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An experimental approach to the replacement of quartz by feldspar

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With 10 figures in the text

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Abstract

Experiments were carried out on rock specimens of nearly pure quartzite in reaction with saturated alkali aluminate solutions in the temperature range of 400 to 650° C and at pressures up to 3 kb. A reaction rim is formed consisting of K-feldspar (sanidine), or Na-feldspar (albite), respectively. Microphotographs show replacement textures analogous to those observed in natural quartzites, or other quartz-bearing rocks, affected by feldspar metasomatism.

A simple reaction rim of feldspar is only formed if the hydrothermal fluid is separated by pressure release after reaction. Cooling without removing the hydrothermal phase leads to secondary alteration processes including partial sericitization of the sanidine, and to the formation of opale or lussatite at essentially lower temperatures when SiO_2 is in excess.

Auszug

Es werden Experimente an Probekörpern von fast reinem Quarzit in Kontakt mit gesättigten Alkali-Aluminat-Lösungen beschrieben, die bei Temperaturen zwischen 400—650° C und bei Drucken bis zu 3 kb vorgenommen wurden. Es bildete sich eine Reaktionszone aus K-Feldspat (Sanidin) bzw. Na-Feldspat (Albit) mit mikroskopischen Verdrängungsstrukturen von Quarz durch Feldspat, die natürlichen metasomatischen Gefügen sehr ähnlich sind.

Eine einfache Reaktionszone von Feldspat wurde nur dann gebildet, wenn die hydrothermale Phase nach der Hauptreaktion durch Druckentlastung entfernt wurde. Abkühlung ohne Entfernen der Hydrothermalphase führt zu einer teilweisen Umbildung des Sanidins in Muskowit sowie zur Bildung von Opal oder Lussatit als niedrig-thermale Phasen bei Gegenwart von überschüssigem SiO_2 als Bodenkörper.

Preliminary note

(by K. R. MEHNERT)

The replacement of quartz by feldspar is a very important process in petrogenesis, especially in magmatic and metamorphic rocks of the deep crust, e. g. granites and migmatites. Feldspar phenocrysts replacing quartz and other minerals are formed by a process of alkali metasomatism in rocks of any composition, a process generally known as "feldspathization" or "granitization".

Whilst the petrographical and geochemical aspects of these metasomatic processes are relatively well known, there is lack of information about the physicochemical conditions of the replacement process itself. It is the

purpose of the present paper to approach this problem by a simplified experiment.

A rock sample of relatively pure quartzite is brought into contact with a supercritical fluid phase saturated with Al and K, or Na, respectively. The fluid phase obviously is introduced into the solid rock by migration mainly along the grain boundaries. By reaction with the fluid phase the quartz crystals are replaced by K-feldspar (sanidine) or Na-feldspar (albite) showing replacement forms similar to those found in natural quartzites which have undergone a feldspathization process.

These investigations should be considered as a continuation of a series of former experiments on the dissolution phenomena of quartz single crystals in various agents, including hydrothermal solutions (R. HEIMANN et al.: "The kinetics and morphology of the dissolution of quartz", part I—VI 1969—70).

Introduction

The present investigation began with a series of experiments on quartz single crystals, mainly spheres of 2 or 4 mm diameter, and their changes in size and shape by dissolution in various fluid agents. The experiments started with hydrofluoric acid and solutions of NH_4HF_2. In this way dissolution forms with rounded faces could be obtained. Nevertheless, goniometric measurements resulted in crystallographically well defined forms (HEIMANN et al. 1969, Parts I and II). In another series of experiments quartz spheres were dissolved in melts of NaF and NaF-$NaPO_3$ which were used in order to lower the rate of reaction (HEIMANN et al. 1969, Parts III and IV).

Hydrothermal experiments began with the dissolution of quartz spheres in pure water under 0.5—4 kb H_2O pressure and at temperatures between the critical temperature of water and that of the high/low inversion point of quartz (Part V). Experiments were continued by using supercritical solutions of alkali salts, mainly carbonates, phosphates, chlorides, fluorides and hydroxides. The morphology of the resulting dissolution forms of quartz were determined and their relations to the compositions of the dissolving solutions and their pH values (Part VI) were studied.

