

## Microdiamonds from Tonian plume-related LIP, North China Craton (NCC)

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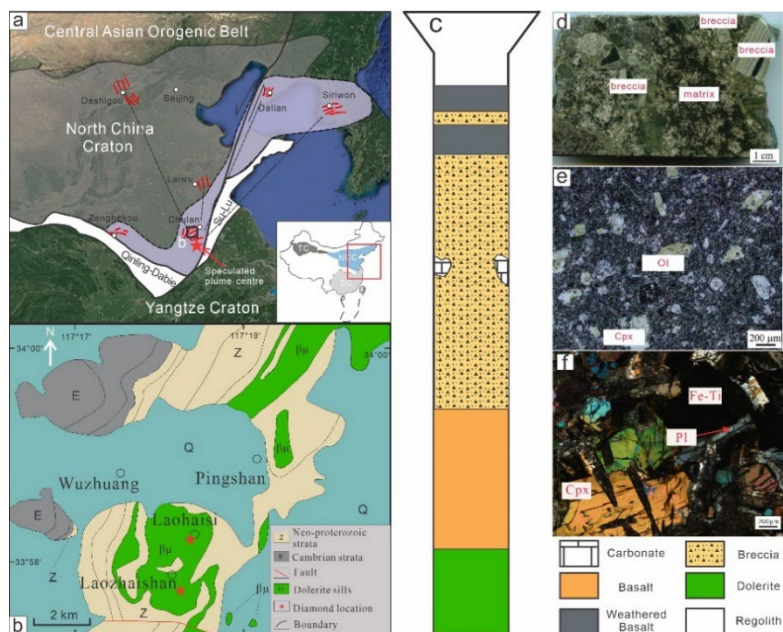
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### Introduction

Diamonds that contain deep-seated mineral/fluid inclusions represent the only direct samples of the deep mantle currently available to scientists. Diamonds have been reported in various environments over the last few decades, including meteorite impacts, metamorphic rocks, ophiolites, and volcanic eruptions in addition to kimberlites and lamproites. These non-kimberlitic diamonds were hotly debatable several tens of years ago, but at present are a common phenomenon (Kaminsky and Voropaev, 2021), their possible formation mechanisms are still of great scientific and practical significance. Recently, thousands of microdiamonds have been discovered in alkaline dolerites within a plume-related large igneous province (LIP), the typical grain size ranging from 200-600  $\mu\text{m}$  (Cai et al., 2021). These microdiamonds are characterized by negative C-isotopes ( $-18.6$  to  $-21.1\%$ ) and low N-aggregation (Ib-IaA diamonds), which is similar to diamonds from the Dachine komatiite (French Guyana) reported by Cartigny in 2010. Despite their significance, little attention was received since the possibility of contamination has yet been excluded. The small size of both diamond host and mineral inclusions has made it difficult to study the origin and formation mechanism of these microdiamonds. We have provided unquestionable evidence on the deep Earth origin of these microdiamonds in this presentation.

### Geology background of diamond-bearing dolerite and sample description

The diamond-bearing dolerite is located within the Chulan-Dalian-Sariwon (CDS) LIP domain situated in the present southern-eastern margin of North China Craton (NCC). Two LIP events were recorded in the eastern NCC i.e. (ca. 1.3 Ga Yanliao LIP and ca. 0.92 Ga CDS LIP)(Zhai et al., 2015). The CDS LIP is composed of several radiating dyke swarms (e.g., Dashigou dyke) and sill complexes (e.g., Chulan sills; Dalian sills and Sariwon sills) with an outcrop extent ca. 0.65 Million  $\text{km}^2$  and are considered as sourced from a  $\sim 900 - 920$  Ma Neoproterozoic mantle plume (e.g. Peng et al., 2011)(Fig.1). Interbedded olivine basalts and basaltic breccial lavas associated with diamond-bearing dolerites were recorded in this region according to drill core compiling record (Zhu et al., 2018). Dolerites are constituents of clinopyroxene, plagioclase with minor apatite, olivine and opaque minerals including ilmenite, titanite and magnetite.



**Figure 1:** Tectonic setting, simplified geological map, vertical shaft map of diamond-bearing dolerites. (a) Satellite image with sketch draw showing the distribution of Neoproterozoic Chulan-Dalian-Sariwon (CDS) LIP mafic dykes/sills in the North China Craton, and speculated location of mantle plume center. (b) Simplified geological map of diamond-bearing dolerites. (c) Vertical shaft map (un-scaled) showing interbedded olivine basalts and basaltic breccial lavas above diamond-bearing dolerites. (d-f) Samples of basaltic breccial lava, olivine basalts and dolerites.

Though rare, garnets exist amongst these dolerites. Since 2010, thousands of microdiamonds have been reported from dolerite sills in this area, the concentration of diamond varies widely within diamond-bearing dolerites (up to 3.43 mg/m<sup>3</sup> to scarcely any). Microdiamond samples are provided by the Second Hydrologic Engineering Geological Survey Institute of Anhui Province. These microdiamonds are mainly cubic-octahedral in shape and show laminar growth, triangular and/or tetragonal dissolution, resorption, plastic deformation lines, and corrosion textures on the surfaces (Fig.2).

