

# Protogenetic sulfide inclusions in diamonds date the diamond formation event using Re-Os isotopes

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## ABSTRACT

Sulfides are the most abundant inclusions in diamonds and a key tool for dating diamond formation via Re-Os isotopic analyses. The manner in which fluids invade the continental lithospheric mantle and the time scale at which they equilibrate with preexisting (protogenetic) sulfides are poorly understood yet essential factors to understanding diamond formation and the validity of isotopic ages. We investigated a suite of sulfide-bearing diamonds from two Canadian cratons to test the robustness of Re-Os in sulfide for dating diamond formation. Single-crystal X-ray diffraction (XRD) allowed determination of the original monosulfide solid-solution (Mss) composition stable in the mantle, indicating subsolidus conditions of encapsulation, and providing crystallographic evidence supporting a protogenetic origin of the inclusions. The results, coupled with a diffusion model, indicate Re-Os isotope equilibration is sufficiently fast in sulfide inclusions with typical grain size, at mantle temperatures, for the system to be reset by the diamond-forming event. This confirms that even if protogenetic, the Re-Os isochrons defined by these minerals likely reflect the ages of diamond formation, and this result highlights the power of this system to date the timing of fluid migration in mantle lithosphere.

## INTRODUCTION

Diamonds, forming at depths up to ~700 km, provide us with unique probes to investigate the evolution of Earth's otherwise inaccessible mantle (Shirey et al., 2013). To place this information in the correct time context, it is crucial to determine their age and crystallization environment. Diamond age determinations are based upon their entrapped mineral inclusions. Re-Os isotope analysis of sulfides is the most commonly used dating technique (Pearson et al., 1998, 1999; Pearson and Shirey, 1999; Aulbach et al., 2009, 2018; Wiggers de Vries et al., 2013; Harvey et al., 2016).

An important aspect to consider in dating diamonds is whether the mineral inclusions formed at the same time as the diamond (syngenetic), as assumed by early studies (Harris, 1968), or whether the diamonds enclosed pre-

existing mineral grains (protogenetic) (Thomasot et al., 2009; Nestola et al., 2014, 2017). For example, garnet inclusions in diamonds from the main diamond-producing cratonic areas have been recently determined to be protogenetic, based on crystallographic relations (Nestola et al., 2019). However, despite being protogenetic, the majority of radiometric ages based on garnets have been shown to effectively correspond to the time of diamond formation, provided certain conditions are met (Nestola et al., 2019). Thus, inclusions and diamond hosts can be synchronous even if not syngenetic (Nestola et al., 2017). As new evidence reveals that the majority of sulfides could be also protogenetic (Thomasot et al., 2009; Jacob et al., 2016), it is necessary to verify whether the most common decay system, <sup>187</sup>Re-<sup>187</sup>Os, is effectively reset by diffusion during encapsulation and therefore provides the correct isochron age of diamond formation.

Sulfides are included into diamond as high-temperature monosulfide solid solution (Mss), exsolving to Fe-, Ni-, and Cu-rich end members during cooling associated with volcanic exhumation (Kullerød et al., 1969). This exsolution causes fractionation of major and trace elements within the inclusions (Richardson et al., 2001), and unless the inclusions can be extracted and studied in their entirety, this process limits the ability to extract accurate isotopic information for geochronology.

To assess whether sulfide inclusions in diamonds are protogenetic, the sulfides must be well characterized *in situ* to understand their original composition and crystallographic relationship with respect to the diamond. We present new results from a set of sulfide inclusions still entrapped in their diamond hosts. By conducting *in situ* X-ray diffraction (XRD) analyses on each inclusion, we determined, for the first time, both the original composition of the Mss inclusions and their crystallographic orientation with respect to the diamond. This knowledge is fundamental to understanding sulfide-host relationships, with implications for the interpretation of Re-Os ages obtained from sulfides. In combination with a diffusion model of Os in sulfides, the new data allowed us to confirm the ability of the Re-Os isotopic system in sulfide inclusions to date diamonds even when they are protogenetic.

