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ON ISOMORPHISM OF THE STRUCTURE OF BASIC ALUMINUM SULPHATES OBTAINED BY MEANS OF HYDROLYSIS OF ALUMINUM SULPHATE AT HIGHER TEMPERATURES

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ABSTRACT

Basic aluminum sulphates are formed by the thermal hydrolysis of aluminum sulphate. An algorithm was formulated defining coordinates x, y, z, taken from any lattice node of alunite type of basic aluminum sulphates. It was hypothesized that basic aluminum sulphates with different compositions can exist with the alunite structure.

INTRODUCTION

Basic aluminum sulphates appear in nature as alunite $KAl_3(OH)_6(SO_4)_2$. They are formed by means of the hydrolysis of aluminum sulphate at elevated temperatures (373–550K). This thermal hydrolysis is very delicate and at high temperatures these compounds are decomposed to aluminum oxide. As one can realize from the literature [1–16], the chemical composition of the products of the thermal hydrolysis varies between the different researches. In order to control this thermal process, the structure and composition of the basic aluminum sulphate should be known. In the present paper a recognized structure is described with computer technique in which the computer is used to simulate the thermal decomposition and also it is used as a tool of theoretical verification of hypotheses referring to thermal decomposition. This work is the first in a series of studies in which this procedure is applied.

The structure of natural alunite which was suggested by Hendricks [5], served as the base for the present study. In the second stage of this study we tried to specify more accurately our model according to published data [2, 3, 7, 8, 10, 11, 13]. The alunite has a layer structure. According to Hendricks, the unit cell is

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composed of three molecules $KAl_3(OH)_6(SO_4)_2$, having the shape of a prism whose base is a rhombus with angles of 60 and 120°. The height of this prism is a threefold axis of symmetry. This threefold axis is perpendicular to two different layers occurring alternately one above the other. The first layer consists of the ions SO_4^{2-} and K^+ with a thickness of 20 nm. The second layer consists of the ions OH^- and Al^+ with a thickness of 37.5 nm (Fig. 1 a and b). There are three such sequences along the height of the unit cell and they differ from one another as to a linear and angular shift towards axis *x* and *y* of the coordinate system. There are strong bonds between the layers which result from Al^{3+} and K^+ ions reacting with oxygens of SO_4^{2-} and OH^- ions, respectively.

INTRODUCING OF THE STRUCTURE OF ALUNITE INTO A COMPUTER MEMORY

The following assumptions were made as to the spatial distribution of the points representing six types of ions (K^+, Al^{3+}, S^{4+}, axial oxygen O^{2-}, nonaxial oxygen O^{2-} and hydroxyl OH^-) in the unit cell of alunite:

- the coordinate system begins with K^+,
- all four sulphur-oxygen bonds are of the same length,
- SO_4^{2-} ions lie exactly between planes 1 and 2 (Fig. 1a),
- independent variables of the system are lattice constants *c* and *a*, the length of sulphur-oxygen bond and the distance between axial oxygen and hydroxyl, respectively,
- distances between potassium-hydroxyl or hydroxyl-aluminum ions are considered as optimalization parameters of localization of hydroxyls.

An alogarithm was formulated defining coordinates *x*, *y* and *z* taken from any lattice node. Table 1 shows algebric expressions which enable to calculate these three coordinates. They are the base which is introduced in the computer memory as the structure of alunite. This notation was recorded by means of the program "ALUNITE 2" (language Basic, text of the program-7kB) and carried out on the "AMSTRAD PC".

Beside calculations and ordering the computer memory by means of coordinate matrices *x*, *y*, and *z*, this program allows to calculate distances between selected ions and prints the list of the closest points in six series of different types. Table 2 shows different kinds of ions and their closest surroundings.

BASIC ALUMINUM SULFATES WITH DIFFERENT COMPOSITIONS BUT WITH THE SAME STRUCTURE

The place in the spatial lattice of alunite occupied by K^+ is designated as M^+. The place occupied by Al^{3+} is designated as M^{3+}. The place occupied by OH is designated as X. The following has been assumed:

1. Places of M^+ can be substituted, in sequence, by cations such as K^+, Na^+, NH_4^+, H_3O^+ and water molecules, or they can be empty.
2. Places of X can be substituted by water molecules or they can be empty.
3. Places of SO_4^{2-} can sometimes be replaced by the tetrahedron $Al(OH)_4^-$.
4. The above substitutions or vacancies occur in the spatial lattice with statistical distribution without forming distinguishable phases.

