Impact of blasting on groundwater composition in a fracture in Canada's Underground Research Laboratory

Mel Gascoyne and David A. Thomas¹

Applied Geoscience Branch, Atomic Energy of Canada Limited, Whiteshell Laboratories, Pinawa, Manitoba, Canada

Abstract. Groundwater composition in a discrete, water-bearing fracture in granitic rock at the Underground Research Laboratory, Manitoba, was monitored during a period of underground excavation of adjacent rock to determine the impact of conventional blasting techniques and rock fracturing on the concentration of dissolved constituents. This work has relevance to the study of hydrogeochemical anomalies associated with seismic activity. Short-lived anomalies such as decreases in dissolved anion (Cl, F, Br, SO₄) and gas (He, Rn) concentrations and concurrent increases in NO₃ and O₂ concentrations were seen shortly after two blasts located opposite the groundwater sampling site. A third blast downstream of the site resulted in variability in dissolved gases concentrations but showed no impact on dissolved anion concentrations. The results are compared with various models used to account for hydrogeochemical fluctuations associated with earthquakes. The data best fit a general form of the aquifer breaching/fluid mixing model in which hydrochemical responses are caused by localized changes in hydraulic conductivity along the plane of a fracture which, in turn, cause changes in mixing ratio of groundwater at the monitoring site.

Introduction

The composition of groundwater is affected by a number of processes as it moves through a rock formation. These processes include leaching and dissolution of soluble salts and minerals at rock-water interfaces and the release of gases formed by decay of radioactive elements in the rock. The processes are influenced by the degree of weathering and fracturing of the rock body. Tectonic activity causing disturbance and new fracturing of the rock has been observed to induce changes in groundwater composition in surface springs or in wells and boreholes. Similarly, when the rock is exposed to large vibrations, as occurs during blasting for excavation, it is often disrupted and the degree and frequency of fracturing in the rock body may change. These changes may also affect the chemical composition of the groundwater flowing through the rock, and if they can be monitored they may be used as a means of determining the effect that tectonic activity might have on groundwater composition, albeit at a much smaller and more detailed scale than in natural seismic events.

Variations in groundwater composition due to sudden tectonic fracturing of rock have been observed in advance of or during natural seismic events [Birchard and Libby, 1980; Finkel, 1981; O'Neil and King, 1981; Barsukov et al., 1985; Rao et al., 1994]. These variations are usually recorded in deep wells, and mineral and thermal springs. Variations that are commonly seen include changes in concentration of dissolved gases (CH₄, CO₂, He, H₂S, and Rn), major ions (Na, K, Ca, Mg, SO₄, Cl, F, and HCO₃), and

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trace elements (Hg, Ra, U, Li, Sr, and Ba). Detailed reviews have been given by *King* [1986], *Thomas* [1988], and *Röshoff* [1989]. While the cause of many of the observed variations in chemical composition remains largely conjectural, several models have been proposed to account for these phenomena [*Thomas* 1988]: (1) physico-chemical release by ultrasonic vibration, (2) chemical release due to pressure-sensitive solubility changes, (3) physical release of salts by pore collapse, (4) chemical release by increased loss from or reaction of groundwater with freshly created rock surfaces, and (5) physical mixing due to aquifer breaching/fluid mixing (AB/FM).

Most of the changes in temperature and dissolved ion and gas concentrations can be accounted for by the AB/FM model in which breakdown of hydrogeological barriers allows groundwaters of different composition to mix. This hypothesis requires permeability changes that would permit large-scale mixing of groundwater. Thomas [1988] proposed that changes in hydraulic head could effectively account for chemical variations in wells prior to or concurrent with seismic events. The head changes could be brought about by a stress change in the rock surrounding the fault prior to rock movement.

This paper describes the influence of man-made seismic events (blasting during underground excavation) on the composition of groundwaters close to the site of excavation. The results are examined in terms of existing theories that account for hydrogeochemical responses in wells and springs to earthquakes and other tectonic events. Because several of the variables that might influence groundwater composition in a natural seismic event (e.g., spatial separation of the event and the water-bearing fracture, timing, and energy of the event) are either absent or reasonably well defined in this work, it was expected that causes of changes in composition due to seismic events could be resolved. Man-made seismic activity (e.g., underground explosions) have been occasionally studied in previous work to determine the impact of seismic activity on groundwater

¹Now at Department of Geology and Geophysics, University of Calgary, Calgary, Alberta Canada.

composition. Changes in Rn, O₂, CO₂, and dissolved ion contents of groundwater have been observed after underground explosions in China and Japan (see review by *King* [1986]). One such study by *Li et al.* [1985] proposed that these changes were a result of stress loading which forced rock pore fluids to migrate into aquifers.

The work described here allows the mechanisms that induce groundwater chemical changes associated with man-made seismic events to be better resolved because many of the variables that influence groundwater composition are known or can be controlled. These results can then be compared to changes associated with natural seismic events.

Background and Site Description

In the Canadian Nuclear Fuel Waste Management Program (CNFWMP), research is being performed on the concept of nuclear fuel waste disposal in a vault located deep within a crystalline rock formation on the Canadian Shield. The primary mechanism for transport of radionuclides from the waste disposal

vault to the biosphere is expected to be via advection and diffusion in groundwater within pores and fractures in the rock. The concept developed by the CNFWMP requires an understanding of the characteristics of potential sites in plutonic rock of the Canadian Shield to optimize the design of the vault and minimize the risks of unacceptable radionuclide releases to the environment. The disposal concept has been recently presented in an Environmental Impact Statement by *Atomic Energy of Canada Limited* [1994].

