Eur. J. Mineral.
2010, **22**, 453–457

Discreditation of ‘‘orthobrochantite’’ (IMA 78–64) as the MDO_1 polytype of brochantite

Stuart J. MILLS[1,2,*], Anthony R. KAMPF[3], Marco PASERO[4] and Stefano MERLINO[4]

[1] Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, BC, V6T 1Z4, Canada
[2] Geosciences Section, Museum Victoria, GPO Box 666, Melbourne, Victoria, 3001, Australia
*Corresponding author, e-mail: smills@eos.ubc.ca
[3] Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA
[4] Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 56126, Pisa, Italy

Abstract: ‘‘Orthobrochantite,’’ IMA 78–64, was originally approved by the Commission on New Minerals, Nomenclature and Classification (IMA) as the orthorhombic polymorph of brochantite. Described by Wilson W. Crook III and Stanley G. Oswald from the Douglas Hill mine, Yerington, Nevada, USA, the mineral description was never formally published; however, the name and some data have been widely available since the late 1970s. Investigation of material from the Douglas Hill mine shows ‘‘orthobrochantite’’ to consist mostly of the MDO_1 polytype of brochantite, but probably also to contain small domains of the MDO_2 polytype. The crystal structure of the MDO_1 polytype [$a = 13.1117(4)$, $b = 9.8654(4)$, $c = 6.0307(9)$ Å, $\beta = 103.255(7)^\circ$ and $V = 759.31(12)$ Å^3] has been refined to $R_1 = 6.37$ % for 1245 unique reflections [$F_o > 4\sigma F$] and 8.83 % for all 1724 reflections. The incorrect unit cell for ‘‘orthobrochantite’’ is either due to the choice of the *B*-centered pseudo-orthorhombic cell, which is virtually identical to the MDO_1 cell, or indexing based on {100} twinning of the MDO_1 polytype. New optical determinations for ‘‘orthobrochantite’’ suggest that the indices of refraction reported by Crook and Oswald were significantly in error.

Key-words: orthobrochantite, brochantite, polytype, Douglas Hill mine, IMA–CNMNC, discreditation.

1. Introduction

Only a handful of minerals which have been approved since the Commission on New Minerals, Nomenclature and Classification (IMA) began its work about 50 years ago remain unpublished. In a systematic approach to investigating the validity of these unpublished minerals, we obtained samples of ‘‘orthobrochantite,’’ IMA 78–64, for investigation and report the findings here. The mineral description was submitted by Wilson W. Crook III and Stanley G. Oswald based upon crystals from the Douglas Hill mine, Yerington, Nevada, USA and was unanimously approved by the Commission in 1978. ‘‘Orthobrochantite’’ was approved based on the orthorhombic cell: $a = 25.579(6)$, $b = 9.865(4)$ and $c = 6.058(2)$ Å and the fact that the powder X-ray diffraction (PXRD) pattern included lines that were not present in the published brochantite patterns. The formal description of ‘‘orthobrochantite’’ was never published, but both the name and specimens have been in general circulation since the late 1970s.

Brochantite, $Cu_4SO_4(OH)_6$, is a common secondary mineral typically formed from the alteration of primary copper sulphides (Woods & Garrels, 1986) and is found in hundreds of locations worldwide (*e.g.*, Anthony *et al.*, 2003). Because of its abundance, brochantite has been the subject of much research. Merlino *et al.* (2003) recently demonstrated the order–disorder (OD) character of brochantite, and solved the crystal structures of the MDO_1 and MDO_2 monoclinic polytypes. The present study provides important information for re-examining the status of ‘‘orthobrochantite’’ and provides the formal discreditation, which was approved by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) prior to publication (Voting Proposal 09–E).

2. Experimental procedure

2.1. Sample provenance

According to the new mineral proposal (IMA 78–64), type material was to be deposited in the U. S. National Museum of Natural History (NMNH), Washington D.C., USA.

0935-1221/10/0022-2029 $ 2.25
DOI: 10.1127/0935-1221/2010/0022-2029

Table 1. Comparative data for ‘‘orthobrochantite’’ and brochantite.

