SILICON ALUMINIUM ORDERING IN THE FRAMEWORK OF ZEOLITES

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The (Si, Al) ordering scheme in the framework of zeolites is reviewed, and four classes are recognized: 1 — zeolites with Si: Al = 1 : 1 and a simple order given by the alternation of Si and Al; 2 — zeolites with Si > Al and an ordered distribution; 3 — zeolites with Si > Al and partial Al-enrichment in some tetrahedra; 4 — zeolites with Si > Al and complete disorder, or at least with a framework that in principle favours disorder.

A crystallization model requiring the formation of cages of tetrahedra around a hydrated cation acting as a template is suitable for classes 3 and 4, but not for classes 1 and 2, which require the standard crystal growth scheme.

Key words: zeolite, framework, (Si, Al) order, crystallization.

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Introduction

The distribution of silicon and aluminium in the centre of the tetrahedra of framework silicates may be ordered or disordered, and every mineralogist knows how hard it is to solve the enigma of the real (Si, Al) order in plagioclases, concealed in their modulated domain structure.

The (Si, Al) distribution in the framework of zeolites has certainly not been the subject of investigations so detailed as those on feldspars: our paper therefore aims to give the present status of the subject matter for natural zeolites and to draw some conclusions on their crystallization.

From this particular point of view and without any other purpose, zeolites may be subdivided into four classes:

Class 1: Zeolites with Si: $(Si+Al) \simeq 0.50$. These obey Loewenstein's rule and exhibit ordered distribution given by the alternation of Si and Al in the tetrahedra. An obvious consequence is that the rings with an odd number of tetrahedra are prohibited in their frameworks; (Si, Al) disorder is possible only if Si: (Si + Al) is slightly over 50 %.

Class 2: Zeolites with Si: $(Si+Al) > 0.5$, which normally have nearly perfect (Si, Al) order; disorder is possible but rare.

Class 3: Zeolites with Si: $(Si+Al) > 0.5$ and a small but definite Al-enrichment repeatedly found in the same tetrahedra.

Class 4: Zeolites with any ratio Si: (Si + Al), in which disorder is highly favoured by their structural features, although order is possible, and has been detected clearly in some cases.

The Al fraction in a tetrahedron is normally deduced from the average T—O distance, for instance, using Jones' relation, 1968; here this relation will be used in a qualitative way only. We use T as a code for both the tetrahedral node and the tetrahedron. Extraframework cations are normally located near the tetrahedra occupied by Al and hence with a deficit of positive charge. On the other hand, if a framework oxygen is at bond distance from an extraframework cation, its T—O bond length is increased (see, for instance, Baur, 1978), but by such a small amount as to be negligible for the conclusions to be drawn in this article.

Class 1

This class contains only a few structurally well known species: gismondine, amicite, thomsonite and willhendersonite.

Gismondine (Fischer and Schramm 1971) and *amicite* (Alberti and Vezzalini 1979) share the same framework of tetragonal topological symmetry, and all tetrahedra are topologically equivalent, but the extraframework cations are positioned so as to reduce symmetry. The order is dominated by the Al—O—Al avoidance (Loewenstein's) rule: the presence of Ca, which strongly favours order in many cases, is not decisive here, as the same order is also found in amicite too, which contains only K and Na.

Thomsonite (Alberti *et al.* 1981) has a different framework but here, too, the order is simply imposed by Loewenstein's rule.

Willhendersonite (Peacor *et al.* 1984; Tillmanns and Fisher 1981) has a chabazite framework, and hence all tetrahedra are topologically equivalent. Nevertheless, Loewenstein's rule imposes ordered alternation of Si and Al.

If the ratio Si: (Si + Al) is slightly over 50 % in one of these frameworks, the probability of antiphase domains grows rapidly. There are thus some thomsonites that are microcristalline and botryoidal and in which up to 55 % of tetrahedra are occupied by Si. They feature X-ray powder patterns with a weakening of all diffractions with 1 odd, clear evidence of disorder (Wise and Tschernich 1978). When describing the refinement of their thomsonite with Si: (Si + Al) = 51 %, Alberti *et al.* (1981) showed that even with such a small increase in Si, there is a slight tendency to disorder with a detectable increase of Al in one tetrahedron, which should be occupied by Si only. In other words, given an average Al decrease, the Si increase in the Al tetrahedra is larger than that strictly necessary to counterbalance the Al deficit, hence some Al is shifted to the Si-tetrahedra. This is a consequence of the »extended Loewenstein's rule»: if two nearby tetrahedra are both occupied by Si, there is a greater likelihood of finding Al in the next tetrahedron.

