Evolution of Mineralizing Fluids of Greisen and Fluorite Veins, Evidence from Fluid Inclusions

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Citation

Abstract
The late-Proterozoic Homrit Waggat granite complex contains Sn-F bearing quartz-muscovite greisen zone as well as fluorite veins. Fluid inclusions study in quartz and fluorite from greisen indicates the same fluid inclusion types. Fluid inclusions trapped in greisenized granite are represented mainly by two-phase (L+V) aqueous and immiscible three-phase (H₂O-CO₂) inclusions which probably trapped from one homogeneous fluid (H₂O-CO₂-NaCl) due to immiscibility process. Two-phase aqueous inclusions (type 1) are represented by three generations (subtype 1a, subtype 1b and subtype 1c). Immiscible three-phase inclusions are conformable and coexisting with the three generations of aqueous inclusions. Based on paragenetic distribution of the inclusions, subtype 1a and subtype 2a are primary, subtype 1b and 2b are pseudosecondary, while subtype 1c and 2c are secondary distributed. Microthermometric results for the first generation (subtypes 1a and 2a) inclusions revealed that the greisenization probably starts at temperature > 330°C. Greisenization as well as cassiterite deposits probably continuous with decreasing temperature (330°C - 270°C) and pressure estimated between 1.4 kb and 0.65 kb. Subtypes 1b and 2b as well as fluorite deposits may be taken place due to dilution at temperature and pressure (260°C - 180°C and 536 - 441 bars). The latest fluid generation is represented by high saline poly-phase, two-phase (subtype 1c) and mono-phase aqueous inclusions. Such coexistence of inclusions is an evidence of boiling. In fluorite veins only primary two-phase aqueous inclusions were observed. The minimum pressures of trapping are between 181 and 212 bars at temperatures between 140°C and 200°C.

1. Introduction

Fluid inclusions form whenever a small volume of fluid is captured in cavities of crystallizing minerals and are virtually the only piece of direct evidence for the pressure, temperature and composition of the mineral-forming fluids. Their study provides important tools for understanding the genesis and genetic type of hydrothermal mineral systems [1, 2, 3]. Fluid inclusions in granites have been extensively studied to give information on ore-forming processes in high-level magmas [4].

Granites with associated mineral deposits usually undergo metasomatic alteration leading to changes in the original texture and mineral composition. These alteration
processes are usually followed by high temperature hydrothermal activities, resulting in the development of mineralized veins as the final stage in the sequence of events controlling the solidification of rare-metal granitic magma and ore-formation [5 - 9]. Homrit Waggat area lies between latitudes 25° 7’ - 25° 12’ N and longitudes 34° 16’ - 34° 22’ E (Fig. 1). In Homrit Waggat granite metasomatic alterations are represented by K-feldspathization (amazonite-bearing marginal pegmatite), albitionization and greisenization [10]. The aim of this paper is the evolution of mineralized hydrothermal fluids and their relation to greisenization and deposition of cassiterite and fluorite mineralizations in the study area.

2. Geological Setting

The Homrit Waggat area comprises a volcano-sedimentary association and a metagabbro-diorite complex intruded by a granodiorite suite, which is in turn intruded by biotite granite and hypersolvus alkali feldspar granite (Fig. 2). The Homrit Waggat pluton displays elongated oval shape bodies in a NW-SE direction (long axis 9 km) separated by Wadi El Faliq. It covers an area of about 50 km² and rises about 1096 m above sea level. The pluton intrudes the metamorphosed volcano-sedimentary association and the metagabbro-diorite complex to the east and north and tonalite-granodiorite suite to the south and northeast (Fig. 2). The studied area is intersected by major sets of faults trending approximately northwest and due north (Fig. 2). The granitic rocks possess a system of jointing well developed in two main sets, trending NE-SW and NW-SE with less dominant N-S trends. These joints are gently to steeply inclined and sometimes are vertical.

Petrographically, the pluton consists of four different
granite phases. Biotite granodiorite forms a wide incomplete zone. It occupies the southern and northeastern parts of the study area. Biotite granite occupies the core of the pluton. It is hard, massive and homogeneous, and contains a few xenoliths of granodiorite with sharp intrusive contact. The third granitic phase is mylonitized granite which forms the northeastern part of the pluton and shows striking features of both brittle and ductile-plastic deformation. Hypersolvus alkali feldspar granite is the latest phase. It makes up the southeastern and western parts of the pluton. The contacts between hypersolvus alkali feldspar granite and both of biotite granite and mylonitized granite are sharp.

