

GENERATION OF HIGH PH GROUNDWATERS AND H₂ GAS

BY GROUNDWATER-KIMBERLITE INTERACTION, NORTHEASTERN ONTARIO, CANADA

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Introduction

Low-temperature serpentinization reactions occur where waters interact with ultramafic minerals, commonly resulting in atypical hydrogeochemistry. These water-rock interactions result in reducing waters (i.e., as reducing as the H₂-H₂O couple) at high pH (~ 12.4), and OH⁻ alkalinity (Sader et al., 2007). Low-T serpentinization has predominantly been studied in association with seawater circulation through oceanic crust (e.g., Janecky and Seyfried, 1986; Palandri and Reed, 2004 Kelley et al., 2005b; Ludwig et al., 2006; Proskurowski et al., 2006; Proskurowski et al., 2008). There are fewer studies of water-ultramafic rock interaction in terrestrial settings (Barnes and O'Neil, 1969; Neal and Stanger, 1983; Abrajano et al., 1988; Fritz et al., 1992). These reactions are also associated with kimberlites (Kosolapova and Kosolapov, 1962; Sader et al., 2007), as they are also ultramafic rocks, dominated by olivine and pyroxene, both unstable minerals at Earth surface conditions.

Through isotopic modelling we demonstrate that groundwater interaction with kimberlites from the Kirkland Lake and New Liskeard, Ontario kimberlite fields produces significant amounts of H₂ and/or CH₄ gas at low temperatures (< 25 °C). The modelled groundwater-kimberlite reactions and production of elevated concentrations of H₂ gas provides the basis for surficial exploration using soil gas. It

also suggests a new use for diamond-production tailings as a carbon capture mechanism. Hydrogen production in crustal rocks at these low temperatures has only been reported in a handful of studies (Neal and Stanger, 1983; Abrajano et al., 1988; Fritz et al., 1992; Sherwood Lollar et al., 2006).

Methodology

Field Sampling

Groundwater samples were collected from exploration boreholes during the month of June in 2002 and 2003 using a Grundfos™ down-hole mechanical pump. In 2002, waters were collected for elemental concentrations, whereas in 2003 samples were collected from the same boreholes at the same depth for gas concentration and isotope ratios. The pH, oxidation-reduction potential (ORP), and temperature were measured in situ. The ORP results are corrected with reference to the standard hydrogen electrode (SHE) and are reported as Eh. Waters were collected for cations, anions, H and O isotopes, were filtered through 0.45 µm Millipore Sterivex-HV filters, and were stored in Nalgene high-density polyethylene sample bottles (filtered cations and anions) and polypropylene bottles for O and H isotopes.

To sample gas, groundwater was pumped through a flow-through cell fitted with a large funnel that was allowed to continuously overflow with sample water. A 125 ml Wheaton™ borosilicate sample bottle, filled with sample water was then inverted inside the funnel and exsolved gas displaced the water in the sample bottle (Fig. 1). The glass sample bottles were sealed and crimped with an aluminium rim and a grey butyl septum submerged in the funnel to ensure that there was no introduction of air. Samples were stored upside-down so that the bottle headspace was at the bottom part of the bottle.

Laboratory Analysis

Groundwater samples were analysed at the University of Texas at Dallas for element concentrations. The methods used have been previously reported by Sader et al. (2007). Stable isotopes in water samples were measured for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ at the G.G. Hach Stable Isotope laboratory, Department of Earth Sciences, University of Ottawa by isotope ratio mass spectrometry (IRMS). Compositional analyses of hydrocarbon gas were performed at the Stable Isotope Laboratory at the University of Toronto with a Varian 3400 GC equipped with a flame ionization detector (FID). Analyses for $\delta^{13}\text{C}$ values were performed by continuous flow compound specific carbon isotope ratio mass spectrometry with a Finnigan MAT 252 mass spectrometer interfaced with a Varian 3400 capillary GC. Hydrogen gas concentration and $\delta^2\text{H}_{\text{H}_2}$ isotopic analyses were performed with a HP 6890 gas chromatograph (GC) interfaced with a micropyrolysis furnace (1465 °C) in line with a Finnigan MAT Delta+-XL isotope ratio mass spectrometer.



