

Whole-grain evaporation for $^{207}\text{Pb}/^{206}\text{Pb}$ -age-investigations on single zircons using a double-filament thermal ion source

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Abstract. A technique has been developed and tested to analyse $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages by thermal evaporation of radiogenic lead directly from untreated whole zircon grains (≤ 0.3 mm). The evaporation analyses are performed in the double-filament arrangement of a thermal ion mass spectrometer (ThIMS). The method is a powerful tool to distinguish between different lead components occurring in the same grain because differing activation energies of the competing lead components cause their sequential evaporation from the zircons. The evaporation of test samples results in $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages in good agreement with U/Pb ages known from literature: single zircons from a granite of the 'Marble Mountains'/California yield an age of crystallization of $1,410 \pm 30$ Ma; 'Ceylon' zircons from heavy-mineral bearing gravels yield 560 ± 40 Ma as age of crystallization of the pegmatitic gravel sources; individuals from a heterogeneous zircon population of a diatexite from the Southern Schwarzwald/SW-Germany indicate metamorphic zircon formation around 500 Ma and the existence of Middle-Proterozoic relics (1.95 ± 0.05 Ga).

The evaporation analyses revealed closed-system U/Pb evolution of the crystalline domains of all investigated zircons irrespective of discordancy-trends documented by U/Pb analyses on related zircon concentrates. Therefore the majority of 'discordia'-lines derived from U/Pb isotope distributions of zircon samples are supposed to be due to phase mixing. Lead components from the crystalline domains are 'concordant' end members of the mixing arrays. Open-system behaviour and U/Pb fractionation should be attributed only to phases with low Pb activation energies eg. metamict zircon domains or intergrown non-zircon minerals.

Introduction

Zircons are among the most important minerals used for geochronological investigations. Under certain conditions their crystal lattices are extremely resistant and are able to preserve the U/Pb isotope information from the time of crystallization till present despite alteration, metamorphic events or even magmatic episodes. Their closed-system behaviour is influenced by structural properties and by the radioactive trace elements. High U- and Th-contents may cause radiation damage to varying degrees and thus enhance loss or gain of U, Th or Pb. Therefore the isotopic clocks within different zircons of the same population or even within different domains of single grains may have

varying response to metamorphic conditions. In simple cases diverse geochronological information can be extracted from one zircon population by U/Pb isotope analyses of different kinds of zircon fractions using 'discordia'-correlations in 'concordia'-plots (Wetherill 1956). The geochronological significance of U/Pb isotope distributions in multi-grain zircon samples however can be strongly obscured by polymetamorphism. The resulting crystal assemblages with multi-episodic histories may elude simple 'concordia'/'discordia' treatments (e.g. Steiger and Wasserburg 1966; Al-egre et al. 1974).

Methods have been developed to analyse small zircon individuals in order to reveal the complex geochronological record of a zircon population. Digestion techniques with low-level lead blanks make it possible to analyse sub-mg-quantities of zircons by teflon-bomb digestion (Krogh 1973) followed by a non-chemical procedure (Tatsumoto et al. 1973; Tera and Wasserburg 1975; Lancelot et al. 1976). Various studies using this kind of single-grain processing were successful in decoding the geochronological information carried by the U, Th and Pb isotopes of zircon individuals (e.g. Lancelot et al. 1976; Pin and Lancelot 1982; Oberli et al. 1985). However, these procedures fail if the zircons are of complex composition, for instance if they are characterized by repeated crystal growth or by the intergrowth of crystalline with non-crystalline zircon domains (amorphous gels; Lipova et al. 1965; Fig. 1). As will be discussed below in more detail, the amorphous phases in particular can be subject to complex U/Th/Pb chemical fractionation, for instance caused by weathering (e.g. Steiger and Wasserburg 1966). The evaluation of the U/Pb isotope distributions may get even more complicated by isotope influx from non-zircon inclusions and by (analytical) element fractionation during the chemical treatment.

The analysis of multiple-phase zircons requires methods which allow the physical distinction between different phases generated by different events but residing in the same mineral. A powerful approach to the analysis of different lead components is ion-microprobe mass spectrometry with spatial resolution of distinct crystal areas. Various Precambrian zircon individuals and their spatial U/Th/Pb isotope distributions have successfully been analysed using mass analysers with medium to high mass resolution (e.g. Hinthorne et al. 1979; Compston et al. 1984; Williams et al. 1984). However the present techniques have a limited spatial resolution of only 10–40 μm for zircon individuals whose homogeneous parts may be very small (0.1–1 μm ;

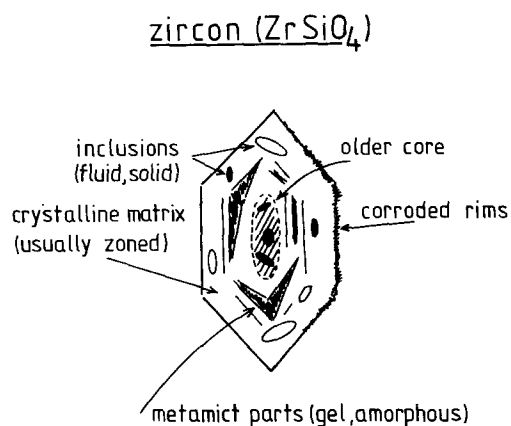


Fig. 1. Schematic presentation of the internal structure of zircon crystals. Zircons often show a complex composition with manifestations that may considerably vary from individual to individual. The grains may be characterized by intergrowth of metamict (= amorphous) and crystalline domains. Relic cores surrounded by younger material can be observed. The grains may contain inclusions of various kinds and may be corroded by hydrothermal alteration

Shukolyukov 1964). Moreover, ion probe mass spectrometry is time-consuming and requires complicated sample preparation as well as adjustment and calibration procedures to guarantee useful isotope data (Hinthorne et al. 1979). Routine application is only possible in few laboratories and is therefore restricted to a very limited number of investigations.

