Aphthitalite in high-temperature fluid inclusions in quartz from the Eikeren-Skrim granite complex, the Oslo paleorift

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Aphthitalite, $(K, Na)_3Na(SO_4)_2$, occurs as a daughter mineral in magmatically derived fluid inclusions in quartz from the Eikeren-Skrim granite complex in the Oslo paleorift. Laser Raman microspectrometry (LRM) was performed on daughter grains and reference samples of aphthitalite. The identity of the mineral was also checked using energy dispersive X-ray spectra (EDS) from opened fluid inclusions.

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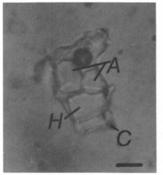
Introduction

Aphthitalite (formerly called glaserite), (K, Na)₃Na (SO₄)₂, has been described both from evaporite sequences and from incrustations on rocks which are spatially associated with fumarole activity (e.g. Palache et al. 1951; Oskarsson 1981; Mötzing 1988). This article describes the common occurrence of aphthitalite as a daughter mineral (e.g. Roedder 1984) in high temperature fluid inclusions in quartz from a mildly peralkaline granite (ekerite; Brøgger 1906).

Occurrence

The quartz samples studied are from the Eikeren–Skrim granite complex in the Oslo paleorift, and have been described by Hansteen (1988) and Hansteen & Burke (1990). Aqueous fluid inclusions containing aphthitalite were formed through entrapment of magmatically derived brines in the temperature interval from ca. 700 to 400° C (Hansteen 1988). Upon cooling, various daughter minerals precipitated. The inclusions with aphthitalite are strong brines saturated with Na⁺, K⁺, Ca²⁺, Cl⁻ and S⁶⁺ (as sulphate) (Hansteen & Burke 1990). Such fluid inclusions are common both in miarolitic and rockforming quartz. Inclusion sizes are $10-80~\mu\text{m}$, and sizes of the aphthitalite grains are $2-30~\mu\text{m}$.

Figure 1 shows two fluid inclusions with aphthitalite, which is recognized by its rounded to equant or short-prismatic shape, its moderate birefringence and a refractive index (RI) higher than the surrounding brine (RI of NaCl \pm KCl \pm CaCl₂ saturated brines have been reported as 1.367 to 1.395; Shepherd et al. 1985). In the studied inclusions, this sulphate always coexists with



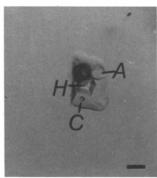


Fig. 1. Photomicrographs of two fluid inclusions containing aphthitalite (A). Other identified minerals are halite (H) and calcite (C). The dark spheres in the inclusions are vapour bubbles. Scale bars are $10~\mu m$. (A) Fluid inclusion containing a twinned, subhedral aphthitalite grain. (B) Fluid inclusion containing a sub to anhedral aphthitalite grain.

halite and calcite, and commonly with sylvite (Hansteen & Burke 1990). Other daughter minerals include one or two opaques and at least one unidentified, colourless grain.

Laser Raman microspectrometry

Laser Raman microspectrometry (LRM) was performed at the Faculty of Earth Sciences, the Free University of Amsterdam, on a Dilor Microdil-28 instrument. In this system, an Ar-laser beam with a wavelength of 514.5 nm is focused inside the inclusion cavity through a microscope objective. The Raman-scattered light is collected at an angle of $\approx 180^{\circ}$ through the same objective, and spectra are recorded by a multichannel detector system. Optical resolution is in the 1 μ m range and is limited by

the diameter of the laster beam (Burke & Lustenhouwer 1987). Spectral resolution is about 3 cm⁻¹.

Analytical results

Aphthitalite was analysed in situ in several fluid inclusions using LRM (Fig. 2). The resulting spectra were compared to spectra obtained from two reference grains of aphthitalite which originate from incrustations on basalt from Vesuvius (grain sizes about 0.5 mm). Figure 2 also shows an energy-dispersive X-ray spectrum (EDS) of an aphthitalite daughter grain from an opened fluid inclusion (from Hansteen & Burke 1990). This and other daughter minerals were located and identified using a JEOL JSM 840 scanning electron microscope fitted with a Link energy-dispersive analyser unit, located at the Department of Geology, University of Oslo.

