## A495

## Tidal variations of gas composition in groundwater

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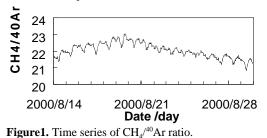
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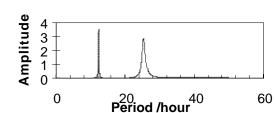
We observed periodic variations in time series data on gas composition in groundwater at Omaezaki, central Japan. Omaezaki is the most important place to be watched for premonitoring signals of the forth-coming great Tokai earthquake in the Japan's earthquake prediction program. We have started continuous monitoring of the gas composition in groundwater at a 100m-deep well.

Groundwater is pumped up directly from an aquifer through a plastic tube. Dissolved gases in groundwater are extracted by a gas extraction module, which has 3000 silicone hollow fibers in a housing. The composition of extracted gases is analysed by a quadrupole mass spectrometer in every 1 minute.

Temperature dependences of the efficiency and the selectivity of a gas extraction module are determined from laboratory experiments. The efficiency depends on water temperature but the selectivity does not. Periodic variations in the gas composition were observed. Figure 1 is an example of the  $CH_4/^{40}Ar$  ratio, which clearly shows diurnal and semi-diurnal fluctuations. Frequency analysis was curried out for all gas compositions. In the case of the  $CH_4/^{40}Ar$  ratio, two distinguishable components: the O1 and M2 tidal constituents were obtained (Figure 2).

This indicates that the gas composition in groundwater is able to respond to small strain changes such as earth tides. Therefore, the gas composition is one of useful parameters to monitor the earthquake activities.





**Figure 2.** Amplitude spectrum of  $CH_4/^{40}$ Ar ratio.

## The marine distribution of molybdenum

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Molybdenum (Mo) was initially classified as conservative in seawater, despite scavenging of Mo by Mn oxides and anoxic sediments. Mo is also utilized by phytoplankton and bacteria as an important micronutrient involved in, among other enzymatic processes,  $N_2$  fixation and nitrate reduction. This study re-examines the dissolved distribution of Mo in the world ocean using isotope dilution ICP-MS analyses. We also present some of the first measurements of Mo in suspended particulate matter.

Thirteen dissolved Mo profiles were measured, four from the California Borderland Basins, seven from the Eastern Equatorial Pacific and one each from the Arabian and Sargasso Seas. The average salinity (35 ppt) normalized concentration of Mo for the Arabian Sea and Sargasso Sea profiles were 107.78±0.32 and 107.50±0.34 nmol kg<sup>-1</sup>, respectively, in agreement with previous measurements of the Mo concentration of seawater. Profiles from the Santa Barbara and San Nicholas Borderland Basins showed Mo depletions in waters below sill depth of up to 2.5 nmol kg<sup>-1</sup> relative salinity. Likely related to Mo uptake by anoxic sediments. The Eastern Tropical Pacific profiles show both enrichment and depletion (up to +5 and -3 nmol kg<sup>-1</sup>) of water samples after salinity normalization. These deviations from the Mo salinity trend suggest that Mo behavior is nonconservative in the Equatorial Pacific.

Particulate matter samples were collected from regions of N<sub>2</sub> fixation and denitrification to evaluate the Mo requirements of phytoplankton and bacteria utilizing Mo containing enzymes. Particulate Mo concentrations were too low to deplete the dissolved phase given reasonable carbon flux. Particulate Mo concentrations did not correlate with particulate Mn, suggesting that water column Mn oxides do not scavenge Mo. Uptake of Mo from coastal anoxic sediments is likely the cause of Mo depletion in stratified basins. Along coastal the eastern tropical Pacific fluctuations in the depth of the oxygen minimum zone my result in enrichment or depletion of the overlying water. However, the flux of Mo in or out of sediments required to support the propagation of these features into the open ocean where the Eastern Tropical Pacific depleted and enriched profiles were measured appears to be unreasonably large. Further work investigating the link between Mo pore water flux and water column concentration with high precision analyses should elucidate this question.