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40Ar/39Ar Dates from the West Siberian Basin: Siberian Flood Basalt Province Doubled

Marc K. Reichow, *et al.*

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magma reservoir between 8.5 Ma and the cessation of volcanism at 7.5 Ma, or during ~0.4 million years of quiescence before emplacement and hydrothermal mineralization of the Alumbrera stock.

Sulfide MIs in amphibole phenocrysts of the intrusion emplaced immediately after Cu ore formation at Alumbrera have mean Au/Cu/Fe ratios similar to those of the earlier sulfide phases and are interpreted as the closest record of the magmatic state of the ore metals during hydrothermal fluid generation (*9*). Their greater variation in Cu content (Fig. 3, A and D) and inverse correlation between Cu and Au (Fig. 3E) may result from the separation of the sulfide melts into two phases, one enriched in Cu and the other close to FeS but rich in Au. Both phases may be liquid, as shown by experimental phase relations suggesting unmixing of a homogeneous sulfide melt into Cu-rich and FeS-rich melts around 1000°C (*20*).

The mean Au/Cu ratio of each population of sulfide MIs overlaps, within a factor of 2, with the bulk Au/Cu ratio of the large Bajo de la Alumbrera ore body, which in turn is identical to the average Au/Cu ratio in fluid inclusions of the earliest hydrothermal brine before ore mineral saturation in the deposit (*3*) (Fig. 3E). We conclude that the ore-forming hydrothermal fluid acquired its high metal content and characteristic Au/Cu ratio by bulk destabilization of magmatic sulfides with similar metal ratios. Bulk resorption of the sulfide liquid is expected to result from the exsolution of a volatile phase, which causes oxidation through H_2 loss and removal of sulfur as SO_2 and H_2S (*21*, *22*). A link between wholesale destabilization of sulfide melt and the generation of the ore fluid is substantiated by similar Fe/Cu ratios (Fig. 3D), despite the contrasting chemical behavior of these two elements in sulfide and volatile phases. In addition to ore metals and Fe, most of the S in the ore fluid is probably derived from the magmatic sulfide liquid. Preliminary results from the Elatsite porphyry deposit in Bulgaria, which has a lower Au/Cu ratio in the bulk ore and in the magmatic sulfide, are consistent with this interpretation.

Our data indicate that magmatic sulfide melts can act as intermediate metal hosts contributing to metal enrichment in large hydrothermal porphyry-Cu-Au deposits. Sulfide melts have previously been proposed (*22*, *23*) as a key factor in the genesis of the giant porphyry deposit at Bingham (Utah). It remains to be tested whether exsolution of sulfide liquid is a ubiquitous and essential prerequisite for ore formation, but it is probably a favorable step in the genesis of extensive porphyry-type ore deposits, by preconcentrating Cu and Au during the evolution of the magmatic system before volatile saturation. During later exsolution of a chloride-rich volatile phase, the sulfide liquid can be instantaneously destabilized, leading to bulk transfer of metals and sulfur to the hydrothermal ore fluid. Although the availability of ore metals ultimately depends on the contribution from the mantle and the history of interaction with the crust, sulfide melts may exert an immediate control on the metal composition of magmatic-hydrothermal ore deposits.