Figure 1. Gas sampling apparatus

Gas sampling was conducted using a flow-through cell where dissolved gas could exsolve into an inverted bottle, displacing sample water.

Results

Groundwater geochemical compositions

Kimberlite groundwaters have elevated pH (7.7 to 12.3), with the Eh values (SHE corrected) ranging from +66 to -69 mV. Water temperatures were fairly consistent and ranged from 6 to 8.4°C. The field measured Fe²⁺ and H₂S ranges from 0.00018 to 0.029 mmol/L, and 0.00059 to 0.013 mmol/L, respectively. Kimberlite water geochemical data from Sader et al., 2007 (waters collected in 2002) showed that with increasing pH, Mg concentrations decrease and K/Mg increases (pH vs K/Mg is well correlated, $r^2 = 0.808$). The low Mg concentrations are due sequestration processes where brucite is precipitating in waters with predominantly OH⁻ alkalinity (Fig. 2). Dissolved inorganic carbon decreases and Ca increases (up to 77 mg/L) with increasing pH, especially where the alkalinity is dominantly OH⁻.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values in groundwaters are predominantly non-radiogenic (0.7064 - 0.7076) for gas-rich groundwaters. In contrast, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in groundwater from rocks elsewhere in the Superior Province, or from Silurian sedimentary formations are typically more radiogenic (0.708 – 0.746) (McNutt et al., 1987).

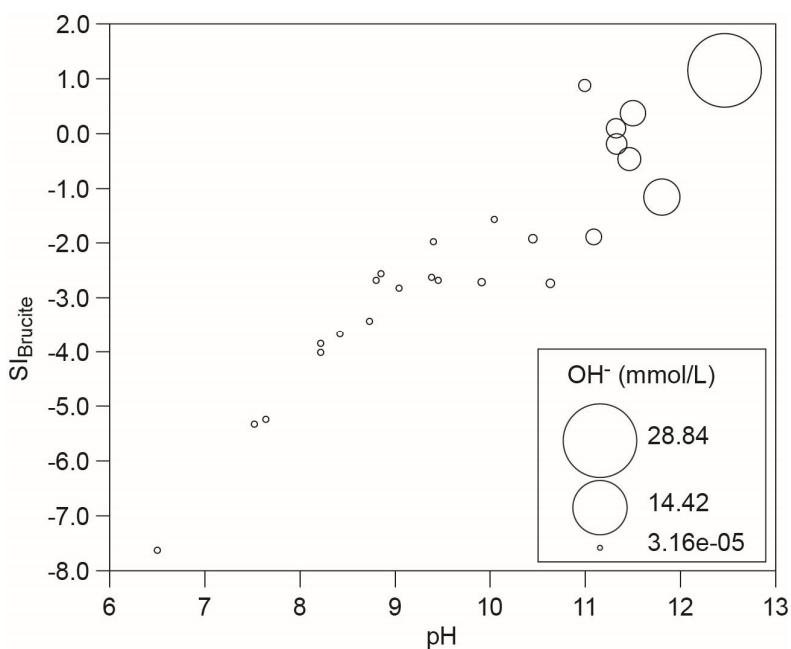


Figure 2. Brucite saturation in reduced waters

Brucite is above saturation in waters with high pH and high concentrations of OH.

Gas compositions

Hydrogen (up to 0.301 mmol/L) is present where the pH is high, the alkalinity is dominated by OH⁻, and DIC is low (defined as Group 2 kimberlite waters). Most samples with H₂ do not contain CH₄ and samples with measureable CH₄ concentrations are only present in Group 1 waters (defined as being dominated by carbonate alkalinity) (Fig. 3). H₂S concentrations correlate negatively with H₂ gas for samples with measureable concentrations of H₂ ($r^2 = -0.87$; $n=6$) and indicate that the reduction of available sulphur in the system likely proceeds before H₂ gas formation, as sulphur reduction is farther up the redox chain. The $\delta^2\text{H}_{\text{H}_2}$ is extremely depleted, ranging from -771 to -801‰.