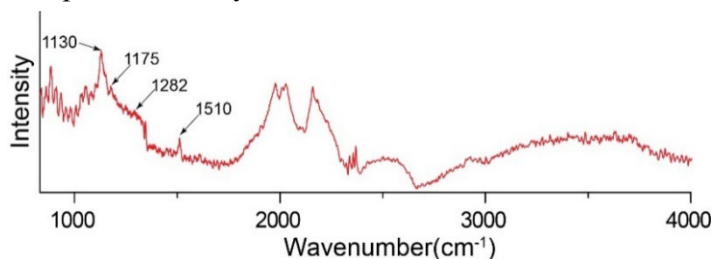


**Figure 2:** Morphology of diamonds from LIP dolerites

## Results and discussion

Our diamond samples contain relatively high nitrogen contents, ranging from 267 to 464 ppm (n=14, median 337 ppm) and low aggregation state. Generally, most of our analyzed sample exhibit weak N absorption near 1282 cm<sup>-1</sup>, accompanied by a broad peak near 1215 cm<sup>-1</sup> (A center); more than half of our tested diamonds not only display IR absorption peaks near 1282 cm<sup>-1</sup> (A center) and 1130 cm<sup>-1</sup> (C center) but also exhibit absorption peaks at 1175 cm<sup>-1</sup> (B center) (Fig.3). Natural type Ib diamonds commonly contain some A-aggregates but B-aggregate IR absorption is rare observed. The only report of the coexistence A, B and C centers in natural diamond crystal has been reported as "ABC" diamond (Hainschwang et al., 2006). We disprove the HPHT treatment origin of our microdiamonds since single nitrogen atom (C center) should convert rapidly by HPHT treatment to A center but farther aggregation to B center is much slower, making the C center absorption extremely weak in HPHT-treated diamonds. The existence of both intense C center and aggregated A center in our diamond samples indicates a complex process during diamond formation.

Most dark-colored flocculence inclusions have a characteristic Raman peak at approximately 1580 cm<sup>-1</sup>, identifying themselves as graphite. Hematite, ilmenite, magnetite, coesite, Fe-Ni and a series of high-



**Figure 3:** Representative FTIR spectra of A center-bearing microdiamond

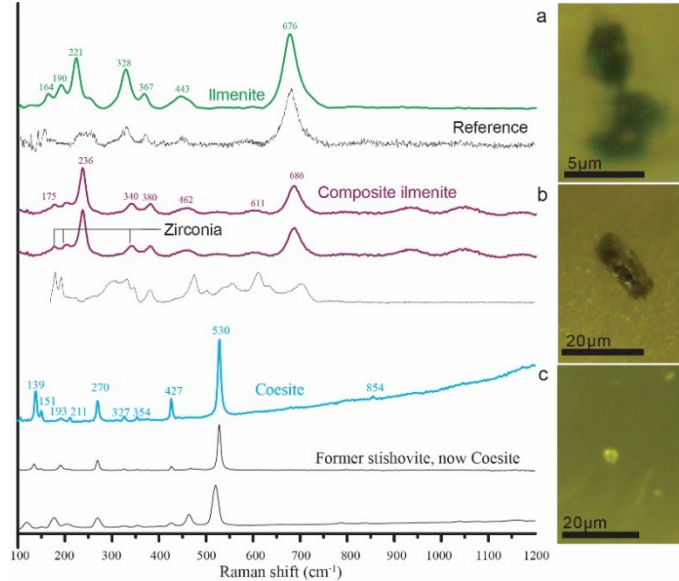
pressure mineral inclusions assemblage ( $> 12.5$  GPa) are also identified by Raman and transmission electron microscope. This coesite has similar spectra with former stishovite, now coesite inclusion from a superdeep diamond reported by Smith et al. (2018). Our coesite inclusion has a high residual pressure ( $P_{\text{Inc}} = 3.24 \pm 0.1$  GPa) based on its Raman spectroscopy shift (Sobolev et al., 2000).

The Fe-Ni alloy (fcc structure) exists as intergranular mineral or independent mineral inclusion during TEM observation. Some of Fe-Ni alloys are closely associated with coesite. Such mineral association is most likely sourced from a basaltic protolith within a reduced deep mantle, indicating these microdiamonds have an eclogitic protolith. The high-pressure mineral inclusions assemblage ( $> 12.5$  GPa) and eclogitic protolith have linked the diamond formation model closely with the mantle plume process. Therefore, it excludes the possibility of anthropogenic contamination.

We have reported the natural origin of a cluster microdiamonds that originate from a LIP associated with a mantle plume. Our analysis suggests that the formation of these microdiamonds was triggered by the mantle plume process. These microdiamonds offer a new perspective to study the deep mantle material and the recycling of carbon in the deep Earth.

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**Figure 4:** Selected Raman spectra of inclusions in microdiamond from dolerites. (a) Ilmenite from sample 11DK11rz01-x-1. (b) a composite spectrum of ilmenite plus zirconia (verified by scanning electron microscopy/energy-dispersive X-ray spectroscopy (EDX)). (c). Coesite spectrum from sample 15LDzk09rz02-a-5. Black thin lines are the reference spectra of ilmenite (R060149), baddeleyite (R100171) and coesite (X050094) from the RRUFF database. Spectra are stacked vertically for clarity.