In the following an alternative approach is presented which allows the separation of different lead components of a single zircon crystal. It is, however, not based on spatially sensitive procedures but separates the competing lead components by physicochemical means.

Evaporation techniques for lead isotope analyses on mass spectrometers

The geochronological decoding of lead isotope distributions generated by multiple events is feasible because various kinds of fixation exist for the different lead components residing in single zircon grains: Accessory lead components as evidenced by radiogenic and/or common lead isotope patterns are only weakly adsorbed to crystal surfaces or caught in cracks and fissures from which they are easily stripped off. Processes of unmixing and demolition by radiation damage yield the mentioned amorphous gel structures that occasionally occur on a sub-microscopic scale in small areas of the grains but may also dominate in large domains all over the crystals. These metamict zones and their in-situ generated radiogenic lead are highly sensitive to low-grade metamorphic overprint as well as to alteration and even decompression during uplift of the host rocks (e.g. Holland and Gottfried 1955; Catanzaro and Kulp 1964; Stern et al. 1966; Pidgeon et al. 1966, 1972; Goldich and Mudrey 1972; Oosthuyzen and Burger 1973; Sommerauer 1976; Zartman 1982). Recrystallisation, dehydration and leaching events induce severe lead loss because of the low activation energy

of the lead isotopes in the amorphous zircon domains (0.1–0.4 eV; Tilton 1960). Crystalline domains of the zircon grains, on the other hand, are much more retentive (Pb activation energy: 2.2–2.5 eV; Mamedov 1970; Shestakov 1972). Therefore lead is mobilized from the crystalline domains only under high-grade conditions (>900 K, Sommerauer 1976). The extremely distinct mobility of lead from the variably structured zircon domains on the one hand is a prominent cause for the hard-to-interpret U/Pb patterns resulting from conventional digestion methods. On the other hand, it is this particular property which offers a chance for analytically separating these lead components. Thermal heating of the zircon in the vacuum of a thermal ion source mass spectrometer successfully sets free the lead components from the crystal according to the differing activation energies. Thus the phenomenon itself, which causes the complexity of U/Pb isotope distributions, is utilized for the separation of the competing lead components hosted in the differently structured zircon domains.

A first attempt to establish an evaporation technique for lead isotope analyses of single zircon grains by ThIMS has been carried out by Kosztolanyi (1965). He proposed to grind zircon individuals to fine powder and to place the ground material on the filament of a solid source mass spectrometer in a HF/H_3PO_4 solution. Chukhonin (1978) discussed the results of Coppens et al. (1965) who applied the procedure to zircons from a granite. Their spectra did not clearly demonstrate the influence of accessory lead components. Moreover, H_3PO_4 solutions form stable phosphoric lead complexes which are for instance utilized by the 'Si-gel method' for advanced isotope analyses of common and radiogenic lead (Akishin et al. 1957; Cameron et al. 1969). These complexes keep common lead components on the filament up to temperatures of 1,500 K thus obstructing the sequential evaporation of competing lead components. Therefore Chukhonin replaced the acid solution by H_2O . Application of the modified procedure to single zircon grains from various rocks demonstrated the geochronological significance of directly evaporated radiogenic lead (Sunin and Malyshev 1983).

Nevertheless, the described suspension techniques arouse problems which do not encourage a routine application for zircon single grain analysis:

1. Because of short migration distances in the small zircon fragments, the lead components are quickly released from the powdered matter deposited on the evaporation filament (~2–3 min, Sunin and Malyshev 1983). This means fast succession of competing lead components with analyses of minor statistical quality because of short measuring intervals and hasty focussing operation.
2. The zircon powder deposited on the filament is inevitably distributed over several millimeters and it thus subject to the temperature profile of the filament. Temperature gradients in the small fragments (one-sided contact to the source of heat) and all over the deposited powder reduce the analytical resolution of the different lead components.
3. Grinding of the minerals enhances the danger of cross-contamination between subsequently processed samples. Moreover badly fixed zircon powder may crumble off and contaminate the instrumentation. The difficulties are overcome by analysing the *unground* grain. For this purpose a mounting procedure was used which independently was proposed by Gentry et al. (1982) for zircon investigations in the context of nuclear waste containment.

