U, Th–^{21}Ne, a new dating tool: A case study of apatites from Hogenakal carbonatites

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Nucleogenic ^{21}Ne produced through (a, n) reaction on ^{18}O in U, Th-rich minerals can be used as a dating tool. We have demonstrated the application of this method to apatite in carbonatite from Hogenakal, South India. Sm–Nd whole rock-mineral isochron of the same hand sample has yielded an age of 2400 Ma and Rb–Sr mica-whole rock isochron method has yielded a reset age of 1900 Ma. Using nucleogenic ^{21}Ne we derive a gas retention age of 845 ± 127 Ma for the apatite from this carbonatite. This age is considerably younger than the reset Rb–Sr mica (blocking temperature: 350°C) age, but is in good agreement with the younger 770 Ma carbonatite–syenite–alkali granite emplacement event in the region. This system therefore has the potential to identify low-temperature thermal events and to estimate cooling histories of large igneous complexes.

CARBONATITES are mantle-derived igneous rocks, consisting of more than 50% (by weight) of carbonate minerals. They range in age from Archean to Recent[1]. Several dating techniques like Rb–Sr, Sm–Nd and Pb–Pb have been employed to determine the emplacement ages of these rocks[2]. Apatite is common in most carbonatites, often constituting up to 2–5% by volume. Most apatites form early in carbonatites, but can persist up to late-stage mineralization as well. Apatites are rich in U and Th and radioactive decay of ^{238}U and ^{232}Th generates alpha particles, while spontaneous fission of ^{238}U produces heavy isotopes of Xe and Kr. Figure 1 schematically represents the production of such *in situ* noble gases in U, Th-rich minerals. The production of a-particles from U and Th is time-dependent, and thus U–Th/^{4}He systematics can be used as a dating tool[3]. Furthermore, the fissiogenic Xe that accumulates in U-rich minerals over geological time has also been used for age determinations[4,5].

Alpha particles produced from the decay of U and Th have energies between 4.01 MeV, and 8.75 MeV, which is sufficient to induce various (a, n) reactions with low threshold energies on suitable target elements like ^{18}O(a, n)^{21}Ne, ^{19}F(a, nb^{+})^{22}Ne, ^{35}Cl(a, nb^{+})^{38}Ar, to generate various nucleogenic noble gases. Also, the neutrons produced by these (a, n) reactions induce various other (n, a and n, g) reactions in samples, like ^{35}Cl(n, gb^{-})^{36}Ar (Figure 1) during their slowing down and interaction with the surrounding atoms[6]. In any U, Th-rich mineral, if the U, Th and target element concentration are known, by measuring the relevant nucleogenic isotope, the systematics can be used as a potential chronometer if the production rate for that isotope in that mineral is known. However, till date, the potential of nucleogenic isotopes for chronological purposes has not been exploited.

In carbonatites, apatites commonly occur as fluoroapatite, with the ideal formula – $Ca_{10}(PO_4)_6F_2$. They contain appreciable F and O atoms thus providing the required target elements for the nucleogenic reactions ^{18}O(a, n)^{21}Ne and ^{19}F(a, n)^{22}Ne. Therefore, U, Th–^{21}Ne and U, Th–^{22}Ne in apatites should serve as chronometers. However, the fluoroapatite may be characterized by appreciable substitution of F by Cl^{-} or OH^{-} ions or both. Also, unlike O, the F distribution in the apatites may not be homogeneous within the 10–40 μm range of the 4–9 MeV a-particles produced by U, Th decay. Thus, it is possible that all the a-particles produced do not encounter target F atoms within their reaction spheres of <40 μm. Such a discrepancy has also been observed from the study of crustal fluid samples, where the O/F ratio of 110 calculated from ^{21}Ne/^{22}Ne is 4–10 times lower than the average crustal ratio, the discrepancy being accounted for by an enhanced O/F ratio within the range of the U, Th-generated a-particles[7]. Thus ^{19}F(a, n)^{22}Ne may not always be an ideal dating tool. Hence, we have attempted to check the potential of U, Th–^{21}Ne as a geochronological clock in apatite.