The most prominent feature in the Raman spectra from aphthitalite in fluid inclusions is a characteristic sulphate peak which occurs in the range 985-996 cm⁻¹ (v₁ band; Ross 1974) (Fig. 2). Depending on crystal orientation, this peak may be replaced by two peaks at 981 and 991 cm⁻¹, respectively (cf. Ross 1974; Bensted 1976). Other characteristic bands occur at 1201-1206, 1084, 626-627, 617-618 and 451-452 cm⁻¹, respectively (Fig. 2). The intensities of these additional bands are strongly dependent on crystal orientation. The 1084 and 451-452 cm⁻¹ peaks occur very close to characteristic bands from the quartz host at 1081-1082 and 462-463 cm⁻¹, respectively, and therefore occur as 'shoulders' on these quartz peaks in Fig. 2.

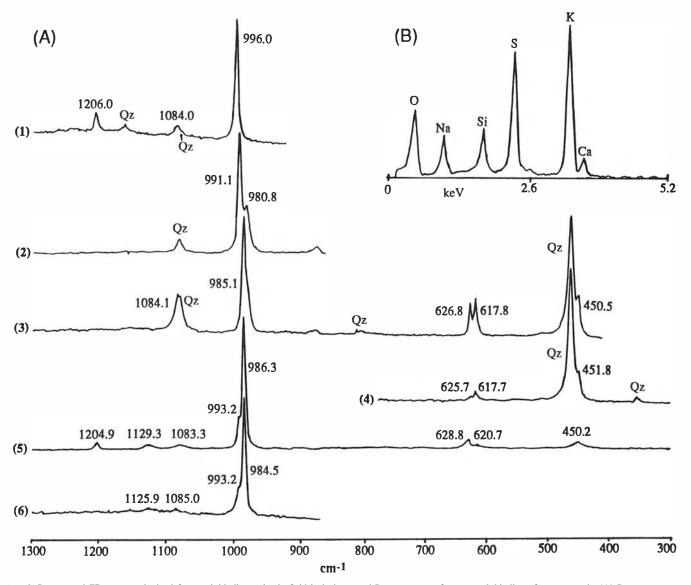


Fig. 2. Raman and ED spectra obtained from aphthitalite grains in fluid inclusions, and Raman spectra from an aphthitalite reference sample. (A) Raman spectra corresponding to different orientations of aphthitalite grains in unopened fluid inclusions (spectra 1 through 4) and of the aphthitalite reference sample (spectra 5 and 6). The horizontal scale is in wave numbers. Identified Raman bands (corresponding to peaks and peak shoulders of aphthitalite in the spectra) are labelled in the figure. Peaks from the host quartz are labelled 'Qz'. (B) EDS from aphthitalite in an opened fluid inclusion, containing prominent peaks for Na, K and S (from Hansteen & Burke 1990). The Si peak is from the host quartz, and the small Ca peak from a neighbouring calcite daughter grain.

The strongest Raman band from the reference specimens occurs at 984-986 cm⁻¹, or as a double peak at 985-986 and 993 cm⁻¹, respectively (Fig. 2). Additional, partly orientation-dependent peaks occur at 1205, 1125-1129, 1083-1085, 629, 621 and 450 cm⁻¹, respectively. This corresponds well with the spectra obtained from aphthitalite in the fluid inclusions, especially when the spectral resolution of about 3 cm⁻¹ is considered. Ross (1974) reports a Raman spectrum for aphthitalite in which the sulphate group v_1 band appears at 991 cm⁻¹. Additional bands occur at 1190, 1109, 621 and 450 cm⁻¹. This agrees only reasonably well with our data. J. Dubessy (pers. comm. 1987) reports a strong 996-997 cm⁻¹ band for aphthitalite, which fits well with our data. EDS from an opened fluid inclusion, containing peaks for Na, K and S (Fig. 2), strengthens the conclusion that the mineral in question is aphthitalite.

Conclusions

The occurrence of aphthitalite as a daughter mineral in high-temperature fluid inclusions was proven through the combined use of LRM and ED X-ray spectra. This shows that the combination of detailed optical microscopy, non-destructuve LRM and scanning electron microscopy provides a powerful tool for identification of daughter phases and trapped minerals grains in fluid inclusions. For LRM, however, the lack of reference spectra for many mineral species often requires that reference specimens are available.

High sulphate contents are expected in fluids derived from alkaline to peralkaline granites (e.g. Burnham 1979; Burnham & Ohmoto 1980). Thus, there are good possibilities for identifying other species of rare sulphate minerals in fluid inclusions from other granites, using the methods described above.

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