



## Coeval argon-40/argon-39 ages of moldavites from the Bohemian and Lusatian strewn fields

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**Abstract**— $^{40}\text{Ar}/^{39}\text{Ar}$  ages of four tektites (moldavites) from southern Bohemia (near České Budějovice, Czech Republic) and a tektite from Lusatia (near Dresden, Germany) have been determined by 11 step-degassing experiments. The purpose of the study was to enlarge the  $^{40}\text{Ar}/^{39}\text{Ar}$  data base of moldavites and to check the age relations of the Bohemian and Lusatian samples. The mean plateau-age of the Bohemian samples, which range from 14.42 to 14.70 Ma, is  $14.50 \pm 0.16$  (0.42) ( $2\sigma$ ) Ma (errors in parentheses include age error and uncertainty of standard monitor age). The plateau age of the Lusatian sample of  $14.38 \pm 0.26$  (0.44) ( $2\sigma$ ) Ma confirms the previously published  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $14.52 \pm 0.08$  (0.40) ( $2\sigma$ ) Ma, and demonstrates that the fall of Lusatian and Bohemian tektites were contemporaneous. Because of their geochemistry and their ages there is no doubt that the Lusatian tektites are moldavites. Accepting that moldavites are ejecta from the Nördlinger Ries impact, the new ages also date the impact event. This age is slightly younger (about 0.2–0.3 Ma) than the age suggested by earlier K-Ar determinations.

### INTRODUCTION

Moldavites are natural glasses which are found in late Tertiary sediments in Bohemia and Moravia, Czech Republic (Suess, 1900). They are tektites (*i.e.*, glasses formed by impact melting and ejection of molten terrestrial rocks over a long distance during the impact of a kilometer-sized cosmic body). Their name refers to the river Moldau/Vltava, a tributary of the Elbe/Labe river.

The Nördlinger Ries basin in Germany is interpreted as a ~25 km wide impact crater which has been identified as the source of the moldavites (*e.g.*, Bouška *et al.*, 1973). In Bohemia and Moravia several well-known moldavite strewn fields have been distinguished (Bouška, 1998; Fig. 1). There are small differences in average chemical compositions, shapes and structures of the tektites in these fields.

In 1967, H. Nicht recognized that moldavite-like tektites occur in late Tertiary sediments in Lusatia (Lausitz) northeast of Dresden, Germany (Fig. 1). It took several years before Žebera (1974) introduced this discovery to the literature. Initially, the Lusatian tektites were taken for moldavites transported from the Bohemian strewnfield to Lusatia by the Moldau and Elbe rivers (*e.g.*, Rost *et al.*, 1979; Lange and Störr, 1991; Störr and Lange, 1992); while the possibility of fluvial transport from Moravian sites to Lusatia was excluded. However, because the majority of Lusatian tektites resemble the Moravian moldavites and because transport from Bohemia was not possible before Pliocene times, Lange (1996) considers Lusatia to be a separate moldavite strewn field because it is

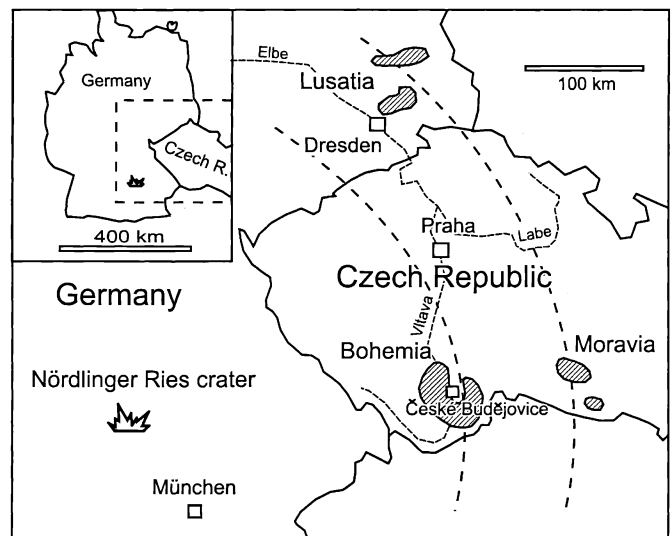


FIG. 1. Schematic map of moldavite occurrences (hatched areas) in Bohemia, Moravia and Lusatia, formed by the Nördlinger Ries impact event (not included are minor occurrences in Lower Austria, the Cheb area and elsewhere; cf., Koeberl *et al.*, 1988; Lange, 1996; Bouška, 1998).

about the same distance to the Nördlinger Ries basin as the Moravian field (Fig. 1).