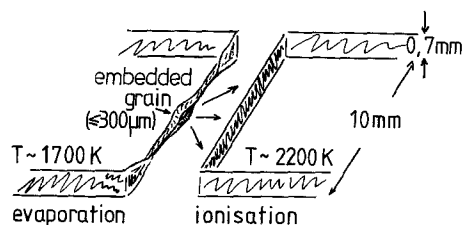


Fig. 2. Rhenium-double-filament arrangement used for Pb evaporation analyses of the present study. The arrangement is part of the thermal ion source of the MAT261 mass spectrometer

Whole-grain evaporation

The technique used in this study is based on the evaporation of uncrushed whole zircon grains (maximum size 0.3 mm). The grain under investigation is embedded into the evaporation filament of a MAT261 mass spectrometer (Fig. 2). Similar to the single-filament treatment of Gentry et al. (1982) the embedding is carried out in three steps: First, the evaporation filament is given a canoe-shaped form, second, the respective grain is placed in the center of the trough, third, the rhenium metal is folded around the grain. Only a little slit remains open which faces the ionisation filament. No pre-treatment of the grain before the mounting procedure is necessary. Enveloping of the whole grain guarantees a uniform temperature all over the crystal so that all zircon domains and all lead components are subject to equal evaporation conditions irrespective of their location within the grain. In the mass spectrometer the temperatures of both the filaments are slowly raised (ionisation filament: $\sim 2,200$ K, evaporation filament: $\sim 1,600$ – $1,700$ K) until a lead ion beam on the order of 10^{-14} A is generated. The very small extension of the evaporating sample volume (<0.3 mm) optimises the beam focussing conditions. A conventional multiplier is used as detector. The linearity of the amplifier system is kept under control by analyses of the NBS isotope standards SRM981 and SRM983. The data acquisition is carried out by peak hopping of the scan-sequence 204-206-207-208-207-206. The ratio $^{204}\text{Pb}/^{206}\text{Pb}$ monitors the accessory lead components. The ratio $^{207}\text{Pb}/^{206}\text{Pb}$ derived from the average of the first and the second $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of each scan carries the geochronological information. The $^{208}\text{Pb}/^{206}\text{Pb}$ ratios are used for the control of fractionation trends and as an additional means for the recognition of differing radiogenic lead components.

The lead ion beams generated at low to intermediate evaporation temperatures (500–1,500 K) generally turned out to be unstable and less intense. Their isotope patterns often demonstrated a rapidly varying mixture of common with radiogenic lead. The approach in the present study was therefore to reject the analysis of these early components and to focus attention on lead from the most stable (=crystalline) phases which evaporated at high temperatures (1,650–1,750 K). The slow raising of the evaporation temperature to the running temperature is thus regarded as beam conditioning ensuring proper information from the crystalline domains undisturbed by the influence of less stable phases.

The acquired data were evaluated for geochronological purposes only in the case of stable ion beams (relative beam

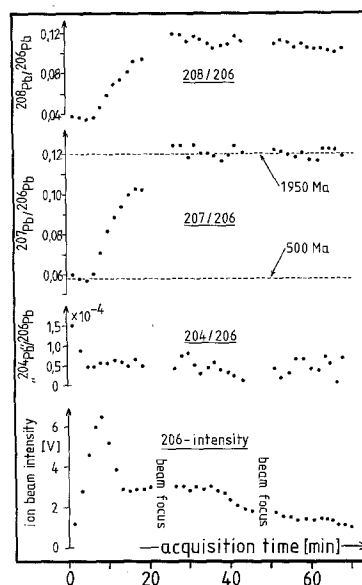


Fig. 3. Record of ^{206}Pb beam intensity and lead isotope ratios 204/206, 207/206 and 208/206 versus acquisition time. This record has been derived from a metamorphic zircon (diatexite 'S235'). The graphs only present the high-temperature evaporation (1,670–1,720 K) which is clearly dominated by an early Paleozoic radiogenic lead component in the rim parts (evaporating at the beginning) and a Middle-Proterozoic one from a relic core (evaporating during the rest of the acquisition interval)

fluctuations $\Delta I/I < 5\%$) with a minimum 206/204 ratio of 5,000, when a common Pb correction can be neglected. This ratio then reflects the minimum distance of the generated Pb signal from the amplifier noise level. From the different case studies carried out to test the power and efficiency of the procedure (presented below) it can be estimated that 1 ng of radiogenic lead in the crystalline domains of the zircon grains yielded on ion beam in the order of 10^{-14} A during about 10–15 min. That means that about $5 \cdot 10^4$ lead atoms are needed from the evaporated crystal in order to register one single-charged ion by the detector. The lead components from the retentive domains of all investigated zircons appeared within the narrow temperature range of 1,650–1,750 K which is in good agreement with Chukhonin (1978). Lead evaporation at temperatures approaching 2,300 K as mentioned by Sunin and Malyshev (1983) has never been observed. Their conclusions may have been influenced by the rapid increase of the evaporation temperature above 1,700 K necessary to keep the ion beam intensity of the evaporating zircon powder above a certain minimum.

The double-filament technique of the present study is superior to the single-filament technique of Gentry et al. (1982): A generally better stability of the generated Pb ion beam and an increased Pb ion yield guarantee improved statistical quality of the data which has been severely criticized for the single-filament technique (Ludwig et al. 1984; c.f. Gentry 1984). Decoupling of evaporation and ionisation facilitates the fine-tuning of the running-temperature. Indirect heating of the evaporation filament by the ionisation filament impairs redeposition of the lead components evaporated during the beam conditioning and thus avoids re-mixing of sequentially evaporated lead components.

