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Boron sources and transport mechanisms in river waters collected from southwestern Taiwan: Isotopic evidence

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ABSTRACT

Boron (B) isotopes are sensitive tracers for constraining water–rock interactions and pollution sources in river systems. In this study, we analyzed $\delta^{11}B$ using multi-collector inductive coupled plasma mass spectrometry, in addition to major and trace elements, to delineate B sources and transport mechanisms in two river catchments, the largest Kao-ping River and the most polluted Erren River in southwestern Taiwan.

Dissolved $\delta^{11}B$ values vary more than 35‰ in Kao-ping River, but keep relatively constant in Erren River, 12.2–26.7‰. Four major B sources identified in these river waters are cyclic seasalt, water/rock interaction, geothermal water and anthropogenic inputs. All specimens collected near the estuaries were influenced strongly by the seawater, B = 4.5 mg/L and $\delta^{11}B$ = 39.5‰. The Erren River results provide unique information on B and $\delta^{11}B$ compositions in anthropogenic sources, in particular for fertilizer and hog manure, characterized with high B (up to 3.43 mg/L) and intermediate $\delta^{11}B$ (average 13‰). The low $\delta^{11}B$ values in 2006 Kao-ping River are attributed to contributions from local geothermal inputs, average 2.5 ppm and 2‰, prior to massive landslides caused by 2009 Morakot typhoon. Mass balance calculations suggest that major contribution of B in river waters was derived from silicate weathering, characterized by low B and intermediate $\delta^{11}B$, contributed approximately 49–97% in 2010 Kao-ping River. The detected changes of $\delta^{11}B$ ($\Delta_{\text{w-rock}}$) reaches a maximum variation of 18‰ during chemical weathering in catchment and highlights the importance of water/rock interaction enhancement after major climatic events.

1. Introduction

River systems are among the most dynamic components of the hydrosphere, with direct links to interactions among atmosphere, lithosphere and biosphere. Previous investigations have examined patterns in water chemistry to delineate weathering sources and transport processes of elements in river catchments (Gibbs, 1970; Santos et al., 2002; Yuan and Miyamoto, 2005; Chu and You, 2007; Moon et al., 2007). In recent years, new isotopic tracers for chemical weathering have been utilized to answer questions related to sources identification and to quantify their respective contributions, including B and B isotopes (Lemarchand and Gaillardet, 2006; Chetelat et al., 2009).

B has two stable isotopes, ^{10}B and ^{11}B, in natural environments. In aqueous solutions, B bonds with oxygen to form tetrahedral borate, $B(OH)_4^-$, and trigonal boric acid, $B(OH)_3$. The relative proportion of the two dissolved species is a function of aliquot pH (Hershey et al., 1986; Kakihana et al., 1977). B isotopic compositions in river and groundwater have been used to trace the source of dissolved B and to understand the extent of water–rock interactions (Rose et al., 2000; Chetelat and Gaillardet, 2005; Pennisi et al., 2006; Lemarchand and Gaillardet, 2006; Chetelat et al., 2009). Rose et al. (2000) found large $\delta^{11}B$ variation in Himalayan rivers, up to 35‰, and applied this signal to quantify sediment denudation and weathering processes. Patterns in dissolved $\delta^{11}B$ in the Seine River agreed well with the Cl/Na and NO_3/Na variations, suggesting the potential use of B isotopes for investigating anthropogenic pollution (Chetelat and Gaillardet, 2005). Lemarchand and Gaillardet (2006) proposed a transport/reaction model to explain dissolved $\delta^{11}B$ in the Mackenzie basin, proposing that water/rock interaction controlled the $\delta^{11}B$ distribution in groundwater. Both dissolved phases and suspended particles collected from Changjiang River suggested competitive processes between leaching and incorporation of B in secondary minerals to affect $\delta^{11}B$ (Chetelat et al., 2009).

In this study, river waters were sampled from two drainage systems in southwestern Taiwan, the Kao-ping River and the Erren

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River. Detailed chemical and isotopic compositions were applied to study chemical weathering and pollutant distribution in the high denudation Kao-ping River and heavily contaminated Erren River. The main objective is to identify the sources and the transport mechanisms of B in the two mountainous river systems.

2. Geological settings and sample preparations

2.1. The Kao-ping River system

The Kao-ping River (22°27′ to 23°28′N, 120°23′ to 121°E) is the largest river in southern Taiwan. This river originates from the Jade Mountain and flows into the Taiwan Strait, and has a total drainage area of 3257 km^2. Compared with other major rivers in the world, the Kao-ping River is characterized by (1) rather short length; (2) relatively steep slope, 1/150; (3) high precipitation rate, and (4) fragile watershed geology. Five major tributaries in the Kao-ping River are Laonong, Cishan, Ailiao, Baolai, and Chukou; the former two contribute more than 70% of the total discharge (Hydrological Year Book of Taiwan, 2004). The upstream Laonong is associated with Eocene–Oligocene slate (or quartzite) and Paleozoic–Mesozoic schist, whereas the Cishan is associated with Miocene-Pliocene sandstone/shale and Pleistocene terrace deposits. The Kao-ping River downstream catchment drains through modern alluvium, where silicate rocks are dominant (Fig. 1).

