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und Magnetit ist die Bildungstemperatur des Granits zwischen 650° C und 710° C bestimmt worden. Das O<sup>18</sup>/O<sup>16</sup>-Verhältnis in den Feldspäten und den Glimmern ist nach der Erstarrung des Magmas durch sekundäre Effekte verschoben worden. Der mittlere  $\delta$ -Wert ( $\delta_{\text{SMOW}}$ ) beträgt für den Quarz 8,7 °/<sub>00</sub>, für die Feldspäte 8,3 °/<sub>00</sub> und für den Magnetit 0,5 °/<sub>00</sub>; die  $\delta$ -Werte der Biotite streuen stark zwischen 1,3 und 5,7 °/<sub>00</sub>.

Oxygen isotope fractionation between coexisting minerals

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#### Abstract

The oxygen isotope content of the phases quartz, alkali feldspar, plagioclase, biotite, and magnetite has been investigated in 20 samples of the Grimstad-granite complex. From the O<sup>18</sup>/O<sup>16</sup> fractionation between quartz and magnetite, temperatures of formation have been calculated between 650° and 710° C with a revised magnetite/H<sub>2</sub>O curve. The temperatures are in good agreement with the melting temperatures of granite magmas determined by hydrothermal bomb experiments. The feldspars and the biotites are not in isotopic equilibrium with the pure phases due to retrograde effects. The mean  $\delta$ -values ( $\delta_{\rm SMOW}$ ) for quartz are 8.7 % 0.00, for feldspar 8.3 % 0.00 and 0-1 % 0.00 for magnetite. The  $\delta$ -values of the biotites show a larger variation between 1.3 and 5.7 % 0.00



Fig. 1. Map showing the Grimstad-granite with the locations of the samples.

#### Introduction

The fractionation of oxygen isotopes between the different minerals of a rock can give us valuable information on the temperature of the last reequilibration between the phases. It was the purpose of this investigation to calculate the "temperature of formation" of the minerals of a granitic magma and to see, whether the various phases are in equilibrium as far as

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reziproken Raum wurde schließlich eine Schnittfläche ausgewählt, die in etwa die Indizierung (109) aufweist. Ihr reziproker Gitterpunkt liegt für Kupferstrahlung und alle längerwelligen Strahlungen außerhalb der Ausbreitungskugel. Ihr Vektor bildet mit dem Vektor der ihm am nächsten gelegenen reziproken Gitterpunkte (001) einen Winkel von annähernd 7°. Dieser Winkel ist wesentlich größer als die üblichen Schwenkwinkel der Präparate.

Die Beugungsaufnahme dieser Schnittfläche eines Quarzkristalls ist im oberen Diagramm von Abb. 1 wiedergegeben. Die darunterliegenden Diagramme zeigen unter gleichen Aufnahmebedingungen die Streukurven von Plexiglas und Glas (Objektträger), das Beugungsdiagramm von Aluminium und zuunterst die Leerstreukurve ohne Präparateträger. Der Beugungsuntergrund der Aufnahme des Quarzkristalls liegt deutlich niedriger als bei Aluminium. Die Streukurven von Plexiglas und Glas sind um ein Vielfaches höher. Es ist ein noch besseres Ergebnis zugunsten einer Schnittfläche (109) von Quarz zu erwarten, wenn ausgesucht gute Kristalle für das Schneiden der Quarz-Einkristall-Präparateträger verwendet werden.

Die Verwendung von Quarzeinkristallen als Ausgangsmaterial für Präparateträger für Beugungsaufnahmen an sehr dünnen Pulverpräparaten ist nicht zwangsläufig. Quarz ist jedoch genügend hart und noch ausreichend leicht zu bearbeiten. Unabhängig von dem verwendeten Ausgangs-Einkristall ist jedoch wesentlich, daß der reziproke Gittervektor seiner Schnittfläche einen genügend großen Winkel zu anderen reziproken Gittervektoren bildet und der reziproke Gitterpunkt seiner Schnittfläche außerhalb der Ausbreitungskugel liegt.