References and Notes

1. J. W. Hedenquist, J. B. Lowenstern, *Nature* **370**, 519 (1994).
2. R. H. Sillitoe, *Aust. J. Earth Sci.* **44**, 373 (1997).
3. T. Ulrich, D. Günther, C. A. Heinrich, *Nature* **399**, 676 (1999).
4. ———, *Econ. Geol.* **96**, 1743 (2001).
5. Commonly used techniques, such as electron or ion microprobe, require thermal homogenization of crystallized MIs and subsequent exposure to the sample surface before analysis.
6. E. J. Llambias, *Rev. Asoc. Geol. Argent.* **27**, 161 (1972).
7. J. C. Caelles, A. H. Clark, E. Farrar, S. L. McBride, S. Quirt, *Econ. Geol. Bull. Soc. Econ. Geol.* **66**, 961 (1971).
8. A. M. Sasso, A. H. Clark, *Soc. Econ. Geol. Newsl.* **34**, 8 (1998).
9. W. E. Halter, C. A. Heinrich, and T. Pettke (in preparation) show that volcanic rocks are samples of magma extracted from the central part of a large magma chamber, where new melt is periodically injected. Intrusive stocks are rooted in a chemically structured boundary layer, developed at the contact of the hot magma with the colder host rock. Successive intrusions sample progressively deeper, more basic parts of the boundary layer. Each intrusion is accompanied by a pressure drop, inducing volatile exsolution from the magma portion intruded as the following batch. Thus, each magma pulse is hydrothermally altered and mineralized by fluid from deeper parts of the reservoir; that is, from magmas intruded at a later stage. Accordingly, the last melt to intrude has lost its volatiles to previously emplaced intrusions, but its phenocrysts still record sulfide MIs from the fluid source region.
10. J. B. Gill, *Orogenic Andesites and Plate Tectonics* (Springer Verlag, New York, 1981).
11. J. B. Lowenstern, G. A. Mahood, M. L. Rivers, S. R. Sutton, *Science* **252**, 1405 (1991).
12. W. E. Halter, T. Pettke, C. A. Heinrich, B. Rothen-Rutishauser, *Chem. Geol.* **183**, 63 (2002).
13. D. Günther, A. Audetat, R. Frischknecht, C. A. Heinrich, *J. Anal. At. Spectrom.* **13**, 263 (1998). The prototype Excimer LA-ICPMS has been commercialized as *GeoLas* by Microlas (Göttingen, Germany).
14. H. P. Longerich, S. E. Jackson, D. Günther, *J. Anal. At. Spectrom.* **11**, 899 (1996).
15. P. J. Jugo, P. A. Candela, P. M. Piccoli, *Lithos* **46**, 573 (1999).
16. G. A. Gaetani, T. L. Grove, *Geochim. Cosmochim. Acta* **61**, 1829 (1997).
17. J. Koepke, H. Behrens, *Geochim. Cosmochim. Acta* **65**, 1481 (2001).
18. C. Jaupart, S. Tait, *J. Geophys. Res. Solid Earth* **100**, 17615 (1995).
19. K. Hattori, J. D. Keith, *Miner. Deposita* **36**, 799 (2001).
20. D. J. Vaughan and J. R. Craig [in *Geochemistry of Hydrothermal Ore Deposits*, H. L. Barnes, Ed. (Wiley, New York, 1997), pp. 367–434] and C. Ballhaus, M. Tredoux, and A. Spath [*J. Petrol.* **42**, 1911 (2001)] also demonstrated the presence of two sulfide liquids at these conditions, albeit in Ni-bearing systems.
21. P. A. Candela, H. D. Holland, *Econ. Geol.* **81**, 1 (1986).
22. A. C. L. Larocque, J. A. Stimac, J. D. Keith, M. A. E. Huminicki, *Can. Miner.* **38**, 1233 (2000).
23. J. D. Keith *et al.*, *J. Petrol.* **38**, 16790 (1997).

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$^{40}Ar/^{39}Ar$ Dates from the West Siberian Basin: Siberian Flood Basalt Province Doubled

Marc K. Reichow,[1] Andrew D. Saunders,[1]* Rosalind V. White,[1] Malcolm S. Pringle,[2] Alexander I. Al'Mukhamedov,[3] Alexander I. Medvedev,[3] Nikolay P. Kirda[4]

Widespread basaltic volcanism occurred in the region of the West Siberian Basin in central Russia during Permo-Triassic times. New $^{40}Ar/^{39}Ar$ age determinations on plagioclase grains from deep boreholes in the basin reveal that the basalts were erupted 249.4 ± 0.5 million years ago. This is synchronous with the bulk of the Siberian Traps, erupted further east on the Siberian Platform. The age and geochemical data confirm that the West Siberian Basin basalts are part of the Siberian Traps and at least double the confirmed area of the volcanic province as a whole. The larger area of volcanism strengthens the link between the volcanism and the end-Permian mass extinction.

Basaltic magma that erupted simultaneously over large areas of Earth's surface—so-called flood basalts—may have released prodigious volumes of SO_2, CO_2, HF, and other gases; hence, it is argued, such an event would trigger climatic disruption and a destabilization of major ecosystems, leading to mass extinction (*1*). The Siberian Traps (Fig. 1) are the largest Phanerozoic continental flood basalt province. They were erupted at the end of the Permian, about 250 million years ago (Ma) (*2, 3*), coincident with the largest known mass extinction event, the Permo-Triassic (P-Tr) crisis (*4–6*). Several authors have proposed that the flood volcanism triggered the mass extinction event (*4–6*), although the precise causal links are not understood (*7, 8*).

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The present-day outcrop of the Siberian Traps is mostly on the Siberian Platform, an area of stable, thick continental lithosphere (Fig. 1) (*2, 3*). However, deep boreholes and seismic sections reveal that similar basaltic lavas are also buried deep within the West Siberian Basin (WSB) (*9, 10*). We have obtained samples from 15 boreholes that drilled these buried formations (Fig. 1).

