Contrib. Mineral. Petrol. 59, 13–32 (1976)

Contributions to Mineralogy and Petrology

U-Pb Zircon and Rb-Sr Whole-Rock Dating of Low-Grade Metasediments Example: Montagne Noire (Southern France)

D. Gebauer and M. Grünenfelder

Laboratory for Isotope Geochemistry and Mass Spectrometry,
Swiss Federal Institute of Technology, Zurich, Switzerland

Abstract. Three detrital, Proterozoic zircon suites extracted from siltstones progressively metamorphosed between chlorite- and staurolite-grade independently date the major Caledonian metamorphism within the gneiss dome of the Montagne Noire (Southern France). From this, the following conclusions concerning U-Pb systematics of zircons in low-, medium- and high-grade metamorphic rocks can be drawn:

1) *Temperatures of at most 350–400°* C are sufficient to *open U-Pb systems* of metamict zircons or domains within zircons.

2) The observed open U-Pb system behaviour during metamorphism of the host rocks was found to be due to a *low-temperature recrystallisation of highly radiation damaged zircon lattices,* probably enhanced by high concentrations of fluid phases in the dehydrating rock volumes.

3) Recrystallisation of metamict zircons under low temperatures causes *maximum U-Pb ages for the thermal climax of metamorphism* of medium- and high-grade metamorphic rocks, as annealing and accompaning closing of U-Pb systems took place *before* the maximum temperatures of metamorphism were reached.

4) *Low-temperature recrystallisation* of old – generally Proterozoic – zircons can readily help to explain the fact that the numerous zircon suites from ancient shield areas yield "lower intercept ages" which are not correlated to any known geological event. Thus, either a weak thermal pulse, not necessarily registered by the mineral assemblage of the host rock, and/or elevated temperatures during burial in the crust might supply enough energy for a structural reordering and simultaneous lead loss of at least the most disordered lattice domains.

In contrast to the U-Pb zircon method, no unambiguous dating of the Caledonian main metamorphism was possible using the *Rb-Sr whole-rock technique* for phyllites and mica schists sampled in the same metamorphic profile from which the zircon samples were taken. The scatter of data points can best be explained by their rotation around a probable Caledonian isochron. This rotation very probably took place during the later Hercynian orogeny, not significantly affecting the slope of the least square regression line through the scattered data points.

1. Introduction

1.1. U-Pb Zircon-Suite Method

Since its introduction by Silver and Deutsch in 1963, the U-Pb zircon-suite method has been applied almost exclusively to the dating of magmatic and/or high-grade metamorphic rocks. The U-Pb systematics of detrital zircon populations from low-grade metasediments, however, are still surprisingly unknown, and the only published data to be found in this field (Michot and Deutsch, 1970; Grauert et al., 1973 and Grauert et al., 1974) were difficult to interpret due to too few or scattered data points. Furthermore, unknown reasons for the strong discordance of the analysed fractions left one without an answer to the question whether it is possible to date metamorphic events in low-grade metasediments or not. The main objective of this study, therefore, was to try to answer this question. The most promising approach seemed to us to be the analysis of zircon populations from samples taken along a profile of regionally metamorphosed rocks progressing from low- via medium- to high-grade metasediments of similar depositional age and – as the strictest condition – of identical geological history. Thus, it should be possible to control the U-Pb zircon data from the low-grade rocks by the results obtained from the high-grade equivalents which are known to give reliable age results provided the U-Pb systems were open during not more than one metamorphic event. Furthermore, Rb-Sr data from the same rocks were expected to serve as an additional control over the U-Pb results from the low-grade rocks.

1.2. Rb-Sr Whole-Rock Method

In contrast to the U-Pb zircon method, the Rb-Sr whole-rock method has been widely applied to the dating of low-grade metamorphic sediments. The interpretation of the isochron ages, however, has not been at all uniform. Some of the authors (e.g. Compston and Pidgeon, 1962; Allsopp and Kolbe, 1965; Peterman et al., 1967; Bell, 1968; Faure and Kovach, 1969) claimed the obtained isochron ages to be the result of a Sr-isotopic homogenisation during sedimentation and/or diagenesis. Consequently, these rocks must have remained closed systems for Rb-Sr during the subsequent metamorphic overprint(s). In a few other cases (e.g. Allsopp et al., 1968; Hurley et al., 1972, and Grauert et al., 1973) the question of having dated either time of diagenesis or metamorphism was left open, and in the remainder of the studies (Peterman, 1966; Clauer and Bonhomme, 1970; Roques et al., 1971) the isochron ages were interpreted in favour of a Sr-isotopic homogenisation during a metamorphic event.

In order to try to solve this dilemma which has lasted now for more than ten years, the present authors analysed fossiliferous Middle Cambrian and Lower Ordovician pelites, silt- and sandstones from the Montagne Noire which were folded between the Lower and Upper Carboniferous. Thus, the time of sedimentation and very low-grade metamorphism was well known for palaeontological and structural evidence. The results (Gebauer and Grünenfelder, 1974) clearly proved that a very slight metamorphism (zeolite facies) which did not even succeed in recrystallising the rounded quartz-grains is sufficient to cause a Sr-isotopic homogenisation in these sedimentary whole-rock systems. From this it was concluded that the numerous isochrons obtained from slightly metamorphosed sediments might be reinterpreted as determining the time of metamorphism and/or deepest burial. As we are dealing in this work with sediments which were on the whole more strongly metamorphosed than the ones cited above, metamorphic ages are all the more expected and could so serve as a further control of the U-Pb results from zircon-suites of chlorite- and garnet-grade rocks.

2. Geological Setting

All samples were taken from the crystalline complex of the Montagne Noire (Southern France) (Fig. 1). This region represents one of the best localities within the Hercynian belt of Middle and Southern Europe for studying regionally metamorphosed sediments between chlorite- and sillimanite-grade in a range

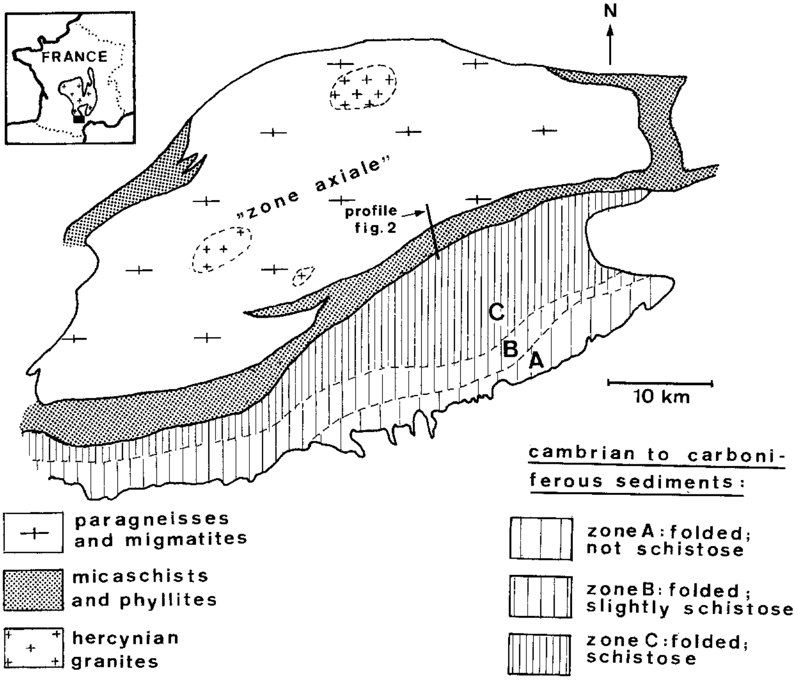

Fig. 1. Schematic, geological map of the Montagne Noire (Southern France). The gneisses and migmatites of the "zone axiale" form together with the Precambrian mica schists and phyllites a dome-like structure. The Cambrian to Carboniferous sediments south of the "zone axiale" belong to a series of nappe units overthrusted during the updoming of the basement in the course of the Hercynian orogeny. Their degree of deformation and zeolite-facies metamorphism decreases with increasing distance from the basement (Arthaud, 1970)

