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## Discordant Absolute Age Values and Their Significance for the Determination of Temperatures and Duration of Rock-Forming Processes

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### ABSTRACT

The degree of divergence of mineral ages of a rock can be taken as an estimate of the intensity of superimposed processes. Kinetic experiments performed in vacuum simulate conditions predominating in meteorites, those performed in the atmosphere are more adequate for weathering processes. For igneous rocks, the use of natural contact haloes for estimates of reactive rates is believed to be the most correct procedure; involving reference temperatures obtained from other considerations, such as the temperature of the granite eutectic.

The discordance of absolute age values, observed sometimes in routine lead determinations, indicates a disturbance of the equilibrium of the radioactive system. On the other hand, this phenomenon can be used for further deductions. First, it should be mentioned that the divergence of the experimental points from the "concordia" towards an intersecting straight line attests to the lack of lead isotope fractionation in natural metamorphic processes. The isotopes are mobilised in a congruent manner in the "episodic metamorphic event" of G. WETHERILL (1956), as well as in the continuous process of G. WASSERBURG (1963). This fact is reaffirmed by the hydrothermal experiments of PIDGEON, O'NEIL and SILVER (1966) and it follows from an expansion in a Taylor series by the power of  $\Delta m/m$  of the relationship between the mobilities of the isotopes and their masses (CRAIG, 1968;  $m$  = mass of the lighter isotope,  $\Delta m$  = mass difference of the extreme isotopes). Besides this, constructions with the "concordia" curve can give the time of the metamorphic event, the true absolute age value and the parameters of a continuous diffusive process.

In the case of the argon method, similar constructions can be made, considering the concordance (or discordance) of the ages of mineral fractions and the whole rock, which might have occurred due to contact and other superimposed processes disturbing the radioactive equilibrium. A few examples of discordant ages are given in Table 1. Instructive data on the age of cogenetic micas and feldspars are given in the papers of LIVINGSTON et al. (1967) and AMARAL et al. (1967) on the alkaline granites of southern Brazil.

Considering first the couple "mica-feldspar": On first sight, these minerals seem unfit for causal deductions; a traditional interpretation of data is that feldspars always give low age values as compared with micas, supposedly due to their lower retentivity

Table 1. Values of argon ages for cogenetic minerals.

Rock	Mineral	K%	Ar <sup>40</sup> nmm <sup>3</sup> /g	Age m. y.
Biotite granite, Mongolia	Biotite	8.0	0.0563	188
	Whole rock	4.1	0.0289	183
Biotite granite, Mongolia	Biotite	8.4	0.0640	192
	Feldspar	10.1	0.0745	192
Biotite granite, Mongolia	Biotite	7.8	0.0747	235
	Feldspar	10.8	0.0930	223
Granodiorite, Transbaik. reg.	Biotite	7.9	0.0709	225
	Whole rock	3.7	0.0281	192
Fine-grained granite, Transbaik. reg.	Biotite	6.0	0.0775	320
	Feldspar	10.2	0.0805	202
Alkaline felsite, Touva	Aegirine	—	—	1110
	Riebeckite	—	—	462
	Feldspar	—	—	300
Leukocratic granite, Transbaik. reg.	Biotite	5.24	0.0396	195
	Feldspar	10.4	0.0815	202
Medium-grained granite, Transbaik. reg.	Biotite	7.0	0.0656	238
	Feldspar	10.4	0.0815	202
Quartz diorite, Touva	Biotite	6.9	0.128	405
	Plagioclase	1.7	0.0123	310
Phlogopite-plagioclase rock, Aldan.	Phlogopite	8.05	0.918	1840
	Plagioclase	2.05	0.112	1090