U, Th–^{136}Xe systematics can yield crystallizing ages of mineral unless reset by some high-temperature event. In fact,

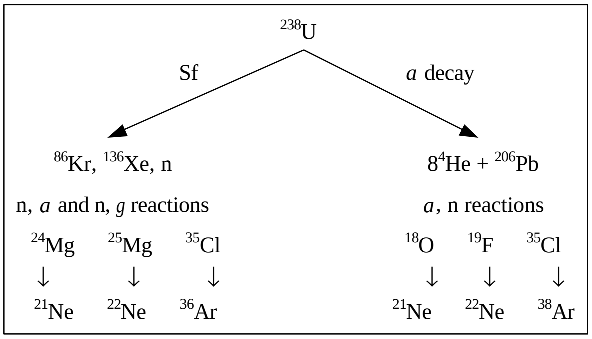

Figure 1. Noble gas isotopes produced by radiogenic, nucleogenic and fission processes of U, Th in minerals like apatite.

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*For correspondence. (e-mail: murty@prl.ernet.in) it has been found to survive up to greenschist facies metamorphic conditions corresponding to $T \approx 350°C$ and $P \approx 0.4$ GPa[4,5]. Unlike the U, Th–^{136}Xe systematics, because of the low closure temperature (~70°C) of He in apatite, the U–Th/He ages of apatite record cooling through lower temperatures[8]. As Ne is expected to have diffusion characteristics intermediate between He and Xe, U, Th–^{21}Ne in conjunction with U, Th–^{136}Xe and U, Th–^{4}He systematics can place valuable constraints on thermal histories. For example, an event that may not reset Xe in the sample may be able to reset both the Ne and He systematics. However, a subsequent lower temperature event may be able to further reset only the He systematics, in which case the imprint of the previous event will be only recorded by the U, Th–^{21}Ne geological clocks. To investigate its potential as a geological clock, we apply the U, Th–^{21}Ne dating method to apatite from the Hogenakal carbonatite.

Geological setting

The Hogenakal carbonatites (about ten bodies) occur about 45 km west of Dharmapuri on the banks of the river Cauvery close to Uttamalai village in Tamil Nadu, South India[9,10]. The Hogenakal carbonatites occur as veins and lenses in pyroxenite dykes that intruded 2550-Ma-old charnockite gneisses along NNE to NE trending fractures[11,12]. The mineral composition of the carbonatites varies from sovite with > 95% calcite and rare phlogopite and apatite grains to silicosovite with about 60% calcite and varying modal abundances of apatite, pyroxene and phlogopite. Sm–Nd isotope data suggest an emplacement age of 2400 Ma, while many other carbonatites in the province are 770 Ma old.

Experimental procedure

About ~ 175 mg of apatite has been separated under optical microscope from the carbonatitic complex of Hogenakal. Coarse (length ≈ 0.25 cm, diameter ≈ 0.15 cm) and cylindrical grains were selected for the study because they retain gases much more than the rounded ones[13]. In fact, retentivity of He in cylindrical apatites of radius ~ 250 μm can be ~ 95%. Therefore, for the present study, the size and shape of the grains are such that corrections for a-stopping distances as well as Ne loss from the samples after being reset due to diffusion loss are not necessary.

The apatite separates were subsequently cleaned ultrasonically with distilled water and ethanol for the removal of surficial contaminants. Then they were completely dried by infrared lamps before packing them in gold foil for loading into the extraction system of the mass spectrometer. In order to release the gases completely, the apatites were heated up to their melting temperature of ~1800°C. In an attempt to separate the different components of noble gases, the gases were extracted by stepwise heating. Initially the sample was combusted (in 2 torr of O_2) at 400°C in an attempt to release all surface-sited gases of atmospheric origin or from organic contaminants and then pyrolysed at temperature steps of 600, 950, 1200, 1400, 1600 and 1800°C. The gases extracted were purified and separated into He, Ne, and Ar, Kr, Xe fractions by differential adsorption on charcoal, before being introduced into the mass spectrometer (VG1200) for analyses following the procedures described elsewhere[14]. Blanks for all temperature steps were done and used for corrections. Isotopic compositions of the blanks were roughly atmospheric within experimental uncertainties. Besides blanks, corrections for isobaric interference and mass discrimination were also done. The noble gases have been analysed by a VG1200 micromass at Physical Research Laboratory, Ahmedabad using the standard procedures of extraction, purification and separation. U and Th have been measured on the same aliquot of apatite that has been analysed for noble gases by ICPMS at the National Geophysical Research Institute, Hyderabad[15]. Errors in U, Th determinations are ± 2%.

