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Preparation and Crystal Structures of Technetium Phosphides*

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The system technetium–phosphorus was investigated for the first time. Samples prepared at 1220 K using the tin-flux technique or iodine as a mineralizer showed the existence of six technetium phosphides. Only those with the lowest and highest phosphorus content are isotypic with known manganese or rhenium phosphides. Tc_3P crystallizes in the tetragonal Mn_3P (Fe_3P type) structure: $a = 9.568 \pm 0.005$, $c = 4.736 \pm 0.003$ Å; TcP_4 has the orthorhombic ReP_4-type structure: $a = 6.238 \pm 0.001$, $b = 9.215 \pm 0.003$, $c = 10.837 \pm 0.003$ Å. The crystal structures of these two compounds were refined from single-crystal X-ray diffractomer data to conventional residual values of $R = 0.039$ for Tc_3P (19 variables, 1698 F values) and $R = 0.031$ for TcP_4 (23 variables, 1848 F values). The crystal chemistry of these two compounds is discussed.

Introduction

Although numerous investigations deal with the binary systems manganese–phosphorus and rhenium–phosphorus, the corresponding system with technetium has not been examined. It is interesting that none of the corresponding manganese and rhenium phosphides have isotypic structures. In the system manganese–phosphorus the compounds Mn_3P with Fe_3P structure, Mn_2P with Fe_2P structure, and MnP (prototype) are known (*1–3*). More recently the three polytype polyphosphides 2-, 6-, and 8-MnP_4 have been prepared and characterized (*4–7*). In the system rhenium–phosphorus the compounds Re_2P with (anti-) $PbCl_2$ structure (*8*), Re_3P_4 (*9, 10*), Re_6P_{13} (*11, 12*), Re_2P_5 (*13*), and ReP_4 (*14*) are well characterized. We wanted to see whether this great variety of compositions and structural types is matched or augmented in the intermediate system technetium–phosphorus.

Syntheses

Starting materials were powders of technetium metal (^{99}Tc, Oak Ridge National Laboratory, nominal purity 99.8%), red phosphorus, tin, and iodine (all from Merck, "rein"). The red phosphorus was purified by boiling in diluted NaOH solution (*15*). Because of the radioactivity of ^{99}Tc

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* Dedicated to Professor A. F. Wells on his 70th birthday.

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only very small samples were prepared and the necessary precautions for working with radioactive materials were followed (*16*). For the total of 18 samples we used 0.35 g ^{99}Tc.

The samples were prepared in evacuated, sealed silica tubes in two different ways: with the tin-flux technique and with iodine as a mineralizer using annealing conditions which have been successfully applied for corresponding manganese and rhenium compounds (*4–7, 10, 12–14*). Starting compositions for samples prepared with the tin flux varied between Tc : P : Sn = 3 : 1 : 18 and 3 : 30 : 18. Thus the ratio Tc/Sn was kept at $\frac{1}{6}$ for all samples. For the samples prepared in the presence of iodine the Tc : P ratios varied between 3 : 1 and 1 : 6. About 1 to 2 mg of iodine was enclosed in the silica tubes of 0.5 to 1 cm^3 volume. All samples were heated to 1220 K within 1 or 2 days and kept at this temperature between 1 and 4 weeks. To prevent radioactive contamination of the furnace by a possible rupture of a silica tube, these tubes were sealed in another larger tube. Thus, on quenching in cold water, the inner tube with the sample took some minutes to reach room temperature. The samples prepared in the tin flux were treated for 1 day with diluted hydrochloric acid to dissolve the tin-rich matrix.

Results

Powder diffraction patterns were recorded with a Guinier camera. A total of six technetium phosphides were identified. All of them were observed in both the tin-flux samples and the samples with iodine as mineralizer. Two of them were recognized to be isotypic with known manganese or rhenium phosphides: Tc_3P which (like Mn_3P) has Fe_3P-type structure, and TcP_4 with ReP_4-type structure. A third compound which we have designated D exhibits a powder pattern similar to that of a rhenium phosphide with unknown structure.[1] The other compounds, called A, B, and C, do not seem to be isostructural with any manganese or rhenium phosphide. Rough estimates of their compositions TcP_x are $x_A \sim 0.7$, $x_B \sim 1.2$, $x_C \sim 2.0$, and $x_D \sim$

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[1] The structure of these isotype compounds was determined recently (*17*).