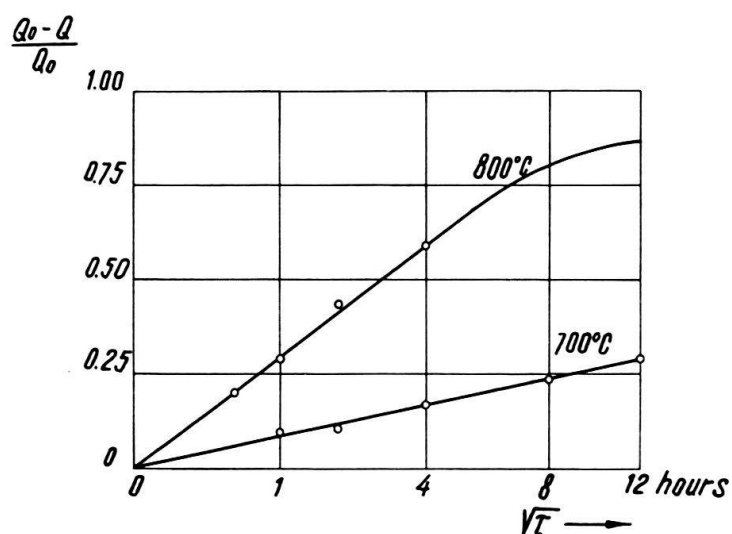


Fig. 1. Isothermal curves of radiogenic argon extraction from muscovite.  $\tau$  = time,  $Q_0 - Q/Q_0$  = relative quantity of expelled argon.

of argon. However, as may be seen from Table 1 and the papers mentioned above, a concordance sometimes takes place and in specially significant cases the age of feldspar is sometimes higher than that of paragenetic mica. These peculiarities which have been observed in quite different regions (Brazil, Mongolia, Transbaik. region), have a general similarity and can be explained on the basis of kinetic investigations on

argon losses by micas and feldspars. In the paper of BRANDT (1964) it was shown that the loss of argon by micas is controlled by a diffusion mechanism and accompanies the loss of hydroxyl water. The diffusion mechanism expells the argon content in the mica.

At the same time, the pattern of argon loss by potassium feldspars is quite different (Fig. 2, BRANDT et al., 1964). During isothermal heating of feldspar in atmosphere, diffusion does not reduce the argon content to zero, the argon approaching rather asymptotically a definite limit, which depends on the temperature. This remarkable feature of feldspars, in that the argon content remains constant during tens of hours of heat treatment at elevated temperatures of 800–1000°C sharply distinguishes them from other minerals. We have worked out theoretical interpretations of this peculiarity in terms of the phenomenological diffusion of binary systems given by J. BARDEEN and C. HERRING (1952). Diffusion, proportional to the gradient of chemical potential, ceases after levelling of the chemical potential difference between the phases of the system.

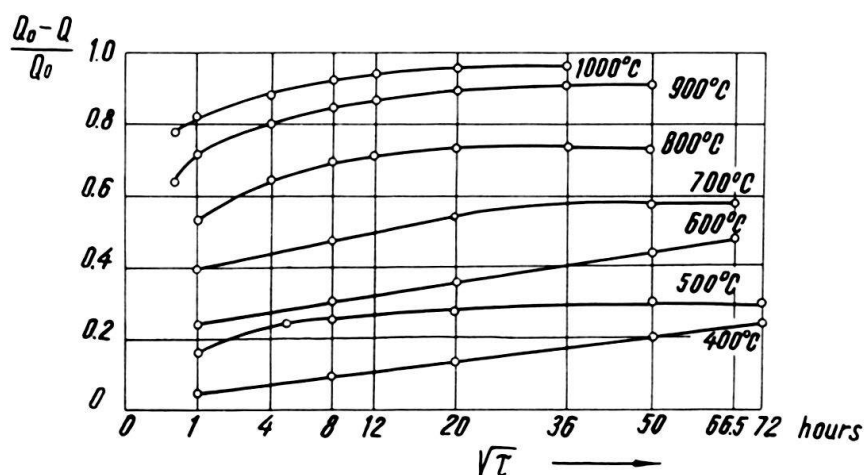


Fig. 2. Isothermal curves of radiogenic argon extraction from a feldspar.

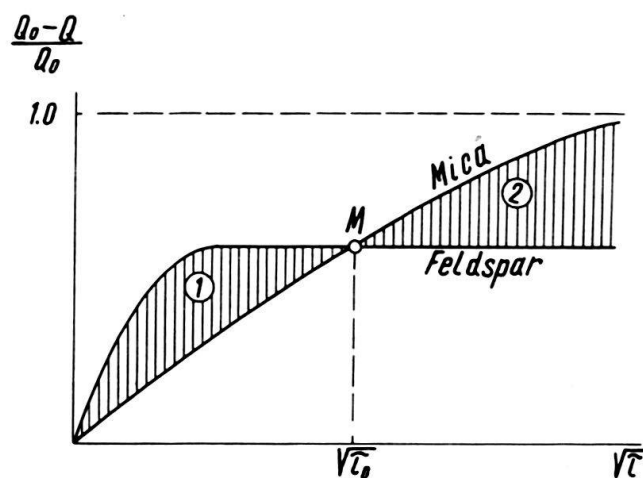


Fig. 3. Comparison of kinetic properties of mica and feldspar.