The Underground Research Laboratory (URL) has been constructed by Atomic Energy of Canada Limited (AECL) in a previously undisturbed portion of the granitic Lac du Bonnet batholith near Lac du Bonnet, Manitoba, Canada (Figure 1), and a number of experiments are being performed in it to assess aspects of the disposal concept. The rock mass surrounding the URL has been well characterized over the period of site selection and construction. The facility now provides researchers with access to rock with a range of geologic conditions in which to carry out a variety of in situ measurements and experiments designed to (1) understand the transport of vault contaminants in

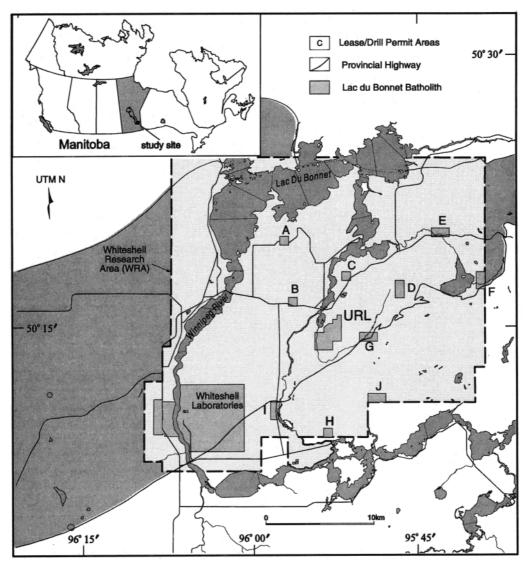


Figure 1. Location of the Underground Research Laboratory (URL) Lease Area and drill permit areas with respect to the Whiteshell Laboratories, the Whiteshell Research Area, and the outcrop of the Lac du Bonnet granite batholith. The inset shows the location of this region in southeastern Manitoba.

the surrounding rock, (2) test vault design and sealing technologies, and (3) determine interactions between the vault and the surrounding rock [Simmons et al., 1992]. The in situ measurements include determination of the chemical composition of groundwater in fractures and fault zones in the rock close to the facility to give an understanding of the variations and origins of dissolved salts in the groundwater. Groundwater in the batholith are dilute, Na-Ca-HCO₃ types in the upper ~300 m, becoming more saline, Na-Ca-Cl-SO4 types below this depth [Gascoyne and Kamineni, 1994]. Monitoring groundwater compositions over the period of construction and operation of the URL has raised awareness of a number of processes by which groundwater composition may change [Gascoyne et al., 1995]. These include the introduction of contaminants caused by use of surface-derived drill waters, the influence of hydrogeologic testing, and the potential for contamination arising from grouting and blasting operations.

The URL facility consists of a main shaft, 440 m deep, two main levels for experimental work at 240 m and 420 m deep, and inclined ventilation raises interconnecting the levels with the surface (inset Figure 2). Recently, excavation of a room for the Quarried Block Migration Experiment (QBME) was performed to accommodate in situ laboratory experiments. The QBME facility (Rooms 217, 218, and 219, Figure 2) is constructed in relatively unfractured grey and pink granite adjacent to a well-characterized,

water-bearing fracture known as the Room 209 subvertical fracture.

Methods

Pressure Pulses

Rock vibration levels (measured by peak particle velocities) and borehole hydraulic pressures were monitored to assess the physical impact of the blasts on the surrounding rock. Four blasts were monitored during the construction of the QBME facility. The blasts are described in Table 1, and their locations are shown in Figure 2. In all cases, ammonium nitrate/fuel oil was the main type of explosive used in the excavations. The relative sizes of the blasts can be seen by comparing the amount of explosives used, the powder factor (i.e., the amount of explosives per volume of rock removed), and the rock vibration as measured at the G2 and G3 sensors installed in other rooms at the 240-m level (Figure 2). Blasts A and B were located approximately 5 m to the NW of the fracture with the explosives placed in holes parallel to the fracture. They removed an entire rock face in the room. Blasts C and D were immediately adjacent to the fracture, and each removed an entire rock face. The explosives for these two blasts were placed in holes which extended directly toward the fracture. Blasts A, B, and C involved full monitoring (for groundwater chemistry, rock vibration, and borehole hydraulic

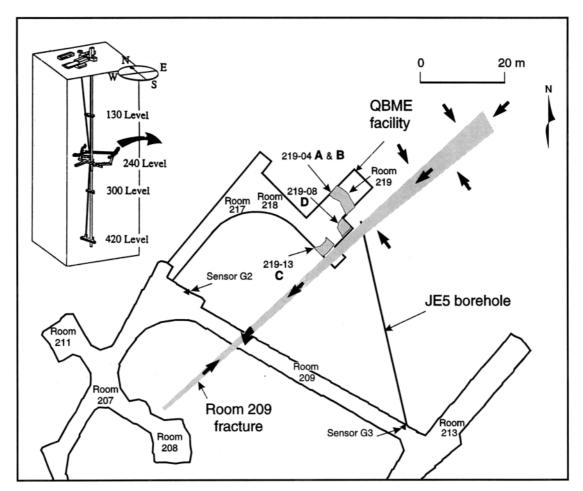


Figure 2. Partial plan of the 240-m level of the Underground Research Laboratory showing the proposed QBME facility, the blasts for which groundwater composition was monitored, and the location of blast monitoring sensors. Arrows indicate groundwater flow directions for the Room 209 fracture.

