Manganese valency and the colour of the Mn$_2$AsO$_4$(OH) polymorphs eveite and sarkinite

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ABSTRACT

Polarized optical absorption spectra of single crystals of the two dimorphic Mn$_2$AsO$_4$(OH)-minerals eveite and sarkinite show that minor concentrations of Mn^{3+} at the octahedral site determine the colour and cause the distinct pleochroism in green and yellow of eveite. In the sarkinite spectra only absorption bands due to spin-forbidden $d-d$ transitions in Mn^{2+} at six- and five-coordinated sites are observed, which produce a weak flesh-red mineral colour and a very faint pleochroism.

KEYWORDS: eveite, sarkinite, optical spectroscopy, Långban, Sweden.

Introduction

EVEITE and sarkinite, two naturally occurring polymorphs of Mn$_2$AsO$_4$(OH), display contrasting properties which reflect their different structural character. Eveite, which is a member of the orthorhombic adamite group and thus is structurally related to the rock-forming silicate andalusite (Moore and Smythe, 1968) has, e.g. considerably lower density than the closer packed monoclinic sarkinite (Fig. 1), which is structurally related to wagnerite (Dal Negro et al., 1974). However, the causes for the contrasting colours observed for the two minerals are less obvious. In spite of large similarities with respect to Mn^{2+} coordination, sarkinite is faintly pleochroic in flesh-red hues while eveite displays a distinct pleochroism with X(a) = Z(b) = green and Y(c) = yellow. In eveite there is one Mn-centred octahedral site and one independent five-coordinated Mn-site, while in sarkinite there are four independent octahedral Mn-sites as well as four unique five-coordinated Mn-centered sites. The individual octahedral sites in the two minerals are comparable, each displaying two OH-ligands in cis-configuration, and mean $M-L$ distances in the

range 2.19–2.23 Å. The trigonal bipyramidal sites in the two minerals also show comparable features including the presence of one OH-ligand and mean $M-L$ distances ranging from 2.11 to 2.15 Å. The observed difference in colour was commented on by Moore (1968), who ascribed it to a possibly higher crystal field strength at the Mn-sites in eveite as compared to the Mn-sites in sarkinite. In the present study polarized crystal field spectra of chemically well-characterized single crystals of eveite and sarkinite have been recorded with the aim to shed some light on the effects responsible for the observed colour difference.

Materials and methods

Natural single crystals of eveite (NRM # 390271) and sarkinite (NRM # 741004) from Långban, Sweden were ground and polished to produce self-supporting double-sided polished thin sections. The crystals used were selected on the basis of their crystal morphology, transparency and lack of inclusions. Two eveite crystal sections (cut perpendicular to (010) and (001)) were prepared, while three sections (cut
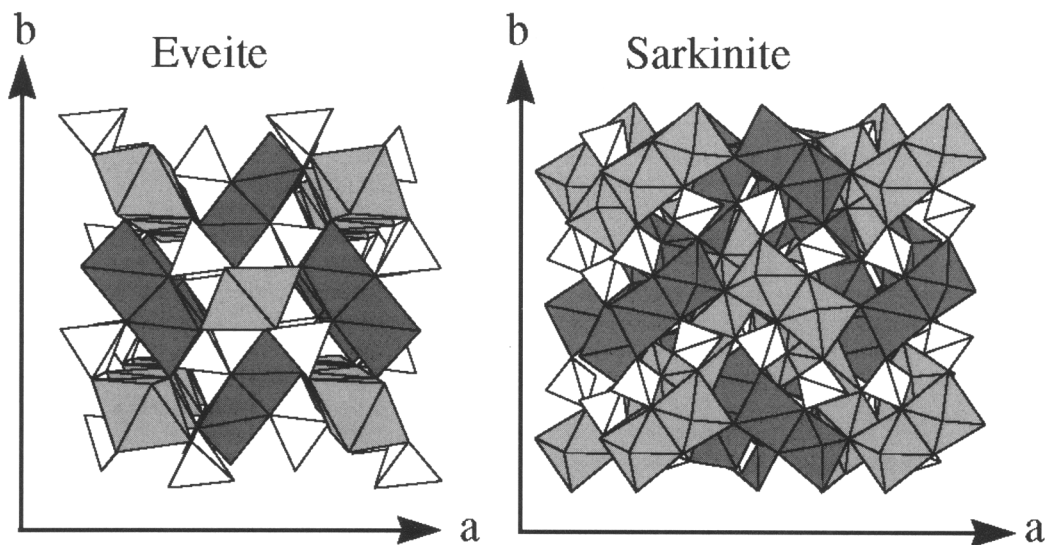
b Eveite

b Sarkinite

FIG. 1. The crystal structure of eveite and sarkinite projected on (001). Strongly shaded, intermediately shaded and open polyhedra represent five-coordinated Mn-centred sites, Mn-octahedra and As-tetrahedra, respectively.