Garronite has Si: (Si + Al) = 0.60 and probably the same framework as gismondine. Its tetragonal space group gives some evidence for disordered zeolite, but the diffuseness of its X-ray diffractions suggests the presence of ordered domains with four orientations (Gottardi and Alberti 1974).

There is no evidence of order in the X-ray powder patterns of chabazite, even if only 59 % of the tetrahedra are occupied by Si (Passaglia, 1970). Unfortunately the samples are not suitable for single crystal work, which could provide better information.

Class 2

This class includes some fibrous zeolites plus laumontite, wairakite and yugawaralite.

Edingtonite: this zeolite may be orthorhombic (Galli 1976; Kvick and Smith 1983) or tetragonal (Mazzi *et al.* 1984). The average T—O distances (see Table 1) show nearly perfect (Si, Al) order in the orthorhombic mineral and complete disorder in the tetragonal one. There is no correspondence between the Al fraction in a tetrahedron and the vicinity of an extra-

Table 1. Average T—O distances (Å) in edingtonites.

Sample	Symmetry	T1—O	T2—O	T3—O	Reference
Böhlet Mine	orthorhombic	1.609	1.623	1.752	Galli (1976)
New Brunswick	orthorhombic	1.617	1.621	1.743	Kvick and Smith (1983)
Kilpatrick Hill	tetragonal	1.660	1.666		Mazzi *et al.* (1984)
Ice River	tetragonal	1.658	1.668		Mazzi *et al.* (1984)

Note: in tetragonal edingtonites T2 is equivalent to T3.

framework cation barium; in fact Ba is linked to three framework oxygens, O1, O2, O3, all of which are vertices of both T2 (Al free) and T3 (Al filled).

Natrolite and *tetranatrolite:* although two names are used, the situation is similar to that of edingtonite; orthorhombic natrolite is a very common mineral and is usually perfectly ordered (see the first three samples in Table 2); as in edingtonite, there is no relation between the Al fraction in a tetrahedral node and the vicinity of an extraframework cation Na at bond distance from O2, O3, O4, all of which are vertices not only of site Al but also of Si2. The last two samples in Table 2 are partially disordered, and the existence of the tetragonal equivalent (Krog-Andersen *et al.* 1969) termed tetranatrolite proves beyond doubt that complete (Si, Al) disorder is also possible in this framework, even though this structure has never been refined because suitable crystals are not available. Tetranatrolite is much less common than orthorhombic natrolite, but it is still not a rare mineral.

Mesolite: Adiwidjaja (1972) found the following average T—O distances for the tetrahedral nodes coded Si1 to Si5: 1.619, 1.620, 1.623, 1.620Å, and for the nodes coded Al1 to Al3: 1.737, 1.750, 1.736Å. It is obvious that there is nearly perfect (Si, Al) order. As in the other fibrous zeolites, no relation exists between the Al fraction in a node and the vicinity of an extraframework cation. Thus Ca is linked to O4, O6, O8, O11, which are part of the tetrahedra Si2, Si3, Si4, Al1, Al2, Al3, and Na is linked to O5, O7, O10, which are part of the tetrahedra Si2, Si3, Al1, Al2.

Table 2. Average T—O distances (Å) in natrolites.

Sample	Si1—O	Si2—O	Al—O	Reference
Bergen Hill	1.617	1.621	1.741	Peacor (1973)
Techloviche	1.622	1.617	1.746	Pechar (1981)
Zalezly	1.621	1.626	1.738	Pechar *et al.* (1983)
Gulacs Hill	1.627	1.631	1.729	Alberti and Vezzalini (1981a)
Zeilberg	1.628	1.629	1.723	Hesse (1983)

Scolecite: there are five non-equivalent tetrahedral nodes with the following T—O distances (Smith *et al.* 1984): 1.616, 1.620, 1.620, 1.743, 1.749Å. This means nearly perfect (Si, Al) order. Ca is at bond distance from framework oxygens O2, O3, O5, O6, which are part not only of the tetrahedra Al1 and Al2 but also of Si2 and Si3.