	‘‘Orthobrochantite’’		Brochantite[a]	
	Original data	New data		
Formula	$Cu_4SO_4(OH)_6$	$Cu_4SO_4(OH)_6$	$Cu_4SO_4(OH)_6$	
Polytype	–	MDO_1	MDO_1	MDO_2
Space group	$P2_12_12_1$	$P2_1/a$	$P2_1/a$	$P2_1/n$
a Å	25.579(6)	13.1117(4)	13.140(2)	12.776(2)
b Å	9.865(4)	9.8654(4)	9.863(2)	9.869(2)
c Å	6.058(2)	6.0307(9)	6.024(1)	6.026(1)
β	–	103.255(7)°	103.16(3)°	$\alpha = 90.15(3)°$
D_{meas}, D_{calc}	3.968(5), 3.919[b]	nd, 3.945[b]	3.97, 4.09	
Optics				
α	1.769(2)	1.727(2)	1.728	
β	1.797(2)	1.768(2)	1.771	
γ	1.814(2)	1.795(2)	1.800	
$2V$ (meas.)	72°–74°	77(2)°	77(2)°	
Orientation	$X = a, Y = b, Z = c$	$X \approx a, Y = b, Z = c$	$X \approx a, Y = b, Z = c$	
X (color)	Pale blue-green	Bluish-green $X \approx Y < Z$	Bluish-greens (slightly pleochroic)	
Y (color)	Blue-green			
Z (color)	Dark blue-green			

Notes: nd = not determined; [a]Data from Merlino *et al.* (2003) and Anthony *et al.* (2003); [b]Based on the empirical formula of Crook and Oswald.

Contact with the Curator and Collections Manager of the Department of Mineral Sciences at the NMNH failed to reveal any samples of ‘‘orthobrochantite’’ or material deposited by either of the authors from the Douglas Hill mine. Without type material to investigate, we sought and located a specimen from the collection of Stanley G. Oswald identified as ‘‘orthobrochantite’’ from the Douglas Hill mine. This specimen is consistent with the description of the material by the original authors and, in the absence of deposited type material, should be regarded as a neotype. This specimen was used in the present study and has been deposited in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County (900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.); catalogue number 62565. We also located a sample of ‘‘orthobrochantite’’ (M34879) in the collections of Museum Victoria (PO Box 666, Melbourne, Victoria, 3001, Australia), which was sourced from an American mineral dealer in the late 1970s. How the dealer obtained the specimens was not recorded; therefore, we restrict the information to that obtained from the aforementioned Stanley G. Oswald specimen. It is possible and likely, however, that the Museum Victoria specimen originated from Stanley Oswald. We note that there is little difference between the crystal-structure refinements obtained from crystals from each specimen.

2.2. Optical properties

The physical properties reported by Crook and Oswald (*e.g.*, color, streak, fracture, hardness, cleavage and density) match well with those of brochantite. The optical properties are a reasonably good fit as well; however, the indices of refraction that they reported were significantly higher than those of brochantite (Table 1). Consequently, we measured the optical properties of the crystals on the neotype. The indices of refraction that we determined (Table 1) are marginally lower than those reported for brochantite. We note that, using the chemical analyses and cell parameters of Crook and Oswald, the Gladstone–Dale compatibility index (Mandarino, 1981) for their average index of refraction (1.793) is -0.055, in the range of only good compatibility, while that for the average index of refraction from the present study (1.763) is -0.015, in the range of superior compatibility (using our newly determined cell parameters yields similar compatibility indexes of -0.048 and -0.008, respectively). This seems to indicate that the determinations of the indices of refraction by Crook and Oswald were significantly in error.

2.3. X-ray crystallography

Both powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Spider curved imaging plate microdiffractometer utilizing monochromatized Mo$K\alpha$ radiation. A prismatic single crystal with the dimensions 100 × 20 × 20 μm was used for collection of intensity data at 295 K (Table 2). The Rigaku Crystal Clear software package was used for processing of the structure data and the SHELX–97 software (Sheldrick, 2008) was used for the solution and refinement of the structure.