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Oxygen isotope fractionation between coexisting minerals of the Grimstad-granite

By Hans Friedrichsen, Marburg

With 4 figures and 1 table in the text

#### Auszug

An 20 Proben des Grimstad-Granits (300 km SW Oslo an der Küste Südnorwegens gelegen) wurde das O<sup>18</sup>/O<sup>16</sup>-Verhältnis in den Phasen Quarz, Alkalifeldspat, Plagioklas, Biotit und Magnetit gemessen. Aus der Isotopenfraktionierung zwischen Quarz

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the oxygen isotope composition is concerned. We analyzed about 20 mineral assenmblages of the Grimstad-granite complex.

The Grimstad-granite (or Fevik-granite) (Fig. 1) is situated about 300 km SW of Oslo at the coast of South Norway. OFTEDAL (1938, 1945) suggested that the Grimstad-granite is of magmatic origin, referring to the sharp contacts and to some intrusion breccias. But other modes of emplacements are suggested too (CHRISTIE et al. 1965). The Grimstad-granite is a coarse grained, red microcline granite, the alkali feldspar is maximum triclinic. The temperature of formation of this granite has been determined by the two-feldspar thermometer, which showed successive lower temperatures from the contact to the center (600 to 450° C). These temperatures are rather low and probably can only be applied to the feldspars.

#### Oxygen isotope geothermometry

The fractionation of the oxygen isotopes O<sup>16</sup> and O<sup>18</sup> is closely related to the temperature. Generally speaking we may conclude, the lower the temperature, at which the phases have equilibrated, the higher the difference in the O<sup>18</sup>/O<sup>16</sup> ratio between the individual phases. The fractionation curves have been determined experimentally for some systems. For the interpretation of our analytical data, we used the fractionation curves of the systems quartz/water (see TAYLOR & EPSTEIN 1968), feldspar/water resp. salt solution (O'NEIL & TAYLOR 1967) and magnetite/water (BERTENRATH et al., in prep.). From these data we can calculate the fractionation between any two of the four mentioned phases for a given temperature between 800° and 350° C (Fig. 2).

### Experimental procedure

The minerals have been separated and purified by standard techniques (hand-picking, heavy-liquid fractionation, magnetic separation). Only monophasic portions have been analyzed, controlled by X-ray methods in the case of quartz, feldspar and biotite, and by wet-analytical technique for magnetite. The purification of magnetite turned out to be the most difficult problem. Only substances for further experiments have been used with more than 96 % Fe<sub>3</sub>O<sub>4</sub> (96.5-99.6 % Fe<sub>3</sub>O<sub>4</sub>). The samples were dried at 150° C. Residual water was converted to HF and oxygen by reaction with BrF5 at about 70-90° C. The oxygen was pumped off. About 5 to 30 mg of the sample were decomposed with BrF5 at 500 to 650° C. The oxygen was converted to CO<sub>2</sub>. The mass-spectrometric analysis was carried out with a 60° single focussing mass-spectrometer similar to the technique described by McKINNEY et al. (1950). The  $\delta$ -values reported in Table 1 are the differences in per mil to SMOW (CRAIG 1961). The analytical reproducibility was less than  $\pm$  0.2  $^{0}/_{09}$ , larger differences reported in Table 1 are due to isotopic inhomogenities of the samples.

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#### Isotopic results

The whole rock isotopic composition of the granite-complex is about  $+8^{\circ}/_{00}-8.5^{\circ}/_{00}$  relative to SMOW (Table 1). This is the O<sup>18</sup>/O<sup>16</sup> ratio of almost all plutonic granites investigated (TAYLOR 1968). The whole rock  $\delta$ -value is calculated from the  $\delta$ -values of the individual phases.



Fig. 2. Fractionation curves of quartz/H2O, feldspar/H2O and magnetite/H2O.

Quartz shows the highest  $\delta$ -values around  $8.7^{\circ}/_{00}$  with a few exceptions. The O<sup>18</sup>/O<sup>16</sup>-ratio of the feldspars are randomly scattered between 6.8 and 9.5 °/<sub>00</sub> with a maximum at  $\delta = 8.3^{\circ}/_{00}$ . The values for the magnetites are found between 0.0 and 1.2 °/<sub>00</sub>. The biotites show the largest variations of 4.4 °/<sub>00</sub> between 1.3 and 5.7 °/<sub>00</sub>.