Blast Designation	Blast	Date	Time, UT	Explosives Used, (kg)	Powder Factor, kg/m ³	G2 Vibration, mm/s	G3 Vibration, mm/s
A	219-04 A	Sept. 30, 1994	12:08	124.0	3.27	541.0	450.0
В	219-04 B	Sept. 30, 1994	15:35	35.0	1.38	275.9	197.5
C	219-13	Oct. 24, 1994	12:00	140.1	4.23	n/a	n/a
D	219-08	Oct. 28, 1994	12:00	68.5	2.47	429.0	225.0

Table 1. Summary of the Blasts Monitored for Hydrogeochemical Variations During the Construction of the QBME Facility

From D. Onagi (personal communication, 1994).

pressure). For blast D, only borehole hydraulic pressure was monitored.

Hydraulic pressures of other boreholes intersecting the fracture were monitored by in-line pressure transducers and data loggers which sampled pressures in all the boreholes at 1-hour intervals for the initial part of the QBME facility construction period (blasts A and B). This monitoring frequency, however, provided insufficient resolution for accurately observing the effects of the blasts, and the sampling interval was changed to 1 min for blast C in an attempt to improve resolution. The increase in sampling frequency meant that fewer boreholes could be monitored by the data acquisition system. For blast D, in an attempt to again increase resolution and observe the blast pulse the sampling interval was again changed to 16 s, and only the hydraulic pressures in borehole JE5-4 were monitored. For this blast a digital voltmeter and a chart recorder were also attached, in parallel, to the data logger to supplement the results.

Groundwater Sampling

Groundwater was sampled from the Room 209 fracture using monitoring zone 4 in the horizontal borehole JE5 (JE5-4). Zone 4

was the portion of the borehole that extended into the fracture immediately adjacent to the QBME facility from the junction of Rooms 209 and 213 (Figure 2). The monitoring zone was isolated from the rest of the borehole by a packer, so that only water from the fracture was sampled. Groundwater samples were obtained from a 48.5-m-long, 6-mm nylon tube that opened into the packer-isolated zone. The nylon tube, which had a void volume of 0.7 L, delayed the arrival of blast impacts on groundwater samples by at least 1-2 min, depending on the rate at which groundwater was able to flow naturally from the zone.

The valve on the nylon tube to JE5-4 was opened several hours prior to the blasting event, and the zone was allowed to flush at a rate of at least 0.5 L/min to allow standing groundwater in the borehole zone and sampling line to be replaced and the groundwater composition to stabilize. The groundwater flow was split into two 9-mm nylon tubes near the borehole collar to allow simultaneous collection of groundwater samples for anion and dissolved gas analysis (Figure 3). Both tubes were valved so that flow rates from each could be adjusted depending on the flow required for particular sampling methods. Samples were collected at regular intervals throughout the flushing and monitoring session (about every 30 min). The sampling frequency immediately after

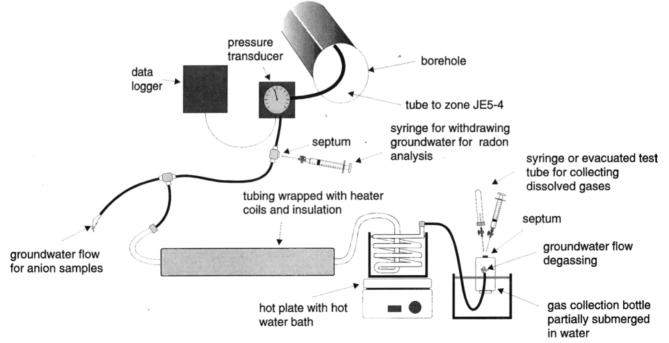


Figure 3. Experimental arrangement to collect groundwater samples and dissolved gases for laboratory analysis.

the blast was increased (to about every 15 min for blasts A and B, 10 min for blast C) to improve monitoring sensitivity. More frequent sampling than this was difficult because of the time required to take a number of samples and their significant volumes. In some cases, sampling methods differed between monitoring sessions. The methods are described below, and their use is indicated.

Radon

Two methods of sampling groundwater for radon (Rn) analysis were used. For blasts A and B, groundwater samples were collected by inserting the tip of a needleless 10-mL hypodermic syringe into the groundwater flow issuing from the nylon tube. The water pressure was generally sufficient to push the plunger of the syringe back and to allow the syringe to fill. If the water pressure in the tube was insufficient to move the plunger, the plunger was pulled back manually to withdraw the groundwater sample. An 8-mL aliquot of groundwater was injected into a 20-mL scintillation vial containing 10 mL of scintillation fluor, and the vial was tightly sealed.

For blast C a septum was installed in line with the 9-mm nylon tube, and a 10-mL hypodermic syringe with a 20-gauge needle was used to withdraw the groundwater sample. An 8-mL aliquot was injected through the needle into a 20-mL scintillation vial containing 10 mL of scintillation fluor. Injection of the groundwater sample into the scintillation vial was done through a needle and under the surface of the fluor to minimize the loss of radon to the atmosphere by degassing. This change in procedure was expected to reduce Rn loss from the sample, thereby improving the accuracy and precision of the measurement. In addition, duplicate samples were taken. All Rn samples were sealed and shaken to ensure mixing and were analyzed in the laboratory by liquid scintillation counting on a Beckman LS 5801 scintillation counter [Watson, 1994]. Count rates were corrected for radioactive decay and daughter ingrowth, and the concentration of Rn was calculated in units of becquerels per liter. For continuous analysis of samples, a set of duplicate analyses for blast C showed that analytical precision was $\pm 2.2\%$ (1 σ).

Helium

Dissolved helium (He) concentrations in groundwater, for the blasts A and B, were determined by collecting groundwater at regular intervals in sealed vessels and subsequently analyzing the headspace gas for He. This method has previously been used to determine He concentrations of surface waters [Stephenson et al., 1992]. The method involves slowly and completely filling 773-mL glass bottles with groundwater, withdrawing 50 mL of the water by syringe to give a known volume of headspace in the bottle, and sealing the bottles with press-on steel crown caps. The bottles are then stored inverted to prevent air leakage before being analyzed in the laboratory.

