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^{14}C AGES OF GROUNDWATER IN ICELAND

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ABSTRACT

During the last few years an effort has been made to date Icelandic groundwater by the radiocarbon dating technique. In Iceland at least three different sources of carbon in the water are expected: atmospheric CO_2, soil CO_2 of organic origin and CO_2 leached from the rock. Moreover, there may be a supply of CO_2 from magmatic sources in some geothermal systems. Addition of carbon from sources other than the atmosphere and organic soil dilutes the ^{14}C concentration of the water and in this way yields higher apparent ^{14}C age. Earlier studies have suggested that boron concentrations of the water samples can be taken as a measure of the amount of ^{14}C-dead CO_2 in groundwater leached from the rock. After applying boron-based corrections, the values for most of the cold and warm groundwaters lie in the range 30 to 110 pMC, which is in accordance with indications from other chemical tracers and the estimated residence time for the groundwater.

The calculated boron based ^{14}C dilution is considerably less in the water samples from the NW-Peninsula and the Southern Lowlands compared to the samples from the Skagafjördur region. This is in accordance with the expected real ages of the groundwater.

The δ^{13}C values in cold surface waters range from -1 to -7 ‰ whereas in soil waters the δ^{13}C is much lighter and ranges from -16 to -22 ‰. In the geothermal waters the δ^{13}C values usually fall in the range -6 to -13 ‰. A linear relationship is observed for the δ^{13}C of groundwater and the calculated ^{14}C boron-based dilution, except where the waters emerge in thick peat soil resulting in low δ^{13}C values.

1. INTRODUCTION

In Iceland, the deuterium content has been used extensively to trace the origin of groundwater, including geothermal water (Árnason, 1976, 1977). Since 1986 extensive oxygen and hydrogen isotope analyses have been carried out on natural waters in Iceland and the relationship between the isotope ratios studied (Sveinbjörnsdóttir, 1989, 1991, Sveinbjörnsdóttir et al., 1995b,1998). These studies have further highlighted the usefulness of stable isotopes to trace groundwater movements and demonstrated the importance of taking into account all available geological, geophysical and geochemical data from any particular system when interpreting the groundwater flow. Árnason (1976) estimated the age of the cold groundwater as relatively young (an average of a few years to a few decades old) and that of the hot water from a few decades to >10.000 BP. More recent stable isotope and geochemical studies have supported the interpretation that the oldest groundwater in Iceland originates from the last glaciation (>10.000 years ago) (Arnórsson et al., 1993, Sveinbjörnsdóttir et al., 1995a, 1995b). Tritium and the ^{14}C radioisotope have since been used to further estimate the age of Icelandic natural waters (Sveinbjörnsdóttir et al., 1995a, 1998). Tritium can be used to date groundwaters in the limited interval back to the beginning of the atmospheric nuclear bomb testing in the late 1950's and the ^{14}C radioisotope, with its half-life of about 5700 years, offers the potential of dating groundwater up to about 40.000 years.

Interpretation of ^{14}C results on groundwater is complex as carbon in groundwater may derive from several sources with different ^{14}C concentration and δ^{13}C. Iceland is mainly made up of basalt (ca. 90%) and the rest is of rhyolitic and intermediate composition. About 90% of the country above sea level consists of volcanic rock and only about 10% are consolidated sediments; mainly interbedded tuffaceous layers of short transport and tillite. Icelandic bedrock contains no calcareous rock, which severely affect the carbon isotopes in groundwater. Geothermal activity is widespread and may yield high apparent ^{14}C ages.

An important development in studying ^{14}C in natural water was the introduction of accelerator mass spectrometry (AMS) to measure ^{14}C in inorganic carbon. The AMS technique allows dating of samples as small as 1 to 0.1 mg carbon - a reduction in sample size of more than a factor of 1000 compared to the traditional ^{14}C dating by radioactive decay counting. The corresponding reduction in sample size from 100 liters to 0.1 liter of water has made it feasible to process large sampling series to test hydrological flow models.

The first measurements of ^{14}C in Icelandic groundwater are reported in Sveinbjörnsdóttir et al. (1992). Since then determined efforts have been made to date Icelandic groundwater by the radiocarbon dating technique (Sveinbjörnsdóttir et al. 1995a, 1998). In this contribution comparison is made of the ^{14}C concentration and δ^{13}C in Icelandic groundwater between geologically different areas with different vegetational cover and how the ^{14}C

concentration can be interpreted as real ^{14}C ages by using the boron concentration in the water as a leaching indicator.

