# New frontiers in radiometric geochronology 

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Abstract. - The recent improvements in mass spectrometry achieved in the last decade have given to the geochronologist the possibilitv of performing extremely precise determinations on very small amounts of material. New techniques in the field of age determination can be in this way utilized, for instance using natural radionuclides with very long half-life (i.e. ${ }^{147} \mathrm{Sm}^{143} \mathrm{Nd} T 1 / 2=106.10^{9} \mathrm{y}$ ) or radionuclides which are very rare like ${ }^{187} \mathrm{Lu}$.

At the same time, older techniques $\left({ }^{57} \mathrm{Rb} /{ }^{57} \mathrm{Sr}\right.$ ) can be employed on nanogram-size samples; besides, the use of particle accelerators as high sensitivity mass spectrometers, casted a new interest on the exploitation of cosmic ray induced radionuclides $\left({ }^{20} \mathrm{Be},{ }^{14} \mathrm{C}\right.$, etc.) for a wider range of application.

Key words: geochronology, mass spectrometry, radionuclides.

Riassunto. - I notevoli progressi ottenuti nell’ultimo decennio nel campo della spettrometria di massa hanno portato alla possibilità di effettuare misure di estrema precisione su quantità molto piccole di materiali. Questo fatto ha reso possibile l'utilizzazione di nuove tecniche radiometriche, ba sate su decadimenti radioattivi naturali aventi tempi di dimezzamento molto lunghi (ad es.: ${ }^{14}{ }^{47} \mathrm{Lu}^{147} \mathrm{Hf}$ ).

Contemporaneamente è stato possibile utilizzare le vecchie sistematiche ( ${ }^{57} \mathrm{Rb}{ }^{5 r} \mathrm{Sr}$ ) usando campioni dell'ordine dei nanogrammi; inoltre l'utilizzazione degli acceleratori di particelle come spettrometri di massa ad alta sensibilità ha rinnovato l'interesse sull'utilizzazione dei radionuclidi prodotti dalla radiazione cosmica ( ${ }^{10} \mathrm{Be},{ }^{14} \mathrm{C}$, ecc.) estendendone notevolmente il campo di applicazione.

Parole chiave: geocronologia, spettrometria di massa, radionuclidi.

The title of this presentation at the meeting on radiometric geochronology may sound somewhat of an overstatement, but
as a matter of fact the present situation, compared to the recent past, justifies the existence of new frontiers. The remarkable improvements in mass spectrometry and the use of new techniques to study cosmic-ray produced radionuclides have, in the first instance, opened up the possibility to utilize isotopic systems until recently thought to be inaccessible, and in the second instance made possible an increase, by at least one order of magnitude, of the applicability range of the geochronology based on that particular class of radionuclides.

A simple enumeration of the new techniques, albeit interesting, would be arid if it did not make connections with new perspectives in research and speculation; I will therefore try to synthesize the new possibilities open to geochronology by giving a few examples, and keeping in mind that any advance in this field is paralleled by an equivalent advance in isotopic geochemistry, which also enjoys new perspectives.

## Recent methods in radiometric dating

Compared to the now-classic methods such as ${ }^{40} \mathrm{~K} /{ }^{40} \mathrm{Ar},{ }^{87} \mathrm{Rb} /{ }^{87} \mathrm{Sr}$ and the so-called lead methods, we consider recent methods those based on the decays of ${ }^{40} \mathrm{~K}$ to ${ }^{40} \mathrm{Ca}$, ${ }^{147} \mathrm{Sm}$ to ${ }^{143} \mathrm{Nd}$ and ${ }^{176} \mathrm{Lu}$ to ${ }^{176} \mathrm{Hf}$. Each one of them has promising special applications fields which we shall now briefly review with the help of some examples.


Fig. 1. - ${ }^{0}{ }^{0} \mathrm{Ca} /{ }^{a{ }^{a} \mathrm{Ca}} \mathrm{vs}{ }^{20} \mathrm{~K} /{ }^{a s} \mathrm{Ca}$ for plagioclase (Pl), whole rock (WR) potassium feldspar (Kf) and biotite ( Bi ) from Pikes Peak granite. The isochron age of $1041 \pm 32 \mathrm{Ma}$ is in good agreement with previously published results. From Marshall \& De Paolo (1982) slightly modified.

