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Chlorine stable isotope evidence for salinization processes of confined groundwater in southwestern Nobi Plain aquifer system, central Japan

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SUMMARY

A confined aquifer system, isolated from modern seawater, is developed in argillaceous marine and freshwater sediments of Pliocene–Holocene age in southwestern Nobi Plain (SWNP), central Japan. A tongue of brackish confined groundwater (Cl^- >1000 mg/L), which extends from the shoreline of Ise Bay inland, mostly has negative δ^{37}Cl values with −0.90‰ to 0.21‰. The Cl isotopic compositions are negatively correlated with paleo seawater Cl^- concentrations discriminated by a Rayleigh distillation model with δ^{34}S values, while they are not correlated with either total Cl^- concentrations or δ^{34}S values. Furthermore, Cl^- concentrations from modern seawater are positively correlated with δ^{37}Cl values. In addition to these observations, diffusion model calculations suggest that paleo seawater Cl^- has diffused out from argillaceous marine sediments whereas modern seawater Cl^- has not been affected by preferential diffusion of Cl isotopes because it has migrated by advection via both an unconfined aquifer and non-pumping wells. Moreover, the brackish groundwater is characterized by an excess of Na/Cl ratio and deficits of Mg/Cl and Ca/Cl ratios compared to those predicted from simple mixing of freshwater with seawater. This would be caused by cation exchange reactions in the confined aquifer system in which groundwater is freshening after salinization by both paleo seawater and/or modern seawater.

1. Introduction

Groundwater salinization is the most common and wide-spread threat to groundwater resources world-wide and is most severe in coastal regions where there has been excessive groundwater abstraction (e.g., Ghassemi et al., 1995). For instance, approximately two-thirds of the United States is underlain by aquifers containing saline groundwater which is unusable for ordinary water supply purpose (Feth et al., 1965). In some cases, the coastal groundwater system is developed in a confined aquifer. Where argillaceous marine sediments form confining beds in the system, groundwater is isolated from modern seawater but the confining beds may act as an additional source of salinity, complicating the salinization process.

In complex cases, the origin of groundwater salinity is often difficult to distinguish on the basis of major ion chemistry (Tellam and Lloyd, 1986) and isotope tracers such as δ^{18}O, δD and ^{87}Sr/^{86}Sr have played an important role in elucidating salinization processes in aquifers (Barker et al., 1998; Mehta et al., 2000; Gattacceca et al., 2009; Han et al., 2011; Monjerezi et al., 2011). According to these studies, the salinization processes can be classified into dissolution of accumulated salts, extensive evapotranspirative concentration and saltwater intrusion. Moreover, saltwater intrusion can be subdivided into modern seawater migration directly into the aquifer and diffusion of saltwater (commonly paleo seawater, trapped in argillaceous marine sediments) into freshwater. If each type of intrusion took place in isolation, sufficient discrimination would be expected using the isotope tracers mentioned above. However, where both types of saltwater intrusion occur simultaneously in an aquifer, the effects of each could not easily be distinguished. This is because isotopic ratios as δ^{18}O, δD and ^{87}Sr/^{86}Sr will often be closely similar in both modern seawater and paleo seawater.

One of potential discriminants for these saline waters is sulfate-δ^{34}S values, which are frequently modified under anaerobic

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conditions associated with decreased SO_4^{2-} concentrations due to microbial sulfate reduction (Strebel et al., 1990; Spence et al., 2001). In the confined aquifer system of the southwestern Nobi Plain (SWNP), for instance, SO_4^{2-} concentrations were variable in brackish groundwater samples with sulfate-δ^{34}S values near that of seawater but they were low in the samples with high δ^{34}S values. By using these as indices for a Rayleigh distillation model, Yamanaka and Kumagai (2006) evaluated influences of both modern seawater and paleo seawater intrusions in the system where paleo seawater, which has been trapped for approximately 10,000 years or longer under anaerobic conditions, would be SO_4-free through sulfate reduction and therefore chemically distinct from modern seawater. An alternative approach is to use chlorine stable isotope ratios (^{37}Cl/^{35}Cl) which have been used as an effective tracer to constrain origins or supplying processes of Cl^- in groundwater studies, especially in environments controlled by physical processes such as diffusion in argillaceous sediments (Desaulniers et al., 1986; Groen et al., 2000; Lavastre et al., 2005; Zhang et al., 2007; Beekman et al., 2011). This is because a separation between ^{35}Cl and ^{37}Cl occurs through diffusion processes due to higher mobility of ^{35}Cl than that of ^{37}Cl, which results in depletion of ^{37}Cl in solution with increasing distance from Cl^- source. Accordingly, δ^{37}Cl values of modern seawater are expected to differ from those of paleo seawater that has been modified by diffusion processes in argillaceous sediments. Thus, difference in chlorine isotope ratios might allow distinction of salinity from different origins and provide further information on seawater intrusions into a confined aquifer system.

