Record of Cycling Operation of the Natural Nuclear Reactor in the Oklo/Okelobondo Area in Gabon

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Using selective laser extraction technique combined with sensitive ion-counting mass spectrometry, we have analyzed the isotopic structure of fission noble gases in U-free La-Ce-Sr-Ca aluminous hydroxy phosphate associated with the 2 billion yr old Oklo natural nuclear reactor. In addition to elevated abundances of fission-produced Zr, Ce, and Sr, we discovered high (up to 0.03 cm^3 STP/g) concentrations of fission Xe and Kr, the largest ever observed in any natural material. The specific isotopic structure of xenon in this mineral defines a cycling operation for the reactor with 30-min active pulses separated by 2.5 h dormant periods. Thus, nature not only created conditions for self-sustained nuclear chain reactions, but also provided clues on how to retain nuclear wastes, including fission Xe and Kr, and prevent uncontrolled runaway chain reaction.

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A natural nuclear chain reaction was predicted by Kuroda [1] 20 years before the remnants of the natural reactor were actually discovered [2–4]. So far, 16 individual reactor zones have been found in the Oklo/Okelobondo area in Gabon. Aside from being a fascinating natural phenomenon, the occurrence of self-sustaining natural nuclear reactors has several important implications, ranging from the verification of variability of the long-term fundamental physical constants [5,6] to storage of nuclear wastes in geological environments [7]. Many elements extracted from the reactor material still carry clear isotopic signatures of ^{235}U and ^{239}Pu fission and neutron capture reactions. Isotopic compositions of these elements allowed for reconstruction of the effective neutron fluence (up to 10^{21} n/cm^2), the amount ^{235}U consumed (>5 tons), the energy released (~15 GW yr). Also, using fission products of 24 000 yr ^{239}Pu, an estimate was made of the effective duration of this nuclear fission chain reaction (150 000 yr). The average power, therefore, was only about 100 kW, equivalent to a small research reactor. The fact that natural reactors did not explode and dissipate themselves right after they went critical was evidently due to some self-regulation mechanism providing a negative feedback. It is not clear, however, whether the reactor was operated continuously or in pulses. This would depend on the mechanism of self-regulation, and/or the time constant for the negative feedback which prevented a runaway chain reaction. One proposed mechanism was related to the burning up of highly neutron absorbing impurities, such as rare earth isotopes or boron, both of which have been detected in Oklo [8]. As the strong absorbers were burned up at one edge of the active reactor zone and uranium was burned at the other, the active zone perhaps shifted along the U vein, like a flame over a wet log. Therefore, different parts of the natural reactor could have operated at different times [8]. Another potential self-regulation mechanism could have involved water, which acts as a neutron moderator [9]. As the temperature of the reactor increased, all unbounded water was converted into steam. This would reduce the neutron thermalization and shut down the chain reaction. The chain reaction could resume only when the reactor cooled down and the water concentration increased again. But until recently, there was no strong evidence in favor of any of these mechanisms. Amazingly, isotopically anomalous xenon we found in Oklo Al phosphate carries the fingerprint of a specific cycling operation with a time scale, which suggests that the self-regulation must indeed involve water.

The material from the natural nuclear reactor was acquired from a Pixie drill with a double swindler in drill hole S2 in the SD.37 gallery on the east face of reactor zone 13. It consisted mainly of massive lustrous uranium oxide grains with numerous 0.1–0.5 mm-sized La-Ce-Sr-Ca aluminous hydroxyl phosphate inclusions [10]. A polished slice (3 × 4 mm, ~1 mm thick) was prepared from this sample and placed into vacuum extraction cell where heavy noble gases were extracted using a slightly defocused beam from acoustically Q-switched Nd-YAG laser (this extraction technique described in details in [11,12]). A typical diameter of the extraction crater was about 25 mm—far smaller than the investigated mineral grains—ensuring mineral specific analysis. All stable Xe and Kr isotopes (except ^{78}Kr) from 28 individual extraction spots on U-bearing minerals and 13 spots on Al phosphates have been analyzed using a high transmission ion-counting mass spectrometer [13]. In all experiments, the amount of extracted gases was sufficient for precise measurement of their isotopic compositions. Various U oxides contained from 10^{-5} to 10^{-3} cm^3 STP/g of ^{136}Xe (Fig. 1), while U-free alumophosphates had even more fission Xe, up to 0.03 cm^3 STP/g, the highest Xe concentration ever found in natural material. Evidently, fission Xe migrated from the U-bearing phase,