TABLE I

GUINIER POWDER PATTERN OF Tc_3P WITH Fe_3P-TYPE STRUCTURE[a]

hkl	Q_c	Q_0	I_c	I_0	*hkl*	Q_c	Q_0	I_c	I_0
110	218	—	2	—	330	1966	1965	50	vs
200	437	—	1	—	112	2002	2002	77	vs
101	555	552	10	vvw	240	2185	2183	0	s
220	874	—	2	—	420	2185		49	
211	992	992	0	vw	202	2220	2220	22	w
121	992		12		141	2303	2303	99	vvs
310	1092	—	2	—	411	2303		38	
130	1092	—	0	—	222	2657	2658	40	vs
301	1429	1429	37	s	510	2840	2843	0	vs
400	1748	—	3	—	150	2840		38	
002	1783	—	5	—	132	2876	2877	0	vs
231	1866	1864	59	vvs	312	2876		40	
321	1866		100						

[a] The pattern was recorded with Cu*Kα* radiation. The Q values are defined by $Q = 10^4/d^2$ (Å^{-2}). The calculated pattern was generated by a computer program (*18*) using the positional parameters of the refined structure.

TABLE II

GUINIER POWDER PATTERN OF TcP_4 WITH ReP_4-TYPE STRUCTURE[a]

hkl	Q_c	Q_0	I_c	I_0	hkl	Q_c	Q_0	I_c	I_0
002	341	340	10	w	142	2482	2482	11	w
111	460	460	52	s	115	2503	—	4	—
020	471	—	1	—	311	2516	2516	10	w
021	556	552	8	vw	025	2600	2602	5	vvw
102	598	598	12	w	043	2651	—	3	—
112	715	715	5	vvw	302	2653	2652	11	w
022	812	—	1	—	134	2679	2681	23	m
121	813	812	26	m	312	2771	2773	7	—
122	1069	—	1	—	233	2854	2855	12	w
210	1146	1145	25	m	125	2857	—	5	—
211	1231	1231	20	w	224	2861	—	1	—
023	1237	1238	100	vvs	321	2869	2869	15	w
212	1486	—	3	—	006	3065	3063	23	m
123	1494	—	1	—	322	3125	—	2	—
220	1499	1499	26	m	044	3247	—	2	—
104	1619		2	—	215	3274	3278	9	m
132	1657	1657	21	m	151	3286		16	
024	1833	—	1	—	106	3322	—	1	—
040	1884	—	1	—	135	3446	—	1	—
213	1912	1912	15	w	234	3450	3449	7	vvw
230	2088	2087	5	vvw	331	3458	—	4	—
042	2225	2225	7	vvw	144	3504	3502	11	vvw
232	2428	2429	22	m					

[a] See footnote of Table I.

3.0. The X-ray powder patterns of all six compounds are recorded in Tables I, II, and III. In both the samples prepared with iodine as mineralizer and in the series of tin-flux samples, all subsequent two-phase equilibria (Tc + Tc_3P, Tc_3P + A, etc.) were observed at 1220 K with the exception of the equilibrium B + C for which apparently no sample with intermediate starting composition was prepared.