Helium is sparingly soluble in water, so it preferentially partitions into air when a gas phase is present. The atmosphere (containing 5.24 ppm He) equilibrates with surface waters at 10° C to give concentrations of 0.047 μ L He/L water. Excess He in the groundwater samples rapidly equilibrates with the headspace gas, resulting in an increased He concentration in the headspace gas. The original aqueous He concentration in the water sample is determined by measuring the He concentration in the headspace.

Helium analysis for the samples from blasts A and B was performed with a Veeco MS-18AB mass spectrometer, which had

been converted to measure absolute He abundance. The mass spectrometer was fitted with a specially designed, adjustable inlet valve and a cryogenic loop that was packed with activated charcoal immersed in liquid nitrogen to remove water and other condensable vapors. Laboratory air (5.24 mL He/L air) and He standards in N_2 (10, 100, 1000 mL He/L N_2) were injected into the mass spectrometer alternately with 10-mL samples of headspace gas.

Two 10-mL gas samples were obtained from the headspace of each sample bottle just prior to analysis and were analyzed sequentially with the standard gases. Helium concentrations in the samples were found to be so large (>15 mL He/L air) that the gas samples were first diluted by factors of up to 900 times before analysis, using the method described by *Gascoyne and Sheppard* [1993].

Difficulties arose using this sampling method, because the concentration of He in the groundwater was much higher than previously encountered in surface waters for which this method had been designed. When filling the sampling bottles from the groundwater supply, gas could be seen to be forming as bubbles and rising to the surface causing a loss of He from the sample and therefore an underestimation of He concentration in the groundwater. The amount of time between filling and sealing of the bottle was also a variable, and so the loss of He was not necessarily constant between samples. To obtain more representative and consistent samples for subsequent blasts, a new method of sampling was developed in which the groundwater was degassed by passing the flow through copper tubing wrapped with heater coils and immersed in a hot water bath (Figure 3). Off gases were collected in an inverted and partially submerged bottle and at regular intervals were sampled through a septum into Vacutainer 8-mL preevacuated test tubes (commonly used for blood sampling). Duplicate gas samples were taken. Analytical precision for He determinations is about $\pm 5\%$ (1 σ).

Gas analysis was performed on a less sensitive mass spectrometer, a VG MM-80 Magnetic Sector instrument. Gas samples were analyzed for He, as well as H_2 , N_2 , O_2 , Ar, CH_4 , and CO_2 . The mass spectrometer was calibrated with gas standards, and the concentrations of gases in the samples were normalized as a percentage of the gas volume. The typical analytical precision for this method of analysis is within $\pm 3\%$ (1σ).

Anions

The groundwater flow from the second nylon tube was used to collect samples for anion analysis, mainly bromide (Br), chloride (Cl), fluoride (F), sulphate (SO_4), and nitrate (NO_3). The samples were collected in 125-mL prewashed sample bottles and were analyzed using a Dionex Ion Chromatograph. Cations were not determined in this work because of their potential change in concentration due to sorption and exchange with other cations on mineral surfaces. Analytical precision is typically \pm 3% (1 σ).

Results

Pressure Pulses

The magnitudes of rock vibration observed during the monitored blasts are shown in Table 1. Figure 4 shows the hydraulic pressure pulse recorded in borehole zone JE5-4 during blast D when the system was maintained at full hydraulic pressure. The hydraulic pressure data are a combination of results from the data logger and a digital voltmeter which was connected in

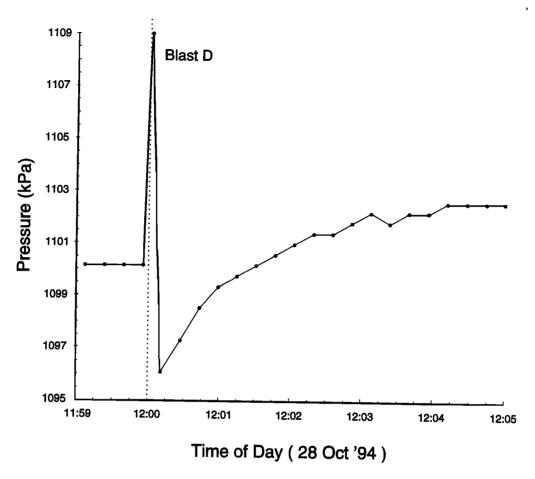


Figure 4. Variation of hydrostatic pressure of borehole JE5-4 in response to blast D.

parallel to the pressure transducer for this blast only. The initial hydraulic pressure pulse is likely to have been greater than the ~9-kPa increase detected here because of the relatively long sampling frequency of the data logger (16 s). However, within 0.5 min following the blast the zone pressure had decreased by ~4 kPa below the preblast level and over the next 5 min slowly increased to stabilize at a pressure slightly greater than the preblast level.

Radon

Radon concentrations often showed variability and inconsistencies between duplicate samplings. Results from monitoring blasts A and B showed a variable baseline throughout the flushing and blasting events, making the identification of blast impacts difficult. The modifications made to the sampling method for blasts C and D, which included taking duplicates, did not seem to improve the reliability of the results but did give a better understanding of how variability was being introduced. Some duplicates had significant deviations indicating either that the sampling procedures were still introducing errors or that real variations in Rn concentration were occurring over the time of sampling the duplicates (~1 min).