These four assumptions are sufficient to explain the existence of alunitic structure, as determined by X-ray, for the basic salts of varied compositions, the formation of which at temperatures 373-550K was reported by many researchers within the last forty years (Table 3). Some researchers were greatly confused because of apparent discrepancy between the composition and its X-ray data [15, 16]. Let us assume for example that the crystal volume includes the 10 following sets: $M^+(M^{3+})_5X_6(SO_4)_2$. Two M^+ places out of ten are empty; six M^{3+} places out of thirty are empty; twenty X places out of sixty are to be occupied by H_2O molecules and not by OH^- ions.

The final molecular formula of this substance would be as follows, $K_2O*3Al_2O_3*5SO_3*10H_2O$. Sets of ion patterns with internally compensated electric charge are shown in Table 4. These sets illustrate concentrations of vacancies and substitutions. There could be more such sets but these are only formal.

CONCLUSIONS

The assumed hypothesis and the example which illustrated it, explains the fact that basic aluminum sulphates with different composition (within some limits), can exist in alunite structure. The presence of H_3O^+ or H_2O in places of M^+ or X in the alunite structure indicates an incomplete thermal hydrolysis.

TABLE 1

Coordinates x, y, z - space lattice of alunite

a=...-2,-1,0,+1,+2... a=...-2,-1,0,+1,+2... b=...-2,-1,0,+1,+2...

A -angle between the base of tetrahedron SO4(2-) and straight line b3

b3=2.52A

c=17.35A(lattice constant)

y0=a$\sqrt{3}$/6=6.96A$\sqrt{3}$/6

x0=a/4=6.96A/4

SO=1.51A(lenght of sulfur-oxygen bond)

HYDROXYL of PLANE 6-1

(4n+2)x0,	(6n+1)y0+b3cosA,	kc+2/3c+2/3SO+b3sinA
(4n+2)x0+$\sqrt{3}$/2b3cosA,	(6n+1)y0-1/2b3cosA,	kc+2/3c+2/3SO+b3sinA
4nx0-$\sqrt{3}$/2b3cosA,	(6n+4)y0-1/2b3cosA,	kc+2/3c+2/3SO+b3sinA
4nx0,	(6n+4)y0-b3cosA,	kc-2/3SO-b3sinA
4nx0+$\sqrt{3}$/2b3cosA,	(6n+4)y0+1/2b3cosA,	kc-2/3SO-b3sinA
(4n+2)x0-$\sqrt{3}$/2b3cosA,	(6n+1)y0+1/2b3cosA,	kc-2/3SO-b3sinA
(4n+2)x0,	(6n+1)y0-b3cosA,	kc-2/3SO-b3sinA
(4n+2)x0+$\sqrt{3}$/2b3cosA,	(6n+1)y0+1/2b3cosA,	kc-2/3SO-b3sinA
4nx0-$\sqrt{3}$/2b3cosA,	(6n+4)y0+1/2b3cosA,	kc-2/3SO-b3sinA

PLANE 1 PLANE 2

OXYGEN of PLANE 2

4nx0,	(6n+2)y0,	kc+2/3SO
4nx0,	(6n+4)y0+2$\sqrt{2}$/3SO,	kc+2/3SO
4nx0+$\sqrt{2}$/3SO,	(6n+4)y0-$\sqrt{2}$/3SO,	kc+2/3SO
4nx0-$\sqrt{2}$/3SO,	(6n+4)y0-$\sqrt{2}$/3SO,	kc+2/3SO
(4n+2)x0,	(6n+5)y0,	kc+2/3SO
(4n+2)x0,	(6n+1)y0+2$\sqrt{2}$/3SO,	kc+2/3SO
(4n+2)x0+$\sqrt{2}$/3SO,	(6n+1)y0-$\sqrt{2}$/3SO,	kc+2/3SO
(4n+2)x0-$\sqrt{2}$/3SO,	(6n+1)y0-$\sqrt{2}$/3SO,	kc+2/3SO

