Inorganica Chimica Acta, 58 (1982) 143–148
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Spectroscopic Studies of Metal Ions Sorbed onto Kaolinite

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Received June 22, 1981

The electron spin resonance spectrum of a specimen of kaolinite is interpreted with the help of a survey of previous literature studies. In particular, the g = 2.0 resonance is not considered to arise from trapped organic radicals.

Surface contamination of the crystals by iron oxide species is demonstrated by staining with 2,2'-bipyridyl coupled with ^{57}Fe Mössbauer studies.

The sorption of vanadium(IV) species is considered. E.S.R. spectroscopy reveals two sites for the vanadyl(IV) species, it is suggested that both are located on the crystal surface and that one is associated with the iron oxide contaminant. A study of sorbed copper(II) leads to the suggestion that the enhanced take up of copper(II) sulphate may relate to specific sulphate-crystal edge interaction. Finally evidence is presented to indicate that hexaaquochromium(III) ions may undergo hydrolysis and release to solution after initial take up by the clay mineral.

Introduction

Interest in the ability of clays to absorb or release heavy metal ions has increased greatly in recent years [1]. The literature indicates that the mechanism of ion-exchange on the clay minerals arises from a range of different phenomena [2]. Exchanged ions are not necessarily permanently held and may be released later by being replaced by other ions.

Previous work [3] has shown that rocks rich in clay minerals, including kaolinite, which are present at waste disposal sites do have the capacity to effect large reductions in heavy metal ion concentrations within typical industrial effluents. The present work was carried out to elucidate the mechanism of ion exchange on the clay minerals. The present paper concentrates on kaolinite.

Recently Angel *et al.* [4–6] studied the e.s.r. spectra of a number of kaolinites from a variety of sources, which were both untreated and subjected to a variety of physical and chemical treatments. They reported that the e.s.r. spectrum of kaolinite contains two main groups of resonance lines centred at about g = 2.0 and g = 4.0 respectively. They suggested that a 3-line resonance centred at g = 4.0 be attributed to iron(III) replacing silicon(IV) in distorted tetrahedral sites; and the asymmetric 2-line resonance at g = 2.0 appears characteristic of an S = ½ system.

In particular [7], it has been suggested that the production of a stable paramagnetic centre (such as that which might account for the g = 2.0 signal in kaolinite) generally requires the presence of some sort of 'pre-centre' which, when irradiated, subsequently traps a hole or an electorn. The 'pre-centre' often takes the form of a foreign ion substituting within the crystal structure and requiring charge compensation. In kaolinite divalent magnesium or divalent iron substituting for trivalent aluminium may provide the necessary pre-centre for the production of a stable defect [7]. These results suggested that divalent iron might be able to perform the same function as divalent magnesium, hence when a synthetic kaolinite was doped with iron(II) the same g = 2.0 was seen after X-irradiation [8]. Thus there seems to be a reasonable evidence for the defect theory. Therefore, an understanding of the e.s.r. spectrum of the particular specimen of kaolinite used in this work is needed before the e.s.r. spectrum of adsorbed paramagnetic ions can be interpreted.

It has been suggested that the exchangeable ions are located on the broken edges of the kaolinite plates [2], where they would compensate charge deficiencies owing from broken bonds. In contrast, Van Olphen [9] has suggested that, the exchangeable cations are located on the flat-layer surfaces and compensate a net negative layer charge which is due to a small degree of isomorphous substitution. Since the basal spacing of kaolinite does not leave room for interlayer cations, all the charge-compensating cations must be adsorbed on the exterior surfaces of the stack of layers representing a particle.

This study attempts to elucidate the properties of the exchange sites of kaolinite by the method of electron spin resonance spectroscopy.

TABLE I. Mössbauer and E.S.R. Data.

Mössbauer Parameters			E.S.R. Data	
δ mm s^{-1} [a]		Δ mm s^{-1}		
Fe^{3+}	0.35	0.92	g = 2.0	g = 4.0
			and new band at	
Fe^{2+}	1.53	2.57		g = 2.115

[a] *vs.* natural iron.