Despite these difficulties, the results shown in Figure 5 suggest that shortly after blast A, dissolved Rn concentrations began decreasing and reached their lowest levels after about 40 min. Radon levels returned to preblast values within an hour after this blast., In contrast, blast B was not followed by an

immediate drop in Rn concentrations, although a small decrease was observed about 2 hours after the blast. Blast B was not expected to produce as large of an impact on the rock mass as blast A (see Table 1) and so a lesser effect on Rn concentrations might be expected.

The uncertainty in the accuracy of the Rn monitoring data for blasts A and B prompted changes to the sampling procedure to try to improve the method. However, the results for blast C (Figure 6) again showed preblast variability and only small, single-point decreases in concentration after the blast.

Helium and Other Dissolved Gases

Variations of dissolved He concentration are shown in Figure 5. Both the blasts A and B resulted in distinctive, multipoint decreases in dissolved He concentrations. The initial decrease in He concentration was observed within 20 min of blast A and within 30 min of blast B. Minimum concentrations occurred about 40 and 50 min after the blast, respectively. The extent of the decreases in concentration in each case corresponded to the relative size of the blast (Table 1).

Results of monitoring blast C are shown in Figure 6. Dissolved gases from the groundwater were collected and analyzed for several gases, including He. Many of the gases showed some response to the blast, although most responses occurred within 5 min after the blast. Methane, H₂, CO₂, N₂, and He all showed decreases in concentration while O₂ showed an increase in concentration. Carbon dioxide concentrations remained low for

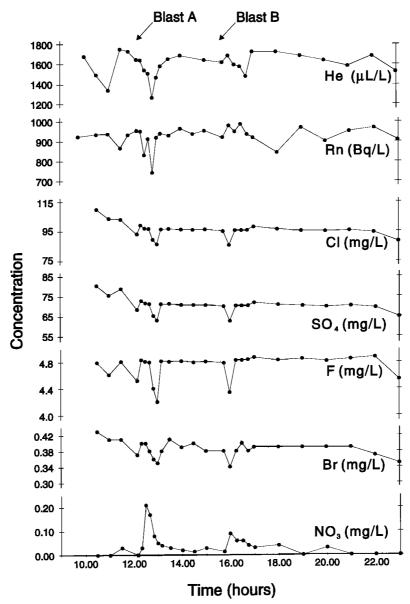


Figure 5. Variation in concentration of dissolved gases and anions over the period of blasts A and B.

only 10 min, and then became erratic for the next few hours. The other gases all began a gradual return to preblast concentrations over the next hour. The higher concentrations of $\rm CO_2$ observed toward the end of the monitoring period may be due to the gradual displacement of the $\rm HCO_3\text{-}CO_2$ chemical equilibrium under the prolonged interval of pressure reduction in the system.

Anions

For blasts A and B the anions Br, Cl, F, and SO₄ all decreased slightly in concentration shortly after the blast (Figure 5). Nitrate (NO₃) was the exception showing a small but distinct increase in concentration. The anions first showed a response to the blast between 30 and 40 min after the blast with the exception of nitrate which showed a response within 20 min. Bromide, Cl, F, and SO₄ all showed multipoint decreases in concentration that lasted at least 20 min. Nitrate took about 2 hours to return to pre-blast levels.

The change in anion concentrations for blast B were smaller than for blast A and, with the exception of NO₃, were seen as distinctive, one-point troughs about 20 min after the blast. Again, the response of NO₃, beginning about 20 min after the blast, was a small increase in concentration that took at least 2 hours to return to preblast levels.

Blast C generated results different than those of blasts A and B, with the exception of NO₃ (Figure 7). A large increase in NO₃ was seen within 15 min of the blast and took over 1 hour to return to background levels. The other anions showed little response to the blast, with only Cl showing an increase 1 to 2 hours after the blast.

Discussion

The changes in composition of the Room 209 fracture groundwater vary depending on the location of the blasting operations with respect to the location where the monitoring zone,

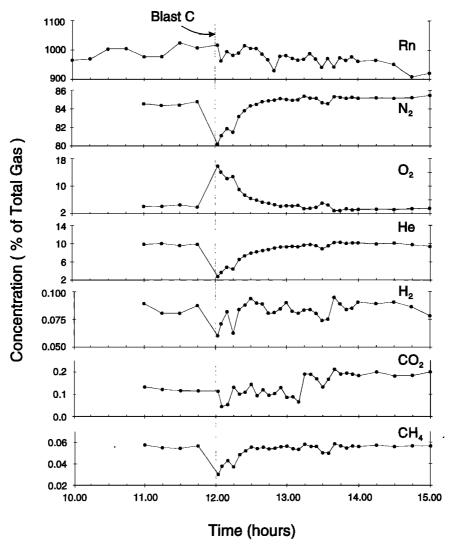


Figure 6. Variation in concentration of dissolved gases over the period of blast C.

JE5-4, penetrated the fracture (Figure 2). In blasts A and B, concentrations of all dissolved gases and anions (excepting NO₃) were observed to decrease at JE5-4 within 1 hour following the blast (Figure 5). In blast C, concentrations remained fairly constant (except for NO₃ and some dissolved gases) despite the fact that blast C was located closer to the fracture than blasts A and B. These results are best understood by examining the hydrogeology of the fracture in conjunction with the hydrochemical changes.