of not more than 4 kilometers. Geologically, the Montagne Noire, lying about 100 km west of Montpellier and about the same distance north of the Pyrenees, forms the southernmost rim of the French Central Massive (Fig. 1). Like the Moldanubicum, the Black Forest, the Vosges and the crystalline basement of the Alps, it is regarded as part of the Hercynian orogen. However, absolute age determinations carried out by over ten European laboratories since about 1967 proved – much to the astonishment and in part also disapproval of field geologists – that these classical Hercynian terranes had already suffered another, strong metamorphism during the Caledonian, i.e. during the Ordovician and Silurian. In fact, the very first hint (Rb-Sr whole-rock errorchron of 413 m.y.) of a Caledonian metamorphism within the Hercynian belt of Europe was obtained by Vachette in 1967 on mica schists taken from all over the Montagne Noire. Further work by Roques and Vachette (1970) supplied new data favouring a Caledonian metamorphism in the crystalline basement of the Montagne Noire.

However, it must be pointed out that due to too few and too scattered datapoints no accurate dating of the probable Caledonian metamorphism was possible. In contrast, the expected Hercynian magmatism and metamorphism is well documented by many Rb-Sr mica ages and isochron ages on granitic rocks and very low-grade, Old Palaeozoic sediments, (e.g. Vachette, 1967; Gebauer and Grünenfelder, 1974; Hamet, 1974, and Gebauer and Grünenfelder, in preparation). Structurally, the crystalline part of the Montagne Noire – the so-called "zone axiale" (Fig. 1) – forms a domelike anticlinorium about 70 km in the NE-SW strike direction and some 25 km perpendicular to it. It consists of highly metamorphosed para- and orthogneisses which are intruded by Hercynian granites (Vachette, 1967 and Hamet, 1974). A nappe structure south of the basement shows a complete stratigraphic sequence from Cambrian to Lower Carboniferous (e.g. Arthaud, 1970). In the north, the borders between the "zone axiale" and the sedimentary cover are tectonic in nature. In the south one

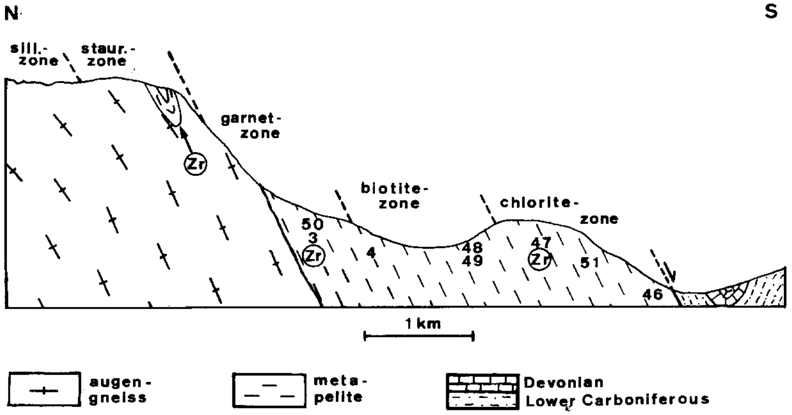

Fig. 2. Geological-petrological profile comprising high-grade to very low-grade metamorphic rocks. The position of the profile is given in Figure 1. The inserted numbers refer to the sample numbers for the Rb-Sr analyses. "Zr" represents the geological-petrological position of the localities from which the samples for the zircon analyses were taken

observes an approximately 4 km thick, metamorphic transition zone separating the Precambrian basement from the overlying, very low-grade, Palaeozoic sediments.

Since the work of De Sitter and Trümpy (in Gèze, 1952) the following interpretation relating to the structural development is generally accepted: during the Hercynian orogeny the Palaeozoic cover of the "zone axiale" was sheared away from its updoming crystalline base and transported to the south, the rocks being folded and in places also foliated.

Figure 2 shows the sample localities inserted into a schematic geologic-petrographical profile through the five mappable mineral zones at the southern rim of the "zone axiale" from which all the samples for the present study were taken.

3. U-Pb Results of Zircons from Staurolite-Grade Metasediments

Before discussing the main objective of this study—i.e. the behaviour of U-Pb systems in zircons from low-grade metasediments—we will first consider the age results from the medium- to high-grade equivalents, in order to find out how much, and when zircons of these rocks were affected by the metamorphic overprint(s).

The sample locality lying within a metasedimentary band folded together with the surrounding augen gneiss is given in Figure 2. The host rock from which the detrital zircons were extracted is a dark gray, fine to medium grained gneiss consisting of quartz (about 35 vol.-%), oligoclase-andesine (about 25 vol.-%), biotite (about 30 vol.-%) and garnet (about 5 vol.-%). The rest is

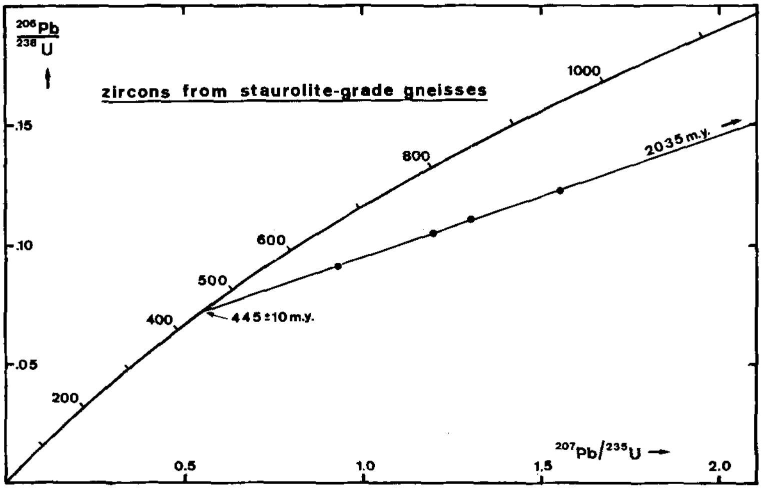

Fig. 3. U-Pb Concordia-diagram with the data points of four size and magnetic fractions of a zircon population extracted from a staurolite-grade paragneiss. The corresponding sample locality is given in Figure 2. The error given for the "lower intercept age" is based on a 95% confidence interval

Table 1. U-Pb analytical data for zircons of chlorite-, garnet- and staurolite-grade metasediments