POTASSIUM

4nx0,	6ay0,	kc
(4n+2)x0,	(6n+3)y0,	kc

SULFUR

4nx0,	(6n+2)y0,	kc-1/3SO
(4n+2)x0,	(6n+5)y0,	kc-1/3SO
4nx0,	(6n+4)y0,	kc+1/3SO
(4n+2)x0,	(6n+1)y0,	kc+1/3SO

OXYGEN of PLANE 1

4nx0,	(6n+2)y0-2$\sqrt{2}$/3SO,	kc-2/3SO
(4n+2)x0,	(6n+5)y0-2$\sqrt{2}$/3SO,	kc-2/3SO
4nx0+$\sqrt{2}$/3SO,	(6n+2)y0+$\sqrt{2}$/3SO,	kc-2/3SO
4nx0-$\sqrt{2}$/3SO,	(6n+2)y0+$\sqrt{2}$/3SO,	kc-2/3SO
(4n+2)x0+$\sqrt{2}$/3SO,	(6n+5)y0+$\sqrt{2}$/3SO,	kc-2/3SO
(4n+2)x0-$\sqrt{2}$/3SO,	(6n+5)y0+$\sqrt{2}$/3SO,	kc-2/3SO
4nx0,	(6n+4)y0,	kc-2/3SO
(4n+2)x0,	(6n+1)y0,	kc-2/3SO

ALUMINIUM of PLANES 2-3

4nx0,	(6n+5)y0,	kc+1/6c
(4n+1)x0,	(3n+1/2)y0,	kc+1/6c
(4n+2)x0,	(6n+2)y0,	kc+1/6c
(4n+3)x0,	(3n+1/2)y0,	kc+1/6c

HYDROXYL of PLANES 2-3

4nx0,	(6n+2)y0-b3cosA,	kc+1/3c-2/3SO-b3sinA
4nx0+$\sqrt{3}$/2b3cosA,	(6n+2)y0+1/2b3cosA,	kc+1/3c-2/3SO-b3sinA
(4n+2)x0-$\sqrt{3}$/2b3cosA,	(6n+5)y0+1/2b3cosA,	kc+1/3c-2/3SO-b3sinA
(4n+2)x0,	(6n+5)y0-b3cosA,	kc+1/3c-2/3SO-b3sinA
(4n+2)x0+$\sqrt{3}$/2b3cosA,	(6n+5)y0+1/2b3cosA,	kc+1/3c-2/3SO-b3sinA
4nx0-$\sqrt{3}$/2b3cosA,	(6n+2)y0+1/2b3cosA,	kc+1/3c-2/3SO-b3sinA
4nx0,	(6n+2)y0+b3cosA,	kc+2/3SO+b3sinA
4nx0+$\sqrt{3}$/2b3cosA,	(6n+2)y0-1/2b3cosA,	kc+2/3SO+b3sinA
(4n+2)x0-$\sqrt{3}$/2b3cosA,	(6n+5)y0-1/2b3cosA,	kc+2/3SO+b3sinA
(4n+2)x0,	(6n+5)y0+b3cosA,	kc+2/3SO+b3sinA
(4n+2)x0+$\sqrt{3}$/2b3cosA,	(6n+5)y0-1/2b3cosA,	kc+2/3SO+b3sinA
4nx0-$\sqrt{3}$/2b3cosA,	(6n+2)y0-1/2b3cosA,	kc+2/3SO+b3sinA

OXYGEN of PLANE 4

4nx0,	6ay0,	kc+1/3c+2/3SO
4nx0,	(6n+2)y0+2$\sqrt{2}$/3SO,	kc+1/3c+2/3SO
4nx0+$\sqrt{2}$/3SO,	(6n+2)y0+2$\sqrt{2}$/3SO,	kc+1/3c+2/3SO
4nx0-$\sqrt{2}$/3SO,	(6n+2)y0-$\sqrt{2}$/3SO,	kc+1/3c+2/3SO
(4n+2)x0,	(6n+3)y0,	kc+1/3c+2/3SO
(4n+2)x0,	(6n+5)y0+2$\sqrt{2}$/3SO,	kc+1/3c+2/3SO
(4n+2)x0+$\sqrt{2}$/3SO,	(6n+5)y0-$\sqrt{2}$/3SO,	kc+1/3c+2/3SO
(4n+2)x0-$\sqrt{2}$/3SO,	(6n+5)y0-$\sqrt{2}$/3SO,	kc+1/3c+2/3SO