Groundwater Flow in the Room 209 Fracture

Because of disturbances introduced by the construction of the URL, groundwater in the fracture currently flows SW toward Room 209 in the URL and discharges at a rate of about 1 L/min into Room 209 (Figure 8). The fracture extends vertically upward to a splay of the FZ2 fault (FZ 2.5). The fracture also extends in a NE direction, tending to converge with FZ2, although hydrogeologic testing and monitoring indicates that there is only a limited hydraulic connection between them [Kozak and Davison, 1992]. Monitoring of groundwater compositions in FZ2, FZ2.5, and this fracture over the period 1987-1995 shows that Vent Raise water (FZ2.5) is generally much lower in Cl concentration than

either the Room 209 inflow or FZ2 groundwater. The long-term decrease in Cl concentration of Room 209 inflow over the period 1988-1992 (Figure 9) suggests that gradual dilution has been occurring due to infiltration of increasing amounts of overlying, more dilute, groundwater from FZ2.5 into the Room 209 fracture, under the influence of the hydraulic gradient. The hydrochemical observations described above suggest that the Room 209 fracture groundwater results from mixing of FZ2 and FZ2.5 groundwater in varying proportions, depending on characteristics of the flow path and hydraulic head conditions in each of the aquifers, as described below.

Hydrochemical Response to Blasting

The groundwater sampled during monitoring was collected through borehole zone JE5-4 which intersects the fracture ~35 m NE of the inflow into Room 209. Blasts A and B were very close to the groundwater sampling point (Figure 2) and would likely have had an impact on the fracture and rock immediately surrounding and upstream of the point. Blast C, however, being farther away (several meters) and downstream from the groundwater sampling point would likely have had a lesser impact on the groundwater sampled. The variations in dissolved anion

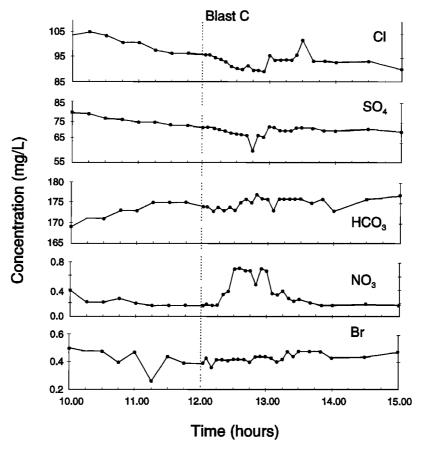


Figure 7. Variation in concentration of dissolved anions over the period of blast C.

concentrations following the blasts are in agreement with this expectation. Blast A showed the largest fluctuation in dissolved anions, followed by blast B. This difference in magnitude of response can be explained by the size of the blast (Table 1), but both affected JE5-4 groundwater as they lie upstream of the borehole. Blast C, however, did not cause any distinct fluctuations in dissolved anions (except for nitrate).

Gas-Phase Flow

As shown in Figure 7, other than NO₃, no anion concentrations varied for blast C, although changes were observed in dissolved gas contents (Figure 6). The increases in NO₃ content were seen in all three blasts (A, B, and C), suggesting that small amounts of residual NO_x gases from the blasting have been forced through the rock matrix by the pressure of the blast (or through microcracks created by the blast) to dissolve in groundwater in the fracture. The presence of this pressure pulse is clearly seen in Figure 4. All three blasts created anomalous dissolved gas concentrations, however. It is likely that the dissolved gas concentrations are more sensitive to rock fracturing and vibration and, because of their greater ease of diffusion, may respond at greater distances from the source.

It is possible that the NO₃ pulse may be a result of sampling the groundwater at the borehole collar in air which could have contained small amounts of NO_x gases. This possibility was not tested at the time of the study (e.g., by monitoring the composition of distilled water blanks open to the air) but is believed to be unlikely because all sampling was done at a location that was constantly up-wind of the blasting area and the NO₃ pulse did not

occur until at least 20 min after the blast, by which time most off gases had been vented from the URL. A similar pulse in dissolved oxygen concentration, soon after blasting is seen in Figure 6, for blast C, suggesting that free O_2 is formed during decomposition of the ammonium nitrate explosive and is driven though the rock matrix. In this case, contamination by the air is not likely because the same sampling method was used throughout the experiment, and dissolved O_2 concentrations are very stable for the remainder of the monitoring. Generation of O_2 from explosives is the most likely mechanism for this pulse as shown by the following equation [Turner and McCreery, 1981]:

$$2NH_4NO_3 \rightarrow 4H_2O + O_2 + 2N_2$$

This reaction shows that N₂ should also be forced through the rock matrix under pressure of the blast. Although data for blast C (Figure 6) show that relative N₂ content decreases while O₂ increases, these data are only expressed as percentages of total gas content and give no indication of absolute concentrations. It was not possible to precisely measure total gas content due to outgassing of the groundwater and bubble entrainment in the sampling vessel. However, a transient increase in both N₂ and O₃ concentrations is consistent with these observations and would lead to "dilution" of the other gases with consequent reduction in their apparent concentrations. This mechanism would be more likely to occur in blast C (and D) than in blasts A or B because microcrack pathways for gas migration would be created in the fracture wall rock during blast C but not in blasts A or B (Figure 2). These results collectively suggest that gases may be forced through the rock matrix, possibly assisted by blast-induced

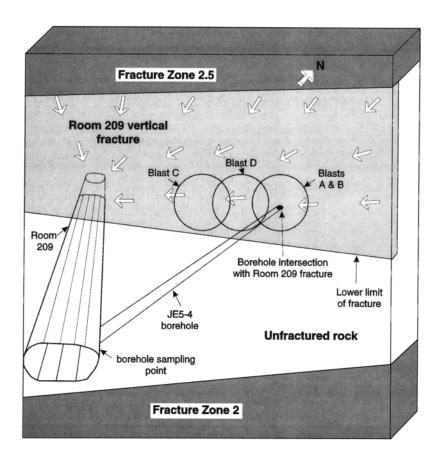


Figure 8. Schematic vertical section through the URL 240-m level showing the Room 209 fracture, groundwater flow directions (arrows), and the position of the blasts A, B, C, and D relative to the fracture and borehole JE5-4.

