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In-situ U-Pb dating of garnet in diamonds from Venetia, South Africa

Brendan Hoare[1,2], Gary O'Sullivan[3], David Chew[3], David van Acken[4], Eszter Badenszki[4], Ulrika D'Haenens-Johansson[1], Evan M. Smith[1], Jeffrey Harris[5], Emma Tomlinson[3]

[1]*Gemological Institute of America, New York, NY, USA*
[2]*National High Magnetic Field Laboratory at Florida State University, USA*
[3] *Geology, School of Natural Sciences, Trinity College Dublin, Rep. of Ireland*
[4]*School of Earth Sciences, University College Dublin, Rep. of Ireland*
[5]*School of Geographical and Earth Sciences, University of Glasgow, UK*

Introduction

During their formation diamonds can entrap inclusions of surrounding mantle. As diamonds are argued to be chemically unreactive they should forever shield these inclusions from later geochemical modification. Since diamonds have formed throughout Earth's history, they provide a unique glimpse of conditions in the Earth's mantle on billion-year timescales, providing their ages can be constrained. As directly dating diamonds is not possible, they must be dated by their inclusions. However, this remains extremely challenging, and at present no in-situ methodology exists for any inclusion type. As the U-Pb system has recently been applied to garnet in peridotite xenoliths using laser ablation inductively coupled plasma mass spectrometry (O'Sullivan et al. 2023), in-situ dating of garnet inclusions in diamond via the U-Pb method is an attractive prospect. Here we provide U-Pb dating and geochemical data for garnets liberated from visually fracture free diamonds from the 524.8 ± 7.3 Ma Venetia Diamond Mine (Griffin et al. 2014). Garnet inclusions from Venetia make a good case study as they have previously been dated by the Sm-Nd method by Koornneef et al., (2017), which provided two isochron ages of 2.95 Ga and 1.15 Ga.

Methods

Trace elements were analyzed using a laser-ablation (LA) system coupled to a quadrupole inductively coupled plasma mass spectrometry (ICP-MS). For U-Pb geochronology a subset of inclusions (n=7/10) were analyzed using an analytical setup that comprised a LA system, coupled to a Thermo Scientific Neptune multiple collector (MC)-ICP-MS. Masses 202, 204, 206, 207, 208 and 238 were all analyzed in static mode on secondary electron multipliers (SEM). The primary reference material was Afrikanda garnet (Salnikova et al. 2019), with Dashkesan garnet used as a secondary reference material (Stifeeva et al. 2019). Using this setup the secondary standard Dashkesan yielded a concordia age of 146.0 ± 1.1 | 2.2 (n=6; MSWD=3.6), relative to the published age of 146 ± 2 Ma (Stifeeva et al. 2019). Nitrogen concentrations and the aggregation state of the host diamonds were obtained by Fourier-transform infrared spectroscopy.

Results

Trace element compositions of the garnets reveal four separate populations (Fig. 1), reflecting the presence or absence of Ti and Zr-Hf anomalies with respective differences seen in rare earth element profiles (REE). Nickel-in-garnet thermometry indicates storage temperatures of 1240-1420°C (median = 1330°C). U-Pb dating of the garnet provides a single U-Pb discordia age of 578 ± 44 Ma (n=8, including one garnet with two 'zones'; MSWD=0.53), despite the significant trace element variation between each garnet population (Fig. 1). The common Pb (Pb_c) composition of the garnet indicated from the upper intercept is radiogenic

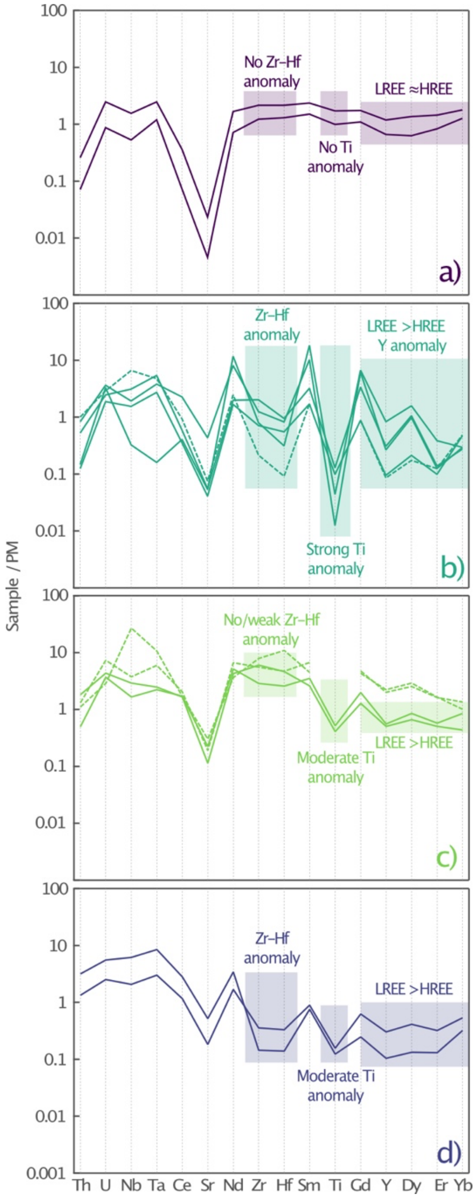

Figure 1: Primitive mantle normalized (McDonough and Sun, 1995) trace element diagrams of garnet from this study and Koornneef et al. (2017), solid and dashed lines respectively.

at $^{207}Pb/^{206}Pb$ = 0.81 ± 0.03 (Fig. 2b), below that expected from the two-stage terrestrial Pb model of Stacey and Kramers (1975) at the lower intercept age of ~600 Ma ($^{207}Pb/^{206}Pb$~ 0.87). One garnet also shows zonation with respect to total U vs Pb_c composition, demonstrated by two discrete zones which were encountered during a single spot ablation. The %B-center aggregation state of the host diamonds ranges from 10-80%, consistent with short residence at relative high temperatures as indicated by garnet thermometry (Fig. 2a). By contrast, the measured %B-center values require lower residence temperatures (~1200°C) than those indicated by thermometry if they had resided in the lithosphere for >0.6 Ga timescales (Fig. 2a).