After these investigations of the basic principles of quartz dissolution, experiments were carried out on polycristalline aggregates, like quartzites, in order to study the effect of dissolution processes along grain boundaries etc. A rock sample of nearly pure quartzite was fixed at the high temperature end of a vessel with a temperature gradient and studied microscopically after partial dissolution under hydrothermal conditions. At the low temperature end another sample of the same quartzite was fixed in order to study crystallization phenomena by replacement of the quartzite by newly

formed feldspar. The formation of feldspar was reached by addition of an alkali aluminate solution and by adding a piece of solid alkali feldspar to the solution so that its concentration remained constant.

This series of experiments led to the formation of microgranular replacement rims of K-feldspar, or Na-feldspar, covering the end planes of the quartzite samples. After their formation the remaining gas phase was removed by pressure release. In this way the final crystallization of low temperature minerals and the formation of secondary alteration products could be avoided.

The replacement of quartz by feldspar has not yet been studied experimentally. Thus the present investigation may be regarded as a first approach to the problem. For instance, one of the petrogenetically most interesting questions can be studied in detail: how the introduced material migrates into the solid rock and, vice versa, how the replaced material leaves its former place and migrates outwards by some kind of counter-current principle. As is well known from natural occurrences, this reciprocal migration mainly occurs along the grain boundaries of the rock. This was corroborated by our experiments since microscopical observations strongly proved this assumption (Fig. 8).

Another problem of replacement processes in general refers to the question whether or not the original mineral, i.e. the "paleosome", is replaced by the newly introduced mineral, the "neosome", in the solid state without any intermediate fluid phase. The alternative would be that the paleosome at first was more or less dissolved, at least partially, and then the neosome crystallized from the interstitial fluid. Hence the question arises how much of the material of the paleosome has remained "in situ" and taken over into the lattice of the neosome. In the case of a replacement of quartz by feldspar essential amounts of the paleosome could re-enter the neosome so that only an addition of alkali and alumina would be necessary. Hence a replacement of this kind can be assumed to work rather easily. Perhaps that may be the reason why replacement processes of this type are rather wide-spread in nature.

Experimental

The quartzite used in the following experiments was taken from glacial boulders found in the diluvial moraines around Berlin. It is a typical Archean quartzite which is very common in Sweden, for instance in the vicinity of Västervik. It consists of more than 99 % quartz, the crystals mostly being directly in contact with each other and forming a polygonal granular fabric with angles close to 120°. The grain size is rather constant, about 150—200 μ in diameter, and only rarely varies from 50—400 μ. Besides quartz very few other detrital components are present, for instance potash feldspar. The

latter is the only component showing rounded primary grains surrounded by a rim of recrystallized quartz. The quartz grains, however, never contain primary internal structures, probably because of a relatively strong recrystallization. A cement between the quartz crystals is generally absent, but locally "spots" of a recrystallized carbonatic cement occur. They are easily distinguished microscopically even after hydrothermal treatment.

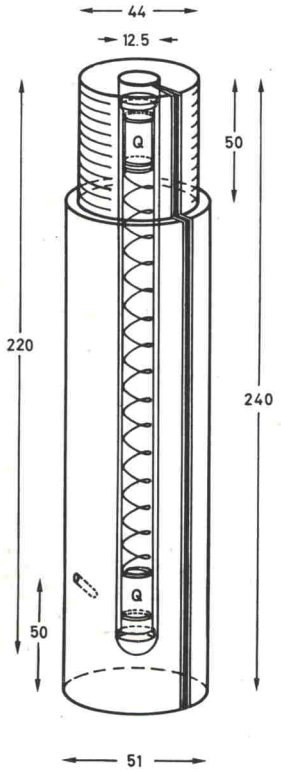


Fig. 1. Reaction vessel and arrangement of the samples.

The hydrothermal vessel (Haynes René 41) had an inner diameter of 1/2″ which corresponds to a volume of 27 cm^3. In a Cu liner of 20 cm length with an internal diameter of 9 mm, at both ends two rod-shaped specimens of the above mentioned quartzite were fixed and held at a constant distance by a NiCr spring (Fig. 1). The rods of quartzite had a diameter of 9 mm and a length of 15—20 mm. The endplanes of the cylindrical bodies were polished.

