

Trace element characteristics of diamond and garnet inclusions from Akwatia, Ghana and De Beers Pool, South Africa

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Summary

REE patterns determined for gem quality diamonds are less fractionated (average $Nd_N/Yb_N = 6.8$) than fluids/melts (average $Nd_N/Yb_N = 518$) modeled from garnet inclusions in the same diamonds. This disparity indicates that the trace element impurities measured in gem diamond likely do not represent the (diluted) composition of diamond precipitating fluids/melts. Microinclusions of minerals that preferentially incorporate HREE over LREE could, however, account for the fairly flat REE_N patterns observed in gem diamonds.

Introduction

The direct investigation of the genesis of monocrystalline gem quality diamonds in the Earth's mantle has been impeded by analytical limitations. Other than nitrogen, most elemental impurities are usually too low to be detected using conventional methods. Researchers, therefore, have relied on a proxy approach by studying mineral (silicate, oxide and sulfide) inclusions to extract information about the formation conditions of the host diamonds. The underlying assumption is that inclusion and host are coeval (syngensis) and hence document the same growth environment.

New analytical protocols with dramatically lowered limits of quantification (McNeill et al., 2009) have now resulted in the ability to analyze gem quality diamond using inductively coupled plasma mass spectrometry (ICP-MS). For this study, we analyzed 10 gem diamonds to test the relationship between the trace element composition of the diamonds and their microscopic (200-100 μm) garnet inclusions. The garnet inclusions were liberated and analyzed in previous studies (Banas et al., 2009; Stachel and Harris, 1997; Phillips et al., 2004). Elemental impurities other than nitrogen (which substitutes for C in the diamond lattice) have previously been interpreted as fluid/melt inclusions captured during the diamond-growth process (Fesq et al., 1973) and thus may represent the composition of the diamond precipitating agent itself. This implies, however, that the incorporation on nanometer sized melt/fluid inclusions is not associated with fractionation processes (Waychunas and Zhang, 2008) related to large surface/volume ratios. Alternatively, the elemental impurities could be interstitial substitutions related to defect structures in diamond lattice or reflect submicroscopic mineral inclusions which again would imply that trace element concentrations would be fractionated relative to the diamond forming melt/fluid.

Samples and methodologies

Seven harzburgitic and three lherzolitic diamond fragments from Akwatia, Ghana and the De Beers Pool kimberlites, South Africa were analyzed using an off-line ICP-MS method. Individual

samples weighed between 1mg and 4mg. The analytical method was developed by McNeill et al. (2009) at Durham University, UK and employs a closed-system laser ablation cell. Diamond ablation products were subsequently leached from the cell and analyzed using sector-field ICP-MS. Twenty-two refractory lithophile elements (RLE), Cs and Rb were measured and only those concentrations above the limit of quantification (10σ above background) are reported.

To compare the trace element patterns of garnet inclusions and their diamond hosts, we converted garnet trace element concentrations to a model fluid/melt composition. Partition coefficients experimentally determined by Johnson (1998) for garnet synthesized in Kilauea basalts at 3GPa were used to model the fluid/melt in equilibrium with each garnet. Although only nine of the analyzed rare earth elements (REE) are represented by this model, it is sufficient to identify overall trends in the CI normalized patterns. Specifically, the Nd_N/Yb_N ratio was used as a proxy for $LREE_N/HREE_N$ ratios to quantitatively compare the slopes of diamond and model melt REE_N patterns.

Results

Absolute REE concentrations in the diamonds are very low, in the parts per trillion (ppt) range. REE patterns for nine of the ten samples show modest enrichment of $LREE_N$ over $HREE_N$ (average $Nb_N/Yb_N=6.8$). High field strength elements (HFSE_N) show greater agreement in their inter-element fractionation than the REE_N .

The modeled fluids/melts in equilibrium with inclusion garnets show much higher $LREE_N/HREE_N$ ratios than their host diamonds. For Ghana, the average Nd_N/Yb_N ratio for diamond is 8.1 as opposed to 53 for the modeled fluids/melts. The De Beers Pool samples show even greater disparity: Average Nd_N/Yb_N in the diamonds is 5.4, for the modeled fluids/melts this ratio is 798.

Discussion

Based on the observations above it is clear that the elemental impurities in the diamonds we have analyzed do not directly reflect fluids/melts in equilibrium with associated garnet inclusions. Furthermore, the only geological melts with similar inter-element REE fractionation to those shown by the diamond are all large degree, shallow melts generated in conditions far removed from any likely diamond-forming environment. Metasomatic fluids that are associated with ancient cratonic regions are characterized by high $LREE_N/HREE_N$, for instance in fluid inclusion from fibrous diamond (Schrauder et al., 1996; Tomlinson et al., 2009; Fesq et al., 1973) or carbonatitic melts that metasomatise some peridotite xenoliths. Hence, it appears reasonable to anticipate that the fluids/melts that precipitate gem diamonds should also have high $LREE_N/HREE_N$. This is clearly not reflected by the REE systematics of the diamonds analyzed in this study. This leads us to conclude that the elemental impurities in gem diamonds from Ghana and De Beers Pool are unlikely to directly reflect the diamond precipitating fluids/melts. Trace element fractionation must have occurred during the incorporation of solid impurities into the gem diamonds. Alternatively, extensive fractionation of a LREE enriched phase may have lowered LREE in the fluid, prior to diamond growth. As there is no evidence of this from any other record of diamond fluid compositions, the latter explanation seems unlikely.

To test if the diamond patterns could be consistent with the incorporation of mineral nano-inclusions, we calculated Nd and Yb concentrations of possible mantle phases in equilibrium with the observed garnet inclusions. The calculated Nd_N/Yb_N ratios were then compared to the measured Nd_N/Yb_N ratios in the diamonds. The results show that minerals with relative distribution coefficients for $LREE_N/HREE_N$ that are similar to olivine and orthopyroxene could produce the observed Nd_N/Yb_N in the gem diamonds analyzed. The observed REE systematic are not consistent with the incorporation of micro-garnet inclusions despite the presence of visible garnet inclusions within these diamonds. The absolute concentrations of REE within the diamonds, however, indicate that possible mineral nano-inclusion assemblages would need to

be overall more enriched in REE than e.g. simple mixtures of olivine or orthopyroxene (otherwise unreasonable volume percentages of nano-inclusions would be required).

Conclusions

Gem diamonds from Ghana and De Beers Pool show low $LREE_N/HREE_N$ ratios. This observation not only disagrees with the generally high $LREE_N/HREE_N$ of low volume mantle fluids/melts but is also inconsistent with melt compositions directly calculated from coexisting garnet inclusions. Therefore, we suggest that the elemental impurities in the studied gem diamonds are not a direct reflection of diamond precipitating fluids/melts. Trace element fractionation associated with mineral-melt or mineral-fluid partitioning, or with nanoparticle behavior may explain the low $LREE_N/HREE_N$ in diamond. A submicroscopic mineral inclusion assemblage with olivine- or orthopyroxene-like inter-element REE fractionation, but with more elevated concentrations, could account for the observed deviation of gem diamond trace element ratios from modeled fluids/melts.

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