The Canadian Mineralogist
Vol. 40, pp. 1411-1419 (2002)

THE MESS THAT IS "ALLANITE"

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Abstract

"Allanite" is a poorly defined collection of species belonging to the epidote group. In the past, "allanite" was defined as merely being lanthanon-bearing, but more recently, it is defined as being *Ln*-dominant at the *A*2 site. Species of the allanite subgroup include allanite-(Ce), allanite-(La), allanite-(Y), androsite-(La), dissakisite-(Ce), dollaseite-(Ce) and khristovite-(Ce). Lack of recognition of the recommendations of Nickel & Mandarino (1987), and of the relation between members of the subgroup with "allanite" in their species name and those without, has led to a number of errors in naming species and in use of the term "allanite". Ten methods have recently been published describing how the relevant formulae may be calculated. Each is reviewed in conjunction with new observations on the behavior of Si, Cr, V, Mn^{2+} and *A*-site vacancies. This evaluation results in a recommended procedure for the calculation of the formula involving a basis of 6 ($M + T$) cations and 12(O,F,Cl) + 1(OH). Recalculation of the formulae of published compositions of allanite-subgroup minerals shows that some *apparently* new species are better interpreted as intermediate solid-solutions between conventional end-members; there are, however, at least five potentially new species awaiting description.

Keywords: epidote group, "allanite", androsite-(La), dissakisite-(Ce), dollaseite-(Ce), khristovite-(Ce), rare-earth elements, formula calculation, electron-microprobe analysis.

Sommaire

Le terme "allanite" fait allusion à un ensemble mal défini d'espèces faisant partie du groupe de l'épidote. Par le passé, "allanite" était utilisé pour représenter un membre du groupe à forte teneur en lanthanes (*Ln*), mais récemment, la précision que la dominance du *Ln* porte sur le site *A*2 est ajoutée. Les espèces faisant partie du sous-groupe de l'allanite incluent allanite-(Ce), allanite-(La), allanite-(Y), androsite-(La), dissakisite-(Ce), dollaséite-(Ce) et khristovite-(Ce). Parce qu'il est courant de passer outre les recommendations de Nickel et Mandarino (1987), et que certains membres du sous-groupe possèdent le mot "allanite" dans le nom de l'espèce et d'autres ne le possèdent pas, il y a eu plusieurs erreurs dans l'attribution d'un nom et dans l'utilisation du mot "allanite". Dix méthodes ont été utilisées dans la littérature pour en arriver à une formule chimique de ces espèces. Chacune de celles-ci est évaluée à la lumière de nouvelles observations sur le comportement de Si, Cr, V, Mn^{2+} et les lacunes sur le site *A*. Cette évaluation mène à une procédure recommandée pour le calcul de la formule sur une base de six cations ($M + T$) et 12(O,F,Cl) + 1(OH). Une ré-évaluation des formules publiées montre que certaines espèces nouvelles semblent mieux interprétées comme membres intermédiaires de solutions solides entre membres conventionnels du sous-groupe. Toutefois, cinq nouvelles espèces potentielles n'ont pas encore été décrites.

(Traduit par la Rédaction)

Mots-clés: groupe de l'épidote, "allanite", androsite-(La), dissakisite-(Ce), dollaséite-(Ce), khristovite-(Ce), terres rares, calcul de la formule, analyse à la microsonde électronique.

Introduction

"Allanite" is the compositionally most diverse part of the epidote group. By far the most common species of "allanite", allanite-(Ce), is defined as $(Ce,Ca,Y)_2(Al,Fe^{2+},Fe^{3+})_3(SiO_4)_3(OH)$. Although this is an adequate description of the chemical composition of allanite-(Ce), it is not an end-member formula; rather, the formula describes a mixture of many distinct end-members. A comparison of the results of the various studies of allanite is difficult without recalculating formulae: there are at least ten methods of formula calculation used in modern studies (post-1980). Without a formal definition of "allanite", much less of allanite-(Ce), it is difficult to accurately name lanthanon-bearing species of the epidote group; indeed, errors in nomenclature are bound to be occasionally made. The following is a review of the current status of "allanite",

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[§] *E-mail address*: sercit@mus-nature.ca and an assessment of procedures for formula calculation and site assignment. Here, lanthanon (*Ln*) is considered to represent the rare-earth elements (*REE*) and yttrium.