K-Ar and fission track dating played an important role in the years 1960 to 1980 when the relations between Nördlinger Ries impactites and moldavites and between the subgroups of

the moldavites were discussed. The  $^{40}\text{Ar}/^{39}\text{Ar}$  dating technique, which increasingly replaces the conventional technique due to its higher dating potential, has not yet been largely applied to moldavites. This omission together with a moldavite dating problem (slight discrepancy between the two known moldavite  $^{40}\text{Ar}/^{39}\text{Ar}$  ages) raised by Lange *et al.* (1995) led us to perform a series of  $^{40}\text{Ar}/^{39}\text{Ar}$  step-dating experiments on four moldavites from Bohemia and one from upper Lusatia.

### MOLDAVITE FORMATION CHRONOLOGY

Although moldavites occur in sediments with known ages, the stratigraphic age of these sediments are only lower age limits for the formation of the moldavites, because they have been redeposited after fluvial transport from the sites where they fell and from earlier sites of redeposition. Moldavites occur in upper Miocene, Pliocene and Pleistocene sediments (*e.g.*, Bouška, 1998; Lange, 1996). The oldest moldavite-bearing sediments belong to the lower Sarmatian, while the Ries impact event happened in late Badenian times (late Tortonian; *sensu* Bolten and Müller, 1969). Therefore, judging from the stratigraphical point of view, and accepting the Ries origin of moldavites as given, the numerical moldavite ages are expected to be higher than ~12 Ma and probably equal to ~15 Ma (middle Miocene; compare with, for example, Haq and Eysinga, 1998). Bouška (1998) as well as Balestrieri *et al.* (1997) estimated the hiatus between the time of moldavite fall and the oldest known redeposition to be ~2 Ma.

Moldavite glasses have been dated by K-Ar and fission track dating techniques since 1961 and 1967, respectively. Simultaneously, the Ries impact glass chronology was developed. The first ~15 Ma K-Ar measurements for Bohemian and Moravian moldavites and Ries impact glass were given by Lippolt (1961) and Gentner *et al.* (1961). Gentner *et al.* (1961) were the first to notice the age coincidence and suggested the Ries impact crater as the source of the moldavites. Geochemical investigations of the main and trace elements of the sediments of the upper Freshwater Molasse from the pre-impact area (consisting of sands, marls, clayed sands and siltstones), Ries glasses and the moldavites led to the same conclusion for the source of the moldavites (*e.g.*, Bouška *et al.*, 1973; Graup *et al.*, 1981; Delano and Lindsley, 1982; v. Engelhardt *et al.*, 1987; Bouška, 1994; Lange, 1996). Zähringer (1963) and Gentner *et al.* (1963) separately determined the ages of eight and six moldavites with identical mean values of  $14.78 \pm 0.13$  Ma and  $14.83 \pm 0.26$  Ma (recalculated with IUGS decay constants of Steiger and Jäger, 1977, factor of 1.0139; errors =  $2\sigma$  standard deviation of the mean; error assignments are described in the "Analytical Procedures" section below). The systematic errors of the age determinations by Zähringer (1963) and Gentner *et al.* (1963) are ~0.5 Ma. Altogether the mean of 16 moldavite K-Ar age determinations was  $14.79 \pm 0.14$  (0.52) Ma. The mean age of eight Ries glasses was  $15.04 \pm 0.42$  (0.65) Ma ( $2\sigma$  standard deviation of the mean; Gentner *et al.*, 1963).