Figure 3 indicates the data record for one single zircon

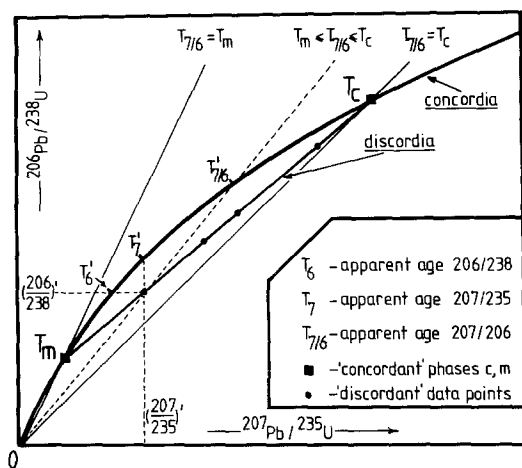


Fig. 4. The conventional concordia diagram (Wetherill 1956) schematically presenting two-episode U/Pb isotope evolution: Crystallization of zircons at $T = T_c$ followed by closed-system U/Pb evolution till a metamorphic event at $T = T_m$. Varying degrees of lead loss and again closed-system evolution till present align the discordant data points (solid circles) along a chord intersecting the concordia at $T = T_c$ and $T = T_m$. Apparent ages T_6 , T_7 and $T_{7/6}$ derived from the $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of discordant data points respectively, yield divergent dates that lead to underestimation of the age of crystallization $T = T_c$ (e.g. the dashed coordinates). Alternatively (re-)crystallization of zircon at $T = T_m$ and mixture with material crystallized at $T = T_c$ yields a mixing array between concordant end members (full squares) having exactly the same trend as the plotted discordia. The two models generate the same discordia lines and are not discernable by conventional U/Pb isotope analyses. However they can be distinguished by the $T_{7/6}$ apparent age distributions derived from evaporation analyses: heterogeneous distribution of $T_{7/6}$ dates with $T_{7/6} < T_c$ reflects episodic lead loss and varying degree of discordancy. Uniform distribution of $T_{7/6}$ centered at $T = T_c$ and $T = T_m$ indicates phase mixing and closed-system evolution of the mixing members

grain of a metamorphic rock (diatexite S235, see below). The example has been chosen from a set of single grain analyses because it well documents the perfect analytical distinction between two competing radiogenic lead components that evaporated one after the other: an early-Paleozoic one residing in the rim parts of the grain, and a Middle-Proterozoic one placed in the core area of the zircon. Separation of both components would not have been possible without the application of very uniform evaporation temperatures all over the treated grain volume.

Testing the method with zircons of known age

The method has been applied to several zircon samples whose conventionally derived U/Pb ages are documented in the literature. Only $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages can be deduced from the evaporated lead isotopes of the studied zircons. Conclusions regarding the geochronological significance must therefore be based on the $^{207}\text{Pb}/^{206}\text{Pb}$ dates and their distribution alone. No element/isotope correlations as in the case of U/Pb isotope studies can be taken into account. Consequently no conventional concordancy/discordancy criteria are available. Nevertheless the $^{207}\text{Pb}/^{206}\text{Pb}$ apparent age distribution reveals general properties of the U/Pb systems contained in the investigated zircons.

As indicated by the scheme of Fig. 4 discordant data points below the concordia curve yield $^{207}\text{Pb}/^{206}\text{Pb}$ dates lower in value than the crystallization age. Discordant data points that are arranged along a linear chord ('discordia') result in $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages which cover a maximum interval given by the upper and lower intercept ages (T_c and T_m in Fig. 4). This will be reflected by a corresponding $^{207}\text{Pb}/^{206}\text{Pb}$ apparent age distribution of the evaporation data if the 'degree of discordancy' is a true property of the crystalline zircon domains and is due to episodic or continuous lead loss. Apparent ages significantly lower than the age of crystallization will be observed. The apparent age distribution will be heterogeneous according to the variation of the 'degree of discordancy'.

For the case of mixing of differently aged concordant phases the application of conventional digestion methods yield discordancy trends in the concordia diagram which are indistinguishable from those generated by episodic lead loss. Evaporation of concordant phases on the other hand yields $^{207}\text{Pb}/^{206}\text{Pb}$ apparent age distributions which are significantly different from those characterized by episodic lead loss. 'Concordancy' of the mixing phases means evaporation of lead components that had evolved in closed U/Pb systems. Consequently the evaporation data are expected to define the ages of crystallization of the mixing phases by distinct and clear-cut centering of the apparent age distributions at the relevant dates (i.e. at $T = T_c$ and $T = T_m$ in Fig. 4). Certainly, the distributions will be more complicated in the unfavourable case when lead components simultaneously evaporate from differently aged parts of the same grain. Note for instance the clearly mixed radiogenic lead composition in the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio record presented in Fig. 3 during the acquisition interval 10 to 25 min. However these radiogenic lead mixtures can be identified by striking trends throughout the ratio records.

The samples analysed are from pegmatitic Ceylon gems, from a Precambrian granite and from an early Paleozoic metamorphic rock. Conventional U/Pb analyses carried out for the granite and for the metamorphic rock have clearly demonstrated discordant U/Pb isotope patterns whereas the Ceylon zircons turned out concordant despite the varying degrees of metamictisation. The Ceylon zircons have been included in the study in order to demonstrate the accuracy of the procedure. The granitic and metamorphic zircons are used to reveal the relation of conventionally verified discordancies to the apparent age distributions derived from the evaporation data. The $^{207}\text{Pb}/^{206}\text{Pb}$ apparent age spectra of the present study are presented in simple histograms by plotting the number N of $X = (^{207}\text{Pb}/^{206}\text{Pb})_{\text{rad}}$ ratios within the ratio class ($X, X + \Delta X$) (see Figs. 5, 6, and 8). This presentation has been preferred to the "thermoisochron"-plot of Sunin and Malyshev (1983) because ^{204}Pb isotopes are absent in the evaluated data of the present study and therefore cannot be used as 'etalon'. Thus X on the horizontal axis of the histogram can be directly interpreted as $^{207}\text{Pb}/^{206}\text{Pb}$ apparent age.

