calculations at pressures >70 GPa, the density of the *Pnc2* structure becomes greater than that of stishovite; at 100 GPa and 300 K the difference amounts to 0.9% and increases with pressure up to 1.8% at 150 GPa. The *Pnc2* structure becomes more stable than the CaCl_2 -like structure at pressures above 93 GPa and 300 K which agrees well with the FPLMTO (full potential linear muffin-tin orbital; see Fig. 3 legend) result where the transition pressure at 0 K is 80 GPa (as discussed below). We find the following sequence of phase transitions; stishovite $\rightarrow \text{CaCl}_2 \rightarrow \text{Pnc2}$ structure $\rightarrow \text{Pa3}$. The first transition takes place at 45 GPa, the second at 80 GPa and the third at 220 GPa. The transition at 45 GPa is in agreement with the calculation by Kingma *et al.*¹⁰. We have found that the *Pa3* structure is stable at pressures above 220 GPa whereas Cohen²⁰ found the *Pa3* structure to be stable already at 157 GPa because he did not consider the new crystal phase. The transition pressure to the *Pnc2* structure, derived from the present zero-temperature calculations (80 GPa), is somewhat lower than that obtained from the room-temperature lattice dynamics¹⁴ (93 GPa) and molecular dynamics¹⁵ (120 GPa) simulations but higher than the experimental result. A possible reason for this small discrepancy between the predictions of theory might be (1) the difference in theoretical methods and/or (2) the influence of the vibrational energy which is not considered in the first-principles calculations. We thus conclude, based on first-principles calculations, that a *Pnc2* structure must be viewed as a strong candidate for explaining the experimentally observed X-ray results of this study. In Table 2 we present theoretically optimized structural parameters for the *Pnc2* structure at two different volumes.

Because the only experimental data we have available so far is for quenched samples at high pressures, we do not know how the density of SiO_2 would increase (owing to its phase transition) along the geothermal gradient in the mantle. However, the demonstrated reversibility of the phase transition shows clearly that the *Pnc2* phase is the densest phase; on release of pressure the *Pnc2* structure reverses to stishovite (or CaCl_2 -type silica). The only constraints we have on the chemical composition of the lower mantle are from the seismic density data. To reproduce this density profile mineralogically, any combination of silicates and oxides may be chosen. It is therefore important that we know the structure and physical properties of any phase which could be a candidate for the mantle. Through this study, we have established that silica with the *Pnc2* structure is such a phase. □

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The age of the Popigai impact event and its relation to events at the Eocene/Oligocene boundary

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Ages ranging from the Late Cretaceous (~65 Myr) to the Oligocene (~29 Myr) have been reported for the 100-km-diameter Popigai impact structure^{1,2} on the Anabar shield, central Siberia. These ages^{3–8} overlap the timing of several possible impact-related features, including the Cretaceous/Tertiary and Eocene/Oligocene stratigraphic boundaries, the North American tektites⁹, and the recently reported occurrences of an iridium anomaly and shocked quartz in Late Eocene deposits in northern Italy¹⁰. Here we report age determinations of several Popigai impact melt rocks using the ⁴⁰Ar–³⁹Ar step heating technique to constrain the age of the impact event. Our results are consistent with a Late Eocene impact age of 35.7 ± 0.2 Myr (2σ)—coincident in time with the impact deposits found in Italy. As this age is also similar to that of the North American tektites, which have been associated with the Chesapeake Bay impact structure in the eastern United States^{11–13}, there seem to have been at least two large and essentially contemporaneous impacts during the Late Eocene.

The target rocks at the Popigai structure (111°E, 71°30'N) are Precambrian, generally granitic, gneisses overlain by ~1.25 km of sandstones and carbonates, ranging in age from Proterozoic to Cretaceous^{1,2}. The impact-related lithologies are capped by several metres of Pliocene and Quaternary alluvial and glacial deposits. In addition to voluminous allochthonous breccias, Popigai contains ~2,000 km³ of impact melt rocks, including glass-bearing suevite breccias, and so-called tagamites, the latter occurring as irregular melt bodies and coherent sheets, up to several hundred metres thick¹.