Also the fission track method (Wagner, 1966; Gentner *et al.*, 1967) yielded coeval ages for moldavite and Ries glasses ( $14.7 \pm 0.3$  and  $14.7 \pm 0.4$  Ma, respectively). Several further publications during the following years confirmed, improved and enlarged these dating results. In 1995, Storzer *et al.* prepared a statistical synopsis of published K-Ar and fission track ages of moldavites and Ries glasses and determined K-Ar mean values of  $14.82 \pm 0.32$  Ma and  $15.14 \pm 0.51$  Ma as well as fission track mean values of  $14.82 \pm 0.18$  Ma and  $14.68 \pm 0.25$  Ma, respectively (errors on  $1\sigma$  level). These authors believe that an age of  $14.87 \pm 0.72$  ( $2\sigma$ ) Ma, which includes all data, is an accurate and binding age for the Ries impact event.

More recently, additional fission track dates of moldavites, excavated from sediments of Sarmatian to Pleistocene ages, have been determined (Bigazzi and de Michele, 1996; Balestrieri *et al.*, 1997; Bouška *et al.*, 2000). The mean values of the "apparent" ages (prior to the track annealing correction) was  $13.8 \pm 0.6$  ( $2\sigma$ ) Ma; the ages after correction of  $15.1 \pm 0.2$  ( $2\sigma$ ) Ma are slightly, however insignificantly, higher than Storzer *et al.*'s fission track mean for moldavites.

However only three  $^{40}\text{Ar}/^{39}\text{Ar}$  data exist (performed in 1982 and 1993; listed in Table 1). Two  $^{40}\text{Ar}/^{39}\text{Ar}$  step-heating experiments, performed on a Czech moldavite and a Ries impact glass from Otting, yielded ages of  $15.21 \pm 0.15$  Ma and  $14.98 \pm 0.49$  Ma (Staudacher *et al.*, 1982; cf., Table 1), the third on a Lusatian moldavite yielded  $14.52 \pm 0.08$  Ma (recalculated with the revised HD-B1 monitor age; cf., Table 1; Bollinger, 1993). The latter is the only Lusatian tektite argon age available. It is slightly younger than the other ejecta ages, especially than Staudacher's  $^{40}\text{Ar}/^{39}\text{Ar}$  age which may indicate loss of radiogenic Ar during fluvial redeposition (Lange *et al.*, 1995). This hypothesis is based on the experience that minerals which are removed from their original places of origin and were transported through the erosional cycle often are altered and show loss of argon. Fission track studies on two Lusatian moldavites had shown that these glasses were heated during the transportation phase (Lange *et al.*, 1995). The (slight) discrepancy between the only two  $^{40}\text{Ar}/^{39}\text{Ar}$  dates for moldavites was a further incentive for our present study.

### ANALYTICAL PROCEDURES

The tektite glasses were crushed gently and sieved into fractions of <100, 100–200 and >200  $\mu\text{m}$ . They were cleaned with demineralised water. Due to the purity of the tektite glass no further cleaning was required to attain a sample purity of >99%.

For  $^{40}\text{Ar}/^{39}\text{Ar}$  age measurements ~500 mg of the 100–200  $\mu\text{m}$  fraction were wrapped in aluminum foil and placed in evacuated and Cd shielded quartz tubes. The irradiations (about 1, 3 and  $6 \times 10^{17}$  fast neutrons/cm<sup>2</sup>, respectively) were performed in three series in the FRG-1 reactor at the Nuclear Research Center Geesthacht, Germany. Monitoring

TABLE 1. Locations, types, isotopic and age data of Bohemian (MOL B) and Lusatian (MOL L) moldavites (this study) and the published  $^{40}\text{Ar}/^{39}\text{Ar}$  data for two moldavites and one Ries impact glass (from the literature).

