Isochemical postkinematic feldspathization : a genetic model

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Isochemical Postkinematic Feldspathization

A Genetic Model

By *Francesco P. Sassi* (Padova, Italy)*)

With 1 figure in the text

Abstract

Isochemical postkinematic feldspathization indicates that the stability of white micas is influenced not only by T and P, but also by other variables. The primary causes of feldspathization are interpreted to be connected with the environmental variations during the passage from the synkinematic phase of metamorphism to the postkinematic one. Such variations entail an increase in the concentrations of oxygen, alkalies (above all Na) and especially of pH in the intergranular fluid. Theoretical and experimental data exist which indicate that these variations produce the destruction of white micas and their replacement by feldspars.

The genetic model proposed explains all the characteristics of isochemical feldspathization, and is applicable also to other similar processes.

Much has been written on the formation of the feldspar porphyroblasts which are so frequently found in metamorphic pelitic rocks, the attention being generally turned towards clarifying the isochemical or allochemical character of these processes.

Allochemical feldspathization has been linked to the more widespread process of metasomatic granitization of crustal rocks in metamorphic environments, and the source of the necessary chemicals has been linked either to the migration of alkaline metasomatic fronts or, directly or indirectly, to magmatic fluids (anatectic or differentiated). As for the mechanisms of the process, insurmountable difficulties do not exist as long as the origin of the metasomatizing fluids can be recognized.

On the contrary, as far as isochemical postkinematic feldspathization in pelitic metamorphic rocks is concerned, nothing is known about the mechanisms

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and the driving forces which lead to the destruction of white micas under P-T conditions consistent with their stability field, and their partial replacement by feldspars. This problem forms the specific subject of this article, while the isochemical formation of new plagioclases through recrystallization of previous plagioclases (ZANETTIN, 1961) is not considered here.

THE PROBLEM

Every attempt at a genetic interpretation of such a process must take the following points into consideration:

1. The phenomenon is to be considered as one of the effects of the metamorphic postkinematic crystallization, whose high frequency makes us think of it as a rule. Within these processes feldspathization is very common.

2. The isochemical character of this feldspathization has been demonstrated several times (*e. g.*, BONDI et al., 1969). To quote MEHNERT (1968, p. 127–128), "geochemical investigations show that the substances essential for the formation of plagioclases are, as a rule, available within the rock itself and can even be concentrated locally by internal exchange of migrating matter". We are dealing with a closed system. Obviously the size of this closed system must be clearly stated, since evidently, on the crystal scale, we are dealing with an allochemical process of the same type as the formation of porphyroblasts and many metamorphic nucleations. The system is to be considered closed not only on a macroscopic scale (dimensions of the rock formation) but also, with some exceptions, on the mesoscopic scale (dimensions of the analysed samples): in fact, it is on this size that demonstrations of the isochemical character of the process are based. It is also to be pointed out that, when speaking of isochemical processes, one refers only to the solid phases: in other words, chemical analyses indicate only that the composition of the solid fraction has not changed during the process, but the fluid phase may have been involved in compositional variations. Consequently, the intergranular fluid phase, the composition of which cannot be analysed, is to be considered available for compositional variations during the process.

3. The widespread occurrence of this phenomenon must be significant and suggests causes and mechanisms which in nature easily occur.

4. The feldspathization takes place at all metamorphic temperatures. On the other hand, it is well known that white micas are stable over the whole P-T range of metamorphism, with the exception of a narrow fringe of very high temperatures (CIPRIANI, SASSI and SCOLARI, 1971). Therefore, temperature should not be considered as the determining cause of isochemical feldspathization, even if the composition of the neogenic feldspars appears to be controlled by temperature.

5. The postkinematic character of the process leads us to search for its primary causes in the environmental variations connected with the passage from the conditions of synkinematic crystallization to those of static crystallization, in a chemical system which is substantially closed except for the very mobile components. In this way, it is possible to detect that the stability of white micas is controlled not only by physical conditions, but also by some chemical variables; this means that the latter are capable of making white micas unstable inside their T-P field of stability.

6. Petrographic experience quite unequivocally indicates that, in metamorphic pelites, the crystallization of new plagioclases is far more common than that of new microcline and that, to the author's knowledge, a true contemporaneity between potash feldspathization and new plagioclase crystallization has never been noted.

