# LIQUID SEPARATION OF TUNGSTEN-TIN-BEARING GRANITIC MELT AT 850 °C AND 150 MPa[①]

Chen Zilong, Peng Shenglin

*Department of Geology, Central South University of Technology, Changsha 410083*

**ABSTRACT**  With two kinds of glasses used as starting material, systematical experiment study had been carried out on liquid separation of granitic silicate melt containing tungsten and tin under the conditions of 850 °C and 150 MPa. The results of the experiments indicated that the quenched product glasses did not contain any newly-formed minerals through observation under microscope (200×) and determination of X-rays diffraction. The final glass of each run consisted of two parts with light and dark color, respectively, which represented two phases of liquid-separated melt. In the quenched glass, the dark part was dominant and took a portion of more than 80%. The data of the compositions for the two portions of glass by determination with electronic probe indicated that the light glass contained relatively much silica and less $Fe_2O_3$, $FeO$, $TiO_2$, $MgO$ and $CaO$. On the boundary between two phases of glass, there did not exist gradually varying zone of the composition, which indicated that complete liquid separation had taken place.

**Key words**  liquid separation  W-Sn-bearing granitic melt  experimental method

## 1  INTRODUCTION

The liquid separation or liquid immiscibility of basaltic or more basic silicate melt has been studied for many years[1-9], and its role in the ore-forming process related to magmatic activity has been recognized for a long time. However, whether the liquid separation of granitic silicate melt may take place or not has not been completely sure, the recognition and identification of the macroscopic and microscopic features or evidences which are formed in the process of granitic magma's cooling or cystallization to form rock by the liquid separation has not been paid enough attention[10-12]. The partitioning of tungsten and tin between the separated silicate melts in the process of liquid separation of the granitic magma at high pressures has not been studied although the behavior of tin and tungsten during the liquid separation of alumosilicate or granitic melts at atmospheric pressure has got some attention[13-15]. Some key techniques such as solid-liquid sample preparation, gold capsule pretreatment are designed in our experiment, and make the experimental results different from the previous ones[10-11], and more proximate to naturally geological phenomena.

## 2  EXPERIMENTAL

### 2.1  *Preparation of Starting Materials and Medium Solutions*

Two kinds of glasses were selected as starting materials. The first (glass F) was made from the Dengfuxian coarse porphyritic biotite granite, occuring in Hunan province of China, being considered as a S-type of granite complex or a type of sial-crust-remelted granite complex. The second (glass D) was made from the Dachang granular biotite-muscovite granite, which occurs in Guangxi, China, and is also considered as a S-type of granite com-

plex or a type of sial-crust-remelted granite complex.

The granites were crushed into powder of − 200 mesh and 20 grams of the powder are put into a solution with a given concentration of dissolved $Na_2WO_4 \cdot 2H_2O$ and $SnO_2$. The mixture was dried up in an electric oven, and repeatedly melted in an electric furnace at the condition of $1\,300 \sim 1\,350$ C. Then, the glass is again crushed into powder of − 200 mesh. The homogeneous distribution of W, Sn and oxides of rock-forming elements in the glass seems to be ensured.

The composition of the glass F were those as folows:

$SiO_2$ 66. 31, $TiO_2$ 1. 01, $Al_2O_3$, 15. 21, $Fe_2O_3 + FeO$ 4. 68, MnO 0. 16, MgO 1. 51, CaO 2. 22, $K_2O$ 3. 19, $Na_2O$ 2. 88;

Those of the glass D were:

$SiO_2$ 73. 10, $TiO_2$ 0. 10, $Al_2O_3$ 13. 56, $Fe_2O_3$ 0. 99, FeO 1. 47, MnO 0. 09, MgO 0. 22, CaO 1. 16, $K_2O$ 4. 84, $Na_2O$ 3. 07.