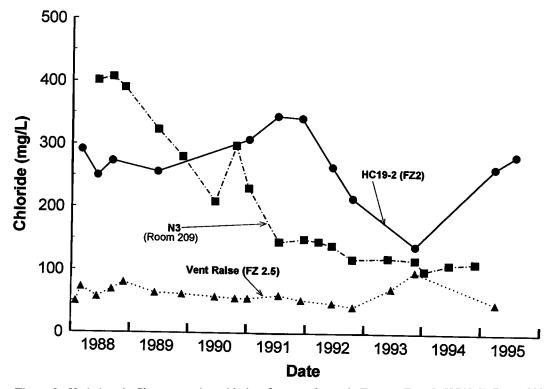


Figure 9. Variations in Cl concentration with time for groundwater in Fracture Zone 2 (HC19-2), Room 209 fracture (N3), and Fracture Zone 2.5 (VentRaise).

fracturing of the matrix, for distances of several meters, under the pressure generated by an underground explosion.

Application to Seismic Models of Hydrogeochemical Change

The hydrogeochemical variations observed after the blasts are similar to anomalies observed in spring and well water prior to and following seismic activity and may be caused by the same processes but on vastly different scales. Of the five models described by Thomas [1988] to account for these anomalies, the AB/FM model best accounts for the changes in groundwater composition observed immediately after the blasts. In this model a stress change or physical impact fractures and breaches the hydrological barriers between two isolated aquifers. breaching results in mixing of the fluids from the two aquifers, which occurs rapidly if they have different hydrostatic pressures. Because of the likely difference in composition of groundwater in these aquifers, this results in either dilution or enrichment of dissolved species in the sampled groundwater and accounts for the variations in concentration of dissolved gases and ions that have been observed both before and after seismic events in wells and springs. The similarity in recovery rates for ionic and dissolved gas concentrations also indicates that hydrological mixing is the principle mechanism causing these characteristics.

In this study, blasts A and B were both located "upstream" of the borehole's intersection with the fracture, while blast C was "downstream" of the intersection (Figure 8). If the blast were located within 1-2 m of the fracture, its effect would likely be to create newly fractured rock into which groundwater would flow. This could cause the decrease in hydraulic pressure following the initial peak in the Room 209 fracture groundwater, as observed in Figure 4. However, blasts A and B were located 5 to 10 m away from the fracture and so the change in groundwater composition is unlikely to be due to creation of newly fractured rock that could temporarily divert the flow of Room 209 fracture groundwater. It is more likely that the shock waves from blasts A and B caused changes in permeability of the fracture, so that more of the dilute groundwater from FZ 2.5 was allowed to flow into the Room 209 fracture at that point. This was seen in JE5-4 groundwater samples as a short period of lower anion concentrations (Figure 5). Recovery to preblast concentrations began once the hydraulic pressures of both groundwater sources stabilized. Because blast C occurred in rock close to the fracture and downstream of the inlet to JE5-4, no changes in ionic concentrations were likely to be seen, but a change in gas concentrations may have occurred.

The hypothesis of localized changes in fracture permeability in response to blasting is supported by observations during sampling that the groundwater flow rate from the borehole zone decreased over the period of the blasts. (Because of the sampling requirements it was not possible to accurately measure changes in flow rate, but an overall reduction in flow was observed.) In addition, the hydraulic pressure data shown in Figure 4 indicate that there was a change in hydraulic conductivity of the borehole zone following blast D. Pressure in the zone stabilized after the blast at a value 2 kPa higher than before the blast.

Four of the five models considered by *Thomas* [1988] only account for increases in concentrations of dissolved constituents prior to seismic activity. They cannot account for decreases in concentration, as have been observed in the monitoring of a number of earthquake events and in this study at the URL. It might be expected that liberation of pore fluids and grain-boundary salts together with the generation of fresh mineral surfaces should inevitably lead to increased groundwater salinity

but, unless groundwater flow is rerouted through this area of damaged rock after the event, this additional source of salinity will tend to remain in situ and only pass into the main flow path by diffusion. This would be a slow process and would be unlikely to cause detectable salinity increases in the groundwater at the monitoring site.

This study suggests that changes in groundwater composition could be caused simply by changes in hydraulic conductivity of the permeable pathway. Seismic activity could lead to increased or decreased permeability at many locations along the fracture plane, and the chemical signal seen at the sampling point (which may be many kilometers away from the epicenter) is a result of change in mixing ratio of local groundwater discharging at that point. Small changes in hydraulic conductivity in a fracture or fault may occur locally in response to distant seismic activity, and this would lead to hydrochemical responses. Release of saline fluids in low-permeability, high-porosity voids associated with the fracture may add to this response. The AB/FM mechanism proposed by Thomas [1988] therefore can be considered as a special case of a more general mechanism in which changes in hydraulic conductivity along the fracture plane influence groundwater mixing ratios and hence give rise to the hydrochemical responses seen in monitoring wells, springs and boreholes, both close to and distant from the epicenter of the seismic activity.

Summary and Conclusions

The main findings of this work are the following.

- 1. Changes in groundwater composition during underground excavation were observed for each of three blasts adjacent to a permeable fracture at the 240-m level of the Underground Research Laboratory, Manitoba.
- 2. Small decreases in concentration of major anions (Cl, Br, SO₄, F) and some dissolved gases (He, Rn), and an increase in NO₃ concentration, were observed when the blasts were located upstream of the groundwater sampling site.
- 3. Only decreases in concentration of some dissolved gases (He, Rn, N₂) and increases in NO₃ and dissolved O₂ were observed when the blast location was downstream of the sampling site.
- 4. The hydraulic pressure in the fracture over the period of a blast showed a sharp initial increase followed by a decrease in pressure, with gradual recovery to slightly above pre-blast levels.
- 5. Evidence was found for the penetration of small quantities of gases (N₂, NO_x, O₂) released from explosives during the blast, through several metres of rock matrix, into groundwater.