The liner was closed by well fitting stoppers fixed by splints. The vessel was filled with saturated (0,06 M) $KAlO_2$- or $NaAlO_2$-solution. In some cases a piece of $KAlSi_3O_8$ or $NaAlSi_3O_8$ glass was added in order to get a

constant concentration gradient. The glass was prepared from potassium carbonate and sodium carbonate, respectively, plus γ-alumina and silica (Malinckrodt). The components were well mixed and then melted in a HF coil. All chemicals were of A. R. grade.

The pressure required was regulated manually by using the overflow valve during the time of heating up.

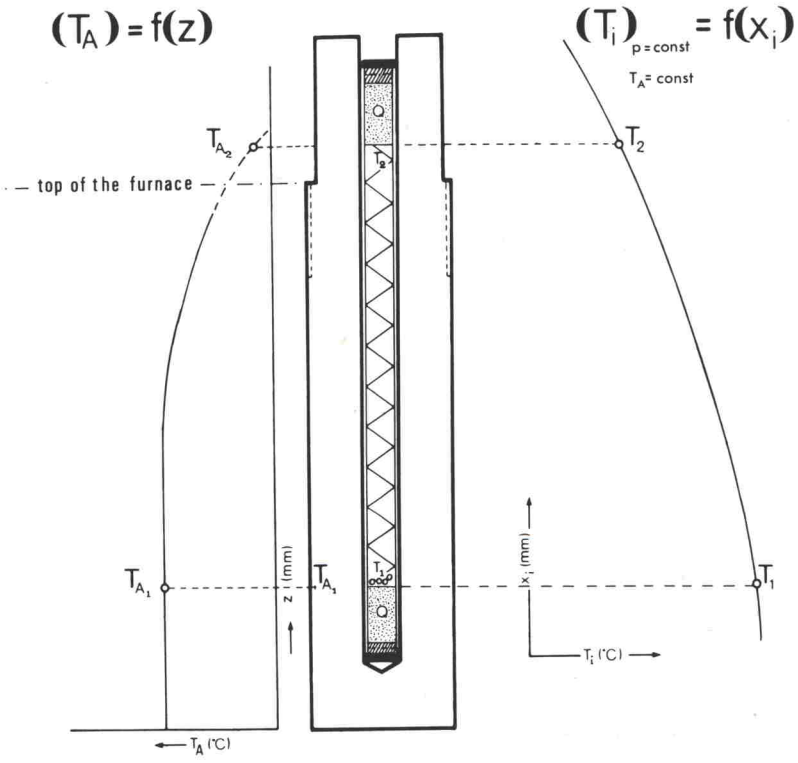


Fig. 2. Temperature distribution inside the vessel (for explanation see text).

Fig. 2 shows the temperature distribution inside the vessel. The left hand diagram represents the temperature measured at the outside of the vessel (T_A). It corresponds to the axial temperature characteristic of the furnace. The right hand diagram represents the temperature measured inside the vessel (T_i). Of special importance are the temperatures T_1 and T_2 which correspond to the temperature measured in the region of dissolution of the lower quartzite rod near the bottom (T_1) and the temperature in the region of crystallization and replacement of the upper quartzite rod near the top of the vessel (T_2). T_1 varied between 500° and 800° C, whilst T_2 varied

between 400 and 650° corresponding to a decrease of temperature of about 100—150° C along the axis of the vessel.

Runs were made from 24 to 100 hours. Pressures varied from 0,5 to 3 kb.