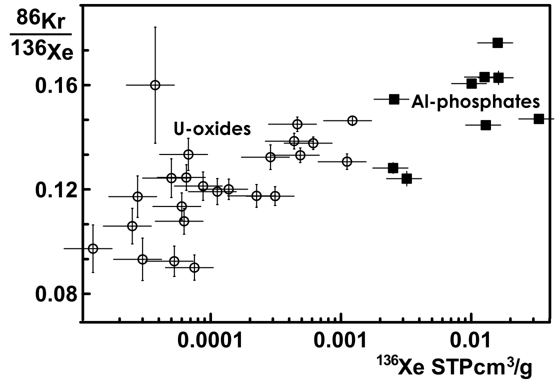

FIG. 1. Fission ^{136}Xe and ^{86}Kr in U oxides (open circles) and Al phosphates (solid squares) after minor correction to account for atmospheric contamination using ^{128}Xe and ^{82}Kr. Xe concentrations were calculated from measured amounts of ^{136}Xe and the amount of degassed material which was estimated from the specific density and geometry of the extraction crater. Fission ^{136}Xe concentration and ^{86}Kr/^{136}Xe ratios in U-rich phases tend to be lower, suggesting a migration of fission products to Al phosphate.

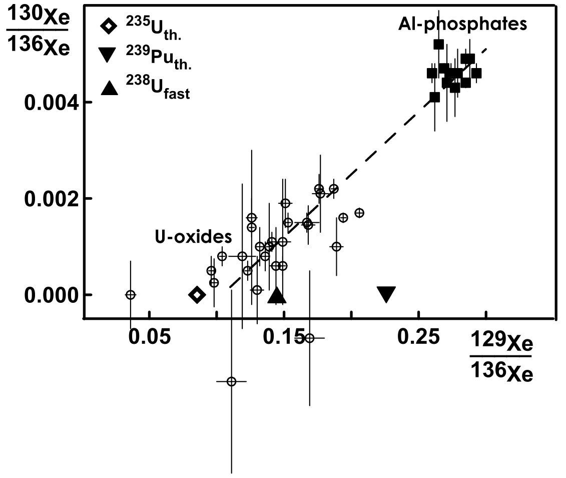

FIG. 2. Excess ^{130}Xe (fission shielded) provides a mean for an estimation of neutron fluence from the slope of the dashed line. Data corrected to account for atmospheric contamination. Negative ^{130}Xe/^{136}Xe values are due to slight overcorrections.

where it has been produced, to the adjacent Al phosphate. ^{86}Kr/^{136}Xe ratios tend to be lower in minerals, which have less fission gases (Fig. 1), providing further evidence for losses of fission products from U oxides. Less than 1% of all fission Xe (as calculated from ^{235}U burnout) is retained in the U-rich phase, with a great fraction of lost Xe apparently recaptured by Al phosphates. It was found earlier that Oklo Al phosphate is enriched in fission Zr, Ce, and Sr, while adjacent uraninite is depleted in those elements [10]. This unique ability of Al phosphate to capture fission products may be useful in man-made reactors and long-term nuclear waste storage.