The carbonate alkalinity groundwaters have $\delta^{18}\text{O}_{\text{SMOW}}$ and $\delta^2\text{H}_{\text{SMOW}}$ ratios that are similar to the Ottawa meteoric water line (OMWL) and are consistent with a meteoric origin (Fig. 4). However, waters that have pH > 10, high K/Mg values, and low DIC (i.e., alkalinity dominated by OH⁻) (Fig. 3) deviate from the OMWL by up to 10‰ in $\delta^2\text{H}_{\text{SMOW}}$ (Fig. 4). These are also the same samples that tend to have measureable H₂ and no CH₄.

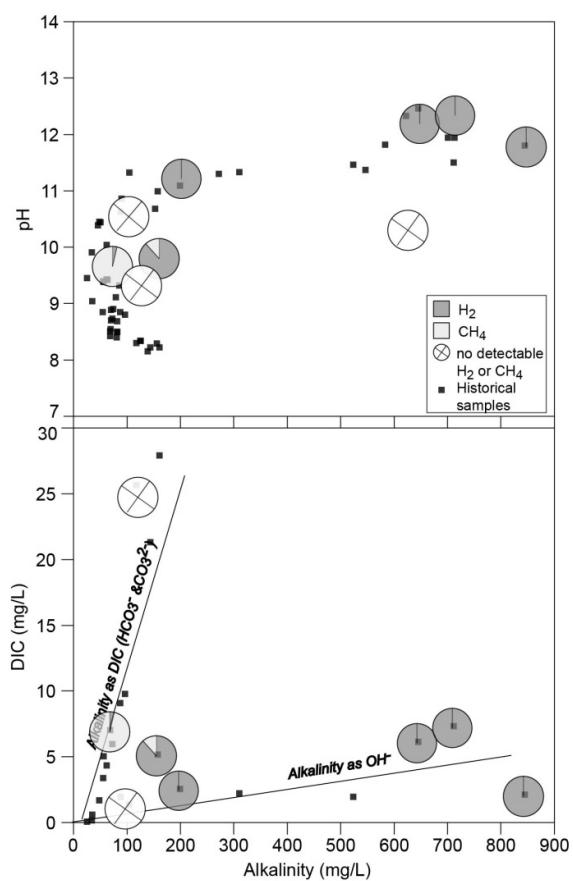


Figure 3. Gas content in relation to alkalinity

Gas samples with OH^- alkalinity only contain H_2 . Whereas, samples that trend towards carbonate alkalinity either have a mixture of H_2 and CH_4 or no measureable gas.