Ceylon zircons

Pegmatite zircons from Ceylon have repeatedly been subject to systematic investigations concerning crystallographical and physicochemical properties (e.g. Holland and Gottfried 1955; Pidgeon et al. 1966, 1972; Vance and Anderson 1972). The grains which are found in heavy-mineral bearing gravels are often of gem-quality. The Ceylon zircons have

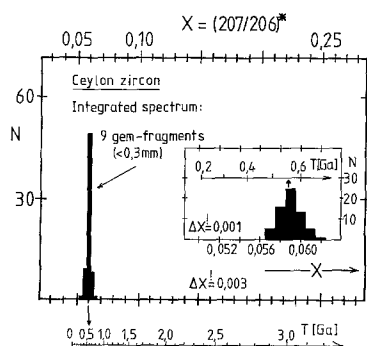


Fig. 5. Distribution of radiogenic lead isotope ratios $X = {}^{207}\text{Pb}/{}^{206}\text{Pb}$ derived from nine Ceylon zircon fragments (green and pink, ≤ 0.3 mm). The spectrum plotted as apparent age histogram has been integrated from the individual evaporation records. N is the number of X -values verified for the apparent age class X to $X + \Delta X$. The distribution is uniform and dates the crystallization of the pegmatites that feeded the gem-bearing gravels, at 560 ± 40 Ma, in agreement with conventional results

been dated at 560 ± 20 Ma (e.g. Tilton and Aldrich 1955; Gottfried et al. 1956; Pidgeon et al. 1966). The samples investigated in the present study have been prepared by crushing translucent green and pink gems. Single fragments not larger than 0.3 mm have been used for evaporation analyses. The results are compiled in the histogram-plot of Fig. 5 by integration of the ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ratio records of 9 different fragments acquired at evaporation temperatures of 1,650–1,750 K. The high-temperature evaporation of radiogenic lead from the pegmatite zircons typically shows a narrow distribution of the ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ apparent ages defining a single geochronological date. The derived age of 560 ± 40 Ma (one standard deviation) corresponds well to the results documented in the literature and it characterizes the age of zircon crystallization. In contrast to the uniformity of the apparent ages in all investigated Ceylon zircon fragments varying U/Th fractionation in the zircons is observed which may depend on the origin of the material. Though the ${}^{208}\text{Pb}/{}^{206}\text{Pb}$ ratio is very homogeneous throughout the respective gem ($< 5\%$), it significantly varies between different gems (green: ${}^{208}\text{Pb}/{}^{206}\text{Pb} = 0.03$, pink: ${}^{208}\text{Pb}/{}^{206}\text{Pb} = 0.05$). From the ${}^{208}\text{Pb}/{}^{206}\text{Pb}$ ratios and the age of crystallization the U/Th ratios can be calculated (green: U/Th = 10, pink: U/Th = 6). They are significantly different from the value of U/Th = 9 estimated by Tilton and reported by Holland and Gottfried (1955). Conventional U/Pb isotope analyses of a metamict Ceylon zircon resulted in an even larger U/Th ratio of 13 which, however, could be significantly reduced by hydrothermal leaching (Pidgeon et al. 1966). The uniformity of the U/Th ratio in the zircons on cm-scales on the one hand and its heterogeneity among different grains on the other is a peculiarity of the gravel-feeding source rocks and may be due to regionally varying U- and Th-concentrations of the differentiates during the crystallization of the pegmatites.

'Marble Mountains' zircons

The sample has been prepared from a Precambrian granite of the 'Marbel Mountains' in San Bernadino County/Southwestern California. This rock contains a morphologically very homogeneous suite of zircons which are preponderantly translucent and hyacinth-coloured. Silver (1963)

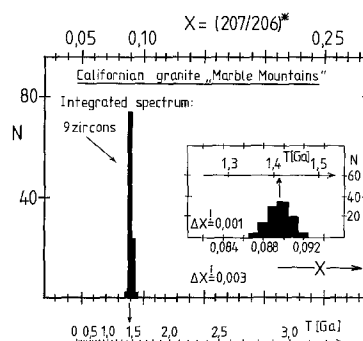


Fig. 6. Distribution of radiogenic lead isotope ratios $X = {}^{207}\text{Pb}/{}^{206}\text{Pb}$ derived from nine zircon individuals (size < 0.3 mm) of a granite from the 'Marbel Mountains'/California. The spectrum has been integrated from the individual evaporation records. The distribution defines a single date of $1,410 \pm 30$ Ma which agrees with the age of crystallization, dated at 1,400 Ma by Silver (1963) on highly discordant zircon fractions

analysed multi-grain zircon fractions of this granite by conventional U/Pb techniques. The fractions had been separated according to grain size and magnetic susceptibility. In the concordia plot the results of Silver are arranged along a linear chord with distinct variation of the 'degree of discordancy'. The lower and the upper intercepts of the chord with the concordia yielded ages of about 180 Ma and 1,400 Ma respectively (recalculated with new decay constants; Steiger and Jäger 1977). The ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ apparent ages of the different fractions ranged from 1,100 Ma to 1,400 Ma (which is important for the discussion of the apparent ages derived from the evaporation data). The U-content appeared to be positively correlated to the size and the magnetic susceptibility of the grains. The mean U-concentration was of the order of 1,000 ppm. The data set of Silver as a whole agrees with intrusion and crystallization of the magmatic body about 1,400 Ma ago.