Sieve fraction (microns)	U (ppm)	Pb rad. (ppm)	$\frac{^{206}Pb}{^{204}Pb}$	Radiogenic lead in %			Atomic ratios			Apparent ages (m.y.)		
				206	207	208	$\frac{^{206}Pb}{^{238}U}$	$\frac{^{207}Pb}{^{235}U}$	$\frac{^{207}Pb}{^{206}Pb}$	$\frac{^{206}Pb}{^{238}U}$	$\frac{^{207}Pb}{^{235}U}$	$\frac{^{207}Pb}{^{206}Pb}$
Chlorite-Zone Metasediments												
−42 m.[a]	1016	100.0	2862	82.28	6.50	11.22	0.09437	1.028	0.07898	581	718	1172
42−53	814	87.1	4538	82.64	6.73	10.63	0.10274	1.154	0.08145	630	779	1232
53−75	741	82.4	2768	82.13	6.88	10.99	0.10614	1.227	0.08381	650	813	1288
+75 n.m.[a]	534	67.7	4273	82.12	7.47	10.40	0.12114	1.520	0.09100	737	939	1447
Garnet-Zone Metasediments												
−42 m.	875	94.8	730	83.38	7.52	9.10	0.10508	1.306	0.09015	644	849	1429
42−53	750	91.9	1233	82.31	7.88	9.81	0.11727	1.548	0.09571	715	950	1542
53−65 n.m.	619	86.0	2206	81.60	8.45	9.95	0.13172	1.880	0.10352	798	1074	1688
+65 n.m.	507	80.9	2134	80.95	8.71	10.34	0.15008	2.227	0.10763	901	1190	1760
Staurolite-Zone Metasediments												
−53 m.	588	54.6	1288	84.30	6.27	9.43	0.09102	0.9335	0.07438	562	670	1052
53−65	565	60.2	4394	84.42	7.01	8.57	0.10455	1.197	0.08306	641	799	1271
65−75	585	66.2	442	84.27	7.19	8.54	0.11067	1.303	0.08537	677	847	1324
+75 n.m.	512	64.5	5354	83.45	7.68	8.87	0.12229	1.552	0.09204	744	951	1468

[a] m. and n.m. refers to fractions which moved along the "magnetic" resp. "not magnetic side" of the Frantz isodynamic separator if it was run at 1.6 amps, 1° tilt and 10° slope

made up mainly by ore minerals, traces of amphibole, apatite and zircon. The mechanical rounding of the detrital zircons can still be recognised, though the surfaces of the crystals are no longer frosted and pitted as is generally found in unmetamorphosed to medium-grade metasediments. Obviously, these energetically unfavourable surface structures are the first areas for a microscopically visible reconstitution of the zircon lattice. The colour of the mostly translucent crystals is light brown, the turbid ones appear slightly darker. The length-width ratio averages about 1.5.

The analytical data are listed in Table 1. As can be seen from Figure 3, four grain-size and magnetic fractions plot linearly in a Concordia diagram, intersecting the Concordia curve at 2035 and 445 m.y. respectively. As is generally observed in the case of young zircon suites, the data do not fit the diffusion models by Tilton (1960) or Wasserburg (1963). Instead, the data pattern can best be explained by a strong episodic lead loss (Wetherill, 1956) during a Caledonian metamorphism. Thus, the Rb-Sr whole-rock results obtained by Vachette (1967) and Roques et al. (1971) on gneisses and micaschists of the same geological unit—two point isochrons and "errorchrons" between 475 and 413 m.y.—are confirmed by the U-Pb zircon method. Including new Rb-Sr whole-rock data of approx. 430 m.y. on gneisses of the "zone axiale" (Gebauer and Grünenfelder, in preparation), a strong Caledonian metamorphism in the Montagne Noire is now well established both by Rb-Sr and U-Pb dating techniques. Mainly for this coincidence of age data the application of complex models like those discussed by Wetherill (1963) and Allègre et al. (1974) seem to be here not necessary for an interpretation of the observed U-Pb pattern.

As to the well-known Hercynian event in this region (Vachette, 1967; Roques and Vachette, 1970; Hamet, 1974 and Gebauer and Grünenfelder, 1974 and in preparation), we must conclude that the U-Pb systems of the analysed fractions remained unaffected about 300 m.y. ago. Obviously, not enough radiation damage was produced in the time span of about 130 m.y. between Caledonian and Hercynian metamorphism to help to reopen the U-Pb zircon systems during the Hercynian event.

4. U-Pb Data from Zircons of Chlorite- and Garnet-Grade Metasediments

The two sample localities are given in Figure 2, the analytical data in Table 1. The same rocks have also been analysed by the Rb-Sr whole-rock method (samples 3 and 47 in Fig. 2). The chlorite-grade quartz phyllites consist of quartz (about 65 vol.-%), white mica and chlorite (about 25 vol.-%), albite (about 5 vol.-%), ore minerals and graphite (about 5 vol.-%). In the case of the garnet-grade metasediments the host rock of the analysed zircons (sample 3) consists of quartz (about 60 vol.-%), biotite (about 20 vol.-%), muscovite and chlorite (about 8 vol.-%), garnet (about 5 vol.-%), albite-oligoclase (about 5 vol.-%) and ore minerals (about 2 vol.-%).

Zircon fractions are similarly heterogeneous in both rocks. They are mechanically rounded, contain frosted and pitted surfaces and range in colour from light to dark brown. The average length—width ratio is about 1.5. The garnet-

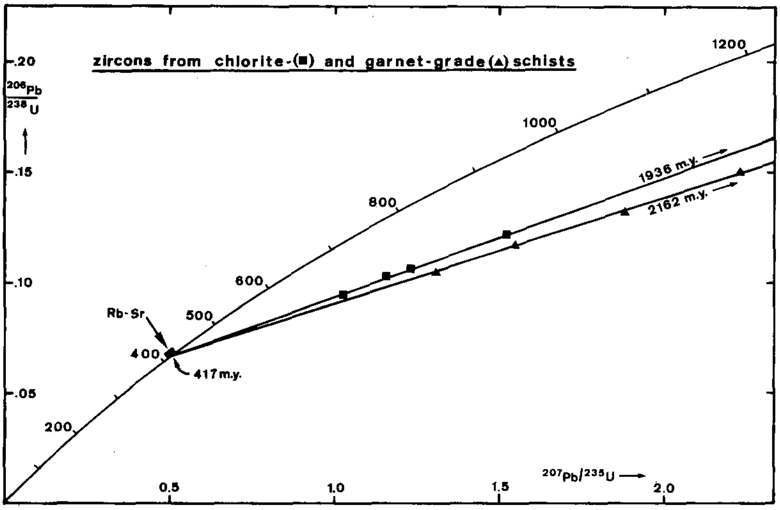

Fig. 4. U-Pb Concordia-diagram showing the data points of size and magnetic fractions from two detrital zircon populations. Squares represent size and magnetic fractions from a chlorite-grade quartz phyllite, triangles represent fractions from a garnet-grade quartz-mica schist. The two sigma errors of the two secondary ages are +35 m.y. and −40 m.y. for the chlorite-grade schist and +30 m.y. and −33 m.y. for the garnet-grade schist

grade zircons, however, show less surface contamination of graphite and are more homogeneous in colour than the chlorite-grade zircons.

As can be seen from Figure 4, the two analysed zircon populations, which were separated into grain-size and magnetic fractions, show an almost identical pattern in an U-Pb evolution diagram to those zircons extracted from the staurolite-grade gneisses. Furthermore, the "intersection ages" also agree within limits of experimental error with the ages obtained from the higher-grade metamorphic sample. Thus, the conclusion that zircon suites can be open systems at temperatures as low as about 350°–400° C, and that they can consequently be very valuable for dating low-grade metamorphic events is straightforward. In the case of the three analysed populations we can further conclude that they are related to a provenance delivering zircon mixtures with average ages of around 2 b.y.