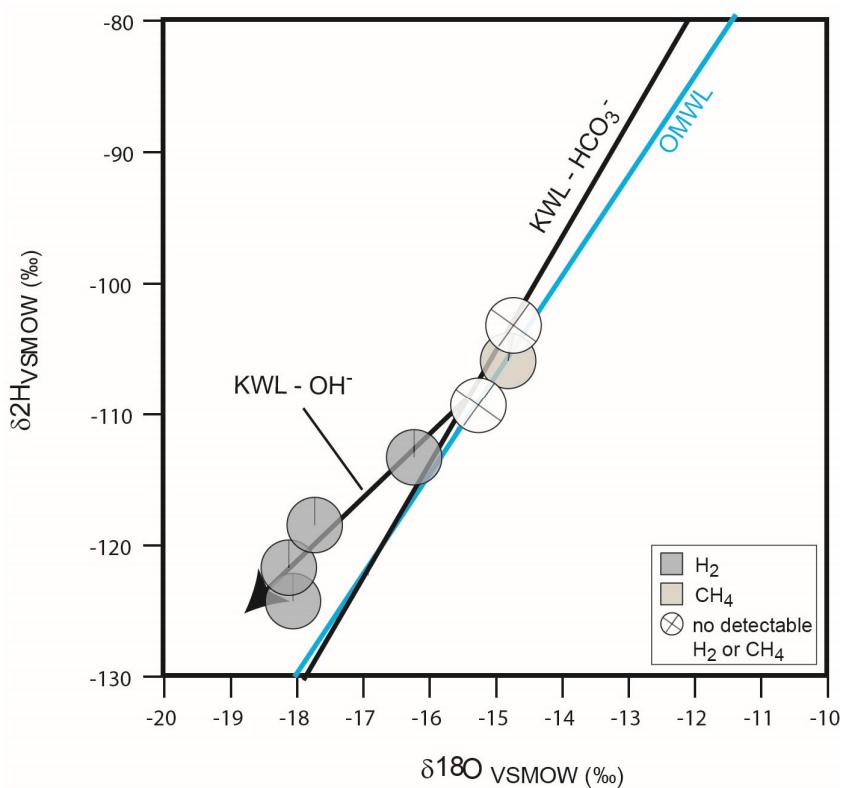


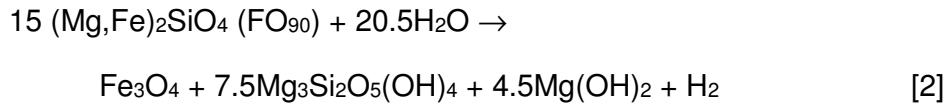
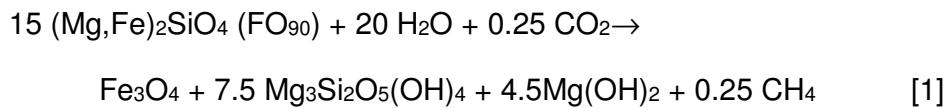
Figure 4. Deviation from the OMWL of samples with H₂

Samples that have H₂ tend to deviate from the OMWL, likely due to the hydrolysis of water in highly alkaline conditions.

Discussion

Effect of serpentinization on reduced gas production

Sader et al. (2007) suggested that based on K/Mg, alkalinity, pH and DIC concentrations, groundwaters can be subdivided into two groups; serpentinization within an open system where the waters have low K/Mg ratios, lower pH, high DIC and alkalinity dominated by carbonate (Group 1; Eq. 1), and serpentinization within a closed system where waters are brucite saturated, have high pH, DIC and, and OH⁻ alkalinity (Group 2; Eq. 2).



In an open system (Eq. 1), there is a continuous supply of DIC, reduced Fe²⁺ liberated from olivine weathering to serpentine oxidizes to Fe³⁺ and will result in the production of CH_{4(g)}. The DIC required for methane production is likely due to an influx (episodic or continuous) of non-kimberlite waters, and is likely the only source. Conversely, in a closed system (Eq. 2) where groundwaters are depleted in DIC, the Fe²⁺ reduces H₂O rather than DIC as Fe²⁺ oxidizes to Fe³⁺. This reaction results in OH⁻ alkalinity, and H₂ gas production, and has been demonstrated experimentally (Foustoukos and Seyfried, 2004; Proskurowski et al., 2008). The elevated OH⁻ contributes to the removal of Mg²⁺ (Fig. 2) as brucite quickly reaches saturation. The trend of increasing proportions of H₂ versus CH₄ gas is consistent with the increasing dominance of OH⁻ alkalinity (shift from Group 1 to Group 2 waters) (Fig. 3). It is assumed that the waters are in equilibrium with kimberlite based on the low ⁸⁷Sr/⁸⁶Sr isotopic ratios in kimberlite waters (c. 0.7065).

Origin of H₂ – isotopic evidence

Under closed system conditions (Group 2 waters), Rayleigh fractionation of δ²H_{H2O} proceeds as H₂O is reduced to H⁺ and OH⁻. These waters have δ²H_{H2O} values that deviate from the kimberlite water line (KWL) and Ottawa meteoric water line (OMWL) by up to -10‰ (Fig. 4). Likewise, they are the only waters that have H₂ gas and extremely depleted δ²H_{H2} values (-770 to -801‰). Waters that contain only CH₄ or do not contain measureable amounts of either CH₄ or H₂, do not deviate markedly from the KML-HCO₃⁻ and the OMWL, presumably due to less H₂O reduction and greater concentrations of DIC as it is reduced first before H₂O will be.

