

Sources of dissolved inorganic carbon in rivers from the Changbaishan area, an active volcanic zone in North Eastern China

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Abstract Major elements and carbon isotopes of dissolved inorganic carbon (DIC) have been measured in the waters of Changbaishan mountain, a volcanic area in northeastern China, between June and September 2016 to decipher the origin of the CO₂ involved in chemical weathering reactions. Spatial variations of major elements ratios measured in water samples can be explained by a change of the chemical composition of the volcanic rocks between the volcanic cone (trachytes) and the basaltic shield as evidenced by the variations in the composition of these rocks. Hence, DIC results from the neutralization of CO₂ by silicate rocks. DIC concentrations vary from 0.3 to 2.5 mmol/L and carbon isotopic compositions of DIC measured in rivers vary from $-14.2\text{\textperthousand}$ to $3.5\text{\textperthousand}$. At a first order, the DIC transported by rivers is derived from the chemical weathering's consumption of CO₂ with a magmatic origin, enriched in ^{13}C (-5%) and biogenic soil CO₂ with lower isotopic compositions. The highest $\delta^{13}\text{C}$ values likely result from C isotopes fractionation during CO₂ degassing in rivers. A mass balance based on carbon isotopes suggest that the contribution of magmatic CO₂ varied from less than 20% to more than 70%. Uncertainties in this

calculation associated with CO₂ degassing in rivers are difficult to quantify, and the consequence of CO₂ degassing would be an overestimation of the contribution of DIC derived from the neutralization of magmatic CO₂ by silicate rocks.

Keywords Carbon isotopes · Dissolved inorganic carbon · Rivers · Chemical weathering · Changbaishan · Active volcanic zone

1 Introduction

Chemical weathering of rocks plays a central role in global biogeochemical cycles and the Earth's climate. Atmospheric CO₂ consumed by chemical weathering of silicate rocks is recognized as the net sink of atmospheric CO₂. Thus, silicate weathering acts as a thermostat for the Earth at geological time-scales.

Silicate rocks do not weather at the same rate, and the weathering of volcanic rocks plays a disproportionate role regarding their surface exposure in the global CO₂ consumption. Responses of chemical weathering to climatic parameters are still debated, but temperature-dependence of basalt weathering has been substantiated (Li et al. 2016 and references therein). In volcanic regions, CO₂ consumed by chemical weathering involved atmospheric CO₂ (including biogenic soil CO₂) and magmatic CO₂. Magmatic CO₂ is involved both in high temperature water/rock interactions and low temperature water/rock interactions (Rive et al. 2013 and reference therein).

The difference in carbon isotopic compositions of CO₂ in soil derived from organic matter decay and root respiration ($-25\text{\textperthousand}$), when compared with magmatic CO₂ ($-5\text{\textperthousand}$), can theoretically be used to apportion the

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respective contributions of the different sources of CO₂ involved in chemical weathering.

In this paper, major elements and C isotopes have been used to constrain sources of CO₂ consumed by chemical weathering and transported as DIC by rivers draining into the Changbaishan area, northeastern China, a volcanic region with a cold temperate climate.

2 Natural settings

The Changbaishan area is located in northeastern China on the northern edge of the Archean-Proterozoic Sino-Korean craton. It is a large basaltic shield platform that includes the headwaters of the Second Songhua, Yalu, and Tumen Rivers (Fig. 1). Tianchi, a volcano that straddles China and North Korea is the largest volcano of the region. It is an intraplate volcano whose activity is related to the Pacific subduction zone.

The basement of the Tianchi volcanic zone and surrounding area consists of Archean to middle-late Proterozoic metamorphic rocks, Paleozoic strata, and predominantly Mesozoic granite. Tianchi's eruptive history has been grouped in three stages characterized by different eruptive products. Alkali and tholeiitic basalts were erupted from the Miocene to the early Pleistocene and form the main part of a shield-like lava plateau that covers an area of 7200 km² centered at Tianchi. The youngest shield basalts are located near Tianchi cone and are overlain by 1000 m thick alkali trachytes erupted during the cone formation stage (Fig. 1). The late eruption stage was associated with comenditic pyroclastic deposits.

