

Sequestration of carbon as carbonate in the critical zone: insights from the Himalayas and Tibetan Plateau

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Received: 18 April 2017/Revised: 23 April 2017/Accepted: 23 April 2017/Published online: 2 May 2017
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Abstract The carbon pool stored in soil carbonate is comparable to the soil organic carbon. Therefore, secondary calcite precipitation in supersaturated catchment could be an important, yet poorly constrained, carbon sink within the modern global carbon cycle. The chemical analysis of some dissolved species transported by rivers, such as elevated Sr/Ca and Mg/Ca ratios but also heavy stable Ca isotopic compositions, witness the formation of secondary calcite in rivers draining arid regions. However, in areas affected by active tectonics and rapid physical erosion, co-variations in the fluvial Sr/Ca and Mg/Ca ratios could also be related to incongruent carbonate weathering processes. Here, we present a model to assess the roles played by incongruent carbonate dissolution and secondary calcite precipitation in modern weathering processes. We tested and applied the model to rivers draining the Himalayan–Tibetan region. The results suggest that regional aridity in the drainage basin promotes carbon sequestration as secondary carbonate but that for a given runoff,

incongruent dissolution of carbonate possibly related to rapid physical erosion amplifies such sequestration. The isotopic compositions ($^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$) of detrital carbonate transported by the main rivers in South and South-East Tibet imply that around 1% of the suspended material transported by those rivers corresponds to secondary carbonate and can represent between 5% and 15% of the alkalinity flux. Most of these alkalinity transported as particulate material is, nevertheless related to the weathering of carbonate lithologies and is also subjected to dissolution prior its final storage in sedimentary basins. However, on glacial-interglacial timescale this will amplify the significant role of mountain weathering on climatic variations.

Keywords Carbonate · Weathering · Isotope · Tectonic forcing

1 Introduction

Stream geochemistry in the headwaters of the rivers draining the Southern and Eastern side of the Tibetan Plateau (TP) suggests that carbonates dissolution dominates the fluvial water alkalinity budget (Wu et al. 2008). In detail, the contribution of aeolian dust can also be significant, especially in the NE part of the Plateau (Jin et al. 2011; Zhang et al. 2013). However, the determination of carbonate chemical weathering flux requires the identification of the carbonate subjected to weathering and a quantification of their detailed chemistry. This task is not easy since traces of bedrock carbonates in fresh plutonic metamorphosed rocks (e.g. Blum et al. 1998; White et al. 1999; Chamberlain et al. 2005) and even trace calcic minerals (Oliva et al. 2003) are generally recognized as key

11th International Symposium on Geochemistry of the Earth's Surface.

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Ca-rich end-member sources. Although disseminated carbonate compositions in silicate rocks are well constrained in the Himalaya (e.g. Blum et al. 1998; Galy et al. 1999; Tipper et al. 2006; Chapman et al. 2015), the composition and variability of carbonate-bearing rocks in the other edges of the TP remain poorly defined. In addition, the determination of the carbonate chemistry and mineralogy in the source rock should improve paleo-reconstruction of this region since proxies derived from soil carbonates, such as $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and trace elements (e.g. Cerling et al. 1993; Quade et al. 1989, 1997; Li and Li 2014) are hampered by the presence of detrital carbonates in sediments (Fan et al. 2007; Li et al. 2013). Here we present a method to determine the Sr/Ca and Mg/Ca ratios of carbonate present in the lithology undergoing weathering from the riverine chemistry and the bulk carbonate composition of terrestrial sediments (e.g. loess, sand and silt and paleosol). This also determines the chemistry and quantity of authigenic carbonate end-member. In addition, we have analysed the suspended material (SM) exported by several large rivers (Yarlung, Salween, Mekong and Chang Jiang rivers) in South-East Tibet. Both types of carbonates (authigenic and detrital) are present and contribute to the export of the alkalinity associated to the chemical weathering of the area.