## ${ }^{40} \mathrm{~K} /{ }^{40} \mathrm{Ca}$ Method

Even if this age determination method cannot be considered as new (the first pioneering applications date back to 1958: Polevaya et al.), it was little employed owing to the difficulties of precisely determining the small amounts of ${ }^{40} \mathrm{Ca}$ produced by the radioactive decay of ${ }^{40} \mathrm{~K}$ compared to that already present in mineral and rocks samples (of the six naturally occurring Ca isotopes, ${ }^{40} \mathrm{Ca}$ represents $96.94 \%$ ). Only recently, following the research by Russell et al. (1978) and the remarkable improvements in solid state mass spectrometry, has it been possible to obtain good results on common minerals with this method. The first data were obtained by Marshall \& De Paolo (1981, 1982) who used the isochron technique on separated minerals to determine the age of the Pikes Peak granitic intrusion (fig. 1); they obtained results agreeing with previous $\mathrm{Rb} / \mathrm{Sr}$ and $\mathrm{U} / \mathrm{Pb}$ age determinations. The relatively short life of ${ }^{40} \mathrm{~K}$ and the production of a non volatile daughter makes this method suitable for the age determinations of sedimentary rocks containing authigenic potassium minerals; moreover, the fact that K and Ca are major constituents of several common minerals makes this method complementary to the
$\mathrm{Rb} / \mathrm{Sr}$ method and applicable to the same minerals.

## ${ }^{147} \mathrm{Sm} /{ }^{143} \mathrm{Nd}$ Method

Sm and Nd belong to the rare earth group and the decay of ${ }^{147} \mathrm{Sm}$ to ${ }^{143} \mathrm{Nh}$ has a half-life of $106 \cdot 10^{9}$ a, which is the longest among systems used in geochronology. The amount of radiogenic nuclide produced in time is therefore very small; hence the impossibility, until a few years ago, to use this method.

The first age determinations were performed on meteorites (Lugmair \& Scheinin, 1975) and lunar rocks (Lugmair et al., 1975) which are the oldest available materials; the first measurements on very old terrestrial rocks ( $2.04 \cdot 10^{9}$ a) are due to Hamiliton et al. (1977). The already advances in mass spectrometry made possible the age determination of increasiongly young rocks, and this method was employed to date recent ophiolitic complexes (McCulloch et al., 1981) (fig. 2).

This is probably the most interesting application of this dating system, i.e. the possibility to determine the age of basic and


Fig. 2. - ${ }^{10} \mathrm{Nd} /{ }^{1 u} \mathrm{Nd}$ vs ${ }^{1 \pi}{ }^{2 \pi} \mathrm{Sm} /{ }^{2 u} \mathrm{Nd}$ for plagioclase (Pl), whole rock (WR) and clinopyroxene ( Cpx ) from a gabbro of the Ibra section (Samail Ophiolite). The $\mathrm{Sm}-\mathrm{Nd}$ isotopic system seems to be essentially unaffected by seawater interaction allowing the possibility of age determination of ophiolitic complexes. From McCulloch et al. (1981) slightly modified.


Fig. 3. - ${ }^{170} \mathrm{Hf} /{ }^{1 \pi 7} \mathrm{Hf}$ vs ${ }^{170} \mathrm{Lu} /{ }^{12 \pi} \mathrm{Hf}$ for samples of total rocks and zircons of the Amitsoq gneiss (Greenland). Zircon samples, with a very low $\mathrm{Lu} / \mathrm{Hf}$ ratios, are represented by black dots. The age of 3550 Ma is in good agreement with the results previousl obtained by $\mathrm{Rb} / \mathrm{Sr}$ and $\mathrm{U} / \mathrm{Pb}$ methods. From Pettingill \& Patchett (1981) slightly modified.
ultrabasic rocks, which has always been a difficult problem with the other well-known methods. This is due to the coherent geochemical behaviour of Sm and Nd : these elements are comparatively immobile, even after a metamorphic event, contrary to the $\mathrm{Rb} / \mathrm{Sr}$ pair, which generally do not manage to behave like a closed system in basic and ultrabasic rocks under metamorphic conditions and therefore forbid the construction of isochrons (which in itself is difficult owing to the low $\mathrm{Rb} / \mathrm{Sr}$ ratios characterizing these rock types).