Experimental and Results

Thermal Treatment

Kaolinite was heated in air for 2 h at various temperatures up to 1200 °C. Marked changes in IR and e.s.r. spectra together with change in X-ray powder data occurred for the sample heated at or above the dehydroxylation temperature. Heating to temperatures of 500 °C and above causes an extinction of the g = 2.0 resonance, together with a collapse of the low-field resonance to a single line at g = 4.0. These transitions in the e.s.r. spectra coincide with both the collapse of the kaolinite X-ray diffraction [10] pattern to the broad, diffuse band characteristic of metakaolin and to the related changes in the hydroxyl bands in the infrared spectrum. Hence this specimen shows similar properties to those used by Angel *et al.* [4].

Tests for Organic Radicals

Kaolinite (0.5 g) was covered with a solution of galvinoxyl (0.5 *M*) in benzene and stirred under nitrogen for one week. The e.s.r. spectrum of the solid was measured and no change was observed in the spectrum compared with spectrum of natural kaolinite.

The Role of Iron(II) and (III)

i) Kaolinite (10 g) was covered with nitric acid (100 ml/4 *M*), stirred for 2 h and the solid was isolated and dried at room temperature in air. This solid (2 g) was covered with a solution of 2,2'-bipyridyl (1 g) in a mixture of ethanol and water (50 ml + 50 ml) and stirred for 24 h. A pink solid was separated from the liquid phase. E.S.R. and Mössbauer spectra of this solid were measured (Table I).

ii) Kaolinite (5 g) was covered with hydrazine (50 ml) and refluxed for 2 h. The e.s.r. spectrum of the solid showed some change at g = 4.0, but no change was observed at g = 2.0.

iii) Kaolinite (1 g) was covered with distilled water (35 ml) and a 10% solution of sodium chloride (5 ml) was added. After addition of sodium dithionite (0.25 g) the mixture was stirred and heated for 15 minutes at 70 °C. This procedure was carried out eight times.

TABLE II. E.S.R. Data for Cu(II) Compounds Sorbed by Kaolinite.

Copper Compounds	g_1	g_2	g_3
Unwashed Material			
$CuSO_4$	2.080	2.140	2.240
$Cu(NO_3)_2$		g_{av} = 2.195	
Washed Material			
$Cu(NO_3)_2$	2.070	2.133	2.238
$CuSO_4$	–	2.150	2.240

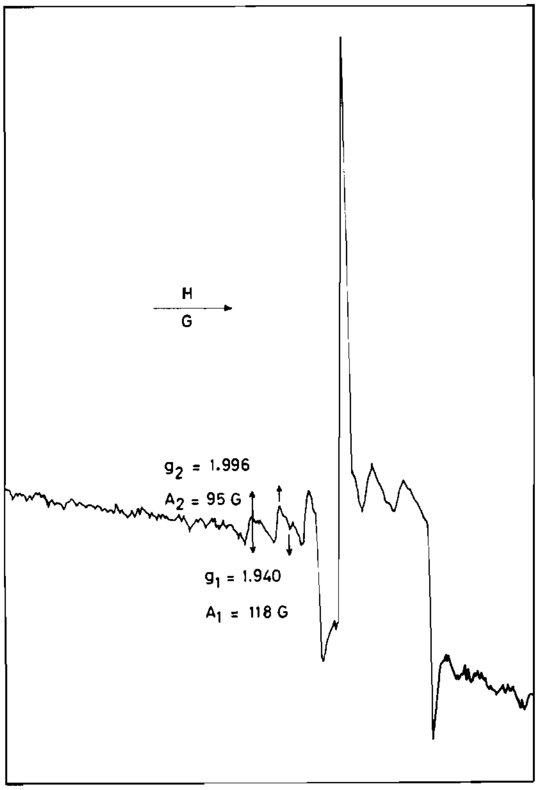


Fig. 1. Sorption of Vanadium(IV) by Kaolinite.

The first time this experiment was carried out, the e.s.r. spectrum showed extinction of the g = 2.0 resonance, however when the total procedure was repeated this observation was not reproducible.