PLANE 4 PLANE 3

POTASSIUM

4nx0,	(6n+4)y0,	kc+1/3c
(4n+2)x0,	(6n+1)y0,	kc+1/3c

SULFUR

4nx0,	6ay0,	kc+1/3c-1/3SO
(4n+2)x0,	(6n+3)y0,	kc+1/3c-1/3SO
4nx0,	(6n+2)y0,	kc+1/3c+1/3SO
(4n+2)x0,	(6n+3)y0,	kc+1/3c+1/3SO

OXYGEN of PLANE 3

4nx0,	(6n+2)y0,	kc+1/3c-2/3SO
4nx0,	6ay0-2$\sqrt{2}$/3SO,	kc+1/3c-2/3SO
4nx0+$\sqrt{2}$/3SO,	6ay0+$\sqrt{2}$/3SO,	kc+1/3c-2/3SO
4nx0-$\sqrt{2}$/3SO,	6ay0+$\sqrt{2}$/3SO,	kc+1/3c-2/3SO
(4n+2)x0,	(6n+5)y0,	kc+1/3c-2/3SO
(4n+2)x0,	(6n+3)y0-2$\sqrt{2}$/3SO,	kc+1/3c-2/3SO
(4n+2)x0+$\sqrt{2}$/3SO,	(6n+3)y0+$\sqrt{2}$/3SO,	kc+1/3c-2/3SO
(4n+2)x0-$\sqrt{2}$/3SO,	(6n+3)y0+$\sqrt{2}$/3SO,	kc+1/3c-2/3SO

ALUMINIUM of PLANES 4-5

4nx0,	(6n+3)y0,	kc+1/2c
(4n+1)x0,	(3n+1/2)y0,	kc+1/2c
(4n+2)x0,	4ay0,	kc+1/2c
(4n+3)x0,	(3n+1/2)y0,	kc+1/2c

HYDROXYL of PLANES 4-5

4nx0,	6ay0+b3cosA,	kc+1/3c+2/3SO+b3sinA
4nx0+$\sqrt{3}$/2b3cosA,	6ay0-1/2b3cosA,	kc+1/3c+2/3SO+b3sinA
(4n+2)x0-$\sqrt{3}$/2b3cosA,	(6n+3)y0-1/2b3cosA,	kc+1/3c+2/3SO+b3sinA
(4n+2)x0,	(6n+3)y0+b3cosA,	kc+1/3c+2/3SO+b3sinA
(4n+2)x0+$\sqrt{3}$/2b3cosA,	(6n+3)y0-1/2b3cosA,	kc+1/3c+2/3SO+b3sinA
4nx0-$\sqrt{3}$/2b3cosA,	6ay0-1/2b3cosA,	kc+1/3c+2/3SO+b3sinA
4nx0,	6ay0-b3cosA,	kc+2/3c-2/3SO-b3sinA
4nx0+$\sqrt{3}$/2b3cosA,	6ay0+1/2b3cosA,	kc+2/3c-2/3SO-b3sinA
(4n+2)x0-$\sqrt{3}$/2b3cosA,	(6n+3)y0+1/2b3cosA,	kc+2/3c-2/3SO-b3sinA
(4n+2)x0,	(6n+3)y0-b3cosA,	kc+2/3c-2/3SO-b3sinA
(4n+2)x0+$\sqrt{3}$/2b3cosA,	(6n+3)y0+1/2b3cosA,	kc+2/3c-2/3SO-b3sinA
4nx0-$\sqrt{3}$/2b3cosA,	6ay0+1/2b3cosA,	kc+2/3c-2/3SO-b3sinA

PLANE 5 PLANE 6

POTASSIUM

4nx0,	(6n+2)y0,	kc+2/3c
(4n+2)x0,	(6n+5)y0,	kc+2/3c

SULFUR

4nx0,	6ay0,	kc+2/3c+1/3SO
4nx0,	(6n+4)y0,	kc+2/3c-1/3SO
(4n+2)x0,	(6n+1)y0,	kc+2/3c-1/3SO
(4n+2)x0,	(6n+3)y0,	kc+2/3c+1/3SO

