



Hydrochemical reactions and origin of offshore relatively fresh pore water from core samples in Hong Kong



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SUMMARY

The existence of relatively fresh pore water offshore has been well recognised over the globe but studies on the chemistry of the pore water from offshore geological formations are extremely limited. This study aims to characterize the hydrochemistry of the submarine groundwater body in Hong Kong. It looks into the major ion concentrations and the stable isotopic compositions of pore water extracted from core samples from an offshore 42.30-m vibrocore in the southwestern Hong Kong waters. A minimum Cl^- level of about one-third of that in typical seawater was noted in the terrestrial sediments, suggesting the presence of offshore relatively fresh water. Unexpectedly high NH_4^+ levels are attributed to organic matter decomposition in the terrestrial sediments. The leaching of shells due to exposure of marine sediments at sea-level low stands raises the Mg^{2+} and Ca^{2+} concentrations. Base Exchange Indices show weak cation exchange reactions in which Na^+ and K^+ are released while Mg^{2+} and Ca^{2+} are adsorbed. Isotopic compositions of pore water reveal that the low-salinity water is probably the relic water sequestered in fluvial systems during relative sea-level low stands. Cores properly stored in a freezer for a long time has been used to study the pore water chemistry. For the first time, this study introduces an approach to correct the measured data by considering the possible evaporation effect during the transportation and storage of the samples. Corrections for evaporation were applied to the major ion concentrations and the stable isotopic compositions of pore water measured. It is found that the corrections determined by the Cl^- mass balance approach are more reliable. The corrected measurements give more reasonable observations and hence allow sensible conclusions on the hydrochemical reactions and the origin of pore water.

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1. Introduction

Low-salinity (<1 g/L) groundwater offshore has been widely recognised (Hathaway et al., 1979; Groen et al., 2000; Cohen et al., 2010; Post et al., 2013). These reserves are mostly located in continental shelves exposed during glacial periods. Evidence for such reserves in Asia has been reported. Examples are Pattani Basin, Bangkok, Japan trench and Nakao trough. The only research with direct observational data in China has been carried out in Zhoushan, Zhejiang in the East China Sea by Zhang et al. (2011). There have not been similar studies in the South China Sea until 2015.

Earlier studies regarding offshore geology in Hong Kong only investigated the engineering properties of inner shelf sediments in order to assess their reactions to construction works. Recent projects look at the sedimentological, geophysical or elemental

characteristics of the sediments so as to understand the morphological changes in the depositional environment and to associate these changes with the global climate and sea-level history (for example, Yim, 1994, 2001; Mok, 2005, 2012; Yim et al., 2008; Zong et al., 2009a,b). Among these studies, offshore hydrogeology has been largely ignored.

The first offshore hydrochemical study in Hong Kong was conducted by Jiao et al. (2015), who showed the presence of low-salinity pore water beneath the low-permeability marine units and modeled the diffusion-controlled solute-transport in one of the boreholes. However, the analysis of the study relies on the reconstruction of concentrations from dried core samples and provides information only on Cl^- concentrations. To attain full understanding of regional offshore groundwater reserves, several other hydrochemical properties deserve more investigation. In this study, ongoing hydrogeochemical reactions in the sediments are discussed based on major ion concentrations. Besides, the origin of the relatively fresh water is investigated through stable isotopic

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signature of water. It is hoped that the results will provide useful insights to the hydrochemistry of groundwater reserves in other places.

2. Regional geology of the study area

The Hong Kong Special Administrative Region (HKSAR) of China is located at the mouth of the Pearl River Delta (PRD) on the northern coast of the South China Sea. The highlands consist of mainly Mesozoic volcanic rocks with younger granite intrusions while the lower lying areas are highly weathered intruded granites (Yim, 2001). Formed predominantly during the Paleogene and Neogene, the landscape has been modified in the Quaternary (Yim, 1994, 2001).

In the Quaternary, multiple glacial-interglacial cycles led to relative sea-level fluctuations and climate zone shifts. These greatly contributed to the submarine geomorphology. Low sediment yields in Hong Kong were reported by Lam (1978). Hence, fluvial sources for offshore sediments are unlikely, especially during interglacial periods (Yim, 2001). During glacial periods, fluvial sediments might be transported and deposited at restricted sites (Berry, 1959), which are submerged by seawater now. The glacial-interglacial cycles have the predominant control on the local submarine stratigraphy, respectively.

At the Last Glacial Maximum (LGM), when the relative sea-level was at approximately 130 m below the present-day sea-level, the coastline receded to approximately 120 km south from Hong Kong. The pre-existing marine sediments were eroded and reworked by rivers. On the exposed continental shelf, fluvial sediments deposited to form the present submarine sand and gravel deposits. Since 19 calibrated thousand years Before Present (ka BP), seawater inundated into the PRD as the relative sea-level rose (Zong et al., 2012). The floodplains and channels were buried by marine sediments. These relict flow systems could have sequestered fresh water and brought about offshore groundwater reserves described by Post et al. (2013).