7. The formation of new plagioclases cannot be genetically explained by presuming that the original micas were paragonite. Although this would certainly simplify the problem of geochemical balance, and there is no doubt that this transformation does take place, a generalization of such an assumption presents many difficulties. Chiefly, there is a great discrepancy between the frequency of the formation of new plagioclases and the relative scarcity of paragonite in metamorphic pelites. Certainly sodic mica is less rare than it now seems to be, considering that it can be detected only by X-ray investigation; there is no doubt, however, that the appearance of paragonite requires a peculiar rock composition, and is therefore relatively scarce in nature (GUIDOTTI, 1968).

Moreover, it is difficult to believe that the two white micas, when they coexist, are heterogeneously distributed in the rocks, to form patches. These two phases must very probably be thoroughly mixed with each other in the mica bands. They are in fact formed from a clayey mixture of suitable composition so that a reciprocal chemical equilibrium is reached, as in a practically binary muscovite-paragonite system (ZEN and ALBEE, 1964). The results obtained by ALBEE and CHODOS (1965) and LADURON and MARTIN (1969) confirm this opinion, although they do not allow us to make a generalized statement. These authors, by means of microprobe analysis, have ascertained that, in the samples they studied, paragonite is thoroughly mixed with the coexisting muscovite so as to form apparently homogeneous flakes consisting, in fact, of compositionally different interlayered plates, the thickness of the paragonitic layers varying from 1 μ to a few tens of a micron. On the other hand, FREY (1969) found a characteristic presence of mixed layers paragonite-phengite in the low-grade pelitic metamorphites of the Glaris Alps. He believes this is general in low-grade pelitic metamorphic rocks and suggests a new reaction for the formation of paragonite, where albite is not involved and from which the formation of intimate associations of phengite and paragonite results. Such a reaction is said to be in agreement with unpublished experimental data by ALTHAUS (FREY, 1969, p. 64).

Finally, if feldspathization was controlled by the composition of the white mica, the wider occurrence of muscovite rather than paragonite in metamorphic rocks would imply the higher frequency of microcline production than plagioclase: in fact, this is not so.

8. Isochemical postkinematic feldspathization is common in the intermediate- and high-pressure facies series, while it is practically absent in the low-pressure facies series. This is shown in the literature and has been observed by the writer too in the rocks of the Central Pyrenees (Bosost Area; ZWART, 1962).

The intermediate- and high-pressure facies series differ from the low-pressure ones not only in the different P_{tot} values, but also for the following reason: according to many authors, tectonic overpressure plays a part in the former, but not in the latter.

In order to recognize the causes of feldspathization, it is clear that P_{tot} differences cannot be used, as white micas are stable in all the facies series. It is therefore inevitable to take the tectonic overpressure into consideration, a very useful concept, but still *sub judice*.

It is not opportune to discuss here the existence of tectonic overpressure and to list all the points in its favour. It is sufficient to keep in mind that until now nobody has demonstrated its inexistence and that, as it has been formerly used to explain otherwise inexplicable phenomena, tectonic overpressure may be invoked once again. This reasoning appears much more convincing if we take into account that the values of tectonic overpressure should decrease to zero in the passage from the synkinematic to the postkinematic phase, that is, just when feldspathization begins.

In conclusion:

1. The composition of the original white micas is not to be considered among the causes of feldspathization, nor among the conditions necessary for it (even if it certainly has its importance in the geochemical balance).
2. Temperature affects the phenomenon but is not the originating factor.
3. The primary causes of feldspathization are to be sought in the chemico-physical variations connected with the passage from the synkinematic to the static environment, i. e. with the decrease of the tectonic overpressure.

THE GENETIC MODEL

Since $P_{tot} \simeq P_f \simeq P_{load} + P_{tect}$¹), when P_{tect} begins to diminish, an overpressure of the intergranular fluid phase develops. This overpressure gradually

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¹) P_{tot} = total pressure; P_f = pressure of the fluid phase; P_{tect} = tectonic overpressure.

decreases as this phase expands into a larger volume by means of diffusion. When this decrease is complete, $P_{tot} \simeq P_{load} \simeq P_f$ results. Since petrographical observations indicate that feldspathization takes place in this lapse of time, the causes of this process must reside in the environmental variations occurring just in this lapse of time.