Sorption of Metal Ions by Kaolinite

a) Vanadium(IV)

Ammonium metavanadate (1.17 g) was dissolved in concentrated (60%) perchloric acid (100 ml) and then this solution was mixed with kaolinite (10 g) in a polythene bottle and was left for one month. After this time the initial orange colour changed into green. The e.s.r. spectrum of solid showed the presence of vanadium(IV) on the kaolinite but no reduction of the g = 2.0 signal. Subsequently this solid was contacted with distilled water (100 ml) and stirred for 24 h. The e.s.r. spectrum of the washed material showed the presence of vanadium(IV), but with less intensity (Fig. 1).

b) Copper(II):

Kaolinite samples (10 g) were covered with an aqueous solution of copper(II) nitrate and copper(II) sulphate (100 ml/0.1 *M*) separately in polythene bottles and were left for one month. After this time a pale-blue solid was separated from the liquid by filtration. E.S.R. spectra of these materials were measured. Then these solids were contacted with distilled water (100 ml) and stirred for 24 h (Table II).

c) Chromium(III):

Kaolinite (10 g) was placed in a polythene bottle and covered with an aqueous solution of chromium(III) nitrate (100 ml/2000 ppm) with pH ≅ 2.0 and shaken for one to fourteen days. Solid was separated from the liquid phase and dried at room temperature in air. The amount of chromium remaining in the solution was determined using atomic absorption spectroscopy. The solid was then covered with distilled water (100 ml) and shaken for 24 h. An e.s.r. spectrum was obtained from the solid, but because of the kaolinite signal it was difficult to determine the g-factor accurately for chromium(III). A graph showing the variation in concentration of chromium in solution with time is given in (Fig. 2).

Physical Methods

Kaolinite used in this work was obtained from English China Clays Sales Co Ltd. Electron spin resonance data were obtained using a JEOL PE-1X instrument operating in the X band; g-factors were measured using a manganese(II) standard. ^{57}Fe Mössbauer spectra were measured by one of us (WRM) using equipment at Simon Fraser University, Burnaby, B.C. Canada (we are grateful to Prof. C. H. W. Jones for access to this spectrometer).

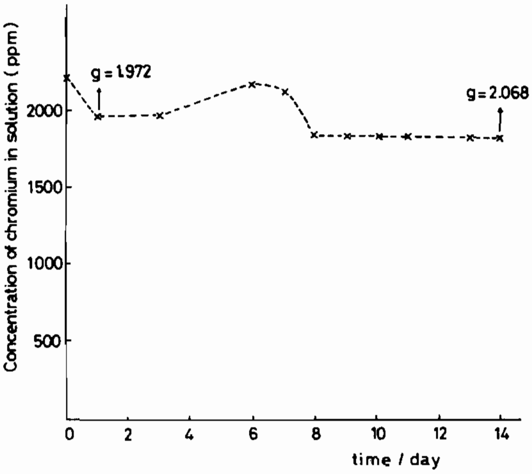


Fig. 2. Plot of uptake of chromium(III) *vs.* time.

Discussion

Kaolinites from a wide variety of locations were found to contain paramagnetic impurities which produce an e.s.r. spectrum [11] the same is true of the specimen used in this work. The spectral details are similar to those reported by Angel [4]. Thus the sample exhibited resonances A and C (Angel's labels), which are centred at g = 2.0 and g = 4.0 respectively. These resonances were not affected by treatment with nitric acid. However, when the acid treated material was treated with 2,2′-bipyridyl, the surface colour was seen to change to pink. This pink colour is attributed to the tris(2,2′-bipyridyl)-iron(II) cation. Re-examination of the e.s.r. spectrum showed that in addition to the unchanged resonances centred on g = 2.0 and g = 4.0, a new signal at g = 2.115 had materialized. The room temperature Mössbauer spectrum of this specimen has two well resolved peaks as well as a less intense unresolved central region of absorption. If the two outer peaks are taken to be both parts of a quadrupole split doublet then δ = +1.04 mm s^{-1} with respect to natural iron and Δ = 2.07 mm s^{-1}. These parameters are consistent with the presence of distorted high spin octahedral iron(II). The similarity between this spectrum and the one reported by Tricker *et al.* [12] is very great. After computation the results indicated (Table I) that there were two iron sites, the second arising from iron(III).