The Kao-ping River catchment is an important resource for agriculture in the Kaohsiung-Pingtung area. Except for the upper Kao-ping River drains in relatively pristine area, the downstream region, especially near the Lin-Yuan and the Dafa station, has been polluted through agricultural, urban and industrial activities. Farming wastes are the main pollution source in the midstream regions due to urban development and population growth. There is a clear seasonal pattern in precipitation in the upstream Kao-ping River, a dry (November–April) and wet season (May–October). The spatial and temporal distribution of rainfall is extremely uneven, decreasing drastically from mountain areas (3400 mm/yr) to the coastal plain (2000 mm/yr), about 90% of the annual total precipitation occurring during typhoon events in summer (Hydrological Year Book of Taiwan, 2004). The annual temperature ranges from 18 °C to 29 °C, a bit lower in the mountain area, 19–21 °C. The lowest temperature occurs in January and the highest in July.

2.2. The Erren system

The Erren River, 22°48′ to 23°02′N, 120°09′ to 120°29′E, originates from the San-Chu Lake and has a drainage area of 350.04 km^2. Relatively steep slopes (1/323) are rather common from headwaters to the Chung-Te Bridge and the slope changes to 1/3500 in the downstream reaches (Hydrological Year Book of Taiwan, 2007). Five major lithologic units are Late Miocene sandstone and shale, Pliocene–Pleistocene sandstone, Pliocene sandstone, mudstone and shale, Pleistocene terrace deposits and modern alluvium (Fig. 1). Erren River is the most contaminated river in southern Taiwan, approximately 20,000 tons/day, where livestock wastes account for the highest proportion of pollutant (~40%). Waste water produced by ~40 industrial companies is discharged into a small tributary, the San-Yeh-Kung River, and affects seriously the river water quality.

2.3. Sampling procedures

Water samples were collected from the Kao-ping River mainstream and major tributaries during three field excursions in dry

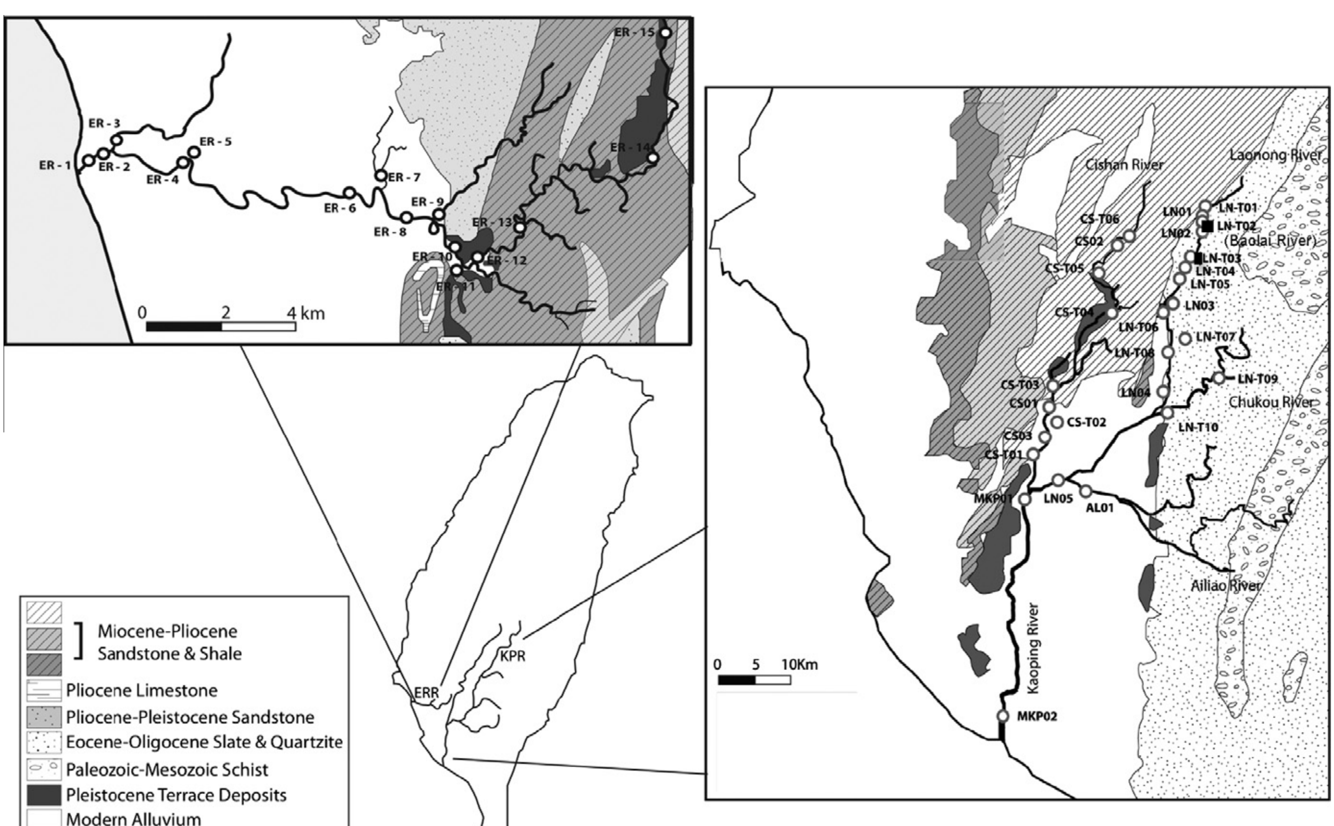

Fig. 1. Geological map of Kao-ping and Erren River catchments in southern Taiwan. The black squares are groundwater sampling points, and LN-T02 is where Baolai River located.