Sample	Location and/or type	K (%)*	$^{40}\text{Ar}^*$ (nl/g) †	$^{40}\text{Ar}^*$ (%)	$^{40}\text{Ar}^*/^{39}\text{Ar}^\ddagger$	$J$ value ( $10^{-4}$ )‡	$t_{\text{int}}$ (Ma)§	$t_{\text{p}}$ (Ma)§
<b>This study</b>								
MOL B 42	(1)		$1.606 \pm 0.032$	88.7	$15.30 \pm 0.26$	$5.24 \pm 0.04$	$14.39 \pm 0.28$ (0.48)	$14.42 \pm 0.14$ (0.42)
	(2) Chlum nad Malši	2.86	$1.664 \pm 0.044$	75.7	$15.33 \pm 0.36$	$5.41 \pm 0.08$	$14.91 \pm 0.40$ (0.56)	$14.64 \pm 0.22$ (0.44)
	(3)		$1.608 \pm 0.038$	69.5	$7.51 \pm 0.16$	$10.67 \pm 0.06$	$14.41 \pm 0.34$ (0.50)	$14.48 \pm 0.10$ (0.40)
MOL B 43	Chlum nad Malši	3.10	$1.762 \pm 0.036$	86.9	$15.60 \pm 0.28$	$5.20 \pm 0.06$	$14.57 \pm 0.30$ (0.48)	$14.49 \pm 0.16$ (0.42)
MOL B 44	Chlum nad Malši	2.74	$1.607 \pm 0.030$	83.0	$15.50 \pm 0.22$	$5.40 \pm 0.06$	$15.03 \pm 0.28$ (0.48)	$14.70 \pm 0.20$ (0.42)
MOL B HA	Habří	3.04	$1.697 \pm 0.042$	77.8	$15.47 \pm 0.30$	$5.15 \pm 0.08$	$14.31 \pm 0.36$ (0.52)	$14.44 \pm 0.24$ (0.44)
MOL L WA	Ottendorf-Okrilla	2.93	$1.722 \pm 0.050$	63.0	$15.66 \pm 0.40$	$5.36 \pm 0.08$	$15.06 \pm 0.44$ (0.60)	$14.38 \pm 0.26$ (0.44)
<b>Literature</b>								
ML-OTT18#	Ottendorf-Okrilla	2.73	$1.564 \pm 0.018$	84.7	–	–	$14.68 \pm 0.30$	$14.52 \pm 0.08$ (0.40)
GM§	Czech moldavite@	2.76	1.60	77.2	–	–	$15.2 \pm 0.4$	$15.21 \pm 0.30$ (0.50)
GO§	Otting/Ries impact glass	2.68	1.66	70.0	–	–	$15.0 \pm 0.6$	$14.98 \pm 0.98$ (1.04)

\*By flame photometry.

†Calculated from measured argon isotopes of samples and standards.

‡Two different irradiation series, higher neutron dose applied.

§Integrated ( $t_{\text{int}}$ ) and plateau ages ( $t_{\text{p}}$ ) with total errors; given in parentheses in columns eight and nine are the age errors including the age uncertainty of the standard monitor (both  $2\sigma$  error level).

#Lusatian moldavite: Bollinger (1993), Lange *et al.* (1995).

§Staudacher *et al.* (1982).

@Sample location not published by Staudacher *et al.* (1982).

of irradiation gradients and ages was achieved by the standard HD-B1 ( $24.21 \pm 0.32$  ( $1\sigma$ ) Ma; Hess and Lippolt, 1994). Argon was extracted in eight temperature steps up to 1600 °C in a resistance-heated tantalum furnace. The Ar isotope compositions were measured in static mode in modified MAT GD-150 mass spectrometers. For the age calculations the IUGS recommended constants (Steiger and Jäger, 1977) were used. All data were corrected for isotope interferences during neutron activation. The isotope ratios and argon dates determined in this study are given with  $\pm 2\sigma$  accuracy. Earlier dating results are given with  $\pm 1\sigma$  errors, unless noted differently. The error assignments of the ages are the propagated analytical uncertainties. Those in parentheses (in Table 1 and the text) additionally include the error of the relevant monitor age as third quadratic summation term. They are needed for comparisons with ages calibrated by other age monitors.

Aliquots of the Bohemian moldavite MOL B 42 were measured several times, applying differing n-doses, in order to check the reproducibility.

### RESULTS: ARGON-40/ARGON-39 AGES

Four Bohemian tektite samples (MOL B) from Chlum nad Malší and Habří (České Budějovice area) and one Lusatian tektite (MOL L) from a quarry near Ottendorf-Okrilla, 6 km north of Dresden, were dated. They were kindly provided by K. Žebera (Praha) and J-M. Lange (Leipzig), respectively.