## 2. 2  *Experimental Procedure*

The experiments were conducted in RQV (Rapid Quenched High-pressure Vessel) system. The reaction took place in a gold capsule with 5. 0 mm OD, 4. 6 mm ID and 50 mm in length. The temperature was controlled by means of RPS − 350 PtRh-Pt thermocouple and DKW-702 automatic temperature-gauge. The errors of the temperature are in a range of $\pm 5$ C. The pressure was measured by means of a tube-shaped spring-gauge high pressure manometer, and the errors of the pressure are in a range of $\pm$ 3 MPa. The length of the isothermal area within the vessel is larger than that of the sample-sealed gold capsule.

The starting material was the powder of glass F enriched in the elements tungsten by 0. 45% and tin by 0. 50% and that of glass D enriched in tungsten by 0. 13% and tin by 0. 16% based on the results of a series of preparatory runs. The starting medium solutions were the following four series of halites-bearing aqueous solutions: Ⅰ. 0. 0~1. 0 mol/L NaF; Ⅱ. 0. 0~2. 0 mol/L KF; Ⅲ. 0. 0~3. 0 mol/L HF; Ⅳ. 0. 0~4. 0 mol/L NaCl. More-

over, for the experiments of the series, 0. 1~ 3. 0 mol/kg LiF (with the highest of 20%) were added into the starting materials, and the starting medium solution is pure water (double-deionized water).

The sample of 200 mg starting material and 200 $\mu$L medium solution were sealed in a pre-treated gold capsule. The capsule was placed in a thermostat and held at 110 C constantly for one to two hours. After that, it was taken out and weighted to check whether the welded seal was in order. If so, the checked gold capsule was sealed within the high-pressure vessel and held at 850 C and 150 MPa for $72 \sim 92$ h. Then, the run was quenched so quickly that the temperature of the capsule and its reacted sample dropped down to 50 C in 20 s. The capsule was removed from the vessel, cleaned up with alcohol (GR) and weighted again. It was confirmed in order during the run if its weight was extremely similar to that before run. So, the capsule could be opened; an aliquot of product liquid was extracted with a micro-hypodermic syringe, and transferred quantitatively into a counting vial. Meanwhile, the pH value of the product liquid was determined. The gold capsule was thoroughly rinsed away with double-deionized water, and the water was collected in another counting vial. On the other hand, the product glass was removed from the capsule as completely as possible. The glasses in the quenched products of each run are proven to contain no newly-formed minerals through observation under 200 times microscope and determination of the X-rays diffraction.

The bulk composition of the product glass was determined by electronic probe microscopic analysis, and the W and Sn contents of all the vials and the product glass was then determined by means of catalysis-polarographic analysis. It was confirmed that the equilibrium of the reaction was attained or nearly attained in most of our runs because of the homogeneous distribution of tungsten and tin in the final product glass and stable similar results of most repeated runs.

# 3　EXPERIMENTAL RESULTS AND DISCUSSION

## 3. 1　Characteristics of Liquid Separation and Affecting Factors

　　Phenomena of the liquid separation observed through the experiments are facts that the final product glass is composed of two kinds of glasses with different color, i. e. light and dark glasses which represent two phases of liquid-separated melt. Between the two kinds of glasses exists a sharply or abruptly boundary(shown in Fig. 1). The color of the light glass varies with the composition of the system of the experiment. In the granite-HF-$H_2O$ and granite-NaCl-$H_2O$ systems, the light glasses are colorless. In the granite-KF-$H_2O$ system, the light part is brownish. In the granite-LiF-$H_2O$ system, the light glass ap-
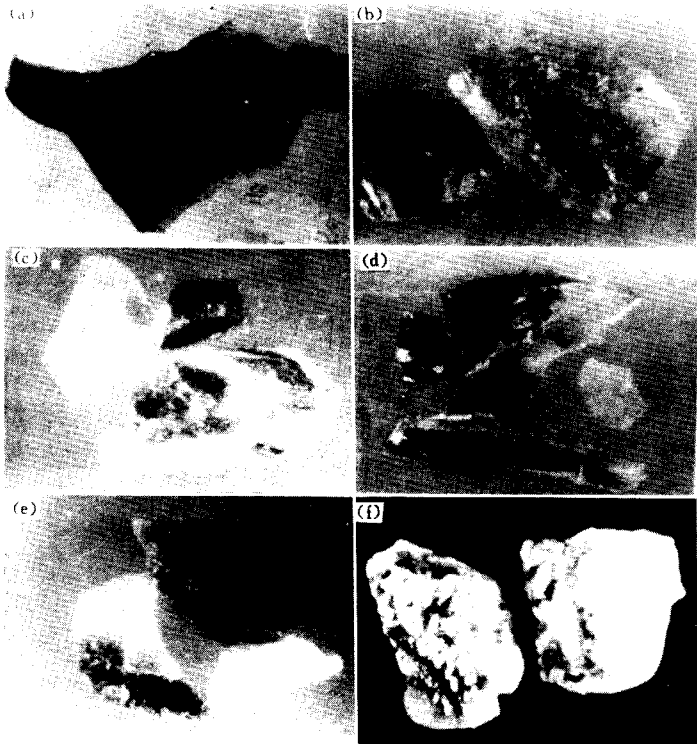


