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HIGHLIGHTS AND BREAKTHROUGHS

Sapphire, a not so simple gemstone

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Abstract: Sapphire is a gemstone of considerable reach and is much researched. It still delivers scientific surprises, as exemplified by a recent paper in American Mineralogist that re-interprets the origin of needle-like rutile inclusions that form "silk" in sapphires. Understanding of variations in sapphire genesis continues to expand. **Keywords:** Sapphire, inclusions, trace elements, genesis

Sapphire as a gem variety of corundum has wide use in the gem trade as one of the more historically valuable colored gem stones (CGS) and is mined from a great variety of continental gem deposits across the world. A masterly compendium on this gemstone and its ramifications is recently available (Hughes 2017). As a gem, sapphire ranges through all the colors of corundum, except where sufficient Cr enters its α-alumina crystal structure and causes the red color of the variety ruby. Sapphire, as a key pillar in a wide economic network of gem enhancing treatments, jewelry and other manufacturing enterprises, has elicited numerous scientific and gemological enquiries into its internal nature and natural genesis and subsequent treatments. A further use of sapphire as a synthetic material with a great variety of purposes also has triggered a proliferation of detailed studies on its growth, properties and other element substitutional effects (Dobrovinski et al. 2009). Even with this vast range of studies, this apparently simple gemstone still yields controversies and breakthroughs in understanding its genetic formation. This short essay discusses some recent enlightenments.

A break through in interpreting the inner growth history of sapphires is proposed within this journal (Palke, and Breeding 2017). In a study on sapphires from East Africa, Madagascar, Sri Lanka and East Australia, this duo analyzed microscopic needle–like crystals of the mineral rutile. Such Ti and Fe oxide mineral inclusions are almost ever-present in gem corundum, forming alignments along crystallographic directions within areas of the host crystal. They impart the effect of 'silk' in the corundum and star effects in fashioned stones. Conventional studies in the published literature normally consider such orientated inclusions as ex-solution features that formed as the host crystal cooled from higher temperatures of formation. In contrast, Palke and Breeding from their case study suggest that the rutile needles and corundum form together in a syngenetic epitaxial intergrowth They also 'finger print' the rutile as the phase that mostly accommodates the unexpected enrichments of "unusual" trace elements found in some sapphires, such as Be, rare-earth and noticeably the high-field strength elements (Zr, Nb, Ta, W). This was attributed to both ionic radii mismatch and the large difference in ionic charge compared with Al (III), which made the pentavalent cations more difficult to substitute into the corundum structure.

Several implications arise from syngenetitic rather than exsolution formation of these aligned rutile inclusions. First, host sapphire formation need not need the higher temperatures that favour slow cooling and annealing processes for rutile exsolution. This provides more flexible parameters for interpreting conditions of sapphire-formation in gem deposits. Second, Ti distribution in sapphire in relation to elements such as Mg and Fe can affect blue coloration (Palke and Breeding 2017), an important criteria in natural and treated sapphire valuations. The 'unusual elements" tend to concentrate in inner sapphire regions (Wathanakul et al. 2004; Palke, and Breeding 2017). A stronger blue color appears where "enriched" rutile inclusions are less conspicuous, presumably related to increased Ti-Fe intervalence charge transfer in the corundum structure. This charge transfer mechanism for blue coloration has been challenged, with the color assigned to other ionic effects (Fontana et al. 2008), but its importance has been reinforced (Bristow et al. 2013). The new findings on genesis of element distribution in sapphire, as indicated by Palke and, Breeding, also affect geochemical assignments and geographic typing of sapphires, placing an onus on researchers for more careful analysis in future studies on sapphires. The Palke and Breeding study clearly opens up scope for follow up investigations of gem corundum, particularly in its application to ruby studies.

Chemical characterization of sapphires from different geological settings has strode ahead in the last decade or so, after detailed trace element, oxygen isotope and statistical sorting studies began to provide considerable consistent comparative data. A trace element study of blue sapphires, helped to 'fingerprint" those of magmatic from metamorphic origins (Peucat et al. 2007), oxygen isotope analyses from word-wide corundum samples initiated a base to indicate various mantle and crustal lithologies (Giuliani et al. 2005) and use of lesser trace element values in statistical multivariant analysis of sapphires (Kochelek et al. 2015) can now yield high success rates for sapphire identification to country of origin (~99%) and deposit of origin (98%). Other studies using new approaches now show that the defined boundaries for sapphire origin classification, although generally useful, become unreliable in some cases. Comprehensive studies on Montana sapphires initially suggested that those from the western alluvial deposits and the Yogo Gulch lamprophyre largely gave metamorphic, metasomatic and crustal trace element values and ratios (Zwann et al. 2015). This led to an interpretation that the igneous carriers that brought the sapphires up had tapped a non-magmatic xenocryst source. By analysing minute melt inclusions in these sapphire groups, Palke et al. (2016, 2017) were able to propose an alternative magmatic explanation for their genesis. In this scenario sapphires grew in a melt formed when old anorthsitic/troctolitic slabs at the base of the crust underwent contact with intruding Cenozoic ultamafic/mafic magmas. Hence, the sapphires were magmatic origin in origin but their more unusual trace element values reflected the Al-rich silicate mafic nature of the parent rock rather than compositions of more usual sources.

A further example of magmatic sapphire formation that breaks new ground is a study of exceptional blue sapphire megacrysts found in a Cenozoic alkaline volcanic field, Siebengebirge, Germany (Baldwin et al. 2014; Baldwin 2016). The sapphires show spinel reaction rims with the host alkali basalt suggesting a megacryst origin. However, they contain a highly unusual mineral inclusion suite of Ca-, Mg- carbonates and Nb, Ti, Fe and Th-rich oxides and are exceptionally enriched in parts in HFS elements relative to primitive mantle (up to X 5). The data raise the feasibility of a petrogenetic origin related to carbonatitic magmatism at mantle conditions which was tested in experimental runs. Other breakthroughs include capability of U-Pb age dating of inclusions in high value sapphires (Link, 2016) and versatile analysis for trace element correlations in sapphires (.Wang et al. 2016). All these studies reveal the complexity inherent in sapphire and overviews of its natural formation (Giuliani et al. 2014) will need continuing refinements.

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