

## Constraints on fluid-rock interaction and magmatic noble gas signatures in hydrothermal fluids

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The noble gases (He, Ne, Ar, Kr and Xe) have extremely variable isotopic signatures that distinguish hydrospheric, crustal and mantle reservoirs. Magmatic fluids are most easily identified by the presence of mantle noble gases. Magmatism involving only crustal rocks can lead to variable noble gas signatures; however, deep-crustal components can be distinguished by a high concentration of radiogenic and nucleogenic noble gases.

As magmatic fluids migrate through the crust, they carry noble gases from their source region and acquire new noble gases through water-rock interaction. The first pulse of a magmatic fluid tends to 'flush' noble gases out from the least retentive minerals in each lithological unit. In contrast, subsequent fluid pulses, passing through lithological units that are already depleted in noble gases, better retain the magmatic noble gas signature. As vein minerals can trap multiple fluid pulses in complex fluid inclusion assemblages, sequential (multiple) noble gas analysis of complex vein samples can enable deconvolution of both the fluid source and subsequent wall-rock reaction history.

We illustrate the effect of wall-rock interaction on magmatic noble gas signatures with examples from a U-rich Fold Belt and an orogenic gold deposit. Both deposit/alteration styles are shown to be related to a complex mixture of crustal fluids that includes a magmatic component. The noble gas isotopic compositions of the fluid inclusions from the U-rich Fold Belt are of further interest because they are distinguished by high concentrations of fissiogenic-Xe and nucleogenic noble gas isotopes (<sup>38</sup>Ar\*, <sup>80</sup>Kr\* and <sup>128</sup>Xe\*). Fluid inclusions with <sup>21</sup>Ne/<sup>22</sup>Ne values of >0.55 (together with <sup>20</sup>Ne/<sup>22</sup>Ne of 8-10) are preserved in both deposit types. These neon isotope compositions are outside the range considered typical of crust-atmosphere-mantle mixtures [1], and reflect high U/Ne ratios and low water-rock ratios in the fluid source regions. These data, indicate the neon isotope composition of the 'crust' may be far more heterogenous than previously realised.

[1] B.M. Kennedy, H. Hiyagon, and J.H. Reynolds, (1990) *Earth Plan. Sci. Lett.* **98**, 277-286.

## Methane clathrate destabilization in equatorial permafrost as a trigger for snowball Earth deglaciation

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The global-warming induced destabilization of oceanic and terrestrial methane clathrates represents a wild card in the climate system. The climate effects of this potentially non-linear response to subtle warming is difficult to accurately access given that it has not been active in historical time. The deep time record, however, provides multiple candidates for climate induced methane clathrate destabilization including examples of abrupt change that may provide analogs for climate change strongly forced by greenhouse gasses in the near future. A potential rapid warming analog occurs during the terminal Proterozoic and what is likely to be the most severe warming event in Earth history and shows a similar 1% increase in greenhouse gas forcing per year as the present atmosphere. Cold temperatures and expansive intracratonic basins exposed to terrestrial conditions during this severe ice house would have optimized the potential for methane clathrate accumulation in both marine and continental permafrost settings. Numerous examples of methane-influence are present in Marinoan-aged (~635 ma) deglacial sediments globally. In South Australia, the presence of carbonate cemented seep horizons that formed within active tidal channels within transgressive deglacial deposits imply catastrophic release of methane from secondary clathrates. These Seep carbonates record the broadest range of  $\delta^{18}\text{O}$  values ever reported from marine sediments (-25‰ to +12‰ PDB), resulting from mixing between ice sheet derived meteoric waters and clathrate derived fluids during flushing and destabilization of a clathrate field by glacial meltwater. Seeps formed in late glacial/deglacial intertidal sandstones requiring a permafrost clathrate origin with clathrate formation coinciding with the sub 0°C land temperatures of the Marinoan ice age. The equatorial paleolatitude implies an order of magnitude increase of the present day highly volatile shelf permafrost pool, providing a massive biogeochemical feedback capable of triggering deglaciation and accounting for the global postglacial marine -5‰  $\delta^{13}\text{C}$  global excursion, abrupt unidirectional warming, cap carbonate deposition, and a critical marine oxygen crisis.