The changes in groundwater composition best fit a more general case of the aquifer breaching/fluid mixing model used to account for compositional changes of groundwaters prior to earthquakes [Thomas, 1988]. Seismic activity causes changes in hydraulic conductivity at many locations along the fracture plane, and it is the change in mixing ratio of groundwater flowing toward the sampling location plus release of saline pore fluids, if present, that causes the hydrochemical response. Support for other models (ultrasonic vibration, pressure-sensitive solubility changes, and release from fresh mineral surfaces) was not found. However, concentration increases observed after earthquakes may be accounted for by these models but require that significant quantities of saline pore fluids are released or the groundwater is redirected through the fractured rock created by the seismic event.

The work described in this study was performed on a scale that is small in comparison with that of natural seismic activity but took place in an environment where the seismic events were controlled, the groundwater flow path was known, and the response travel time was rapid. This work has been useful in providing a better understanding of the causes of geochemical changes in groundwater in association with larger-scale seismic events such as earthquakes.

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References

- Atomic Energy of Canada Limited, Environmental Impact Statement on the concept for disposal of Canada's nuclear fuel waste, AECL-10711, COG-93-1, Pinawa, Man., 1994.
- Barsukov, V.L., G.M. Varshal, and N.S. Zamokina, Recent results of hydrogeo-chemical studies for earthquake prediction in the USSR. Pure Appl. Geophys, 122, 143-156, 1985.
- Birchard, G.F., and W.F. Libby, Soil radon concentration changes preceding and following low-magnitude 4.2-4.7 earthquakes on the San Jacinto Fault in southern California, *J. Geophys. Res.* 85(B6), 3100-3106, 1980.
- Finkel, R.C., Uranium concentrations and ²¹⁴U/²¹⁸U activity ratios in fault-associated groundwater as possible earthquake precursors, *Geophys. Res Lett.*, 8, 453-456, 1981.
- Gascoyne, M., and D.C. Kamineni, The hydrogeochemistry of fractured plutonic rocks in the Canadian Shield, Appl. Hydrogeol., 2, 43-49, 1994.
- Gascoyne, M., and M.I. Sheppard, Evidence of terrestrial discharge of deep groundwater on the Canadian Shield from helium in soil gases, *Environ. Sci. Technol.*, 27, 2420-2426, 1993.
- Gascoyne, M., S. Stroes-Gascoyne, and F.P. Sargent, Geochemical influences on the design, construction and operation of a nuclear waste vault, Appl. Geochem., 10, 657-672, 1995.

- King, C.-Y., Gas geochemistry applied to earthquake prediction: An overview, J. Geophys. Res., 91, (B12), 12269-12281, 1986.
- Kozak, E.T., and C.C. Davison, Hydrogeology of the rock mass encountered at the 240 level of Canada's Underground Research Laboratory, Rep. AECL-10346, COG-92-293, At. Energy of Can. Ltd., Pinawa, Man., 1992.
- Li, G., F. Jiang, J. Wang, and P. Zhang, Preliminary results of seismogeochemical research in China, Pure Appl. Geophys., 122, 218-230, 1985.
- O'Neil, J.R., and C.-Y. King, Variations in stable-isotope ratios of ground waters in seismically active regions of California, *Geophys. Res. Lett.*, 8, 429-432, 1981.
- Rao, G.V., G.K. Reddy, R.U.M. Rao, and K Gopalan, Extraordinary helium anomaly over surface rupture of September 1993 Killari earthquake, India, Curr. Sci., 66, 933-935, 1994.
- Röshoff, K., Seismic effects on bedrock and underground constructions.

 A literature survey of damage on constructions; Changes in groundwater levels and flow; Changes in chemistry in groundwater and gases, SKB Tech. Rep., 89-30, Swed. Nucl. Fuel and Waste Manage. Co., Stockholm, Sweden, 1989.
- Simmons, G.R., D.M. Bilinsky, C.C. Davison, M.N. Gray, B.H. Kjartanson, C.D. Martin, D.A. Peters, L.D. Keil, and P.A. Lang, Program of experiments for the operating phase of the Underground Research Laboratory, Rep. AECL-10554, COG-92-280, At. Energy of Can. Ltd., Pinawa, Man., 1992.
- Stephenson, M., W.J. Schwartz, L.D. Eveden, and G.A. Bird, Identification of deep groundwater discharge areas in the Boggy Creek catchment, southeastern Manitoba, using excess helium, Can. J. Earth Sci., 29, 2640-2652, 1992.
- Thomas, D., Geochemical precursors to seismic activity, Pure Appl. Geophys., 126, 241-266, 1988.
- Turner, C.F., and J.W. McCreery, The Chemistry of Fire and Hazardous Materials, 292 pp., Allyn and Bacon, Needham Heights, Mass., 1981.
- Watson, R, Handling and analysis of groundwater samples within the Hydrogeochemistry Section, Doc. SI002.005, Waste Technol Div. QA Program, At. Energy of Can. Ltd., Pinawa, Man., 1994.

M. Gascoyne, Applied Geoscience Branch, Atomic Energy of Canada Limited, Whiteshell Laboratories, Pinawa, Manitoba, Canada ROE 1L0. (e-mail: gascoyne@aecl ca)

D.A. Thomas, Department of Geology and Geophysics, University of Calgary, Calgary, Alberta TZN 1N4.

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