

Monitoring of hydrogeochemical change in a seismically active region – a possible application for continuous monitoring by voltammetry

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toring of groundwater chemistry in a seismically-active region.

ABSTRACT

Results, presented by Claesson et al. (2004), indicating short-lived increases in the concentrations of Fe, Cr, Mn, Zn and Cu in groundwater taken from a 1.5 km deep borehole on northern Iceland before a major earthquake, are summarised. The sampling and analytical strategies currently implemented in this ongoing study (ICP-AES, Varian Vista Pro Ax) are reviewed in the context of recent advances in off-laboratory analytical capabilities, with specific reference to continual monitoring of low concentrations ($\mu\text{g/l}$) of trace metals by voltammetry. This approach would reduce total analytical time from 1-2 days to < 15 minutes per sample, increase the analysis frequency potential from weekly to every 15-30 minutes, greatly reduce the cost per analysis and permit real time moni-

KEYWORDS

Hydrogeochemistry, groundwater, continuous monitoring, voltammetry, earthquake prediction, Tjörnes Fracture Zone

INTRODUCTION

This paper examines the results of a hydrogeochemical monitoring program conducted on groundwater samples recovered from a 1.5 km deep borehole near the town of Husavik on northern Iceland (Fig. 1). The program began on July 3, 2002 and is ongoing at the time of writing (October, 2004). The paper then focuses on a review of the sampling and analytical strategy which is currently being implemented in the study. The paper concludes with a preliminary assessment of the suitability of this study as a pilot application for continual monitoring by voltammetry

(Reference to article by Øyvind Mikelsen, Silje M. Skogvold, og Knut H. Schrøder, KONTINUERLIG TUNG-METALLOVERVÅKING I RAUBEKKEN, LØKKEN VERK, this volume of «VANN»). During the initial phase of the hydrogeochemical monitoring program (July 2002 to August 2003), a major earthquake (Magnitude 5.8, September 16, 2002) occurred 90 km from the sampling station. Chemical changes were detected in groundwater samples both before and after the earthquake. These results are summarised in this paper for the purpose of providing a basis for a discussion of sampling and analytical strategy. However the interested reader is referred to Claesson et al. (2004) for a more complete discussion.

GEOLOGY

Husavik is situated within the Tjörnes Fracture Zone. This is a seismically active area that displaces the mid-Atlantic ridge, where earthquakes up to magnitude 7 have occurred, with the most recent occurring in 1963 (Saemundsson, 1974; Gudmundsson et al., 1993; Garcia et al., 2002).

HYDROGEOCHEMICAL MONITORING

In July 2002, a hydrogeochemical monitoring program was established within this area in order to **a)** broaden the knowledge of fluid flow and source regions of fluids in the upper crust by studying water/rock migration, **b)** further the understanding of water-rock interaction and brittle deformation in seismically active areas, and **c)** examine the viability of hydrogeochemical monitoring of fluids in active fault zones as a method of stress forecasting and ultimately earthquake prediction.

The monitoring program involved the weekly collection of groundwater samples from a 1500 meter deep borehole (HU-01) in the Tjörnes Fracture Zone. Sampling began on July 3, 2002 and is ongoing at the time of writing. The borehole cuts through a well-stratified sedimentary sequence with basaltic horizons intercalated with the sediments. From borehole HU-01, three water samples are taken once per week: one for cation analysis, one for anionic analysis and one for stable isotope analysis. The water is analysed at Stockholm University using spectrometry (ICP-OES) for the cations, and a chromatographic

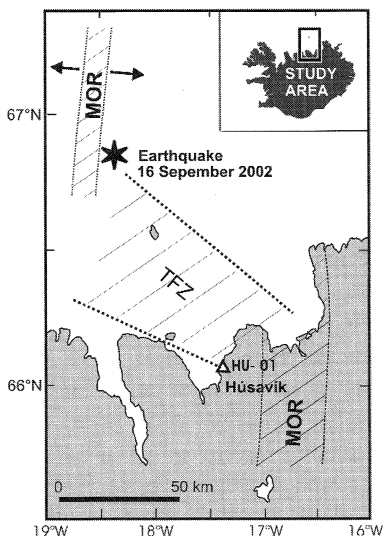


Fig. 1. Map of northern Iceland, showing the location of the sampling station (borehole HU-01) at Husavik, the epicentre of the earthquake which occurred on September 16, 2002, and the approximate locations of the mid-ocean ridge (MOR) and Tjörnes Fracture Zone (TFZ).