In addition to water, the fluid phase consists of other components in various concentrations and with different degrees of relative mobility (KORZHINSKII, quoted in MEHNERT, 1969). Therefore the variation of P_f determined by decreasing P_{tot} brings about a differential variation in the concentration of these components in the intergranular fluid. More precisely, the intergranular fluid phase is indirectly enriched in relatively immobile components with respect to H_2O and CO_2, and in particular there is an increase in the concentrations of oxygen and alkalies. Moreover, K^+ is more mobile than Na^+: an increase in the concentration of Na^+ greater than that of K^+ in the fluid phase is therefore to be anticipated.

It should also be borne in mind that the preferential removal of CO_2 from the system implies a relative increase of the pH inside the fluid phase.

Therefore, in a synorogenic metamorphic event, during the passage from the synkinematic phase to the later static phase, a concentration of oxygen and alkalies (in particular Na^+) takes place in the fluid phase, as well as an increase of pH.

Now, are these environmental variations really capable of limiting the field of stability of white micas, and causing their replacement by feldspars?

The answer is supplied by the experimental results obtained by HEMLEY and JONES (1964) in the systems Na_2O-Al_2O_3-SiO_2-H_2O and K_2O-Al_2O_3-SiO_2-H_2O and by the diagrams presented by GARRELS and CHRIST (1965) for the system Na_2O-K_2O-Al_2O_3-SiO_2-H_2O. These results in fact lead us to conclude that, at constant T, an adequate increase in pH will promote evolution into the field of the feldspars from that of the micas, and, on the other hand, that an increase in the concentration of alkalies will by itself have the same effect as well. Therefore, all predictable environmental variations due to decreasing tectonic overpressure will lead to the chemical instability of white micas inside their own T-P stability field and their replacement by feldspars.

The greater frequency of Na-Ca feldspathization than K feldspathization is clearly explained when considering Fig. 3 of HEMLEY and JONES (op. cit.) and Figs. 10.10 and 10.12 of GARRELS and CHRIST (op. cit.). Since the increase in the concentration of Na^+ is greater than that of K^+, those diagrams indicate that consequently the field of plagioclase rather than that of K-feldspar is usually entered. Moreover, those diagrams explain the non-contemporaneity between K feldspathization and Na-Ca feldspathization: the contemporary postkinematic crystallization of microcline and albite would in fact imply a variation in the concentrations of Na^+ and K^+ along only one definite line, and this would clearly imply the occurrence of very particular conditions.

It is worth remembering that Hemley and Jones (op. cit.) point out that the reactions they studied are pressure-dependent (p. 554), and that a decrease in pressure favours the appearance of feldspars (p. 565).