The second interesting finding in Al phosphate was ^{130}Xe excess (Fig. 2). This isotope is not produced by fission since it is shielded by stable ^{130}Te in the fission chain. ^{130}Xe is a likely product of the reaction $^{129}\mathrm{I}(n, \gamma)\,^{130}\mathrm{I} \rightarrow {}^{130}\mathrm{Xe}$, previously observed only in Oklo uraninites from Zones 2 and 3 [14,15]. The enhancement of ^{130}Xe in Al phosphates is much higher than in U-rich phases (Fig. 2), suggesting that ^{129}I has been displaced from its parent uraninite into adjacent U-free Al phosphate during exposure to the thermal neutrons. The shift in ^{130}Xe/^{129}Xe ratio allows us to estimate the effective neutron fluence of 1.7×10^{21} n/cm^2—more than was previously determined in the same reactor zone (1.0×10^{21} n/cm^2 and 0.78×10^{21} n/cm^2) [16,17], suggesting a possibility that Al phosphate may attract fission ^{129}I.

The most remarkable Xe anomalies were observed in the heavy isotopes (Fig. 3). Xenon in U phase is a relatively normal mixture of fission products of ^{235}U and ^{239}Pu (by thermal neutrons) and ^{238}U (by fast neutrons). Spontaneous fission of ^{238}U, dominant in common rocks, is negligible in Oklo samples. However, Al phosphate once again carries the most extreme anomalies, which are impossible to explain in terms of the mixing of known fissile nuclei and n-capture reactions. The apparent feature of Xe in Al phosphate seems to be a deficit of ^{136}Xe, the end product of the shortest fission chain. The only β-active precursor of ^{136}Xe is 86 s ^{136}I; so, after the onset of the fission chain reaction, ^{136}Xe appears first and hence has more chance of being lost before the other Xe isotopes start to accumulate. This, in itself, suggests a cycling operation of the natural reactor. As the temperature rises during a pulse, diffusion of volatile Xe in Al phosphate accelerates. During dormant periods, the temperature returns to normal, slowing down the diffusion. However, a sole deficit of ^{136}Xe cannot explain experimentally observed Xe isotopic anomalies in Al phosphate (dotted lines, Fig. 3). Evidently, a more complex process was responsible for the transformation of the relatively normal fission Xe in U-rich phase into the anomalous Xe observed in Al phosphate. Such processes must generate isotopes in the following proportions: $^{131}\mathrm{Xe}/^{134}\mathrm{Xe} = 3.4$, $^{132}\mathrm{Xe}/^{134}\mathrm{Xe} = 7.0$, and $^{129}\mathrm{Xe}/^{134}\mathrm{Xe} = 0.95$ (slopes of solid lines, Fig. 3).

Tellurium is known to be the most retentive fission product in Oklo reactors [18]. Measured yields of fission Te isotopes precisely match the fission product yield curve [19]. This implies that Te β-active precursors, such as 2.8 m ^{132m}Sb, 23 m ^{131}Sb, 4.4 h ^{129}Sb, 2.4 m ^{129}Sn, 6.9 m ^{129m}Sn, also retained well in the reactor material. We assume that fission isotopes of iodine, including the long-lived ^{129}I, were retentive as well, otherwise we would not find the excess of ^{130}Xe produced by ^{129}I neutron capture. In addition, numerous observations of ^{129}I and ^{129}Xe in meteorites clearly demonstrate that iodine is much more retentive than xenon (e.g., [20]). Therefore, during a reactor pulse, the radioactive fission tellurium and iodine migrate from U oxide into Al phos-