It was anticipated that any surface iron contaminant would be affected by chemical treatment of the kaolinite which would either modify or remove the iron species. However, when kaolinite was treated with nitric acid no removal of iron was observed. Similar results have been reported by Tricker *et al.* [12] for some other kaolinite specimens. That iron was present on the surface of the clay particles was confirmed by the 2,2′-bipyridyl treatment which produced the familiar red colour of $[Fe(bipy)_3]^{2+}$; however, the Mössbauer spectrum showed no contribution from $[Fe(bipy)_3]^{2+}$, implying that the surface concentration of iron is relatively low compared with the concentration of lattice iron. The presence of a new e.s.r. signal at g = 2.115 after acid/2,2′-bipyridyl treatment probably arises from the change in magnetic properties of the surface iron contaminant. $[Fe(bipy)_3]^{2+}$ possibly may be formed as a result of a redox reaction. This can be explained as an electron transfer across a layer of oxygen atoms in kaolinite. If this is so, then the amount of surface iron contaminant must be small because lattice iron(II) can still be seen by Mössbauer spectroscopy, but $[Fe(bipy)_3]^{2+}$ is not observed.

Heating at temperatures of 500 °C and above causes elimination of the g = 2.0 resonance, together with a collapse of the low-field resonance to give a more intense and isotropic spectrum at g = 4.0. Also one new feature, a broad band centred on g = 2.271 was observed in the e.s.r. spectrum. It is postulated that, the resonance at g = 2.0 is stable at temperatures up to about 400 °C, but at temperatures above 500 °C the collapse of the signal on dehydroxylation suggests that the paramagnetic species is more closely associated with the octahedral layer than the tetrahedral layer, which is virtually unchanged on dehydroxylation [13]. This observation is accompanied by the growth of a broad resonance at g = 2.271, which has also been seen by others [14] when surface contaminated kaolinites are heated. This is attributed to a change in the surface iron, possibly to magnetite [14]. At the same time, the single-line resonance at g = 4.0 exhibits a corresponding increase in intensity. It has been suggested [15] that this is consistent with an increase in the number of ferric ions occupying distorted tetrahedral configurations after the change in aluminium(III) coordination from six to four. These transitions in the e.s.r. spectra coincide with both the collapse of the kaolinite X-ray diffraction pattern to the broad, diffuse band characteristic of metakaolin and to the related changes in the hydroxyl bands in the infrared spectrum.

Angel's [7] explanation was accepted for the resonance at g = 2.0, however it was considered desirable to examine the possibility that trapped organic radicals could be responsible for the signal in this specimen. Interaction with galvinoxyl leaves the resonance at g = 2.0 unaffected, and this is taken to indicate that the signal does not result from organic radicals.

An investigation of the effect of reducing agents, in particular sodium dithionite, which was designed to remove surface and free iron oxide and hydroxide, failed to remove the g = 4.0 signal; however in one experiment the sharp g = 2.0 signal was lost. This experiment was not reproducible, but Angel [14] removed the resonance at g = 2.0 by heating the clay in hydrogen at 500 °C and also observed the isotropic line at g = 4.0 to increase in intensity. Thus there is some evidence that the specimen in this work also may be changed by reducing agents, but the cause of poor reproducibility remains obscure. Finally it was decided to consider hydrazine as a reducing agent. No effect on g = 2.0 was seen, but some change in g = 4.0 was noted. It has been suggested that the g = 4.0 signal may result from two iron(III) sites, hence it appears probable that the iron(III) in one of these sites is more rapidly reduced than the other.

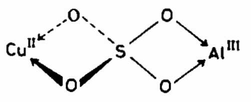
In conclusion, it appears that the specimen of kaolinite, used in this work, is broadly similar to those studied by Angel. Angel's view of the origin of the g = 2.0 and g = 4.0 e.s.r. signals is accepted, but differences of detail in other aspects of the behaviour of the specimen in the present work are noted. However, we are in a position of having a reasonable understanding of our kaolinite and may now move to a discussion of its behaviour in the presence of the metal ions solution.

a) Sorption of Vanadium(IV) by Kaolinite:

