and not on their absolute abundances, result almost independent from both phase transfer processes and the influence of superficial aquifer. Therefore, it is reasonable to consider that the application of geothermometric techniques based on thermodynamic equilibrium of organic gases is a reliable tool to evaluate the temperature of deep systems even by adopting the hydrocarbon composition of natural discharges.

The grid diagram by D'Amore & Truesdell (1985) shows that, using two gas equilibrium equations expressed as gas concentrations versus water, we can evaluate both the temperature of the reserves, and the "y" value representing the steam fraction. This graphical method is based on the Fischer-Tropsch [FT = 4 log (H₂/H₂O) - log (CH₄/CO₂)] and pyrite-magnetite [HSH = 3 log (H₂S/H₂O) - log (H₂/H₂O)] reactions. The diagram shows that an increase in temperature and decrease in "y" could indicate that there has been a contribution of hotter deeper fluids with high saturation in the liquid phase. An increase in both parameters (temp and steam fraction) could mean an apparent increase in temperature caused by secondary vapour with zero saturation in the liquid phase and a strong accumulation of local non-reactive gas in a pure gas phase. A decrease in calculated temperature and steam fraction "y" could be caused by a local source of low temperature water crossed by the gas. A change in temperature accompanied by an increase in the "y" value, often is associated a decreasing in ratio (HSH/H₂O).



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References
 D'Amore F., 1991. Gas geochemistry as a link between geothermal exploration and exploitation. Edit. Application of geochemistry in geothermal reservoir development. 93-117.
 Caprai A., 2005. Volcanic and Geothermal gases and low-enthalpy Natural Manifestations. Methods of Sampling and Analysis by Gas Chromatography. Journal of Applied Sciences, Asian Network for Scientific Information, 5 (1), 85-92.
 Ferrara G., Giuliani A., Magro G., 1981. La composizione isotopica dell'argon nei gas fumarolici di Vulcano (Isole Eolie) e della Solfatara (Campi Flegrei). Rend. Soc. Geol. It., 4, 221-224.
 Giggenbach W.F. & Goguel R.L., 1989. Collection and analyses of geothermal and volcanic water and gas discharges. Report N. CD 2401 (3th ed.), Chemistry Division DSIR, Petone, New Zealand.
 Caprai A., Leone G., Doveri M., Mussi M., Calvi E. Geochemical surveillance of reactive gas from Pozzuoli Solfatara (Naples, Italy): chronological evolution and local ground displacement.

The Giggenbach geothermometer (1991) (fig. 8), expresses the LHA [log (XH₂/XAr) vs the LCA (log X CO₂/ XAr) values, considering an equilibrium line on which are plotted all the dissolved gases within a single liquid phase. The horizontal line corresponds to the predicted composition for equilibrium in the vapor phase. The other lines represent intermediate conditions; the steam increase at equilibrium or the loss of Ar before equilibrium is attained. The following figure shows the historical data relative to the Bocca Grande and Soffionissimo fumaroles plotted against the data measured in Central American wells and fumaroles. Note the similarity between the fumarole gas values at Pozzuoli and for one well. The temperatures obtained at Pozzuoli fall within the 300-350 °C range, whereas in one well the temp values are around 260 °C, with the fumarole showing a value of 300 °C. The results for the other well indicate very low temperature conditions.