WHAT IS "ALLANITE"?

"Allanite" was originally coined to describe unaltered, tabular *Ln*-bearing (predominantly cerian) members of the epidote group. "Orthite" was used to denote prismatic, altered *Ln*-bearing members of the group. Despite western (allanite) *versus* eastern (orthite) preferences for these terms, "allanite" has historical precedence over "orthite", which is now obsolete. With invocation of the Levinson rules, "allanite" became allanite-(Ce) and allanite-(La), and "yttro-orthite" became allanite-(Y), depending upon the dominant lanthanon (Levinson 1966, Nickel & Mandarino 1987). Note, however, that Levinson (1966) incorrectly stated that allanite-(La) comes from *two* granitic pegmatites in Karelia; upon examination, the original data of Zhirov *et al.* (1961) clearly show that it was found only in the Olenchik pegmatite, northern Karelia, Russia.

The distinction between "allanite" and other members of the epidote group is somewhat muddled. First, there is the historical use of "allanite" as merely a *Ln-bearing* member of the epidote group. Many mineralogists and petrologists still use the term in this manner; consequently, *Ln*-bearing epidote is occasionally incorrectly called "allanite", even in modern studies [Gieré (1986), and, in part, Pan & Fleet (1990) and Peterson & MacFarlane (1993)]. Second, the introduction of dissakisite-(Ce), dollaseite-(Ce), khristovite-(Ce) and androsite-(La) as new members of the epidote group with *Ln* dominant at the *A*2 site has confused some investigators, who associate the term "allanite" with *Ln*-bearing or *Ln*-dominant epidote: Zakrzewski *et al.* (1992) originally called the dissakisite-(Ce) from Bergslagen, Sweden "allanite-(Ce)". Third, the formula contents of "allanite" are commonly grouped, rather than assigned to individual sites (or even not grouped at all). Consequently, if samples of a distinct composition are encountered, they are occasionally not recognized or are misidentified: Treloar & Charnley (1987) called their samples of dissakisite-(Ce) and apparent "dissakisite-(La)" (not yet recognized by the IMA) "chromian allanite", not noticing the more important role of Mg; Pan & Fleet (1991) called their samples of lanthanian cerian mukhinite "*REE*-enriched epidote".

The formula for allanite-(Ce) is commonly given as $(Ce,Ca,Y)_2(Al,Fe^{2+},Fe^{3+})_3(SiO_4)_3(OH)$ (*e.g.*, Mandarino 1999). However, note that:

(i) There are two large cation sites, one that strongly prefers Ca, the other, *Ln*; thus the formula is better written as $Ca(Ce,Ln)(Al,Fe^{2+},Fe^{3+})_3(SiO_4)_3(OH)$.

(ii) There are two distinct groupings of silicate anions in the crystal structure, Si_2O_7 dimers and SiO_4 islands, so the general formula is more accurately modified to $Ca(Ce,Ln)(Al,Fe^{2+},Fe^{3+})_3(Si_2O_7)(SiO_4)O(OH)$.

(iii) Octahedrally coordinated *M* cations in epidote-group minerals are highly ordered, and all *other* members of the epidote group are defined on the basis of distinct occupancy of the three *M* sites (Table 1). Given that published structure refinements of allanite-(Ce) show Al to be dominant at two of the three *M* sites and Fe^{2+} to be dominant at the other (*e.g.*, Dollase 1971), the end-member formula for allanite-(Ce) is $CaCeFe^{2+}Al_2(Si_2O_7)(SiO_4)O(OH)$.

Similarly, the end-member formula of allanite-(La) is $CaLaFe^{2+}Al_2(Si_2O_7)(SiO_4)O(OH)$, and allanite-(Y),