Discussion

Prior to discussion regarding the meaning of the U-Pb age from Venetia garnet, one concern is the U concentration difference between the reference materials (>250,000 cps) and the inclusion garnet (~1000 cps). Due to the potential non-linear ion-counting response of the SEMs with increasing count rates, it is possible that the measured ages in the garnet from diamonds are artifically depressed. Assuming a non-linearity of ~1% per decade of ion beam intensity above 100,000 cps (Richter et al. 2001; Hoffmann et al. 2005), the $^{206}Pb/^{238}U$ ages could be 2-3% higher than expected in the garnet from the diamonds using Afrikanda as the primary reference material. As such, it should be borne in mind the reported age could represent a minium value and be as much as ~17 Ma older.

The garnet U-Pb discordia age from Venetia diamonds of 578 ± 44 Ma can be explained by two scenarios: either that the U-Pb age reflects encapsulation (and hence diamond formation) shortly prior to, or contemporaneously, with the eruption of the Venetia kimberlite, or the isotopic closure of the U-Pb system in the garnet during emplacement to the Earth's surface. The radiogenic Pb_c composition of the garnet is more consistent with Pb exchange between the garnet and the surrounding mantle much later than would have been expected based on previous Sm-Nd isochron dating of diamonds from Venetia. Discrete zonation in Pb_c seen in one garnet also strongly supports short-term disequilibration and is not expected for a garnet inclusion in diamond resident at mantle temperatures on >0.6 Ga timescales. Assuming mantle residence temperatures of ~1330°C, the N aggregation state of the host diamond supports diamond growth a Neoproterozoic encapsulation age (Fig. 2a). Collectively, the data here suggest either that the diamond growth event for these diamonds occurred in the late Neoproterozoic or that the surrounding diamonds did not perfectly shield the garnet inclusions from the surrounding mantle prior to the entrainment in their host kimberlite. If in the unlikely event diamonds do not perfectly shield their inclusions from chemical reequilibration with the surrounding mantle, the extremely low concentrations of U and Pb in garnet that should be easily reset by diffusive reequilibriation with any coexisting fluids/melts. Finally, if the garnet age here simply reflects that of its host kimberlite (for any reason), U-Pb dating of garnet inclusions may represent a useful technique for diamond exploration and prospecting. It remains unclear *why* the U-Pb and Sm-Nd systems give conflicting results.

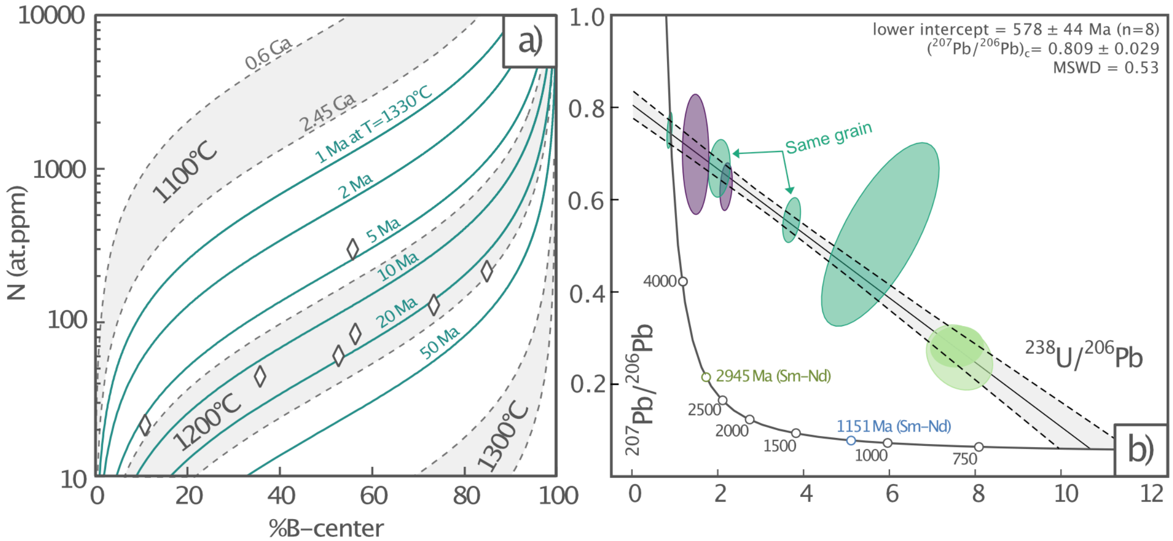

Figure 2: a) Nitrogen aggregation states and residence times for diamonds from Venetia. In green residence times for fixed storage temperature (1330°C) as indicated by Ni-in-grt thermometry. In grey storage temperatures are calculated assuming fixed residence times as indicated from Sm-Nd dating of diamonds from Venetia . b) Tera-Wasserburg concordia of garnet from Venetia diamonds.

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