Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 191 (2016) 165–186

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Age and speciation of iodine in groundwater and mudstones of the Horonobe area, Hokkaido, Japan: Implications for the origin and migration of iodine during basin evolution

Yoko S. Togo [a,*], Yoshio Takahashi [b], Yuki Amano [c], Hiroyuki Matsuzaki [d],
Yohey Suzuki [b], Yasuko Terada [e], Yasuyuki Muramatsu [f,†], Kazumasa Ito [a],
Teruki Iwatsuki [g]

[a] *Research Institute of Earthquake and Volcano Geology, National Institute of Advanced Industrial Science & Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan*
[b] *Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[c] *Horonobe Underground Research Center, Japan Atomic Energy Agency (JAEA), 432-2 Hokushin, Horonobecho, Teshio-gun, Hokkaido 098-3224, Japan*
[d] *The University Museum, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-0032, Japan*
[e] *SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5158, Japan*
[f] *Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan*
[g] *Mizunami Underground Research Laboratory, Japan Atomic Energy Agency (JAEA), 1-64 Akiyo-cho, Mizunam City, Gifu 509-6132, Japan*

Received 5 September 2013; accepted in revised form 10 July 2016; available online 16 July 2016

Abstract

This paper reports the concentration, speciation and isotope ratio ($^{129}I/^{127}I$) of iodine from both groundwater and host rocks in the Horonobe area, northern Hokkaido, Japan, to clarify the origin and migration of iodine in sedimentary rocks. Cretaceous to Quaternary sedimentary rocks deposited nearly horizontally in Tenpoku Basin and in the Horonobe area were uplifted above sea level during active tectonics to form folds and faults in the Quaternary. Samples were collected from the Pliocene Koetoi and late Miocene Wakkanai formations (Fms), which include diatomaceous and siliceous mudstones. The iodine concentration in groundwater, up to 270 μmol/L, is significantly higher than that of seawater, with the iodine enrichment factor relative to seawater reaching 800–1500. The iodine concentration in the rocks decreases from the Koetoi to Wakkanai Fms, suggesting that iodine was released into the water from the rocks of deeper formations. The iodine concentration in the rocks is sufficiently high for forming iodine-rich groundwater as found in this area. X-ray absorption near edge structure (XANES) analysis shows that iodine exists as organic iodine and iodide (I^-) in host rocks, whereas it exists mainly as I^- in groundwater. The isotope ratio is nearly constant for iodine in the groundwater, at $[0.11–0.23] \times 10^{-12}$, and it is higher for iodine in rocks, at $[0.29–1.1] \times 10^{-12}$, giving iodine ages of 42–60 Ma and 7–38 Ma, respectively. Some iodine in groundwater must have originated from Paleogene and even late Cretaceous Fms, which are also considered as possible sources of oil and gas, in view of the old iodine ages of the groundwater. The iodine ages of the rocks are older than the depositional ages, implying that the rocks adsorbed some iodine from groundwater, which was sourced from greater depths. The iodine concentration in groundwater decreases with decreasing chlorine concentration due to mixing of iodine-rich connate water and meteoric

---

[*] Corresponding author.
E-mail address: yoko-togo@aist.go.jp (Y.S. Togo).
[†] Deceased on July 2, 2016.

http://dx.doi.org/10.1016/j.gca.2016.07.012

water. A likely scenario is that iodine-rich brine formed during the long-term basin evolution from the Cretaceous to Quaternary and that this brine was diluted by mixing with meteoric water during uplifting and denudation of the area.

Keywords: Source of iodine; Iodine speciation; Horonobe; Tenpoku Basin; $^{129}I/^{127}I$ ratio; XANES; Micro-XRF

1. INTRODUCTION

The migration of iodine during water–rock interaction is important from various perspectives. For example, iodine has been used as a tracer of crustal fluids, oil field brines, and geothermal fluids (Edwards, 1962; Fehn, 2012). The chemical processes during water–rock interaction are also important in terms of the environmental geochemistry of radioiodine that can be related to the utilization of nuclear energy (Hou et al., 2009). The Japan Atomic Energy Agency (JAEA) began the Horonobe Underground Research Laboratory (Horonobe URL) Project in 2000 to enhance the reliability of disposal technologies for high-level radioactive wastes through investigations of the deep geological environment of sedimentary formations in the Horonobe area, northern Hokkaido, Japan (e.g., Ota et al., 2007; Niizato et al., 2008). The project has focused on the Wakkanai Formation (Fm), which is composed of late Miocene siliceous and diatomaceous mudstone, and the Koetoi Fm, which is Pliocene diatomaceous mudstone (Ota et al., 2007; Hama et al., 2007; Niizato et al., 2008; Iwatsuki et al., 2009). Deep groundwater in the region is characterized by high salinity with high iodine and bromine concentrations (Hama et al., 2007; Iwatsuki et al., 2009). The present study examines the ages and speciation of iodine in both groundwater and rocks to obtain a better understanding of the origin and migration of iodine in the groundwater during the long-term basin evolution and the uplifting and denudation of the Horonobe area in the Quaternary.