Under the experimental conditions used, reduction of vanadium(V) to vanadium(IV) occurred and the uptake of vanadium(IV) by kaolinite was confirmed by e.s.r. spectroscopy, it was also noted that the resonance at g = 2.0 was unaffected. Vanadium(IV) ($3d^1$) is a suitable species with which to probe the exchange sites of kaolinite. The observed spectrum (see experimental section) was isotropic and showed the expected eight line pattern arising from ^{51}V (I = 7/2). The g-value and hyperfine constant for this material was calculated and found to be g = 1.961 and $\langle A \rangle$ = 117.5 G, in excellent agreement with the g-value and $\langle A \rangle$ measured in the aqueous vanadyl solution [16]. When this material was washed with distilled water the signal intensity greatly reduced compared with the signal for kaolinite at g = 2.0. The residual signal however consists of two overlapping isotropic signals (Fig. 1) with g_1 = 1.940 and $\langle A_1 \rangle$ = 118 G; g_2 = 1.996 and $\langle A_2 \rangle$ = 95 G. It is reasonable to deduce that g_1, $\langle A_1 \rangle$ is due to an aqueous vanadyl species, but g_2, $\langle A_2 \rangle$ implies vanadium(IV) in a different environment. In the case of g_1, $\langle A_1 \rangle$ the aqueous vanadyl ion is freely tumbling and may be sorbed onto the surface of the kaolinite. The second signal g_2, $\langle A_2 \rangle$ which is also due to a freely tumbling species might then arise from sorption of aqueous vanadyl ion on the broken edges of the crystalline plates. Another explanation is that, as we have previously shown, some iron surface contamination is present on the kaolinite. Such iron oxide species are effective substrates for sorption of metal ions, hence we must consider that 'surface' sites may in reality also be associated with the iron oxide. McBride [17] has used e.s.r. spectroscopy to investigate kaolinite sorption sites. He concludes that the popularly held view of edge adsorption is not valid at least at acid pH. If this is accepted, then the two sites observed in the present work are likely be located on the layer surface areas of the crystals. One may well be a pure kaolinite site the other associated with surface iron. Also, in agreement with McBride, we note that under normal humidity conditions, all exchange sites seem to offer solution type environments to the metal ion.

b) Sorption of Copper(II) Ion:

Kaolinite was covered with copper(II) nitrate and copper(II) sulphate separately and left for one month. E.S.R. measurement of the solids showed an isotropic spectrum for copper(II) nitrate which can be due to $[Cu(H_2O)_6]^{2+}$ species. The anisotropic signal found for copper(II) sulphate might be due to sorption of a sulphato-complex on the edge of crystals. When these materials were washed with distilled water, a complex signal was observed for copper(II) nitrate which could be an anisotropic resonance (Table II). Alternatively it may arise from the two overlapping isotropic signals of copper(II) ions sorbed in two distinct sites similar to that observation for aqueous vanadium(IV) and following the view of McBride [17]. In the case of copper(II) sulphate a broad signal with a shoulder was observed. Possibly this can be explained following the nitrate argument, or it could be specific edge sorption encouraged by the sulphate anion. Sulphate with two negative charges may have a good affinity for the positive edge of the clay crystal and this could enhance adsorption. Thus, SO_4^{2-} has the correct stereochemistry to interact with the crystal edge:



The copper(II) may now have an enhanced affinity for the edge as shown in the above figure.

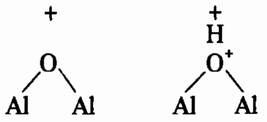
c) Sorption of Chromium(III) Ions:

It has been reported [18] that hydrolytic reactions may occur before or after the sorption of metal ions by clay minerals, e.g. (Cu(II) may be taken up as 'Cu^{II}(OH)$^{+}$'). It is difficult to clearly resolve whether the hydrolytic species are formed in solution or produced *in situ* after sorption of the hydrated ion at specific sites. To consider this phenomenon chromium(III) is potentially useful because of the slow reaction behaviour (kinetically inert). For these experiments kaolinite was covered with an acidic solution of chromium(III) (pH ≅ 2) and stirred from 1–14 days after which the chromium(III) remaining in the solution was determined by atomic absorption, and e.s.r. spectroscopy was used to detect the sorption of chromium(III) onto the clay. When the 'exchanged' kaolinite was in contact with distilled water for 24 h some of the chromium(III) was released into the solution as shown by atomic absorption analysis.

