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Uranium-Lead Radioactive Ages of Monazite and Zircon from the Vire-Carolles Granite (Normandy). A Case of Zircon-Monazite Discrepancy

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“Chargé de Recherches” of the Belgian National Fund for Scientific Research.

ABSTRACT

Uranium-lead age determination performed on two monazite samples from the Upper Precambrian Vire-Carolles granite (Lower-Normandy) suggests an age attribution of 570 ± 25 m.y. for this granite, a result slightly higher or similar to biotite Rb-Sr and K-Ar ages obtained by other contributors. This figure may represent an upper limit for the base of the Cambrian. Two zircon samples yield 207/206 ages which are obviously too high. They are considered as indicative of the presence of zircon xenocrysts.

Introduction

The Vire-Carolles granite massif, and other similar outcrops of Lower Normandy, may be considered, both on the basis of field relationships and geochronology, to date the very end of the Precambrian. They cross-cut the folded and weakly metamorphosed sediments of the Briovérien, considered as Proterozoïc, and are overlain by Lower Cambrian strata (L. CHAURIS 1956, L. CHAURIS et al. 1956, J. COGNÉ 1962). However, it is uncertain whether the Lowermost Cambrian is present (L. CAHEN and F. DORÉ 1964, F. DORÉ 1963).

Available geochronological results concerning these rocks are summarised in Table 1. Calculation is based upon values of the decay constants used normally (Table 2). The highest figures obtained are slightly lower than the commonly accepted figure for the base of the Cambrian, i.e. 570 m.y. (HOLMES symposium 1964). It has therefore been suggested that these highest figures themselves may point to a rather too low age indication – as is often the case with K-Ar and Rb-Sr mineral ages (C. D. J. ADAMS 1967).

The field relationships of the Lower Normandy granites are rather similar to that of southeastern Massachusetts rocks dated at 570 ± 20 m.y. by the Rb-Sr isochron method applied to whole rock samples (H. W. FAIRBAIRN et al. 1967). Allowing for uplift and unroofing prior to the deposition of the first Lower Cambrian strata, the above-mentioned authors tentatively date the base of the Cambrian at 550 m.y. This figure would still be lowered (to 520 m.y.) if the value of the decay constant $\lambda^{87}\text{Rb} = 1.47 \times 10^{-11} \text{ y}^{-1}$, also frequently used, is preferred. The present paper deals

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with an attempt to gather reliable age information for the Vire-Carolles granite and the overlying Lower Cambrian strata.

Analytical procedure

The procedure used for zircon has been described elsewhere (S. DEUTSCH et al. 1964); the only modifications concern the mass spectrometry. For monazite, we chose a procedure which did not attack the zircon and left it behind in the concentrates. It was impossible indeed to obtain a clean mechanical separation of the monazite (see appendix).

About 0,05 g of (impure) monazite was weighed, then placed in a silica glass beaker and mixed with 3 ml of concentrated sulphuric acid (Hopkin and Williams "low in lead"). The beaker was placed into a pyrex tank flushed by filtered nitrogen, in order to minimize contamination by air dust, the tank being placed on a hot plate. After several hours of heating, the solution was allowed to cool, and transferred, together with a greyish solid residue, into a teflon beaker. About 12 ml H₂O (de-mineralized and twice distilled in silica-glass) and 12 ml of concentrated HNO₃ (Hopkin and Williams "low and lead") were added, using for that purpose the silica-glass beaker which itself was rinsed by this way. The solution obtained was transferred into a 100 ml volumetric flask, and diluted almost to 100 ml with hot water. After cooling, dilution to 100 ml and mixing, the ²³⁵U and ²⁰⁶Pb spikes were added to an aliquot for concentration.

The remaining operations are identical to those used for zircon: dithizone extraction of the lead, hexone separation of the uranium. This procedure followed that described by R. A. POWELL and C. A. KINSER (1958). The only solid residue observed in the two analyzed samples, apparently consisted of unattacked zircon and tourmaline (and some undetermined impurities in the case of sample 100.307). Prior to the analysis, it was necessary to proceed to a quick washing with warm diluted HNO₃ of the monazite concentrate of sample 100.307, in order to get rid of the abundant sulphides present. Sulphides were present in a lesser amount in the case of sample 100.197, from which a split was washed in hot 50% HNO₃ for 45 minutes, another split remaining unwashed, and so analyzed.

