Understanding diamond-forming liquids and parental lithology using Fe, Mg, and K isotopes

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Introduction

Recent decades of diamond inclusion research have significantly advanced our understanding of the origin of diamonds within the Earth’s mantle. Diamonds are predominantly sourced from the lithospheric mantle but sometimes sample as deep as the top of the lower mantle. Those from the lithospheric mantle can be further divided into peridotitic and eclogitic in origin, distinguished by their inclusion chemistry, as well as carbon and nitrogen isotopic compositions (see reviews by Stachel et al., 2022a, b). In contrast, the origins of sublithospheric diamonds are less well understood, partly due to their rarity compared to lithospheric diamonds. There has been, however, growing isotopic evidence for the involvement of subducted materials in the source region of sublithospheric diamonds, such as carbon, boron, oxygen, and iron (e.g. Regier et al., 2020, 2023; Smith et al., 2021; Stachel et al., 2022b).

Precipitation of diamonds in the Earth’s mantle requires the presence of a liquid phase. Being C-O-H, saline, carbonatitic, silicic, or metallic in composition, these liquids were released upon dehydration or partial melting of the parental rocks and migrated through the mantle until they reached carbon saturation due to changes in pressure, temperature, or redox conditions. Subducted slabs that contributed to diamond-forming liquid generation, however, are highly heterogeneous in nature as a consequence of fluid-alteration or metasomatism at shallow depths. Common tools utilized for studying lithospheric diamonds, such as carbon and nitrogen isotopes and trace element chemistry, have their limitations in application. Nitrogen isotopes, for example, are less applicable to sublithospheric diamonds due to their low N concentrations. Whereas trace element compositions can be easily manipulated by small fractions of low-degree melt that are enriched in incompatible elements. On the other hand, non-traditional stable isotope systems, such as Fe, Mg, and K, are powerful tools for tracing sources and processes involved in generating the diamond-forming liquids and diamond precipitation itself. As major elements in the mantle, these elements are also less prone to modifications by small fractions of melts or fluids. Combined with carbon isotopes and trace element chemistry, these tools bring new perspectives to studying diamond-forming liquids and parental lithology.

Development of clean lab chemistry and isotope analyses

Existing procedures for measuring non-traditional stable isotope systems are typically designed for rock samples with tens of milligrams of materials. Adapting these procedures to mineral and fluid inclusions in diamonds require careful measures to: 1) extract the inclusion without introducing significant contamination; 2) minimize blanks of the clean lab chemistry; and 3) increase the sensitivity to measure small quantities of the target element.

We previously developed dedicated procedures for Fe isotope analyses of metallic inclusions in CLIPPIR (Cullinan-like, Large, Inclusion-Poor, Pure, Irregular, and Resorbed) diamonds (Smith et al., 2021). The procedure involves identifying crack-free primitive inclusions using Raman spectroscopy, cleaning the
diamond surface to remove contamination prior to inclusion dissolution, an adaption of micro-column chemistry to scale down the amount of resin and acids used for Fe purification, and efforts to maximize the sensitivity of Fe isotope analyses using the Nu Plasma II multi-collector ICP-MS at Carnegie Science. This procedure allowed us to analyze metallic inclusions with as little as 200 ng Fe.

We recently improved the procedure to allow Fe and Mg isotope analyses of ferropericlase inclusions, the most abundant type of mineral inclusion in sublithospheric diamonds. In particular, 200-400 mesh of AG1-X8 resin to achieve better separation of Fe and Mg than 100-200 mesh, and a synthetic ferropericlase solution was used to verify the chemical procedure and mass spectrometry measurements. This allows us to simultaneously measure the Fe and Mg isotope composition of the same ferropericlase inclusion as small as 500 ng in size.