Fig. 1　Product glasses of the systems with different compositions( × 200)

pears milkwhite. The color of dark glass hardly varies with the compositions of the different systems, and appears darkbrown or grey-black. In the quenched glass, for each run, the dark part is dominant and take a portion of more than 80%, whereas the light part is secondary and takes only a portion of less than 20%. Moreover, in the granite-LiF (20%)-$H_2O$ system, the product glass is composed up of three kinds of portions with different color, namely, dark brown glass (about 75% in volume), white opaque glass (about 15% in volume), milkwhite transparent glass (about 10% in volume).

Refractive index of the product glasses are systematically determined with rotational table-needle in a Leitz microscope. The results of the determination show that, for the product glass of the same run, refractive indexs of the two parts of the glasses are obviously different, and ones of the light glass are smaller than those of the dark glass. The value of the differences of the refractive index regularly varies with the system of the experiment and the concentration of the starting medium solution. It has been proven that the difference of the refractive index of silicate glasses indicates the difference of the composition of the glasses. The chemical compositions of the two portions of the glasses are determined with EPM-810 electron probe microscope made in Japan and shown in Table 1. The results of the determination are plotted in Figs. 2~4. The compositions with the multi-

point-determination of the probe show that there does not exist any gradient in contents of oxides of rock-forming elements on the boundary between two portions of the glasses, namely, the compositions from one portion of the glass to another portion of the glass cross the boundary abruptly vary. The marginal and internal parts of the same phase of glass are homogeneous in the composition. Although the different glasses with two kinds of color may appear either in single spherulite or a cluster of spherulite in the product glasses, the glass with the same kind of color possesses the same chemical composition (shown in Table 1) regardless of the shapes of the product glasses. In other word, the glass spherulite and glass block with the light color have no difference between them in the composition, and the glass spherulite and the glass block with the dark color also have no difference between them in the composition. Thus, it is proven that the spherulites of the product glasses are not brought about by so-called quenched-immiscibility which is accepted by some researchers. The extents of the liquid separation in the various experimental systems are different. The scale of the liquid separation, defined as the ratio of the amount (in volume) of the light glass to that of the dark glass in the product glasses, depends on the type of the added aqueous solution and its concentration, namely varies apparently with the systems of the experiment. For the systems granite-NaF-$H_2O$, granite-KF-$H_2O$, and

**Table 1   The compositions (%) of transparent light glasses'spherulites (TLGS) and blocks(TLGB), and dark glass block (DGB)**