The possibility of superposition of effects of isothermal heating in atmosphere of micas and feldspars is somewhat doubtful. Indeed, in the case of realization of, say, a granite eutectic, with melting of all the phases, apparently the diffusion should appear congruently. On the other hand, however, why in actual rocks do discordant ages of mineral fractions occur? Therefore we conditionally accept the possibility of superposition (see Fig. 3). Suppose that the superimposed process has caused losses of radiogenic argon in mica, as well as in the feldspar, as shown in the diagram. In region 1, at a time  $\tau < \tau_0$  the feldspar will be "younger" than the mica. At a definite moment  $\tau_0$ , at point M, the curves intersect, mica and feldspar being of equal age. At  $\tau > \tau_0$ , in region 2, the mica age will be less than that of the feldspar. Hence, kinetic considerations explain all the possible age relations between mica and feldspar. However, it should be noted that so far a theory has not been developed that is adequate for a unique treatment of this mineral couplet.

A contact between a dyke of alkaline granite with quartz diorite wall rocks has been considered (BRANDT et al. 1967). Considering the mineral couplet biotite-plagioclase at the exocontact (see Table 1), involving a diffusion model and a laboratory determination of the activation energy, we estimated the temperature and the duration of the thermal action of the dyke on the country rocks, taking into consideration the latent heat of crystallization.

As to the temperature, we arrived at the formula:

$$T = \frac{E_{Bi} - E_{Pl}}{R \ln \left[ \left( \frac{Fo_{Pl}}{Fo_{Bi}} \right) \left( \frac{D_0/a^2_{Bi}}{D_0/a^2_{Pl}} \right) \right]}$$

( $E_{Bi,Pl}$ ) are the activation energies of diffusion of radiogenic argon in biotite and plagioclase, respectively

$$Fo = \frac{D\tau}{a^2} = \frac{D_0 \exp(-E/RT) \tau}{a^2}$$

the Fourier criterion for diffusion,  $D_0, a^2 = \text{constants}$ ).

The temperature appeared to be 850°C.

The duration of action will be:

$$\tau = \frac{Fo_{Bi} \exp(E/RT)}{(D_0/a^2)_{Bi}}$$

It equals 12 hours.

The same speculation was applied to the couplet phlogopite-plagioclase from a metasomatic halo at the contact of a diopside-slate with a leukocratic granite in Aldan (VOLKOVA et al. 1969). Although the application of the argon geothermometer to metasomatically changed formations is of course not irreproachable, the values obtained (effective temperature 630°C and duration 1–2 years) appear plausible.

The development of an independent procedure for the measurement of temperatures and duration of rock-forming processes is indeed attractive, for it suggests the possibility of estimating the migration properties of petrogenic elements. Fig. 4 shows

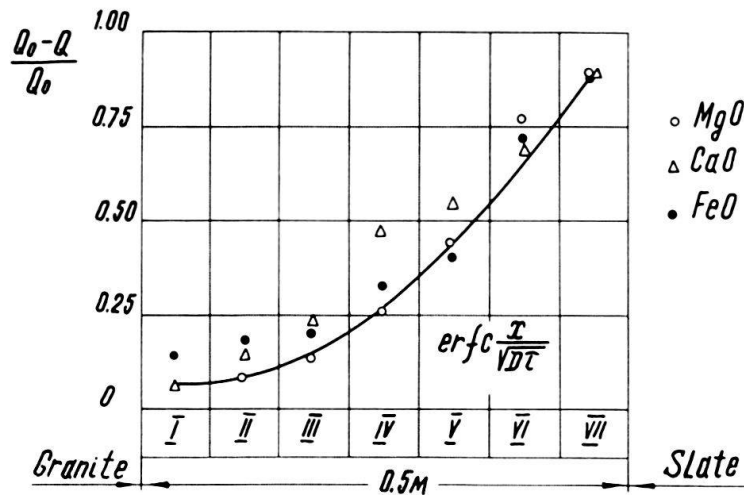


Fig. 4. Halo of magnesium, calcium and iron concentrations at a contact of slate and granite.

