RADIOGENIC ARGON IN GLAUCONITES AS A FUNCTION OF MINERAL RECRYSTALLIZATION

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Natural glauconitic grains were subjected to hydrothermal treatment at a pressure of 2 kbars and temperatures of 200–414°C for the period of one month.

The measurement of radiogenic argon before and after treatment shows that the mica-type glauconite mineral contains 92–96% of the argon initially present up to temperatures as high as 320°C.

After recrystallization of the mixed-layered glauconitic minerals the new phases still contain significant amounts of argon in the structure. The mixed-layered glauconitic minerals are much more sensitive to temperature treatment at elevated pressure than glauconitic-type mica, they, however, still contain up to 84% of the initial argon of the untreated material at temperatures as high as 320°C, i.e., just below the thermal stability of glauconite mica. It is evident that low-temperature metamorphism will affect the apparent radiogenic age of glauconitic grains to an extent which depends upon their composition and the temperature of metamorphism.

1. Introduction

There has been a certain amount of discussion concerning the interpretation of K-Ar dating of glauconites. Numerous authors [1,2] have affirmed that dated glauconitic grains tend to give slightly young ages by K-Ar dating: up to 15% or more. Recent studies [3] have shown that a careful preliminary choice of the material to be dated diminishes the scattering of the apparent ages. The data obtained on the Kreyenhagen Formation [2–4] suggest that an important loss of Ar is possible by burial diagenesis of more than 6000 ft. Hydrothermal treatment [4] shows relatively little diffusion at 300°C at a 1000 psi pressure and 400°C at 1000 psi pressure. The complex situation in which radiogenic Ar and K are held in glauconitic mineral structures has been shown by acid leaching experiments [5] which indicate that
there are several K sites with differing chemical activities and that there is a possible loss of Ar or an enrichment in K in the more open sites. There has also been considerable work done on radiogenic Ar retention by other mica structures — biotites and muscovites [6-8]. These data suggest that Ar diffusion in micas can certainly result in Ar loss but the diffusion rate in micas, is very greatly reduced at temperatures where glauconites are stable, 100—250°C.

It should be possible to lose Ar from a complex phyllosilicate structure during a phase change which is effected by low-grade metamorphic conditions or those of strong diagenesis. Previous work [9] has shown that mixed-layered mica-smectite glauconites recrystallize into two or more optically distinct components one of which becomes a K-rich, mica-like phase. The purpose of the study here is to ascertain the importance of such a recrystallization as it concerns the amount of radiogenic Ar which is retained in the solid phases under hydrothermal conditions. Problems of Ar diffusion in micas have been treated elsewhere [6] and these data will be assumed to be applicable to the present study.

2. Experimental methods

Five samples of pelletal glauconites from Albo-Aptian and Cenomanian levels from the Paris Basin [3, p. 58] were used in the hydrothermal experiments. The range of K content was from 7.9 to 4.9 wt.% K₂O; the minerals were micaceous to 30% expandable in their mixed-layered component.

The hydrothermal experiments were performed by B.V. in rod bomb-type autoclaves at 2 kbars pressure and at temperatures between 200°C and 415°C for durations of one month. This method has been used previously to establish the phase relations of glauconite evolution under various temperatures [9]. 300 mg of glauconitic grains were sealed with 75 μl of H₂O in gold capsules. The Ar determinations were performed (by M.B. and G.S.O.) on a line build in 1974 [10]. Results are given in Table 1.

Using materials which did not recrystallize (GL-O) it was found that a variation of liquid to solid proportions (75—300 μl H₂O to 300 mg solids) did not seem to affect the run products as far as Ar retention was concerned. There was no apparent difference in the results between half and three months’ run durations.

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Radiogenic (rad.; in 10⁻⁶ cm³ g⁻¹) and atmospheric (atm.; in %) Ar content of glauconite grains before and after one-month experiments at 2 kbars. (+) = after three measurements of the Ar content</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Untreated</td>
</tr>
<tr>
<td>rad. atm.</td>
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<tr>
<td>GL-O K₂O = 7.9%</td>
</tr>
<tr>
<td>G 398A K₂O = 6.7%</td>
</tr>
<tr>
<td>G 403A K₂O = 6.1%</td>
</tr>
<tr>
<td>G 407A K₂O = 5.9%</td>
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<tr>
<td>G 409B K₂O = 4.9%</td>
</tr>
</tbody>
</table>
TABLE 2

Radiogenic and atmospheric Ar content in glauconite sample GL-O after various experiments: (a) variation of the duration (15, 30 and 90 days), (b) variation of the water volume with the same quantity of solids

<table>
<thead>
<tr>
<th></th>
<th>250°C</th>
<th>300°C</th>
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<tbody>
<tr>
<td>(a) Variation in experimental duration</td>
<td></td>
<td></td>
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<tr>
<td>15 days</td>
<td>23.99 (19.6% atm.)</td>
<td></td>
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<tr>
<td>30 days</td>
<td>23.98 (20.8% atm.)</td>
<td></td>
</tr>
<tr>
<td>90 days</td>
<td>23.17 (17.8% atm.)</td>
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<tr>
<td>(b) Variation in water content of the experiment for 300-mg solids</td>
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<tr>
<td>75 µl</td>
<td>23.98 (20.8% atm.)</td>
<td>22.85 (25.9% atm.)</td>
</tr>
<tr>
<td>150 µl</td>
<td>24.07 (19.5% atm.)</td>
<td>22.42 (16.0% atm.)</td>
</tr>
<tr>
<td>300 µl</td>
<td>23.77 (18.6% atm.)</td>
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</table>

either (Table 2). Thus in these experiments Ar loss in non-recrystallized glauconites is mostly a function of temperature.