The eruptive history of the Tianchi volcano was marked by the so called “Millennium Eruption” (930–960 AD), one of the largest known volcanic explosive events on Earth in the last 2000 years. This eruption was responsible for a massive input of halogens, and to a lesser extent sulphur, into the atmosphere. The collapse of the upper

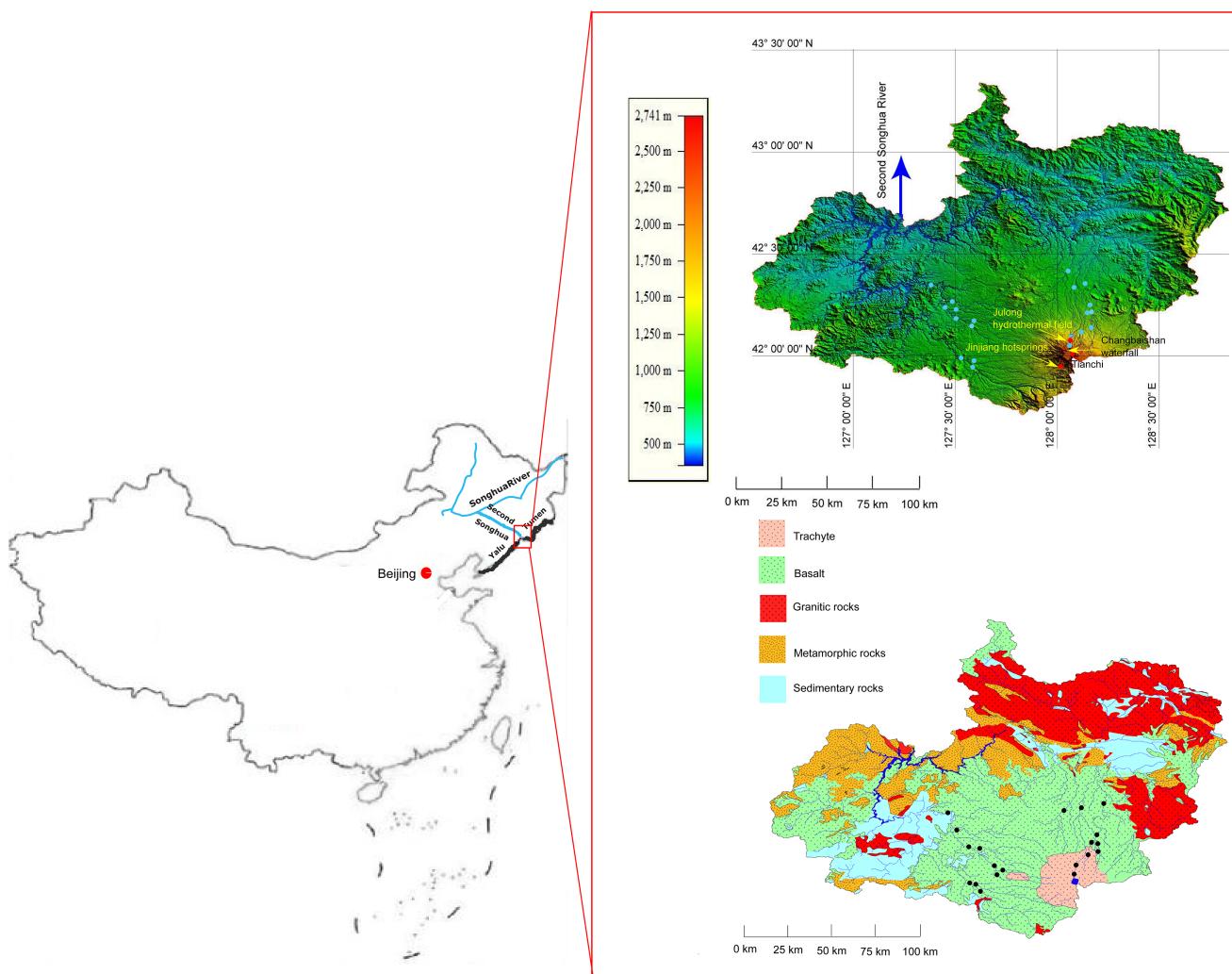


Fig. 1 Study area and samples location

cone during this eruption resulted in the formation of a 5 km-wide caldera, which is now filled by the 384 m deep Tianshi Lake. Subsequently, the Tianshi volcano erupted several times less energetically, with the last eruption to date occurring in 1903.