The sensitivity of Fe isotope analyses is further improved with a Nu Sapphire collision-cell MC-ICP-MS at UCLA. Operated with a collision cell on the low energy path to react away Ar-related interferences, precise analyses of $^{56}\text{Fe}^{54}\text{Fe}$ ratios can be obtained for samples with only 50 ng Fe. The collision cell path of the Sapphire also allows for high-sensitivity isotope analysis of K for fibrous diamonds. Benefited by the use of a powerful green laser at the Hebrew University of Jerusalem, tens of milligram of diamonds can be ablated in a reasonable time to extract fluid inclusions with hundreds of ng K. The ablated material was dissolved in strong acid mixtures, converted to nitric form, and purified for K using Econo-Pac columns loaded with 2 ml AG50W-X8 resin (200-400 mesh) following Moynier et al. (2021). After loading the sample on the column, 15 ml of 0.5 N HNO$_3$ was used to remove the matrix elements and the K fraction of the sample was then collected by eluting another 18 ml 0.5 N HNO$_3$ through the column. The purified K was diluted to 400 ppb in concentration and introduced to the Sapphire using an Aridus III desolvating nebulizer. The two isotopes of K, $^{39}\text{K}$ and $^{41}\text{K}$, were analyzed with a 10$\Omega$ and a 10$^{11}\Omega$ resistor, respectively. Typical sensitivity for $^{39}\text{K}$ was 500 V/ppm with a 50 µL/min nebulizer and 1000 V/ppm with a 100 µL/min nebulizer. The current procedure is capable of analyzing fluid inclusion samples with > 300 ng K.

**A dual-origin for ferropericlase inclusions based on Fe and Mg isotope compositions**

Ferropericlase is by far the most abundant type of inclusions in sublithospheric diamonds (Walter et al., 2022). It is part of the stable mantle assembly below the mantle transition zone, and is therefore typically interpreted as lower mantle in origin. However, experiments have demonstrated the possible formation of ferropericlase in the upper mantle. In addition, ferropericlase inclusions in sublithospheric diamonds show large variations in composition, covering almost the entire range of wustite (FeO) to periclase (MgO) solid solution. The major element variation is also correlated with trace element composition, such as the NiO content. Carbon isotopes of ferropericlases-bearing diamonds, on the other hand, are dominantly mantle-like in composition, which does not provide diagnostic information on the source of compositional variation in ferropericlase inclusions.

Our Fe and Mg isotope analyses of 5 ferropericlase inclusions from Kankan, Guinea (Mg# from 0.85 to 0.88) and 14 inclusions from Juina, Brazil (Mg# from 0.58 to 0.81) show a clear difference between the high Mg# (>0.78) and low-Mg# (<0.78) ferropericlase inclusions. High-Mg ferropericlase inclusions from Kankan and Juina have a narrow range of Fe isotope composition ($\delta^{56}\text{Fe} = 0.00 \pm 0.09\%$; 2 s.d.; n =7) and Mg isotope composition ($\delta^{26}\text{Mg} = -0.24 \pm 0.20\%$; 2 s.d.; n=4) within error of the mantle values. The low Mg# ferropericlases, in contrast, show larger isotopic variations in both Fe ($\delta^{56}\text{Fe} = 0.09 \pm 0.28\%$; 2 s.d.; n=10) and Mg ($\delta^{26}\text{Mg} = -0.48 \pm 0.70\%$; 2 s.d.; n=10) and a skew toward the heavy and light values, respectively.

The mantle-like Mg and Fe isotopic compositions of the high Mg# ferropericlases, along with their major and trace element composition, are consistent with a meta-peridotite protolith from the slab mantle not significantly mixed with recycled crustal materials. This is also consistent with a recent crystallographic
orientation relationship (COR) study of ferropericlase inclusions from Juina and Kankan diamonds that found random COR between high Mg# ferropericlase inclusions and their host diamond lattice, suggesting a protogenetic origin of the high Mg# ferropericlase (Lorenzon et al., 2023). The low Mg# ferropericlase inclusions with larger variations of Fe and Mg isotope compositions have to be formed by a different process. The isotopic fractionation in Fe and Mg relative to the mantle composition has to be a partially preserved signature of the subducted slab or the consequences of diamond-forming liquid formation or diamond precipitation. In particular, the hint of heavy Fe might be related to the magnetite/awaruite source phases forming the metallic liquid in CLIPPIR diamonds (Smith et al., 2021). While the light Mg composition is typically a signature of carbonates or metasomatic fluids in the peridotite mantle (Teng, 2017; Xiong et al., 2024).

Source of silicic fluid inclusions in fibrous diamonds from Koidu based on K isotope analyses
Our K isotope analyses of silicic fluid inclusions in 8 fibrous diamonds from Koidu showed consistently light K isotope compositions of -0.8 to -1.1‰, significantly lighter than the BSE value of -0.42‰. The light K isotope composition of the silicic fluid inclusions from Koidu disputes their possible source of K from seawater, which is expected to have a heavy K isotope composition of +0.1‰. Instead, the light K isotope composition of the Koidu fibrous diamonds is most consistent with an origin from dehydration of subducted eclogite rocks, which became gradually light in K isotope composition due to episodes of fluid loss that preferentially removed the heavy isotopes of K.

References