Figure 6 shows the results of the evaporation analyses on 9 different 'Marble Mountains' zircons (maximum weight ~ 100 μg). Their apparent age distributions are integrated and combined in one common histogram for simplicity of presentation. Obviously the data well-define a single ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ apparent age of $1,410 \pm 30$ Ma (one standard deviation) in close agreement with the result of Silver (1963). Contrary to the discordant multi-grain fractions reported by Silver no ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ apparent age significantly lower than the age of crystallization was found in the high-temperature evaporation spectra. This means that none of the zircon individuals contained crystalline domains with lead components formed significantly after the primary crystallization episode. Consequently a lead isotope evolution in closed U/Pb systems has to be assumed for the crystalline domains of all investigated 'Marble Mountains' zircons. This closed-system evolution lasted from the time of crystallization till present. Silver's linear chord plotted from the discordant multi-grain fractions in the concordia diagram therefore appears to be a mixing line. One end member of the mixing array is a radiogenic lead component with well-defined and (in conventional notation) 'concordant' isotopic composition in the crystalline domains. The rest of the radiogenic lead components which participate in the mixing array are clearly characterized by low Pb activation energies for they do not contribute to the evapo-

ration spectra at high evaporation temperatures. They may be weakly adsorbed to surfaces or carried by non-zircon inclusions or metamict zircon domains.

Zircons from a Southern Schwarzwald diatexite

The zircon samples have been prepared from an aliquot of a diatexite whose isotope composition has been studied by various working groups: Rb/Sr isotope patterns agree with anatectic conditions at about 490 Ma (sample 'S235'; Hofmann and Köhler 1973); a Rb/Sr mineral isochron implies Hercynian Sr homogenization at 331 ± 6 Ma (v. Drach and Lippolt 1975; isochron age recalculated with $\lambda = 1.42 \cdot 10^{-11} \text{ a}^{-1}$); Pb isotope analyses on K-feldspar and whole-rock samples support genetic relations to a nearby orthogneiss area (Kober and Lippolt 1985a, b). Zircons from a similar rock sampled from a location not far away from 'S235' had been analysed by Steiger et al. (1973): The heterogeneous zircon population contained euhedral needle-shaped as well as rounded grains and yielded a complex U/Pb distribution supporting a multi-event history. The majority of fractions enriched in euhedral zircons were arranged along a linear chord in the concordia diagram that intersected the concordia at 100 ± 40 Ma and 490 ± 20 Ma. The upper intercept had been assumed to date the anatectic event and agreed well with the results from the Rb-Sr study on whole rocks (Hofmann and Köhler 1973). The lower intercept was considered to have no geological significance. A Precambrian prehistory was confirmed by the zircon fractions enriched in rounded zircons. However the data of Steiger et al. (1973) did not permit an estimate for precursor ages.

The zircon population of the diatexite S235 investigated in the present study is heterogeneous in morphology, translucence, colour and number and type of inclusions (Fig. 7). The grains are either nearly euhedral or rounded. They are colourless, reddish or brownish and occasionally contain a lot of small dark inclusions. The apparent age spectrum of 13 zircon individuals integrated from their high-temperature evaporation records is presented in the $^{207}\text{Pb}/^{206}\text{Pb}$ apparent age histogram of Fig. 8. The apparent age distribution centers in two different narrow intervals: an early Paleozoic one of about 500 Ma, and a Precambrian one of 1.95 ± 0.05 Ga (one standard deviation). The Middle-Proterozoic date derived from two of the 13 grains is in good agreement with an extrapolated U/Pb concordia/discordia upper intercept reported for zircon-multi-grain fractions from a Central Schwarzwald paragneiss (Todt and Büsch 1981).

The early Paleozoic apparent age distribution agrees well with the results of Steiger et al. (1973). However the application of a smaller interval step ΔX in the histogram reveals a non-statistical spread around the estimated date of 500 Ma (Fig. 8). The evaporation spectrum is asymmetrically extended to higher apparent ages of about 600–650 Ma and, moreover, it appears to be double-centered at about 470 Ma and 520 Ma. The extension to somewhat higher apparent ages is mainly due to a significant increase of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios observed for two among the eleven zircons shortly before their ion beam was dying away. It may point to the influence of Precambrian microreliefs in the two early Paleozoic grains. The bimodal nature of the early Paleozoic apparent age distribution is far from being statistically safe and from being a proof for two inde-

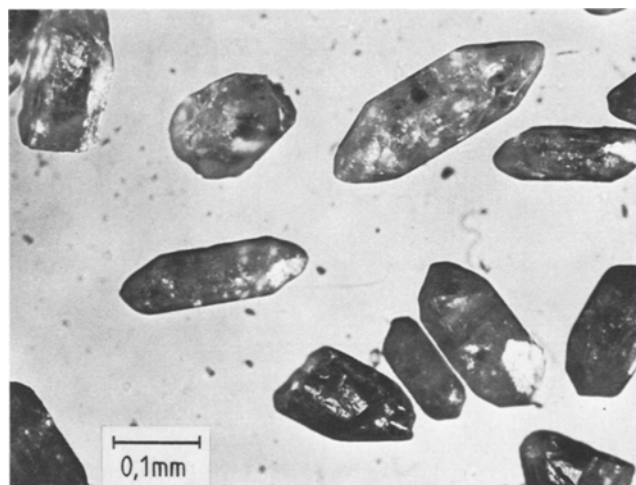


Fig. 7. Zircon individuals from the diatexite 'S235' (Southern Schwarzwald, SW-Germany). The population turns out to be heterogeneous in colour, translucence and morphology. Occasionally grains with numerous dark inclusions are observed. Some of the individuals are strongly rounded