Intense visible hydrothermal activity is present on the North flank where more than 100 hot springs with temperatures between 40 °C and 80 °C are concentrated within the Julong hydrothermal system. These are located after the Changbaishan waterfall, which acts to drain the Tianshi water lake. This crater-lake is partly fed by thermal springs located on its northern shore with temperatures between 20 °C and 40 °C. Few hot springs with a maximum temperature of 60 °C are located in the Jinjiang valley on the western flank of the volcano (Zhang et al. 2015 and reference therein) (Fig. 1).

The climate is characterized by a long cold winter and a short cool summer, of which the latter accounts for 60%–70% of the whole year precipitation. Temperature and humidity are associated with the elevation of the mountain. The mean annual temperatures varies from 3 °C at 700 m to –7.3 °C, at elevations greater than 2000 m. The mean annual precipitation in Changbaishan ranges from 700 to 900 mm, with a maximum value of 1630 mm at the top of the Tianshi volcano, and decreases sharply in the mountain-foot area. The vegetation is also related to the elevation. Areas below 1100 m are covered in mixed coniferous and broad-leaved forests. Between 1100 m and 1800 m, mixed coniferous and sub-alpine coniferous forests cover the slopes. Only birch forests grow between 1800 m and 2100 m, whereas at elevations above 2100 m, only tundra vegetation is present with bare ground. Soils classified as andisols are poorly developed and remain at the initial stage of pedogenesis.

3 Samples collection and analysis

Stream and river water samples were collected monthly between June 2016 and October 2016.

Each month, samples were collected from rivers/streams draining mainly volcanic rocks on the northern and western slopes of Tianshi volcano. We also collected samples from hydrothermal springs from the Julong hydrothermal system located on the northern flank of the Tianshi volcano. In addition, we collected water samples from a small stream that receives geothermal water from the Julong hydrothermal system and outflowing into the Erdaobai River. For stream/river and hydrothermal spring samples, the temperature, pH and EC were measured in the field and alkalinity was determined by titration on the same day of the sample collection.

Samples were filtered using a Teflon filter holder through 0.2 micron poly-ether sulfone membranes.

Acidified (with bi-distilled HNO₃) and non-acidified aliquots were prepared and stored for further analysis.

Samples for carbon isotopes analysis of DIC were stored at 4 °C in evacuated Labco Exetainers until analysis.

Cations and silica concentrations were measured by ICP-OES whereas anions were analyzed by HPLC. Major elements analysis was performed at the Institute of Geochemistry, CAS in Guiyang, China and at Tianjin Normal University, China. Reproducibility for major elements analysis based on duplicated measurements of samples was better than 5%.

Carbon analysis was performed at the SIPERG Stable Isotope Lab at Iowa State University on a Thermo Finnigan Delta XL Plus coupled with an on-line gas preparation and introduction system Thermo Finnigan GasBench II.

Carbon isotopic compositions are expressed in the delta notation relative to the VPDB standard. Reproducibility based on repeated standard analysis and sample duplicates are better than 0.15‰.

4 Sources of inorganic carbon in rivers from the Changbaishan area

For most of the river samples, pH values are comprised between 7 and 8 with the exception of the Erdaobaihe River water samples collected after the Changbaishan waterfall, which displays relatively constant values of about 8.4 and 8.5. Riverine total dissolved solids (TDS) vary from about 40 to 310 mg/L, with the highest values being observed for the Erdaobaihe River whereas DIC concentrations vary from 0.3 to 2.5 mmol/L. With the exception of samples from the Erdaobaihe River collected after the Changbaishan waterfall and the Julong hydrothermal field, which are close to equilibrium with calcite ($SI_{calcite}$ between –0.3 and 0.6) and most of the hydrothermal waters, which are oversaturated with calcite, river samples are undersaturated in regards to calcite ($SI < -1$). Hydrothermal waters and most of the river samples are oversaturated regarding to atmospheric CO₂.

Carbon isotopic compositions of DIC measured in rivers vary from –14.2‰ to 3.5‰, and seasonal variations can reach up to 4‰ for some rivers. With the exception of samples from the Erdaobaihe River collected after the waterfall and the Julong hydrothermal system, all river water samples display negative $\delta^{13}\text{C}$ values, lower than the compositions measured in the hot spring waters.

Elemental ratios (e.g. Ca/Na and Mg/Na) display large variations over one order of magnitude, and river water is usually characterized by higher Ca/Na and Mg/Na ratios

than hydrothermal waters, as illustrated in Fig. 2, where major elements concentrations are corrected from rainwater contribution (Cheng et al. 1993). Ratios show spatial variations, and samples collected at the foot of the volcano usually show enrichment in Ca and Mg relative to the samples collected near the cone. The ratios measured in the river water samples fall into the field defined by the composition of the trachytes constituting the volcanic cone and the basalts from the flank and the ‘shield’ (Fig. 2).