TABLE 1. KNOWN MEMBERS OF THE EPIDOTE GROUP

	Species	Composition	End-Member Site Populations					
		*A*1 *A*2 *M*3 *M*1 *M*2 (Si_2O_7) (SiO_4) *O*4 (OH)	*O*4	*M*2	*M*1	*M*3	*A*2	*A*1
A	Zoisite	$Ca_2Al_3(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Al	Ca	Ca
	Clinozoisite	$Ca_2Al_3(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Al	Ca	Ca
	Epidote	$Ca_2Fe^{3+}(Al,Fe^{3+})Al(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Fe^{3+}	Ca	Ca
	Hancockite	$Ca(Pb,Sr)Fe^{3+}Al_2(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Fe^{3+}	Pb^{2+}	Ca
	Piemontite	$Ca_2(Mn^{3+},Fe^{3+})Al_2(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Mn^{3+}	Ca	Ca
	Strontiopiemontite	$CaSr(Mn^{3+},Fe^{3+})Al_2(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Mn^{3+}	Sr	Ca
	Mukhinite	$Ca_2V^{3+}Al_2(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	V^{3+}	Ca	Ca
B	Allanite-(Ce)	$Ca(Ce,La,Ca)(Fe^{2+},Fe^{3+})(Al,Fe^{3+})Al(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Fe^{2+}	Ce	Ca
	Allanite-(La)	$Ca(La,Ce,Ca)(Fe^{2+},Fe^{3+})(Al,Fe^{3+})Al(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Fe^{2+}	La	Ca
	Allanite-(Y)	$Ca(Y,Ce,Ca)(Fe^{2+},Fe^{3+})(Al,Fe^{3+})Al(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Fe^{2+}	Y	Ca
	Dissakisite-(Ce)	$Ca(Ce,La)MgAl_2(Si_2O_7)(SiO_4)O(OH)$	O	Al	Al	Mg	Ce	Ca
	Dollaseite-(Ce)	$Ca(Ce,La,Nd)Mg_2Al(Si_2O_7)(SiO_4)F(OH)$	F	Al	Mg	Mg	Ce	Ca
	Khristovite-(Ce)	$(Ca,REE)(Ce,Nd,La)Mn^{2+}(Mg,Fe^{2+})Al(Si_2O_7)(SiO_4)(F,O)(OH)$	F	Al	Mg	Mn^{2+}	Ce	Ca
	Androsite-(La)	$(Mn,Ca)(La,Ce)Mn^{2+}Mn^{3+}Al(Si_2O_7)(SiO_4)O(OH)$	O	Al	Mn^{3+}	Mn^{2+}	La	Mn^{2+}

A: epidote subgroup (Y or REE not dominant at *A*2). **B**: allanite subgroup (Y or REE dominant at *A*2)

$CaYFe^{2+}Al_2(Si_2O_7)(SiO_4)O(OH)$. Other cation-ordered variants, such as $CaCeFe^{2+}Fe^{3+}Al(Si_2O_7)(SiO_4)O(OH)$, are possible. Because of the precedents established by dissakisite-(Ce) and dollaseite-(Ce), these variants would probably deserve new trivial names.

Conclusion

Because of (i) the lack of any obvious relation in nomenclature among allanite-(Ce), allanite-(Y), allanite-(La), androsite-(La), dissakisite-(Ce), dollaseite-(Ce) and khristovite-(Ce), (ii) the confusion in nomenclature that already exists, and (iii) the explosion of new species and trivial names that might follow a better definition of the "allanite" problem", it would be prudent to refer to all *Ln*-dominant members of the epidote group as belonging to an allanite subgroup.

THE DERIVATION OF FORMULA CONTENTS FROM ELECTRON-MICROPROBE DATA: A REVIEW

Many approaches have been published on how to calculate formula contents of allanite-subgroup minerals from electron-microprobe data. The following list is a summary of the approaches taken in relatively *recent* publications.

Method 1: 12.5 (O) and all Fe as Fe^{2+}

This method of formula calculation was used by Treloar & Charnley (1987) and Finger *et al.* (1998). The main flaw with the procedure lies with the erroneous assumption that all Fe is Fe^{2+}, *i.e.*, that there is no solid solution between Fe^{2+}-bearing allanite-subgroup minerals and epidote (Fe^{3+}-bearing). In addition, the formulae of Finger *et al.* (1998) are not charge-balanced, and their *Ln*-bearing epidote is really a *Ln*-bearing ferrian clinozoisite.

Method 2: 12(O) + 1(OH,F), and all Fe as Fe^{2+}

Grew *et al.* (1991) used this approach for calculating the formula of dissakisite-(Ce). Although it might give a reasonable estimate of (OH), it incorrectly assumes that F is ordered at *O*10 (OH site), whereas an analysis of hydrogen bonding in dollaseite-(Ce) convincingly showed F to be ordered at *O*4 (Peacor & Dunn 1988). The argument against assuming all Fe as Fe^{2+} is as in method 1, above.