Results and discussion

Release pattern of noble gases by pyrolysis

Stepwise pyrolysis of the apatites indicates that most of the ^{4}He (~93%), which is assumed to be radiogenic in such U, Th-rich minerals, is released at lower temperature (600–950°C). The ^{21}Ne/^{20}Ne and ^{22}Ne/^{20}Ne ratios suggest that the nucleogenic Ne is mostly released at a higher temperature of 1200–1400°C. Apatites from spinel–lherzolite xenoliths of Australia show that the nucleogenic/spallogenic Ne is released at high temperature (1450–1600°C)[16]. Almost all Kr and Xe are of fissiogenic origin and are released during the melting of apatites. Differences in the release pattern of different *in situ* noble gases in the apatites reflect the different diffusion rates for each gas species in apatite. Thus the concentration of different isotopes in apatite would be variably modified at different times depending on thermal temperature imprint subsequent to crystallization. Figure 2 is the Ne three-isotope plot for the apatites from Hogenakal as observed during pyrolysis. Since the normalizing isotope (^{20}Ne) is purely of trapped origin, any increase in ^{21}Ne/^{20}Ne

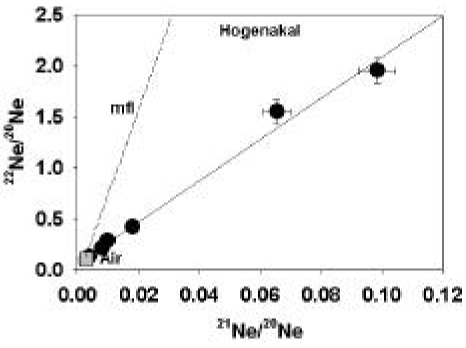

Figure 2. Ne three-isotope plot for apatite from Hogenakal. Clear excesses of ^{21}Ne and ^{22}Ne are seen in all the temperature steps. As the slope of the mass fractionation line (mfl) indicates, these excesses are not due to mass fractionation.

and ^{22}Ne/^{20}Ne over the trapped values has to be either due to mass fractionation or the presence of nucleogenic Ne. The Ne data for apatite show higher than trapped values and also they plot far away from the mass fractionation trend, indicating that the shifts are not due to fractionation and can be attributed to the presence of nucleogenic Ne in them.

Calculation of nucleogenic Ne

The Ne present in the apatites should be a mixture of trapped and *in situ* components and it is necessary to decouple the two. The trapped gases are mostly present in the fluid inclusions because of their incompatible nature, while the *in situ* gases are hosted in the lattice structure.

From two-component mixing between trapped and nucleogenic gases, one can obtain the nucleogenic ^{21}Ne ($^{21}\mathrm{Ne}_\mathrm{n}$) from the equation

$$^{21}\mathrm{Ne}_\mathrm{n} = {}^{20}\mathrm{Ne}_\mathrm{m}[(^{21}\mathrm{Ne}/^{20}\mathrm{Ne})_\mathrm{m} - (^{21}\mathrm{Ne}/^{20}\mathrm{Ne})_\mathrm{t}], \qquad (1)$$

where m, t and n stand for measured, trapped and nucleogenic respectively. The trapped component may be from air (A), upper or lower mantle (UM or LM). Table 1 gives the concentration of *in situ* ^{21}Ne actually present and determined as above.