|  | $SiO_2$/% | $TiO_2$/% | $Al_2O_3$/% | $Fe_2O_3$/% | MnO/% | MgO/% | CaO/% | $Na_2O$/% | $K_2O$/% |
|---|---|---|---|---|---|---|---|---|---|
| TLGB | 75. 25 | 0. 07 | 16. 02 | 1. 39 | 0. 01 | 0. 20 | 0. 64 | 3. 55 | 2. 88 |
| TLGB | 75. 06 | 0. 11 | 16. 44 | 1. 25 | <0. 01 | 0. 31 | 0. 61 | 3. 34 | 2. 89 |
| TLGB | 75. 22 | 0. 06 | 16. 43 | 1. 16 | <0. 01 | 0. 11 | 0. 28 | 3. 67 | 3. 08 |
| TLGB | 74. 91 | 0. 12 | 16. 45 | 1. 14 | 0. 04 | 0. 23 | 0. 65 | 3. 64 | 2. 84 |
| TLGS | 75. 15 | 0. 10 | 16. 26 | 1. 14 | 0. 04 | 0. 28 | 0. 30 | 3. 66 | 3. 06 |
| TLGS | 75. 16 | 0. 04 | 16. 17 | 1. 11 | 0. 05 | 0. 22 | 0. 45 | 3. 67 | 3. 14 |
| TLGS | 75. 30 | 0. 08 | 16. 27 | 1. 00 | 0. 01 | 0. 27 | 0. 20 | 3. 65 | 3. 23 |
| DGB | 65. 57 | 1. 23 | 15. 58 | 4. 80 | 0. 21 | 2. 51 | 2. 51 | 3. 03 | 3. 18 |

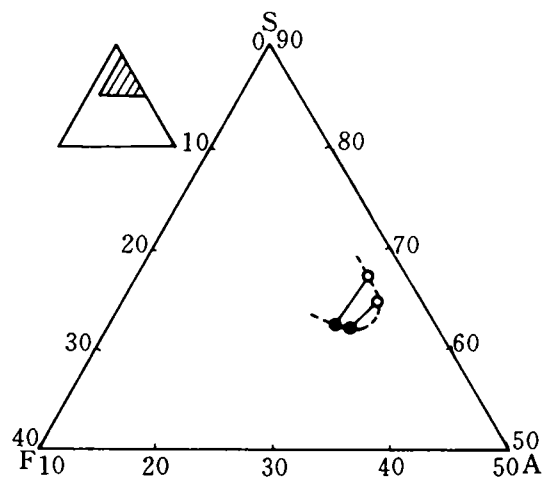\* run number 137, determined by electronic probe

**Fig. 2 The Greig phase diagram of
the system granite-KF-H$_2$O
at** 850 °C **and** 150 **MPa**

●—The composition of the dark glasses;
○—The composition of the transparent light glasses
S=SiO$_2$; F=TFe+TiO$_2$+MgO+MnO+CaO;
A=Al$_2$O$_3$+Na$_2$O+K$_2$O
The field included by the dashed line showing field of immiscibility



**Fig. 3 The Greig phase diagram of
the system granite-HF-H$_2$O
at** 850 C **and** 150 **MPa**

■ —The composition of the starting glasses;
● - The composition of the dark glasses;
○—The composition of the transparent
 light glasses;
S=SiO$_2$; F=TFe+TiO$_2$+MgO+MnO+CaO;
A=Al$_2$O$_3$+Na$_2$O+K$_2$O
The field included by the dashed line showing field of immiscibility

granite-NaCl-H$_2$O, no liquid separation would occur when the concentration of the starting medium solutions is less than 0. 5 mol/L. For the system of granite-HF-H$_2$O, no liquid separation would occur when the concentration of the starting medium solution is less than 0. 25 mol/L. For the system of granite-LiF- H$_2$O, the liquid separation could be expected to occur when the concentration of LiF added into the starting material is equal to or larger than 0. 5 mol/kg. For the same kind of the systems, the scale of the liquid separation increases with the concentration of the starting medium solution or other added material. At the condition of same concentration of the solutions, the intensity and scale of liquid separation for the system containing HF are the largest, that for the system containing NaF are the smallest, that for the system containing LiF, or KF, or NaCl respectively become smaller.