The WSB covers a region of about 2.5×10^6 km^2 located between the Ural Mountains and the Siberian Platform (Fig. 1). The basin is filled with a thick sequence of Triassic continental, and Jurassic and Cretaceous marine, sedimentary rocks (*10, 11*). Thick sequences of basaltic rocks underlie the Mesozoic sedimentary successions. The WSB underwent extension during the late Paleozoic or early Mesozoic, producing north-south–trending rifts in the central part of the basin. From seismic studies and deep boreholes [e.g., borehole SG-6 (*10*)], the basalt sequences are at least 2 km thick in the rifts. The rifts are associated with high magnetic intensity (*12*), consistent with thick accumulations of basaltic rocks.

Samples were taken from depths as much as 4.3 km below the surface, and in two boreholes the sampling interval was almost 1 km. Four holes are located in the rifts, but others are on the flanks of the rifts, indicating that magmatism was not restricted to the rifts. Depths-to-basalt in the boreholes are, on average, deeper in the rift zones than on the flanks, suggesting that rifting continued after basalt emplacement. The units range in thickness from 0.5 to 40 m. Abundant vesicles (now filled with calcite) and thick breccia horizons at the tops and bottoms suggest that many units are extrusive. Sub–meter-thick tuff layers in some boreholes (e.g., Permyakovskaya) and a lack of nonvolcanic sedimentary material suggest short intervals between eruptions. Previous studies have assigned the WSB basalts recovered from borehole SG-6 to the lower Triassic and have attempted to correlate them with the main trap sequences by means of magnetostratigraphy, palynology, and geochemistry (*10, 11*). One radiometric date obtained by ^{40}Ar/^{39}Ar incremental heating on multigrain plagioclase fractions from the Tagrinskaya borehole gave an age of 250.8 ± 2.6 Ma (*13*).

Most of the recovered rocks are basalts and dolerites with rare rhyolites and an olivine gabbro. Most of the basalts contain phenocrysts of plagioclase ± clinopyroxene ± olivine, although some are aphyric. Alteration ranges from slight to severe, with olivine mostly replaced by secondary minerals. The gabbro from Van Eganskaya contains biotite. We selected five of the least altered rocks from three boreholes within the WSB (Table 1). Sample depths range from 2797.1 m to 3434.0 m below surface.

The ^{40}Ar/^{39}Ar age determinations were carried out by incremental heating on multigrain, hand-picked plagioclase and biotite fractions (*14*). Ages obtained for plagioclase from the WSB basalts average 249.4 ± 0.5 Ma. All samples give well-defined age plateaus having 15 to 31 steps (plagioclase) or 8 to 9 steps (biotite) (Fig. 2) and equivalent isochron ages (Table 1) (*15*). The youngest plagioclase age was obtained for sample 3c97-97 (249.1 ± 0.8 Ma) from Hohryakovskaya, and the oldest for 3c97-45 (249.7 ± 0.8 Ma) from Permyakovskaya. Samples 3c97-8 (249.3 ± 0.8 Ma) and 3c97-45 (249.7 ± 0.8 Ma) from Permyakovskaya, but are within error of each other. Biotites 3c97-82 and 3c97-81 were sampled 20 m apart, from within the Van Eganskaya gabbro body. They yield older ages of 252.5 ± 1.5 Ma and 253.4 ± 0.8 Ma, respectively. The resolution of the incremental-heating experiments reported here does not allow us to distinguish whether the age difference between the basalts and gabbros is real, or is due to excess radiogenic ^{40}Ar (^{40}Ar*) in biotite (*16*).