Method 3: 3(Si) apfu and all Fe as Fe^{2+}

Peacor & Dunn (1988) and Rouse & Peacor (1993) used this basis for calculating the formulae of dollaseite-(Ce) and dissakisite-(Ce). Although reasons were not given for using 3(Si) as a basis of normalization, one can reasonably assume that the approach derived from the lack of any correlation between Si–O bond lengths and inferred $^{[4]}Al$ (= 3 – Si *apfu*) for members of the epidote group. However, at the time Rouse & Peacor (1993) published their findings, there were too few refinements of lanthanon-bearing members of the epidote group to be certain that Al $\rightleftharpoons$ Si substitution does not occur in allanite-subgroup minerals. Furthermore, normalization to 3(Si) transfers all errors in Si determination to other cations in the formula, and results in potentially larger absolute errors on numbers of cations. See method 1 for the error in assuming all Fe to be Fe^{2+}.

Method 4: 13(O,OH) and all Fe as Fe^{2+}, assuming 2 wt.% H_2O

This approach, adopted by Campbell & Ethier (1984), is certainly one of the more unusual bases for calculating the formulae of allanite-subgroup minerals. Although it might be safe to assume a *maximum* of approximately 2 wt.% H_2O in allanite-subgroup minerals when assessing the analytical totals of electron-microprobe analyses, one should not use this crude approximation in calculating formulae. As with method 1, the assumption of all Fe as Fe^{2+} is not valid.

Method 5: 12.5(O) and a charge-balance mechanism for Fe^{3+} : Fe^{2+}

In this approach, taken by Pan & Fleet (1989, 1990), the charge-balance mechanism is unstated, and the calculated formulae are actually *not* charge-balanced.

Method 6: 12.5(O) and all Fe^{3+} at M1, all Fe^{2+} at M3

Zakrzewski *et al.* (1992) used this method as a basis of calculation of the formulae of dissakisite-(Ce) samples from the Koberg mine, Bergslagen district, Sweden. Although Fe^{2+} has been shown to avoid the *M*1 site (Dollase 1971, Bonazzi & Menchetti 1995), Fe^{3+} actually *prefers* the *M*3 site over the *M*1 site (hence the species epidote). This is not a valid approach for calculation of the Fe^{3+}:Fe^{2+} ratio.

Method 7: A total of eight cations, open-ended total of anions, and all Fe as Fe^{3+}

Although this was not the approach taken in their structure-analysis work, Bonazzi & Menchetti (1995) and Bonazzi *et al.* (1996) did actually use this approach to calculate the formula contents of allanite-(Ce) and androsite-(La) from electron-microprobe data. Although the assumption of Σcations = 8 is a good approach to take in calculating the formulae of allanite-subgroup minerals, an open-ended total of anions and the assumption of all Fe as Fe^{3+} are not good assumptions to use in calculating formulae.

Method 8: 12.5(O) and a total of eight cations

This is a popular (Chesner & Ettlinger 1989, Sorensen 1991, Carcangiu *et al.* 1997, Liu *et al.* 1999) and reasonably good approach, and one that generates an estimate of Fe^{3+}/Fe^{2+}. In this approach, formulae are first calculated on a basis of a total of eight cations, and Fe^{2+} / Fe^{3+} is varied until the total number of positive charges equals 25 (to balance 12.5 effective O ions). Although the method compensates for the presence of OH, it does not produce a calculated value of H_2O (wt.%). Furthermore, it assumes that no *A*-site vacancies are present in lanthanon-bearing members of the epidote group; the structure refinement of Sokolova *et al.* (1991) and the electron-microprobe data of Peterson & MacFarlane (1993) indicate otherwise.

Method 9: 12(O) + 1(OH) and a total of eight cations

There is really no difference between this approach (Gieré 1986, Wood & Ricketts 2000) and method 8 above, except that an estimate of H_2O (wt.%) is generated.

