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Supplement of

Isotopic evidence for biogenic molecular hydrogen production in the Atlantic Ocean

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Due to the experimental upset and timing the following assumption have been made:

- The glass vessel is initially under vacuum.
- The water sample flows into the glass vessel, equilibrates with the headspace and mix completely with the injected makeup gas.
- No significant exchange between the headspace / makeup gas mixture and the water phase will happen until the sample has been extracted into an evacuated flask.

The following abbreviations and definitions have been used:

- V_h : volume headspace in the glass vessel (1.6 dm³)
- V_w : volume water in the glass vessel (8.4 dm³)
- V_t : volume gas transfer system (0.025 dm³)
- V_f : volume flask and drying tube (1.1 dm³)
- p_h : pressure headspace after transfer from Niskin bottle to glass vessel
- p_{ht} : pressure headspace and gas transfer system before addition of makeup gas
- p_{htm} : pressure headspace and gas transfer system after addition of makeup gas
- p_f : pressure headspace, gas transfer system and flask after expansion to flask
- c_{w0} : initial H₂ concentration in seawater
- c_h : H₂ concentration in headspace after transfer from Niskin bottle to glass vessel
- c_w : H₂ concentration in seawater after transfer from Niskin bottle to glass vessel
- y_h : H₂ wet mole fraction in headspace after transfer from Niskin bottle to glass vessel
- y_m : H₂ dry mole fraction makeup gas
- y_{htm} : H₂ wet mole fraction in headspace and gas transfer system after addition of makeup gas
- y_f : H₂ dry mole fraction sample flask
- R : ideal gas constant (= 8.31446621 J K⁻¹ mol⁻¹)
- T : ambient absolute temperature (assumed to be equal to the gas temperature)

Defining the **extraction efficiency η** as

$$\eta = \frac{c_h V_h}{c_{w0} V_w} \quad (1)$$

the **initial concentration of H₂ in seawater, c_{w0}** , can be calculated from

$$c_{w0} = \frac{c_h V_h}{\eta V_w} \quad (2)$$

The concentration in the headspace, c_h , was not measured directly, but can be derived from the measured H₂ mole fraction in the sampling flask. The sampling procedure following gas extraction under vacuum can be broken into three steps (see Methods section):

1. Expansion of headspace
2. Addition of makeup gas
3. Expansion of headspace/makeup gas mixture into sampling flask

Step 1: The volume of the headspace increases from V_h to $V_h + V_t$, where V_t is the volume of the gas transfer system. The total pressure drops from p_h to $p_{ht} = p_h V_h / (V_h + V_t)$. H_2 mole fraction, y_h , and isotope delta, δ_h , do not change.

Step 2: Adding makeup gas changes the total pressure from p_{ht} to p_{htm} . H_2 mole fraction and isotope delta also change. The H_2 mole fraction after mixing with makeup gas is:

$$y_{htm} = (y_h - y_m) \frac{p_{ht}}{p_{htm}} + y_m \quad (3)$$

The initial headspace H_2 concentration is calculated using the ideal gas law:

$$\begin{aligned} c_h &= \frac{y_h p_h}{RT} = \frac{p_h}{RT} \left[(y_{htm} - y_m) \frac{p_{htm}}{p_{ht}} + y_m \right] \\ &= \frac{1}{RT} \left[(y_{htm} - y_m) p_{htm} \left(1 + \frac{V_t}{V_h} \right) + y_m p_h \right] \end{aligned} \quad (4)$$

Step 3: The gas is expanded from the manifold into a sampling flask, passing through a drying trap. At this stage the mole fractions are changed due to drying of the gas. The volume of the system also changes, but this affects the H_2O and H_2 mole fractions by the same ratio.

Thus, y_{htm} is calculated from the measured dry mole fraction in the flask, y_f , as

$$y_{htm} = y_f \left[1 - \frac{p_h(H_2O)}{p_{htm}} \frac{V_h}{V_h + V_t} \right] \quad (5)$$

where $p_h(H_2O)$ is the initial water vapour pressure in the headspace. Due to the short time periods involved (< 4 min), water vapour equilibration is assumed not to occur upon subsequent pressure changes in the system.

Combining equations (2), (4) and (5), the initial seawater concentration can be calculated as

$$\begin{aligned} c_{w0} &= \frac{(y_{htm} - y_m)(V_h + V_t)p_{htm} + y_m V_h p_h}{\eta V_w RT} \\ &= \frac{y_f \left[\left(1 + \frac{V_t}{V_h} \right) p_{htm} - p_h(H_2O) \right] - y_m \left[\left(1 + \frac{V_t}{V_h} \right) p_{htm} - p_h \right]}{\eta V_w RT} \end{aligned} \quad (6)$$

y_f , y_m , p_{htm} , V_t , V_h and V_w were measured. R is a constant ($= 8.31446621 \text{ J K}^{-1} \text{ mol}^{-1}$).

T is the ambient lab temperature and assumed to be equal to the gas and water temperature. Since ambient lab temperature and surface water temperature were never more than 1.2°C apart, this assumption is unlikely to cause an error of more than 0.4% in c_{w0} .

$p_h(H_2O)$ was assumed to be equal to the equilibrium vapour pressure (calculated following Green and Carritt (1967)) of seawater at temperature T and at its actual salinity, which was measured to within 0.01 g kg^{-1} .