## METHODS

Single-crystal XRD measurements were performed using a Rigaku-Oxford Diffraction Supernova diffractometer, equipped with a PILATUS 200 K (DECTRIS) area detector, an X-ray microsource (MoK $\alpha$  wavelength) and operating at 50 kV and 0.8 mA. The sample to

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detector distance was 68 mm (Nestola et al., 2016). Reciprocal crystallographic orientations between sulfide inclusions and diamond hosts were calculated using OrientXplot ([http://www.rossangel.com/text\\_orientxplot.htm](http://www.rossangel.com/text_orientxplot.htm)). See the Supplemental Material<sup>1</sup> for details.

## RESULTS AND DISCUSSION

### Original Mss Composition

Nine diamonds from the Victor kimberlite (Superior craton, Ontario, Canada) and three diamonds from the Jericho kimberlite (Slave craton, Nunavut, Canada), containing a total of 25 sulfide inclusions, were investigated. Six diamonds contained multiple sulfide inclusions, and six specimens had a single inclusion (see the Supplemental Material). Sulfides in peridotite-suitite diamonds from the Victor kimberlite defined a Re-Os isochron of  $718 \pm 49$  Ma, whereas eclogitic diamonds from the Slave craton defined an isochron of  $1.86 \pm 0.19$  Ga (Aulbach et al., 2009, 2018).

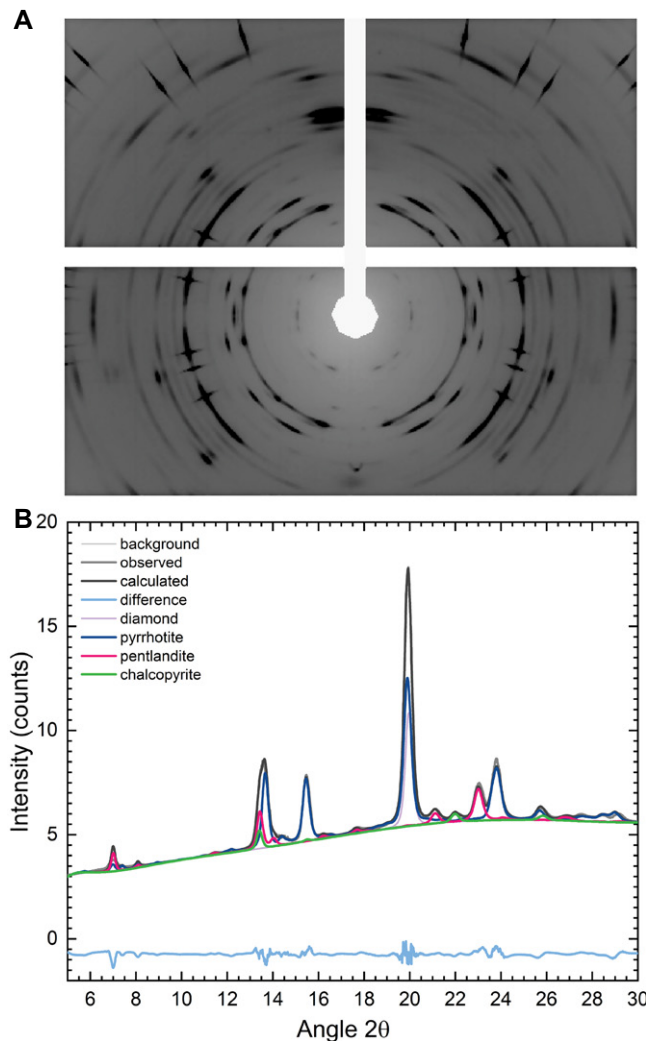
An assemblage of exsolved sulfide minerals is commonly encountered within diamonds (Taylor and Liu, 2009), including in this study (Fig. 1): XRD shows the polycrystalline nature of the sulfide inclusions, dominated by pyrrhotite [Fe<sub>1-x</sub>S] with additional pentlandite [(Fe,Ni)<sub>9</sub>S<sub>8</sub>] and chalcopyrite [CuFeS<sub>2</sub>]. The occurrence of these compositionally distinct phases complicates quantitative reconstruction of the original Mss inclusion.