From experimental work on metamict zircons (e.g. Mumpton and Roy, 1961; Pidgeon et al., 1966) we propose that the main causes for the observed open system behaviour must lie in the strong radiation damage produced over more than 1.5 b.y., and in the high concentration of fluid phases within the host rocks. Under these circumstances recrystallisation, as reflected by the present unit cell dimensions of these zircons, took place. In fact, the measured c_0- and a_0-values (Table 2) fall into the same range as those of zircons from the staurolite-grade gneisses or, generally, those formed or recrystallised during a Caledonian event and having U-contents between 500 and 1000 ppm (Köppel and Grünenfelder, 1971). In an α-dosage versus unit cell dimension plot (Holland and Gottfried, 1955) these cell parameters can easily be distinguished from those found in zircons which did not recrystallise after about 2 b.y. (Table 2),

Table 2. Cell dimensions of several zircon fractions analysed for U-Pb

Sample	a_0 (Å)	c_0 (Å)
Chlorite-grade sediments		
−42 μ m.	6.609 ± 0.001	5.996 ± 0.005
53−75 μ	6.607 ± 0.001	5.984 ± 0.002
Garnet-grade sediments		
−42 μ m.	6.609 ± 0.001	5.991 ± 0.002
+65 μ n.m.	6.608 ± 0.001	5.988 ± 0.002
Staurolite-grade sediments		
−42 μ m.	6.606 ± 0.002	5.984 ± 0.003
42−53 μ n.m.	6.608 ± 0.001	5.987 ± 0.002
Undamaged Ceylon zircon (Holland and Gottfried, 1955)	6.603	5.979
"Practically undamaged" zircon from an alpine peridotite containing ca. 150 ppm U (Gebauer and Grünenfelder, unpublished)	6.605 ± 0.001	5.980 ± 0.001
Strongly radiation damaged Ceylon zircon with an α-dosage comparable to 2 b.y. old zircons containing ca. 500 ppm U (Holland and Gottfried, 1955)	6.700	6.085

an age corresponding to the upper intercepts of the three zircons suites with the Concordia. Here, values of 6.085 for c_0 and 6.700 for a_0, far off the observed values, must be expected. This means that we also can exclude any type of low temperature diffusion or leaching processes of Pb which would not have affected the crystal structure of the metamict zircons. Of course, this recrystallisation and loss or radiogenic lead under low temperatures will also be enhanced by fluid phases within the zircon structure itself, as was first shown by Grünenfelder (1963).

In addition, polished sections of the studied zircons did not reveal any microscopically visible zones or regions which are leached away. Such an effect can only be detected after HF-etching of polished sections (Krogh and Davis, 1973 or Sommerauer, 1974). However, even then far less than one percent of zircon, i.e. euhedral zones with probably very high U-contents and consequently strongest radiation damage, is removed. Thus, the high resistance of the analysed zircon fractions against HF-etching is another factor supporting their recrystallisation during the Caledonian.

The conspicuous relationship between U-content and degree of discordance might best be explained in two ways. One is the chemical reaction model of Shukolyukov (1964) in which zircons with higher U-content contain, due to the higher radiation damage, more micropores and more microchannels than U-poorer Zircons; consequently, they contain higher concentrations of fluid phases and escape of radiogenic lead during recrystallisation is considerably enhanced.

As can be seen from the data spread of the zircon-suite extracted from staurolite grade sediments (Fig. 3), the grain size plays another important rôle in the degree of lead loss. This can be deduced, as in this population there is only a slight (about 15%) increase of U-content between the coarsest (512 ppm U) and finest fraction (588 ppm U) and nevertheless the data spread is comparable to those of the other two populations. In the latter, on the other hand, the U- contents increase by about 73% (507 ppm–875 ppm in the garnet-grade zircons) and about 90% (534 ppm–1016 ppm in the chlorite-grade zircons). Thus, the higher surface-to-volume ratio in the finer fractions is an additional important cause of the relatively stronger lead loss in the small fractions.

It seems astonishing that no correlation between degree of discordance and degree of metamorphism can be observed amongst the 3 zircon suites. In contrast, zircons from the chlorite-grade quartz phyllites are more discordant (on the average about 10%) than zircons from garnet-grade quartz-mica schists which have been formed at temperatures about 150° C higher. Furthermore, both zircon suites from staurolite- and chlorite-grade schists are on the average equally discordant. There is also no correlation between U-content and degree of discordance in all 12 analysed fractions. This pattern is shown, however, only within a single zircon suite. As consequently neither the different degrees of metamorphism nor the average U-contents can explain the relative position of the data points of the 3 suites, other factors, as e.g. the composition of the fluid phase (Pidgeon et al., 1973) and/or the content of trace elements including H_2O

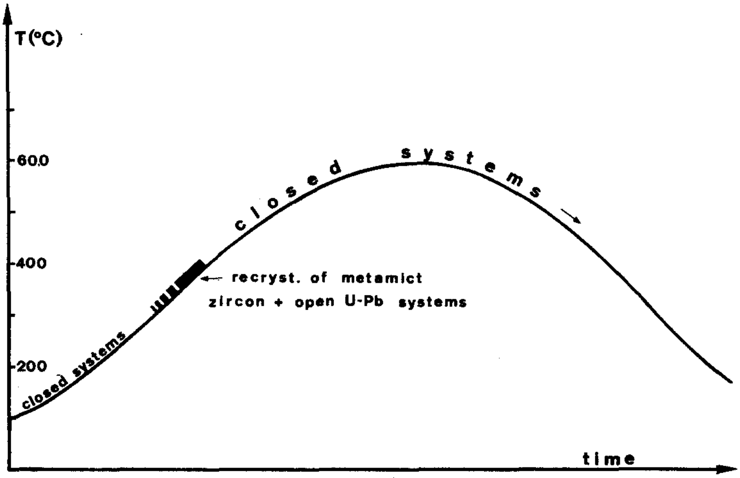

Fig. 5. Temperature versus time diagram illustrating recrystallisation of metamict zircon at temperatures of 300° C–400° C, i.e. *before* the thermal climax of high-grade metamorphism is reached. Consequently, U-Pb systems in zircons of medium and high-grade metamorphic rocks are closed already in an early stage of metamorphism. Above 300° C–400° C closed U-Pb systems in *freshly recrystallised* zircons are demonstrated by many zircon data obtained in the Caledonian-Hercynian basement of Middle Europe (see text). In contrast, laboratory experiments on *metamict* Ceylon zircon (Pidgeon et al., 1973) showed that annealing is possible at temperatures as low as 350° C. These laboratory results are confirmed by the present U-Pb and cell dimension data obtained on zircons which recrystallised in a natural environment

(Grünenfelder, 1963; Köppel and Sommerauer, 1974; Sommerauer, 1974 and in preparation) must have played a prominent rôle.

The results stongly suggest that the conditions for open U-Pb systems in zircons can already exist at temperatures as low as about 350–400° C. Furthermore, this low-temperature recrystallisation and lead loss serves as an argument that zircons from amphibolite facies metasediments already act as closed systems for U and Pb *before* the thermal maximum of the corresponding metamorphism is reached (Fig. 5). The proof that recrystallised zircons behave as closed systems for U and Pb at temperatures well above 350–400° C is given by many zircons of the Middle European basement which recrystallised or newly crystallised during the Caledonian and which were not affected isotopically about 150 m.y. later during amphibolite facies Hercynian metamorphism (e.g. Grauert and Arnold, 1968; Pidgeon et al., 1970; Gebauer and Grünenfelder, 1974a).

In general, under these circumstances, zircon ages from highly metamorphosed gneisses would give maximum ages for the thermal peak of metamorphism as recrystallisation and thus closing of U-Pb systems is completed already in an early stage of metamorphism (Fig. 5). The slightly, but not significantly higher age of metamorphism for the staurolite-grade metasediments might be explained in this way. Naturally, dating of an early stage of metamorphism, as derived by the present study, will only be valid if there was no new growth of zircon during metamorphism. Such a new growth, however, is generally observed only in rocks undergoing anatectic conditions (e.g. Eckelmann and Poldervaart, 1957; Gastil et al., 1967 or Gebauer and Grünenfelder, 1974a).