The fractionation of the oxygen-isotopes between quartz and magnetite varies from 7.5 to 8.7  $^{9}/_{00}$ . This corresponds to a temperature of equilibrium

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of 700 to  $650^{\circ}$  C. These temperatures are derived from the quartz/water and magnetite/water fractionation curves mentioned above. They represent the temperatures of the last equilibration between these phases. The values are in good agreement with other experimental data for granitic melts.

| Table          | 1. | Analytical | data | and | calculated | temperatures | from | the | quartz-magnetite |  |
|----------------|----|------------|------|-----|------------|--------------|------|-----|------------------|--|
| fractionation. |    |            |      |     |            |              |      |     |                  |  |

|   |    | θQ               | ∂ Fsp                       | Ә Мі | 9 Pl | ЭBi    | ∂ Mt  | ∆ Q/Mt           | ⊿ Q/Fsp   | tQ/Mt |
|---|----|------------------|-----------------------------|------|------|--------|-------|------------------|-----------|-------|
| А | 1  | 8,70             |                             | 8,10 | 8,40 | 2,5    | 1.10  | 7.6              | 0.6/0.3   | 700   |
| Н | 4  | 8,70             |                             | , ,  | Ū    | , ,    | 1.2   | 7.5              | 0.6       | 710   |
| A | 3  | 8,76             | 8,2 <sub>0</sub> :<br>+ 0.5 |      | :    | 1<br>1 |       |                  | •,•       |       |
| D | 4  | 9,70             | - 0,5                       |      |      |        |       |                  |           |       |
|   |    | ± 0,3            |                             |      | 1    | 4      |       |                  |           |       |
| G | 4  | 9,0 <sub>0</sub> |                             |      |      |        | 0,95  | 8,0 <sub>5</sub> |           | 690   |
| - |    | ± 0,2            |                             |      | 4    |        |       |                  |           |       |
| F | 4  | 8,7 <sub>0</sub> |                             |      |      |        |       |                  | i i       | 4     |
| A | 4  | 8,80             |                             |      |      |        | 1,20  | 7,60             |           | 705   |
| U | 17 | 8,75             |                             |      |      |        |       |                  |           |       |
| V | 1  | 8,65             | 8,60                        | 8,3, |      | 1.3.   |       |                  | 0.0/0.3   |       |
| F | 3  | 9,00             | 8,05                        |      |      | 3.5.   |       |                  | -,-,-,-,- |       |
| Е | 2  | 7.7.             |                             |      |      | - )- 3 |       |                  |           |       |
| G | 2  | 8.60             | (                           | 9.5₅ | 8.4. | 4.4    | 0.1.  | 8.4.             | 0.2(-1.0) | 660   |
| Н | 1  | 8.3              |                             | 8.0  | -,.0 |        | \$,15 | 0,15             | 03        | 000   |
| S | 1  | 8.8.             | . [                         | -,-0 |      | 15.    |       |                  | 0,5       |       |
| С | 2  | 7.6.             | 7.1.                        |      |      | 3.5    |       |                  | 0.5       |       |
| М | 1  | 8.3              | 7.7.                        | 7.3. | 7.8. | 5,50   | 0.0   | 82               | 1.0       | 670   |
| В | 3  | 8.6.             | . , 0                       | 87.  | 8.5. | 57     | 0.05  | 9 4              | 1,0       | 670   |
| U | 1  | 8.8.             |                             | 0,0  | 6.8  | 31     | 0,25  | 0,40             | 0,2       | 660   |
| R | 1  | 0,00             |                             | 77   | 77   | J,48   | 0,07  | ð,/3             | 2,0       | 650   |
|   | 1  | 0,10             |                             | 1,15 | /,/0 |        | 0,05  | 8,65             | 1,0       | 650   |

WINKLER & v. PLATEN (1960) determined the melting temperatures of granitic melts with differing Ca/Na-ratios. Mixtures of granitic composition with Ca/Na ratio of 0.35 (expressed in weight percent anorthite/albite) were completely liquidized at 675° C, with an An/Ab ratio of 0.45 at 725° C. The experiments were carried out at 2kb water pressure.

