

Protogenetic clinopyroxene inclusions in diamond and Nd diffusion modeling—Implications for diamond dating

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ABSTRACT

Diamonds are witnesses of processes that have operated in Earth's mantle over more than 3 b.y. Essential to our understanding of these processes is the determination of diamond crystallization ages. These cannot be directly determined on diamond, but they can be calculated using radiogenic isotopic systematics of suitable minerals included in a diamond. This method relies on the assumption that the mineral inclusions were in isotopic equilibrium with the diamond-forming medium. We evaluated the validity of Sm-Nd ages yielded by clinopyroxene inclusions by combining crystallographic orientation analyses and Nd diffusion modeling at the relevant conditions for Earth's cratonic mantle. We investigated the crystallographic orientation relationships (CORs) for 54 clinopyroxene inclusions within 18 diamonds from South Africa and Siberia. Clinopyroxene inclusions in some diamonds showed specific CORs with their hosts, indicating possible syngeneses. Other samples had clusters of clinopyroxene inclusions sharing the same orientation but no specific orientation relative to their hosts, indicating that the inclusions are older than the diamond (i.e., they are protogenetic). Diffusion modeling in the temperature range typical for lithospheric diamonds (900–1400 °C) showed that resetting of the Sm-Nd isotopic system in clinopyroxene grains larger than 0.05 mm requires geologically long interaction with the diamond-forming fluid/melt (>3.5 m.y. at average temperature of ~1150 °C). Depending on inclusion size and temperature regime, protogenetic clinopyroxene inclusions may not fully reequilibrate during diamond-formation events. We suggest that small clinopyroxene inclusions (<0.2 mm) that equilibrated at temperatures higher than 1050–1080 °C may be the most suitable for age determinations.

INTRODUCTION

Diamonds and their inclusions are samples of Earth's interior and provide information about the geological processes that have operated over much of our planet's existence (Howell et al., 2020). The temporal significance of information derived from inclusions in diamonds depends on whether the inclusions and diamonds formed simultaneously (syngeneses) or if the inclusions were entrapped as preexisting grains (protogeneses) during diamond growth and failed to reach isotopic equilibrium upon entrapment. However, even protogenetic mineral grains can yield accurate diamond formation ages if their isotopic composition was re-equilibrated upon inclu-

sion in diamond—these are termed synchronous inclusions (Nestola et al., 2019; Pamato et al., 2021).

Distinguishing between proto- and syngenetic inclusions can be challenging. The traditional proof for syngeneses, apart from epitaxial relationships between inclusion and host (e.g., Jacob et al., 2016), has been the imposition of the diamond's morphology on the inclusion. However, this criterion has been disputed by Nestola et al. (2014), who found evidence of protogeneses for some olivine inclusions with diamond-imposed shape. The argument for protogeneses was the finding of clusters of olivine inclusions that are iso-oriented relative to one another but randomly oriented with respect to the diamond hosts. These clusters were inter-

preted as remnants of original olivine single crystals that were partially dissolved during the formation of the host diamond.

Since these findings, many studies have been carried out to study the crystallographic orientation relationships (CORs) between diamond and its inclusions and explore their significance in terms of syn- versus protogeneses (e.g., Neuser et al., 2015; Milani et al., 2016; Davies et al., 2018; Nimis et al., 2018, 2019; Nestola et al., 2019; Sobolev et al., 2020; Pamato et al., 2021). Clinopyroxenes represent ~12% of all inclusions in lithospheric diamonds (Stachel and Harris, 2008), but a statistically significant COR data set for clinopyroxene inclusions is still lacking.

Knowing the temporal relationships between inclusions and diamonds is crucial for the correct interpretation of diamond ages. These are determined by applying radiogenic isotope systematics to mineral inclusions under the assumption of synchronicity. The most used radiogenic isotope chronometers are Re-Os on sulfides and Sm-Nd on garnet and clinopyroxene (e.g., Richardson et al., 1984, 1990, 1993; Pearson et al., 1998; Koornneef et al., 2017; Timmerman et al., 2017; Gress et al., 2021). If inclusions predate the diamond host, obtaining valid isotopic ages from these protogenetic inclusions requires the inclusions to have reequilibrated isotopically at the time of diamond formation. Diffusive reequilibration is mainly a function of temperature and grain size. Several examples in the literature show that reequilibrated protogenetic inclusions in diamond can indeed yield valid diamond ages (Westerlund et al., 2004; Smit et al., 2016, 2019; Aulbach et al., 2018).