Laumontite: according to Bartl (1970), there are three non-equivalent tetrahedral nodes. One is coded Al with an average T—O distance of 1.750Å; the other two are coded Si1 and Si2 with T—O distances of 1.611 and 1.621Å. Thus there is nearly perfect (Si, Al) order. The extraframework cation Ca is at bond distance with O2 and O3, which are both part of the Al tetrahedron; the Si1 and Si2 tetrahedra each contain one of these two oxygens.

Wairakite: Takeuchi *et al.* (1979) have shown that this species has a perfectly (Si, Al) ordered distribution, although its framework is the same as that of analcime, which is disordered or partially ordered. In wairakite, each Ca has two Al tetrahedra on two opposite sides, the other Si tetrahedra being a little farther away.

Yugawaralite: Kerr and Williams (1969) found nearly perfect (Si, Al) order in its framework, with eight independent tetrahedral nodes: the first two, coded Al1 and Al2, have average T—O distances of 1.735 and 1.733Å, the other six, coded Si1 to Si6, have 1.605, 1.613, 1.606, 1.612, 1.603, 1.612Å. The only extraframework cation Ca is linked to framework oxygens O3, O7, O9, O12; Al1 and Al2 are each linked to two of these oxygens, whereas Si2, Si3, Si4 are each linked to one, and Si1, Si5, Si6 to none.

Class 3

This class includes mordenite, dachiardite, epistilbite, ferrierite and bikitaite, all with similar frameworks, plus heulandite and brewsterite, again with similar frameworks, and finally mazzite, and perhaps offretite and levyne, all of which contain 6-rings in their structures.

The frameworks of the first four zeolites may be described as parallel nets with hexagonal meshes, connected by 4-rings (6-rings in ferrierite) normal to the plane of the nets.

Mordenite: in the Na-exhanged form, the data of Gramlich (1971) give very slight evidence for Al enrichment in T3 (a node in the 4-ring) because the distance T3—O (1.639Å) is slightly larger than the other three (1.625, 1.622, 1.607Å). Moreover O1 and O9, all of which are part of tetrahedron T3, are coordinated by the extraframework cation, giving further support in favour of a higher Al fraction in T3. Note that two vertices of T3 are occupied by two symmetrically equivalent O1, which are also a vertex of T1. Mortier *et al.* (1975, 1976a) have refined Ca-exchanged mordenites. In the dehydrated form T3—O is again larger (1.63Å) than the others (1.61, 1.60, 1.59Å), and the oxygens O1 and O9 of this tetrahedron are coordinated by Ca I, the cation site with the highest (42 %) occupancy. The rehydrated form features once more the greatest T—O distance (1.630Å) for T3 comparable with 1.621, 1.615, 1.604Å for the other tetrahedra. Hence, each of these three refinements gives such scanty evidence in favour of Al enrichment in T3 that some doubt could be cast on the significance of the information; however, all three investigations point in the same direction and this could not happen by chance. The Al fraction in T3 is probably ca. 20 or 25 %.

Dachiardite: Vezzalini (1984) refined its structure and coded T1 and T2 the tetrahedra nodes of the hexagonal nets, and T3 and T4, the nodes of the 4-rings. The T—O distances are 1.648 and 1.623Å for T3 and T4, 1.612 and 1.614Å for T1 and T2. The most occupied cation site is bound to O1, O2 and O9: now, of these oxygens, T1 contains only O1 and T2 only O2, whereas T3 has two symmetrically equivalent O1 at its vertices, and T4 two symmetrically equivalent O2 plus one O9. So the highest T—O distances certainly correspond to the highest Al fraction (ca. 30 %) of T4, one of the two nodes of the 4-ring. Also the other one, T3, is definitely higher in Al (ca. 20 %) than the nodes of the hexagonal net.

Epistilbite: Perrotta (1967) coded TA, the nodes of the 4-rings, TB and TC, being in the hexagonal nets. TA—O is 1.65Å as against 1.60 and 1.59Å for the other two. The extraframework cation site is at bond distance from O1 and O3, both of which are part of the TA tetrahedron; O3 is also a vertex of TC. The Al fraction in the nodes of the 4-ring should be ca. 35 %.