All mass-spectrometric measurements were performed on an Atlas CH₄ instrument in Brussels except zircon of sample 100.197 where U and Pb concentration isotopic analyses were made on a similar instrument, at the Laboratory of Physics of the University of Bern, by G. GRÖGLER (I wish to thank Dr. G. Grögler for allowing me to publish these results).

Uranium was loaded as uranyl nitrate on a tantalum filament, lead as nitrate on platinum covered with a zirconium silicate activator (P. A. AKISHIN et al. 1957) except for zircon sample 100.197, where the lead concentration has been measured using the boric acid technique on tantalum.

The errors on the 207/206 radiometric ages are over-all uncertainties, except for the constants used. They include a $\pm 0,2$ (or 1,3%) uncertainty on the 207/204 ratio of the common lead chosen for the correction. Our mass-spectrometric measurements are aligned on the absolute values of E. J. CATANZARO (1968), using the CIT or the NBS 200 lead standards.

Table 1. Lower Normandy granites, Rb-Sr and K-Ar data

Rock or mineral	Athis granite		Vire-Carolles granite	
	Rb/Sr	K/Ar	Rb/Sr	K/Ar
biotite	545 \pm 11 ^{a)}	489 \pm 10 ^{a)}		553 \pm 9 ^{b)} 583 \pm 9 ^{c)}
muscovite	503 \pm 60 ^{a)}	531 \pm 11 ^{a)}		
granite, whole rock			508 \pm 10 ^{a)}	

^{a)} M. J. GRAINDOR and G. J. WASSERBURG (1962).

^{b)} G. KAPLAN and F. LEUTWEIN (1963), recalculated with the constants figuring in Table 2.

^{c)} Same results, with the constants used by these authors in their original publication.

Table 2. Constants used in age calculations

$^{40}\text{K} = 0.0119\% \text{ K}$	$\lambda_{\beta} = 4.72 \times 10^{-10} \text{ y}^{-1}$
	$\lambda_e = 5.84 \times 10^{-11} \text{ y}^{-1}$
$^{87}\text{Rb} = 27.85\% \text{ Rb}$	$\lambda^{87}\text{Rb} = 1.39 \times 10^{-11} \text{ y}^{-1}$
$^{238}\text{U} = 99.27\% \text{ U}$	$\lambda^{238}\text{U} = 1.537 \times 10^{-10} \text{ y}^{-1}$
$^{235}\text{U} = 0.720\% \text{ U}$	$\lambda^{235}\text{U} = 9.72 \times 10^{-10} \text{ y}^{-1}$

No error indication is given for the 206/238 and 207/235 radiometric ages of monazites, since we have not been able so far to check the reliability of the Pb and U concentration measurements with the adopted procedure. It is, however, believed that partial loss of lead as precipitated sulphate is improbable, in view of the satisfactory results obtained by R. A. POWELL and C. A. KINSER (1958) and the very low amounts of lead present.

Discussion of the results

The experimental results are presented in Table 3.

In spite of the presence of impurities in the final monazite concentrates, it is believed that, in the case of the HNO₃ washed samples, the analyzed material was practically pure monazite. In these cases, the weighed material included tourmaline and zircon which remained undissolved, and, for the unwashed split of monazite 100.197 it also included sulphides and other matter which was dissolved together with the monazite. Therefore, the concentrations in uranium and radiogenic lead figuring in Table 2 are not of great significance, only the ratios uranium to radiogenic lead being significant. It is apparent from the data, however, that some material (unidentified mineral phase?) rich in uranium and uranium-derived radiogenic lead has been dissolved by the nitric acid treatment in the case of sample 100.197.

The radiometric 207/206 age is generally considered as the most reliable age indication for uranium bearing minerals (except when a more refined interpretation is possible as, for example, in the case of cogenetic suites). It is equal or nearly equal to the real age if the discordance between the three "apparent ages" is small (which is the case for the monazite samples investigated), and can be too low (or else remains essentially correct) when the following pattern, $t_{206/238} < t_{207/235} < t_{207/206}$, is caused by preferential loss of lead. It is observed that the 207/206 ages of the mona-

zites are close to the radiometric ages previously obtained for the Vire-Carolles granite (Table 1), while the zircon ages are surprisingly high. Our interpretation is that the monazite 207/206 ages provide a reliable age indication, while those of the zircon are spurious – probably because of the presence of zircon xenocrysts. Arguments in favour of this interpretation are the following.