TABLE III

INTENSITIES AND D VALUES (Å) IN GUINIER PATTERNS OF NEW TECHNETIUM PHOSPHIDES

Phase A		Phase B		Phase C		Phase D	
I_0	d_0	I_0	d_0	I_0	d_0	I_0	d_0
s	3.1127	w	4.1898	vs	5.1238	s	4.2747
w	2.8727	vw	3.3437	s	4.3616	m	3.8404
s	2.7350	m	3.1048	w	3.7112	s	3.6299
s	2.5779	vw	2.9139	s	3.4172	m	3.0755
m	2.4695	s	2.8341	m	2.9949	m	2.8679
s	2.4205	vw	2.7915	m	2.9489	s	2.6503
w	2.3988	vs	2.7528	m	2.6599	m	2.6360
vs	2.2299	vw	2.7251	vs	2.6342	s	2.6115
vs	2.2234	w	2.4759	vs	2.4036	m	2.5591
s	2.1951	vs	2.0944	s	2.3056	w	2.5361
s	2.1781	vw	2.0850	vs	2.1730	s	2.1814
m	2.0744	vs	2.0385	vs	2.1315	m	2.0180
m	2.0508	vs	1.9759	vs	2.0805	s	1.9719
m	2.0163	vs	1.9458	vs	1.9320	vs	1.8440
w	1.8733	m	1.8079	s	1.9051	m	1.7985
s	1.8198	s	1.7169	vs	1.8565	w	1.7568

Structure Refinement of Tc_3P

The X-ray powder pattern of Tc_3P resembled that of Mn_3P (*1*, *2*) with Fe_3P-type structure. The tetragonal lattice constants were refined from Guinier powder data with α-quartz (a = 4.9130, c = 5.4046 Å) as a standard: a = 9.568 ± 0.005, c = 4.736 ± 0.003 Å, c/a = 0.4950 ± 0.0006, V = 433.6 ± 0.6 Å^3. The stated variations of the lattice constants are not standard deviations, but denote the whole variation as observed in samples with different overall compositions and different preparation conditions. With $Z = 8$ formula units in the cell, the calculated density is $D_c = 10.04$ g · cm^{-3}.

The crystal used to measure the intensity data on a four-circle diffractometer had approximately globular shape with a radius of 0.05 mm. Graphite monochromatized Mo$K\alpha$ radiation was used with a scintillation counter and a pulse-height discriminator. Scans were recorded along Θ with background counts at both ends of each scan. The scan rate was variable and the optimal rate was determined by a fast prescan. A total of 2031 reflections were measured within one quadrant of reciprocal space up to $(\sin \Theta)/\lambda = 1.0$. This resulted in 1754 independent F values after averaging of equivalent reflections. Because of the small size of the crystal no absorption correction was applied ($\mu_{\mathrm{Mo}K\alpha} = 175.3$ cm^{-1}).

The structure was refined by a full-matrix least-squares program (*19*) with the starting parameters of Mn_3P (*2*) in the space group $I\bar{4}-S_4^2$. Scattering factors for neutral atoms (*20*) were used, corrected for anomalous dispersion (*21*). Weights were assigned according to counting statistics. A secondary extinction parameter was refined and applied to the calculated structure factors. As a check for the correct absolute configuration, least-squares refinements were carried out whereby the indices hkl were changed to $\bar{h}\bar{k}\bar{l}$. The resulting conventional R value was 0.0391. This compares to the value of $R = 0.0389$ assumed to be the correct configuration of the crystal investigated. Both values correspond to refinements with isotropic thermal parameters (a total of 19 variable parameters) and 1698 structure factors, excluding those with counting statistics smaller than three standard deviations. A final difference Fourier synthesis showed as extrema the values -4.0 and $+4.5$ e · Å^{-3}. Final positional and thermal parameters are given in Table IV, and observed and calculated structure factors are available upon request from the authors. Table V lists interatomic distances.

TABLE IV

POSITIONAL AND THERMAL PARAMETERS OF Tc_3P^a

	x	y	z	B (Å^2)
Tc(1)	0.08700(4)	0.10569(4)	0.2204(1)	0.34(1)
Tc(2)	0.35297(4)	0.02591(4)	0.9865(1)	0.32(1)
Tc(3)	0.17672(4)	0.21948(4)	0.7427(1)	0.37(1)
P	0.2916(1)	0.0348(1)	0.4955(3)	0.40(2)

[a] All atoms are in the general position of space group $I\bar{4}-S_4^2$. Standard deviations in the least significant digits are given in parentheses.