a halo of calcium, magnesium and iron at the contact of a slate and granite in Aldan, mentioned above. This halo can be fairly well approximated by the function  $\text{erfc} \frac{x}{\sqrt{D\tau}}$ . Knowing the distance, it follows that

$$D_{0 \text{ Mg, Ca, Fe}} e^{-\frac{E_{\text{Mg, Ca, Fe}}}{RT}} \tau = 196.$$

This expression contains four unknown quantities (functionally interrelated):  $D_0$ , the active time interval of rock-forming  $\tau$ , the temperature  $T$  and the activation energy of diffusion  $E$ . Hence, if at least some of these quantities are not available from some other sources, a natural diffusion halo can give any information, except the Fourier criterion.

Taking  $D_0 = 1$  and introducing the temperature and duration found above, we obtain  $E_{\text{Ca, Mg, Fe}} = 23 \text{ kcal/mole}$ . This is comparable with the activation energy of sodium self diffusion in minerals, as reported by SIPPEL (1963). The estimate obtained, allows us to conclude that the speculation proposed gives values which are comparable with the other data, and justifies the conclusion that the duration of the rock-forming process was short, as compared with the absolute age of the rock.

With reference to the contact interactions of rocks, the outstanding investigations of HART (1964) and of HANSON and GAST (1967) should be mentioned. These investigations are based on a somewhat different approach: the contact zonality of radiogenic products is analyzed in terms of a certain model of the temperature field. Thus, nature is used as a "laboratory furnace". As a result of these speculations the natural activation energy of the migration of radiogenic argon is obtained.

Generally speaking, nature as a "laboratory furnace" should be definitely preferred to simple laboratory furnaces. Heating of minerals (for instance of micas) in vacuum can only simulate the conditions predominating in meteorites. Heating in the atmosphere probably is characteristic for weathering processes. Therefore the success of the methods considered above depends wholly upon the degree of approximation to reality of the conditions of the kinetic experiment.

As an example of the influence of water pressure of 4–6 kbars on the retentivity of radiogenic argon in some minerals we refer the reader to Table 2. Apparently the water pressure hinders the expulsion of argon in the stability range of hydrocrystals but stimulates it outside of this range.

Table 2. Concentration of radiogenic argon in minerals, subjected to hydrothermal treatment. After BRANDT et al. (1967).

Mineral	Before heating nmm <sup>3</sup> /g	In % relative to the initial value after heating for 7 hours			
		In atmosphere		In an autoclave	
		°C	%	°C	%
Phlogopite, Aldan, crushed to powder state	1.08	750	6	750	51
Muscovite, Paleozoic	0.11	700	100	700	100
Biotite (natural scales)	0.105	750	81	750	88
Microcline, Touva	0.093	750	56	750	39
Riebeckite, Touva	0.021	750	52	750	0

A rather effective experiment, unfortunately not concerned with the retentivity of radiogenic argon and not performed with granite, but with peridotite, was recently published by KUSHIRA (1968). It follows from this experiment that the melting temperature of a rock depends on the lithostatic pressure, as well as on the hydrostatic pressure, however in a complex manner.

Similarly it is known that water pressure can lower the melting point of granite from temperatures  $> 1000^{\circ}\text{C}$  to  $500\text{--}600^{\circ}\text{C}$ . It is clear that under certain conditions not only argon but also lead, strontium and other elements can become equally mobile.

The following conclusions can thus be drawn:

1. The equality of argon ages, obtained on whole rocks and on mineral fractions, is a necessary symptom of an undisturbed closed system. However, this symptom becomes insufficient in the case of the realization of an eutectic (congruent losses).
2. A discordance in the ages of mineral fractions of a rock can be utilized for determinations of temperatures and durations of rock-forming processes.
3. Natural diffusion haloes of petrogenic elements only give the Fourier criterion of the process which contains four unknown quantities. A knowledge of temperature and duration can give the activation energy of migration of petrogenic elements.
4. The precision of temperature and duration measurements of rock-forming processes in the experimental determination of kinetic parameters of radiogenic argon depends on the degree of approximation to natural conditions.
5. Mica and plagioclase were used for all the determinations. So far, K-feldspar cannot be used, due to the complexity of its diffusion pattern.

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