2. METHODS

One liter of each water sample is collected and in the first attempt to analyse ^{14}C in Icelandic groundwater, carbon was precipitated from the samples as $BaCO_3$ (Sveinbjörnsdóttir et al., 1995a). The $BaCO_3$ precipitate was then transformed to CO_2 by reaction with 86% phosphoric acid in an evacuated vial placed in a water bath at 20°C. Since 1997 the sample preparation has been done in accordance with McNichol et al. (1994), i.e. the water samples are acidified in a vacuum system and CO_2 extracted directly by nitrogen flow through the water sample. Schematic figure of the sample preparation line is shown in Figure 1. The collected CO_2 is then partly used for $\delta^{13}C$ measurements at the Finnegan Mat 251 mass spectrometer at the Science Institute, University of Iceland and partly converted to graphite for AMS ^{14}C measurements at the Aarhus EN tandem accelerator, Denmark. Further information on the graphitisation system and the AMS system is given in Sveinbjörnsdóttir et al. (1992). ^{14}C results are normalised to a $\delta^{13}C$ value of -25‰ PDB and expressed in "percent modern carbon" (pMC) relative to 0.95 times the ^{14}C concentration of the NBS oxalic acid standard (HOxI).

3. RESULTS

Water samples have been collected from geologically different parts of Iceland (Fig.2) with different types of vegetational cover and with different water temperatures. The Southern Lowlands are located in Quaternary rock between the two active volcanic belts in South Iceland. The area is almost completely covered with relatively thick humus and peat soil. The Northwest Peninsula is located in Miocene flood basalts (10-13 Ma old), where humus and peat soil cover is sparse except along the coast and in low valleys. The Skagafjördur region in N-Iceland is also located in Miocene flood basalt and the vegetational cover is very variable in the area studied. In addition, some glacial rivers were sampled and analysed for carbon isotopes after the subglacial volcanic eruption that took place beneath the glacier Vatnajökull in 1996.

3.1 Surface waters

In the surface water (rivers and streams) the ^{14}C concentration ranges from 85 to 117 pMC corresponding to apparent ^{14}C ages from ca. 1700 BP to modern, bomb influenced values of present atmospheric ^{14}C excess. Soil waters, emerging from soil that is high in organic matter, are all bomb influenced. The surface waters that show some ^{14}C age are either influenced by geothermal water with relatively low ^{14}C concentration or are samples from glacial rivers that have an icemelt component of old glaciers. The $\delta^{13}C$ values in surface rivers are in the range -1 to -7 ‰, whereas the soil waters that have seeped through the organic soil zone, have considerably lower $\delta^{13}C$ values ranging from -16 to -22‰.

Volcanic influence

The carbon isotopes suggested abnormal conditions in the glacier rivers from the Vatnajökull glacier after the subglacial volcanic eruption beneath the glacier in 1996. The increase in $\delta^{13}C$ values is up to 3.8‰ (from -2.3 to +1.5‰) and the increase in ^{14}C apparent age is by about 20.000 BP. The impact of the subglacial eruption on the chemistry of the rivers from the glaciers is comprehensively described in Kristmannsdóttir et al. (1999) and Gíslason et al. (1999).

3.2 Groundwater

For the cold (<10°C) groundwater samples the ^{14}C concentration ranges from 70 to 117 pMC corresponding to apparent ^{14}C ages from ca. 3000 BP to modern. The $\delta^{13}C$ values for these samples range from -7.2 to -21‰, where the lowest $\delta^{13}C$ values are found in water samples emerging in thick peat soil. The warmer groundwater samples have generally lower ^{14}C concentration as is demonstrated on Figure 3a, and slightly narrower range in the $\delta^{13}C$ values (Fig. 3b).

4. DISCUSSION

The component of carbon in the water samples that is derived from the rock due to water-rock interaction dilutes the ^{14}C concentration of the water and in this way yields a high apparent ^{14}C age. Sveinbjörnsdóttir et al. (1995a) demonstrated that the simple two component (i.e. rock and organic derived carbon) $\delta^{13}C$ model (Mook, 1980) to correct for dissolution of old carbon is inadequate for Icelandic water samples. Sveinbjörnsdóttir et al., 1995a proposed that boron concentrations of the water samples can be taken as a measure of the amount of ^{14}C-dead CO_2 in groundwater leached from the rock. Boron acts as a mobile element in the Icelandic basalt-water environment (Arnórsson and Andrésdóttir, 1995) and can thus be used as a leaching indicator, i.e. its aqueous concentration is a measure of the amount of rock dissolution caused by reaction with the water. A negative correlation is observed between the boron concentration and the ^{14}C concentration of the water samples and fits a hyperbolic function, as expected if the boron concentration is a measure of dilution with ^{14}C dead CO_2. By assuming that the ratio of boron to CO_2 is the same in the rock and groundwater it is possible to correct the ^{14}C concentration for the contribution of rock derived carbon in the groundwater and thus calculate the initial (undiluted) ^{14}C concentration. Figure 4 demonstrates the different amount of water-rock interaction that has occurred in the Skagafjördur region on one hand where the carbon concentration derived from rock is up to 4 mmoles/kg (Fig. 4a) and the Southern