A confined groundwater system has developed in argillaceous marine and freshwater sediments in the southwestern Nobi Plain (SWMP) of central Japan (Figs. 1 and 2), where groundwater salinization of a confined aquifer has been observed. In this study, chemical and chlorine stable isotopic compositions of the groundwater in the SWNP aquifer system were determined to better understand the origins of seawater intrusions into the system and characterize the geochemical reactions taking place around the salt/fresh water interface.

2. Study area

The SWNP is located about 20 km west of Nagoya City in an estuarine delta environment formed by the Kiso, Ibi and Nagara Rivers, and is bounded by the Yoro mountain range, composed mainly of slate and sandstone of the Yoro Group of Permian to Jurassic age (Fig. 1). Subsurface geological setting in the SWNP is well described by GSSTP (1985) and summarized as follows.

The Nobi Plain lies in a tectonic basin where block faulting has taken place along its western margin since middle Pleistocene (Kuwahara, 1968). Basement rocks of the basin are composed

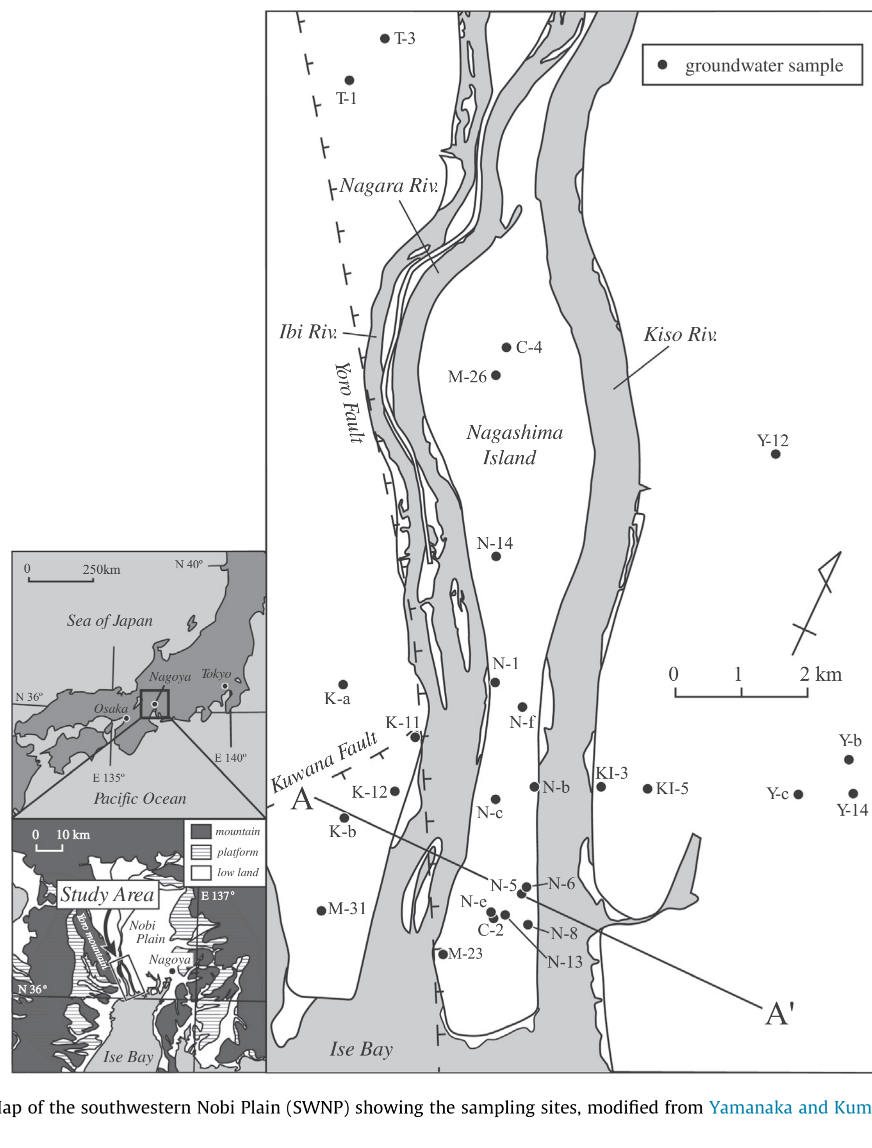

Fig. 1. Map of the southwestern Nobi Plain (SWNP) showing the sampling sites, modified from Yamanaka and Kumagai (2006).