Evaluation of geochemical characteristics of groundwater in Wailpally watershed, Nalgonda District, Andhra Pradesh, India

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Major ion chemistry in a hard rock fractured subsurface aquatic system indicates significant difference in mean content of many parameters. The ionic dominance pattern is in the order of $Na^+ > Ca^{2+} > .Mg^{2+} > K^-$ among cations and $HCO_3^- > Cl^{--} > SO_4^{-2} > NO_3^- > F^-$ among anions in pre monsoon. In post monsoon Mg replaces Ca^{2+} and NO_3^- takes the place of SO_4^{-2}. Soltan's classification categorizes the groundwater as Normal sulphate type with 66% of samples in pre monsoon and 92% in post monsoon having SO_4^{-2} content in <6 meq/l. The Base Exchange Indices of majority of the gound water samples are of Na^+-SO_4^{-2} type and rest belong to Na^+-HCO_3^- type. The groundwater based on meteoric genesis index show that almost all the samples belong to shallow meteoric percolation type. Weathering of silicate rocks in the region is one of the important processes responsible for the higher concentration of the Na^+ in groundwater. The Ca^{+2}/Mg^{+2} ratio of 1 to 2 in many (80% in pre and 74% in post monsoon) indicate dissolution of dolomite and calcite for Ca^{+2} and Mg^{+2} content in groundwater. Ca^{+2}+Mg^{+2} and Cl^- (m mol/l) plot confirm that ion exchange is the dominant process as Ca^{+2} and Mg^{+2} increase with increasing salinity, negative chloralkali indices in both the seasons further prove that ion exchange between Na^+ and K^+ in aquatic solution took place with Ca^{+2} and Mg^{+2} of host rock. The molar ratio of Ca^{+2}/Na^+ (0.60 to 0.90), Mg^{+2}/Na^+ (0.70 to 0.72) and Mg^{+2}/HCO_3^- (0.33 to 0.48) together with Na^++K^+/T_z^+ ratio (0.49 to 0.41) and $(Ca^{+2}+Mg^{+2})/\ T_z^+$ ratio (0.51 to 0.60) suggest weathering of silicate rocks are responsible for major ion chemistry of groundwater in Wailpally watershed. The correlation coefficient and t test also prove that the groundwater has under gone substantial seasonal variations.

Methanethiol: A geochemical link between carbon and sulfur in hydrothermal systems?

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Current 'metabolism-first' models for a hydrothermal origin of life on Earth invoke abiotic formation of methanethiol (CH_3SH) as the crucial link between carbon and sulfur that may have led to primitive thioester-based (Acetyl-CoA) metabolism [1, 2]. However, the origin and distribution of CH_3SH in modern vent fluids has not been adequately constrained.

To evaluate this possibility, we conducted a survey of CH_3SH abundance in vent fluids from ultramafic (Rainbow, Lost City), basaltic (Lucky Strike, TAG, 9°N EPR) and sediment-hosted (Guaymas Basin) hydrothermal systems. These systems are characterized by a broad range of temperature, redox and sulfur fugacity. Highest levels of CH_3SH (15–16μM) were observed in Guaymas Basin fluids influenced by hydrothermal alteration of unconsolidated organic-rich sediment. Lowest levels (1.7nM) were observed in H_2-rich fluids at Lost City. A key finding is that CH_3SH concentrations in many high temperature (>300°C) fluids from H_2-poor basalt-hosted systems (3.98–20.1nM) were comparable to or greater than those in H_2-rich fluids at Rainbow (7.5–8.4nM). This observation strongly suggests that CH_3SH in vent fluids is not forming by CO_2 reduction as previously assumed [1,3], and is consistent with experimental evidence that CH_3SH formation from CO_2, H_2 and H_2S is kinetically inhibited under hydrothermal conditions.

Thermodynamic considerations suggest that the source of CH_3SH to many high-temperature fluids may instead be reaction of CH_4 with H_2S at reaction zone or upflow conditions. Unlike CO_2 reduction, CH_3SH formation by this mechanism is more favorable in higher temperature, more oxidizing fluids. Results of this study indicate that low temperature, high-pH reducing fluids emanating from serpentinite-hosted hydrothermal systems (such as Lost City) may not have been favorable for the production of critical 'prebiotic' carbon-sulfur compounds.

[1] Martin & Russell (2006) *Phil. Trans. R. Soc*. doi:10.1098/rstb.2006.1881 [2] Huber & Wächterhäuser (1997) *Science* **276**, 245-247. [3] Schulte & Rogers (2004) *Geochim. Cosmochim. Acta* **68**, 1087-1097.