Recent numerical modeling of Os diffusion in sulfides showed that the Re-Os system can

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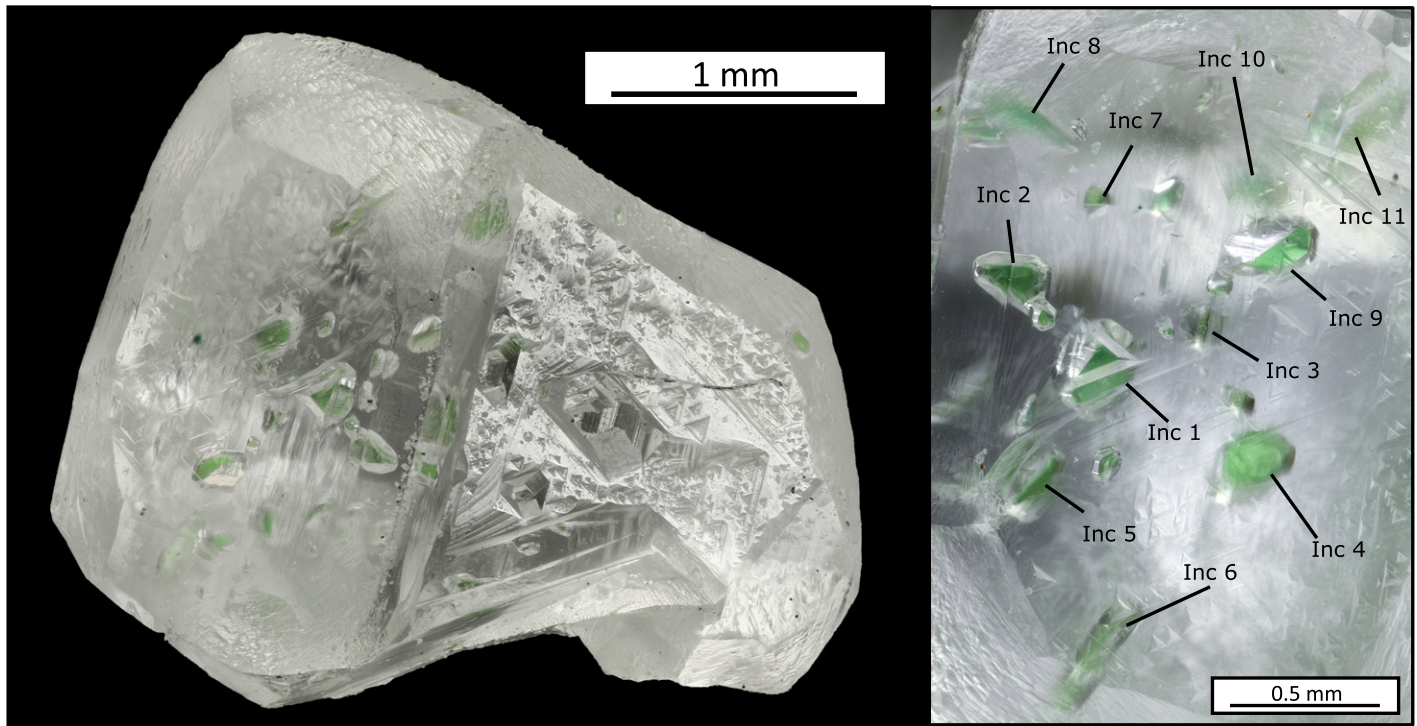


Figure 1. Diamond L22S36 from Voorspoed, South Africa, containing at least 25 optically visible intense green inclusions. Out of all inclusions (Inc), we analyzed 11 clinopyroxene (cpx) inclusions (zoomed-in image on right).

rapidly reequilibrate at the relevant conditions for diamond formation (Pamato et al., 2021). Similar results were also obtained for the Sm-Nd method in protogenetic garnet inclusions, except for uncommon diamond formation conditions, e.g., at low temperature (900–1000 °C), as well as for large inclusion sizes (>0.2 mm) (Nestola et al., 2019). Clinopyroxenes coexisting with garnets in the same diamond host allow a two-mineral Sm-Nd isochron approach, which is likely more accurate than diamond model ages based on one mineral alone (e.g., Richardson, 1986; Richardson et al., 1993; for an extensive review, see Pearson and Shirey, 1999). It is therefore crucial to know whether clinopyroxene inclusions in diamond are protogenetic and, if they are, whether they are likely to have been in diffusive equilibrium with the diamond-forming medium.