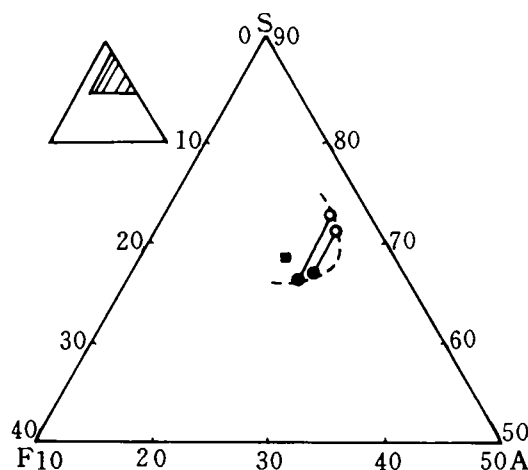## 3. 2 *Partitioning of* W *and* Sn *Between Separated Silicate Melts*

Contents of tungsten and tin in the two phases of glasses for the systems of the experiments, determined with the electron probe, are shown in Table 2.

The liquid-liquid partitioning coefficient $D^{L1/L2}$ of W or Sn is defined as the ratio of the concentration of element W or Sn in melt phase one (L1) to that in melt phase two (L2). In this paper, the melt phase one represents that relatively rich in silica, or the light glass, and the melt phase two represents that relatively rich in FeO, MgO, CaO, or the dark glass. Apparently, the value of $D^{L1/L2}$ can reflect the tendency of preferentially partitioning of W or Sn between the two phases of melts in the process of liquid separation of granitic magma.

From the Table 2, it is known that the liquid-liquid partitioning coefficient of W ( $D_W^{L1/L2}$ ) or Sn ( $D_{Sn}^{L1/L2}$ ) varied with the type of the system of the experiment and with the concentration of the starting medium solu-

tions. At the condition of the same concentration of the solutions, in the system containing HF, the liquid-liquid partitioning coefficient $D^{L1/L2}$ of W or Sn is the largest, that in the system containing KF is the smallest, and that in the system containing NaCl is between them. For the system with the same kind of starting medium solution, the liquid-liquid partitioning coefficient $D^{L1/L2}$ of W or Sn increases with the concentration of the starting medium solution.

## 4  CONCLUSION

The features of the product glass show undoubtedly that the liquid separation of the granitic magmas containing fluorine or containing NaCl is objectively present. The liquid separation of the granitic magma is much more complicated than that of basaltic magmas. In the system of the granitic magmas, both the intermediate-acid to ultra-acid type of liquid separation and silicate-fluoride type of liquid separation may occur at the same time. The controlling factors of the liquid separation of the granitic silicate melt mainly are the com-
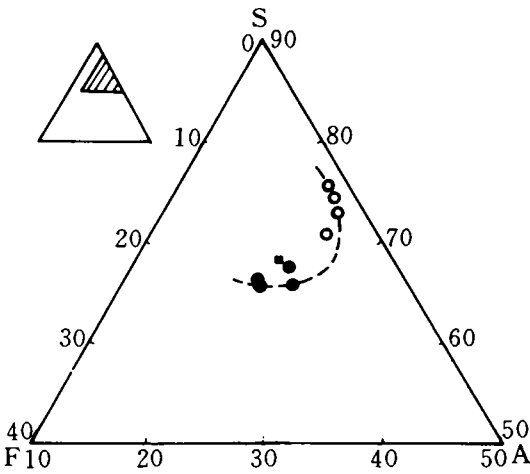


Fig. 4    **The Greig phase diagram of the system granite-LiF-H$_2$O at** 850 ℃ **and** 150 MPa

■ ·· The composition of the starting glasses;
● The composition of the dark glasses;
○ · The composition of the transparent light glasses;
S = SiO$_2$; F = TFe + TiO$_2$ + MgO + MnO + CaO;
A = Al$_2$O$_3$ + Na$_2$O + K$_2$O
The field included by the dashed line showing field of immiscibility