perpendicular to (100), (010) and (001)) were prepared from three sarkinite crystals. The orientation of the crystal sections were confirmed by means of crystal morphology and conoscopic microscopy. As determined by means of digital micrometer measurements the thickness of the eveite absorbers were 265 and 266 μm and the sarkinite absorbers were 530, 560 and 753 μm. In addition to this, approximately 2 mg of each mineral was separated under a binocular microscope and ground to a powder suitable for FTIR-measurements.

The self-supporting crystal sections were measured in polarized light by optical microscope-spectrometry in the range 333−2,000 nm (30 000−5000 cm^{-1}) using a Zeiss MPM 800-instrument. The general instrumental set up (light sources, lenses, monochromators, detectors and polarizers) in the different wavelength regions has been described by Hålenius and Lindqvist (1996). In the present study the spectral slit widths adopted were 1 nm in the range 333−800 nm and 5 nm in the range 800−2,000 nm. The field aperture and the object aperture were in all measurements 100 and 60 μm, respectively. The measurements were performed at ambient temperature and air served as a reference medium. Raw spectra were analysed by means of peak resolution using the Peak Fit 4 computer

program under the assumption of Gaussian band shapes.

Subsequent to the optical absorption measurements the five absorbers were analysed at the spots used for these recordings by means of a Cameca SX50-microprobe running at an acceleration voltage of 20 kV and a sample current of 12.0 nA. At each spot 7−8 analyses were performed. Standard samples included synthetic CaSiO$_3$ (Ca), Cu-metal (Cu), Fe$_2$O$_3$ (Fe), GaAs (As), MgO (Mg), MnTiO$_3$ (Mn, Ti), ZnS (Zn) and natural vanadinite (Cl). Neither Ti nor Cl were found in detectable concentrations. Corrections of raw data were performed by means of the ZAF-related PAP-program (Pouchou and Pichoir, 1984).

Fourier Transform Infrared (FTIR) spectra of the separated mineral powders were obtained with a Biorad-instrument using Nujol emulsions placed on a transparent CaF$_2$ disc. The spectra were recorded during 64 cycles at a spectral resolution of 2 cm^{-1}.

Results

The chemical analyses of the two eveite and three sarkinite crystals are summarized in Table 1. The obtained analyses show that the crystals used in the present study are compositionally very close

TABLE 1. Electron microprobe analyses of sarkinite and eveite

	Sarkinite A N = 8	Sarkinite B N = 8	Sarkinite C N = 8	Eveite A N = 7	Eveite B N = 8
As$_2$O$_5$	44.09	44.41	44.23	43.34	42.44
MgO	0.19	0.15	0.19	1.78	0.50
CaO	0.29	0.25	0.29	0.32	0.68
MnO	51.77	51.52	51.49	49.26	51.32
FeO	0.02	0.02	0.02	0.02	0.00
CuO	0.01	0.00	0.01	0.01	0.00
ZnO	0.15	0.08	0.10	0.00	0.02
H$_2$O$_{calc}$	3.40	3.40	3.40	3.38	3.34
Total	99.93	99.84	99.72	98.10	98.29
Cations on the basis of 9 negative charges					
As	1.015	1.022	1.019	1.006	0.994
Mg	0.013	0.010	0.013	0.118	0.033
Ca	0.014	0.012	0.014	0.015	0.032
Mn	1.931	1.920	1.922	1.852	1.948
Fe	0.001	0.001	0.001	0.001	0.000
Cu	0.000	0.000	0.000	0.000	0.000
Zn	0.005	0.003	0.003	0.000	0.001

to the nominal mineral chemistry. The analyses also confirm the chemical homogeneity of the individual crystals. Substitutions at the Mn-sites are limited and mainly restricted to Ca and Mg proxying for Mn. The total extent of the substitutions is less than 7% in the present samples. The eveite analyses also show a low oxide sum, apart from the presence of detectable concentrations of Mg, which were not observed in previous analyses of the mineral (Moore, 1968). The only microprobe analyses of eveite so far published (Moore,1968) similarly display low totals. A series of WDS-scans on the present eveite crystals down to Z = 10 did not reveal detectable concentrations of any elements other than those reported in Table 1.