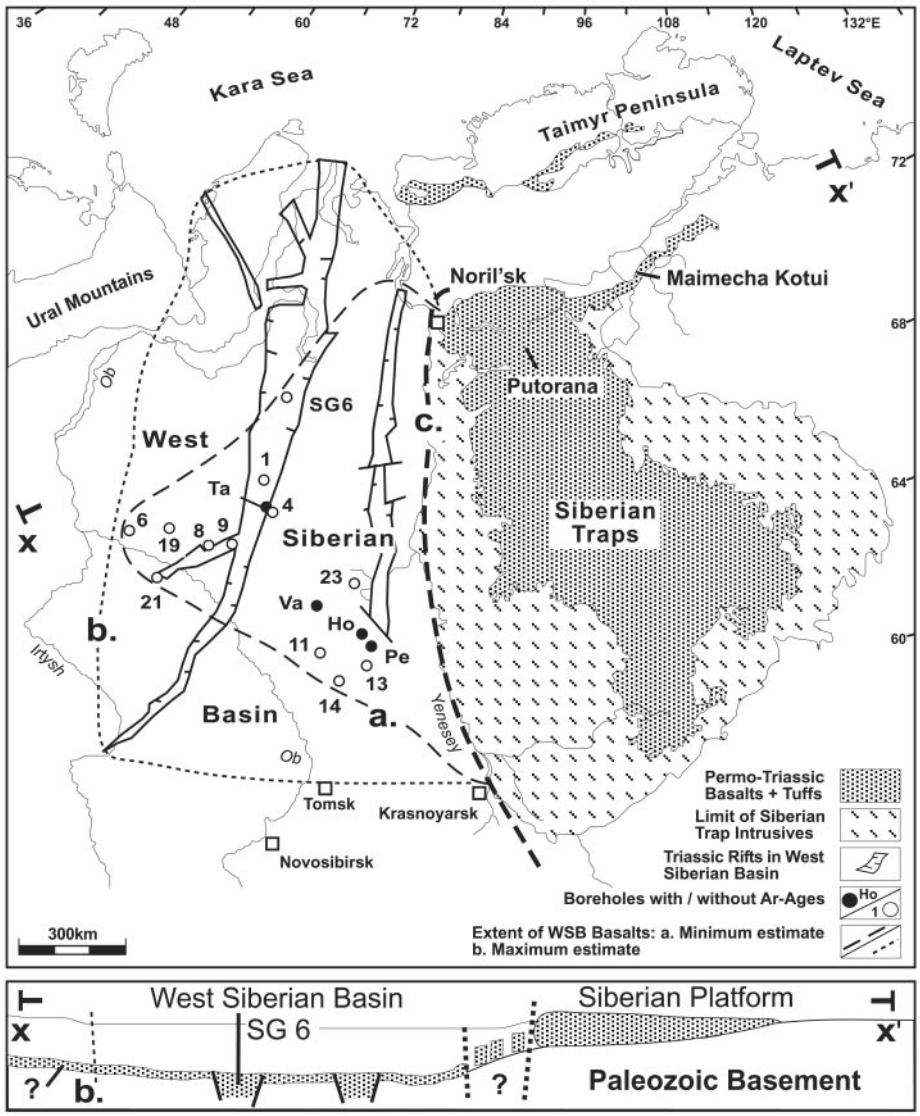


Fig. 1. Map and schematic cross section of the West Siberian Basin and Siberian Platform. All indicated boreholes penetrated basaltic rocks sampled for geochemical analysis [see also (*11*)]; those with letters were sampled for ^{40}Ar/^{39}Ar analysis [this study and (*13*)] (Ta, Tagrinskaya; Va, Van Eganskaya; Ho, Hohryakovskaya; Pe, Permyakovskaya). Lines a and b represent minimum and maximum estimates, respectively, of the area of basalt buried beneath the West Siberian Basin. Line c represents the estimated western limit of the Siberian Platform.

[1]Department of Geology, University of Leicester, Leicester LE1 7RH, UK. [2]Scottish Universities Environmental Research Centre (SUERC), Scottish Enterprise Technology Park, Rankine Avenue, East Kilbride G75 0QF, UK. [3]Institute of Geochemistry, Favorsky Street, Post Office Box 4019, Irkutsk 664033, Russia. [4]Institute of Geology Oil and Gas, Koptyug Avenue 3, Novosibirsk 630090, Russia.

*To whom correspondence should be addressed. E-mail: ads@le.ac.uk

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High-precision dating and magnetostratigraphy imply a short duration for the Siberian Trap volcanism in the Noril'sk and Putorana areas (Fig. 3) (*2–6, 17, 18*), with a uniform age of about 250 Ma throughout a 3.5 km thickness of basalts (Fig. 3). $^{40}Ar/^{39}Ar$ ages on biotites from a dike (Fig. 3) intruding the lower lava suites of the Noril'sk area indicate a minimum age of 253.7 ± 1.2 Ma for the onset of the volcanism (*17*). This is older than the basalts themselves, but this discrepancy can be ascribed to excess $^{40}Ar^*$ in the dike rock and/or $^{40}Ar^*$ loss due to alteration of the lavas (*16*). When normalized to the same standard (*14*), the new plagioclase ages from WSB basalts are indistinguishable from ages obtained for the Noril'sk and Putorana basalts (Fig. 3).