Method 10: 6 (M + T) cations and 12(O) + 1(OH)

With this basis of calculation, one assumes that there are no vacancies at the octahedral or tetrahedral sites, but the possibility of vacancies at the *A* sites is left open. One also assumes that there is no substitution of O for OH at *O*10. These assumptions are supported by all structure refinements published to date. Formulae are first calculated by normalizing the (*M* + *T*) cations to 6; this step is followed by varying Fe^{2+}/Fe^{3+} until the total number of positive charges equals 25. A method similar to this was used by MacFarlane (1987); note, however, that his results are not quite charge-balanced.

Conclusion

Methods 8 to 10 are the only statistically and crystal-chemically valid approaches to calculating the formulae of allanite-subgroup minerals, and of these, method 10 is superior.

SPECIAL CONSIDERATIONS

T-site populations

The *T* sites are generally considered to be fully occupied by Si (*e.g.*, Bonazzi & Menchetti 1995). However, there is a weak, but significant ($P[H_0] = 0.004$) negative correlation between total Si and total Al for *Ln*-bearing members of the epidote group from the Grenville Province (Fig. 1a). Given that (i) the plot has a negative slope, (ii) a plot of total Si *versus* total Al is independent of errors in $Fe^{2+}:Fe^{3+}$, O:OH estimation and site assignment, and (iii) data for these samples represent the results of two independent studies, Figure 1a indicates that very minor Al does occur in the *T* sites of *Ln*-bearing members of the epidote group. Figure 1b shows the most likely form of charge balance: Al $\rightleftharpoons$ Si is balanced by *Ln* $\rightleftharpoons$ Ca.

The role of Mn^{2+}

Because of the (generally) minor amounts of Mn^{2+} present in allanite-(Ce), there is no consensus as to the location of Mn^{2+}. It is known that Mn^{2+} can occupy either *M*3 or *A*1 (Bonazzi *et al.* 1996), but nothing is known of its relative preference for these sites. By calculating formulae on the basis of a total of eight cations, the issue is avoided; the role of Mn^{2+} does not affect the basis of formula calculation. However, in order to calculate a formula on 6 (*M* + *T*) cations, it is essential to know whether Mn^{2+} occupies *M*3, *A*1 or both.

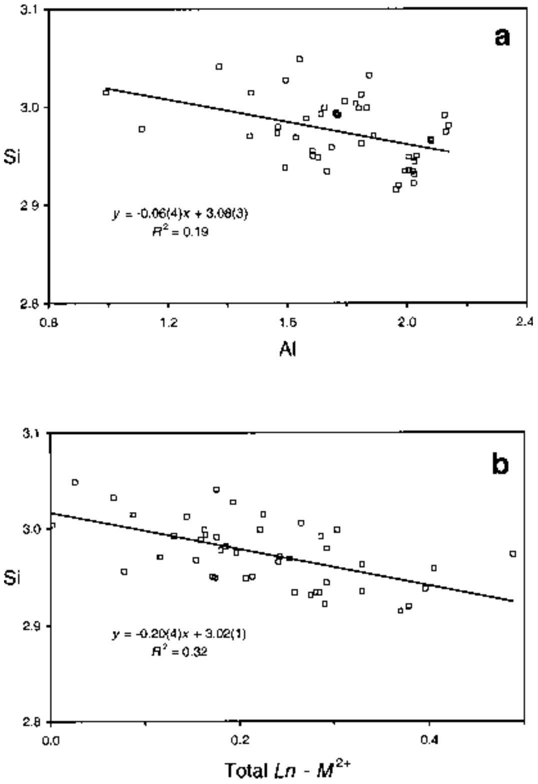

FIG. 1. Behavior of Si in *Ln*-bearing members of the epidote group from the southwestern Grenville Province, Canada: (a) Si *versus* total Al; (b) Si *versus* excess *Ln*. Data from Peterson & MacFarlane (1993) and to a minor extent, unpublished data of the author.