XRD data collected on single crystals were converted into two-dimensional powder patterns to perform Rietveld refinements of the polycrystalline assemblage diffraction pattern (Fig. 1) to quantify the relative amounts of each phase. Different inclusions showed similar phase proportions of chalcopyrite, pentlandite, and pyrrhotite, with two exceptions where pentlandite or chalcopyrite was not detectable. From the relative abundances and chemical formulae of the individual phases, the original compositions of the Mss were derived (see the Supplemental Material). These accurately reconstructed, original Mss compositions are key features for interpreting the state of the sulfide inclusions at the time of incorporation into the diamond.

### Crystallographic Evidence for Protogenesis

Among all inclusions investigated, 17 contained pyrrhotite as single crystals, allowing us to investigate the crystallographic orientation relationships (CORs) with respect to their diamond hosts (Milani et al., 2016; Nimis et al., 2019).

<sup>1</sup>Supplemental Material. Description of Rietveld refinements and composition of the Mss, reciprocal crystallographic orientations and Os diffusion model, unit-cell parameters of pyrrhotite single crystals, and orientation matrices for both inclusions and hosts. Please visit <https://doi.org/10.1130/GEOL.S.14347016> to access the supplemental material, and contact editing@geosociety.org with any questions.

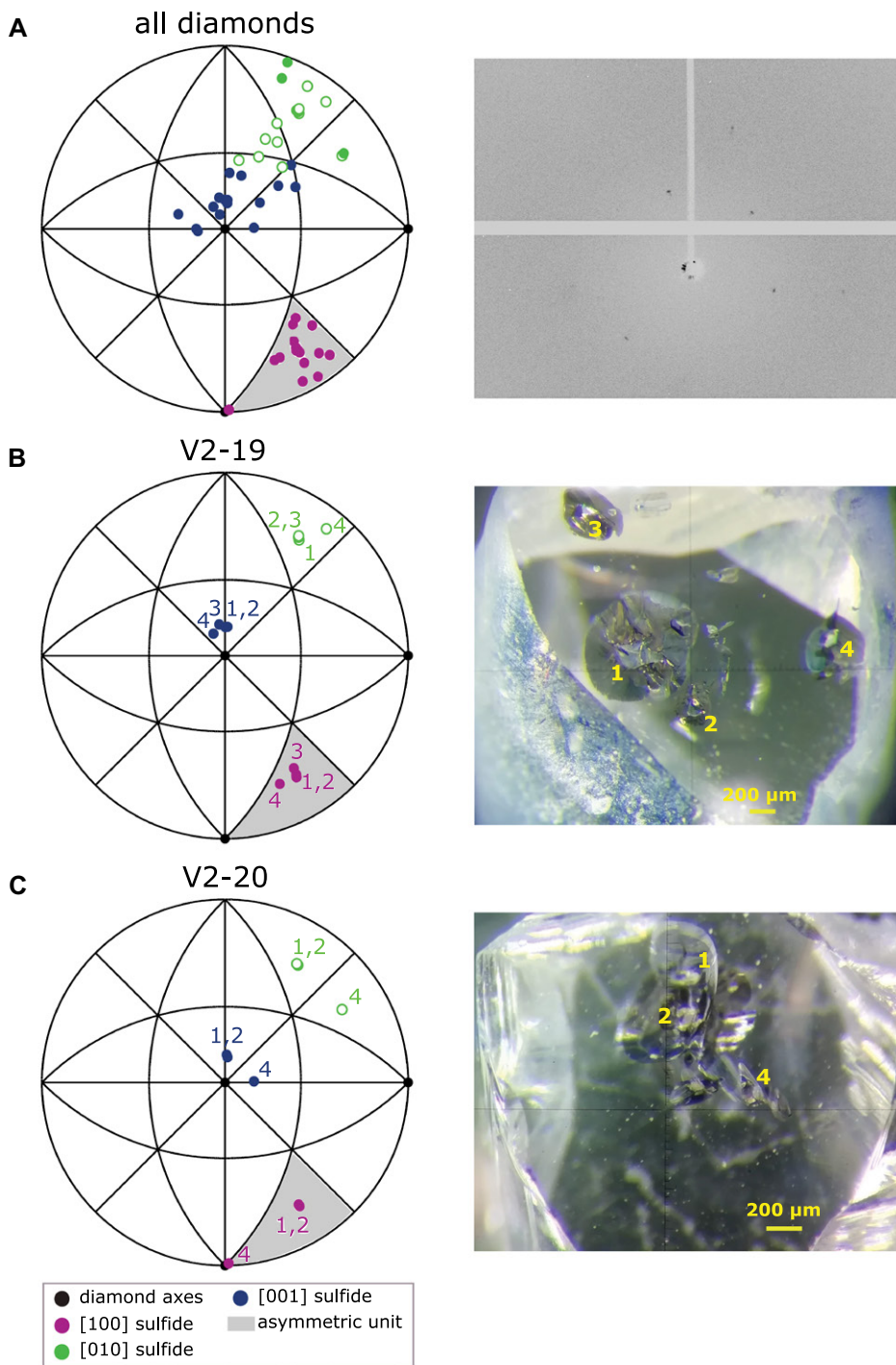


**Figure 1.** (A) X-ray diffraction (XRD) image showing the polycrystalline nature (diffraction rings) of inclusion V2–17 from Victor Mine (Ontario, Canada). (B) Reconstructed powder diffraction pattern revealing the presence of exsolved pyrrhotite, pentlandite, and chalcopyrite.

Importantly, 14 of the 17 sulfide inclusions had random CORs, while just three had a specific COR characterized by one crystallographic axis coincident with one of its host (Fig. 2A). The general lack of correlation indicates the absence of crystal growth control between the diamond and inclusions, implying two