The stratigraphic age of Popigai is between the end of the Cretaceous (~65 Myr) and the beginning of the Pliocene (~5 Myr). Dating impact events using isotopic methods is often not straightforward^{14,15} and previous attempts to date the Popigai impact have given age estimates that range from Late Cretaceous to Oligocene. Earlier whole-rock K–Ar age estimates include: 40–45 Myr (mean 42.5 Myr; ref. 3) for four tagamites and 29–46 Myr (mean 38.7 Myr; ref. 4) for five tagamites and one glass fragment

from a suevite breccia. Fission track analyses of six glass fragments from suevite breccia yielded 32.4–44.0 Myr (mean 38.9 Myr; ref. 1). An additional fission track analysis gave 30.5 ± 1.2 Myr (ref. 5). Deino *et al.*⁶ reported five total fusion ^{40}Ar – ^{39}Ar ages ranging from 52.2 to 65.9 Myr on glass from suevite breccia, and plateau ages of 65.5 ± 5 Myr and 65.4 ± 0.3 Myr, that is, a Cretaceous/Tertiary (K/T) age. Most recently, Deino *et al.*⁷ failed to reproduce a K/T age from additional samples. They obtained a highly discordant ^{40}Ar – ^{39}Ar spectrum from a fused gneiss fragment and an integrated age of 37.7 ± 0.3 Myr from four impact melt glasses, which they considered to be a maximum for the Popigai impact event. An age for Popigai of 39 ± 9 Myr, consistent with both the whole rock K–Ar and most of the fission track ages, has been generally quoted⁸.

We have undertaken a stepwise heating ^{40}Ar – ^{39}Ar analyses of six tagamite samples from Popigai in an attempt to resolve the uncertainty in age and the possible relationship to various events in the stratigraphic record. Our previous experience with ^{40}Ar – ^{39}Ar has shown that analyses from a suite of well re-equilibrated impact melt rocks gives the least ambiguous estimate of the true age of impact¹⁵. The tagamite (impact melt rock) samples analysed here range from glassy (P72, P22), through cryptocrystalline (sub-microscopic crystals; P1, P84), hypocrySTALLINE (crystals in a glassy ground-mass; P21) to holocrystalline (all crystals; P9). Paralleling the increasing matrix crystallinity, there is a reduction in clasts from

~20% to <10%. The clasts are dominantly quartz and feldspar and, in the relatively coarser-grained varieties, have indications of partial melting and reaction with the matrix, with the development of so-called chequerboard feldspar and orthopyroxene-high silica glass coronas around quartz^{16,17}. Where identifiable, the matrix mineralogy is hypersthene (40–60% ferrosilite molecule) and labradorite (55–65% anorthite molecule) laths in a ground-mass of glass or an intergrowth of quartz and potassium feldspar. The major-element chemistry of the samples is similar to previous analyses of Popigai tagamites². Trace-element data indicate variable, but elevated, siderophile abundances compared to the Archaean target rock gneisses. Iridium and nickel abundances in the samples analysed here range from 0.54 to 1.7 p.p.b. and 77 to 112 p.p.m., respectively, and it has been suggested that Popigai was formed by the impact of an ordinary chondrite body¹⁸.

The ^{40}Ar – ^{39}Ar age spectra have a variety of shapes, which reflect the complex underlying argon systematics in the tagamites. We show the spectra from the least to the most disturbed. Replicate runs are denoted by the letters A and B following the sample identifier. The age spectra from holocrystalline sample P9 and hypocrySTALLINE sample P21 show the classic pattern of mild disturbance in the lower-temperature fractions, where argon loss from the less retentive sites lowers the age of the early fractions. As gas is released from the more retentive sites at higher temperatures, the ages stabilize around a

Figure 1 ^{40}Ar – ^{39}Ar incremental heating spectra for holocrystalline (P9; **a**) and hypocrySTALLINE (P21; **b**) impact melt rocks from Popigai. The vertical width of each fraction represents the experimental error for that fraction at the 1σ level. The integrated or total gas ages for each run (corresponding to conventional K–Ar ages) are also indicated for each sample. The standard used for these determinations was hb3gr with an age of 1,071 Myr (refs 21, 22). Details of the experimental data are available; see Supplementary Information.

Figure 2 ^{40}Ar – ^{39}Ar incremental heating spectra for cryptocrystalline impact melt rocks from Popigai. **a**, P1; **b**, P84.

plateau that typically involves at least 80% of the gas released (Fig. 1a, b). Spectrum 21A has a plateau age of 35.7 ± 0.2 Myr (2σ), whereas spectra from 9A (plateau, 36.7 ± 0.2 Myr) and 9B (plateau, 36.3 ± 0.2 Myr) give a slightly older apparent age. The replicate tagamite chip in run 21B has lost a larger percentage of its argon in the lower fractions and displays a stepwise rise throughout most of its release, never reaching a true plateau.