OXYGEN of PLANE 6

4nx0,	(6n+4)y0,	kc+2/3c+2/3SO
4nx0,	6ay0+2$\sqrt{2}$/3SO,	kc+2/3c+2/3SO
4nx0-$\sqrt{2}$/3SO,	6ay0-$\sqrt{2}$/3SO,	kc+2/3c+2/3SO
4nx0+$\sqrt{2}$/3SO,	6ay0-$\sqrt{2}$/3SO,	kc+2/3c+2/3SO
(4n+2)x0,	(6n+1)y0,	kc+2/3c+2/3SO
(4n+2)x0,	(6n+3)y0+2$\sqrt{2}$/3SO,	kc+2/3c+2/3SO
(4n+2)x0+$\sqrt{2}$/3SO,	(6n+3)y0-$\sqrt{2}$/3SO,	kc+2/3c+2/3SO
(4n+2)x0-$\sqrt{2}$/3SO,	(6n+3)y0-$\sqrt{2}$/3SO,	kc+2/3c+2/3SO

ALUMINIUM of PLANES 5-1

4nx0,	(6n+1)y0,	kc+5/6c
(4n+1)x0,	(3n+5/2)y0,	kc+5/6c
(4n+2)x0,	(6n+4)y0,	kc+5/6c
(4n+3)x0,	(3n+5/2)y0,	kc+5/6c

HYDROXYL of PLANES 5-1

4nx0,	(6n+4)y0+b3cosA,	kc+2/3c+0/3SO+b3sinA
4nx0+$\sqrt{3}$/2b3cosA,	(6n+4)y0-1/2b3cosA,	kc+2/3c+2/3SO+b3sinA
(4n+2)x0-$\sqrt{3}$/2b3cosA,	(6n+1)y0-1/2b3cosA,	kc+2/3c+2/3SO+b3sinA

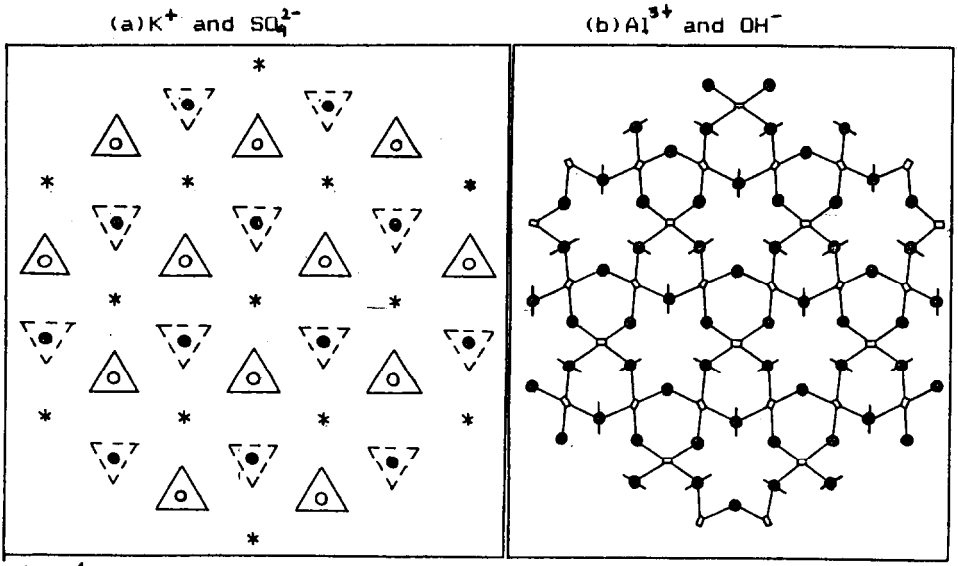

Fig.1.Sections (a) and (b) of alunite crystal.
(a) The space with ions K^+ and SO_4^{2-}
Equation of section plane(1-2) is z=0
* potassium ion
● oxygen of tetrahedron SO_4^{2-} over the plane 1-2 (axial)
o oxygen of tetrahedron SO_4^{2-} under the plane 1-2 (axial)
△ base of tetrahedron SO_4^{2-} over the plane 1-2 (nonaxial)
▽ base of tetrahedron SO_4^{2-} under the plane 1-2 (nonaxial)
(b)The space with ions Al^{3+} and OH^-
Equation of section plane(2-3) is z=1/6 c
⊕ hydroxyl ion over the plane 2-3
● hydroxyl ion under the plane 2-3
□ aluminium ion