3. Methodology

3.1. Vibrocore collection

Located about 2.3 km south to Shek Pik, Lantau Island (Fig. 1), HKUV12 (at 22°12'5.34"N, 113°53'38.50"E) was drilled at –8.30 m below Principle Datum (mPD). It ended at –50.70 mPD where alluvium deposits were noted. The vibrocoreing took place on 20–21 January 2009. 6-m core tubes were used. The total core recoveries were over 80%. The collected cores were then spilt at 1-m intervals, sealed in PVC tubes and stored in the freezer before analysis. The cores were transferred for whole-core geophysical measurement once before this study.

The vibrocore is in close proximity to paleo-river tributaries. Extensive alluvial deposits comprised of coarse gravelly sand with pebbles and cobbles fill the river valley currently occupied by the Shek Pik Reservoir (Fyfe et al., 2000). The site, now being submerged, was a river valley (Fyfe et al., 2000) and received terrestrial sediments from southern Lantau Island during the last sea-level low-stand. These deposits probably contribute to a submarine groundwater body. The pore water from the core is thereby believed to show the hydrochemical properties of the reserve.

3.2. Pore water extraction

Pore water samples were extracted by mechanically squeezing sediment samples taken at 0.20-m intervals from HKUV12. Before sub-sampling, the loose or watery sediments at the upper and lower 10-cm section and the disturbed sediments a few mm near

the cut surface and from the column wall were removed. The subsampling was carried out in November 2013, followed by pore water extraction and hydrochemical measurements. The samples were sealed in polyethylene bags immediately. The water samples were analysed for their major ion concentrations and stable hydrogen and oxygen isotope compositions. The ion concentrations were corrected for possible evaporation in storage. The corrected values were then plotted as piper diagrams and used in saturation index calculations.

A mechanical squeezing method, described by Reeburgh (1967), Patterson et al. (1978), Ridout and Pagett (1984), Böttcher et al. (1997) and Warnken et al. (2000), was employed for pore water extraction from the core samples. The apparatus was designed according to Patterson et al. (1978), except that the cylinder holding the sediments was made up of stainless steel and that the squeezer was modified from a triaxial compression test apparatus. Thanks to the dominant clay and silty clay sediments in the core, this method was chosen because it is suitable for fine-grained and organic-rich sediments (Patterson et al., 1978).

The samples were sealed in polyethylene bags to avoid air exposure. The peripheral sediments about 1 cm from the edges were not used so as to minimize the effect of evaporation. The extraction followed the procedures described by Patterson et al. (1978) and Böttcher et al. (1997). With the help of the compression machine, the pressure applied to the sediments was increased at a rate of about 0.1 kg cm⁻² per 10 s. Any temperature increase, which may alter the pore water chemistry (Patterson et al., 1978), was thereby minimized. The maximum pressure was limited to 40 kg cm⁻² to prevent sediments from being squeezed out and making the extracted pore water turbid. Pressures over 600 kg cm⁻² can alter the soil structures and therefore change the pore water chemistry (Böttcher et al., 1997). Hence, pressures under the reported limit were adopted. The first few drops of extracted pore water were discarded before collection. After passing through a 0.45 µm hydrophilic PTFE syringe filter, the water sample was stored in polypropylene centrifuge tubes and refrigerated for analyses.

3.3. Major ion concentration measurements

The concentrations of major ions (Cl⁻, Na⁺, Mg²⁺, K⁺, Ca²⁺, SO₄²⁻, F⁻, Br⁻, NH₄⁺, NO₂⁻ and NO₃⁻) in pore water samples were measured by ion chromatography (Thermo Scientific Dionex ICS-1100). The equipment has been calibrated with Dionex Six Cation-II and Dionex Seven Anion Standards every month. During calibration, three injections of the original standards and standards freshly prepared by two-, three-, five- and ten-fold dilutions are run. The same was carried out before the sample measurements. The analytic errors were about 5%. Since high Cl⁻ concentrations have been expected for the shallow samples, 100-fold dilution was performed to avoid any damage to the instrument. 18.2 MΩ deionized water was used in the dilution. In addition, 2 drops of hydrochloric acid were added to samples for cation measurement so as to prevent precipitation of calcium compounds in the chromatography column.

Phenolphthalein and total alkalinity were measured using the HACH Method 8203. Bromcresol Green-Methyl Red and Phenolphthalein indicator powder and sulphuric acid (0.16 N) were used. Given the Ca²⁺ concentrations measured by ion chromatography, the sample volume extracted and the instructions in the HACH manual, 10 ml of each sample was used and diluted ten times for the test. Since the phenolphthalein alkalinity was always found to be zero, HCO₃⁻ concentration was determined from the total alkalinity with the following formula:

$$\text{Alkalinity as HCO}_3^- \text{ (mg/L)} = 1.22 \times \text{Alkalinity as CaCO}_3 \text{ (meq/L)},$$

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