The recorded polarized optical absorption spectra of eveite (E//X(a), E//Y(c) and E//Z(b)) and sarkinite (E//X, E//Y(b), E//Z, E//a and E//c) are illustrated in Figs 2 and 3. Due to the non-orthogonality of the sarkinite cell five polarized spectra were recorded in order to obtain a complete absorption character (see, e.g. Dowty, 1978). The sarkinite spectra which are weakly polarized show a number of sharp to relatively sharp absorption bands in the UV−VIS spectral range. A very similar set of absorption bands are also observed in the eveite spectra, although the

absorption bands in the UV-region are less well-resolved due to stronger L−M absorption, which pushes the UV-absorption edge further into the visible spectral region. In addition to these absorption bands, which are common to the two
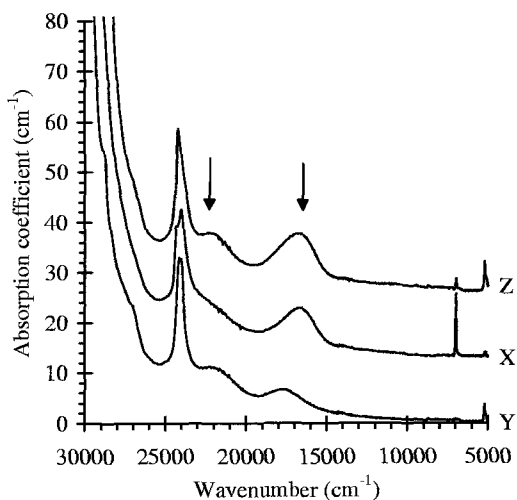

FIG. 2. Polarized absorption spectra of eveite. Arrows indicate absorption bands assigned to trivalent manganese. The X- and Z-spectra are for the sake of clarity offset with respect to the absorption baseline.
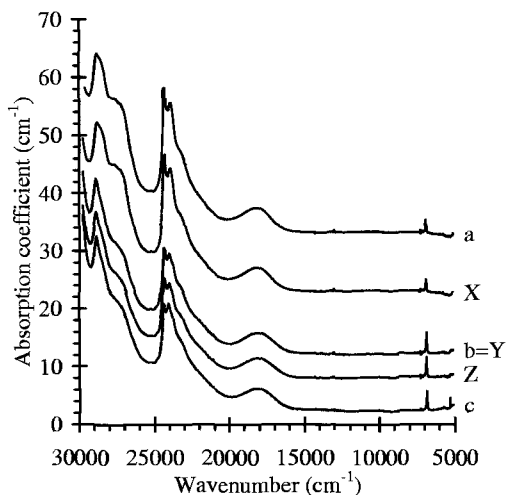
FIG. 3. Polarized absorption spectra of sarkinite. All spectra except E//c are offset with respect to the absorption baseline.

FIG. 4. Unpolarized powder FTIR absorption spectra of eveite and sarkinite.

minerals, the eveite spectra reveal two absorption bands at 22160 and 16485 cm^{-1}. These two broader bands are distinctly anisotropic and they determine the colour and pleochroism of eveite. In addition to the bands in the UV and visible spectral ranges there are two strongly polarized narrow absorption features in the NIR-range of the eveite spectra at 6965 cm^{-1} and at 5200 cm^{-1}. In the sarkinite spectra just one polarized NIR-absorption feature at approximately 6920 cm^{-1} is recorded. This feature is, from detailed recordings at a spectral resolution of 2 nm, demonstrated to be composed of at least four absorption bands at 6855, 6875, 6915 and 6940 cm^{-1}. All the NIR-bands in the spectra of the two minerals are distinctly anisotropic.