Ferrierite: in this mineral, 6-rings (instead of 4-rings) represent the connections between the nets with hexagonal meshes. There are four non-equivalent tetrahedral nodes, T3 and T4 forming the nets, and two T1 and four T2 the 6-rings. According to Vaughn (1966), the average T2—O distance (1.626Å) is greater than the other three (1.613, 1.599, 1.596Å); according to Alberti and Sabelli (oral communication) T2—O = 1.638Å, the other three dimensions being 1.610, 1.609, 1.600Å. In any case these data are sufficient to state that Al is enriched in T2, that is, in the 6-rings and not in the nets. In this particular case the oxygens of the T2 tetrahedron are not linked to extraframework cations, because Mg is fully surrounded by water molecules only, and the other cation sites, occupied mainly by Na and K, are too far from the T2 tetrahedron.

Bikitaite: this zeolite also contains parallel nets with hexagonal meshes, which, however, are connected by chains similar to those of pyroxenes. Kocman *et al.* (1974) coded T1 and T3 the nodes in the hexagonal nets, and T2, the nodes of the chains. The average T—O distances are 1.681Å for the first two, and 1.610Å for the T2 of the chains. These values differ so much that they prove a 50 % Al fraction in the nets and nearly zero Al in the chains. What is more, the extraframework cation Li coordinates O1, O2 and O6, all vanrtices of the T1 and T3 tetrahedra, but not of the T2 tetrahedron.

Heulandite: this framework, which can be considered as an assemblage of units called 4—4—1—1 or heulandite units, is topologically monoclinic with five non-equivalent tetrahedral nodes. Table 3 lists the average T—O distances in nine minerals with this framework; five are Si-poor and all show definite Al enrichment in T2, in good agreement with the fact that three of its vertices (O1, O2, O10) are bound to the two main cation sites coded C1 and C2, or M1 and M2, and so on. T2 should contain ca. 40 % of the Al in these five samples. Four samples (clinoptilolites) are Si-rich, and all show smaller T—O distances, although the T2 tetrahedron remains the largest and the T1 tetrahedron shows only limited shrinkage, probably because clinoptilolites have another important cation site (M3 of Koyama and Takeuchi 1977) at bond distance from O2, O3, O4, all vertices of T1.

Brewsterite: this framework too can be assembled connecting the heulandite units. There are four topologically different tetrahedral nodes, coded TA, TB, TC and TD by Perrotta and Smith (1964). The first three show T—O average distances of 1.66, 1.66, 1.67Å, whereas for TD the value is 1.58Å. Schlenker et al. (1977) confirmed these data, giving 1.645, 1.664, 1.660 for the first three and 1.607Å for the fourth tetrahedron. Hence all the Al is present in the first three tetrahedra; evidence for the validity of this assertion is given by the coordination around Sr, the only extraframework cation that includes O1 and O2, which are vertices of the first three tetrahedra but not of the fourth tetrahedron.

Offretite: there are two kinds of tetrahedral node in the framework: T1 in the double 6-rings and T2 in the simple 6-rings. The T—O distance is 1.66Å for T1 and 1.62Å for T2 (Gard and Tait 1972). Nearly all the Al is therefore present in the double rings, even more so considering that K, the only cation linked to framework oxygens, is bound to O2 and O3, both part of the double rings. On the other hand, the refinement performed on dehydrated natural offretite

Table 3. Average T—O distances (Å) in heulandites and clinoptilolites refined in space group C2/m.

Sample	Si: (Si + Al)	T1—O	T2—O	T3—O	T4—O	T5—O	Reference
Nadap	0.74	1.635	1.658	1.624	1.629	1.637	Alberti and Vezzalini (1983)
Faroes	0.75	1.630	1.658	1.640	1.615	1.635	Alberti (1972)
Iceland	0.75	1.633	1.655	1.637	1.629	1.654	Bartl (1973)
Mossyrock Dam	0.75	1.631	1.657	1.628	1.619	1.640	Galli et al. (1983)
Azerbaijan	0.79	1.624	1.658	1.630	1.620	1.628	Bresciani-Pahor et al. (1980)
Siusi	0.81	1.612	1.667	1.617	1.615	1.615	Alberti (1975)
Kuruma Pass	0.81	1.627	1.659	1.610	1.606	1.618	Koyama and Takeuchi (1977)
Agoura	0.83	1.625	1.645	1.612	1.607	1.615	Alberti (1975)
Agoura	0.83	1.624	1.645	1.618	1.615	1.614	Koyama and Takeuchi (1977)

(Mortier *et al.* 1976b) gives nearly equal values (1.632 and 1.629Å) for the two tetrahedra, and hence (Si, Al) disorder may also be possible in offretite.