We investigated the CORs of 54 clinopyroxene inclusions in 18 diamonds and provide evidence that the inclusions are protogenetic in several cases. Based on diffusion modeling of Nd in clinopyroxene at conditions typical for lithospheric diamonds, we provide boundary conditions for the reliability of the Sm-Nd method on clinopyroxene for dating diamonds.

MATERIAL AND METHODS

The crystallographic orientations of 54 clinopyroxene (cpx) inclusions within 18 diamonds from three kimberlites were studied by single-crystal X-ray diffraction (for details on data col-

lection and processing, see the Supplemental Material¹). More specifically, we studied 46 cpx (8 eclogitic, 27 websteritic, 3 peridotitic/websteritic, and 8 peridotitic) in 13 diamonds (3 eclogitic, 5 websteritic, 2 peridotitic/websteritic, 3 peridotitic) from Voorspoed, South Africa; 5 cpx (3 eclogitic, 2 peridotitic) in 2 diamonds (1 eclogitic, 1 peridotitic) from Cullinan, South Africa; and 3 cpx (1 eclogitic, 2 peridotitic) in 3 diamonds (1 eclogitic, 2 peridotitic) from Udachnaya, Siberian Russia (Table S1 in the Supplemental Material). A representative diamond studied in this work is shown in Figure 1.

RESULTS AND DISCUSSION

Crystallographic Orientations

The relative crystallographic orientations between cpx inclusions and their diamond hosts are shown in Figure 2A. Fourteen (14) out of 54 cpx inclusions (~26%, all from Voorspoed) showed a specific COR, according to the terminology defined by Griffiths et al. (2016) for inclusion-host systems. In particular, for all these inclusions, the cpx (100) and (111) planes coincided within 4° with the diamond (111) and (001) planes, respectively (Fig. 2B; Table S1). More detail about the statistical method we used

¹Supplemental Material. Data for the reciprocal orientations between diamonds/clinopyroxene (cpx) and the Nd diffusion model. Please visit <https://doi.org/10.1130/GEOL.S.19783150> to access the supplemental material, and contact editing@geosociety.org with any questions.

for determining and interpreting these specific CORs is reported in the Supplemental Material.

In all other cases, the cpx showed no special COR with the diamond. Nonetheless, pairs of nearby inclusions located less than 0.5 mm from each other and showing nearly identical orientations (within 4°) were found in diamonds L22S36 and L41S1 from Voorspoed and diamond PR4 from Cullinan (Figs. 1 and 2C). The other inclusions in the same three diamonds were randomly oriented.

The presence of clusters of multiple inclusions with similar crystallographic orientations but unrelated to their hosts may be explained if the diamond-forming fluid/melt forced the selective partial dissolution of mantle minerals, and the remaining portions of a preexisting cpx were encapsulated upon diamond growth. A very similar interpretation was proposed for 12 similar clusters of iso-oriented inclusions in diamonds worldwide (Nestola et al., 2014; Milani et al., 2016; Nestola et al., 2019; Nimis et al., 2019; Pamato et al., 2021), as well as for two iso-oriented cpx grains: one enclosed within and one external to a diamond in a diamondiferous xenolith from Finsch, South Africa (Nestola et al., 2017). The orientation patterns observed for cpx inclusions in diamonds L22S36, L41S1, and PR4 thus support a protogenetic relationship between at least these specific inclusions and their diamond hosts.

Nd Diffusion Model for Clinopyroxene

Dating methods using radiogenic isotope systems record the time of the last diffusive