What has been stated so far is represented diagrammatically in Fig. 1a,

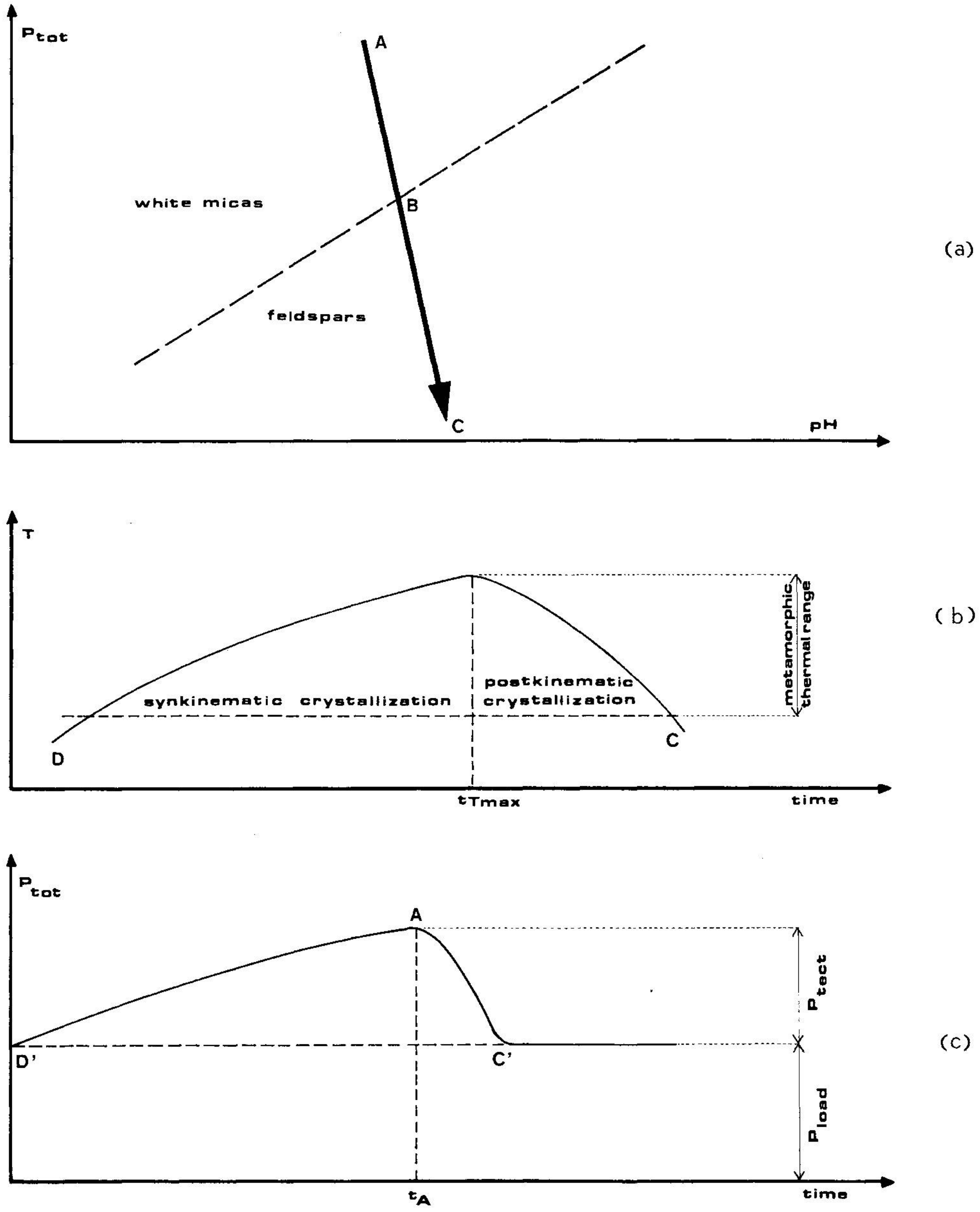

Fig. 1.

where the arrow AC outlines the variations of pH (and, if desired, also of the alkalies or oxygen concentrations) with decreasing P_{tot}. The boundary between the fields of white micas and feldspars is purely indicative, and its slope is established only by the fact that micas are favoured by high pressure and relatively low pH (or alkalies or oxygen concentrations).

Along the line AB pH varies for the above-mentioned reasons. During this time, if Na^+ is enriched more than K^+ (as very frequently happens), the following effects are to be expected: thermal conditions being suitable, ionic exchanges between the fluid phase and minerals develop and consequently the Na content of white micas increases, in agreement with the experimental results of IIYAMA (1964); moreover, if metamorphic nucleations occur, postkinematic Na-rich white mica crystallizes; then, following the line BC, postkinematic plagioclases replace the white micas. On the contrary, if the enrichment of K^+ is greater than that of Na^+, in the same lapse of time (line AB) a postkinematic nucleation of K-rich white mica may occur, and successively, along the line BC, postkinematic microcline crystallizes at the expense of the white micas.

The process does not end at C′, where P_{tot} and P_{load} have the same value (Fig. 1 c), but in C (Fig. 1 b), where the regional temperature reaches low values at which the mobility of the elements becomes insignificant and metamorphic nucleation impossible.

The time at which point A is reached (t_A) need not necessarily coincide with that of the thermal maximum ($t_{T\,max}$; Figs. 1 b and 1 c). On the contrary, in the writer's experience, the maximum temperature is often reached during the late static phase. There is no way of anticipating the chronological lapse between C and C′, and between D and D′.

Other conditions being equal, the crossing of the boundary between the fields of white micas and of feldspars depends on the value of the tectonic overpressure; more precisely, it depends on how much P_{tot} decreases while the thermal conditions favourable to metamorphic nucleation persist. Thus, in the absence of metasomatism, the distribution of postkinematic white micas and feldspars in a metamorphic belt can be used as an index of the regional variations of tectonic overpressure and/or of the chronological relationships existing between regional cooling and disappearance of P_{tect}.

However, the patchy development of isochemical feldspathization may also be due either to other environmental factors determining heterogeneous nucleation on the meso- and macroscopic scales, or to compositional heterogeneities of the original intergranular fluid.

From the diagrams mentioned above, and especially Fig. 10.10 of GARRELS and CHRIST, it can also be inferred that suitable variations in the concentrations of the intergranular fluid phase may lead to the following effects, before the formation of new plagioclases: a later increase in the Na-content in the already crystallized white potassic micas; the appearance of paragonite replacing muscovite. The writer thinks that this process is responsible for numerous occurrences of paragonite in rocks belonging to the high-pressure facies series, and of Na-rich muscovites in low-grade and very high-grade metamorphic rocks.