The Bohemian moldavites (B 42-44, B Ha; cf., Table 1) are from fluvio-lacustrine sediments (K. Žebera, pers. comm.), which belong to the late lower Pliocene (lower Romanian, 3.7 to ~2.5 Ma; Bouška, 1998). They are rounded, green and have deep pits, indicating long transport before redeposition (Balestrieri *et al.*, 1997) and corrosion of the surface by chemical attack in a weekly acidic environment. The Ottendorf-Okrilla tektite was also found in fluvio-lacustrine sediments which, after Lange (1996), are of upper Miocene/lower Pliocene age (older Senftenberg Elbe gravels, ~7 to 4 Ma). Bouška (1998), however, does not exclude the possibility that they are younger and belong to the later part of the lower Pliocene as do the sediments containing the České Budějovice moldavites. The stratigraphic evidence of the five moldavite samples therefore defines a lower age limit of ~4 Ma, which is ~10 Ma younger than the formation ages.

Due to an insufficient n-irradiation dose, the first series of measurements yielded only ages with relatively high errors in the order of magnitude of the conventional K-Ar moldavite dates. The degassing spectra, however, showed adequate plateaus (>70 to 85% of  $^{39}\text{Ar}$  degassing). The  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages and their errors (all on  $2\sigma$  level) are MOL B 42:  $14.8 \pm 1.8$  (2.0) Ma; MOL B 43:  $15.2 \pm 0.8$  (1.0) Ma; MOL B 44:  $14.4 \pm 1.4$  (1.6) Ma; MOL L WA:  $13.9 \pm 0.8$  (1.0) Ma, based on  $J$  values ( $\times 10^{-4}$ ) of  $1.96 \pm 0.24$ ,  $1.81 \pm 0.08$ ,  $1.56 \pm 0.14$  and  $1.66 \pm 0.08$ , respectively. These ages are not sufficiently precise to settle the aforementioned problem, but they are in

agreement with earlier results for moldavites and with the more precise data of this study.

Table 1 presents the results of the seven measurements with correct neutron irradiation, including K contents determined by AES (atomic emission spectrometry) flame photometry and radiogenic Ar concentrations derived from the neutron activation results. The plateau ages of the three Mol B 42 aliquots agree within 1.5%. The integrated ages of the Bohemian tektites (total argon ages) show a slight variation from 14.31 Ma (B HA) to 15.03 Ma (B 44), and the plateau ages from 14.42 Ma (B 42(1)) to 14.70 Ma (B 44). But they agree within the  $2\sigma$  error limits. The mean age of the Bohemian moldavites is 14.50 Ma with  $2\sigma$  deviations of  $\pm 0.16$  and ( $\pm 0.42$ ), respectively. The Lusatian tektite yields an integrated age of  $15.06 \pm 0.44$  (0.60) Ma. Its plateau age is  $14.38 \pm 0.26$  (0.44) Ma.

Figure 2 presents the corresponding age and Ca/K spectra for the Bohemian tektites; Fig. 3 presents those of the Lusatian tektite. In three age spectra of Figs. 2 and 3 the first temperature step yields a higher age, similar to Bollinger's Lusatian tektite spectrum. This increase could possibly be due to a kind of excess argon (Lanphere and Dalrymple, 1976), minor sample impurities or from the absence of this increased first step age in the equivalent spectra of the first dating series as an analytical artifact. The Ca/K spectra are flat and only one sample shows a higher first value.

### DISCUSSION

The  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau age of  $14.38 \pm 0.26$  (0.44) Ma of the Lusatian tektite agrees well with the mean of the Bohemian tektite ages of  $14.50 \pm 0.16$  (0.42) Ma reported here. Both are slightly lower than the mean of the hitherto published moldavite ages ( $14.8 \pm 0.5$  Ma), but well within the  $2\sigma$  error margins.