Figure 2 shows the total occupancies of the *M*3 and *A*1 sites as a function of Mn^{2+} content of the relatively Mn-rich *Ln*-bearing members of the epidote group from the Grenville Province. In Figure 2a, one assumes that Mn^{2+} is exclusively at *M*3. If Mn^{2+} has been correctly assigned, there should be no correlation between total site-occupancy and Mn^{2+} content. This is clearly not the case; the *M*3 occupancy rises to excessive levels (>>1 atoms per formula unit, *apfu*) as Mn^{2+} increases, and the total occupancy of *A*1 decreases as Mn^{2+} increases, *by an amount that matches the increase in M3 occupancy*. If one assumes that all Mn^{2+} is at *A*1, trends opposite and equal in magnitude to those of Figure 2a are observed (not shown here). Figure 2b is similar to Figure 2a, except that Mn^{2+} is disordered equally over *M*3 and *A*1. The absence of a correlation between Mn^{2+} content and total site-occupancy in Figure 2b indicates that Mn^{2+} shows no ordering preference for either *M*3 or *A*1.

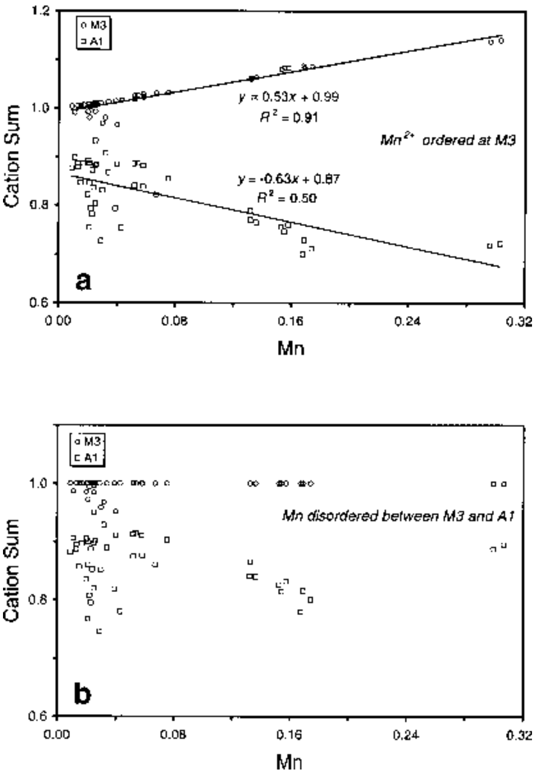

FIG. 2. Partitioning of Mn^{2+} in *Ln*-bearing members of the epidote group from the southwestern Grenville Province. (a) Behavior of cation sums at the *M*3 and *A*1 sites if one assumes that all Mn^{2+} orders at *M*3. (b) Behavior of cation sums if one assumes disorder of Mn^{2+} between *M*3 and *A*1. Data sources are as in Figure 1.

The role of Cr^{3+}

The partition of Cr^{3+} between *M*1 and *M*3 is problematic in that $^{[6]}Cr^{3+}$ is intermediate in size to $^{[6]}Al$ and $^{[6]}Fe^{3+}$ (albeit closer to Fe^{3+}). Chromian dissakisite-(Ce) (Treloar & Charnley 1987) is so magnesian and aluminous that Cr^{3+} must be ordered primarily at *M*3 with Mg. In more typical compositions of allanite-subgroup minerals (*i.e.,* those poor in Mg and rich in Fe^{2+}), Cr^{3+} is likely to order at *M*1. For compositions in which abundant Fe^{3+} is present at *M*3, some disorder of Cr^{3+} between *M*1 and *M*3 is expected.

The role of V^{3+}

To date, no structure refinement exists for any vanadium-rich epidote-group mineral. However, mineral compositions and results of spectroscopic analyses impose constraints on the behavior of V^{3+}. On the basis of optical absorption spectra, Burns & Strens (1967) proposed that V^{3+} prefers the more highly distorted *M*3 site in epidote-group minerals. However, the observations of Burns & Strens (1967) are based only on Al-rich members of the group, and their conclusions should be applied only to such compositions. The electron-microprobe data of Kato *et al.* (1994) for vanadian "allanite-(Ce)" (more likely ceroan vanadian *epidote*) unambiguously show that V^{3+} is disordered between *M*1 and *M*3 in highly ferrian compositions of allanite-subgroup minerals. This can be easily rationalized on the basis of ionic radius: $^{[6]}Fe^{3+}$ and $^{[6]}V^{3+}$ have nearly identical radii (Shannon 1976); some disorder of V^{3+} between *M*1 and *M*3 thus is to be expected for Fe^{3+}-rich compositions.