CONCLUDING REMARKS

It seems to the writer that the model described above explains all the characteristics of isochemical feldspathization, including its distribution in nature. Furthermore, it is also applicable to other analogous processes taking place during the postkinematic phase of metamorphism as, for instance, the replacement of one feldspar by another. In this specific case the experimental results of ORVILLE (1962, 1963), IIYAMA (1965) and CHRISTOPHE-MICHEL-LÉVY (1967, 1968) are very useful.

The extension of this model to syn-slip feldspathization (ZWART, 1962) does not involve serious difficulties. In fact, movements along the S planes characterizing this type of deformation (which generally turns out to be small when the trains of inclusions are analysed), take place after the main dynamic and metamorphic phase. They can therefore be considered just as movements of settling which take place during the relaxation phase of P_{tect}.

This opinion is supported by the heterogeneous distribution of such movements observed by the writer in the crystalline basement of Recoaro (Northern Italy) (SASSI and ZIRPOLI, 1968, pgs. 234–235.).

The problem of the geochemical balance remains open, as does the question of the fate of K^+ released from micas and added to the intergranular fluid phase. No definite opinions on this difficult problem can be given, since: a) the composition of the original solid phase (micas) cannot be recognized with certainty, not even by analysing the mica inclusions still present in the neogenic feldspars; b) the composition of the fluid phase is never quantitatively known, and therefore it cannot be reproduced in the laboratory in other than an extremely simplified form.

An appraisal of the fluid phase composition, however, can be based on the chemical data on the composition of sea water, pore solutions (ENGELHARDT, 1960; HEIER and ADAMS, 1964), and fluid inclusions in metamorphic minerals.

Regarding the latter, a good support to the present model is given by ORVILLE (1963): "Fluid inclusions data strongly support the assumption that a vapor phase rich in alkali salts is present during the crystallization of most metamorphic rocks" (p. 236); "Most of the samples determined were enriched in Na relative to K" (p. 224).

If the system can be considered partially open for K^+, some amount of this cation could leave the system due to its mobility, but this would imply a partially metasomatic character for the process. On the other hand, some K^+ could be removed from the fluid phase through adsorption at the boundaries of the crystals (De Vore, 1955); some K^+ could enter already existing minerals, producing for example a partial replacement of plagioclases by microcline, or of the amphiboles by biotite (phenomena observed by the writer; see also B. Zanettin, 1964). Finally, small amounts of K^+ could enter the plagioclases.

Inclusions of white micas in feldspars seems to occur, to the writer's knowledge, only in the plagioclases, never in microcline²). It is clear that we are dealing with microstructural relics but there are many doubts as to whether we are dealing also with relics in a chemical sense, considering the high sensitivity of white micas to new environmental conditions (Cipriani, Sassi and Scolari, 1971), and bearing in mind the experimental data obtained by Iiyama (1964). Moreover, it should be noted that the amount of these inclusions is very variable, and does not depend on the size of the plagioclase neoblasts and on the intensity of the feldspathization. This could suggest that the amount of mica inclusions in feldspars might represent an index of the degree of local mobility of K^+.

If one accepts the presupposition that Na^+ did not come from outside but was already present in the *intergranular phase-rock* system, no problems remain: at the end of the process, Na^+ is fixed in the solid phase and K^+, freed from the replaced micas and not fixed in other minerals, is added to the fluid phase of the same system. On the other hand, "the transfer of large amounts of alkalis between adjacent volumes of rock does not require that large quantities of alkalis be present in solution at any given time, but only that diffusion of alkali ions takes place through a pervasive vapor phase" (Orville, 1963, p. 235); this condition seems to occur in nature.

Notwithstanding this, the problem of the fate of K^+ in this process still remains, as do the analogous ones posed for other elements in many metamorphic reactions (for example, De Vore, 1955; Angel, 1965). However, the genetic mechanism proposed here is substantially independent of this problem, so that the impossibility of solving it does not weaken this genetic model at all.

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²) A relatively wide formation of microcline at the expense of white mica was detected by the writer only in metamorphosed Raiblian beds from the Fleres Valley, Alto Adige, Northern Italy, in samples kindly supplied by Prof. C. Friz.

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