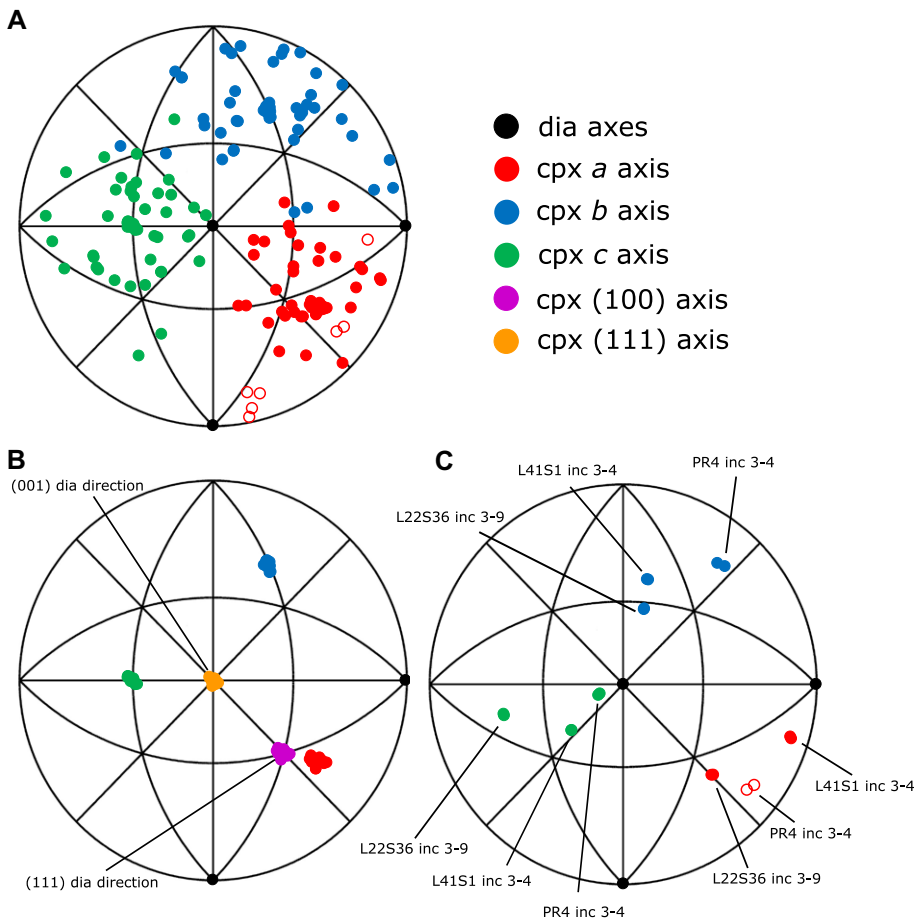


Figure 2. (A) Stereographic projection of all collected clinopyroxene (cpx) inclusions. Empty symbols plot on the lower hemisphere. (B) Stereographic projections for 14 inclusions having specific crystallographic orientation relationships (CORs) with respect to their diamond (dia) hosts. In this case, (100) and (111) cpx directions are coincident (within 4° of angular mismatch) to (111) and (001) diamond directions, respectively. More detail about specifically oriented pairs and the method we applied for their detection may be found in the Supplemental Material (see footnote 1). (C) Stereographic projection of inclusions 3–9 in diamond L22S36 (Fig. 1), inclusions 3–4 in diamond L41S1, and inclusions 3–4 in diamond PR4. These couples show very similar orientations to each other, but they have random CORs with respect to their host diamonds. These stereographic projections were plotted using OrientXplot software (Angel et al., 2015).

equilibration, namely, the point in time when the mineral was effectively isolated from diffusional interaction with its surroundings. This can be achieved by cooling below the system-specific closure temperature (Ganguly and Tirone, 1999), at which diffusive exchange becomes inefficient, and/or when a mineral is entrapped by its diamond host and thus effectively is shielded from further interaction with Earth's mantle. Since diffusional reequilibration rates for a specific element in a mineral grain mainly depend on temperature and grain size, protogenetic minerals may not entirely reequilibrate at the time of diamond formation. Depending on the degree of reequilibration, isochrons and model ages obtained from such protogenetic inclusions can vary from providing no valid time information to presenting significant scatter and high uncertainty on the isotopic age if they experienced partial isotopic reequilibration (Nestola et al., 2019; Pamato et al., 2021).

We modeled the diffusion of Nd in cpx between 800 °C and 1600 °C and 2 and 12 GPa. This range includes the typical pressure-temperature conditions for diamond formation in the cratonic mantle; i.e., 900–1400 °C and 4–7 GPa (Stachel and Harris, 2008). The average diamond formation temperatures were estimated to be 1160 ± 110 °C ($\pm 1\sigma$; $n = 164$) for peridotitic and 1170 ± 110 °C ($n = 144$) for eclogitic diamonds based on geothermobarometry of various types of mineral inclusions in diamonds worldwide (Stachel and Harris, 2008; Stachel and Luth, 2015). Average residence temperatures based on the nitrogen-aggregation state of diamonds were also very similar, i.e., 1146 ± 50 °C ($n = 399$) for peridotitic and 1141 ± 48 °C ($n = 256$) for eclogitic diamonds, assuming a mantle residence of 3 b.y. (Stachel and Harris, 2008). In comparison, diamond formation at temperatures above 1300 °C is very rare for cratonic diamonds, and temperatures above

1400 °C are even rarer, since these temperatures exceed the mantle adiabat (Stachel and Harris, 2008). The typical temperature range for cratonic diamond formation includes temperatures that may be either below or above the closure temperature for the Sm–Nd system in cpx of 1000–1150 °C (Van Orman et al., 2002). At temperatures above the closure temperature, diffusive equilibration is efficient, depending on grain sizes and potential pressure effects, which are small for Nd in cpx (see the Supplemental Material).