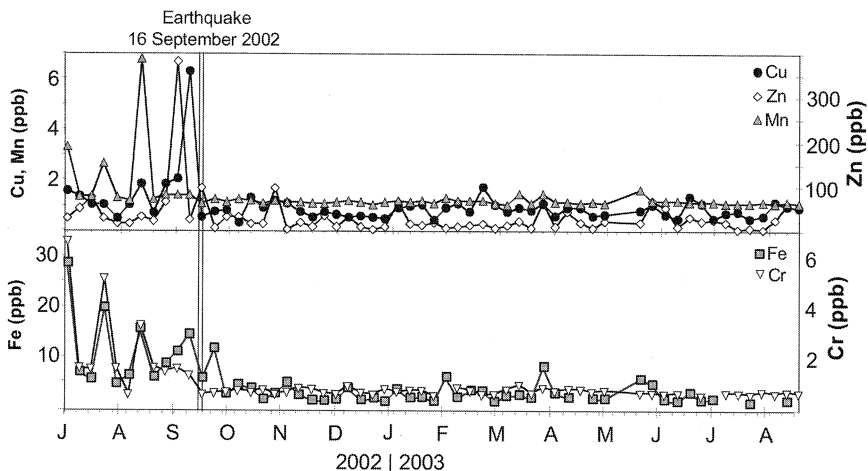


Fig. 2. Hydrogeochemical changes measured in groundwater recovered from the 1.5 km deep borehole, HU-01 which is located near Husavik, northern Iceland. Analytical errors are <2% (estimated from replicate analysis of standards). The magnitude 5.8 earthquake on September 16, 2002 is shown. Other chemical data is presented by Claesson et al. (2004).

system for the anions. Additionally, stable isotopes are analysed with mass spectrometry.

METHODS

Water samples are taken with acid clean syringes (50 ml) and filtered through 20 μm filters into three 50 ml acid clean polypropylene bottles. The purpose of filtering the water upon collection is inhibiting suspended particles from reacting with the water, and changing its composition during storage. Samples intended for cation analysis are also acidified with ultra pure HNO_3 during collection. The purpose of this is two-fold: 1) to prevent precipitation of solid particles that could occur during sample storage (e.g. precipitation of ferric hydroxide or calcium carbonate from CO_2 rich waters) and 2) to prevent adsorption of ions onto the bottle

walls. These samples are filtered into acid washed bottles and acidified with 1 ml ultra pure HNO_3 during collection. This is because water with pH as low as 1 has a tendency to dissolve dust, rock or other particles present in the water in unfiltered samples (Árnorsson and D'Amore., 2000).

Acid cleaning is completed as follows: bottles are soaked in a 5% NaOH bath for 24 hours, rinsed in deionised water, soaked in a bath consisting of 5% ultra pure HNO_3 for 72 hours, rinsed in ultra pure water and finally soaked in an ultra pure water bath and dried in an air-clean laboratory for 5-7 days. Samples intended for anion and isotope analysis are filtered into bottles carefully rinsed with sample water prior to filling in order to remove any contaminants. Sampling of the water from HU-01 is carried out by affili-

ated personnel at Húsavíkurkaupstadur. Samples are stored for up to 12 weeks at a temperature of maximum 8 °C at the sample location, and are subsequently freighted to Stockholm University. If an earthquake occurs, samples can be sent more quickly to Stockholm University for analysis.

All analyses are carried out at Stockholm University. Cation concentrations are determined with a ICP-AES, Varian Vista Pro Ax and anion concentrations with a Dionex DX-300 ion chromatography system. Due to a high Si and Na content some samples intended for cationic analysis need to be diluted, in order to prevent silica polymerisation (Arnórsson and D'Amore, 2000). Dilution is prepared as follows: 1 ml sample is diluted with 9 ml of ultra pure water and finally 100 µl ultra pure HNO₃ is added. Dilution is also performed for some samples intended for anionic analysis, if Na and Ca concentrations are high.

To prepare, obtain and analyse one water sample from borehole HU-01 requires 24-48 hours, excluding the time taken to freight the samples to Stockholm. Included in this calculated time period is the actual analytical running time in the laboratory, which is on the order of a few hours for both spectrometry and chromatography.

SUMMARY OF RESULTS

Claesson et al. (2004) report hydrogeochemical changes both before and after the earthquake. Hydrogeochemical changes detected before the earthquake are summarised below. Hydrogeochemical changes detected after the earthquake do not

involve elements which are of interest for continual monitoring by voltammetry and are consequently not discussed further.

Before the magnitude 5.8 earthquake on September 16, 2002, we detected short-lived increases in the concentrations of Fe, Cr, Mn, Zn and Cu. These occurred as statistically-significant anomalies which arrived at the sampling station on or before the start of sampling (Fe and Cr), and 5, 2 and 1 week(s) before the earthquake (Mn, Zn and Cu, respectively).