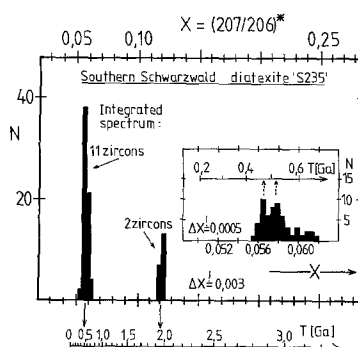


Fig. 8. Distribution of radiogenic lead isotope ratios $X = ^{207}\text{Pb}/^{206}\text{Pb}$ derived from 13 grains of the diatexite 'S235'. The spectrum has been integrated from the individual evaporation records. It proves the anatectic event to have occurred around 500 Ma ago, in agreement with U/Pb isotope analyses on zircon fractions from an adjacent anatexite by Steiger et al. (1973). Moreover, a Precambrian relic component of two zircon individuals can be dated at 1.95 ± 0.05 Ga by the evaporation records

pendent events. It is also not possible to recognize different euhedral zircon generations on the basis of morphological or U/Th fractionation criteria. Nevertheless a memory in the present data set from an early Paleozoic magmatic episode preceding the diatexite to the nearby orthogneiss area. The intrusion of the precursor magmas has been dated by conventional U/Pb isotope analyses at 520 ± 20 Ma (Todt and Büsch 1981).

As a whole the spectrum in Fig. 8 is well suited to demonstrate the power as well as the current limitations of the mass spectrometric zircon evaporation under discussion. The procedure clearly allows a significant quantification of Precambrian relic ages. However geological events that affected the investigated rocks during later episodes of the earth's history can hardly be resolved within 30–50 Ma by analyses of a single zircon population.

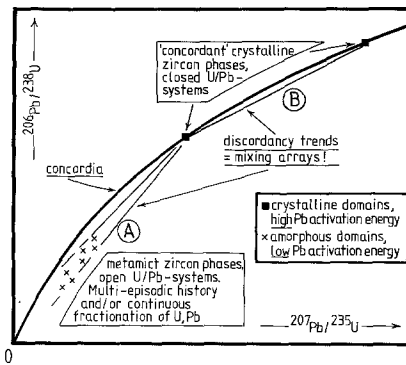


Fig. 9. Discordancy trends in U/Pb concordia diagrams interpreted as mixing arrays. The general closed-system behaviour of crystalline zircon domains with regard to U and Pb favours mixing models instead of multi-episodic lead loss models for the explanation of discordia lines. Two types of 'discordia' can be distinguished: *Type A* due to mixing of (concordant!) crystalline phases with (usually discordant) metamict ones or with radioactive non-zircon minerals. The lower concordia-intercept may be without geochronological significance because of open-system U/Pb isotope evolution of the less retentive phases. *Type B* due to mixing of concordant crystalline phases with different ages of crystallization. In the case of two-phase mixing the upper as well as the lower concordia-intercept are of geochronological significance

Reinterpretation of U/Pb discordancy trends

From the crystalline domains of all investigated zircons apparent Pb/Pb dates have been derived which are distributed closely around the respective ages of crystallization. From the high-temperature evaporation spectra no discordancy could be ascertained as would have been indicated by $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages significantly lower than the respective age of crystallization (Fig. 4). This implies *undisturbed* lead isotope evolution in the crystalline domains from the time of crystallization till present. Consequently general *closed-system* behaviour with respect to the U and Pb isotopes can be postulated for the zircon domains characterized by high Pb activation energies. Lead loss phenomena which had been proven for the zircons from the Precambrian granite and from the early Paleozoic metamorphite by conventional U/Pb isotope studies are obviously not a property of the crystalline zircon phases. Open-system behaviour in the geological environment can therefore only be attributed to the phases which released their lead at low or intermediate evaporation temperatures and which did not contribute to the high-temperature evaporation spectra governed by the stable phases.

These conclusions suggest a reinterpretation of discordancy trends in U/Pb isotope distributions. The crystal assemblages that appear discordant according to U/Pb element/isotope correlations may be mixtures of at least two different phases (Fig. 9):

- a) One or several phases that are characterized by low Pb activation energies. Their open-system lead isotope evolution may be modelled by multi-episodic lead loss and/or continuous fractionation of U and Pb. These characteristics are assumed for the metamict zircon domains or for intergrown non-zircon phases (e.g. uranothorite; Steiger and Wasserburg 1966).
- b) One or several phases which are characterized by high

Pb activation energies. They are usually concordant in the notation of conventional U/Pb isotope studies because of their closed-system behaviour with regard to U and Pb. General closed-system behaviour is postulated for the crystalline zircon domains.