The extraction efficiency, η can be calculated from the following mass balance

$$V_w c_{w0} = V_h c_h + \alpha V_w c_h \quad (7)$$

Assuming that headspace and water phase are in equilibrium, the ratio of the H₂ concentration in water and in the headspace is given by the Ostwald coefficient

$$\alpha = \frac{c_w}{c_h} \quad (8)$$

This gives for the initial concentration in the water

$$c_{w0} = \left(\frac{V_h}{V_w} + \alpha \right) c_h \quad (9)$$

and for the extraction efficiency as defined in equation (2)

$$\eta = \left(1 + \alpha \frac{V_w}{V_h} \right)^{-1} \quad (10)$$

In the present case, $\alpha = \alpha(\text{H}_2)$ was equal to 0.0163 ± 0.0001 , which gives $\eta = 92\%$ for $V_w/V_h = 8.4/1.6 = 5.25$.

p_h was not measured and had to be estimated from the gas concentrations in the water.

$$\begin{aligned} p_h &= p_h(\text{N}_2) + p_h(\text{O}_2) + p_h(\text{Ar}) + p_h(\text{CO}_2) + p_h(\text{H}_2\text{O}) \\ &= RT \left[c_h(\text{N}_2) + c_h(\text{O}_2) + c_h(\text{Ar}) + c_h(\text{CO}_2) \right] + p_h(\text{H}_2\text{O}) \\ &= RT \left[\frac{c_{w0}(\text{N}_2)}{\frac{V_h}{V_w} + \alpha(\text{N}_2)} + \frac{c_{w0}(\text{O}_2)}{\frac{V_h}{V_w} + \alpha(\text{O}_2)} + \frac{c_{w0}(\text{Ar})}{\frac{V_h}{V_w} + \alpha(\text{Ar})} + \frac{c_{w0}(\text{CO}_2)}{\alpha(\text{CO}_2)} \right] + p_h(\text{H}_2\text{O}) \end{aligned} \quad (11)$$

The extraction efficiencies of all gases were assumed to follow their solubilities. Due to the buffering effect of the CO₂ system (CO₂(w), H₂CO₃, HCO₃⁻ and CO₃²⁻), the dissolved CO₂ concentration changes by only 1 or 2 % during extraction, so that the headspace concentration can be estimated from $c_{w0}(\text{CO}_2)/\alpha(\text{CO}_2)$.

p_h was estimated to vary between 98 and 111 hPa, with contributions of 46 to 52 hPa from N₂, 23 to 27 hPa from O₂, 1.1 to 1.3 hPa from Ar, 0.4 hPa from CO₂ and 17 to 40 hPa from H₂O.

Based on equation (4), the **isotope delta of the headspace gas** can be calculated as follows

$$\delta_h = \frac{\delta_{\text{htm}} y_{\text{htm}} \left(1 + \frac{V_t}{V_h} \right) p_{\text{htm}} - \delta_m y_m \left[\left(1 + \frac{V_t}{V_h} \right) p_{\text{htm}} - p_h \right]}{y_{\text{htm}} \left(1 + \frac{V_t}{V_h} \right) p_{\text{htm}} - y_m \left[\left(1 + \frac{V_t}{V_h} \right) p_{\text{htm}} - p_h \right]} \quad (12)$$

Two alternative scenarios were considered to derive the initial isotope delta of dissolved H₂, with scenario 1 assuming equilibrium isotopic fractionation between headspace and water, and scenario 2 assuming kinetic isotopic fractionation during extraction from Niskin bottle to glass vessel.

Scenario 1: Correction of δ_h for equilibrium isotopic fractionation between headspace and water

The equilibrium isotope fractionation between water and headspace is defined as

$$\varepsilon = \frac{1 + \delta_w}{1 + \delta_h} - 1 \quad (13)$$

The isotopic mass balance equation between headspace and water can then be described via

$$V_w c_{w0} \delta_{w0} = V_h c_h \delta_h + V_w c_w \delta_w \quad (14)$$

which gives for the isotope delta of the original dissolved gas:

$$\delta_{w0} = \frac{\varepsilon(1 + \delta_h)}{1 + \frac{V_h}{V_w} \frac{1}{\alpha}} + \delta_h \quad (15)$$

The equilibrium isotope fractionation between dissolved phase and gas phase is $\varepsilon = (37 \pm 1) \%$ at 20 °C (Knox et al., 1992). The temperature dependence of ε is unknown and was neglected here.

Scenario 2: Correction for kinetic isotopic fractionation between headspace and water

If kinetic isotope fractionation applies, then the isotopic composition of the residual gas in the water is

$$\delta_w = (1 + \delta_{w0}) \left(\frac{c_w}{c_{w0}} \right)^{\varepsilon_k} - 1 = (1 + \delta_{w0}) (1 - \eta)^{\varepsilon_k} - 1 \quad (16)$$

Then, the isotope delta of the accumulated gas in the headspace is

$$\delta_h = (1 + \delta_{w0}) \frac{1 - (1 - \eta)^{1 + \varepsilon_k}}{\eta} - 1 \quad (17)$$

which gives for the isotope delta of the original dissolved gas:

$$\delta_{w0} = \frac{(1 + \delta_h) \eta}{1 - (1 - \eta)^{1 + \varepsilon_k}} - 1 \quad (18)$$

The kinetic isotope fractionation during gas evasion is $\varepsilon_k = (-18 \pm 2) \%$ at 20 °C (Knox et al., 1992). The temperature dependence of ε_k is unknown and was neglected here.

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