Structure Refinement of TcP_4

A comparison of the Guinier powder diffractogram of the most phosphorus-rich technetium phosphide with that of ReP_4 (*14*) indicated isotypy of the two compounds, which was confirmed through the subsequent structure refinement of TcP_4. The powder pattern of TcP_4 was readily indexed with the orthorhombic cell of ReP_4. Least-squares refinements with α-quartz as a standard resulted in the lattice constants $a = 6.238 \pm 0.001$, $b = 9.215 \pm 0.003$, $c = 10.837 \pm 0.003$ Å, $V = 623.0 \pm 0.1$ Å^3. The calculated density is 4.75 g · cm^{-3} assuming $Z = 8$ formula units in the cell.

For the collection of the single-crystal diffractometer data a crystal with approximately globular shape and a radius of about 0.03 mm was used. The experimental setup and the least-squares refinement procedures were similar to those described above for Tc_3P. A total of 2489 intensity data were collected, which, after averaging of equivalent reflections and omitting those with counting statistics smaller than three standard deviations, resulted in 1848 independent F values. Because of the small size of the crystal and because of the relatively small linear absorption coefficient ($\mu_{\mathrm{Mo}K\alpha} =$

TABLE V

INTERATOMIC DISTANCES IN Tc_3P[a]

Tc(1):	P	2.448	Tc(2):	P	2.400
	P	2.517		P	2.466
	Tc(1)	2.620		P	2.482
	Tc(3)	2.654		P	2.487
	Tc(2)	2.780		Tc(3)	2.652
	Tc(1)	2.791 (2×)		Tc(3)	2.736
	Tc(3)	2.814		Tc(3)	2.758
	Tc(3)	2.835		Tc(1)	2.780
	Tc(2)	2.879		Tc(2)	2.857
	Tc(3)	2.990		Tc(1)	2.879
	Tc(3)	3.015		Tc(2)	3.017 (2×)
	Tc(1)	3.231 (2×)		Tc(2)	3.211 (2×)
Tc(3):	P	2.387	P:	Tc(3)	2.387
	P	2.418		Tc(2)	2.400
	P	2.655		Tc(3)	2.418
	Tc(2)	2.652		Tc(1)	2.448
	Tc(1)	2.654		Tc(2)	2.466
	Tc(2)	2.736		Tc(2)	2.482
	Tc(2)	2.758		Tc(2)	2.487
	Tc(3)	2.813 (2×)		Tc(1)	2.517
	Tc(1)	2.814		Tc(3)	2.655
	Tc(1)	2.835			
	Tc(1)	2.990			
	Tc(1)	3.015			

[a] All distances shorter than 3.58 Å are given. Standard deviations are all 0.003 Å or less.

58.3 cm^{-1}) no absorption correction was made. As a result of this neglect, the thermal parameters obtained in the least-squares refinement are slightly too small. The structure was refined in the space group *Pbca* with the starting parameters as determined for ReP_4 (*14*). The final *R* value is 0.031 for the refinement with isotropic thermal parameters and a total of 23 variables (Table VI). A final difference Fourier analysis resulted in no peaks with less than -1.6 or more than $+1.7$ e · $Å^{-3}$. A listing of observed and calculated structure factors are available from the authors. Interatomic distances are shown in Table VII.

TABLE VI

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS OF TcP_4[a]

	x	*y*	*z*	*B* ($Å^2$)
Tc	0.12136(3)	0.10916(2)	0.07538(2)	0.173(2)
P(1)	0.05916(12)	0.28166(8)	0.23571(6)	0.297(8)
P(2)	0.19065(12)	0.94640(8)	0.23853(6)	0.306(8)
P(3)	0.75589(11)	0.04366(8)	0.08122(6)	0.287(7)
P(4)	0.49952(12)	0.20803(7)	0.06899(6)	0.302(7)

[a] All atoms are in the general position of space group *Pbca*. Standard deviations in parentheses are in the least significant digits.

TABLE VII

INTERATOMIC DISTANCES IN TcP_4[a]

Tc:	P(3)	2.334			
	P(2)	2.358			
	P(3)	2.359			
	P(1)	2.387			
	P(4)	2.421			
	P(4)	2.530			
	Tc	3.002			
P(1):	P(2)	2.177	P(3):	P(2)	2.187
	P(2)	2.193		P(4)	2.207
	P(4)	2.253		Tc	2.334
	Tc	2.387		Tc	2.359
P(2):	P(1)	2.177	P(4):	P(3)	2.207
	P(3)	2.187		P(1)	2.253
	P(1)	2.193		Tc	2.421
	Tc	2.358		Tc	2.530

[a] Standard deviations are all 0.002 Å or less. All distances shorter than 3.6 Å (for Tc atoms) or 3.1 Å (for P atoms) are listed.