scenarios: (1) pyrrhotite was protogenetic with respect to the diamond, with very low adhesion energy between each face of the inclusion and the host; or (2) pyrrhotite was syngenetic with the diamond, but the adhesion energy between each face of pyrrhotite and the diamond was high and identical, allowing syngenetic growth without developing any specific CORs. For olivine inclusions in diamonds, where the results are applicable to other silicates, the adhesion energies are close to zero regardless of the orientation (Bruno et al., 2016). Adhesion energy data confirming protogeneity are unavailable for pyrrhotite-diamond.

Conversely, crystallographic systematics observed in diamonds with multiple sulfides suggest a protogenetic scenario. In sample V2–19 (Fig. 2B), inclusions 1, 2, and 3 were spatially clustered with similar orientation, whereas inclusion 4 was displaced, indicating

a different orientation. The inclusions, however, showed random COR with respect to the diamond. Similarly, in sample V2–20 (Fig. 2C), inclusions 1 and 2 were clustered, showing similar crystallographic orientations, but random with respect to the diamond. Inclusion 4 showed a specific COR with respect to the host (one axis coincident) but different orientation with respect to inclusions 1 and 2. In the other diamonds with multiple inclusions, sulfides showed no specific orientations. The iso-orientation of multiple inclusions showing no epitaxial relationship with the diamond can only be explained if the inclusions are remnant portions of single preexisting grains, as interpreted for other inclusions in diamonds (e.g., Nestola et al., 2019). Therefore, we only state with certainty that sulfide inclusions in two diamonds (V2–19, V2–20) are protogenetic, but a similar origin is likely for many if not all other inclusions investigated. This is supported by the recognition of mass-independent S isotope fractionations in sulfides included in diamonds and by the presence of plastic deformation only in the inclusion and not in the diamond (Thomassot et al., 2009; Jacob et al., 2016).