Hydrothermal waters and samples collected from the Erdaobaihe River after the Changbaishan waterfall and Julong hydrothermal field display the lowest Ca/Na, Mg/Na and Mg/Ca ratios in the same range as those reported for the alkali trachytes. Rivers draining the flank and the basaltic shield are characterized by ratios similar to the basalts or intermediate between a trachytic and a basaltic composition. At a first order, the difference in chemical composition between the volcanic rock end-members seems to control the chemical composition of waters, although lowering of the Ca/Na and Mg/Na ratios due to carbonate precipitation for the Julong hot spring waters and the Erdaobaihe River samples cannot be ruled out. Hence, DIC concentrations probably result from the neutralization reaction between CO₂ and silicate rocks. As observed in the case of the Lesser Antilles volcanic islands by Rive et al. (2013), a relationship exists between the δ¹³C values of DIC and the ratio between total dissolved cations (μeq/L) corrected from atmospheric contribution and silicon (μmol/L), thereafter mentioned as TDScat/Si (Fig. 3).

This ratio varies from about 1–6 and cannot be explained by the diversity of chemical composition of the

volcanic rocks. Although trachytes are depleted in Ca and Mg relative to basalts, the range of chemical compositions in the rocks is much smaller than the range observed in river waters. In addition, rivers draining mostly trachytes (e.g. Erdaobaihe River) display the highest (Na + K + 2 * Ca + 2 * Mg)/Si ratios, whereas trachytes are characterized by the lowest ratios. In agreement with the conclusions of Rive et al. (2013), the TDScat/Si ratio reflects different regimes of water/rock interactions at low and high temperatures. Rivers displaying low TDScat/Si are characterized by low δ¹³C values whereas rivers showing high δ¹³C values have high TDScat/Si ratios in the range of hydrothermal waters. Hence, variations of carbon isotopic compositions and TDScat/Si ratios seem to trace the different contributing sources of CO₂ and different temperatures of water/rock interactions. The best candidates for the sources of CO₂ are biogenic soil CO₂ characterized by low C isotopic compositions and magmatic CO₂ usually enriched in ¹³C.

Carbon isotopic compositions reported for wood samples collected around the Tianchi volcano are around –24‰ (Yin et al. 2012), similar to the composition measured in particulate organic carbon transported by the Tumen River (Han and Hu 2009). By taking into account a diffusional fractionation factor of 4.4‰, the δ¹³C of soil CO₂ should be around –20‰. However, variable contribution of atmospheric CO₂ (–8‰) and dissolution of CO₂ in open or closed system (Jin et al. 2009 and references therein) might affect the δ¹³C of soil DIC resulting from the interaction of silicate and biogenic soil CO₂. The lowest values measured in our set of samples approach

Fig. 2 Variations of the Ca/Na and Mg/Na ratios corrected from rain contribution measured in waters from the Changbaishan area. By comparison, the range of compositions for the shield basalts and trachytes is also reported (Andreeva et al. 2014)