The FTIR-spectrum of eveite (Fig. 4) is characterized by one sharp absorption band at 3560 cm^{-1} and two broad and less intense bands at 3340 and 3450 cm^{-1}. In the FTIR-spectrum of sarkinite (Fig. 4) a set of overlapping sharp absorption bands centred at 3505, 3515, 3525 and 3535 cm^{-1} are evident.

Discussion

In view of the nominally identical set-up of transition metal cations (Mn^{2+}) and the similarities in symmetry and geometry 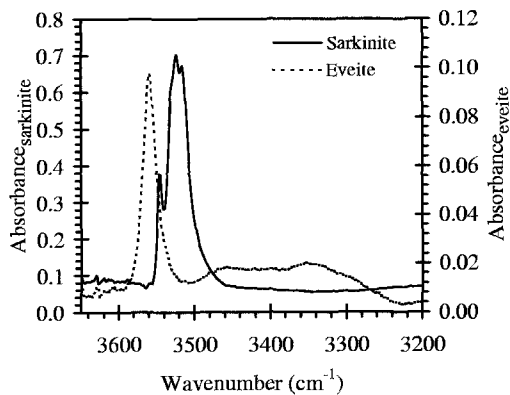of the Mn-centred sites in the two minerals one would expect absorption spectra of the two minerals to be very similar, with possibly only minor shifts in peak positions and band intensities. With the exception of the absorption bands at 22160 and 16485 cm^{-1}, and a stronger UV-absorption in the eveite spectra, the strong similarities in the spectral character of the two minerals are indeed evident. The absorption bands in common to the two minerals are all relatively weak ($\varepsilon <$ 0.8 l/mole·cm) and have energies and band widths comparable to those recorded in a large number of Mn^{2+}-bearing minerals (Rossman, 1988a; Burns, 1993). These bands are tentatively assigned to different spin-forbidden $d-d$ transitions in divalent manganese at six- and five-coordinated sites (Fig. 5 and Table 2). In this assignment scheme, the Racah B- and C-parameters for six-coordinated Mn^{2+} in eveite are calculated at 639 and 3583 cm^{-1}, respectively, and in sarkinite at 646 and 3578 cm^{-1}, respectively. For the five-coordinated divalent manganese, B- and C-values are determined to be 623 and 3550 cm^{-1} in eveite and 619 and 3563 cm^{-1} in sarkinite. The crystal field splitting parameter Dq for divalent manganese at the five-coordinated sites in eveite and sarkinite, 556 and 569 cm^{-1}, are found to be considerably smaller than for the six-coordinated manganese, 907 and 902 cm^{-1}, in the two minerals. For this assignment the resulting Dq-ratio for Mn^{2+} at the two different types of coordination sites is ~0.62, which is very close to the theoretical ratio of 0.52 (Burns, 1993).This theoretical value is based on coordination sites having equal $M-L$ distances. As the $M-L$ distances of the five-coordinated sites in eveite
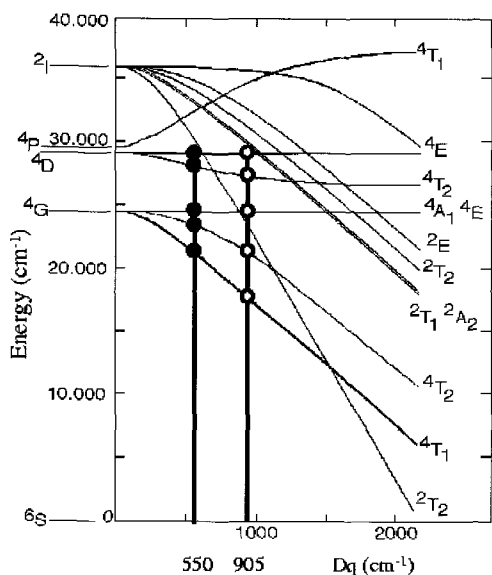
FIG. 5. Energy level diagram of Mn^{2+} (d^5) with B = 664 and C = 3560 cm^{-1} (Modified from Moore and White, 1972). Vertical lines and open and filled circles indicate the approximate positions of bands caused by six- and five-coordinated Mn^{2+}, respectively, in eveite and sarkinite.

and sarkinite are slightly shorter than those of the six-coordinated sites, the Dq$_V$/Dq$_{VI}$-ratios in the present cases are expected to be 10−30 % higher. The lower B-values found for Mn^{2+} at the five-coordinated sites as compared to the octahedrally

bonded divalent manganese, indicate a slightly higher degree of covalent bonding, which is consistent with the shorter M−L distances for the five-coordinated sites.

