

Paleo-Asian Oceanic slab under the North China Craton revealed by carbonatites derived from subducted limestones

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Our report (Chen et al., 2016) on a carbonatite intrusion with geochemical features of recycled limestone in the Hannuoba region provides evidence for subduction of sedimentary carbonates to mantle depths, followed by their return to Earth's surface by buoyant diapirism and high-degree melting. Yang (2017) prefers the interpretation that the carbonatite is a limestone block (i.e., xenolith) by comparing the Hannuoba carbonatite with "typical carbonatites." Here, we clarify some misrepresentations in the comments raised by Yang and explain that they do not alter our original interpretation.

Yang criticizes the identification of the Hannuoba intrusion as a carbonatite on the basis of a number of features that differ from what he calls "typical" or "true" carbonatites. These are a lack of associated peralkaline igneous rocks and fenitization, low trace element contents, and carbon and oxygen isotopes that are similar to sedimentary limestones. However, none of these are part of the definition of a carbonatite, which is an igneous rock (i.e., a rock that has crystallized from a melt) that contains more than 50% modal carbonates. Yang's criticisms could only be accepted if the approved definition of a carbonatite were to be modified to insist on these additional features.

Carbonatite melts are generally attributed to either late-stage separation from an alkaline silicate magma by liquid immiscibility, or to low-degree melting of carbonated peridotite, carbonated basaltic oceanic crust, or carbonated sediments. Contrasting with most carbonatites, the Hannuoba carbonatite is not associated with peralkaline intrusive rocks, and does not exhibit enriched incompatible trace element contents and steep light rare earth element (LREE)-enriched patterns (Jones et al., 2013). We never claimed that the Hannuoba occurrence is a typical carbonatite, but rather suggested that the carbonatite was formed by high-degree melting of subducted limestone, which penetrated into the cold cratonic mantle in the form of solid buoyant diapirs. Because limestone is mostly composed of a single calcite phase, high modes of melting would occur once melting initiates. Carbonatite melt formed in this way would experience only limited chemical exchange with the mantle, retaining many of the chemical characteristics of limestone such as low alkali contents and low trace element contents.

Here, we use five lines of evidence to refute Yang's assertion that the Hannuoba carbonatite is a limestone xenolith. (1) *Field evidence for intrusive form*: The Hannuoba carbonatite occurs in *xenolith-free* basalt layer and has a sharp boundary with the basalt layer, and the overlying basalt is domed upward by the invasion of the carbonatite melt (Chen et al., 2016, our figure 1B). (2) *Mineralogy of the carbonatite*: The medium- to coarse-grained silicate macrocrysts are set in the fine-grained calcite matrix at random and not concentrated close to the contact between carbonatite and basalt (our figures 1C and 1D). The chemical compositions of Ol (CaO < 0.1 wt%) and Cpx (Mg# = 91.9–93.3 and SiO₂ > 50.1 wt%) in the carbonatite intrusion are those of mantle-derived peridotite xenocrysts and cannot be the products of contact metamorphism proposed by Yang. The highly disordered graphites (our figure

DR1) might be transformation products from diamond during rapid upward migration, and are thus further evidence that the precursor of the carbonate body resided at some stage in the deep mantle, as suggested by the graphite-diamond-bearing carbonatite xenoliths (Liu et al., 2015). The occurrence of moissanite require complex devolatilization during ascent (Shiryaev and Gaillard, 2014), eliminating the possibility that the moissanites in the Hannuoba carbonatite are mantle-derived xenocrysts. These robust petrological observations disqualify Yang's reinterpretation. (3) *High Ni contents and high ¹⁴³Nd/¹⁴⁴Nd ratios*: The carbonate components in the carbonatite intrusion have high Ni contents and high ¹⁴³Nd/¹⁴⁴Nd ratios, indicating interaction between carbonate melt and mantle peridotite. Yang's assertion that the Ni contents in the calcite (1.4 to 133 ppm) are within the uncertainty of the LA-ICP-MS technique is incorrect: our analytical results on reference material MACS-3 (Ni = 57.9 ± 1.8 [1σ, n=8] ppm) agree well with reference values (Ni = 57.4 ± 4.9 [1σ] ppm) and indicate a small uncertainty relative to the range observed. Furthermore, the similarity of Nd isotopes but widely differing Sr isotope compositions is compatible with mixing, with a large difference in concentration between the two elements (White, 2013). Nd is an immobile element in hydrothermal fluids, so that the Nd isotopic compositions of the Hannuoba carbonatite would not be modified by the post-magmatic fluid that deposited the aragonite veins. (4) *Light carbon isotopes*: Complex devolatilization during rapid ascent of carbonatite melts could have resulted in their low δ¹³C_{V-PDB} values (−14.4‰ to −11.2‰). The carbonatite samples were attacked with H₃PO₄ to collect inorganic carbon from calcite for carbon isotopic analysis, thus their low δ¹³C_{V-PDB} values could not result from organic carbon materials, as suggested by Yang. (5) *Positive Eu anomaly*: The Hannuoba carbonatites show much lower Rb, Ba, and HREE contents and positive Eu anomalies compared to limestone, suggesting modification by subduction-related CO₃²⁻-rich aqueous fluids, hence supporting the subduction interpretation.

The geochemical evidence for mixing between limestone and mantle peridotite, but *not* the host basalt, reinforces our interpretation that the carbonatite interacted with the mantle during the subduction cycle.

The Hannuoba carbonatite is not a unique case where sedimentary limestone subduction followed by melting can be traced. Liu et al. (2015) provided direct evidence for the recycling of limestone into the mantle in the form of carbonatite xenoliths in the Dalihu basalts, ~250 km north of Hannuoba (our figure 1). Those carbonatite xenoliths also exhibit the geochemical signatures of limestone, but contain diamond, indicating a history of subduction to at least 120 km and an origin by high-degree melting of a subducted limestone.

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