5. Rb-Sr Results from Chlorite- to Garnet-Grade Metasediments

For the Rb-Sr whole-rock analyses eight samples on the order of 15–25 kg each were collected within a profile about 3 km long, running perpendicular to the critical mineral zones and comprising metasediments of chlorite-grade (samples 46, 47, 51), biotite-grade (samples 4, 48, 49) and garnet-grade (samples 3 and 50). Samples 49, 48, 50 represent very fine grained, phyllitic schists; samples 47 and 3, from which the zircons were separated, are quartz phyllites and quartz-mica schists.

The results of the eight whole-rock samples and one sericitic muscovite separated from the biotite-grade schist (sample 49) are given in Figure 6, the analytical data are listed in Table 3. From the scatter of the data points no reliable age information can be deduced. Nevertheless, the "Caledonian age" of the least square reference isochron agrees astonishingly well with the U-Pb results of the zircons from the same rocks. To explain the strong scatter, 3 independent or interacting causes can be considered: Firstly, the data points might still reflect the isotopic heterogenieties within the freshly deposited sediment; secondly, the Caledonian metamorphism was not strong enough to wipe out completely the varying contents of inherited radiogenic Sr within the sediment and, thirdly, there was a complete Sr-isotopic homogenisation during the Caledonian. The subsequent Hercynian event, however, was strong enough to destroy this linear relationship, but too weak to cause a complete Sr-rehomogenisation.

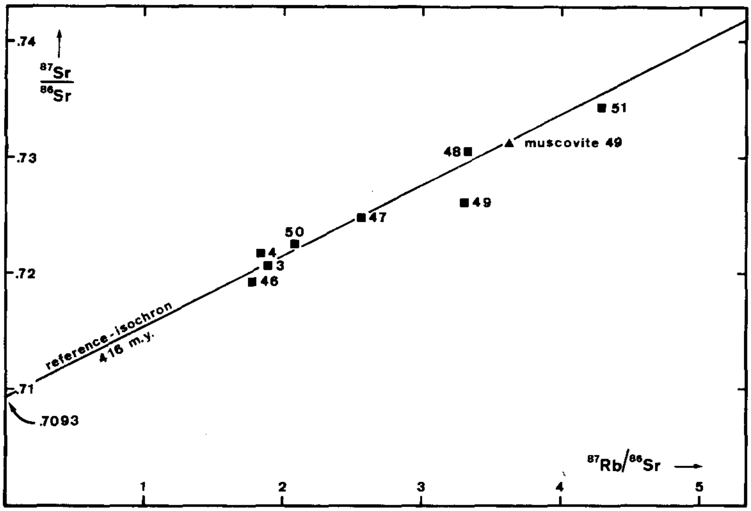

Fig. 6. Rb-Sr evolution diagram for metasediments of chlorite-grade (46, 47, 51), biotite-grade (4, 48, 49) and garnet-grade (3, 50). The "least-square" reference isochron was calculated using all nine datapoints

From the many good isochrons reported in the literature on very low-grade and low-grade metasediments, the first hypothesis—scatter of data points due to varying amounts of not homogenised, inherited, radiogenic Sr—seems to be highly improbable. Furthermore, it has been shown (Gebauer and Grünenfelder, 1974) that these "sedimentary isochrons" are generally not based on a Sr-isotopic homogenistion during sedimentation and/or diagenesis, as is widely assumed in the literature, but on a Sr-isotopic equilibration during deepest burial and/or very low-grade metamorphism. Thus, we know that there is the possibility of Sr-isotopic homogenisation in even lower-grade metasediments. Because of this fact, the second hypothesis, namely that there was only an incomplete Sr-isotopic exchange within whole-rock systems, does not seem to be likely either. In fact good isochrons on low-grade metasediments have been obtained by various authors (e.g. Peterman, 1966; Allsopp et al., 1968; Clauer and Bonhomme, 1970; Hurley et al., 1972). We are therefore left with the third hypothesis, which is based on a Sr-isotopic homogenisation during the Caledonian and a later partial reopening during the Hercynian orogeny. Of course, no direct proof of such a process is possible. However, the fact that the correct age can still be statistically deduced is in favour of a rotation of data points around a former Caldeonian isochron. Thus, the distance of the actual data points from such a presumed Caledonian isochron depends on the quantity of radiogenic Sr lost or gained in the analysed whole-rock system during the Hercynian metamorphism.

Since such opened whole-rock systems can only be explained by the presence of open mineral systems, one must expect Hercynian ages for at least a part of the Rb and Sr-containing mineral phases within the whole-rock systems.

Table 3. Rb-Sr analytical data for whole-rocks and muscovite

Sample No. in Figs. 2 and 6	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$(^{87}Sr/^{86}Sr)_{norm.}$
3	96.2	148	1.88	0.72070 ± 25
4	166	264	1.82	0.72170 ± 14
46	93.0	151	1.78	0.71924 ± 11
47	57.7	65.5	2.55	0.72474 ± 23
48	121	105	3.32	0.73049 ± 11
49	125	109	3.30	0.72608 ± 28
49 (muscovite)	133	107	3.61	0.73125 ± 11
50	116	163	2.06	0.72250 ± 11
51	136	91.8	4.29	0.73446 ± 108

In fact, such a pattern was already observed by Vachette (1967) in muscovites, biotites and plagioclases extracted from mica schists of the Montagne Noire. From this we suspect that in cases in which the whole-rock points fall below the Caledonian reference isochron, radiogenic Sr released mainly from the micas could not be completely trapped by other minerals during the Hercynian metamorphism. In case this excess radiogenic Sr could be incorporated for example into the feldspars of a neighbouring whole-rock system, the data point would be above the Caledonian reference isochron. If such a mechanism involving migration of radiogenic Sr over distances smaller than the sampling distance is correct, an increasing number of data points would improve the precision of the "errorchron" so that geologically significant ages can still be obtained. Of course, enlargement of the sample volumes might contribute to a reduction of the data scatter; however, in this case a very limited migration of radiogenic Sr during the Hercynian metamorphism must be assumed.

As can be seen from Figure 6 the muscovite extracted from sample 49, a biotite-grade schist, was not in isotopic equilibrium with its corresponding whole-rock system during the Hercynian event. Without more data points from other mineral phases, however, the position of whole-rock sample 49 cannot be fully explained. Nevertheless, it is probable that highly radiogenic biotite making up about 20 vol.-% of this sample lost its radiogenic Sr during the Hercynian metamorphic overprint whilst coexisting muscovite remained closed for Rb and/or Sr after its Caledonian formation. In such a case there were no or not enough acceptor phases for the radiogenic Sr released from the biotite so that the position of the whole-rock point was shifted below the Caledonian isochron.

The fact that the muscovite sample still plots on the Caledonian regression line is a further indication for the geological significance of the corresponding age. In addition, also the extrapolated initial Sr-isotopic ratio yields a value (ca. 0.71) identical to the numerous other initial ratios of rocks formed during a Caledonian event in Central Europe.