2 Methods

For carbonate, sediment were crushed to <200 mesh powder and leached with 10% acetic acid (liquid/powder ratio >10) for 1 h in an ultrasonic bath at room temperature. Supernatants were then separated by centrifugation and analysed using a Leeman Labs ICP-OES at the Institute of Tibetan Plateau Research, Chinese Academy of Sciences. Sr, Mg and Ca concentrations were expressed in parts per million (ppm) of the weight of dry powder. Replicate analyses of samples show that relative standard deviations from the mean value were <2%. Comparison with literature data are restricted to carbonate composition data based on diluted acetic acid leaching (Liu et al. 2002; Yokoo et al. 2004; Jin et al. 2010) or HNO_3 leaching using careful multi pre-treatments (Li and Li 2014). Crushed sediments were also analysed for the amount and isotopic composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of carbonate by reaction with >100% H_3PO_4 at 70 °C overnight on a Thermo Finnigan GasBench system coupled to a MAT 253 mass spectrometer by the continuous flow method at the Centre de Recherches Pétrographiques et Géochimiques, CNRS. The determination of the chemistry and quantity of authigenic carbonate is based on the careful analysis of $\log \text{Sr}/\text{Ca}$ – $\log \text{Mg}/\text{Ca}$, since authigenic carbonate precipitation is characterised by a constant gradient of $(D_{\text{Sr}} - 1)/(D_{\text{Mg}} - 1)$ in

this space, dependent only on the partition coefficients (e.g. Yang et al. 2015).

3 Results and discussion

River data in northern China are characterised by a very strong correlation between their Sr/Ca and Mg/Ca ratios. These observations would suggest that carbonate weathering and precipitation dominate fluvial water composition changes. However, secondary calcite precipitation and incongruent calcite dissolution (Yang et al. 2015) are unable to represent the overall picture found in northern China and in the large rivers of the northern China and the Himalayan–Tibetan region (NCHT) region. Some of the differences can be related to a widespread contribution of aeolian sediments (Yang et al. 2017). However, the best explanation is a combined effect of incongruent dissolution and secondary carbonate precipitation, albeit variable from catchment to catchment. In line with the findings in rivers draining the Himalayan region (e.g. Galy et al. 1999; Jacobson et al. 2002; Tipper et al. 2008; Bickle et al. 2015; Chapman et al. 2015), many more NCHT rivers are affected by secondary calcite precipitation. For instance, based on the chemistry of the dissolved species, around 2/3 of the Ca released in the catchment of the Yellow River by the weathering of rock has precipitated as calcite. Such value implies a secondary calcite precipitation flux of $0.14 \text{ Tmol yr}^{-1}$, more than the carbonate precipitation flux induced in the oceans by the alkalinity flux of the Yellow River. This clearly highlights the significance of the secondary calcite precipitation. This also illustrates the underestimated role of arid region rivers in regulating the global carbon cycle. Other rivers, such as the Yarlung Tsangpo upstream the Eastern syntaxis (Hren et al. 2007) have left behind more than 50% of the Ca as pedogenic carbonate. Part of those carbonates can still be exported by the river but as particulate. The $\delta^{18}\text{O}$ of the bulk carbonate of the SM is negatively correlated with the reciprocal of the carbonate concentration. The high carbonate content display $\delta^{18}\text{O}$ values characteristic of the detrital metamorphic Himalayan carbonate (e.g. Galy et al. 1999). The lower $\delta^{18}\text{O}$ values can only be produced by low-temperature precipitation from ^{18}O -depleted waters, characteristic of rainwater and river water sampled in Tibet. Therefore a low carbonate content of around 1% by weight in the SM in Southern Tibet corresponds to the export of secondary calcite. In the case of the Yarlung Tsangpo–Brahmaputra catchment, those pedogenic carbonate do not reach the ocean since under-saturated waters characteristic of the very wet south flank of the Himalayan range in this catchment dissolve all the carbonate in the SM exported from Tibet (Singh et al. 2005). However, weaker monsoon

condition around the Eastern syntaxis of the Himalaya in the past might have exasperated the precipitation of pedogenic carbonate in Tibet and promoted its export to the Ocean.

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

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