Final solution of the crystal structure of ‘‘orthobrochantite’’ was complex. Initial post-processing of the data indicated that the MDO_2 polytype with the unit cell $a = 12.7856$,

Table 2. Summary of data-collection conditions and refinement parameters for ''orthobrochantite.''

Crystal data	
Cell parameters	$a = 13.1117(4)$ Å $b = 9.8654(4)$ Å $c = 6.0307(9)$ Å $\beta = 103.255(7)°$ $V = 759.31(12)$ Å^3
Space group	$P2_1/a$
Data collection	
Temperature (K)	293(2)
λ (Mo$K\alpha$)	0.710747
Crystal shape, size	Prism, 100 × 20 × 20 μm
$2\theta_{max}$ (°)	54.96
Reflection range	$-17 \le h \le 17$; $-12 \le k \le 12$; $-6 \le l \le 7$
Total no. reflections	12,655
No. unique reflections	1724
No. reflections, $F_o > 4\sigma F$	1245
Absorption correction	$\mu = 8.526$ mm^{-1}
R_{merg} on F^2	0.0429
Refinement	
No. parameters refined	137
R_1, $F_o > 4\sigma F$	0.0637
R_1, all data	0.0883
wR_2 F^{2a}, all data	0.1116
GOF	1.099
$\Delta\sigma_{min}$, $\Delta\sigma_{max}$ (e/Å^3)	−1.511, 6.354

Notes: [a] $w = 1/[\sigma^2(F_o^2) + (0.0001P^2 + 42.49P)]$, $P = [2F_c^2 + \mathrm{Max}(F_o^2, 0)]/3$.

$b = 9.8807$, $c = 6.0416$ Å, $\alpha = 90.005$, $\beta = 90.000$ and $\gamma = 90.000°$ was most probable; however, a careful inspection of the reflection files showed that reflections with l = odd were extremely weak – the presence of these reflections suggests that small zones within the crystal correspond to that of the MDO$_2$ polytype, but that the majority of the crystal does not. Processing of the data using the unit cell for the MDO$_1$ polytype [$a = 13.1117(4)$, $b = 9.8654(4)$, $c = 6.0307(9)$ Å, $\beta = 103.255(7)°$ and $V = 759.31(12)$ Å^3] was then undertaken. Atoms were first located by direct methods using SHELXS–97 (Sheldrick, 2008) and then by subsequent Fourier and difference Fourier syntheses, followed by anisotropic full-matrix least-squares refinements on F^2 using SHELXL–97 (Sheldrick, 2008). The final model was then compared to that of Merlino *et al.* (2003) and found to be in excellent agreement (Fig. 1). The final model converged to $R_1 = 6.37$ % for 1245 unique reflections [$F_o > 4\sigma F$] and 8.83 % for all 1724 reflections (Table 2). The relatively high R factors are probably due, at least in part, to the presence of small domains of the MDO$_2$ polytype, which cannot be modelled with the MDO$_1$ structure. The refined atomic coordinates, site occupancies and displacement parameters are given in Table 3 and polyhedral bond distances in Table 4.

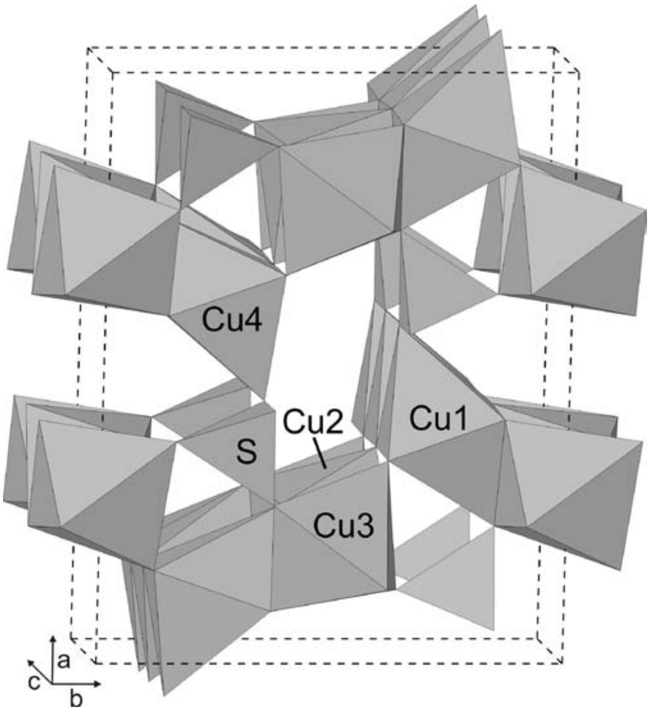

Fig. 1. Crystal structure of ''orthobrochantite,'' equivalent to the MDO$_1$ polytype of brochantite.