Alternative Mn^{2+}-assignment models, including the eveite spectral bands at 16 485 and 22 160 cm^{-1} were explored in addition to the one presented in Table 2 and Fig. 5. These additional schemes yielded unreasonably high Dq-values for five-coordinated Mn^{2+} in eveite, which equalled or even exceeded those obtained for divalent manganese at the six-coordinated sites of the two arsenates. Considering the strongly similar Mn^{2+}-coordination in terms of site geometries, ligand types and next-nearest neighbours in the two minerals, as well as the theoretically predicted Dq$_V$/Dq$_{VI}$-relationship, the parameters obtained from the alternative assigment models seem unrealistic and so these models are judged to be less likely than the one presented in Table 2 and Fig. 5.

The two additional absorption bands observed at 22 160 and 16 485 cm^{-1} in the eveite spectra, and which cause the colour and pleochroism of the mineral, are thus obviously not related to divalent manganese at the five- or six-coordinated site. Furthermore, the EMP-analyses of the present eveite crystals show that no other 3d-elements other than Mn are present in concentrations likely to produce detectable absorption bands. Even an assumed and highly overestimated ε-value of 200 l/ mole·cm for a potential Fe^{2+}-band in eveite, in combination with the observed maximum FeO-concentration of 0.02 wt.% would result in bands with extinction coefficients of < 2.0 cm^{-1}.

TABLE 2. Band positions and assignments

Band energy (cm^{-1})		Band assignment	
Sarkinite	Eveite	Cation	Transition
28 870	28 770	Mn^{2+}[VI]	^{6}A$_{1g}$(S)→ ^{4}E(D)
28 330	28 340	Mn^{2+}[V]	^{6}A$_{1g}$(S)→ ^{4}E(D)
27 610	27 630	Mn^{2+}[V]	^{6}A$_{1g}$(S)→ ^{4}T$_2$(D)
27 070	26 950	Mn^{2+}[VI]	^{6}A$_{1g}$(S)→ ^{4}T$_2$(D)
24 350	24 300	Mn^{2+}[VI]	^{6}A$_{1g}$(S)→ ^{4}A$_1$^{4}E(G)
24 000	23 980	Mn^{2+}[V]	^{6}A$_{1g}$(S)→ ^{4}A$_1$^{4}E(G)
23 150	23 570	Mn^{2+}[V]	^{6}A$_{1g}$(S)→ ^{4}T$_2$(G)
–	22 160	Mn^{3+}[VI]	^{5}B$_{1g}$(D)→ ^{5}B$_{2g}$(D)
21 800	–	Mn^{2+}[VI]	^{6}A$_{1g}$(S)→ ^{4}T$_2$(G)
21 000	21 470	Mn^{2+}[V]	^{6}A$_{1g}$(S)→ ^{4}T$_1$(G)
18 190	18 130	Mn^{2+}[VI]	^{6}A$_{1g}$(S)→ ^{4}T$_1$(G)
–	16 485	Mn^{3+}[VI]	^{5}B$_{1g}$(D)→ ^{5}A$_{1g}$(D)