A plot of uptake of chromium(III) against time (Fig. 2) agrees well with that reported by Carter [3]. Thus an initial fairly rapid uptake is followed by a period in which chromium is released to the solution after which a new equilibrium appears to be established. Much of the chromium(III) taken up is labile as demonstrated by the fact that it is released into pure water. This observation is considered to result from simple sorption onto the surface of kaolinite crystals. The small release of iron detected by atomic absorption may arise from the surface contaminant detected in the previous section. Indeed this contaminant may play an active role in the uptake of metal ions since one of our group has demonstrated [19] quite remarkable affinities for cations to exist for various hydrated iron oxides of the type found in some geological environments. It is suggested that initial rapid adsorption occurs on the surface of the kaolinite. Chromium(III), as the $[Cr(H_2O)_6]^{3+}$ species, will be efficiently adsorbed because of high charge. When the chromium(III) ion is attached to the clay mineral, deprotonation of the hydrated ion may occur, in which a hydrogen ion is lost from one of the water molecules acting as ligands. The effect would be to reduce the charge in the chromium, thus making the ion less competitive for occupation of exchange sites. A reduction in the rate of adsorption of chromium(III) can thus result after a period of time. Indeed new equilibria will have to be established and the curve shown in (Fig. 2) becomes understandable in these terms.

The e.s.r. spectrum initially showed an extremely broad signal at g = 1.972. A g-factor for 1.976 has been reported [20] for $[Cr(H_2O)_6]^{3+}$ species. The environment of the chromium(III) ions thus is obviously similar on the clay surface to that in $[Cr(H_2O)_6]^{3+}$, the isotropic signal may indicate a solution-like environment on the clay, but the breadth of the line suggests that the chromium ions may not be well separated, this would of course be the case if the surface iron compounds were involved in the sorption process. With time, the g-factor changed to 2.068 (14 days see Fig. 2), hence we may deduce that some change in the chromium environment has occurred. This is entirely consistent with the view that hydrolytic reactions may occur on the clay. Also use of the kinetically inert species supports the view that this might be generally the case. There would certainly be no shortage of proton acceptor sites on the clay and this might enhance the essential deprotonation step:

e.g. $[Cr(H_2O)_6]^{3+} \rightarrow [Cr(H_2O)_5(OH)]^{2+}$



After this dimers and oligomers may rapidly form accounting for both the enhanced breadth of the e.s.r. signal and also for the shift in g-factor.

References

1 H. Farrah, D. Hatton and W. F. Pickering, *Chem. Geol., 28,* 55 (1980).
2 R. E. Grim, 'Clay Mineralogy', McGraw-Hill (New York), (1953).
3 M. Carter, Ph.D. Thesis, The University of Aston in Birmingham, (1975).
4 B. R. Angel and P. L. Hall, *Proc. Int. Clay Conf., P47,* 71 (1972).
5 P. L. Hall, B. R. Angel and J. Braven, *Chem. Geol., 13,* 97 (1974).
6 J. P. E. Jones, Ph.D. Thesis, University of London (1974).
7 B. R. Angel, A. H. Cuttler, K. S. Richards and W. E. J. Vincent, *Clays Clay Min., 25,* 381 (1977).
8 B. R. Angel, J. P. E. Jones and P. L. Hall, *Clay Miner., 10* (1) 247 (1974).
9 H. Van Olphen, 'An Introduction to Clay Colloid Chemistry', 2nd Edition, Houston Texas, (1963).
10 G. B. Mitra and S. Bhattacherjee, *Am. Mineralogist, 54,* 1409 (1969).
11 E. Boesman and D. Schoemaker, *C.R. Acad Sci., 252,* 1931 (1961).
12 D. A. Jefferson, M. J. Tricker and A. P. Winterbottom, *Clays Clay Min., 23,* 355 (1975).
13 R. W. Grimshaw, 'The Chemistry and Physics of Clays and Other Ceramic Materials', 4th Edition, Benn, (1971).
14 B. R. Angel and W. E. J. Vincent, *Clays Clay Min., 26 (4) 263 (1978).*
15 G. W. Brindley and M. Nakahira, *J. Am. Ceram. Soc., 42,* 311 (1959).
16 R. N. Rogers and G. E. Pake, *J. Chem. Phys., 33,* 1107 (1960).
17 M. B. McBride, *Clays Clay Min., 24,* 88 (1976).
18 W. F. Pickering, *Copper Environ., Part 1,* 217 (1979).
19 A. Park, unpublished work, 1980.
20 H. Levanon, S. Charbinsky and Z. Luz, *J. Chem. Phys., 53,* 3056 (1970).