Lowlands and North-western Peninsula on the other hand where the highest concentration of rock derived carbon in the water is only 1.8 mmoles/kg (Fig. 4b). This difference was expected as the samples from the Southern Lowlands and the NW-Peninsula were all selected to characterise young groundwaters in contrast to the Skagafjördur samples where some of the waters are > 10.000 BP.

The only available data on boron and carbon in Icelandic rocks are on tholeiites from Eastern Iceland (1.2 ppm B and 0.05 % (wt) CO_2) and these numbers may not characterise well Iceland as a whole. Part of the observed difference in rock derived carbon concentration between Figure 4a and b can be explained by different concentration of these elements in the host rock. In the Skagafjördur regions the boron-based calculations indicate that a substantial fraction of the carbon entering the water has precipitated, probably as calcite. Subsequently the ^{14}C dilution was calculated by assuming the average CO_2 composition of surface waters as the initial CO_2 concentration of the water. After application of the boron-based corrections, the values for most of the cold and warm groundwaters lie in the range 30 to 110 pMC, which is in accordance with indications from other chemical tracers and the estimated residence time for the groundwater. Where tritium analyses are available they also support the boron based calculated ^{14}C ages.

Figure 5 suggests a linear relationship for the $\delta^{13}C$ and the calculated ^{14}C dilution for groundwater in the Skagafjördur region, except where the groundwater emerge in thick peat soil and cause particularly low $\delta^{13}C$ values. The samples for the NW-Peninsula show considerably less ^{14}C dilution (<1.8) than the Skagafjördur samples (up to 7.6) and quite uniform $\delta^{13}C$ values, ranging from -12.6 to -15.3 ‰. Figure 5 suggests very little ^{14}C dilution for the samples from the Southern Lowlands. They represent cold springs on one hand, where the $\delta^{13}C$ values are in the range -11 to -13 ‰ and warm groundwater from shallow drillholes at farmhouses on the other, where the $\delta^{13}C$ values are around -16 ‰.

5. CONCLUSIONS

Stable isotopes of oxygen and hydrogen have been used successfully in Iceland to trace the origin of groundwater and to delineate regional movement of groundwater. The first attempts to use carbon isotopes to trace groundwater movements and study water-rock interaction are promising. By using boron concentration in the water samples to correct for the ^{14}C dilution it is possible to interpret ^{14}C concentration as real ^{14}C ages.

6. ACKNOWLEDGEMENTS

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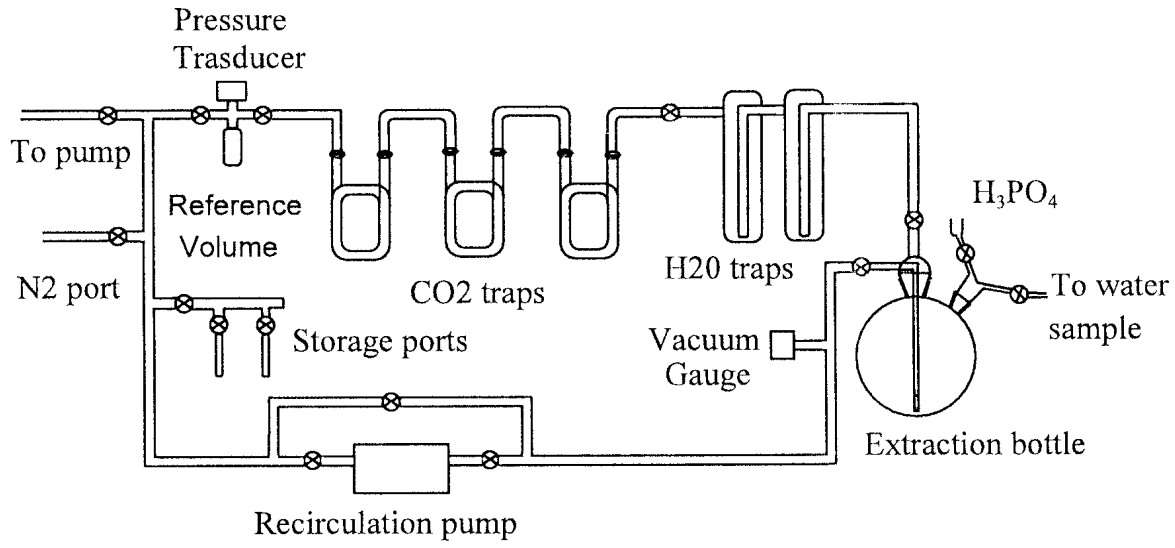

CO2 stripping line for water samples

Figure 1. Schematic figure of the water preparation line for ^{14}C and $\delta^{13}C$ analyses.