We have also analyzed 61 basalts from the WSB for a range of major and trace elements. In the Noril'sk area, the traps have been divided into 11 distinctive lithological suites (*2, 3, 19, 20*). On the basis of minor and trace elements (*21*), the WSB samples most closely match the low-TiO_2 basalts of the Nadezhdinsky Suite at Noril'sk (*19, 20*). The data strongly indicate that the basalts in the WSB are an integral part of the Siberian flood basalt province.

Little is known about the area (and consequently the volume) of basalts within the WSB. No basalts were recovered from boreholes near Krasnoyarsk and Tomsk, in the southern part of the WSB (Fig. 1). The western boundary is unconstrained. Assuming that the basalts and tuffs recovered from boreholes delineate the area of the volcanic province in the WSB, and assuming that the igneous rocks occur continuously beneath this region and extend to the Siberian Platform, a minimum area of 0.75×10^6 km^2 (enclosed by line a in Fig. 1) is derived. However, the true extent of the volcanic region may be much larger if the basalts continue farther west and follow the major rift zones beneath the Rivers Ob and Irtysh, and north to the Arctic Ocean (line b). This would give a total area of basalts within the WSB of more than 1.3×10^6 km^2. The combined area of the basaltic flows, volcaniclastic rocks, and intrusive rocks on the Siberian Platform is about 2.6×10^6 km^2, although the present-day area of basalts is much smaller ($\sim 0.34 \times 10^6$ km^2) (*2, 3, 19, 22*). Thus, the area of the basaltic flows is at least doubled—and possibly more than tripled—by inclusion of the WSB basalts, giving a combined area of basalts of as much as 1.6×10^6 km^2, or a total area of basalts, pyroclastics, and intrusives of 3.9×10^6 km^2.

Deriving volume estimates for the basalts in the WSB is difficult; borehole SG-6, in the western rift zone, penetrated more than 1 km of basalt, and seismic data indicate an additional 1 km of basalt below this (*10*). Other boreholes indicate smaller thicknesses. In the absence of high-quality seismic data for the WSB, it is not possible to produce a reliable figure for the volume of the basalts. The combined volume of exposed lavas, tuffs, and intrusives on the Siberian Platform is estimated to be as much as