**Figure 2.** (A) Stereographic projection of all inclusions where pyrrhotite was detected as a single crystal (diffraction spots on the right). Empty dots are directions plotting in the lower hemisphere. (B) Stereographic projections (left) of four sulfides in sample V2-19 (from Victor Mine, Ontario, Canada) (right) where inclusions 1, 2, and 3 are iso-oriented. Inclusion 4 (~1.4 mm from other inclusions) shows different orientation. (C) Stereographic projections (left) of three sulfides in V2-20 (right) where inclusions 1 and 2 (0.16 mm apart) are iso-oriented but have random crystallographic orientation relationships (CORs) with respect to diamond, while inclusion 4 shows specific COR (a axes coincident).

High-pressure experiments suggest Mss is typically subsolidus in the subcratonic lithosphere under conditions relevant for diamond formation (Bockrath et al., 2004; Zhang and Hirschmann, 2016). However, the sulfide solidus can be depressed by up to ~80 °C for carbon-

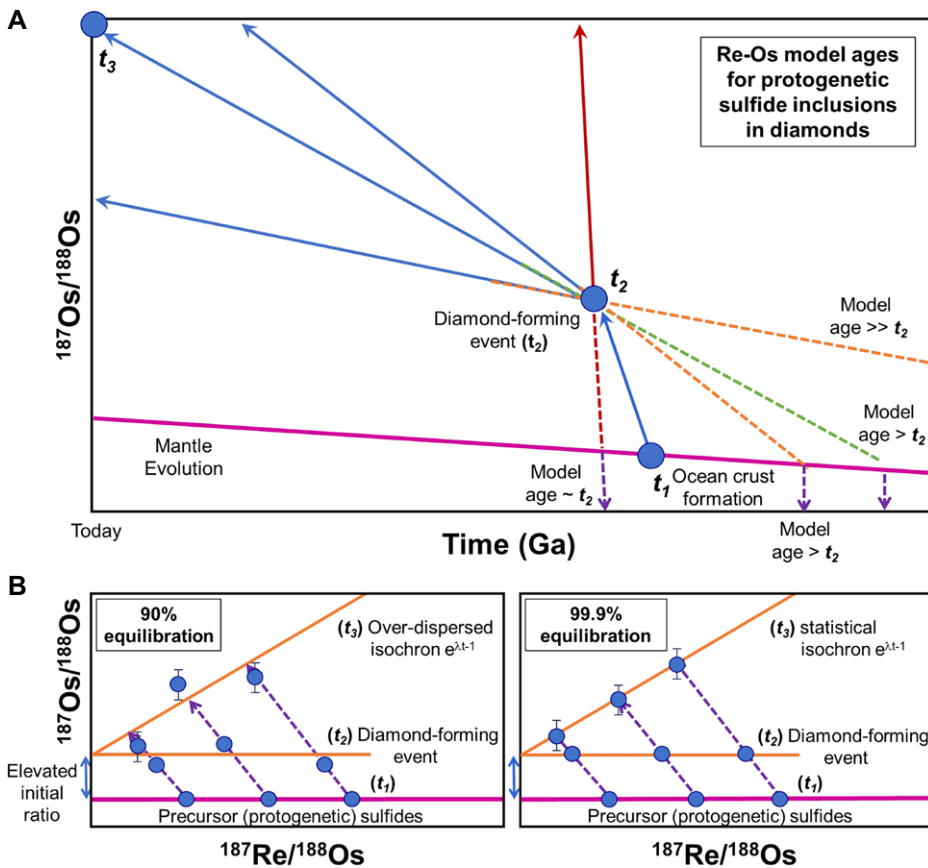
bearing sulfides and is depressed even further with increasing metal/sulfide ratio and oxygen contents (Ballhaus et al., 2006; Zhang et al., 2015). The depressed carbon-bearing solidus intersects the hot end of the pressure-temperature (*P-T*) field of diamond inclusions (Zhang

et al., 2015), suggesting that some sulfides could have been molten at the time of their encapsulation and thus are truly syngenetic (Spetsius et al., 2002). However, inclusion-based geothermobarometry indicates formation of Victor kimberlite diamonds at  $180 \pm 6$  km and temperatures of  $1129 \pm 16$  °C (Stachel et al., 2018), well below the solidus of Mss (Zhang et al., 2015). Similar *P-T* conditions have been determined for the formation of Jericho kimberlite diamonds (De Stefano et al., 2009). The accurate bulk composition of the Mss determined here allows us to estimate their likely solidus temperature. Hence, formation conditions for Victor and Jericho diamonds and the compositions of the Mss support our findings from the COR results showing that the sulfide inclusions were encapsulated in diamonds as solid grains and are therefore prothegenetic.