Levyne: There are again two kinds of tetrahedral node, which may be part of double (T1) and single (T2) 6-rings. The T1—O distance is slightly greater (1.66Å) than the T2—O one (1.645Å) (Merlino *et al.* 1975). Out of the five extraframework cation sites, only C1 has a high occupancy (100 %) and is at bond distance from O2, a vertex of T1. So actually one cannot exclude a small Al enrichment in T1, even though evidence thereof is sparse (levyne, like erionite, could also be placed in class 4).

Mazzite: two kinds of tetrahedral node are also present in this framework: T1 in the 6-rings and T2 in the walls of the gmelinite cages, with T1—O = 1.653Å and T2—O = 1.639Å (Galli 1975). Alberti and Vezzalini (1981b) were able to give some evidence, based on crystal energy calculations, showing that the small (0.014Å) difference in bond lengths is significant and that there is more Al in Tl (33 %) than in T2 (24 %).

Class 4

Typical representatives of class 4 are those zeolites whose tetrahedra are all topologically equivalent: a tendency to (Si, Al) disorder is foreseeable and could be counteracted either by a Si: Al = 1:1 ratio or by the presence of a divalent medium-sized cation such as Ca. Typical examples are gmelinite, chabazite, faujasite, merlinoite and analcime.

Gmelinite: Galli *et al.* (1982) did not find any deviation from the maximum possible symmetry, which means that perfect (Si, Al) disorder only can be deduced from their refinement. On the other hand, the fact that sodium is the common extraframework cation does not favour order.

Chabazite: most of the refinements for this zeolite, with Si: (Si + Al) usually ca. 66 %, (see Alberti *et al.* 1982, and quoted references) have been performed with the maximum symmetry allowed by the framework, and hence with only one kind of tetrahedron and without hope of finding any order. This simple situation is certainly not valid when Si: (Si + Al) is lowered to 50 % as in willhendersonite, which exhibits perfect order (see class 1), and probably also not in many of the chabazites that show a symmetry lower than trigonal not only in optics (Majer 1953; Gottardi, 1978; Akizuki 1980, 1981) but also in structure (Mazzi and Galli 1983). These latter authors were able to demonstrate significant deviations in the tetrahedra dimensions from the average values when the symmetry was lowered from trigonal to triclinic. This partial (Si, Al) ordering in a framework in which the tetrahedra are in principle equivalent, is certainly related to the presence (in the mineral and in the solution from which it crystallized) of calcium, which, being divalent and medium-sized, strongly favours order.

Faujasite: all the refinements for this cubic zeolite were carried out in space group Fd3m, with only one independent tetrahedron, so that no deviation from disorder was detectable (Baur 1964; Bennett and Smith 1968).

Merlinoite: the framework of this zeolite, which is topologically tetragonal but really orthorhombic, contains two T—O distances, 1.64 and 1.65Å (Galli *et al.* 1979); hence no order is present. In agreement with this disorder, oxygens of the two tetrahedra are equally bound to extraframework cations.

Analcime: analcime may be cubic and, if so, all tetrahedra are symmetrically equivalent and hence exhibit perfect (Si, Al) disorder; the mineral can also be tetragonal, orthorhombic (Mazzi and Galli 1978) or even monoclinic (Hazen and Finger 1979). Schematically, the orthorhombic analcime has three non-equivalent tetrahedral nodes, each with a particular Al fraction; in the tetragonal analcime two of these three are equivalent and have the same Al fraction. The Al enrichment is always associated with a corresponding location of the extraframework cations, Na, which have some freedom of choice, because there are only 16 Na in a site of multiplicity 24. With its perfectly ordered (Si, Al) distribution, wairakite is inserted in class 2.