1. The two rock samples have been collected not very far from the contact with the Brioverian slates.
2. In both cases, rather numerous but very minute fine-grained hornfelsic inclusions are observed, dispersed within the rock (see appendix for description).
3. Somewhat similar cases have been reported in the literature. This point will be discussed in a further paragraph.

Age of the Vire-Carolles granite and of the base of the Cambrian

From the preceding discussion, it appears that the age assignment of 570 ± 25 m.y. can be accepted for the accessory monazite of the Vire-Carolles granite.

The question arises whether this figure really dates the crystallisation of the monazite or, as for the micas, a significantly later time at which the migration of the radiogenic element ceased. We may accept, provisionally, that the behaviour of the micas, especially of biotite, is to some extent peculiar. Though the subject may deserve further investigation, the uranium-bearing minerals are not considered to behave in a similar way with regard to the radiogenic lead loss. Sphene might possibly be subject to extensive post-crystallisation lead loss, but becomes closed at much higher temperature than biotite does for strontium and most probably for argon escape (P. PASTEELS 1969; P. PASTEELS and J. MICHOT 1970).

As noted above, the age obtained is hardly different from the biotite K-Ar ages of G. KAPLAN and F. LEUTWEIN (1963). Since we are dealing with a post-tectonic epizonal granite, it can be assumed that its cooling time is short, and that, in general, the mica ages and the ages obtained on other minerals, such as monazite, closely indicate the emplacement time. The lower radiometric ages figuring in Table 1 might be due to local effects (Hercynian influence or weathering).

The crystallisation or, possibly, an early stage of the cooling of the granite is thus dated at 570 ± 25 m.y. The overlying Lower Cambrian sediments are, at least, several million years younger (allowing for uplift and erosion)²). There is thus a clear suggestion that the 570 m.y. figure generally accepted for the base of the Cambrian is too high.

It may be argued that definitive stratigraphical proof that the granite emplacement predates the lowermost Cambrian is lacking, since the oldest well-dated layers which, very probably, post-date the granite emplacement are of middle Lower Cambrian age (L. CAHEN and F. DORÉ 1964, F. DORÉ 1963). Therefore it cannot, on the base of the present data, definitively be concluded what the age of the base of the Cambrian is.

²) Because of the epizonal character of the Vire granite, this time gap may be appreciably smaller than the 20 m.y. assumed by H. W. FAIRBAIRN et al. (1967) in another, more or less comparable case.

Table 3. Analytical data and radiometric ages

Sample	Mineral	U ppm	Pb rad ppm	Lead isotope abundances relative to Pb ²⁰⁶			Radiometric ages in m.y.			
				204	206	207	206/238	207/235	207/206	
100.197	Zircon	544	51.0	0.1114	100	8.003	11.95	595 ± 16	760 ± 35	
	Monazite (unwashed)	2449	1046	0.3554	100	11.164	454.7	550	606 ± 60	
	Monazite (HNO ₃ -washed)	1925	1017	0.0972	100	7.277	654.0	510	564 ± 26	
100.307	Zircon	462	39.9	0.1218	100	8.112	10.57	593 ± 20	738 ± 50	
	Monazite (HNO ₃ -washed)	1098	746	0.1153	100	7.580	741.7	568	579 ± 30	

Common lead correction: 204 = 1; 206 = 18.6; 207 = 15.7; 208 = 38.9.

A thorough discussion of this point of the time-scale should include considerations on the stratigraphical correlations, on other localities of interest, on the validity of the decay constants, on the implications of experimental and methodological uncertainties, and others. This is beyond the scope of the present investigation.

Zircon xenocrysts in granite

Several cases of isotopic evidence on the presence of zircon xenocrysts in granites have been reported (P. PASTEELS 1964, P. P. BANKS and L. T. SILVER 1968 etc.). In other instances, this presence has been postulated but not demonstrated. From a rapid survey of the isotopic data relative to granitic zircons, it would appear that cases of high 207/206 ages indisputably caused by the presence of zircon xenocrysts are rare.