3. Discussion of 40Ar measurements

Fig. 1 gives the data from Table 1 plotted on temperature-composition coordinates which indicate the phase fields of the silicates encountered in the experiments [9]. Essentially five regions are pertinent; that where glauconitic mica exists (Mi), that where various amounts of mixed-layered glauconitic minerals exist (Mi2), that where glauconitic mica coexists with an expandable trioctahedral phase (Mi + Exp3), that where glauconitic mica and a mixed-layered chlorite-saponite phase coexist (Mi + Mi3), and finally that where biotite, feldspar, quartz and oxides coexist in the region above glauconitic mica stability. This last region represents total reorganization of the mineral assemblage used as starting materials. The numbers on the diagram (in circles) indicate percent radiogenic Ar found in the solids after the experiment compared to the initial amount in the starting material. These are essentially the type of values one would expect to obtain when dating diagenetic and metamorphic glauconitic grains [1–3,5].

Due to the limited number of experiments for the five samples studied, and the uncertainty in knowing the distribution of grain sizes of the individual phyllosilicate structures (they range from 10 µm in the micaceous types to <1 µm for others) in each sample, it is probably not pertinent to use the data presented to construct Arrhenius-type plots. However, the sample GL-O, a micaceous glauconite, can be used to indicate the Ar loss when the mineral subjected to hydrothermal treatment does not recrystallize. We see that a difference of 100°C in the experiments decreases the Ar content of this glauconite by 5%. As a first approximation one can attribute most
of this Ar loss to diffusion. Further, in the experiments at 200°C, all of the samples show about the same Ar loss when they show no apparent recrystallization, i.e., no new phases appear in X-ray diagrams or under the microscope. Again one can most likely attribute the 2–4% Ar loss in the samples to diffusion.

In the samples which recrystallize, i.e., where new phases are found in the run products, but in which glauconitic mica is stable, the Ar content of the solids seems to be a function of temperature more than bulk composition. This means that although various proportions of mica layers are present in the initial material, the Ar which is found in the solids at the end of the experiment is not influenced by the composition of the starting material. The most important factor is that the glauconitic material has recrystallized or experienced a change of phase. Comparison between non- or little recrystallized glauconitic mica (GL-O) and less micaceous (lower K2O content) glauconites for run temperatures of 250 and 300°C indicates that the appearance of new phases decreases the amount of 4°Ar in the solids to a much greater extent than 4°Ar loss through diffusion or other processes.

When glauconitic mica is no longer stable (>300°C) the amount of Ar retained in the solids is much less than in the other experiments. It appears also that the amount of 4°Ar present is a function of the bulk composition of the charge. However, a surprising amount of 4°Ar is still present in the new phases suggesting some sort of partitioning between solids and fluids. As has been noted for experiments on phlogopite [8], the amount of Ar present in the micas is much higher under hydrothermal conditions than that retained at similar temperatures but under vacuum conditions [3,4].

It is possible to explain the variation in Ar content of the solids which change phase under the experimental conditions in two ways:

1. Ar diffuses from the solids. Recrystallization is effected by ionic migration of certain elements in the phyllosilicate structure. These minerals segregations produce new phases in individual grains which are seen under the microscope [9]. Ar then is mobile as are other ions—notably K, Fe and Si. There is, however, no relation between 4°Ar retained and the amount of mica present.

2. Ar is involved in an equilibrium between solid and liquid when minerals are precipitated from solution. During a recrystallization process of the type; mixed-layered mica-smectite → mica + expandable saponitic mineral, all elements pass into ionic complexes in solution and precipitate new phyllosilicates. Oxygen isotope studies ([11], B. Velde, unpublished data) indicate that mineral's recrystallization under hydrothermal treatment is effected by transfer of polymeric silicate units which are smaller than the original phyllosilicates but which are larger than monomeric silica units. There is no way to determine whether Ar remains in these units during the process or whether it enters the fluid phase. The latter possibility is more probable in the authors' opinion. In this instance, the Ar is involved in a fluid/solid partitioning. If the ionic-polymeric structures in solution are small, mica unit cell size, the diffusion of Ar from them must be great and one would not expect much to be retained in the “solids” during the recrystallization process.

4. Conclusions

Several observations can be made concerning the dating of glauconites by the 4°Ar method. First, the most reliable material will be a purely micaceous mineral. However, a certain amount of diffusion should be expected at high temperatures even though the material does not experience phase changes. This has been demonstrated by for natural glauconites [12]. Glauconites with low as well as those with high smectite components will give roughly the same amounts of 4°Ar.

If relatively large amounts of radiogenic Ar should be released into a rock fluid, for example by the destabilization of authigenic potassic zeolites, the 4°Ar could be incorporated into a mica structure giving an older age. The most important factor to respect in dating glauconites is to avoid material which has experienced recrystallization through diagenetic processes.

Acknowledgements

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References