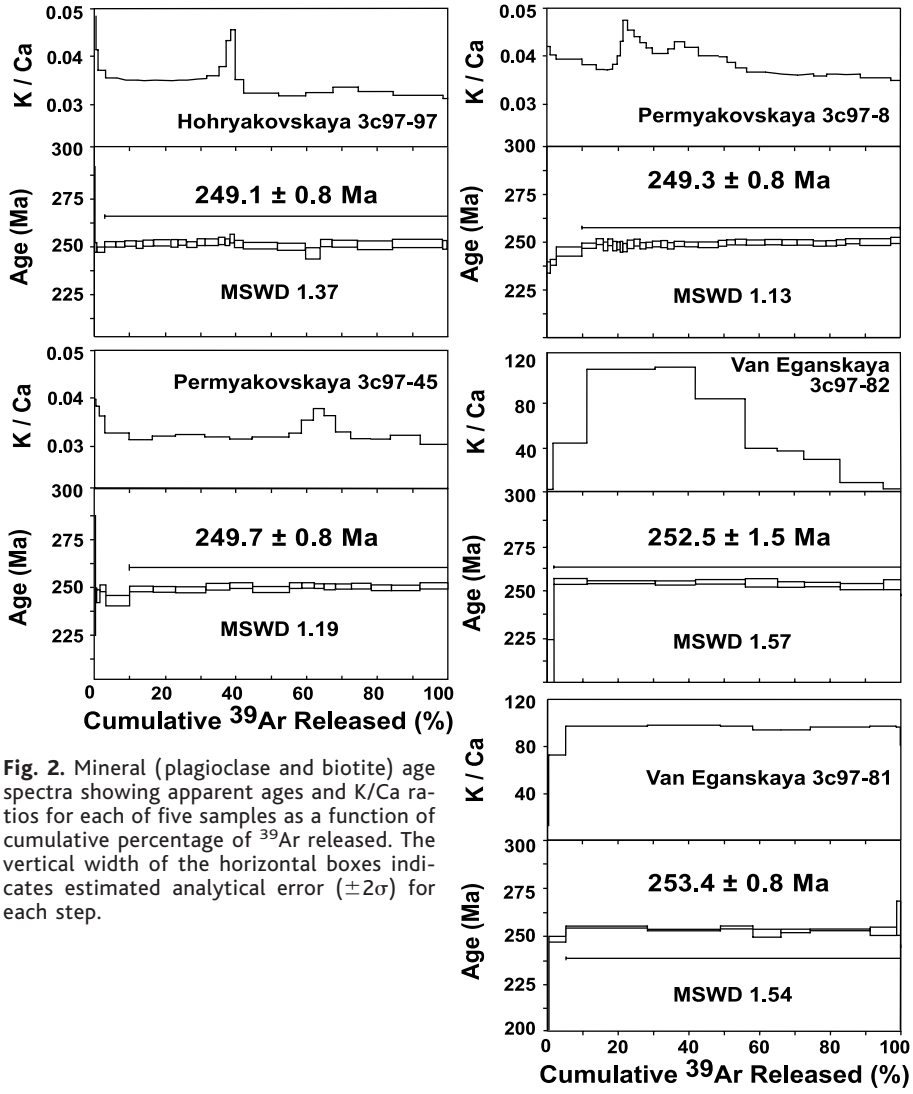


Fig. 2. Mineral (plagioclase and biotite) age spectra showing apparent ages and K/Ca ratios for each of five samples as a function of cumulative percentage of ^{39}Ar released. The vertical width of the horizontal boxes indicates estimated analytical error ($\pm 2\sigma$) for each step.

Table 1. $^{40}Ar/^{39}Ar$ ages for West Siberian Basin basalts and gabbros. All ages are relative to biotite standard GA 1550 at 98.79 Ma.

	Location				
	Permyakovskaya		Hohryakovskaya	Van Eganskaya	
Sample	3c 97-8	3c 97-45	3c 97-97	3c 97-81	3c 97-82
Depth from surface (m)	2865.3	2985.5	2797.1	3348.8	3368.6
Sample type	Plagioclase	Plagioclase	Plagioclase	Biotite	Biotite
Fraction (μm)	250 to 500	125 to 250	250 to 500	250 to 500	250 to 500
Total fusion age ± 2σ (Ma)	248.8 ± 0.8	249.0 ± 0.8	248.7 ± 0.9	252.6 ± 0.8	251.7 ± 1.5
^{39}Ar in plateau (%)	90%	90%	97%	94%	98%
Steps	31 of 34	15 of 21	23 of 26	8 of 11	9 of 10
Weighted plateau age ± 2σ (Ma)	249.3 ± 0.8	249.7 ± 0.8	249.1 ± 0.8	253.4 ± 0.8	252.5 ± 1.5
MSWD	1.19	1.13	1.37	1.54	1.57
Inverse isochron age ± 2σ (Ma)	249.7 ± 0.8	250.4 ± 1.0	249.0 ± 1.0	253.4 ± 1.0	252.3 ± 1.7
MSWD	1.06	0.89	1.40	1.78	1.63
$^{40}Ar/^{36}Ar$ intercept	266.3 ± 24	269.6 ± 22	298.1 ± 13	295.3 ± 31	298.9 ± 8

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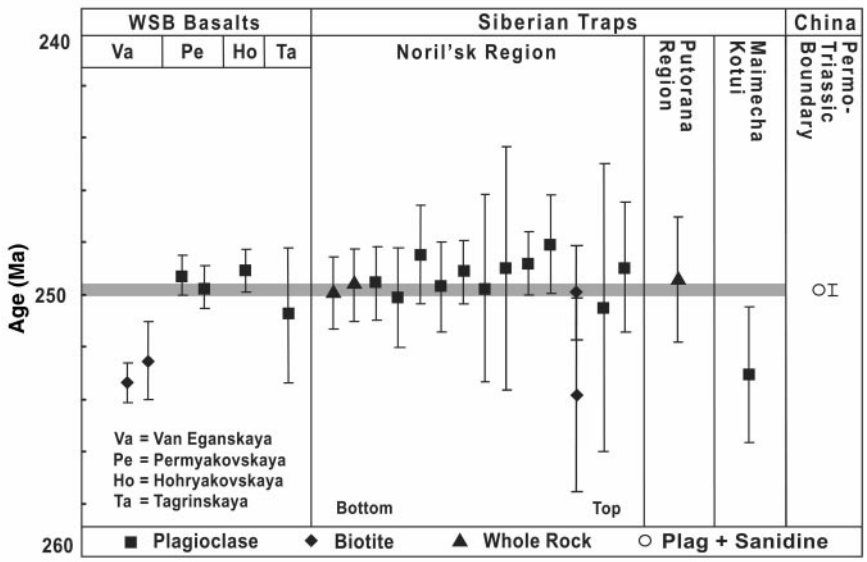


Fig. 3. Compilation of $^{40}Ar/^{39}Ar$ ages of basalts from the West Siberian Basin [this study and (*13*)], Noril'sk (*4, 5, 16, 17, 39*), Putorana (*4, 5*), and Maimecha-Kotui (*18*) areas. Proposed age, with error bars, of the P-Tr boundary is based on $^{40}Ar/^{39}Ar$ dating (gray bar) (*6*).