Obviously the cause for the two strong (approaching 10 cm^{-1}), relatively broad ($\omega_{1/2}$ approximately 2000 cm^{-1}) and anisotropic bands in the visible region of the eveite spectra must be sought elsewhere. In the absence of significant concentrations of additional 3d-elements only one likely alternative remains, i.e. a fraction of the manganese is present in the trivalent state. The broadness of the two bands, their strong polarization as well as their energies are also consistent with an assignment to spin-allowed $d-d$ transitions in trivalent manganese. The band energies are comparable to those observed for spin-allowed $d-d$ bands in Mn^{3+} at distorted octahedral sites in a number of minerals (Burns, 1993), and in particular to the Mn^{3+}-bands (22 100 and 16 000 cm^{-1}) recorded in the spectra of the isostructural mineral kanonaite (Smith *et al.*, 1982). In analogy with the observed ordering of the Jahn-Teller cation Cu^{2+} (3d^9) in isostructural Cu-substituted adamite (Chisholm, 1985) it is proposed that Mn^{3+} (3d^4), which is also susceptible to large Jahn-Teller distortions, has a strong preference for the octahedral site in eveite. Taking an ε-value of 200 l/mole·cm, which corresponds to the upper limit of ε-values observed for spin-allowed Mn^{3+} $d-d$ bands at the octahedral site in the isostructural mineral kanonaite (Smith *et al.*, 1982), the concentration of Mn_2O_3 in the present eveite samples is calculated to be ~0.10 wt.%. Based on the present assignment of trivalent manganese exclusively to the octahedral site in eveite, this implies that only 0.4% of the octahedra are Mn^{3+}-centred and the remaining 99.6% are mainly occupied by Mn^{2+}. A number of coupled cation substitutions for incorporating trivalent cations under charge balance conditions in eveite are possible. These alternatives involve the presence of reduced As-cation species, dehydroxylation and cation vacancies. The IR-spectrum of eveite does not show any evidence for As^{3+}-clusters, which possess IR-active modes that should give rise to absorption bands at energies lower than bands caused by As^{5+}-clusters. On the other hand it is questionable if the low concentrations of As^{3+} required to enable the minor degree of Mn^{3+}-incorporation would be detectable in the IR-spectrum. It is concluded that it is not possible on the basis of the present data sets to unequivocally assign a mechanism for the substitution of trivalent Mn in eveite. An on-going laser Raman study with the aim to obtain information on the As valence state distribution in eveite may give some further useful results.

The sharp IR-band recorded at 3560 cm^{-1} in the powder spectrum of eveite is in accordance with previous studies on the isostructural Zn-arsenate adamite assigned to a stretching mode of the structural OH-group (Braithwaite, 1983). The slightly higher energy of the OH-stretching band in eveite as compared to adamite (3540 cm^{-1}, from Braithwaite, 1983) is ascribed to the lower electronegativity of Mn relative to Zn. The absorption bands found between 3400 and 3600 cm^{-1} in the sarkinite IR-spectrum are also assigned to OH-stretching modes. The more complex IR-absorption in sarkinite, which displays a number of overlapping OH-bands, is explained by the fact that in sarkinite there are four independent OH-ligands as compared to one in adamite. The absorption bands recorded in the NIR-spectra of both minerals between 6800 and 7000 cm^{-1} represent overtones of the fundamental OH-stretching modes. The very pronounced pleochroism of the OH-stretching overtone in eveite (E||a>>E||b>E||c) is in agreement with the major alignment of the O−H vector along the *a*-direction determined by X-ray structural refinement of the isostructural mineral adamite (Hill, 1976).

In addition to the sharp bands representing fundamental frequencies and overtones of the OH-stretching modes there are two absorption features observed in the NIR and IR-spectra of eveite that suggest that structurally bound H_2O-molecules are present. The distinctly polarized absorption band at 5200 cm^{-1} observed in the single crystal spectra and the two broad bands at 3340 and 3450 cm^{-1} in the eveite powder spectrum display band features (energies and band widths) typical for H_2O-combination modes (bend+stretch) and OH-stretching modes, respectively, in water (Rossman, 1988*b*). This indication of additional water molecules in the structure may be one explanation for the low oxide sums obtained from the EMP-analyses of eveite.

Conclusions

The colour and pleochroism of eveite is mainly determined by the presence of two distinctly anisotropic absorption bands at 22 160 and 16 485 cm^{-1}, which are caused by spin-allowed $d-d$ transitions in six-coordinated trivalent Mn. Remaining absorption bands in the UV−VIS spectral region in eveite are caused by spin-forbidden $d-d$ transitions in Mn^{2+} at the five- and

six-coordinated sites. In the optical absorption spectra of sarkinite all bands in the same spectral range are assignable to divalent manganese at comparable five- and six-coordinated cation positions. The main cause for the distinct difference in colour between the two $Mn_2AsO_4(OH)$-polymorphs is the presence of small amounts of Mn^{3+} in eveite.

The presence of structurally bound H_2O in eveite has been indicated by NIR-spectra of single crystals as well as by IR-spectra of powdered samples. The low analytical sums recorded for the mineral by EMP-methods may be partially due to the presence of water molecules.

Acknowledgements

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