3. Discussion

The difference in the PXRD between ''orthobrochantite'' and published patterns in 1978 can be attributed to the difference between the MDO$_2$ and the MDO$_1$ polytype; the published pattern was that of the MDO$_2$ polytype, whilst Crook and Oswald had described the MDO$_1$ polytype. New powder data (Fig. 2) confirm the match to the MDO$_1$ polytype.

Based on the data compiled by Crook and Oswald in the original proposal, plus the structure determinations completed here and by Merlino *et al.* (2003), we contend that there is no orthorhombic polymorph (or polytype) of brochantite and that the unit cell reported by Crook and Oswald for ''orthobrochantite'' was incorrectly derived. Their error may simply have involved the choice of the *B*-centered pseudo-orthorhombic cell ($a = 25.579$, $b = 9.865$ and $c = 6.058$ Å), which is virtually identical to the MDO$_1$ cell. More rigorously, it is also possible that the crystals they studied were twinned on {100}. If such were the case, the twinned MDO$_1$ lattices would be geometrically superimposed and, if the ratios between the two twin individuals were close to 1 (*i.e.*, perfect merohedral twinning), the distribution of intensities would simulate orthorhombic symmetry; and in the doubled-volume cell the reflections that are specific to the MDO$_2$ polytype would have integer indices as well (Fig. 3). That {100} twinning in brochantite points to a wrong, doubled-volume orthorhombic cell was previously noted by Palache (1939) and

Table 3. Atomic coordinates and displacement parameters ($\mathring{A}^2$) for ‘‘orthobrochantite.’’

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0.38150(10)	0.74087(12)	0.3167(2)	0.0077(3)	0.0108(6)	0.0072(6)	0.0054(5)	0.0001(5)	0.0027(4)	−0.0021(5)
Cu2	0.20272(10)	0.50997(13)	0.4761(2)	0.0095(3)	0.0117(6)	0.0091(6)	0.0075(6)	−0.0007(5)	0.0020(5)	−0.0016(5)
Cu3	0.20549(9)	0.50995(12)	−0.0217(2)	0.0082(3)	0.0095(6)	0.0077(6)	0.0077(6)	0.0002(5)	0.0026(4)	−0.0011(5)
Cu4	0.38001(10)	0.74252(13)	0.8146(2)	0.0085(3)	0.0123(6)	0.0081(6)	0.0054(5)	−0.0010(5)	0.0028(4)	−0.0020(5)
S1	0.1128(2)	0.8028(3)	0.1819(5)	0.0150(5)	0.0172(12)	0.0099(12)	0.0181(13)	0.0010(11)	0.0046(10)	−0.0008(10)
O1	0.4152(6)	0.8671(7)	0.5827(12)	0.0097(14)	0.012(3)	0.012(4)	0.006(3)	0.001(3)	0.004(3)	0.000(3)
O2	0.3444(6)	0.6181(7)	0.5506(12)	0.0126(15)	0.012(4)	0.012(4)	0.012(4)	−0.004(3)	−0.001(3)	−0.006(3)
O3	0.1368(6)	0.6048(9)	0.6938(12)	0.0194(18)	0.025(4)	0.035(5)	0.003(3)	−0.005(3)	0.011(3)	−0.012(4)
O4	0.2587(6)	0.4011(10)	0.2561(13)	0.026(2)	0.020(4)	0.048(6)	0.012(4)	−0.005(4)	0.008(3)	−0.018(4)
O5	0.3413(5)	0.6170(7)	0.0435(11)	0.0059(13)	0.007(3)	0.007(3)	0.005(3)	0.003(3)	0.004(2)	0.001(3)
O6	0.4087(5)	0.8678(7)	0.0800(11)	0.0075(14)	0.012(3)	0.008(4)	0.004(3)	0.001(3)	0.004(3)	−0.002(3)
O7	0.2228(7)	0.8594(11)	0.2394(14)	0.030(2)	0.020(4)	0.054(6)	0.016(4)	0.005(4)	0.002(3)	0.016(4)
O8	0.5577(7)	0.6496(9)	0.3665(18)	0.029(2)	0.011(4)	0.016(4)	0.058(6)	0.008(4)	0.005(4)	0.001(3)
O9	0.1185(8)	0.6500(9)	0.1867(16)	0.029(2)	0.035(5)	0.015(4)	0.032(5)	0.001(4)	0.001(4)	−0.010(4)
O10	0.5583(6)	0.6507(9)	0.9457(18)	0.031(2)	0.009(4)	0.016(4)	0.062(7)	−0.006(4)	−0.003(4)	0.000(3)