6. Significance of the Results for the Interpretation of Geologically "Meaningless" Secondary Ages of Zircons

Open U-Pb systems caused by low-temperature annealing of metamict zircons might be an important contributing if not ruling factor for the frequently made observation that zircons from ancient shield areas yield young secondary ages (500–0 m.y.) which are not understood as they are not in agreement with a known geological event. Early attempts of Tilton (1960) and Wasserburg (1963) to explain this phenomenon by either continuous or time dependent diffusion loss of radiogenic lead so far could not be substantiated due to the lack of U-Pb data in the "non linear" region of the corresponding diffusion trajectories. Furthermore, diffusion experiments on zircons showed (Shestakov, 1972) that diffusion coefficients of lead are low by many orders of magnitudes to explain the observed apparent lead loss rates.

In another model Goldich and Mudrey (1968) suggested that radiogenic lead is lost from zircons during crustal uplift as water held in the microchannels of the zircon lattice (Shukolyukov, 1964) could escape during pressure relief together with dissolved radiogenic lead. Applying this model Goldich and Mudrey found agreement between various secondary ages and the probable time of uplift of the corresponding basement as derived by palaeogeographical evidence. Naturally, it is very difficult to discuss this model as the hypothesis of lead loss due to dilatancy cannot be directly checked by experimental techniques in the laboratory. Furthermore, information on crustal uplift in the late Precambrain or Phanerozoic is generally very hard to obtain and if so of only limited application if multiple and/or differential uplift and burial occurred.

Recently, Krogh and Davis (1973) and Krogh and Davis (1975) were able to demonstrate a "contributing factor if not the major cause of the discordance" of zircons. The authors found that alteration zones within metamict zircons yield younger U-Pb ages than the metamict rest which can be analysed separately after leaching away the altered regions. The time of lead loss in the altered zones was found in a few cases to be correlated with the well-known Grenville event in Northern America, in another with an "event" at 500 m.y. which is not supported by any other geological evidence except possible uplift at that time. However, the dilatancy model fails to explain the data points obtained from an unleached sample and its residue (Krogh and Davis, 1975). Obviously, lead loss due to low-temperature annealing did not occur either, probably as the rock remained at too high levels within the earth's crust and consequently under temperatures too low for an annealing of metamict and/or altered regions within the zircons.

Unfortunately, from the data presented in this paper we cannot give minimum temperatures necessary for the beginning of recrystallisation of metamict zircons as the Precambrain metasediments do not extend into regions of less than chlorite-grade metamorphism. However, U-Pb data on zircons extracted from zeolite-facies siltstones of the innerbohemian Algonkian in the CSSR indicate (Gebauer and Grünenfelder, in prep.) that temperatures below about 300° C are sufficient to cause recrystallisation and thus open U-Pb systems. Assuming this minimum temperature range to lie within 200° C and 300° C a burial of about 6–10 km – assuming a "normal" geothermal gradient of 30° C/km – would be enough to start annealing of the most disordered regions or domains within the single zircon grains. Of course, it is very hard to find out by independent evidence whether or not temperatures of that order were reached in the late stages of the history of ancient shield areas. Very probably, both conditions are possible. However, from the very few published papers reporting geologically unsupported secondary ages as well as the corresponding unit cell parameters (e.g. Fairbairn and Hurley (1957), Kuovo (1958), Silver and Deutsch (1963) or Pidgeon and Hopgood (1975)) it can be seen that most zircons are better crystallised than one would expect from their radiation dosage. Mainly for this reason radiation damage ages obtained on these zircons are generally too low when compared with the time of the last known magmatic or metamorphic event which can be derived from the corresponding upper intercept ages. Thus, low temperature annealing and with it open U-Pb systems, e.g. lead loss, occurring in the late stages of the history of zircon can readily explain both the relatively well ordered crystal lattices and the low secondary ages of Proterozoic or Archaean zircons.

Though knowledge of cell parameters of isotopically dated zircons is, as previously mentioned, extremely scarce, the most obvious example for an application of this new low temperature annealing model is demonstrated by the zircon data from the Precambrian basement of the Western United States (e.g. Silver and Deutsch, 1963; Catanzaro and Kulp, 1964; Naylor et al., 1970; Nunes and Tilton, 1971). In this area secondary ages around 120 m.y. and primary ages around 1600–1900 m.y. and 2700 m.y. are indicated by U-Pb zircon data. The 120 m.y. "event" coincides with the well documented Laramide orogeny in this area. Mainly for this reason, but also because some of the data points did not fit any tpye of diffusion model an episodic lead loss during the very weak Laramide event was taken as the simplest explanation of the observed data patterns, though no mechanism for the assumed lead loss could be given in any of the papers. Lead loss due to partial or complete recrystallisation of metamict zircon was thought, if discussed at all, to be not possible as temperatures during the probable Laramide event seemed to have been too low to start this mechanism. As shown in the present paper this assumption is no longer valid as low temperature annealing of of metamict zircon probably starts already at temperatures below 300° C. Unfortunately, data on cell dimensions were found to be available only from zircons of the Johnny Lyon Granodiorite in Arizona (Silver and Deutsch, 1963). Nevertheless, the weak degree of metamictisation of these zircons – c_0 varies from 6.009 to 6.010, a_0 from 6.607 to 6.610 – strongly supports the low temperature annealing model. According to Holland and Gottfried (1955) or Fairbairn and Hurley (1957) cell dimensions of at least 6.08 for c_0 and 6.69 for a_0 must be expected if there was no annealing after the primary crystallisation of zircons in the granodioritic melt at 1655 m.y. (Silver and Deutsch, 1963).

Admittedly, the numerous secondary ages around 400–600 m.y. which led to the hypothesis that volume diffusion might be a mechanism for discordant U-Pb ages (Tilton, 1960) do not seem to find a satisfactory explanation either using the low-temperature annealing model. However, unless there is more information on the crystallographic state and the possible presence of alteration zones (Krogh and Davis, 1973 and 1975) partial annealing due to a weak thermal "event" possibly caused by epeirogenic depression of large crustal blocks cannot be excluded either.

In any case, strongly metamict zircons seem to be able to respond to events which cannot be detected by other standard minerals used in geochronology.

Conclusions

From the study of U-Pb systems in zircon suites and Rb-Sr systems of whole-rocks from a profile of progressively metamorphosed metasediments, i.e. chlorite- to staurolite-grade, the following conclusions can be reached:

1. U-Pb Zircon-Systems

a) Open U-Pb systems in approx. 2 b.y. old detrital zircon suites (Montagne Noire, Southern France) were found to be the reason for a successful dating of the time of Caledonian metamorphism of only chlorite- and garnet-grade metasediments.

b) From determinations of the unit-cell dimensions of the analysed fractions – including those of zircons from amphibolite facies paragneisses giving the same age results – a recrystallisation and simultaneous loss or radiogenic lead at the time of metamorphism must be concluded. This strongly indicates that there were no low-temperature leaching processes which could have likewise explained the observed strongly discordant data patterns of zircons from chlorite- and possibly also garnet-grade host rocks.

c) There is no correlation between degree of metamorphism (chlorite-, garnet- and staurolite-grade) and degree of discordance, suggesting that not so much maximum temperatures during metamorphism but much rather the high concentrations of fluid phases in the low-grade rocks are responsible for the early recrystallisation and Pb-loss during metamorphism.

d) From the presence of annealed zircons in metasediments formed at temperatures as low as 350° C or even less, it is concluded that zircons from higher metamorphosed schists and gneisses, not containing zircons newly formed during metamorphism give ages in excess of the climax of metamorphism; this is because the annealing of the crystal lattices and simultaneous closing of the U-Pb systems took place *before* the maximum temperatures during metamorphism were reached.

e) Low temperature recrystallisation of metamict zircon or at least metamict zones within the zircon grains might also be a contributing factor to the general observation that zircon suites from ancient shield areas yield lower intercept ages not corresponding to a known geological event. Such a mechanism might overlap with those caused by alteration of zircons as shown by Krogh and

Davis (1975) or possibly also dilatancy as supposed by Goldich and Mudrey (1972).