The cryptocrystalline samples P1 and P84 display more structured spectra (Fig. 2a, b), where the individual fraction ages fluctuate around a common age but with more scatter than expected from the experimental errors (indicated by the vertical thickness of the box for each fraction on the figure). Whereas P1A shows a good plateau, with 84% of its release indicating an age of 36.9 ± 0.6 Myr, the spectra of the replicate, P1B, oscillates around this value. Both P84A and P84B oscillate around means of 35.6 ± 1.2 Myr and 37.5 ± 0.8 Myr, but with inter-fraction differences ranging up to 5 Myr.

Spectra from the glassy samples P72A and P72B (Fig. 3a) superficially resemble structured plateaux and are the result of two different phases releasing the bulk of their argon at different temperatures. The phase preferentially releasing its gas at lower temperatures is characterized by a low apparent Ca/K ratio (as indicated by the ratio of $^{37}\text{Ar}/^{39}\text{Ar}$). The higher-temperature phase, dominating the last 50% of the gas released, has a Ca/K ratio that is

30% higher. The integrated ages of 37.7 ± 0.6 and 35.8 ± 1.8 Myr are broadly concordant with the ages of the better-behaved tagamite samples, which give plateaux. This is consistent with sample P72 having undergone an internal redistribution of argon between mineral phases without loss, presumably due to ^{39}Ar recoil during neutron irradiation¹⁹. Spectra P22A and P22B (Fig. 3b) display broad U-shaped spectra, which are characteristic of contamination by clasts partially degassed by the event that reset the argon clock²⁰. In samples displaying this shape, the minimum in the trough of the U gives an upper limit to the age of the resetting event. The minimum age is 52 Myr for sample P22A and 42 Myr for P22B, indicating an upper limit for the impact event of 42 Myr.

As the formation of impact melt involves the melting of target rocks and the incorporation of clastic debris, argon ages can range from the age of impact up to the age of the target rock, depending on how well the argon clock was reset in the various components of the melt rock. This suite of tagamite samples displays such an array of argon behaviour, as evidenced by their varied spectral shapes. There is a correlation between the degree of structure in the spectra and the petrographic character of the tagamite samples. The best behaved argon spectra come from the rocks which show greater matrix crystallinity and degree of thermal equilibration of the relict mineral inclusions (for example, P9, P21). Non-plateau spectra come from the tagamites with a higher proportion of glass and unequilibrated inclusions. In a situation where we are dealing with contamination by older material and some modification of the argon clock—either by differential mineralogy or thermal resetting of lower-retentivity sites—we consider the best estimate of the age of impact is given by the sample which displays the best developed plateau and youngest age: sample P21A. Using the four fractions which make up the plateau portion of P21A, we find an age of impact of 35.7 ± 0.2 Myr (2σ). For comparison, the average of the plateau ages of the next best behaved samples, P9A and P9B, is 36.5 ± 0.4 Myr (2σ), which we believe reflects some relict argon contamination. This age (35.7 Myr) is broadly consistent with earlier reported Late Eocene age determinations, using conventional K/Ar and fission track dating, but the resolution and interpretative techniques possible with ^{40}Ar – ^{39}Ar dating allow an improved determination of the time of impact. In comparing age determinations of contemporaneous events, it should be noted that there is an uncertainty in the age of the standard (monitor) of the order of 1% (refs 21,22), and measures of laboratory precision do not always fully reflect the underlying geological complexity.

There is no evidence to support the involvement of Popigai in the K/T event (65 Myr). The difference in our determination of the age of Popigai (35.7 ± 0.2 Myr) and the Eocene/Oligocene boundary (33.7 ± 0.5 Myr)²³ would also preclude a role for Popigai. The Late Eocene stratigraphic record, however, contains at least two Ir anomalies¹⁰ and deposits marked by microspherules and microtektites^{9,24}, as well as shocked quartz and coesite^{25,26}. In the Eocene/Oligocene stratotype section at Massignano, Italy, a distinct Ir peak occurs at the lower calcareous nanofossil NP19/20 zone (mid-lower foraminiferal P16 zone, top of chron 16n2). Based on dating by various isotopic methods of volcanic ash in the same section, the age of this Ir anomaly is 35.7 ± 0.4 Myr (ref. 10). The Ir anomaly is associated with shocked quartz containing planar deformation features^{27,28}. Given the almost identical age for Popigai and that it has been suggested¹⁸ that it was caused by the impact of a chondritic projectile, the Popigai impact event would seem a logical source for both the Ir and the shocked quartz in the Late Eocene section in northern Italy.