### True Age of Diamonds

One of the fundamental prerequisites for the Re-Os decay system to reliably record the age of diamond formation is that, for a volume of diamond substrate affected by a particular datable diamond-forming event, the inclusion minerals attained chemical diffusive equilibrium with the diamond-forming fluid before their encapsulation. While this is evident for syngenetic inclusions, it is not a given for prothegenetic minerals. Depending on grain size, temperature, specific diffusivities, and the presence of fluids/melts, prothegenetic inclusions could potentially retain older model ages that are unrelated to the formation of their diamond host (Thomassot et al., 2009), and failure to re-equilibrate preexisting grains would seriously disrupt isochron systematics. Most sulfides take in very large amounts of initial, “common” Os from their environment, which becomes integrated with the “radiogenic” Os produced after system closure through diamond encapsulation. In fact, even if a sulfide is “reset” during diamond crystallization, if it has experienced significant prehistory, for instance, via derivation from old subducted oceanic crust carrying radiogenic Os, then a model age is unlikely to reflect the diamond crystallization age when calculated with reference to a model evolution line for the typical mantle (Fig. 3A). This was discussed by Aulbach et al. (2018) in relation to their isochron versus model ages determined for Victor kimberlite diamonds and is well illustrated by other studies (e.g., Smit et al., 2016). The “gold-standard” for diamond inclusion dating is the isochron approach, which itself requires proof of the relation between all data points on the isochron. Diffusive re-equilibration with the diamond-forming fluid environment is one of the critical requirements for each sulfide being regressed on the isochron (Fig. 3B).

We modeled chemical diffusive equilibration between a prothegenetic pyrrhotite grain (0.1–0.4 mm diameter, the common size of eclogitic



**Figure 3. (A) Model age evolution diagram for sulfide within subducting oceanic crust that was extracted from the mantle at time  $t_1$ . Diamond forms shortly after subduction ( $t_2$ : when Os isotopes are reset). Re/Os (reflected in slope of blue evolution lines) may or may not be fractionated at this stage, and evolution continues until time of measurement at  $t_3$ . Calculated model age from this evolution (intersection of green dashed line with mantle evolution curve) and all other Re/Os fractionations (orange dashed lines projected to model age) will fail to reflect the age of the diamond-forming event at  $t_2$ . Only in rare circumstance where a diamond-forming event dramatically increases the Re/Os ratio of a sulfide inclusion (red line) will it be likely to yield a model age (red dashed line projected) close to  $t_2$ . In suites of diamonds, multiple sulfides would be represented on the diagram. (B) Isochron diagrams representing different degrees of chemical diffusive equilibration (90% and 99.9%), showing that with increasing equilibration, statistical quality of the isochron increases (decreased scatter of data points around the isochron) because of a closer adherence to the “uniform initial ratio” required to produce a statistically perfect isochron.**

sulfide inclusions in diamonds, with P-type sulfides generally being <0.2 mm) and a fluid/melt as a function of temperature (Fig. 4A) using available diffusivity data for Os (Brenan et al., 2000). Many lines of evidence point toward a critical role of fluids or melts in diamond formation, and Os and Re concentrations in these media vary strongly (Pearson et al., 1995). Our calculations show that chemical equilibration is achieved in a matter of hours and days for sulfides between 0.1 and 0.4 mm, respectively, at 1150 °C (Fig. 4A). In the absence of a published pressure term for the diffusion coefficient, these model calculations can be projected onto the  $P$ - $T$  field for diamond inclusions (Fig. 4B; Zhang et al., 2015), allowing us to bracket the fastest and slowest equilibration times between ~10 min for a 0.1 mm grain at 1380 °C and 7 GPa and ~1 month for a 0.4 mm grain at 950 °C and 4 GPa.