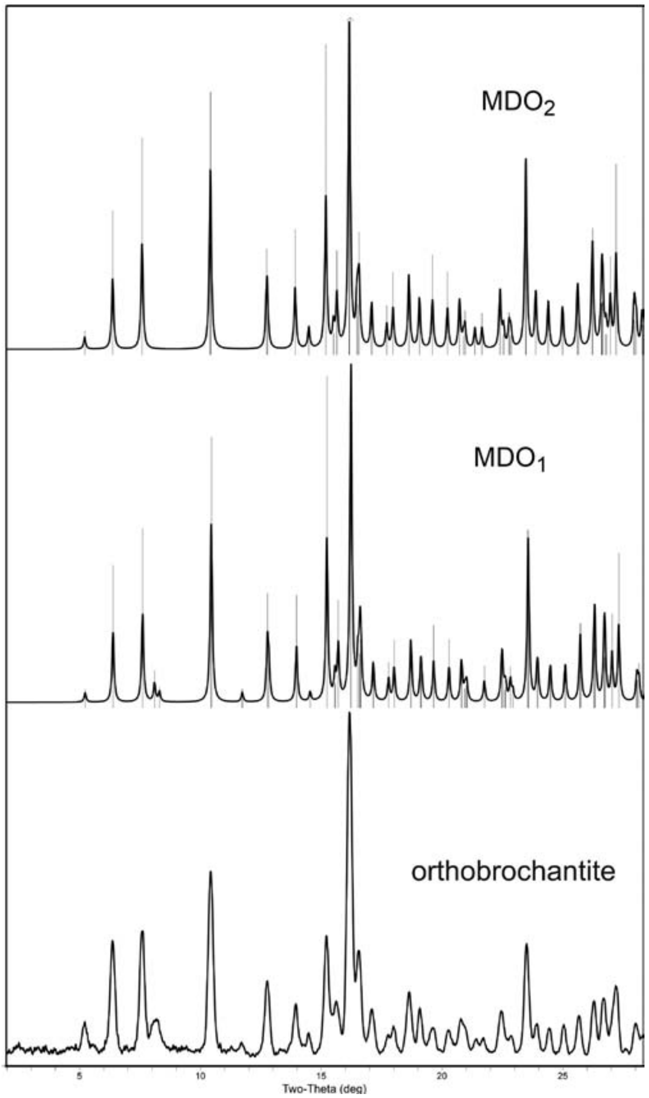

Fig. 2. Powder X-ray diffraction of ‘‘orthobrochantite’’ compared with the patterns simulated from the structure data for the brochantite polytypes (Merlino *et al.*, 2003).

discussed in detail by Cocco & Mazzi (1959). Hence, ‘‘orthobrochantite’’ is equivalent to the MDO_1 polytype of brochantite and is now regarded as a discredited species.

Acknowledgements: Dr Jeffrey Post and Ms Cathleen Brown (NMNH) are thanked for attempting to locate type ‘‘orthobrochantite’’ in their collection. Dr Bill Birch is thanked for providing a specimen of ‘‘orthobrochantite’’ for study. Mr Thomas Loomis is especially thanked for donating the Stanley Oswald specimen used for the discreditation. Part of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County and by MIUR (Italy) through the PRIN project ‘‘Compositional and structural complexity in minerals (crystal chemistry,

Table 4. Polyhedral bond distances (Å) in ''orthobrochantite.''