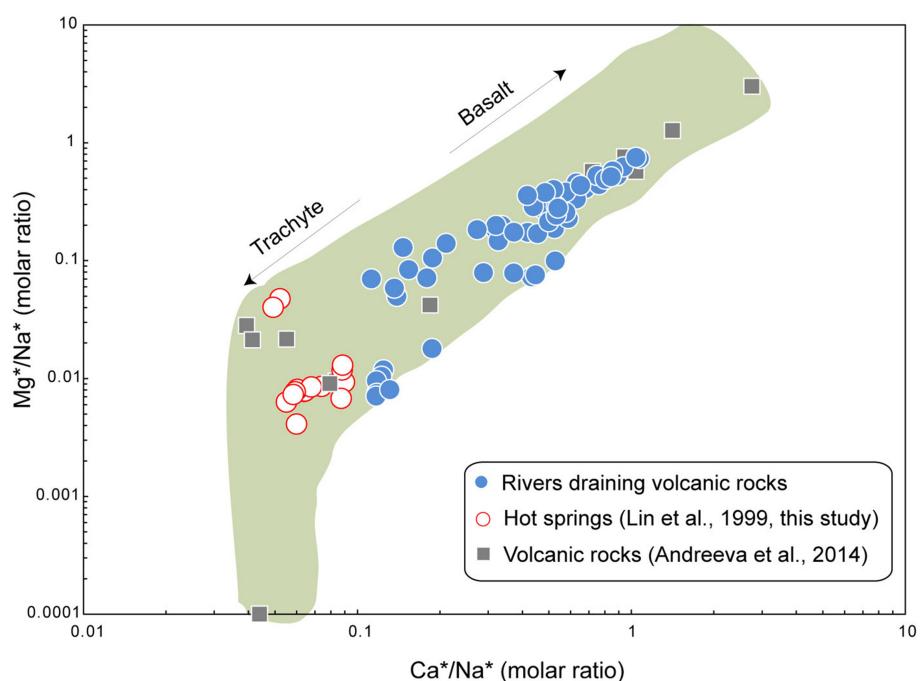
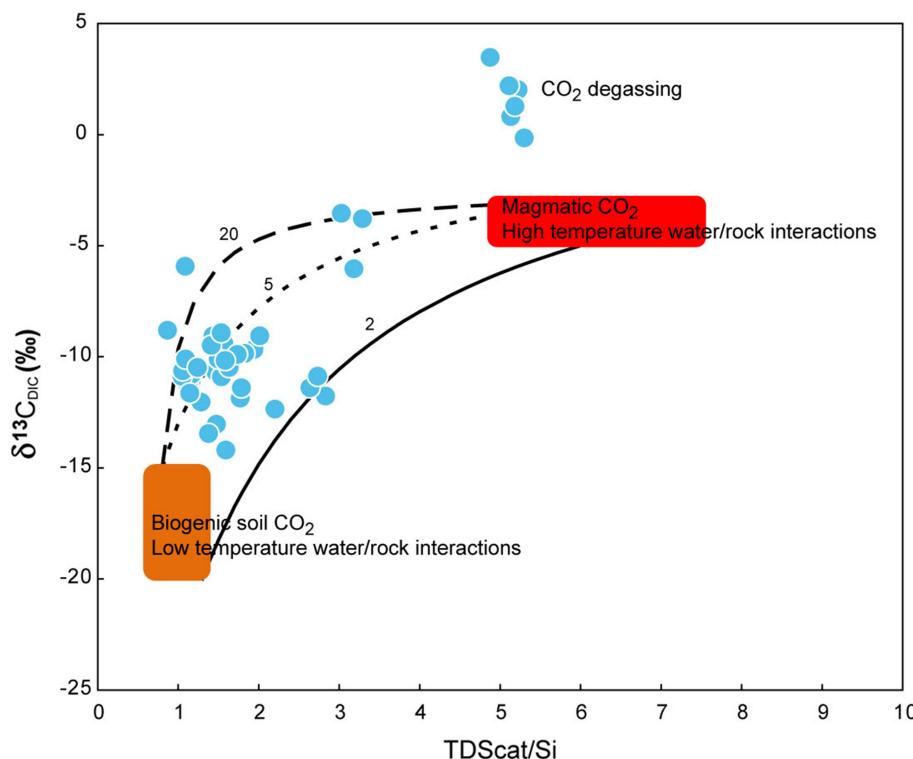


Fig. 3 Relationship between the TDScat/Si ratios corrected from rain contributions and the C isotopic compositions of DIC measured in waters from the Changbaishan area. The curvature of the mixing curves is a function of the $(\text{DIC}/\text{Si})_{\text{magma}}/(\text{DIC}/\text{Si})_{\text{soil}}$ ratio. For the composition of the different end-members, the reader is invited to refer to the text



−14‰ and are associated with concentrations of Cl close to 0 μmol/L within uncertainties after correction from atmospheric contribution, indicating the negligible hydrothermal contribution for these samples. These values are similar to those measured in soil seep samples in the Lesser Antilles volcanic islands by Rive et al. (2013). In the following discussion, a range of carbon isotopic composition of DIC derived from reaction between silicate minerals and biogenic soil CO₂ from −20‰ to −15‰ will be assumed.