1×10^6 km^3 (*19, 22*). Assuming an average thickness of 1 km, the WSB probably contains as much as 1.3×10^6 km^3 of lavas and intercalated pyroclastic rocks, at least doubling the volume of lavas and pyroclastics found on the Siberian Platform.

Flood basalts have been implicated in major climatic changes (*23*) and mass extinctions (*1, 24, 25*). The Siberian Traps and our new data from the WSB are both within error of the P-Tr boundary and mass extinction event (Fig. 3). An average $^{40}Ar/^{39}Ar$ age of 249.9 ± 0.2 Ma has been obtained on sanidine and plagioclase grains separated from the ash layers immediately below and above the biostratigraphic P-Tr boundary section at Meishan in China (*6*). Recent zircon U/Pb dates (*26, 27*) for the same section consistently give slightly older ages than the $^{40}Ar/^{39}Ar$ dates, and the cause of this discrepancy is unclear (*28*). However, for the purpose of this report, it is the relative age of the P-Tr boundary, the WSB basalts, and the Siberian Traps that is important; thus, we have restricted our discussion to a comparison of the $^{40}Ar/^{39}Ar$ age data.

Unlike the Deccan Traps and the end-Cretaceous extinction, there is no unequivocal evidence for a large extraterrestrial impact at the time of the P-Tr extinction (*29*). The close timing between the Siberian Traps and the collapse of marine and terrestrial ecosystems at the end of the Permian suggests a causal linkage between the two events. The rapid and prolonged effusion of large volumes of lava may cause climate change by injection of volatiles and aerosols into the atmosphere (*1*). High magma and volatile fluxes maintained for long periods of time (hundreds or thousands of years) may be a prerequisite for substantial climate forcing and ecological collapse by global cooling and acidification (release of particulates and SO_2), by local poisoning (HF and HCl), or by global warming (CO_2). We have shown that the basalts in the WSB were erupted at the same time as the traps on the Siberian Platform, adding substantially to the total flux and volume of gases released into the atmosphere. This observation must strengthen the argument for some causation between the Siberian flood basalts and the end-Permian crisis.