Typical grain sizes for inclusions in diamonds are between 0.05 and 0.2 mm, and 0.1 mm is the typical average size, whereas larger grains of ~0.2 mm are rare, and sizes of 0.5 mm are exceptional (Stachel et al., 2005). Modeling results for the diffusivity of Nd in cpx for these grain sizes are shown in Figure 3 (see the Supplemental Material for a detailed description of the diffusion model). For a typical cratonic geotherm of 40 mW m⁻² (Hasterok and Chapman, 2011) (Fig. 3B) and at 1160 °C, a 0.05 mm cpx grain would require reequilibration with the diamond-forming fluid for around 3.5 m.y. to reset the isotopic clock and accurately record the age of diamond formation once included in the diamond. For larger grain sizes, the model predicts ~14 m.y. for 0.1 mm, 56 m.y. for 0.2 mm, and ~350 m.y. for a 0.5 mm inclusion (Fig. 3A).

At higher temperatures, the calculated equilibration times for cpx are shorter. For instance, at 1300–1400 °C (near the upper limit for lithospheric diamond formation), the equilibration times range from tens of thousands of years for a 0.05 mm grain, to hundreds of thousands of years for a 0.1 mm grain, and to a few million years for a 0.5 mm grain. Nevertheless, these times are an order of magnitude longer than for similarly sized garnets (Nestola et al., 2019). At lower temperatures of 900–1000 °C (near the lower end for cratonic diamonds), the equilibration times are significantly longer, ranging from 450 m.y. at 1000 °C to 20 b.y. at 900 °C for even the smallest grain size of 0.05 mm, reflecting the inefficiency of Nd diffusivity at such low temperatures (Van Orman et al., 2002). These time spans are geologically significant or even unrealistic. Therefore, cpx inclusions in diamonds from such temperature regimes are unlikely to yield statistically meaningful isochrons nor valid model ages.

Our model considered the ideal cases of perfectly crystallized cpx grains in diffusional exchange with a rare earth element-rich fluid. In reality, lattice defects in minerals may significantly accelerate diffusion, and partial dissolution/precipitation may further enhance chemical reequilibration. Therefore, the calculated equilibration times should be intended as the maximum possible times required for a specific cpx grain to reset its isotopic clock by