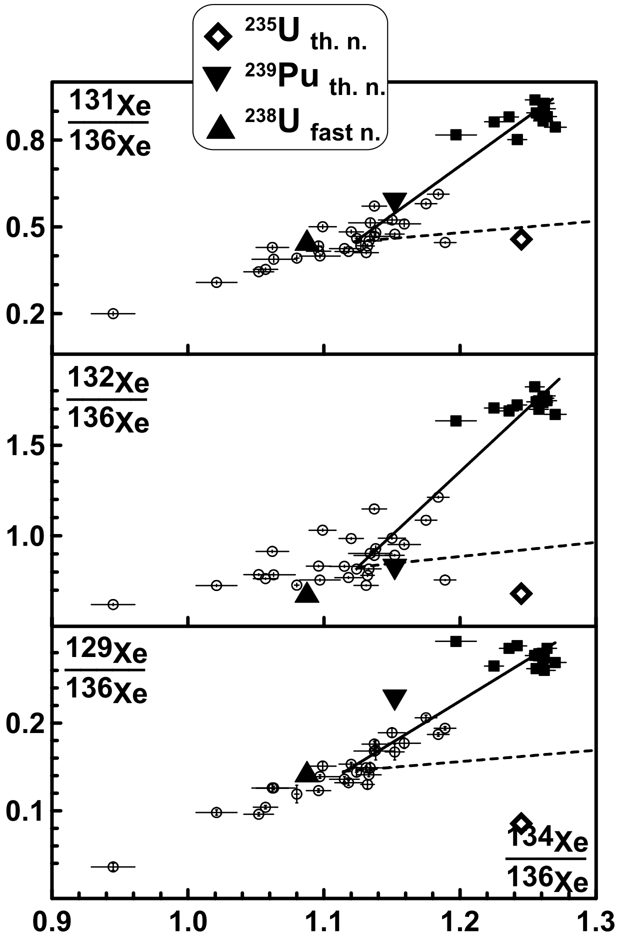

FIG. 3. Xe isotopic composition in U oxides and Al phosphates are related by a process that shifted points along the solid lines. Dotted lines illustrate a sole deficit of ^{136}Xe, which cannot explain the Xe anomalies in Al phosphate. Migration of all isotopes in each isobaric chain must be considered. Also shown are Xe components produced by the three potential progenitors (^{235}U$_{\rm th}$, ^{239}Pu$_{\rm th}$, ^{238}U$_{\rm fn}$).

phate, where they subsequently decay to Xe. The latter, however, is volatile and is retained in Al phosphate only when the reactor cools down between operational pulses. There is only one apparent problem: why is not the Xe produced in the first pulse given off at the next one? This problem can be resolved considering the conditions at which Al phosphate has been formed. The high concentration of short-lived intermediate fission products in Al phosphate without significant quantities of uranium implies that it precipitated during the operation of the Oklo reactor. Hydrothermal experiments demonstrate that Al phosphate grows fast at relatively low temperatures (270–300 °C) [21]. After being captured by growing Al phosphate, fission products decay into Xe which remains imprisoned in Al phosphate because of its framework crystalline structure [22] (similar to the cagelike structure of zeolite). Then Xe can be released from the alumophosphate only after destroying its crystalline structure, which requires temperatures higher than those during the operational pulse of the Oklo reactor.

To calculate the evolution of isotope ratios of accumulating Xe precursors during and after the active pulses of the fission chain reaction, we considered only those fission fragments which have a fission yield greater than 0.1% and/or a half-life shorter than 1 min. We also assumed that the three major fissile nuclei in the Oklo reactor—^{235}U$_{\rm th}$, ^{239}Pu$_{\rm th}$ (thermal neutron fission) and ^{238}U$_{\rm fn}$ (fast neutron fission)—have relative contributions of 75%, 7%, and 18%, accordingly. These numbers were determined [16] using Ru, Pd, Nd, Sm, and Gd isotopic compositions measured in the same reactor zone where our sample came from. Then, using known individual and cumulative fission yields [23] for ^{235}U$_{\rm th}$, ^{239}Pu$_{\rm th}$, and ^{238}U$_{\rm fn}$, we calculated independent and cumulative yields for each fission fragment relevant to Xe production in our reactor zone. Finally, cumulative accumulation of Sn, Sb, Te, and I in each isobaric chain was computed and plotted in the form of isotope ratios on Fig. 4.