Discussion

At the outset of this investigation we had hoped to prepare several new technetium phosphides, most of which we had expected to be isostructural with analogous rhenium phosphides. This could be anticipated because of the close resemblance of many other technetium and rhenium compounds (*16*, *22*). We were surprised that only TcP_4 and probably $TcP_{\sim3}$ (compound D of the present investigation) are isotypic with corresponding rhenium phosphides. Apparently there are many thermodynamically stable, or almost stable, atomic arrangements possible for phosphides of the two elements, and none of these are that overwhelmingly stable that the others get suppressed.

Tc_3P has Fe_3P-type structure which is also found for Cr_3P, Mn_3P, Ni_3P, and several other transition metal pnictides with this composition. Three other closely related structure types occur frequently for such compounds: the Ti_3P type (e.g., for Nb_3P and α-Ta_3P), the α-V_3S type (for Mo_3P and W_3P), and the β-V_3S type (for β-Ta_3P). Rundqvist *et al.* (*23*) have recently discussed these four structure types extensively. They pointed out that in these structures the coordination numbers of the phosphorus atoms decrease with increasing cohesive strength of the elemental transition metal. Thus in the series Ti_3P, V_3P, Cr_3P, Mn_3P, Fe_3P the coordination number of the phosphorus atom is lowest in V_3P, and actually vanadium has the highest melting and boiling point of the corresponding transition metals. It is gratifying to see that Tc_3P fits this rule nicely. In the second transition metal series, the highest melting and boiling point occurs for molybdenum, and the coordination numbers (CN) of the phosphorus atoms decrease first from Zr_3P (CN = 9), via Nb_3P (CN = 8(+1)) to Mo_3P (CN = 8), and increase again with Tc_3P, where the P atom has coordination number 9. The rationale for this rule is as follows: The maximum in cohesive strength of the transition metal occurs where the *d*–*d* interactions are highest. With increasing *d*–*d* interactions, a smaller fraction of the *d* states is available for bonding to the P atoms, which leads to lower coordination numbers of the P atoms. Rundqvist *et al.* (*23*) have pointed out that such a rule can only be expected to work for structures which are very closely related.

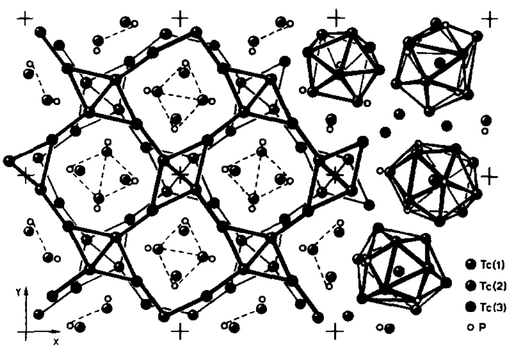

FIG. 1. Crystal structure of Tc_3P. On the left-hand side atoms at $z \sim \frac{3}{4}$ and $z \sim \frac{1}{4}$ are connected by thick and thin lines, atoms at $z \sim \frac{1}{2}$ are joined by broken lines, and atoms at $z \sim 0$ are unconnected. On the right-hand side the corodination polyhedra are drawn with all near neighbors as listed in Table V.

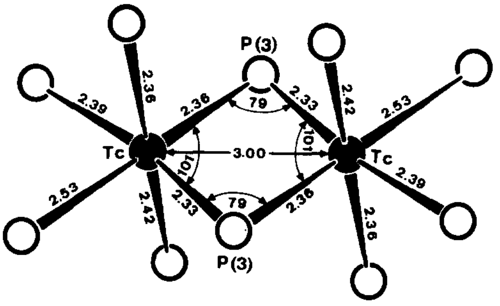

FIG. 2. Near-neighbor environments of the Tc atoms in TcP_4.