Results

The solubility relations of quartz and potassium feldspar are represented in Figs. 3 and 4, according to ANDERSON & BURNHAM (1965) and SCHLOEMER (1962). The diagrams show that the mass of quartz dissolved in pure water at a given temperature and pressure is about five to ten times greater than

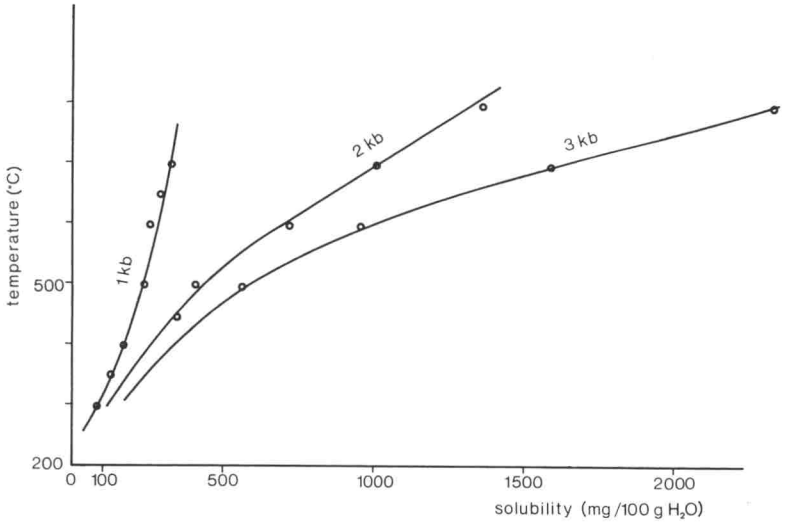


Fig. 3. Isobars of the solubility of quartz in pure water according to ANDERSON & BURNHAM (1965).

that of feldspar. From Fig. 4 it is evident that potassium feldspar shows a retrograde congruent solubility in the temperature range between 450 and 700° C. Hence the following has to be considered: By cooling the system down to about 450° C the solubility of K feldspar increases, and the formerly crystallized feldspar is partially resolved. Beneath the temperature of about 450° C feldspar again crystallizes mostly in the form of relatively big crystals.

An excess of silica in the fluid phase, for instance by using a second quartzite rod (see above), leads to the crystallization of late quartz, likewise in the form of relatively big crystals. They mostly consist of prism-free forms only showing steep rhombohedra like (40$\bar{4}$3), (20$\bar{2}$1) and (70$\bar{7}$5) (FLÖRKE 1963, BROWN et al. 1955, AUGUSTIN & HALE 1958).

By further cooling, the surplus of silica was precipitated in the form of colloidal aggregates of opale or lussatite (= cristobalite-opale), and uncertain keatite. This mineral forms very thin shells covering spherical aggregates of lussatite and showing a refractive index of 1.47. According to CARR & FYFE (1958) keatite is easily formed on rapidly growing surfaces of cristobalite. Hence it is commonly observed in hydrothermal experiments that spherical aggregates of cristobalite are covered by a skin of keatite.

To avoid the formation of these low-temperature minerals, as well as the secondary crystallization of feldspar, it is necessary to eliminate the hydro-

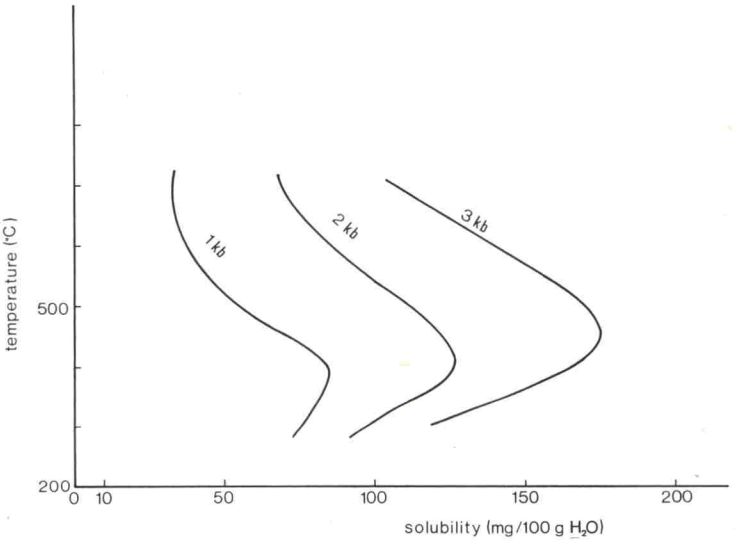


Fig. 4. Isobars of the solubility of potash feldspar in pure water according to SCHLOEMER (1962).

thermal fluid phase after the main formation of feldspar by reaction with quartz. This was done by opening the overflow valve after the main reaction, but before cooling. The condensed portion of the escaping gas phase was collected and analyzed.