2. *Rb-Sr Whole-Rock Systems*

a) In contrast to the U-Pb zircon method, no unambiguous dating of the Caledonian main metamorphism was possible using the Rb-Sr whole-rock technique for phyllites and mica schists.

b) The scatter of data points can best be explained by their rotation around a probable Caldedonian isochron. This rotation very probably took place during the later Hercynian orogeny, not significantly affecting the slope of the least square regression line through the scattered data points.

Analytical Techniques

1. Rb-Sr Method

For details of the chemical procedure, mass spectrometry including data evaluation, preparation and calibration of spikes as well as precision and accuracy of standards and spikes, we refer here to an earlier paper (Gebauer and Grünenfelder, 1974). Age calculations are based on the $1.47 \times 10^{-11} y^{-1}$ decay constant for ^{87}Rb.

2. U-Pb Method:

2.1. Borax Fusion – Lead Sulfide Method

As this method, which was applied only for the zircon measurements of the garnet-grade sediments, has been repeatedly described (Grauert and Arnold, 1968; Grauert, 1969; Pidgeon, 1969; Grauert et al., 1973), we will mention here only a few modifications. This is the application of a combined ^{235}U-^{208}Pb tracer (Grauert et al., 1973) and the calculation of Pb/U – ratios and ages using 137.88 for $^{238}U/^{235}U$ (Shields, pers. commun.) and the U-decay constants given by Jaffey et al. (1971). The estimated relative errors are less than .5% for the $^{207}Pb/^{206}Pb$, 1% for the $^{206}Pb/^{238}U$ and 1.5% for the $^{207}Pb/^{235}U$.

2.2. Teflon Bomb – Silicagel Method

This technique was used for the dating of chlorite- and staurolite-grade sediments. It is fully described by Krogh (1973) and Cameron et al. (1969). The following modifications were introduced:

1) Application of a combined Pb/U tracer (Grauert et al., 1973) and 2) separate zircon dissolutions for determining the Pb-isotopic composition on one hand and the Pb- and U-concentrations on the other. The latter modification of the standard method introduced by Krogh (1973) was chosen since it was found from the first tests that spiking of aliquot solutions did not always give reproducible results. This is thought to be due to varying amounts of precipitates which were formed during or after cooling down of the bombs following decomposition, and which then did not equilibrate isotopically with the spike solutions. Zircon fractions, therefore, were ground before dissolution in an agate mortar and split into two fractions. One – comprising about two thirds of the powdered zircons – was decomposed unspiked for the determination of the Pb-isotopic composition; the rest was spiked and decomposed separately for the U- and Pb-concentration runs.

For the isotopic measurements the same mass spectrometer as described in Gebauer and Grünenfelder (1974) was used for U-analyses using the Re-double filament mode of ionization and Pb-analyses using the silicagel-phosphoric acid technique. For both elements typically obtained ion currents were on the order of 10^{-11} to 10^{-10} amps for the most frequent isotopes. The precision for isotopic ratios is generally better than 0.03% for $2\sigma_m$. Only for the $^{206}Pb/^{204}Pb$ determinations were errors of up to 1.5% obtained.

Total blanks—referring to 9–25 mg of sample—average about 5 nanograms. The isotopic composition for the lead correction, as determined from an unspiked blank-run, was 17.46 for the $^{206}Pb/^{204}Pb$, 15.25 for the $^{207}Pb/^{204}Pb$ and 36.65 for the $^{208}Pb/^{204}Pb$.

To determine the reproducibility of the whole technique, one zircon fraction was analysed five times indicating maximum errors of .3% for the $^{206}Pb/^{238}U$, .6% for the $^{207}Pb/^{235}U$ and .3% for the $^{207}Pb/^{206}Pb$.

Acknowledgements. We are indebted to Drs. V. Köppel, R.W. Page, and J. Sommerauer for reading and criticizing the manuscript. The able assistance of O. Krebs both in the field and the laboratory work is gratefully acknowledged. We further wish to thank W. Wittwer for performing the zircon separations and I. Ball for taking the trouble to improve the English text.

References

Allègre, C.J., Albarède, F., Grünenfelder, M., Köppel, V.: Zircon geochronology in alpine and non-alpine environment. Contrib. Mineral. Petrol. **43**, 163–194 (1974)

Allsopp, H.L., Kolbe, P.: Isotopic age determination on the Cape Granite and intruded Malmesbury sediments, Cape Peninsula, South Africa. Geochim. Cosmochim. Acta **29**, 1115–1130 (1965)

Allsopp, H.L., Ulrych, T.J., Nicolaysen, L.O.: Dating some significant events in the history of the Swaziland System by the Rb-Sr isochron method. Can. J. Earth Sci. **5**, 605–619 (1968)

Arthaud, F.: Etude tectonique et microtectonique comparée de deux domaines hercyniens: Les nappes de la Montagne Noire (France) et l'anticlinorium de L'Iglesiente (Sardaigne). Ser. Géol. Struct. 1, Montpellier, 1970

Bell, K.: Age relations and provenance of the Dalradian Series of Scotland. Bull. Geol. Soc. Am. **79**, 1167–1194 (1968)

Cameron, A.E., Smith, D.H., Walker, R.L.: Mass spectrometry of nanogram-size samples of lead. Anal. Chem. **41**, 525–526 (1969)

Catanzaro, E.J., Kulp, J.L.: Discordant zircons from the Little Belt (Montana), Beartooth (Montana) and Santa Catalina (Arizona) Mountains. Geochim. Cosmochim. Acta **28**, 87–124 (1964)

Clauer, N., Bonhomme, M.: Datations Rb-Sr dans les schistes de Steige et la Série de Villé (Vosges). Bull. Serv. Carte Géol. Alsace Lorraine **23**, 191–208 (1970)

Compston, W., Pidgeon, R.T.: Rubidium-Strontium dating of shales by the total-rock method. J. Geophys. Res. **67**, 3493–3502 (1962)

Eckelmann, F.D., Poldervaart, A.: Geologic evolution of the Beartooth Mountains, Montana and Wyoming. Geol. Soc. Am. Bull. **68**, 1225–1261 (1957)

Fairbarn, H.W., Hurley, P.M.: Radiation damage in zircon and its relation to ages of Palaeozoic igneous rocks in northern New England and adjacent Canada. Trans. Am. Geophys. Union **38**, 99–107 (1957)

Faure, G., Kovach, J.: The age of the Gunflint Iron Formation of the Animikie Series in Canada. Geol. Soc. Am. Bull. **80**, 1725–1736 (1969)

Gastil, G.R., Delisle, M., Morgan, J.R.: Some effects of progressive metamorphism on zircons. Geol. Soc. Am. Bull. **78**, 879–906 (1967)

Gebauer, D., Grünenfelder, M.: Rb-Sr whole-rock dating of late diagenetic to anchimetamorphic, Palaeozoic sediments in Southern France (Montagne Noire). Contrib. Mineral. Petrol. **47**, 113–130 (1974)

Gebauer, D., Grünenfelder, M.: Comparative studies of U-Pb systems in zircons and monazites as well as Rb-Sr systematics in minerals and whole-rocks during the anatexis of a polymetamorphic paragneiss (crystalline basement of NE-Bavaria) Internat. meeting for geochronology, cosmochronology and isotope geology, Paris, abstracts (1974a)