While Tc_3P has a structure with high coordination numbers for all atoms (Fig. 1), as is typical for intermetallic compounds and other electron-deficient compounds with high metal content, TcP_4 has low coordination numbers for all atoms, where all near-neighbor interactions can be rationalized with classical two-electron bonds. Thus the Tc atoms have the formal oxidation number +2 (d^5 system) and form pairs with a Tc–Tc bonding distance of 3.00 Å (Fig. 2). The compound should be diamagnetic and semiconducting, as was discussed before for isoelectronic and isotypic ReP_4 (*14*).

The lattice constants of TcP_4 and ReP_4 are very similar with *a* being greater in TcP_4, and *b* and *c* being greater in ReP_4. The slightly smaller cell volume of TcP_4 (623.0 ± 0.1 Å^3 for TcP_4 vs 623.9 ± 0.4 Å^3 for ReP_4) suggests that in these compounds the atomic volume of Tc is slightly smaller than that of Re. This need not be concluded, because varying amounts of impurities (like the incorporation of silicon from the silica tubes) could also be responsible for such small differences. However, a comparison of the interatomic distances also suggests that Tc is slightly smaller: The average Tc–P distance is 2.398_2 Å, and the average Re–P distance is 2.402_3 Å; the average P–P distances, on the other hand, are slightly larger in TcP_4 (2.203_4 Å) than in ReP_4 (2.202_0 Å). Thus the smaller cell volume of TcP_4 is only due to the smaller Tc–P distances. We note that the octahedral ionic radii (in fluorides and oxides) for various oxidation states given by Shannon (*24*) are larger for technetium than for rhenium. On the other hand, for tetrahedral oxygen coordination Tc(+7) is smaller than Re(+7) (*24*, *25*).

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References

1. O. Årstad and H. Nowotny, *Z. Phys. Chem. B* **38**, 356 (1937).

2. S. Rundqvist, *Acta Chem. Scand.* **16**, 992 (1962).

3. S. Rundqvist, *Acta Chem. Scand.* **16**, 287 (1962).

4. W. Jeitschko and P. C. Donohue, *Acta Crystallogr. Sect. B* **31**, 574 (1975).

5. D. J. Braun and W. Jeitschko, *Z. Anorg. Allg. Chem.* **445**, 157 (1978).

6. W. Jeitschko, R. Rühl, U. Krieger, and C. Heiden, *Mater. Res. Bull.* **15**, 1755 (1980).

7. R. Rühl and W. Jeitschko, *Acta Crystallogr. Sect. B* **37**, 39 (1981).

8. S. Rundqvist, *Acta Chem. Scand.* **15**, 342 (1961).

9. S. Rundqvist, *Acta Chem. Scand.* **20**, 2075 (1966).

10. W. Jeitschko and R. Rühl, unpublished results (1978).

11. R. Guérin, M. Potel, and M. Sergent, *Mater. Res. Bull.* **14**, 1335 (1979).

12. R. Rühl and W. Jeitschko, *Z. Anorg. Allg. Chem.* **466**, 171 (1980).

13. R. Rühl and W. Jeitschko, *Inorg. Chem.* **21**, 1886 (1982).

14. W. Jeitschko and R. Rühl, *Acta Crystallogr. Sect. B* **35**, 1953 (1979).

15. G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," 3rd ed., Enke, Stuttgart (1975).

16. K. Schwochau, *Chem. Ztg.* **102**, 329 (1978).

17. R. Rühl and W. Jeitschko, *Acta Crystallogr.*, in press (1982).

18. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).

19. G. Sheldrick, "SHELX 76," Program system for the determination of crystal structures (1976).

20. D. T. Cromer and J. B. Mann, *Acta Crystallogr. Sect. A* **24**, 321 (1968).

21. D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).

22. R. D. Kemmitt and R. D. Peacock, "The Chemistry of Manganese, Technetium, and Rhenium," Pergamon, New York (1973).

23. S. Rundqvist, Y. Andersson, and S. Pramatus, *J. Solid State Chem.* **28**, 41 (1979).

24. R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976).

25. B. Krebs and K.-D. Hasse, *Acta Crystallogr. Sect. B* **32**, 1334 (1976).