In this way, the reaction was stopped and the reaction products were preserved without being transformed by secondary alteration processes analogous to "retrogressive metamorphism" in nature.

Dissolution and replacement of quartz by feldspar

In the following experiments a small sample of quartzite fixed at the high-temperature end of the vessel was dissolved in a hydrothermal fluid

containing K-aluminate. This fluid reacted with another sample of quartzite fixed at the low-temperature end.

Fig. 5 shows some typical dissolution forms of quartz grains having been in contact with the hydrothermal fluid at 625° C and 2 kb H_2O pressure for 23 hours. The dissolution mainly proceeds along the grain boundaries of the quartzite (below) and leaves behind partially dissolved quartz grains with crystallographically shaped contours (above). The crystal faces thus formed could not be measured, and therefore they could not be compared with the crystal faces obtained from the dissolution of single crystals (HEIMANN et al. 1969/70, Part V and VI). However, the similarity with natural

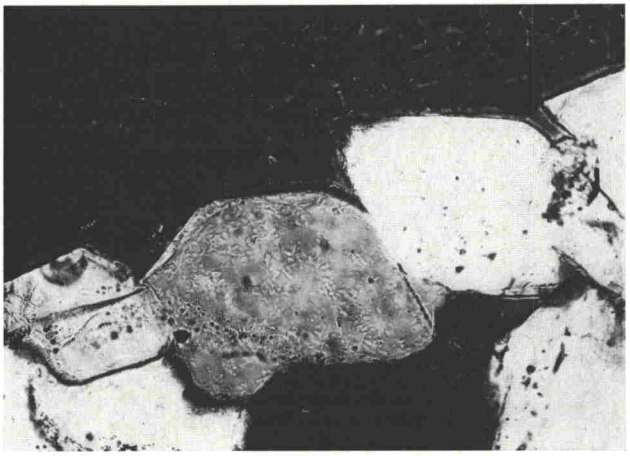


Fig. 5. Dissolution forms of quartz grains at the boundary between a quartzite sample (below) and the hydrothermal fluid phase (above). (625° C, 2 kb). Magn. 320×. Crossed nicols.

dissolution forms of quartz is striking. This will be discussed in detail in a later publication.

Fig. 6 gives an impression of the crystallization and replacement phenomena at the surface of the second sample of quartzite being fixed at the low-temperature end of the vessel. It was taken from an experiment carried out at 615° C and 3 kb H_2O pressure after 24 hours. The quartzite (below) is partially replaced by a fine-grained aggregate of K-feldspar (sanidine) with a grain size of about 5—10 μ. The somewhat coarser sanidine crystals at the upper end of the quartzite rod (grain size about 25—50 μ) have been formed at a relatively late stage and crystallized towards the fluid (above).

The colored Fig. 7 once more demonstrates the process of replacement in greater detail and clearly shows that the reaction proceeds along the grain boundaries of the quartz aggregate. The depth of the penetration of feldspar

into the quartzite can approximately be seen in Fig. 6. Under the conditions of this experiment, microscopically visible feldspar crystals in coherent clusters could be observed as far as about 0.5 mm from the surface.

The depth of penetration increases with the time of reaction and finally leads to a separation of more or less replaced quartz grains from the former quartzite aggregate. The separated quartz grains generally show irregular