Isotopic calculations were used to determine the quantity of gas and whether water temperatures are consistent with calculated temperatures. Using an isotopic mass balance equation, we calculated the quantity of H₂ gas that formed based on the deviation of δ²H_{H2O} from the OMWL for samples that plot along the KML-OH⁻ line. The mass balance calculations indicate that enrichment in δ²H_{H2O} of 8‰ due to H₂O reduction would result in the production of a substantial amount of H₂ (up to 1.01 moles/L). It should be noted that these calculated H₂ concentrations are up to 3 orders of magnitude greater than the concentrations observed in kimberlite groundwaters. The higher calculated values versus measured are likely due to oversaturation and ebullition related to pressure change (i.e., change in hydraulic head). The solubility of H₂ at the observed temperature and pressure where gas was collected is low (9.51 × 10⁻³ moles/L at 3.5 to 6.3 ATM).

Using the stable isotopic compositions of the groundwaters and hydrogen gas, we calculated temperatures of serpentinization of 5–25 °C based on H₂O-H₂ geothermometry calculations (Horibe and Craig, 1995), only slightly higher than measured temperatures. This similarity provides further support for significant modern serpentinization reactions occurring at observed groundwater temperatures

(5.8 to 8.4 °C). The H₂ formation conditions (measured or calculated) in our study are similar to previous studies of terrestrial systems (i.e., Neil and Stanger, 1983, Fritz et al. 1996), however, our formation temperatures are lower than have been previously identified (i.e., ~ 40 to > 90°C) (Kelley et al., 2005).

Gas formation and groundwater residence time in kimberlite

The most simplistic model for serpentinization and reduced gas production is abiotic (slow kinetics) and would require significant residence times. The kinetics of the H₂O – H₂ system indicate that below 200 °C, and especially below 50°C, reactions will progress orders of magnitude more slowly (Proskurowski et al., 2008). Water-ultramafic rock modelling reactions have indicated that the lower the water-rock ratio, the more reducing kimberlite waters become (Palandri and Reed, 2004; Sader et al., 2007). Kimberlite hydrogeological studies by Morton and Mueller (2003) have shown that hydraulic conductivities are 4.3×10^{-2} to 1.5×10^{-4} m/day for coarse sedimentary to breccia facies South African Kimberlites, similar to the Kirkland Lake kimberlites. Such hydraulic conductivities, in conjunction to the estimated groundwater gradients and porosities in our study, suggest groundwater residence times on the order of tens of years for the Kirkland Lake kimberlites are not unreasonable.

Conclusions

Hydrogen gas production is attributed to oxidation of Fe²⁺ under high pH conditions and the subsequent reduction of water as hematite and magnetite stability are reached. This process appears to be greatest where it occurs under conditions closed to the input of DIC. In kimberlites where the groundwater environment is open to the input of DIC, CH₄ is the dominant gas produced. The production of reduced gases in kimberlites compared to host rock may be useful in diamond exploration applications where geophysical targets have already been identified, but which are covered by Quaternary sediments. In both the phreatic and vadose zones, vapor-phase gases are much more mobile than dissolved solids, especially vertically. Because the measurement of gas is relatively straightforward (Sader, 2010), H₂ and CH₄ measurements of groundwater or soil gas could be easily implemented in an exploration program and geophysical targets could be ranked based on reduced gas anomalies. However, setting is important, as the Attawapiskat kimberlites (emplaced into Silurian limestone and overlain by extensive bog terrain) had pH values of 7.5 to 8.5 (Sader, 2010), potentially due to the abundance of soluble fulvic acids.

We also suggest the possibility that CO₂ generated from combustion of diesel fuel at mine sites could be sequestered by alkaline effluent produced in kimberlite tailings piles. The strongly alkaline water and high Ca content result in over saturation of calcite. The addition of CO₂ into the Ca-OH water from serpentinization reactions would result in the precipitation of carbonate. The idea of sequestering CO₂ with naturally occurring highly alkaline waters has been suggested in the Oman

ophiolites (Kelemen and Matter, 2008), ultramafic mining waste at two Quebec, Canada nickel projects (Pronost et al. 2011) and in California by a handful of commercial enterprises.

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