By comparison, carbon isotopic composition of magmatic CO₂ is less variable. Hydrothermal CO₂ gas samples display δ¹³C values from −7.1‰ to −4‰ (median −4.6‰) and from −7.5‰ to −4.8‰ (median −7‰) for the Julong and Jinjiang hot springs, respectively (Zhang et al. 2015 and reference therein). Comparatively, carbon isotopic compositions of DIC from the Julong hydrothermal waters are slightly enriched in ¹³C, with values ranging from −3.5‰ to 0.6‰ (this study, Hahm et al. 2008). This difference probably results from isotopic fractionation during phase changes at the surface conditions. By comparison, hot springs from the Himalaya-Tibet Plateau (Supporting Information) display large differences between the carbon isotopic compositions of outgassed CO₂ and DIC (up to 17‰), suggesting large CO₂ degassing (up to 97%). In the case of the Changbaishan area, up to 40% of initial DIC can be lost by degassing and need to be taken account in carbon budget. In the following discussion we

will assumed a composition between −5‰ and −3‰ for the δ¹³C value of the magmatic carbon end-member.

Curvatures of the mixing curves in Fig. 3 are a function of the DIC/Si ratio acquired by water during high temperature water/rock interaction, normalized to the same ratio acquired by water at low temperature. In hydrothermal waters the DIC/Si ratios are around 5 (this study, Lin et al. 1999). Although the DIC/Si ratios in soil water have not been directly measured, the DIC/Si ratios associated to the lowest δ¹³C values are close to 1, similar to those estimated for the low temperature weathering regime by Rive et al. (2013). Hence, given the uncertainties related to the compositions of the different end-members, the relationship in Fig. 3 can be interpreted as a result of water/rock interactions at high and low temperatures associated to two distinct sources of CO₂ of magmatic origin and biogenic origin.

Respective contributions of biogenic soil CO₂ and magmatic CO₂ consumed by silicate weathering is estimated based on a mass balance equation written for carbon isotopes of DIC as followed:

$$f_{\text{magma.}} = \frac{\delta^{13}\text{C}_{\text{riv}} - \delta^{13}\text{C}_{\text{soil}}}{\delta^{13}\text{C}_{\text{soil}} - \delta^{13}\text{C}_{\text{magma.}}}$$

where f_{magma.} is the proportion of carbon with a magmatic origin, δ¹³C_{riv} the C isotopic composition of DIC transported by the rivers, δ¹³C_{magma.} and δ¹³C_{soil} the isotopic

compositions of the magmatic and biogenic soil end-members, respectively.

Any biological or physical process fractionating carbon isotopes impair the use this equation to calculate the source of DIC. As mentioned above, carbonate precipitation is unlikely due to the low calcite saturation index of the river waters ($-2 < \text{SI}_{\text{calcite}} < -1$). Due to the oversaturation relative to atmospheric CO₂ [$\log(p\text{CO}_2)_{\text{atm}} \approx -3.5$] of most of the rivers [$-3.55 < \log(p\text{CO}_2)_{\text{river}} < -2.7$, median -3.15], CO₂ degassing is the most plausible mechanism, which could fractionate carbon isotopes. Such effect is evidenced by the carbon isotopic compositions of the samples collected from the Erdaobaihe River, which display $\delta^{13}\text{C}$ values higher than those measured in the hydrothermal waters.

The consequence of CO₂ degassing would be an overestimation of the contribution of DIC derived from the neutralization of magmatic CO₂ by silicate rocks.

Given the uncertainties related to the choice of the end-members and the effects of CO₂ degassing, contribution of magmatic CO₂ range from less than 20% to more than 70% for rivers (excluding Erdaobaihe River) draining the Changbaishan area. Seasonal variations of might reflect changes of contribution between magmatic CO₂ and atmospheric/biogenic soil CO₂ although variability of the end-members composition or degassing cannot be ruled out.

5 Conclusions

Variations in the chemical composition of rivers reflect the variability of composition between the volcanic rocks in the Changbaishan area. For instance, the evolution of the Ca/Na ratios with the Mg/Na ratios of the rivers can be explained by a mixture between waters interacting with trachytes and basalts.

Hence, the DIC transported by rivers is derived from the neutralization of CO₂ by silicate rocks. At a first order, variations of the C isotopes ratios can be explained by a mixture between CO₂ of magmatic origin, enriched in ^{13}C (−5%) and biogenic soil CO₂ with lower isotopic compositions. The highest isotopic values can be explained by C isotopes fractionation during CO₂ degassing in rivers. The coupling of elemental ratios with the $\delta^{13}\text{C}$ values of

DIC evidences two water/rock interaction regimes at low and high temperature.

A mass balance based on carbon isotopes suggest that the contribution of magmatic CO₂ vary from less than 20% to more than 70%.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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