BOETTCHER & WYLLIE (1968) determined the curve for the beginning of melting of granite with  $34.8 \, ^{0}/_{0}$  quartz,  $31.5 \, ^{0}/_{0}$  plagioclase,  $29 \, ^{0}/_{0}$  orthoclase and  $4.7 \, ^{0}/_{0}$  mafics. At 1 kb water pressure the granite begins to melt at 715° C, the curve passes through  $675^{\circ}$  C and  $655^{\circ}$  C at 2 and 3 kb and  $620^{\circ}$  C at 10 kb.

The experimental data show that the melting temperature of a granite is distinctly dependent

1. on the pressure,

2. on the chemical composition, mainly the Ca/Na-ratio.

The highest temperatures of formation are calculated for the samples from the contact (sample A 1, H 4), the lowest for the samples from the center. But there is no systematic ralitionship between equilibration temperature and distance from the contact. The variations are probably due to small deviations in the chemical composition as may be concluded from WINKLER's data.



The differences of the  $\delta$ -values of quartz and the coexisting feldspars  $(d_q - \delta_{fsp})$  is about 0.3 to  $1^{0}/_{00}$  with a maximum at about 0.5  $^{0}/_{00}$ . For a temperature of 650 to 700° C this difference should be 1.5 to  $1.7^{0}/_{00}$ . There exists no reasonable temperature where quartz and feldspar show as low differences in equilibrium as in these parageneses. The only possible explanation for this phenomenon is, that the feldspars have undergone secondary reactions, probably during the cooling period of the magma. It is known from experimental data (O'NEIL & TAYLOR 1967), that the feldspars reequilibrate their oxygen isotopes and their cations with a vapour phase (salt



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solution) at lower temperatures within reasonable time. Any reaction with the vapour phase of the magma in the subsolidus field would enrich the  $O^{18}$ -content in the feldspars and deplete the  $O^{18}$ -content in the fluid phase. Cogenetic feldspars, which have been formed at the melting temperature are in chemical nonequilibrium in the subsolidus field. The temperature, at which the reequilibration of these phases "freezes in", is dependent on the amount of fluid phases, the cation content of those phases and the cooling rate. From this point of view the temperatures of formation of the feldspars, calculated from the two-feldspar thermometer proposed by BARTH (1962) (600° C at the contact, 450° C at the center of the granite complex) are quite reasonable; these temperatures indicate the temperature of the last equilibration of the feldspars.

The  $\delta$ -values of the biotites show a broader scattering than any other phase. We know from RbSr-age determination (JÄGER, pers. communication) that the biotites exchange the cations, if they are heated to a temperature higher than 300° C. The scattering of our data is probably due to some retrograde effects. We do not yet know the precise fractionation of the O<sup>18</sup>/O<sup>16</sup>-ratios between biotite and other rock forming minerals. But if we compare our data with the biotite values of GARLICK & EPSTEIN (1967), we must conclude that the micas with extrem light values (1.3 and 1.5 %) are not in equilibrium with the oxygen isotope ratios of the other minerals. They are probably caused by interaction with meteoric water (for complete discussion see TAYLOR 1968). This hypothesis is checked by hydrogen isotope analysis of the OH-hydrogen of the biotite.

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# Distribution of cobalt between coexisting biotite and hornblende in igneous rocks\*

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With 2 figures and 3 tables in the text

#### Abstract

Cobalt has been determined by neutron activation in 95 pairs of coexisting biotite and hornblende from igneous rocks ranging in composition from gabbro to syenite. The distribution ratio of Co in hornblende to Co in biotite averages 0.66 with a standard deviation of 0.13. The distribution coefficient apparently is unaffected by initial crystallization temperature, cooling history, or major element composition of the minerals or magmas. Partition of Co between biotite and hornblende appears to provide a useful estimate of the degree of equilibrium attained by a given rock system but has no potential application as a geothermometer.

#### Introduction

The distribution of a trace element between coexisting minerals at equilibrium is a function of temperature, pressure, and major element composi-

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