References and Notes

1. S. Self *et al.*, in *Large Igneous Provinces*, J. J. Mahoney, M. F. Coffin, Eds. (Geophysical Monograph 100, American Geophysical Union, Washington, DC, 1997), pp. 381–410.
2. V. V. Zolotukhin, A. I. Al'Mukhamedov, in *Continental Flood Basalts*, J. D. Macdougall, Ed. (Kluwer Academic, Amsterdam, 1988), pp. 273–310.
3. M. Sharma, in *Large Igneous Provinces*, J. J. Mahoney, M. F. Coffin, Eds. (Geophysical Monograph 100, American Geophysical Union, Washington, DC, 1997), pp. 273–295.
4. I. A. Campbell *et al.*, *Science* **258**, 1760 (1992).
5. P. R. Renne, A. R. Basu, *Science* **253**, 176 (1991).
6. P. R. Renne *et al.*, *Science* **269**, 1413 (1995).
7. D. H. Erwin, *Nature* **367**, 231 (1994).
8. R. J. Twitchett *et al.*, *Geology* **29**, 351 (2001).
9. C. Mitchell *et al.*, *Mineral. Mag.* **58A**, 617 (1994).
10. M. E. L. Westphal *et al.*, *Geophys. J. Int.* **134**, 254 (1998).
11. A. I. Al'Mukhamedov *et al.*, *Rus. Geol. Geophys.* **40**, 1550 (1999).
12. D. Schissel, R. Smail, in *Mantle Plumes: Their Identification Through Time*, R. E. Ernst *et al.*, Eds. (Geological Society of America, Boulder, CO, 2001), pp. 291–322.
13. M. S. Pringle *et al.*, *Terra Nova* **3/95**, 120 (1995).
14. Plagioclase and biotite crystals were crushed and sorted into two size fractions: 125 to 250 μm and 250 to 500 μm. Plagioclase was magnetically separated and ultrasonically cleaned with 6 N HCl and distilled water before hand-picking; biotite was ultrasonically cleaned with distilled water before hand-picking. The minerals were wrapped in 99.99+% pure Cu foil and irradiated in the Cd-lined RODEO facility at the European Commission HFR at Petten, Netherlands. Biotite standard GA1550 was used as the fast neutron fluence monitor with a reference age of 98.79 Ma (*30*). All $^{40}Ar/^{39}Ar$ data referred to in this paper are reported relative to 98.79 Ma for GA1550 using the values given in (*30*); all errors are reported as internal errors only given at the 2σ significance level.
15. The proportion of ^{39}Ar released in the age spectra plateau ranges from 90 to 98%. Low apparent ages in the lowest temperature release fraction for all samples indicate that minor amounts of $^{40}Ar^*$ were lost as a result of alteration. This is also indicated by the high K/Ca ratios for the same temperature range (Fig. 2). Slightly elevated K/Ca ratios at higher temperatures may be the result of melting of the Cu foil capsule. Weighted plateau ages were calculated using the inverse of the variance for each step; isotope correlation diagrams of $^{40}Ar/^{36}Ar$ versus $^{39}Ar/^{36}Ar$ (normal isochron, not shown), and inverse isochrons (Table 1) were calculated using a weighted York-2 fit (*31*). Ages for all three calculations are within error (2σ), and the mean squared weighted deviation (MSWD) for the age plateau is lower than 1.6 for all samples.
16. P. R. Renne, *Earth Planet. Sci. Lett.* **131**, 165 (1995).
17. G. B. Dalrymple *et al.*, *Geochim. Cosmochim. Acta* **59**, 2071 (1995).
18. A. R. Basu *et al.*, *Science* **269**, 822 (1995).
19. V. A. Fedorenko *et al.*, *Int. Geol. Rev.* **38**, 99 (1996).
20. P. C. Lightfoot *et al.*, *Contrib. Mineral. Petrol.* **114**, 171 (1993).
21. The basalts we analyzed all have Gd/Yb ratios of <2 and La/Sm ratios between 1.8 and 6.0. TiO_2 is mostly less than 1.5% between 5 and 10% MgO.
22. M. L. Lur'ye, V. L. Masaytis, in *Flood Basalts*, V. S. Sobolev, Ed. (Nauka, Moscow, 1964), pp. 13–26. (in Russian).
23. P. B. Wignall, *Earth Sci. Rev.* **53**, 1 (2001).
24. V. Courtillot, *Isr. J. Earth Sci.* **43**, 255 (1994).
25. _____, *Evolutionary Catastrophes* (Cambridge Univ. Press, Cambridge, 1999).
26. Bowring *et al.* (*32*) obtained a U/Pb age of 251.4 ± 0.3 Ma on zircons (multi- and single-grain) from the ash layer (Bed 25) below the P-Tr boundary at Meishan, China.
27. Mundil *et al.* (*33*) obtained a U/Pb age of 252.5 ± 0.3 Ma on zircon grains from the ash layer (Bed 28) above the P-Tr boundary at Meishan.
28. The small but significant discrepancy between U/Pb (zircon) and $^{40}Ar/^{39}Ar$ ages is supported by recent detailed studies such as (*34–36*). An explanation for the discrepancy is that the currently accepted ages for $^{40}Ar/^{39}Ar$ standard minerals are too young and/or the currently accepted potassium decay constant is too high.
29. Becker *et al.* (*37*) report fullerenes (from P-Tr boundary sediments) that contain trapped noble gases with isotopic ratios indicative of an extraterrestrial source. Attempts to replicate these results have been unsuccessful (*38*).
30. P. R. Renne *et al.*, *Chem. Geol.* **145**, 117 (1998).
31. D. York, *Earth Planet. Sci. Lett.* **5**, 320 (1969).
32. S. A. Bowring *et al.*, *Science* **280**, 1039 (1998).
33. R. I. Mundil *et al.*, *Earth Planet. Sci. Lett.* **187**, 131 (2001).
34. K. Min *et al.*, *Geochim. Cosmochim. Acta* **64**, 73 (2000).
35. M. D. Schmitz, S. A. Bowring, *Geochim. Cosmochim. Acta* **65**, 2571 (2001).
36. K. Min *et al.*, *Earth Planet. Sci. Lett.* **185**, 121 (2001).
37. L. R. Becker *et al.*, *Science* **291**, 1530 (2001).
38. K. A. Farley, S. Mukhopadhyay, *Science* **293**, 2343 (2001).
39. T. R. Venkatesan *et al.*, *Chem. Geol.* **138**, 303 (1997).

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