These results show that Os exchange in sulfides is very rapid, implying that even in protogenetic sulfides, diamond formation is likely to be reflected by Re-Os isochrons due to resetting—an observation supported by the isochronous relationship in Victor Mine samples (Aulbach et al., 2018). The typically observed statistical scatter on isochron regressions for sulfide inclusions (Fig. 3B), including that for Victor Mine samples, may relate to a combination of incomplete equilibration together with small-scale heterogeneity in the diamond-forming fluid (Aulbach et al., 2018). We conclude that while many sulfide inclusions in diamonds are likely to be protogenetic, diffusional equilibration during the diamond-forming event was likely rapid enough to generate isochronous relationships, with the degree of statistical dispersion dictated, in part, by incomplete re-equilibration. Furthermore, our results show that the rapid Os equilibration times

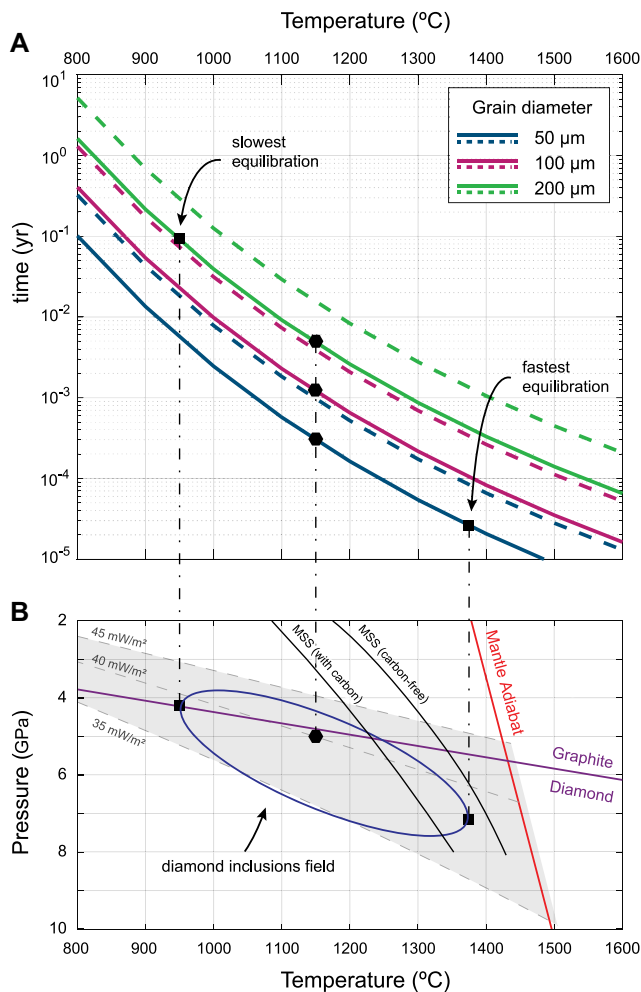
for fluid-sulfide interaction at mantle temperatures provide a way to constrain the timing and scale of fluid migration in mantle rocks at 100–200 km depths, far beyond conditions for fluid processes during metamorphism in crustal rocks.

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**Figure 4. (A) Chemical diffusive equilibration (90% solid lines and 99.9% dashed lines) for Os between defect-free pyrrhotite grains of different sizes and diamond-fluid, as a function of temperature. (B) Pressure-temperature (P-T) diagram for diamond inclusions in Earth's mantle (modified after Zhang et al., 2015) showing that sulfide inclusions are typically subsolidus (note monosulfide solid-solution [Mss] solid). Black dashed lines project example spots from the diffusion model in A to pressures within the diamond inclusion field in B.**

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