There is a second, smaller Ir anomaly in the same section within magnetic chron 16r1, some 0.2 Myr earlier¹⁰. In addition, an Ir anomaly associated with microspherules and microtektites is known from Barbados and several Deep Sea Drilling Program cores in the Late Eocene²⁵. All, or some of these, are related to the North American tektite strewn field. Unfortunately, uncertain

Figure 3 ^{40}Ar – ^{39}Ar incremental heating spectra for glassy impact melt rocks from Popigai. **a**, P72; **b**, P22.

biostratigraphic correlations precludes a determination of whether they are strictly coeval¹⁰. ⁴⁰Ar–³⁹Ar plateau age determinations of tektite fragments in DSDP 612 give 35.5 ± 0.3 Myr (ref. 29), indistinguishable from 35.4 ± 0.6 Myr for tektites from Barbados³⁰. It is highly unlikely that Popigai is also the source of the North American tektites, as isotopic evidence, as well as geographical location, tends to exclude Popigai as a source³¹. The best candidate seems to be the recently discovered 85-km-diameter Chesapeake Bay impact structure¹¹ ($76^\circ 5' \text{ W}$, $37^\circ 15' \text{ N}$), which formed during the early part of the foraminiferal P15 zone and the calcareous nanofossil NP 19/20, that is, at 35.5–35.2 Myr (ref. 12). The Chesapeake Bay structure has the advantage of having much more suitable target rocks¹³ and location close to the occurrence of North American tektites.

Isotopic dating can not prove that the Ir and shocked quartz in the Massignano section are from Popigai or that the North American tektites are from Chesapeake Bay. This will require the discovery of appropriate geochemical and/or mineralogical markers from the source crater in the corresponding distal ejecta. It is clear, however, that two large impact events resulting in 100- and 85-km diameter structures occurred within, at most, a few hundred thousand years of each other in the Late Eocene. In terms of the terrestrial cratering rate, this represents an unusually small time between events; the expected³² repeat rate of impact structures of this size is of the order of ten million years. □

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Earliest known Old World monkey skull

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Similarities of the skull are commonly used to support hypotheses of ancestor–descendant relationships between fossil and living ape genera, especially between the late Miocene apes *Sivapithecus* and *Dryopithecus* from Eurasia and the living orang-utan (*Pongo*) from Borneo and Sumatra^{1–4}. Yet determining whether craniofacial traits shared by extant and Miocene apes are primitive or derived is severely hampered by the rarity of well-preserved fossil crania, particularly of early members of their closest outgroup, the Old World monkeys (Cercopithecoidea). The discovery of a complete and undistorted skull of *Victoriapithecus* at middle Miocene deposits from Maboko Island, Kenya, provides evidence of intact cranial-vault and basicranial morphology, brain size and craniofacial hafting for a primate from between 32 and 7 million years ago. *Victoriapithecus* represents a branch of Old World monkey that is intermediate between extant cercopithecids (Colobinae and Cercopithecinae) and the common ancestor they shared with apes (Hominoidea)^{5–8}. The skull preserves traits widely thought to be derived for extant and fossil members of a proposed *Sivapithecus/Pongo* clade, but which now appear to be primitive features of ancestral Old World higher primates in general.

Victoriapithecus cranium KNM-MB 29100 was found *in situ* during excavation of sediment at Maboko Island that has been radiometrically dated as older than 14.7 Myr (ref. 9), and biostratigraphically dated as younger than 16 Myr (ref. 10). The cranium has preserved left male canine and postcanine teeth on both sides (Fig. 1, Table 1). Anatomy of the teeth and skull show *Victoriapithecus* to be a catarrhine (Old World higher primate) of modern aspect, and more specifically an Old World monkey (Fig. 2). The absence of at least 30 derived dental features shared by the living Old World monkey subfamilies Colobinae and Cercopithecinae demonstrates that *Victoriapithecus* belongs to neither extant group, but represents the sister taxon (Victoriapithecidae) of modern Cercopithecidae^{5–8}.

The cranial vault of *Victoriapithecus* differs from those of all extant Old World monkeys in being narrower and lower relative to length (Table 1), a configuration found only in the early Pliocene African colobine *Libypithecus*¹¹. *Victoriapithecus* and *Libypithecus* also share unusually well-developed sagittal and nuchal crests. Relative to a body-weight estimate of 4.5 kg for large male postcrania¹², the cranial capacity of KNM-MB 29100 at 54 cm³ falls between regressions for extant anthropoids and strepsirrhines, and is significantly higher than that of the Oligocene archaic catarrhine *Aegyptopithecus*¹³ (Fig. 3). The relative brain size of *Victoriapithecus* is more similar to that of the red colobus than to any other living cercopithecoid¹⁴.

The craniofacial hafting and upper facial morphology of *Victoriapithecus* are unique among Old World monkeys, adding to the list of traits which demonstrate that victoriapithecids represent