Gèze, B., Sitter, L.U., Trümpy, R.: Sur le sens de déversement des nappes de la Montagne Noire. Bull. Soc. Geol. France **6**, 491–535 (1952)

Goldich, S.S., Mudrey, Jr.: Dilatancy model for discordant U-Pb zircon ages, in Contributions to recent geochemistry and Analytical chemistry (Vinogradov Volume), A.I. Tugarinov, ed., pp. 415–418 Moscow: Nauka Publ. Office 1972

Grauert, B., Arnold, A.: Deutung diskordanter Zirkonalter der Silvrettadecke und des Gotthardmassivs (Schweizer Alpen). Contrib. Mineral. Petrol. **20**, 34–56 (1968)

Grauert, B., Haenny, R., Soptrajanova, G.: Age and origin of detrital zircons from the pre-Permian basement of the Bohemian Massif and the Alps. Contrib. Mineral. Petrol. **40**, 105–130 (1973)

Grauert, B., Haenny, R., Soptrajanova, G.: Geochronology of a polymetamorphic and anatectic gneiss region: the Moldanubicum of the area Lam-Deggendorf, Eastern Bavaria, Germany. Contrib. Mineral. Petrol. **45**, 37–63 (1974)

Grünenfelder, M.: Heterogenität akzessorischer Zirkone und die petrogenetische Deutung ihrer Uran-Blei-Zerfallsalter. I. Der Zirkon des Granodioritgneiss von Aquacalda (Lukmanierpass). SMPM **43/1**, 235–257 (1963)

Hamet, J.: Montagne Noire: résultats géochronologiques. Internat. Meeting for Geochronology, Cosmochronology and Isotope Geology. Excursion géologique, Montagne Noire and Pyrénées, Paris 1974

Holland, H.D., Gottfried, D.: The effect of nuclear radiation on the structure of zircon. Acta Cryst. **8**, 291–300 (1955)

Hurley, P.M., Pinson, W.H., Nagy, B., Teska, T.M.: Ancient age of the Middle Marker Horizon Onverwacht Group, Swaziland Sequence, South Africa. Earth Planet. Sci. Lett. **14**, 360–366 (1972)

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., Essling, A.M.: Precision measurement of the half-lives and specific activities of ^{235}U and ^{238}U. Phys. Rev. C **4**, 1889–1906 (1971)

Köppel, V., Grünenfelder, M.: A study of inherited and newly formed zircons from paragneisses and granitised sediments of the Strona-Ceneri zone (Southern Alps). Schweiz. Mineral. Petrog. Mitt. **51**, 387–411 (1971)

Köppel, V., Sommerauer, J.: Trace elements and the behaviour of the U-Pb system in inherited and newly formed zircons. Contrib. Mineral. Petrol. **43**, 71–82 (1974)

Krogh, T.E.: A low contamination method for hydrothermal decomposition of zircon and extraction of U and Pb for isotopic age determination. Geochim. Cosmochim. Acta **37**, 3, 485–494 (1973)

Krogh, T.E., Davis, G.L.: Alteration in zircons with discordant U-Pb ages. Carnegie Year Book 1973, 560–567 (1973)

Krogh, T.E., Davis, G.L.: Alteration in zircons and differential dissolution of altered and metamict zircon. Carnegie Year Book 1974–1975, 619–625 (1975)

Kouvo, O.: Radioactive age of some Finnish pre-Cambrain minerals. Comm. Geol. Finnlande Bull. **182**, 1–70 (1958)

Michot, J., Deutsch, S.: U/Pb zircon ages and polycyclism of the gneiss de Brest and the adjacent formations (Brittany). Eclogae Geologicae Helvetiae **63**, 215–227 (1970)

Mumpton, F.A., Roy, R.: Hydrothermal stability studies of the zircon-thorite group. Geochim. Cosmochim. Acta **21**, 217–238 (1961)

Naylor, R.S., Steiger, R.H., Wasserburg, G.J.: U-Th-Pb and Rb-Sr systematics in 2.7 b.y. old plutons from the southern Wind River Range, Wyoming (1970)

Nunes, P.D., Tilton, G.R.: Uranium-lead ages of minerals from the Stillwater igneous complex and associated rocks, Montana. Geol. Soc. Am. Bull. **82**, 2231–2250 (1971)

Peterman, Z.E.: Rb-Sr dating of Middle Precambrian metasedimentary rocks of Minnesota. Geol. Soc. Am. Bull. **77**, 1031–1044 (1966)

Peterman, Z.E., Hedge, C.E., Coleman, R.G., Snavely, P.D.: ^{87}Sr/^{86}Sr ratios in some eugeosynclinal sedimentary rocks and their bearing on the origin of granitic magma in orogenic belts. Earth Planet. Sci. Lett. **2**, 433–439 (1967)

Pidgeon, R.T., Hopgood, A.M.: Geochronology of Archaean gneisses and tonalites from north of the Frederishabs isblink, S.W. Greenland. Geochim. Cosmochim. Acta **39**, 1333–1346 (1975)

Pidgeon, R.T., Köppel, V., Grünenfelder, M.: U-Pb isotopic relationships in zircon suites from a para- and orthogneiss from the Ceneri zone, Southern Switzerland. Contrib. Mineral. Petrol. **26**, 1–11 (1970)

Pidgeon, R.T., O'Neil, R.J., Silver, L.T.: Observations on the crystallinity and the U-Pb system of a metamict Ceylon zircon under experimental hydrothermal conditions. Fortschr. Mineral. **50**, 3, p. 118 (1973)

Roques, M., Vachette, M.: Ages au strontium sur roches totales des migmatites de la zone axiale de la Montagne Noire et du Massif de granite du Mendic (Massif Central français). (Compt. Rend.) **270**, 275–278 (1970)

Roques, M., Vachette, M., Vialette, Y., Bernard-Griffiths, J., Cantagrel, J.-M., Duthou, J.-L.: Géochronologie du socle du Massif Central. Abstracts. European Colloquium of Geochronology, Brussels 1971

Shestakov, G.I.: Diffusion of lead in monazite, zircon, sphene, and apatite. Trans. from Geokhimiya **10**, 1197-1204 (1972).

Shukolyukov, V.A.: Interpretation of discordant ages calculated from the isotopic ratios: $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$. Transl. from Geokhimiya, No. 9, 855–865 (1964) in Geoch. Int. **1**, 843–852 (1964).

Silver, L.T., Deutsch, S.: U-Pb isotopic variations in zircons: a case study. J. Geology **71**, 721–758 (1963).

Sommerauer, J.: Trace element distribution patterns and the mineralogical stability of zircon – an application for combined electron microprobe techniques. Elektronenmikroskopievereniging van Suidelike Afrika. Johannesburg 1974

Tilton, G.R.: Volume diffusion as a mechanism for discordant lead ages. J. Geophys. Res. **65**, 2933–2945 (1960)

Vachette, M. Etude géochronologique de la Montagne Noire dans le Massif Central français. Ann. Fac. Sci. Univ. Clermont **36**, Fasc. 16 (1967)

Wasserburg, G.J.: Diffusion processes in lead-uranium systems. J. Geophys. Res. **68**, 4823–4846 (1963)

Wetherill, G.W.: Discordant uranium-lead ages, I. Trans Am. Geophys. Union **37**, 320–326 (1956)

Wetherill, G.W.: Discordant uranium-lead ages, II. Discordant ages resulting from diffusion of lead and uranium. J. Geophys. Res. **68**, 2957–2965 (1963)

Received August 16, 1976 / Accepted August 30, 1976