The age of the Lusatian tektite confirms the age of  $14.52 \pm 0.08$  (0.40) ( $2\sigma$ ) Ma published previously for an Ottendorf-Okrilla tektite (Bollinger, 1993; Lange *et al.*, 1995, cf., Table 1). As seen from Table 1, the age data show no age difference between the Bohemian and Lusatian tektites as was tentatively discussed by Lange *et al.* (1995) in referring to the  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $15.21 \pm 0.15$  Ma for a Czech moldavite given by Staudacher *et al.* (1982). Although the mentioned age discrepancy is larger than the analytical  $2\sigma$  error, it is still within the external  $2\sigma$  error margins, which have to be applied because both Bollinger's and our dates are calibrated with the HD-B1 monitor, while Staudacher's result is based on B4M (using  $t = 18.5 \pm 0.2$  ( $1\sigma$ ) Ma; Jäger, 1970). The ages of the two monitors have been well intercalibrated against other international standards (cf., Charbit *et al.*, 1998 for HD-B1; Rex and Guise, 1995 and Baksi *et al.*, 1996 for Bern 4M).

When the previously determined two moldavite  $^{40}\text{Ar}/^{39}\text{Ar}$  ages are combined with our new data the mean of the  $^{40}\text{Ar}/^{39}\text{Ar}$  moldavite ages (14.50 Ma) is increased by 0.02 Ma to  $14.52 \pm 0.14$  (0.42) ( $2\sigma$ ) Ma. This mean  $^{40}\text{Ar}/^{39}\text{Ar}$  age of nine