Greisen zone up to 30 m² of fine- to medium-grained, greenish-grey granite composed mainly of quartz, muscovite, fluorite and cassiterite (Fig. 3a, b); topaz, zircon and allanite, occurs at the eastern contact between hypersolvus and mylonitized granites. Fluorite veins trending NNW–NW (up to 2 m wide and 30 m long) were recorded close to the contact between biotite granodiorite and mylonitized granite. At the vein contacts, highly altered zone is represented by very friable kaolinitic rock. This zone fades away from the vein passing to the proper granite.

3. Methods of Study

Double-polished wafers 200-300 µm thick were prepared from the greisenized granite and fluorite vein samples. The present study includes the genetic and non-genetic description of fluid inclusions as well as the phase transition (microthermometry). Microthermometry was carried out at fluid inclusion lab., Geology Department, Faculty of Science, Assiut University using a Linkam THMS 600 heating/freezing stage. The stage was calibrated for temperatures between -56.6°C and +400°C using Merck chemical standards, melting point of distilled water (0°C), and phase transition in natural pure CO₂ inclusions with triple point at (-56.6°C). From microthermometric results, the bulk composition and density of the fluids are calculated using equation of state of Zhang and Frantz [12] for H₂O-NaCl system and Brown and Lamb [13] for volatile-rich system. Isochores for different fluid densities are calculated until a fit with the known homogenization temperature is calculated using Flincor computer program [14]. The minimum conditions of trapping are estimated from the constructed P-T diagrams.

4. Fluid Inclusions

Fluid inclusions were investigated in fluorite and quartz from greisenized granite and fluorite veins cutting the Homrit Waggat granites.

4.1. Petrography and Chronology

4.1.1. In Greisenized Granite

Four types of fluid inclusions were detected in fluorite and quartz from greisenized granite samples:

Type (1): Two-phase (L+V) aqueous inclusions. These inclusions are easily recognizable by their clear appearance, and usually present (at room temperature) as two-phase (L+V). According to paragenetic classification of Roedder [1], three generations of fluid inclusions were observed: The first generation (subtype 1a) is distributed either in three dimensions or as individual isolated inclusions (Fig. 4a) as primary inclusions. The second generation (subtype 1b) is distributed in short lines as pseudo-secondary inclusions. The third generation (subtype 1c) is distributed along lines of healing microfractures as secondary inclusions. They show rounded, negative, oval to elongated shapes. The sizes of type 1a and b inclusions range from 10 to 50 µm with vapor phase range from 10 to 25% of the total inclusion volume. The secondary (type 1c) inclusions are characterized by size ranging from 5 to 25 µm.

Type (2): Three-phase immiscible (H₂O - CO₂ L - CO₂ V) inclusions with a wide range of CO₂ content, are paragenetically classified into three generations: primary (subtype 2a), pseudo-secondary (subtype 2b) and secondary (subtype 2c). These generations of inclusions are coexisting with type 1 (three generations) aqueous inclusions (Fig. 4b to 4f). The shape of inclusions is variable from subrounded,
Type (3): Poly-phase (L+V+S) inclusions, these inclusions are distributed along lines and fluid inclusions planes (Fig. 4g). The solid phase is cubic or elongated in shape and the size up to 3 µm. Petrographic investigation indicates that these crystals are probably halite and sylvite.

Type (4): Mono-phase liquid inclusions are associated with subtype 1c (two-phase) aqueous inclusions and type 3 (poly-phase) inclusions.

4.1.2. In Fluorite Veins

In fluorite veins, fluid inclusions are represented mainly by two-phase aqueous inclusions. Three generations of aqueous inclusion were observed. The first and early one, is primary, which is distributed randomly or as isolated groups (Fig. 4h). The second generation is distributed in short lines as pseudo-secondary inclusions. The third and latest generation is secondary distributed along lines and fluid inclusions planes of healing microfractures.

In the first and second generations, the shapes are variable from oval, elongate, triangular, irregular and negative crystals. The sizes range from 10 to 40 µm with regular vapor phase (10–20%) from the total volume of the inclusion. The third generation is smaller in size and generally up to 5 µm.

Fig. 4. Photomicrographs show types, distribution and description of fluid inclusions. (a-h) in fluorite and quartz from greisenized granite. (a) Negative crystal primary distribution of subtype 1a (two-phase) aqueous inclusions. (b to f) Coexistence of type 1 (H$_2$O inclusions) and type 2 (H$_2$O-CO$_2$ inclusions with variable content of CO$_2$) at room temperature. (g) Secondary distribution of type 3 (poly-phase) inclusions with cubic solid phase. (h) Primary distribution of the first generation of fluid inclusions in vein fluorite. L = liquid-H$_2$O, V = vapor-H$_2$O and S = solid.
4.2. Microthermometry

The following table 1 summarizes the microthermometric results.