To investigate the behavior of iodine in geological environments, it is necessary to determine the speciation of iodine because solubility, volatility, and mobility differ completely among various iodine species (Hou et al., 2009). Iodine is an electronegative element with its possible oxidation states of −1, 0, +1,+3, +5, and +7. Moreover, iodide (I^-), hypoiodous acid (HOI), elemental iodine (I_2), iodate (IO_3^-), and organic iodine are the most common species in geological environments (Hou et al., 2009). Organic iodine compounds with low molecular weights such as CH_3I are mainly volatile, whereas the behavior of larger organic iodine molecules, which are bound to humic substances, are controlled by the behavior of the host organic matter (Hou et al., 2009; Shimamoto et al., 2011). Speciation analysis of iodine in both solid and liquid phases is needed to investigate its migration in the environment. X-ray absorption near edge structure (XANES) is a powerful tool for analyzing the speciation of iodine and other elements without destruction of samples (Shimamoto and Takahashi, 2008; Shimamoto et al., 2011; references therein), and provides useful complementary information to other analyses such as micro-focused X-ray fluorescence (micro-XRF) and chemical extraction because the speciation of elements may change with chemical treatment. High-performance liquid chromatography connected to an inductively coupled plasma mass spectrometer (HPLC–ICP–MS) is also useful for determining the speciation of iodine in liquid phases (Shimamoto et al., 2011). This paper reports iodine speciation from analyses using these methods.

The iodine behavior in sedimentary rocks also has important implications for the recycling of iodine in the earth's crust because 68.2% and 27.7% of iodine in the crust are estimated to be present in ocean sediments and sedimentary rocks of the upper continental crust, respectively (Muramatsu and Wedepohl, 1998). The $^{129}I/^{127}I$ ratio in the ocean is considered to be constant because the marine residence time of iodine, at ~400 ka, is significantly longer than the ocean circulation time (Fehn, 2012; references therein). Previous studies used ^{129}I for environmental tracing and age determinations. The initial value of the $^{129}I/^{127}I$ ratio used for age calculations ranges from 5.7×10^{-13} to 1.5×10^{-12} (Fabryka-Martin et al., 1985; Fehn et al., 1986, 1990, 2000; Moran et al., 1998; Muramatsu et al., 2001; Tomaru et al., 2007a,b). Fehn et al. (2007) examined the value of the pre-anthropogenic $^{129}I/^{127}I$ ratio and suggested a best estimate of 1.5×10^{-12}, which is the same value as that reported by Moran et al. (1998). This initial ratio is consistent with the hemipelagic sediments in the Nankai Trough area, which have $^{129}I/^{127}I$ ratios of $(1.5 \pm 0.3) \times 10^{-12}$ (Tomaru and Fehn, 2015). Thus, this initial ratio is used for age determination in this study, assuming that the initial value was constant and was not disturbed locally before the modern nuclear age.

Most previous work compares the ages of iodine in groundwater with the age of sedimentary rocks (e.g., Muramatsu et al., 2001; Tomaru et al., 2007a, 2009a). However, the present study reports the ages of iodine extracted from host rocks in addition to the iodine ages of groundwater. The concentrations and ages of iodine in groundwater and host rocks, in comparison with the sedimentation ages of the formation, give insight into the behavior of iodine in the formations. A groundwater sample from a nearby mud volcano was also analyzed to obtain information on the deeper part of the basin. On the basis of the data, a possible scenario is suggested for the formation and migration of iodine-rich brine during the long-term basin evolution and for the mixing of the brine with meteoric water during the uplifting and denudation of the Horonobe area. Moreover, we also discuss the procedure for modeling the geological, hydrological, and chemical processes recognized in the Horonobe area in a future study.

Further, we expect that our study will have implications for understanding the behavior of ^{129}I produced by