Consequently two kinds of discordia lines can be distinguished: Either the trend lines are due to phase mixing between (concordant!) crystalline domains and less stable phases (type A in Fig. 9). Or the discordancy trends are generated by mixture of crystalline zircon phases of different age (type B in Fig. 9). Examples for case B are old cores surrounded by newly-grown rims, zircons intergrown with domains which have been recrystallized after having been radiation-damaged and unmixed, mixture of zircons from different sources in a sedimentary environment. All crystalline mixing members are concordant. Thus in the case of simple two-phase mixing both concordia-intercepts are of geochronological importance. Obviously the interpretation remains heavily dependent on the basic model of rock genesis which has to be constrained by petrographical investigations. The occurrence of metamict zircon domains in the crystal assemblage may result in geologically meaningless concordia-intercept ages and obscure the geochronological information recorded by the crystalline phases.

Irrespective of the kind of crystal structure that characterize the material involved, the discordancy trends are due to *phase mixing* and thus have to be treated as mixing arrays. This inference agrees well with the conclusions of Steiger and Wasserburg (1966). They proved zircon concentrates from the Sandia Mountains granite/New Mexico to be multi-phase assemblages and suggested that they are mixtures of highly discordant (metamict) zircon phases with high radioactivity and of "relatively concordant" zircon phases with low Th- and U-concentrations. The conclusions of the present study are also in agreement with those of Allegre et al. (1974) based on studies of Alpine and non-Alpine zircons. They postulated that zircon crystals present *closed* U/Pb systems provided there are no unmixing phenomena that open the U/Pb systems and may result in multi-phase assemblages with varying Pb activation energies. High lead retention of zircons under adverse environmental conditions has been concluded by Gentry et al. (1982) from single zircons of five granitic bore hole samples using single-filament whole-grain evaporation. Phase mixing as the main cause for the generation of discordancy trends is also supported by the studies of Krogh (1982) who succeeded in reducing the discordancy of zircon concentrates by air abrasion.

Summary and conclusions

The application of the evaporation technique to zircon individuals of pegmatitic, granitic and metamorphic origin and with known ages has proved the geological significance of the $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages which were derived from the lead ion beams evaporated from untreated zircon grains. Using the whole zircon grain as lead emission source eliminates serious difficulties which arise with conventional U/Pb analyses and with evaporation methods based on suspension techniques. With the highly different evaporation activation energies of lead components residing inside and outside of the crystalline zircon domains the geochronological information carried by the stable phases can be 'filtered'.

The procedure is insensitive to cross-contamination of any kind as already stated by Gentry (1984). The preservation of the internal structure of the zircons (e.g. relic cores) allows variable path lengths of diffusion to be used as an additional means for the separation of lead components, which otherwise would be homogeneously mixed by bomb-digestion or by zircon-powdering and suspension. Moreover the much longer migration paths compared to powder-evaporation make it easier to compromise between maximum ion current and maximum lifetime of the ion beam. For the conditioning of the ion beam the decoupling of evaporation and ionisation by application of the double-filament arrangement turned out to be very important with respect to fine-tuning the evaporation temperature and with respect to improvement of the Pb ion beam stability and of the Pb ion yield compared to single-filament techniques. Contrary to the ion microprobe application the evaporation technique has a spatial resolution down to submicroscopic scales. This means that the MS evaporation analysis also works in the case of zircon micro-crystallites which are closely intergrown with gel-structures involving a complex U/Pb geochronology. Therefore, the MS evaporation technique is well-suited to analyse 'normal' and not only 'perfect' zircons. There can be no doubt that the preparation procedures to mount the whole zircon individual onto the evaporation filament are less time-consuming and quite suitable for rapid spot checks of zircon populations. This facilitates identification of rare relic components, for instance in metasedimentary rocks.

The application of the method to the various zircon individuals has revealed some important features of the crystalline zircon domains:

1. Generally the amount of common lead in these domains is less than 10^{-2} picomoles (estimated from the $^{204}\text{Pb}/^{206}\text{Pb}$ ratios).
2. The activation energies of uranium and thorogenic lead in the zircon lattice are usually not different. The lead isotopes of different radiogenic origin appear to be similarly bound to the crystal. However, they evaporate from domains of varying U/Th ratios which reflect trace element heterogeneities of the minerals and perhaps also of the mineral sources during their crystallization episode. This can be inferred from the observation that the record of $^{208}\text{Pb}/^{206}\text{Pb}$ ratios is usually characterized by constant values in the case of the pegmatite zircons or by only slightly increasing or decreasing values in the case of the granitic and metamorphic ones.
3. The crystalline domains within the zircon grains generate radiogenic lead in closed U/Pb systems.

This means, the respective crystalline domain usually contains only one single radiogenic lead component with a single-stage evolution, and not different radiogenic components with a multi-episodic history. Problems in the case of evaporation studies may therefore only arise from the intergrowth of crystalline domains with different ages of crystallization. However, even with this complication there is the chance to identify the competing components by sequential evaporation (e.g. see Fig. 3), if the crystallization events have not succeeded each other as closely as in the case of diatexite 'S235' (Fig. 8).

The postulated simple U/Pb isotope evolution of the crystalline domains implies that the majority of published discordancy trends are due either to mixing of concordant crystalline domains or to mixing between concordant crys-

talline phases and less-retentive mineral domains. Radiation-damaged amorphous zircon glasses and/or non-zircon minerals are considered to be the less stable mixing partners. In any case the discordancy trends should be reinterpreted as mixing arrays, that means, as results of contrasting response of individual components in a phase assemblage treated by a given event.

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