<table>
<thead>
<tr>
<th>Mineralization Types of fluid inclusions</th>
<th>Sn-F mineralization in greisen</th>
<th>F mineralization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1: Two-phase aqueous inclusions</td>
<td>-50°C to -53°C</td>
<td>-49°C to -53°C</td>
</tr>
<tr>
<td>Te</td>
<td>-0.4°C to -5.1°C</td>
<td>-3°C to -10.5°C</td>
</tr>
<tr>
<td>Salinity in wt.% NaCl eq.</td>
<td>0.71 to 8</td>
<td>4.96 to 14.46</td>
</tr>
<tr>
<td>Tm(Tot)</td>
<td>180°C to 310°C</td>
<td>100°C to 270°C</td>
</tr>
<tr>
<td>Distribution</td>
<td>P, PS</td>
<td>P, PS</td>
</tr>
<tr>
<td>Th(Tot)</td>
<td>120°C to 170°C</td>
<td></td>
</tr>
<tr>
<td>Distribution</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Type 2: Three-phase (H₂O+CO₂) inclusions</td>
<td>Not observed</td>
<td></td>
</tr>
<tr>
<td>Tm(CO₂)</td>
<td>-56°C to -57°C</td>
<td></td>
</tr>
<tr>
<td>Tm(CO₂)</td>
<td>4.5°C to 9.5°C</td>
<td></td>
</tr>
<tr>
<td>Salinity in wt.% NaCl eq.</td>
<td>1.43 to 9.84</td>
<td></td>
</tr>
<tr>
<td>Th(CO₂)</td>
<td>26°C to 31°C</td>
<td>Not observed</td>
</tr>
<tr>
<td>Distribution</td>
<td>P, PS</td>
<td></td>
</tr>
<tr>
<td>Th(Tot)</td>
<td>210°C to 330°C</td>
<td></td>
</tr>
<tr>
<td>Distribution</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Type 3: Poly-phase (L+V+S) inclusions</td>
<td>Not observed</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>125°C to 180°C</td>
<td></td>
</tr>
<tr>
<td>Ts</td>
<td>275°C to 330°C</td>
<td></td>
</tr>
<tr>
<td>Salinity in wt.% NaCl eq.</td>
<td>36.51 to 40.79</td>
<td></td>
</tr>
<tr>
<td>Distribution</td>
<td>S</td>
<td></td>
</tr>
</tbody>
</table>

P: primary, PS: pseudosecondary, S: secondary

4.2.1. In Greisenized Granite

In subtype 1a and subtype 1b (primary and pseudo-secondary aqueous inclusions), the eutectic temperature (Te) was observed in many inclusions at temperatures between -50°C and -53°C. This indicates the presence of CaCl₂ in addition to NaCl dissolved in the aqueous phase [15]. The final melting of ice observed at temperatures between -2°C and -5.1°C, corresponding to salinity ranging from 3.39 to 8 wt.% NaCl eq. with maximum peak at 7 wt.% NaCl eq. (Fig. 5a). The total homogenization temperatures were measured between 180°C and 310°C with two peaks at 240°C and 280°C (Fig. 5b). In subtype 1c (secondary inclusions) the temperatures of final ice melting (Tmice) were measured between -0.4°C to -1.6°C, corresponding to salinity between 0.71 and 2.74 wt.% NaCl eq. Total homogenization were measured at temperatures range from 120°C to 170°C, with the majority at 150°C.

Fig. 5. Histograms show the distribution of salinity and homogenization temperatures for fluid inclusions in the greisenized granite.

In type (2), three-phase immiscible (H₂O + CO₂ (L+V)), the melting temperature of solid CO₂ was measured at temperatures between -57°C and -56°C, very near to the triple point of pure CO₂. The temperatures of last clathrate melting (Tm_clath) can give an estimate of the salinity [16, 17]. Clathrate melting were measured at temperatures between 4.5°C and 9.5°C, giving salinity estimate between 1.43 and 9.84 wt.% NaCl eq. with maximum peak at 5 wt.%
NaCl eq. (Fig. 5a). CO$_2$–phases were homogenized to liquid at temperatures between 26°C and 31°C with majority at 29°C. In subtypes 2a and 2b, total homogenization temperatures were measured between 210°C and 330°C with maximum peaks at 230°C and 280°C (Fig. 5b). In subtype 2c, the total homogenization was measured at temperatures range from 160°C to 190°C, with the majority at 170°C.

In type (3), ploy-phase inclusions, the aqueous phases (liquid +vapor) are homogenized (Th$_{L+V}$) to liquid at temperatures between 125°C and 180°C. The dissolution temperature (Ts) of the daughter crystals were achieved at temperatures between 275°C and 330°C, corresponding to high salinity between 36.51 and 40.79 wt.% NaCl eq.

