DIOPSIDE NEEDLES AS INCLUSIONS IN DEMANTOID GARNET FROM RUSSIA: A RAMAN MICROSCOPIC STUDY

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Straight, acicular, colorless solid inclusions in demantoid garnet from the Ural Mountains of Russia were investigated by laser Raman microspectrometry. These “needles,” which occur in association with “horsetail" inclusions (curved, fibrous chrysotile), were identified as diopside. This study also demonstrated that Raman analysis is a highly sensitive method for distinguishing even between isomorphous mineral inclusions in gems, that is, minerals with similar crystal structures but different chemical compositions.

Studies of the inclusions in demantoid garnet from Russia’s Ural Mountains have focused mainly on the “horsetail” fibers that historically were referred to as byssolite—an obsolete name for fibrous amphibole—in the literature (see, e.g., Gübelin and Koivula, 1986; Webster, 1994). Recent investigations by A. Peretti, however, identified these fibers as chrysotile, a serpentine mineral (Phillips and Talantsev, 1996). Similar horsetail inclusions have been seen in demantoid garnets from Val Malenco, Italy. However, only very few stones from this locality have been cut and have appeared in the gem trade.

In recent years, the historic demantoid deposits have been reworked and new deposits have been uncovered in the Urals. Demantoid garnets recently mined from these Russian deposits have been observed to contain distinctive acicular inclusions (see, e.g., figure 15 of Phillips and Talantsev, 1996), sometimes accompanied by horsetails. The goal of the present study was to identify these acicular inclusions by means of laser Raman microspectrometry.

Although Raman analysis has been used in mineralogical research for many years (see, e.g., Moore et al., 1971; Griffith, 1987), it is a relatively new technique in most gemological laboratories. Nevertheless, several authors have described geological applications of Raman microspectrometry, which is an excellent tool for the nondestructive analysis of inclusions in gemstones (see, e.g., Delé-Dubois et al., 1980; Hänni et al., 1998; Koivula and Elen, 1998).

The Raman-shift effect measured by the instrument is due to the molecular vibrations within a substance during its exposure to an intense monochromatic light source, usually a visible laser (Long, 1977; McMillan and Hofmeister, 1988). Minerals that have

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different crystal structures can be distinguished by different peak positions in their respective Raman spectra (Maestrati, 1989). However, even isomorphous minerals (i.e., those that have similar crystal structures but different chemical compositions) may be distinguished from one another by Raman analysis (see, e.g., Pinet and Smith, 1993, 1994; Mernagh and Hoatson, 1996).

**MATERIALS AND METHODS**

Recently, the author had the opportunity to investigate the inclusions in 11 demantoid garnets from Russia’s Ural Mountains, which were sent to the SSEF Swiss Gemmological Institute for certification. The origin of the samples was determined by SSEF on the basis of their inclusions and chemical compositions. All of the samples were faceted, most as round brilliants. They ranged from 0.55 to 3.06 ct, and from yellowish green to intense green (figure 1). Similar demantoid garnets from Russia have been reported on the market since the mid-1990s (Phillips and Talantsev, 1996; ICA Gazette, 1998).

Each stone was examined with a gemological microscope and darkfield illumination at 10×–50× magnification. The inclusions were analyzed with a Renishaw Raman system, using a 514 nm argon laser and an Olympus gemological microscope at 20× magnification to focus the laser on the inclusion. For each analysis, 20 scans (5 seconds/scan) were accumulated. On the basis of a preliminary computerized identification, the spectra were compared to reference samples to make a positive identification.

**RESULTS**

**Microscopic Investigations.** In all 11 samples, the long, thin, curved chrysotile fibers (horsetails) characteristic of Russian demantoid were present. Three samples also contained colorless acicular inclusions that were accompanied by horsetail inclusions (figure 2). The acicular inclusions showed no specific orientation relative to the garnet structure or to the horsetails. They were characterized by a rhombic cross-section and distinct striations parallel to the long axis (figure 3). In two of the three demantoid

![Figure 1. These demantoid garnets (0.55 to 3.06 ct) from the Ural Mountains of Russia were among those studied for this article. Photo by Henry A. Hänni.](image1)

![Figure 2. When observed with magnification, the straight, colorless diopside needles appeared very different from the curved chrysotile fibers ("horsetails") typically seen in Russian demantoid garnet. Photomicrograph by Henry A. Hänni; magnified 30×.](image2)

![Figure 3. The acicular inclusions, which appeared rhombic in cross-section, revealed striations parallel to the long axis. Photomicrograph by Henry A. Hänni; magnified 50×.](image3)
samples, the acicular inclusions were accompanied by hollow tubes that appeared to have the same shape. Where they reached the surface, these tubes were partly filled with residues of the polishing compound.

**Identification of Inclusions by Raman Analysis.**

The Raman spectra of the acicular inclusions analyzed in the three samples showed only slight differences in peak intensity, due to the anisotropy of the crystal structure (Ostertag, 1996). They were always superimposed over the peaks of the host demantoid (figure 4). A careful subtraction of the spectra (Ostertag, 1996; Hänni et al., 1997) was required to avoid any misinterpretation. When the Raman spectra of the acicular inclusions were compared with the spectra in the digital SSEF Raman library (Hänni et al., 1997), they were identified as diopside (again, see figure 4).

Diopside, a Ca-Mg pyroxene, forms an isomorphous series with hedenbergite (a Ca-Fe pyroxene; Deer et al., 1992). The general patterns of the peak positions in the Raman spectra of diopside and hedenbergite are similar. This is not surprising, as both have the same crystal structure (monoclinic C2/c) and thus have similar vibrational spectra in Raman microspectrometry. However, the two similar structures contain slightly different molecules, which results in slightly higher wavenumbers for diopside than for hedenbergite. Thus, Raman analysis can distinguish between members of an isomorphous series, even if the size of the ions involved in

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**Figure 4.** When a representative Raman spectrum of the acicular inclusions was compared to reference spectra for diopside, hedenbergite, and demantoid garnet, it was evident that the study sample correlated well with diopside (Ca-Mg pyroxene). The peaks that are not labeled correspond to demantoid.
the exchange mechanism (0.72 Å for Mg²⁺ in diopside versus 0.78 Å for Fe²⁺ in hedenbergite) is not significantly different. The literature reveals similar results, for example, for clino- and orthopyroxenes [Mernagh and Hoatson, 1996] and for garnets (see, e.g., for andradite-umarovite-grossular: Pinet and Smith, 1993, for spessartine-almandine-pyrope: Pinet and Smith, 1994).

In the mineralogical literature, Deer et al. [1982] mention the presence of relics of an unspecified pyroxene in demantoid garnet from the western Carpathian Mountains of central Europe. With the current study, however, diopside is identified for the first time as an inclusion in gem-quality demantoid garnet.

**CONCLUSIONS**

Colorless acicular inclusions of diopside were identified in demantoid garnet from Russia’s Ural Mountains. In the samples examined, these colorless acicular inclusions occurred together with classic horse-tail inclusions. Consequently, they may provide further microscopic evidence for the Russian origin of a demantoid garnet.

This study also represents the successful use of Laser Raman microspectrometry in geology to differentiate between isomorphous minerals of the pyroxene group (diopside and hedenbergite), by revealing slight general shifts in the peaks of their respective Raman spectra.

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