Other zeolites, *e.g.* erionite, phillipsite, harmotome, stilbite, stellerite and barrerite, are known to have fully disordered (Si, Al) distribution yet two or more topologically non-equivalent tetrahedra.

Erionite: like offretite, it contains double and single 6-rings (Kawahara and Curien 1969; Gard and Tait 1973), and hence tetrahedra of two kinds but with the same dimensions and both containing O1 and O2, the framework oxygens linked to the extraframework cation.

Phillipsite and *harmotome:* here we have only two topologically non-equivalent tetrahedra, but in the real monoclinic structure (Rinaldi *et al.,* 1974), there are four non-equivalent tetrahedral nodes with average T—O distances (in increasing order) of 1.651, 1.654, 1.655, 1.664Å; every tetrahedron contains two or three oxygens at bond distance from the extraframework cations. So there is not even the slightest evidence for order, which is consistent with the even distribution of the positive charges in the extraframework space.

Stilbite, stellerite and *barrerite:* Table 4 gives the average T—O distances in these zeolites, all with the same framework. No (Si, Al) order is apparent in their framework, in compliance with the fact that the main extraframework cation, Ca, is fully surrounded by water molecules and not in contact with framework oxygens. The other cation, Na, is monovalent and dispersed in many sites with low occupancy.

Conclusions

The (Si, Al) distribution in the tetrahedral framework of zeolites may be mainly ordered, as in our classes 1 and 2, or mainly disordered (with some partial enrichment in some tetrahedra), as in our classes 3 and 4.

According to a generally accepted model (see for instance Breck 1974, p. 340), during a crystallization of a zeolite from an alumino-silicate (true or colloidal) solution, rings or cages of tetrahedra are formed around a hydrated cation. This acts as a template, and so the newly formed cage tends to a definite, constant shape. Subsequently this fragment sticks to the growing crystals, partly changing its arrangement to fit the structure better if necessary. In our opinion, this particular model of crystal growth may be applied only to zeolites of classes 3 and 4, in which the order is either absent or present in a partial, statistical way; any partial order is always related to the location of the extraframework cations as required by the model. In one special case (analcime-wairakite), any situation from perfect disorder to perfect order is possible. One disturbing case is that of ferrierite, which displays some partial order in its framework, even though no extraframework cation is in contact with framework oxygens. Stilbite reveals a similar situation but is fully

Table 4. Average T—O distances (Å) in stilbite, stellerite and barrerite.

Mineral	Si1—O	Si2—O	Si3—O	Si4—O	Si5—O	Reference
Stilbite, Iceland	1.648	1.638	1.645	1.640	1.630	Galli (1971)
Stilbite, Nova Scotia	1.652	1.640	1.645	1.636	1.638	Slaughter (1970)
Stellerite, Sardinia	1.630		1.640	1.630	1.640	Galli and Alberti (1975a)
Barrerite, Sardinia	1.637		1.638	1.625	1.630	Galli and Alberti (1975b)

Note: Si1 and Si2 are symmetrically equivalent in stellerite; for barrerite, the value given for Si1 is the average of Si1 and Si1P, which together are equivalent to Si1 and Si2 of stilbite.

disordered; hence a certain tendency towards order is probably inherent in the structure type.

The template model cannot however be applied to the ordered zeolites of classes 1 and 2. During their growth, the parts added to the crystal surface are single ions or anionic groups such as AlO_4 and SiO_4, but not larger clusters. In other words they grow like normal crystals, the type of the new linked atom (Si or Al) depending only on the crystal structure already grown, and not on the »structure« of the solution (lato sensu).

In class 1 the choice between Si and Al is imposed by Loewenstein's rule, in class 2 probably by the »extended Loewenstein's rule« (Merlino, 1984): if Si: (Si + Al) > 0.5, Al must be distributed so as to minimize Al—O—Si—O—Al linkages. Such a rule may have importance only if the ratio Si: (Si + Al) is low; this is true for zeolites of class 2. The value of ratio is 60 % in natrolite, mesolite and scolecite; 66 % in wairakite and laumontite; and 75 % in yugawaralite. It is to be noted that in all three last-mentioned zeolites the extraframework cation is Ca, whose presence certainly favours order. All zeolites of class 2 always have a composition very near to the stoichiometric formula.

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