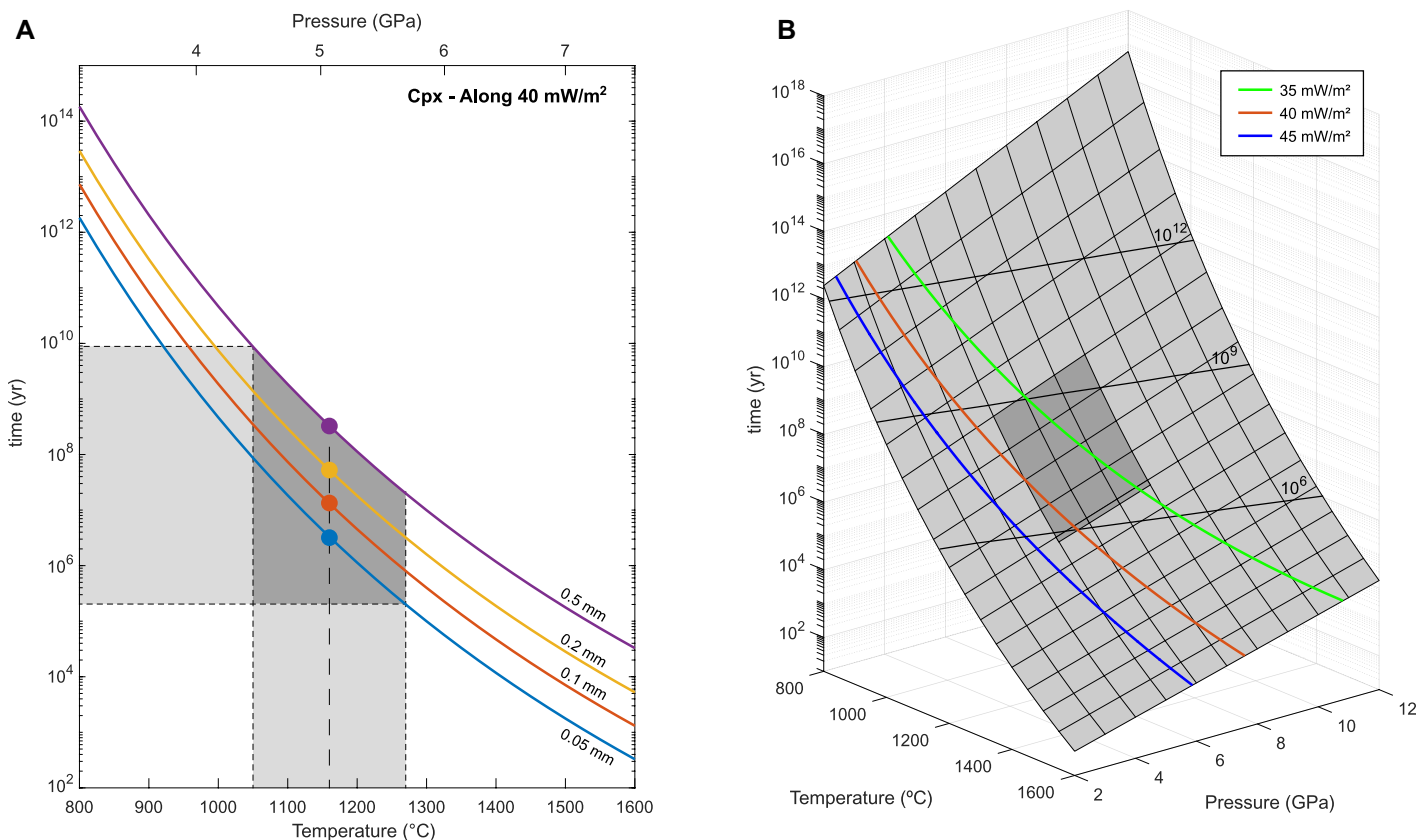


Figure 3. (A) Diffusion model for Nd for diamond-bearing fluid and a defect-free clinopyroxene (cpx) grain along the 40 mW m⁻² cratonic geotherm (from Hasterok and Chapman, 2011). Violet, orange, red, and blue lines indicate equilibrium for 0.5, 0.2, 0.1, and 0.05 mm cpx grains, respectively. (B) Pressure-temperature-time diagram for 0.5 mm cpx grain. Estimated average pressure-temperature conditions for cratonic diamond formation (Stachel and Harris, 2008; Stachel and Luth, 2015) are highlighted by dark gray boxes in A and B.

interaction with the diamond-forming medium, before the grain is fully enclosed in the diamond.

CONCLUSIONS

The closure temperature of the Sm-Nd system in cpx is significantly higher than that in garnet (1000–1150°C versus 750–900°C; Ganguly and Tirone, 1999; Van Orman et al., 2001, 2002) and closer to the average temperature of diamond formation in the cratonic upper mantle (1150°C). The time spans required for efficient isotopic equilibration of a protogenetic cpx with the diamond-forming fluid before encapsulation in the diamond host (namely, during any specific diamond growth episode) are orders of magnitude longer for cpx than for garnet, depending on the grain size. While our diffusion model used ideal scenarios, it did place realistic limits on the suitability of cpx inclusions to date their host diamonds. It raises awareness to the fact that, when dealing with protogenetic grains, cpx may be a less reliable timekeeper for diamond formation than garnet. More generally, among the most widely used methods for dating diamonds, Re-Os dating of sulfide inclusions stands out for being least affected by the proto- versus syngenetic nature of the inclusions (e.g., Smit et al., 2016, 2019; Aulbach et al., 2018; Pamato et al.,

2021), whereas Sm-Nd dating of cpx inclusions appears to be the least robust to inclusion-host timing relationships. Therefore, careful selection of suitable cpx samples (i.e., small grain size and/or higher equilibration temperatures) would always be desirable. Single-cpx thermometry of peridotitic cpx (Nimis and Taylor, 2000) may help to discard excessively low-temperature samples in advance of isotopic analyses.

ACKNOWLEDGMENTS

We thank the European Research Council for support provided to F. Nestola (grant 307322) and the European Union's Horizon 2020 research for support to M.G. Pamato (Marie Skłodowska-Curie grant 796755). D.E. Jacob was supported by the Australian Research Council (CE110001017). We thank Matteo Chinellato for the photos in Figure 1. An anonymous reviewer, S. Mikhail, and particularly K. Smit are also thanked for constructive comments that strongly improved this work.

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