Cu1	O6	1.992(7)	Cu3	O3	1.981(8)	S1	O9	1.509(9)
Cu1	O1	1.998(7)	Cu3	O4	1.978(9)	S1	O10	1.511(10)
Cu1	O2	2.002(8)	Cu3	O6	2.023(7)	S1	O7	1.510(10)
Cu1	O5	2.022(7)	Cu3	O5	2.030(7)	S1	O8	1.534(10)
Cu1	O7	2.339(9)	Cu3	O7	2.320(10)			
Cu1	O8	2.433(8)	Cu3	O9	2.333(10)			
Cu2	O3	1.966(8)	Cu4	O2	1.979(7)			
Cu2	O4	1.975(9)	Cu4	O6	1.988(7)			
Cu2	O1	2.062(7)	Cu4	O1	1.994(7)			
Cu2	O2	2.100(7)	Cu4	O5	2.004(7)			
Cu2	O7	2.310(10)	Cu4	O4	2.362(8)			
Cu2	O9	2.300(9)	Cu4	O10	2.458(8)			

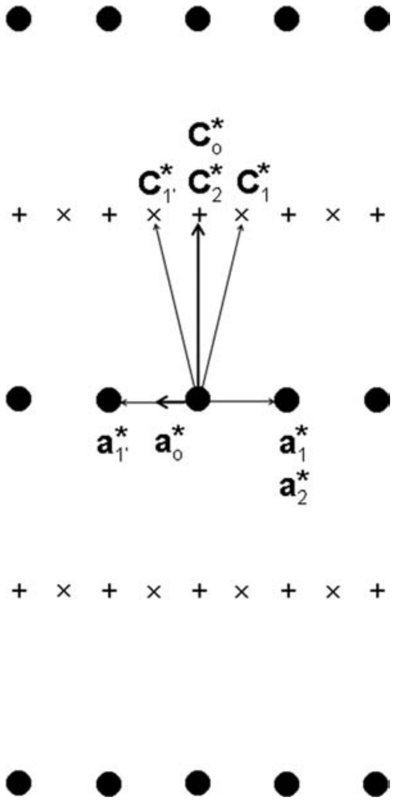

Fig. 3. Simplified drawing of the reciprocal lattice plane ($h0l$) for brochantite. Reciprocal vectors of the MDO_1 polytype, of the twin MDO_1' polytype, of the MDO_2 polytype, and of ''orthobrochantite'' by Crook and Oswald have subscripts 1, 1', 2, and o, respectively. The family reflections (l = even) are denoted with ''•'', and the non-family reflections (l = odd) are denoted with ''x'' (MDO_1) and ''+'' (MDO_2).

modularity, modulations): analysis and applications.'' Prof. Ekkehart Tillmanns and Christian Chopin are thanked for editorial assistance and members of IMA Commission on New Minerals, Nomenclature and Classification for their comments and suggestions during the review procedures.

References

Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C. (2003): Handbook of mineralogy. Volume V. Borates, carbonates, sulfates. Mineral Data Publishing, Tucson, AZ.

Cocco, G. & Mazzi, F. (1959): La struttura della brochantite. *Period. Mineral.*, **28**, 121–149.

Mandarino, J.A. (1981): The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Can. Mineral.*, **19**, 441–450.

Merlino, S., Perchiazzi, N., Franco, D. (2003): Brochantite, $Cu_4SO_4(OH)_6$: OD character, polytypism and crystal structures. *Eur. J. Mineral.*, **15**, 267–275.

Palache, C. (1939): Brochantite. *Am. Mineral.*, **24**, 463–481.

Sheldrick, G.M. (2008): A short history of SHELX. *Acta Crystallogr. A*, **64**, 112–122.

Woods, T.L. & Garrels, R.M. (1986): Use of oxidised copper minerals as environmental indicators. *Appl. Geochem.*, **1**, 181–187.

Received 11 February 2010
Modified version received 25 February 2010
Accepted 11 March 2010