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Origin of methane in high-arsenic groundwater of Taiwan – Evidence from stable isotope analyses and radiocarbon dating

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ABSTRACT

Groundwaters in the confined aquifers of the Chianan and Ilan coastal plains of Taiwan are rich in dissolved methane (CH_4). Serious endemic "blackfoot disease", which occurred in the Chianan plain, especially during AD1950-1970, has been demonstrated to have arisen from drinking highly reducing groundwater with abnormal arsenic and humic substance levels. In order to explore the origin of CH_4 and its hydrological implications, stable carbon isotope ratios ($\delta^{13}C$) and radiocarbon (^{14}C) ages of exsolved CH_4, dissolved inorganic carbon (DIC), and sedimentary biogenic sediments from a total of 34 newly completed water wells at 16 sites were determined. The main results obtained are as follows: (1) The $\delta^{13}C_{CH_4}$ (−65‰ to −75‰) values indicate that, except for one thermogenic sample ($\delta^{13}C_{CH_4} = 38.2‰$) from the Ilan plain, all CH_4 samples analyzed were produced via microbially mediated CO_2 reduction. Many $\delta^{13}C_{DIC}$ values are considerably greater than −10‰ and even up to ~10‰ due to Rayleigh enrichment during CO_2 reduction. (2) Almost all the ^{14}C ages of CH_4 samples from the shallow aquifer (I) (<60 m depth) are greater than the ^{14}C ages of coexisting DIC and sediments, suggesting the presence of CH_4 from underlying aquifers. (3) The ^{14}C ages of coexisting CH_4, DIC and sediments from aquifer (II) of the Chianan plain are essentially equal, reflecting in-situ generation of CH_4 and DIC from decomposition of sedimentary organic matter and sluggishness of the groundwater flow. On the other hand, both CH_4 and DIC from each individual well of the relatively deep aquifers (III) and (IV) in the Chianan plain are remarkably younger than the deposition of their coexisting sediments, indicating that current groundwaters entered these two aquifers much later than the deposition of aquifer sediments. (4) Each CH_4 sample collected from the Ilan plain is older than coexisting DIC, which in turn is distinctly older than the deposition of respective aquifer sediments, demonstrating the presence of much older CO_2 and CH_4 from underlying strata.

1. Introduction

Considerable amounts of dissolved methane (CH_4) are often present in groundwaters pumped from wells tapping confined aquifers in the Chianan and Ilan alluvial coastal plains of SW and NE Taiwan, respectively (Fig. 1). These groundwaters are also characterized by high concentrations of dissolved humic substances and arsenic (Chen and Liu, 2007), both of which were considered to be responsible for endemic "blackfoot disease" through drinking of groundwater (Tseng et al., 1961; Lu, 1990). It has long been recognized that occurrence of CH_4 generally implies a considerably reducing state in the geochemical environment (Stumm and Morgan, 1996). In addition, strongly reducing waters tend to be contaminated by heavy metals and natural discharges are likely to be minimal (Smedley and Kinniburgh, 2002; Gooddy and Darling, 2005). Previous studies of dissolved gas from the six water wells drilled by the Chinese Petroleum Corporation in the Chianan plain focused mainly on the potential for profitable production (Hsu, 1984), and the composition of the gas was shown to contain more than 90% CH_4, up to 6% CO_2, and a few percent N_2. However, the origins and source of CH_4 in these aquifers have not been well studied.

Dissolved methane in groundwater can be formed via bacterial reduction, or from thermogenic decomposition of organic matter at relatively high temperatures. Furthermore, the former type can proceed through either reduction of dissolved forms of CO_2 (i.e., $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) or acetate fermentation (i.e., $CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$) (Schoell, 1980, 1988; Oremland et al., 1982).

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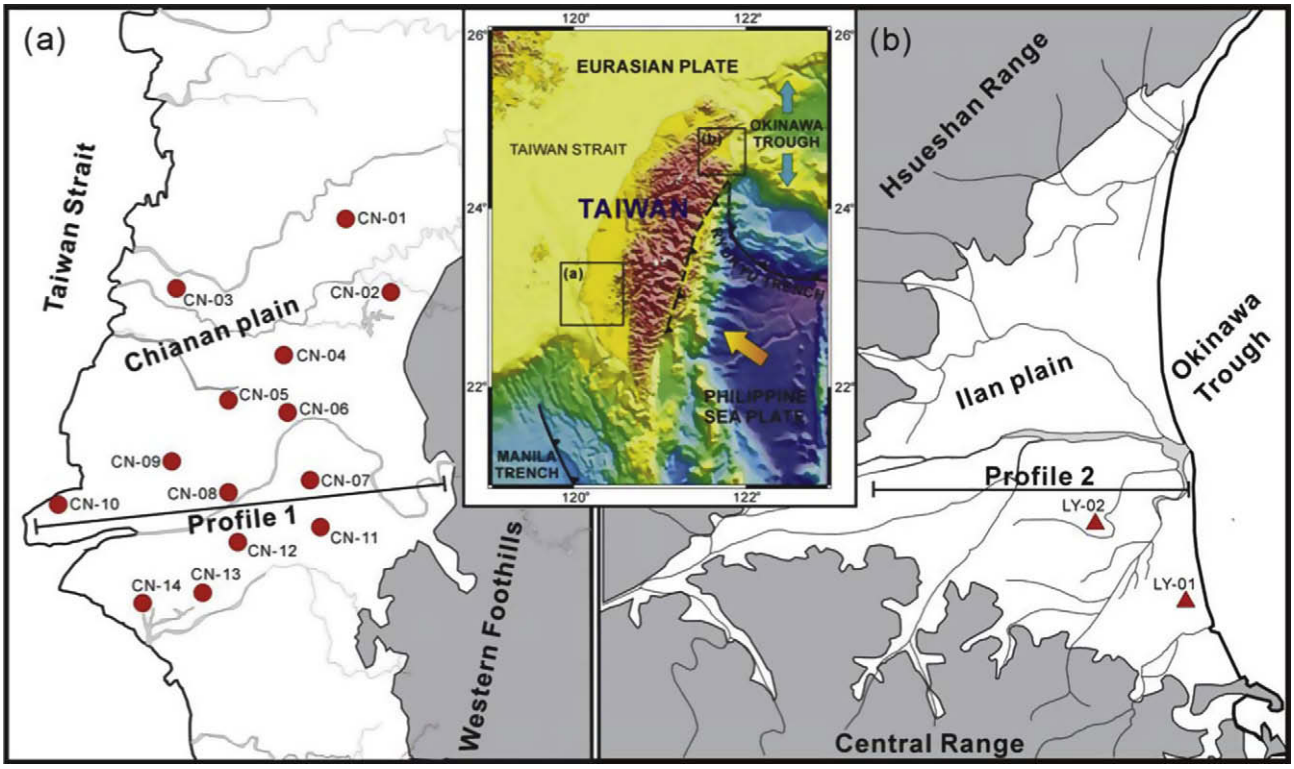