In the two cases which we have investigated, the present one and that of the Mont Orfano granite, Italian Alps, the granite is epizonal³), exhibits at least some evidence of wall-rock contamination, and is relatively poor in zircon. This last observation could be common for granites containing zircon xenocrysts in non-negligible proportions (B. R. DOE, personal communication 1968). However, neither in the case of the Mont Orfano granite (P. PASTEELS 1964), nor in the present one, is the morphology of the zircon population indicative of the presence of zircon xenocrysts. It can even be said that in the two samples of the Vire-Carolles granite presently investigated, the zircons are more elongated and more euhedral than is generally the case, and that the proportion of nuclei (often observed in granitic zircons) is rather small. It may therefore be assumed that the xenocrysts are not numerous but of considerable age, and that the bulk of zircon is truly magmatic (see appendix).

³) This observed fact may be worthwhile noting, though evidently it may have no bearing on the presence or absence of zircon xenocrysts.

Whenever a granite sample is collected with the purpose of dating the zircon by the U-Pb method, care must obviously be exercised in eliminating rocks which are *visibly* contaminated. However, this is not always easily achieved. In the present case, the fresh outcrops (quarries) expose a contaminated rock, sample 100.197, at some distance from the mapped contact (2 km).

The xenocrysts are very minute. Hand specimens may fail to contain any of them. Thus if a similar case was encountered in the course of a routine dating work intended to decipher the poorly-known geology of a region of difficult accessibility, the erroneous 207/206 values or the erroneous age indication extrapolated on the "Concordia" diagram would, in all probability, be considered as reliable. Inasmuch as a sensible increment of the 207/206 apparent age is more likely to be due to wall-rock contamination in the case of zircon-poor granites, and since these latter (Ca-poor granites in general) often contain monazite (D. E. LEE and F. C. W. DODGE 1964), it may be preferable in such cases to select monazite, and not zircon, for dating purposes.

The case of deep-seated, gneissic granites with gradational contacts is obviously different and in such case the presence of old relict zircons may be indicative that a truly magmatic stage never existed.

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APPENDIX

Sample location

100.197: Saint-Michel de Montjoie, 13 km W-SW from Vire. Quarry north of the village, which is located 2 km N-NE from the mapped contact.

100.307: Saint-Michel de Montjoie, quarry south of the village.

Short sample description

Both rock samples are very similar and composed of plagioclase, quartz, orthoclase (perthitic), biotite, the accessories being muscovite, myrmekite, opaques, apatite, sphene, zircon.

Plagioclase occurs in automorphic crystals exhibiting a distinct zonation and often an albitic rim. The outer part of the crystals is composed of oligoclase; the inner part is badly sericitized and undeterminable in most cases. Orthoclase is often poikilitic. Biotite is automorphic, dark reddish-brown, locally transformed into chlorite.

Minute inclusions of modified country-rock material are observed in the two rock samples, being somewhat larger and more abundant in sample 100.197, collected, however, at further distance from the observed contact than the other sample. These xenoliths do not exceed 1 cm in maximum size. They are composed of fine stubby automorphic plagioclase and biotite crystals often embedded in poikilitic orthoclase, and randomly orientated. Cordierite, light yellowish, is locally abundant. Accessory muscovite often occurs associated with this.

The same description applies of the zircon populations extracted from the two rocks. The colourless, clear zircons are euhedral and exhibit generally a combination of the dipyrmaid face 331,

well developed, with only less developed 111. Subeuhedral and rounded forms occur only in very subordinate amounts. The mean elongation ratio L/l is very high. Nuclei (recognizable inclusions of a zircon with different optical properties) are rare. Monazite occurs in very fine euhedral or subeuhedral crystals in sample 100.197, in irregular and euhedral forms in sample 100.307. Before the acid-washing, monazite concentrate sample 100.197 contained about 7% unidentified opaques, 8% zircon, 1% tourmaline. Sample 100.307, after dissolution of the very abundant sulphides, still contained about 12% tourmaline, 10% zircon and, unidentified, 4% whitish minerals and 2% translucent coloured minerals.

The morphology of the accessory monazite and zircon of the Lower Normandy granites has been described by L. BERTHOIS (1935).

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