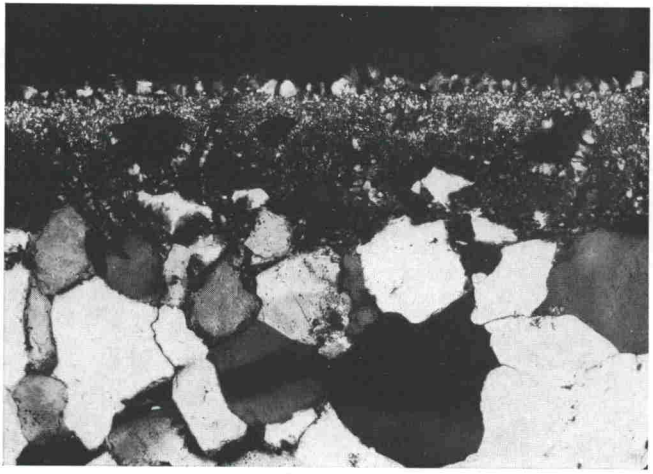


Fig. 6. Replacement of a quartzite sample by a fine-grained aggregate of potash feldspar (615° C, 3 kb). Magn. 75×.

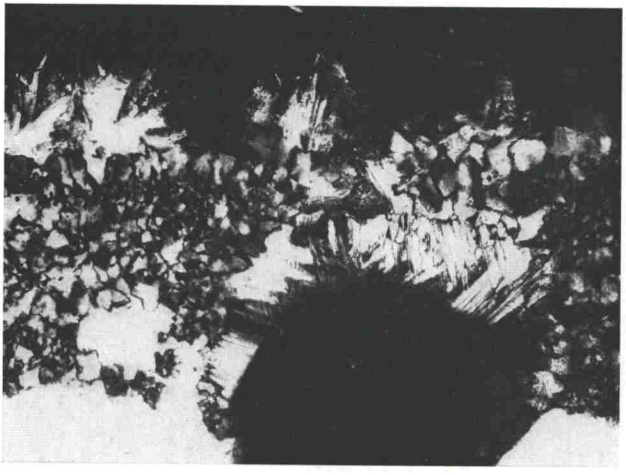


Fig. 9. Replacement of a quartz crystal (dark) by potash feldspar along preferred lattice directions (640° C, 3 kb). Magn. 215×.

forms, often with convex roundings, but sometimes also with concave cavities (Fig. 8, see also below).

Another type of replacement is portrayed in Fig. 9. The emplacement of feldspar begins again at grain boundaries, but in this case a quartz crystal is partially replaced by preferential growth of feldspar along particular lattice directions. This can be explained by a replacement process which was mainly governed by diffusion of the introduced substances into the quartz crystal and by an exchange of matter "volume per volume". In contrast to this, the structure seen in Fig. 8 can probably better be explained by first a dissolution of quartz and a following crystallization of feldspar from an interstitial fluid phase (see the alternative on p. 64).

Fig. 10 demonstrates the effects of secondary processes caused by the crystallization of low-temperature phases in the presence of a cooling hydrothermal phase. The picture shows the replacement of a quartzite by a fine-grained K-feldspar aggregate. Above this zone we see a streak of flaky muscovite, and above that a second generation of K-feldspar appears with relatively large crystals.

This formation of muscovite can be explained by the following equation (NORTON 1939, GILLINGHAM 1948, O'NEILL 1948; additional literature see SEKI & KENNEDY 1965, LAGACHE 1965):

$$3\ KAlSi_3O_8 + H_2O \rightleftharpoons KAl_2((OH)_2AlSi_3O_{10}) + 6\ SiO_2 + K_2O.$$

The muscovite is of the 2 M type as ascertained by X-ray investigations corresponding to the results of YODER (1959) who pointed to the pressure induced synthesis of the more closely packed 2 M muscovite in contrast to the less dense 1 M type.

Experiments in the system Na_2O-Al_2O_3-SiO_2-H_2O

Along with the experiments described above, similar investigations were made in the corresponding system using Na-aluminate dissolved in a hydrothermal fluid.

In principle, the reactions are analogous to the reactions in the K-bearing systems. However, the reaction rate of the Na-bearing systems is distinctly greater than that of the K-bearing systems. Thus the replacement of quartzites in Na-rich hydrothermal fluids is much easier and quicker than in the corresponding K-rich solutions. For instance, the typical dissolution forms shown in Fig. 8 were only obtained in Na-bearing fluids.