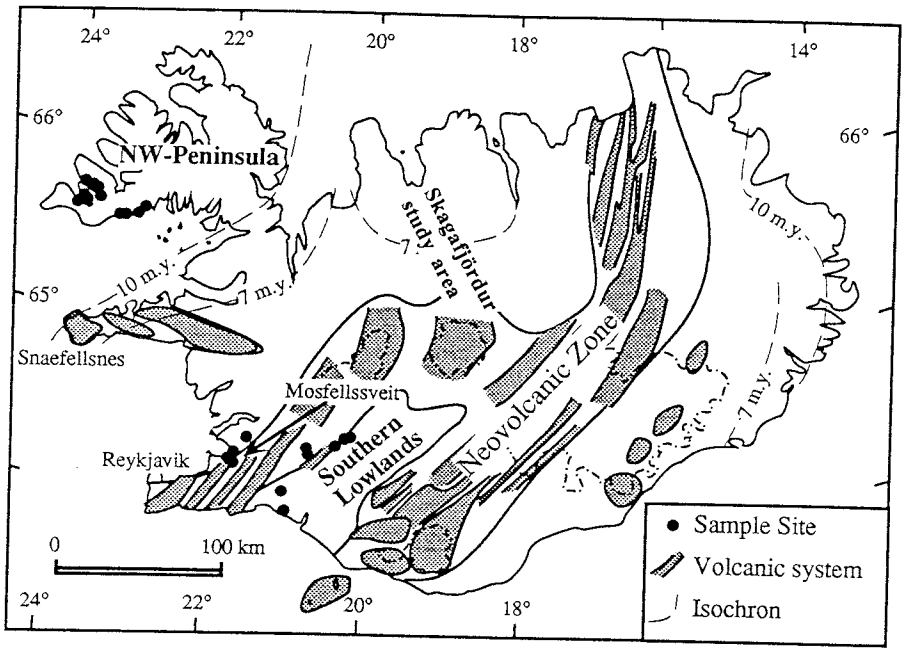

Figure 2. The locations of the studied areas.

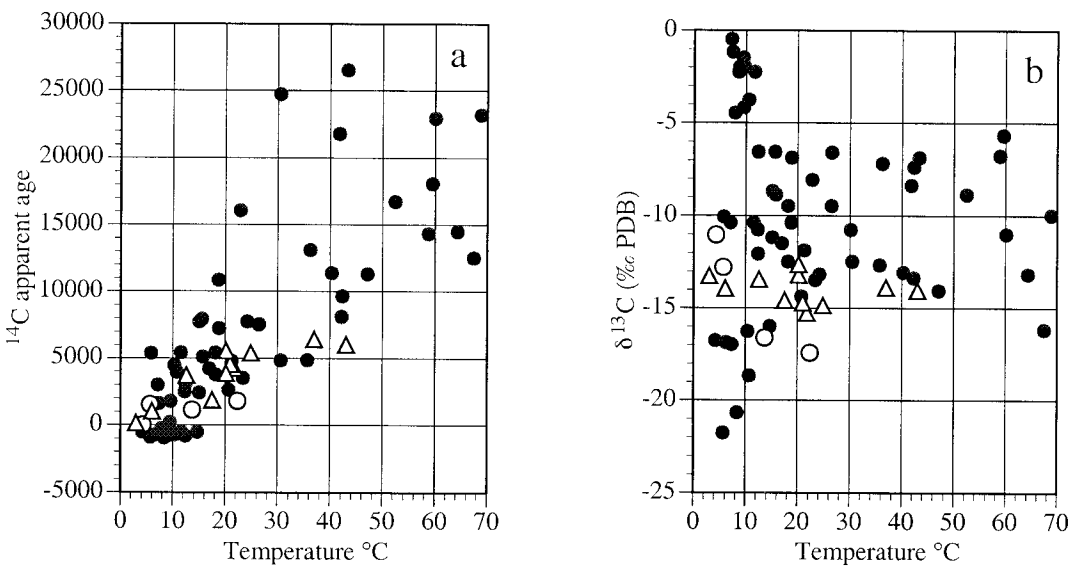

Figure 3. The relation between water temperature and a) ^{14}C apparent age of the water and b) δ^{13}C values. Dots: Skagafjördur natural waters, open circles: S-Lowlands, triangles: NW-Peninsula.