Table 2:Distances A-B(angstroms)and number of neighbors B from ion A point of view

Kind of ion	A \ B	1	2	3	4	5	6
potassium	1	6.96*6	3.52*6	4.05*6	4.14*6	2.78*6	2.85*6
aluminium	2	3.52*2	3.48*4	3.12*2	3.96*4	1.97*2	2.03*4
sulfur	3	4.05*3	3.12*3	6.96*6	1.51*1	1.51*3	3.50*3
axial oxygen	4	4.14*3	3.96*6	1.51*1	3.77*1	2.47*3	2.52*3
nonaxial oxygen	5	2.78*1	1.97*1	1.51*1	2.47*1	2.47*2	2.60*2
hydroxyl	6	2.85*1	2.03*2	3.50*1	2.52*1	2.60*2	2.60*2

Table 3.Composition of the basic sulphates obtained experimentally

Formula of oxides	Ref	Formula of oxides	Ref
$3Fe_2O_3*4.24SO_3*7.33H_2O$	[12]	$3Al_2O_3*3.9SO_3*8.6H_2O$	[4]
$3Fe_2O_3*3.99SO_3*7.93H_2O$	[12]	$3Al_2O_3*8H_2O$	[10]
$1.86NH_3*3Fe_2O_3*4SO_3*6.15H_2O$	[12]	$0.97K_2O*3Al_2O_3*5SO_3*9H_2O$	[16]
$K_2O*3Al_2O_3*5SO_3*9H_2O$	[1]	$K_2O*3Al_2O_3*5SO_3*9H_2O$	[15]
$K_2O*3Al_2O_3*4.67SO_3*9.93H_2O$	[11]	written by authors as	
$Na_2O*3Al_2O_3*5SO_3*10H_2O$	[6]	$K_2[Al_6(OH)_{10}(SO_4)_6]*4H_2O$	

Table 4. The exemplary sets of ionic formulas with full electrical compensation. System $4(K_2O*3Al_2O_3*5SO_3*10H_2O)$

N°	Ionic formulas
1	$2K_2[Al_4(OH)_6(H_2O)_6](SO_4)_4 = 4K^+, 8Al^{3+}, 12OH^-, 12H_2O, 8SO_4^{2-}$
	$2K_2[Al_5(OH)_9(H_2O)_3](SO_4)_4 = 4K^+, 10Al^{3+}, 18OH^-, 6H_2O, 8SO_4^{2-}$
	$[Al_6(OH)_{10}(H_2O)_2](SO_4)_4 = 6Al^{3+}, 10OH^-, 2H_2O, 4SO_4^{2-}$
	$\sum = 8K^+, 24Al^{3+}, 40OH^-, 20H_2O, 20SO_4^{2-}$
2	$4K_2[Al_5(OH)_9(H_2O)_3](SO_4)_4 = 8K^+, 20Al^{3+}, 36OH^-, 12H_2O, 16SO_4^{2-}$
	$[Al_4(OH)_4(H_2O)_8](SO_4)_4 = 4Al^{3+}, 4OH^-, 8H_2O, 4SO_4^{2-}$
	$\sum = 8K^+, 24Al^{3+}, 40OH^-, 20H_2O, 20SO_4^{2-}$
3	$3K_2[Al_5(OH)_9(H_2O)_3](SO_4)_4 = 6K^+, 15Al^{3+}, 27OH^-, 9H_2O, 12SO_4^{2-}$
	$K_2[Al_4(OH)_6(H_2O)_6](SO_4)_4 = 2K^+, 4Al^{3+}, 6OH^-, 6H_2O, 4SO_4^{2-}$
	$[Al_5(OH)_7(H_2O)_5](SO_4)_4 = 5Al^{3+}, 7OH^-, 5H_2O, 4SO_4^{2-}$
	$\sum = 8K^+, 24Al^{3+}, 40OH^-, 20H_2O, 20SO_4^{2-}$

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