Fig. 1. Location of wells sampled and the simplified geologic provinces around (a) the Chianan plain, and (b) the Ilan plain in Taiwan. Profiles 1 and 2 in Fig. 2 are also shown.

The best diagnostic tool for identifying the origin of CH_4 in the groundwater environment appears to be the ^{13}C and ^{2}H fractionation between coexisting CH_4 and CO_2 (Oremland, 1988; Coleman et al., 1988; Whiticar et al., 1986; Whiticar, 1999; Lansdown et al., 1992; Aravena et al., 1995, 2003). It has long been recognized that the stable carbon isotope ratios ($\delta^{13}C$) of thermogenic methane range from −30‰ to −50‰, and are mostly greater than −45‰ (Barker and Fritz, 1981; Tyler, 1991). By contrast, $\delta^{13}C$ values for microbial CH_4 are less than −50‰ and mostly fall in the range −50‰ to −65‰ for acetate fermentation pathway and −65‰ to −90‰ for CO_2 reduction pathway. In addition to the problem of the origin of CH_4, it is also interesting to know whether CH_4 was formed in-situ. The purpose of this study is to verify the origin and source of CH_4 associated with groundwater in the Chianan and Ilan plains by using stable carbon isotopes and radiocarbon dating of CH_4, DIC and shell (or plant) sediments collected from 34 recently drilled groundwater-monitoring wells. A $\delta^{2}H$ value was measured for a CH_4 sample to further support its origin identified by $\delta^{13}C$ criterion.

2. Hydrogeological setting

2.1. Chianan plain

The Chianan plain is a part of the coastal plain of southwestern Taiwan, covering about 1100 km^2 with a N–S length of approximately 40 km and an average E–W width of 30 km. The ground surface slopes seaward with a very low gradient. It is bounded on the east by the western edge of the Western Foothills, which is mostly composed of siltstone and fine-grained sandstone of the late Tertiary epoch and provides the source rocks for the Chianan plain (Ho, 1975). Accordingly, the upper-most ~300 m of which is mostly silt and clay, intercalated with thin lenticular fine-sand layers (Fig. 2a; Chen and Liu, 2007); these sediments were deposited in mixed sedimentary environments, including lagoon, estuarine, shallow marine, and fluvial plains during late Pleistocene and Holocene. The average rate of sediment accumulation during Holocene reached a high value of ~1 cm/yr in the coastal areas as determined by radiocarbon dating (Liu et al., 1997).

Based on grain-size of sediments, the upper ~300-m thick strata at each well locality are generally divided into four aquifers: I, II, III and IV from top to bottom. Unconfined aquifers are limited to the upper few meters of the plain, even at the eastern parts adjoining the hills. Hydrogeological characteristics are consistent with the very low permeability shown in pumping tests and the occurrence of saline water in the aquifers deposited in a marine environment. Chen and Liu (2007) interpreted the high chlorinity for some wells in aquifer (I) as being due to strong evaporation in the coastal zone.

2.2. Ilan plain

The Ilan plain is located in the western tip of the rifting back-arc basin of the Okinawa Trough. This plain is triangular in shape and bounded by low-grade metamorphic rocks of the Hsueshan Range and medium-high grade metamorphic rocks of the Central Range to the northwest and the south, respectively. The upper 120-m thick layer was deposited during Holocene and its average sediment accumulation rate is similar to the Chianan plain, also reaching a high of ~1 cm/yr. Grain-sizes of sediments in most parts of the plain decrease distinctly from gravel in the proximal part to silt/clay in the coastal area. A relatively shallow (<20 m depth) and thick (~10 m) clayey layer acts as the upper-most aquitard overlying the confined aquifers in the middle and distal parts. The CH_4 samples analyzed were taken from the southern margin of the plain, where the whole pile of strata drilled through for this study is basically composed of dark-gray clay intercalated with thin layers of silt and fine-grained sand (Fig. 2b).