U, Th–^{21}Ne as dating tool

The retention of Ne in apatites will be recorded by the U, Th–^{21}Ne clock that will correspond to the timing of the event that has reset this systematics after crystallization. The equations that relate the accumulation of *in situ* Ne to the relevant age of their retention are discussed below.

Since the production of α-particles inducing the nuclear reaction $^{18}\mathrm{O}(\alpha, \mathrm{n})^{21}\mathrm{Ne}$ depends on the age of the samples and U, Th concentration in the mineral, the ^{21}Ne($^{21}\mathrm{Ne}_\mathrm{n}$) so produced will also depend on the age of the samples along with target element O and U, Th concentrations of the mineral. Since the cross-sections for the reaction $^{24}\mathrm{Mg}(\mathrm{n}, \alpha)^{21}\mathrm{Ne}$ is low (~<1–200 millibarns), and Mg concentration measured in these apatites is also small (0.04%), production of $^{21}\mathrm{Ne}_\mathrm{n}$ via this reaction can be considered to be negligible. On the other hand, in fluorapatite the abundance of the target element O is ~38% and the cross-section for the reaction $^{18}\mathrm{O}(\alpha, \mathrm{n})^{21}\mathrm{Ne}$ is much higher (~300–650 millibarns), and for all practical purposes produces almost all the ^{21}Ne in the samples. From the decay systematics of ^{238}U, ^{235}U and ^{232}Th, we can estimate the expected α-particle fluence ($\sum\alpha$) over the crystallization age of the sample (2400 Ma) as,

$$\sum\alpha = \mathrm{U}[7.942(e^{\lambda 238t}-1) + 0.0504(e^{\lambda 235t}-1) + 6\{(\mathrm{Th/U}) \times (e^{\lambda 232t}-1)\}]. \qquad (2)$$

The production rate of $^{21}\mathrm{Ne}_\mathrm{n}$ has been estimated for U, Th-rich minerals and given as[17]

$$^{21}\mathrm{Ne}_\mathrm{n} = \{W(\mathrm{O})\sum\alpha\} \times [A + B(\mathrm{Th/U})]/[21.29 + \{4.87(\mathrm{Th/U})\}] \times 0.2534, \qquad (3)$$

where $^{21}\mathrm{Ne}_\mathrm{n}$ is expressed in 10^{-10} cm^3 STP/g, U in ppm and W(O) is the weight fraction of oxygen. A and B are coefficients used for calculating nucleogenic production rates in monazite, zircon and apatite. For apatites, A and B are 5.62 and 1.91 respectively, and $W(\mathrm{O}) = 0.38$. Substituting these values, we can express eq. (3) as

$$^{21}\mathrm{Ne}_\mathrm{n} = 0.0963 \times \sum\alpha \times [5.62 + 1.91(\mathrm{Th/U})]/[21.29 + \{4.87(\mathrm{Th/U})\}]. \qquad (4)$$

From the above equations we obtain $\sum\alpha = 232.5 \times 10^{-4}$ cm^3 STP/g, the $^{21}\mathrm{Ne}_\mathrm{n}$-expected ($^{21}\mathrm{Ne}_\mathrm{e}) = 8.2 \times 10^{-10}$ cm^3 STP/g for the apatites since their formation, using measured U (25.4 ppm) and Th (189 ppm) concentration in the samples and their crystallization age. In Hogenakal apatite, the retention of nucleogenic ^{21}Ne ($^{21}\mathrm{Ne}_\mathrm{n}/^{21}\mathrm{Ne}_\mathrm{e}$) is observed to be 33%. It is interesting to note that the retentivity of $^{21}\mathrm{Ne}_\mathrm{n}$ in the sample is intermediate between the retentivities of ^{4}He (8.5%) and ^{136}Xe (52.5%), implying an intermediate diffusional character. This implies a closure temperature also between that of ^{4}He and ^{136}Xe. Thus, constraining its closure temperature in apatite in future should yield information about the thermal history of the terrain.