The concentration of Cu (detection limit = 0.34 µg/l) increased from an average baseline of 0.90 ± 0.37 µg/l (based on 48 samples) to 6.28 µg/l *one week before the earthquake*, and then decreased to baseline. The concentration of Zn (detection limit = 1.1 µg/l) increased from an average baseline of 26 ± 23 µg/l (based on 48 samples), to 381 µg/l *two weeks before the earthquake*, and then decreased to baseline. The concentration of Mn (detection limit = 0.12 µg/l) increased from an average baseline of 1.25 ± 0.35 mg/l (based on 48 samples) to 6.76 µg/l *five weeks before the earthquake*, and then decreased to baseline. Fe (detection limit = 0.80 µg/l) decreased erratically from >25 mg/l to an average post-earthquake baseline of 2.8 ± 2.2 µg/l (based on 48 samples) shortly after the earthquake. Cr (detection limit = 0.48 µg/l) decreased erratically from >6 µg/l to an average post-earthquake baseline of 0.65 ± 0.10 µg/l (based on 48 samples) shortly after the earthquake.

INTERPRETATION

Claesson et al. (2004) interpret stress-induced source mixing as a possible cause of these pre-earthquake anomalies, with leakage of water from an external (hotter) basalt-hosted source-reservoir, where water-rock interaction was more rapid. Their interpretation is supported by the experimental results of Seewald and Seyfried (1990), which show that basalt alteration by saline fluids at 300–400 °C will sequentially enrich Fe, Mn, Zn and Cu in the fluid. This sequence corresponds to the sequence of chemical anomalies detected at HU-01.

CONTINUAL MONITORING

The pre-earthquake signals detected by Claesson et al. (2004) are of obvious interest because they could represent earthquake precursors. Critical to evaluating their significance is testing whether or not these results are reproducible. This requires continued monitoring. Ideally this would involve several sampling stations to test whether or not the anomalies represent some effect that is specific to borehole HU-01 and/or to assess the affect of distance between the earthquake focus and the sampling station. In addition, the sampling frequency would ideally be increased. The anomalies that were detected were short-lived and thus each anomaly is only supported by a single data point. This both lowers confidence in the data and renders it highly likely that the true size of the anomaly is unknown.

(Reference to article by Øyvind

Mikkelsen, Silje M. Skogvold, og Knut H. Schrøder, KONTINUERLIG TUNGMETALLOVERVÅKING I RAUBEKKEN, LØKKEN VERK, this volume of «VANN»). Presents a new method for continual monitoring and on-line surveillance of dissolved heavy metals in water using off-laboratory automatic voltammetry. This method has proven highly successful in pilot studies that are ongoing at the Trondheim River and Løkken Verk, yielding measurement of Fe, Zn and Cu, present only in low concentrations (µg/l), which are fully reproducible using ICP analysis. Even at these low concentrations, measurement times are generally <15 minutes. Thus, by applying this method to monitor groundwater chemistry on northern Iceland, a 500-fold increase of analysis frequency is realistic and therefore full characterisation of any future concentration anomalies. The method has been in operation without maintenance for a period of 8 months at the Trondheim River. This level of operational reliability together with ease of operation satisfies essential prerequisites of the Icelandic groundwater monitoring program which arise because of the remote location of the sampling station. The sampling station has both electricity and GSM coverage, which are prerequisites for the operation of the on-line surveillance equipment. On-line installation at the borehole may require some modification to the standard setup and the high temperature of the groundwater (ca. 90°C) can be handled through output calibration. Finally, continual monitoring, with remote

data access would introduce the possibility of observing and documenting changes in groundwater chemistry before an earthquake actually occurs, which is of obvious benefit if the pre-earthquake hydrogeochemical changes observed by Claesson et al. (2004) can be shown to be precursory.

CONCLUSIONS

Claesson et al. (2004) observed short-lived increases in the concentrations of Fe, Cr, Mn, Zn and Cu in groundwater taken from a 1.5 km deep borehole on northern Iceland before a major earthquake. This result is part of ongoing monitoring of groundwater chemistry in two seismically active regions on Iceland, where samples are bottled and shipped to a laboratory for chemical analysis. This study is ideally suited for continual monitoring by voltammetry (Reference to article by Øyvind Mikkelsen, Silje M. Skogvold, og Knut H. Schrøder, KONTINUERLIG TUNG-METALLOVERVÅKING I RAUBEKKEN, LØKKEN VERK, this volume of «VANN»), which would reduce the analytical time from 1-2 days to < 15 minutes, increase the analysis frequency from weekly to every 15-30 minutes, reduce the cost per analysis and permit real time monitoring of hydrogeochemical change.

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