**Table 2    Experimental results (%) of liquid-liquid partitioning of W and Sn**

| Nos. of run | Medium solutions | | | Contents in light glasses | | Contents in dark glasses | | $D_{W}^{L1/L2}$ | $D_{Sn}^{L1/L2}$ | Yield | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | C (NaCl) | C (HF) | C (KF) | W/% | Sn/% | W/% | Sn/% | | | W/% | Sn/% |
| | /mol·L$^{-1}$ | | | | | | | | | | |
| 229 | 4.0 | | | 1.01 | 1.29 | 0.39 | 0.42 | 2.85 | 3.07 | 89.5 | 107.1 |
| 231 | 4.0 | | | 0.98 | 1.35 | 0.34 | 0.49 | 2.88 | 2.76 | >96.4 | 66.8 |
| 245 | 3.0 | | | 0.96 | 1.05 | 0.40 | 0.40 | 2.40 | 2.63 | 91.6 | 89.4 |
| 247 | 3.0 | | | 0.90 | 1.05 | 0.35 | 0.40 | 2.57 | 2.63 | 88.6 | 98.7 |
| 234 | 2.0 | | | 1.00 | 0.97 | 0.42 | 0.39 | 2.38 | 2.48 | 101.7 | 99.1 |
| 232 | 2.0 | | | 0.92 | 0.91 | 0.39 | 0.39 | 2.36 | 2.33 | 97.5 | 106.9 |
| 233 | 1.0 | | | 0.92 | 0.90 | 0.47 | 0.48 | 1.96 | 1.88 | 96.8 | 87.4 |
| 227 | | 3.0 | | 1.59 | 1.26 | 0.38 | 0.33 | 4.18 | 3.82 | 93.0 | 93.5 |
| 219 | | 3.0 | | 1.46 | 1.40 | 0.38 | 0.40 | 3.84 | 3.50 | 77.4 | >87.5 |
| 230 | | 2.0 | | 1.00 | 1.33 | 0.30 | 0.40 | 3.33 | 3.33 | 75.8 | 99.5 |
| 222 | | 1.0 | | 0.97 | 1.20 | 0.43 | 0.37 | 2.26 | 3.24 | 61.0 | 91.5 |
| 221 | | 0.5 | | 0.79 | 0.86 | 0.35 | 0.47 | 2.26 | 1.83 | 79.4 | 93.5 |
| 203 | | | 2.0 | 0.45 | 0.47 | 0.40 | 0.41 | 1.13 | 1.15 | 93.8 | 71.8 |
| 205 | | | 2.0 | 0.48 | 0.45 | 0.42 | 0.38 | 1.14 | 1.18 | 88.5 | 72.5 |
| 202 | | | 1.0 | 0.41 | 0.44 | 0.37 | 0.39 | 1.11 | 1.13 | 82.5 | 85.9 |
| 239 * | 4.0 | | | 0.68 | 0.76 | 0.13 | 0.14 | 5.23 | 5.43 | 110.6 | 114.5 |

*   Glass D used as the starting material, determined by electronic probe

such as heights and areas of caved region of the orebody are also in good agreement with in-situ measument results. Guided with the predicted results, no boundary weakening is used up to now in the mine, and the orebody caves normally as predicted. In the engineering point of view, the predicted method is accepatable.

# 5　CONCLUSION

Block caving method is used in the mine with developed joints, the caving of orebody is induced by subcritical growing of crack in ore and the action of joints in orebody, it is a fracture process related with time which can be simulated by combining the subcritical growing rate of crack in ore and numerical analysis method. The subcritical crack growing rate of rock can be tested with double torsion testing method effectively and conveniently. As an application of rock fracture mechanics in ming engineering, the caving rate of orebody of TKY mine is predicted with the subcritical crack growth of the orebody. Comparing the predicted results and in-situ measument results, it can be considered that the predicting method is useful and preferable to the prediction of cavability for block caving mining.

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(*From page 13*)　　position, the pressure and the temperature of the system. Not all of the granitic magmas may bring about the liquid separation at any conditions. The dominant oxides of the granitic magmas such as $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $FeO$, $CaO$, $MgO$, etc. do not excert a significant or apparent influence on the liquid separation. The contents of the volatile components such as F or Cl and alkaline metal elements such as Li , Na, and K could excert an important influence on the liquid separation.

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