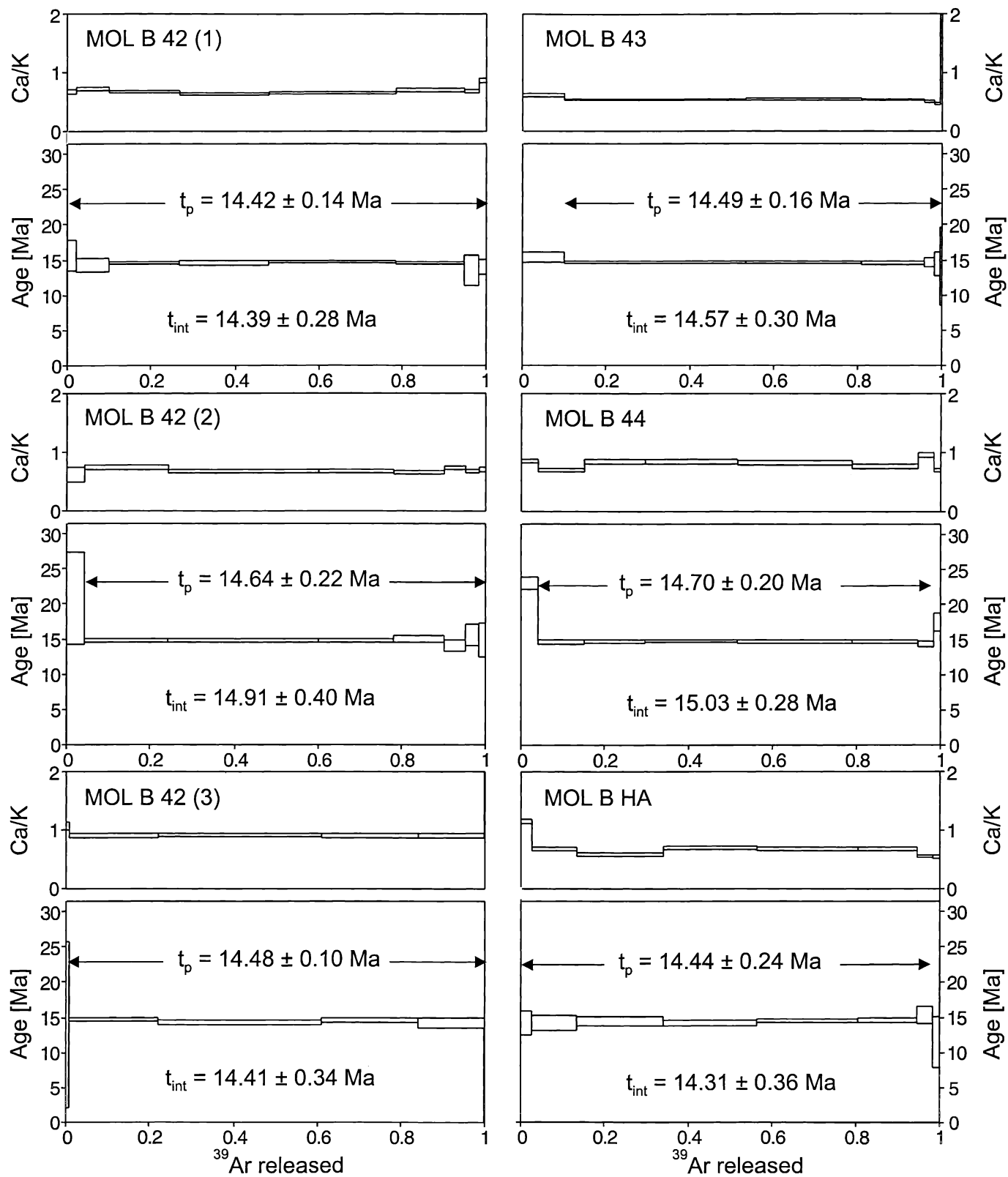


FIG. 2.  $^{40}\text{Ar}/^{39}\text{Ar}$  age and Ca/K degassing spectra for Bohemian moldavite samples. Included are the integrated ( $t_{\text{int}}$ ) and plateau ( $t_{\text{p}}$ ) ages.

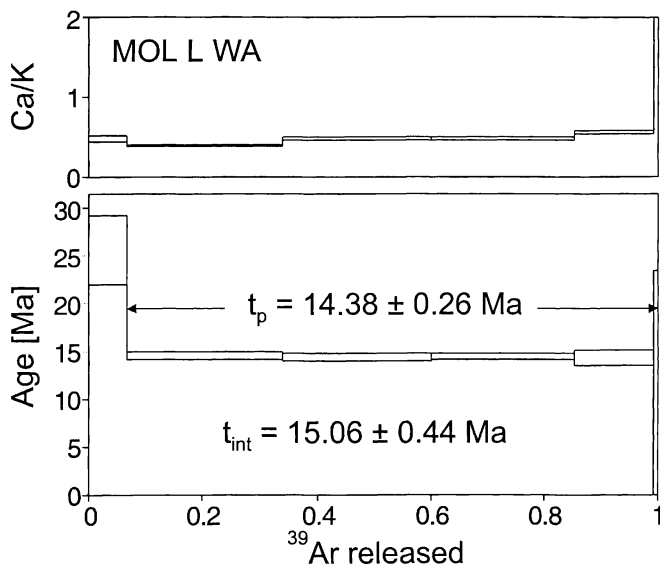


FIG. 3.  $^{40}\text{Ar}/^{39}\text{Ar}$  age and Ca/K degassing spectra of a Lusatian moldavite (from Ottendorf-Okrilla, Lusatia).

moldavites specimen is slightly lower ( $\sim 0.3$  Ma) but well within the error margins of the known mean of the conventionally determined Ar ages of 16 samples. However, this small difference in age possibly indicates that further work will result in a slightly lower mean value for the moldavite ages. It is noteworthy that the calibration of the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages is better documented than that of the conventionally determined moldavite ages.

The argon and fission track age evidence for moldavites is still in agreement, although the moldavite fission track ages determined by the Pisa researchers are nominally slightly higher than the Storzer *et al.* fission track mean value for moldavites.

### CONCLUSIONS

The  $^{40}\text{Ar}/^{39}\text{Ar}$  dating results of this study do not show any significant age difference between the Bohemian and Lusatian tektites. The possibility of argon-loss from the Lusatian tektites is ruled out.

The coevality shows that Lusatian and Bohemian tektite strewing was contemporaneous. The chemistry and the age of the Lusatian tektites demonstrate they are moldavites. Accepting that moldavites are ejecta from the Nördlinger Ries impact the new ages also date the impact event. The presented mean age of  $14.52 \pm 0.14$  (0.42) ( $2\sigma$ ) Ma is only slightly younger ( $\sim 0.3$  Ma) than earlier K-Ar determinations.

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