### 4.2.2. In Vein Fluorite

In the first and second generations (primary and pseudo-secondary) two phase aqueous inclusions: the eutectic temperatures (Te) were measured between -49 and -53, indicating the presence of CaCl$_2$ dissolved with other salts in the fluid. The final melting of ice (T$_{mice}$) was measured at temperatures between -3°C and -10.5°C, indicating salinities range between 4.96 and 14.46 wt.% NaCl eq. with two peaks at 6 and 12 wt.% NaCl eq. (Fig. 6a). Total homogenization was achieved to liquid at temperatures between 100°C and 270°C, with two peaks at 140°C and 200°C (Fig. 6b). In the third generation, phase changes have been never observed due to the small sizes of fluid inclusions.

5. Discussion

**Interpretation of fluid inclusion data**

In greisenized granite associated with cassiterite and fluorite mineralizations the two–phase aqueous and immiscible three-phase inclusions are the main fluid inclusions detected in the studied samples. The presence of these fluid inclusion types may be interpreted as due to partial immiscibility of one homogenous fluid (H$_2$O-CO$_2$- NaCl) or due to mechanical mixing of two heterogeneous fluids (H$_2$O-rich and CO$_2$-rich). In the present study, the coexistence of these two fluid inclusions is interpreted as partial immiscibility of one homogeneous fluid (H$_2$O-CO$_2$- NaCl) for the following reasons:

a. The presence of two end members (H$_2$O-rich and CO$_2$-rich inclusions).
b. Similarity in microthermometric results of the two fluid inclusion types (Fig. 5).
c. The occurrence of the two fluid inclusion types in the same region of the same sample considered as an evidence of contemporaneous trapping [18, 19].

The homogenization temperature of the two end member fluids in an immiscible system defines the temperature of mineralization [15]. Therefore, it can be assumed that greisenization as well as cassiterite deposits have taken place at temperature between 330°C and 270°C (bulk homogenization of subtype 1a).

The minimum pressure of trapping was estimated to be about 1.4 kb at 330°C for Sn-bearing fluids. Dilution trends observed for the homogeneous fluids (Fig. 7) at decreasing temperature are characteristics of many cassiterite deposits in the world [20 - 23]. Jackson and Helgeson [24, 25]; Keppler and Wyllie [26]; Hu et al. [27] suggest that in chlorine–fluorine-rich systems, chloride complexing is the most effective and dominant Sn transporting mechanism in the hydrothermal solution. The studies on melt and fluid-inclusions in a highly evolved halogen-rich granite–pegmatite system [28, 29] demonstrate that fluorine might have a much greater influence in the extraction and transport of Sn in such systems. Therefore, it can be considered that tin might have been transported by this homogeneous fluid most probably as fluoride and chloride complexes. When the fluid expanded into the low-pressure spaces T and P would have suddenly changed. The beginning of greisenization seems to have taken place at temperature > 330°C. Subsequent greisenization and deposition of cassiterite probably took place due to immiscibility at temperature and pressure between 330°C and 270°C, 1.4 and 0.65 kb (Fig. 8) according the following reactions:

\[
\text{SnCl} + 2\text{H}_2\text{O} = \text{SnO}_2 + 2\text{H}^+ + \text{Cl}^- + \text{H}_2
\]
SnF + 2H₂O = SnO₂ + 2H⁺ + F⁻ + H₂

Fluorite mineralization may have taken place with decreasing temperature and pressure between 180°C and 260°C, and 441 and 536 bars (T and P of trapping of subtype b inclusions). Decreasing salinity with decreasing temperature of homogenization (Fig. 7) may indicate the presence of dilution process due to mixing of hydrothermal fluids with low temperature-low saline fluids (may be meteoric water). The latest fluid generation is represented by high saline association of poly-phase, two-phase and mono-phase aqueous inclusions. This coexistence of inclusions is an evidence of boiling.

![Fig. 7. Salinity versus homogenization temperatures (Th °C) of two-phase aqueous inclusions from greisenized granite.](image)

6. Conclusions

From the foregoing discussion of fluid inclusions study of Sn-F bearing greisen and fluorite veins, it can be concluded that:

In greisenized granite: Sn-mineralization was transported by a homogeneous fluid composed mainly of (H₂O-CO₂-NaCl). Greisenization seems to have begun at temperature > 330°C. Subsequent greisenization and deposition of cassiterite may be due to the immiscibility of the homogeneous fluid which probably took place with continuous decreasing temperature between 330°C and 270°C, and pressure between 1.4 kb and 0.65 kb. Fluorite deposition have taken place due to dilution process at temperature between 260°C and 180°C and pressure between 536 and 441 bars. Coexistence of high saline poly-phase, two-phase and mono-phase aqueous inclusions in the latest fluid generation is an evidence of boiling.

In fluorite veins: Fluorite was probably deposited due to dilution process. Pressure is estimated between 181 and 212 bars at temperatures between 140°C and 200°C. These conditions may be the minimum condition of fluorite deposits.

References