U, Th–^{21}Ne age (timing of disturbance) of Hogenakal apatite

The U, Th–^{21}Ne age obtained (using eq. (4)) from the present study for the Hogenakal apatite is 845 ± 127 Ga. This age within errors corresponds to the age of emplacement of the younger adjacent carbonatites, syenites and alkali granites (~770 Ma)[2] and is coeval with rifting and alkaline magmatism events within other continental blocks related to the break-up of Rodinia[18]. We believe that the U, Th–^{21}Ne

Table 1. Excess concentration of ^{21}Ne ($^{21}\mathrm{Ne}_\mathrm{n}$) in Hogenakal apatite calculated considering air (A), lower mantle (LM) or upper mantle (UM) to be the trapped components (where excess ≈ *in situ*) and the measured ^{20}Ne, ^{21}Ne/^{20}Ne and ^{22}Ne/^{20}Ne values. The expected $^{21}\mathrm{Ne}_\mathrm{n}$ ($^{21}\mathrm{Ne}_\mathrm{e}$) considering no loss of gas since formation and the resulting retentivity of ^{21}Ne ($^{21}\mathrm{Ne}_\mathrm{n}/^{21}\mathrm{Ne}_\mathrm{e}$) in the Hogenakal apatite are also given. Concentrations of noble gases are in cm^3 STP/g with errors of ± 10%. Age is taken from Kumar *et al.*[2]

					$^{21}\mathrm{Ne}_\mathrm{n}$ (10^{-10})				
	Age (Ma)	^{20}Ne (10^{-10})	^{21}Ne/^{20}Ne	^{22}Ne/^{20}Ne	A	LM	UM	$^{21}\mathrm{Ne}_\mathrm{e}$ (10^{-10})	Retentivity (%)
H–A	2400	412.2	0.0096 ± 0.0001	0.2469 ± 0.0021	2.7	2.6	2.0	8.2	33

age so obtained from this study corresponds to the disturbance associated with this major event. Overprinting of ~700–800 Ma thermal event is demonstrated by the Ar age spectrum of single plagioclase grains from dolerite dykes in the same Dharmapuri region[19].

It is to be noted that the younger local rejuvenation event (~ 0.5 ± 0.1 Ga) reported from Peninsular India, associated with various shear zones from the northeastern part of Eastern Ghats Belt collision[20], does not leave its imprint on the Hogenakal carbonatites. In fact, between 2.4 Ga and the time of emplacement of the Neoproterozoic carbonatite complexes, apart from the 1900–2100 Ma low temperature event recorded by micas from the Hogenakal carbonatite[2], no significant metamorphic or igneous event is reported in this region. The Hogenakal carbonatites appear to be undeformed with well-preserved magmatic textures, unlike the other neighbouring carbonatites like Sevattur and Samalpatti that show distinct effects of tectonic stresses[21]. It would be interesting to check in these younger carbonatites if U, Th–^{21}Ne ages correspond to any event that might be related to the stress effects observed in these rocks.

The large errors involved in the measurements are because of the errors associated with mainly the noble gas concentrations and could be improved by isotope dilution technique in future. Also, the error accommodates the difference in ages that would be obtained by assuming different trapped components, namely air or the mantle. It is more likely that samples have a mixture of both air and mantle as trapped components.

This is an attempt to check the feasibility of U, Th–^{21}Ne as a dating tool and it should be noted that it records events that may otherwise go undetected, and hence may be applied in U, Th-rich minerals (like monazites and zircons) from other terrains as well.

Conclusion

The present work demonstrates the feasibility of using U, Th–^{21}Ne as a dating tool in U, Th-rich samples like apatite. In conjunction with the already existing dating tools like U, Th–^{4}He and U–^{136}Xe, valuable information regarding the thermal history of the geological terrain may be obtained. Also, it is possible that an event unrecorded by U, Th–^{4}He systematics (since it might be subsequently reset by a lower temperature event) and which only partially (or does not) reset the U–^{136}Xe dating tool, is recorded by the U, Th–^{21}Ne clock that is reset completely. For Hogenakal apatite, the U, Th–^{21}Ne age of 845 ± 127 corresponds to the Neoproterozoic disturbances associated with the break-up of Rodinia.

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