In contrast to the results with K-solutions, no hydrolysis phenomena could be observed in the Na-bearing systems. In all experiments the Na-feldspar was stable and proved to be high-temperature albite ($2\vartheta_{131}$—$2\vartheta_{1\bar{3}1}$ = 1.92 — 2.05). Experiments carried out at temperatures lower than 500° C showed analcite, beside albite, at the wall of the liner.

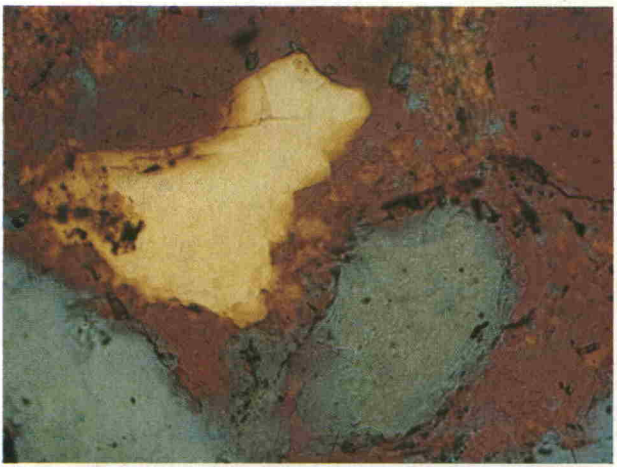


Fig. 7

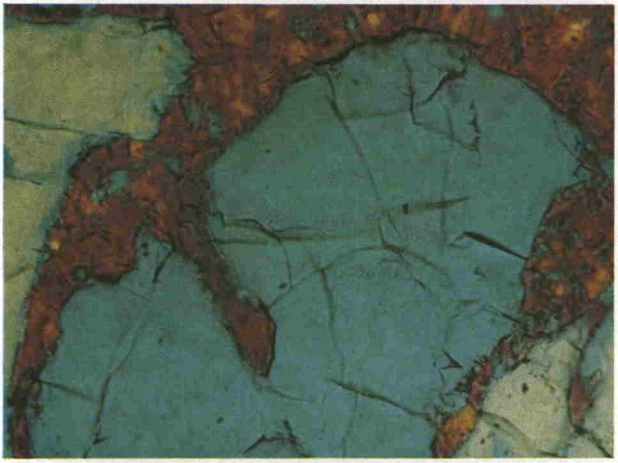
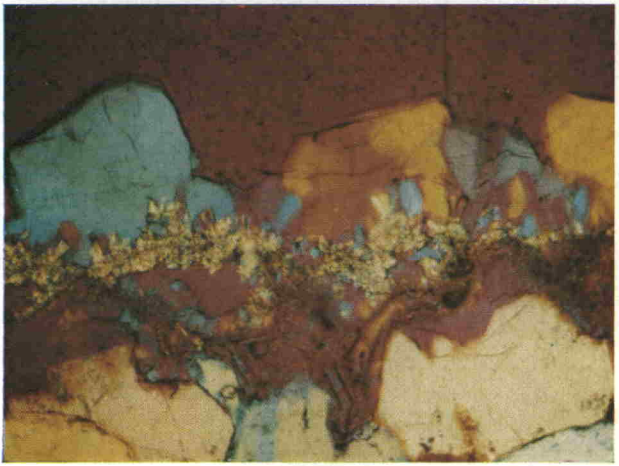


Fig. 8



4

3

2

1

Fig. 10

Acknowledgements

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Fig. 7. Detail of the replacement of quartzite (yellow and blue) by a fine-grained aggregate of potash feldspar (red, orange, blue) in an advanced stage. The replacement mainly proceeds along the grain boundaries (615° C, 3 kb). Magn. 320×.

Fig. 8. Detail of the replacement of quartz grains (light and dark blue) at the edge of a quartzite sample by a fine-grained aggregate of albite. The quartz grain in the center shows a cavity filled by albite (600° C, 3 kb). Magn. 320×.

Fig. 10. Replacement of quartzite (1) by fine-grained potash feldspar (2), followed by a zone of muscovite (3) and by a second generation of relatively large crystals of potash feldspar (4). In this experiment the hydrothermal fluid phase remained in the vessel during cooling and caused "retrogressive" replacement and crystallization Magn. 160×.

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