## ${ }^{176} \mathrm{Lu} /{ }^{176} \mathrm{Hf}$ Method

The application of this decay to geochronology is still at the beginning; very interesting results were obtained on meteorites and lunar rocks (Patchett \& Tatsuмото, 1980). The long half-life ( $30.3 \cdot 10^{9}$ a) and the very low natural abundance of ${ }^{176} \mathrm{Lu}$ confine this method to very old rocks, which can generally be easily dated with other methods. To data, one whole-rock isochron obtained with this method was reported, on Amitsoq gneiss samples (Pettingill \& Patchet, 1981); the resulting
age (fig. 3 ) agrees with those already obtained with the $\mathrm{Rb} / \mathrm{Sr}$ and Pb methods, and thus demonstrates the possibility to date whole rocks with this technique.
As pointed out earlier, the precision and sensitivity achieved today by mass spectrometry also entails the possibility to perform measurements on microscopic amounts of material, even on nanogram-sized samples. In a recent work (1981), Papanastassiou \& Wasserburg obtained a $\mathrm{Rb} / \mathrm{Sr}$ isochron using five samples weighting $6 \cdot 10^{-6} \mathrm{~g}$ and called this isochron a «microchron». The used material is a lunar basalt, already dated with routine methods. These special techniques can also be used on terrestrial materials to solve special problems. One of them is the dating of mineralization, which usually do not contain minerals suitable for age determination.

Shepherd \& Darbyshire (1981) utilized successfully the fluid microinclusions contained in quartz crystals associated with sulphide mineralization. These inclusions range in size between 5 and $30 \mu \mathrm{~m}$ and contain Rb and Sr in a comparatively high ratio, but in extremely low amounts, just of the order of nanograms.


Fig. 4. - ${ }^{\pi r} \mathrm{Sr} /{ }^{*} \mathrm{Sr}$ vs ${ }^{*} \mathrm{Rb} /{ }^{*} \mathrm{Sr}$ for samples of fluid inclusions in quartz from the Carrock Fell tungsten vein deposits (Cumbria). Fluid inclusions in quartz behave as closed systems, with favourable ${ }^{n} \mathrm{Rb} /{ }^{*} \mathrm{~S}$ r ratios as can be seen from the diagram. The age result is in good agreement with the mean $\mathrm{K} / \mathrm{Ar}$ age obtained from vein micas of the same mineralization ( $387 \pm 6 \mathrm{Ma}$ ). From Shepard and Darbyshire (1981) slightly modified.

These authors nevertheless obtained an isochron yielding an age in accordance with previously known data (fig. 4).

## Radionuclides produced by cosmic radiation

In the field of cosmic-ray produced radionuclide measurements ( ${ }^{3} \mathrm{H},{ }^{10} \mathrm{Be},{ }^{14} \mathrm{C}$...) we observe a great increase in the employment of these methods, following the utilization of accelerators (cyclotrons) as high-energy, extremely sensitive mass spectrometers (Muller, 1977; Raisbek et al., 1978). The low-level counting techniques used so far had strongly hampered the utilization of these radionuclides because of their laboriousness and of the low yield of the counting
systems. With the help of the cyclotron it is possible to analyze very small samples and to expand the detection limit to several half-lives. For instance, with the ${ }^{14} \mathrm{C}$ method it is possible to measure ages as high as 40,000 to 100.000 years with carbon samples between 1 and 100 mg , while with the ${ }^{10} \mathrm{Be}$ method it is possible to perform age measurements of $10-30$ million years with rock samples weighting a few mg to a few g (Muleer, 1977).

One of the most important results obtained by this technique is the determination of ${ }^{10} \mathrm{Be}$ in island arc volcanoes (Brown et al., 1982), which proved for the first time the existence of recent oceanic sedimentary material in the lavas of these volcanoes, and therefore of the subduction.

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