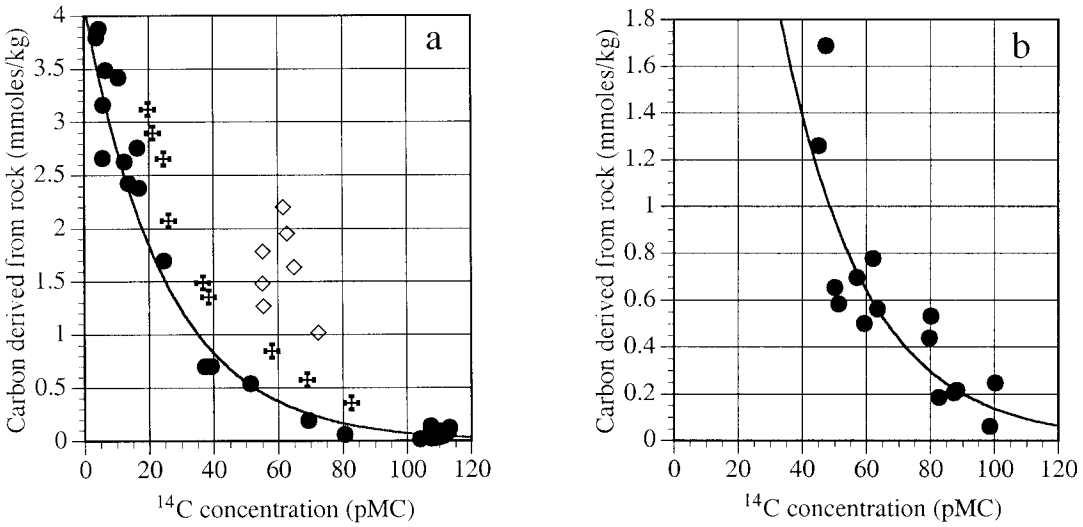

Figure 4. Correlation between CO_2 leached from rock and the ^{14}C concentration of a) the Skagafjördur natural waters (Crosses and diamonds represent waters where the boron based correction model overestimates the ^{14}C dilution) b) the Southern Lowlands and the NW-Peninsula.

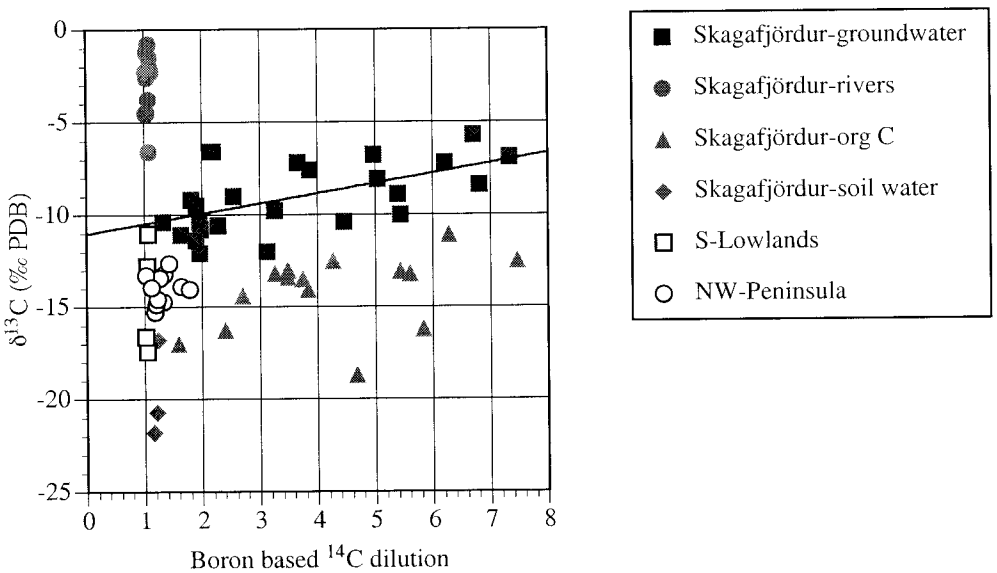

Figure 5. The relation of $\delta^{13}C$ and the calculated ^{14}C dilution.