Evidently, the calculated isotopic ratios are changing with time, and the final Xe composition will depend on how long the operational pulses last (*d*) and when the Al phosphate cools down enough to retain Xe (*p*). We tried to vary these two free parameters *d* and *p* until all three measured Xe ratios (determined from Fig. 3 and shown as gray horizontal lines on Fig. 4) matched the calculated isotope ratios. This turned out to be impossible. However, if we considered only two ratios $\langle 131\rangle/\langle 134\rangle$ and $\langle 132\rangle/\langle 134\rangle$, there is one single solution $d = 30$ m and $p = 2.5$ h. And there is no solution for $\langle 129\rangle/\langle 134\rangle$ combined with either one of the two others. To match all three ratios the value of ^{129}Xe/^{134}Xe needs to be adjusted from the measured 0.95 to about 1.5 (light gray line on Fig. 4). This can be done assuming that 37% of ^{129}I has been lost by Al phosphate subsequent to the termination of the reactor 2 Ga ago, which is not unreasonable. ^{129}I has a 16×10^6 yr half-life, several orders of magnitude longer than all other Xe precursors, is chemically active, forms water soluble compounds and, therefore, has a chance of being partially leaked out from Al phosphate in the aqueous environment of the reactor. Indeed, there is clear evidence for ^{129}I migration from uranium deposits [24].

Interestingly enough, the 30 min pulses of natural nuclear reactor activity and 2.5 h dormant periods recorded in the Oklo Al phosphate resemble a typical geyser operation. Similar time scales suggest similar processes. This similarity suggests that 0.5 h after the onset of the chain reaction, unbounded water was converted to steam, decreasing the thermal neutron flux and making the reactor subcritical. It took at least 2.5 h for the reactor to cool down until fission Xe began to retain. Then the water returned to the reactor zone, providing neutron moderation and once again establishing a self-sustaining chain.

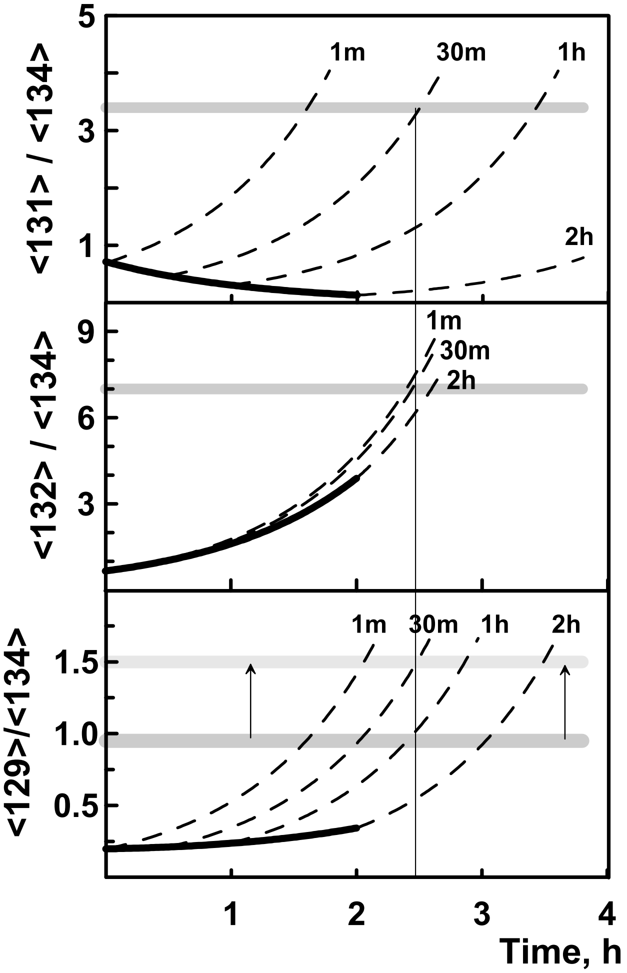

FIG. 4. The calculated evolution of isotopic composition of intermediate fission products Sb, Te, and I, which hold up the production of stable Xe isotopes. Bold black lines correspond to the active period of the reactor, with the numbers indicating the duration of that period. Dashed lines illustrate free decay of Xe precursors. The gray horizontal lines show the compositions required to make Xe in Al phosphate from Xe in U oxides (as inferred by the slope of the solid lines observed in Fig. 3). The light gray line represents adjusted $\langle 129\rangle/\langle 134\rangle$ ratio assuming 37% losses of ^{129}I.

It is fascinating that Xe in Al phosphate measured today provides us with such pristine timing records for a natural reactor operated 2 billion yr ago.

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