A-site vacancies

Both compositional data (Peterson & MacFarlane 1993) and structure refinements (Sokolova *et al.* 1991) imply the presence of vacancies (□) at the *A* sites. Where formulae of *Ln*-bearing members of the epidote group of the present study are calculated on the basis of 6 (*M* + *T*) cations, many samples show significantly low *A*-cation sums. Peterson & MacFarlane (1993) showed that the total occupancy of the *A* sites correlates with "excess" *Ln* content (*i.e.*, excessive with respect to the amount required to charge-balance the substitution of M^{2+} cations for M^{3+} cations: $Ln - M^{2+}$). This is illustrated in Figure 3, a reproduction of Figure 3 of Peterson & MacFarlane (1993), less compositional data for altered samples. The question exists whether the low occupancy of the *A* sites is actually due to low numbers of *A* cations, or is perhaps an artifact of the basis of formula calculation. To this effect, three times the *A*-cation sum divided by the (*M* + *T*)-cation sum will produce values that are independent of the basis of formula calculation. In the absence of *A*-site vacancies, the frequency distribution of these values should be normal, and have a mean of 1 and a standard deviation of 1 to

1.5% (based on typical operating conditions for electron-microprobe analysis). Figure 4 shows the frequency distribution for the present study (123 samples, mean 0.961, standard deviation 3.8%). The 99% confidence limits are ±0.009, thus the mean of 0.961 is significantly different from the ideal value of 1, and *A*-site deficiencies are statistically significant. Note, however, that the data of Figure 4 do not show significant skewness or kurtosis, which is not surprising given the high standard deviation.

Are vacancies ordered or disordered between the two *A* sites? In their refinement of the crystal structure of khristovite-(Ce), Sokolova *et al.* (1991) inferred that vacancies are disordered over *A*1 and *A*2. However, given the high proportions of Ca, *Ln* and vacancies in khristovite-(Ce), and the small number of vacancies at *A*2 (7%), a statistically similar, if not identical, result can be obtained by modeling *A*2 as fully occupied by *Ln* + Ca and by ordering all vacancies at *A*1. This model is supported by bond-valence considerations: higher-charge cations (Ln^{3+}, Th^{4+}) strongly prefer *A*2, and the bond-valence contributions from the [12]-coordinated cation at *A*1 to its coordinating anions are much less than those from the [9]-coordinated cation at *A*2.

Most *Ln* is introduced in epidote–allanite solid solution by means of the mechanism:

$$^{M3}\mathrm{Fe}^{2+} + {}^{A2}Ln^{3+} \rightleftharpoons {}^{M3}\mathrm{Fe}^{3+} + {}^{A2}\mathrm{Ca} \qquad (1)$$

However, the mechanism of Peterson & MacFarlane (1993) for excess *Ln* involves:

$$3\mathrm{Ca} \rightleftharpoons 2Ln^{3+} + \square \qquad (2)$$

This mechanism relates epidote–clinozoisite, $\mathrm{Ca}_2M3^{3+}\mathrm{Al}_2(\mathrm{Si}_2\mathrm{O}_7)(\mathrm{SiO}_4)\mathrm{O(OH)}$, to a set of hypothetical end-members, $(\mathrm{Ca}_{0.5}\square_{0.5})LnM3^{3+}\mathrm{Al}_2(\mathrm{Si}_2\mathrm{O}_7)(\mathrm{SiO}_4)\mathrm{O(OH)}$, that, unlike allanite-(Ce), allanite-(La) and allanite-(Y), are devoid of Fe^{2+}.

Linear combination of (1) and (2) gives the relation between the end-members allanite-(Ce), allanite-(La), and allanite-(Y) and hypothetical end-members $(\mathrm{Ca}_{0.5}\square_{0.5})LnM3^{3+}\mathrm{Al}_2(\mathrm{Si}_2\mathrm{O}_7)(\mathrm{SiO}_4)\mathrm{O(OH)}$:

$$2\,{}^{M3}\mathrm{Fe}^{2+} + {}^{A1}\mathrm{Ca} \rightleftharpoons 2\,{}^{M3}\mathrm{Fe}^{3+} + {}^{A1}\square \qquad (3)$$

The proportions of the three *groups* of end-members [epidote–clinozoisite *versus* allanite-(Ce), allanite-(La) and allanite-(Y) *versus* $(\mathrm{Ca}_{0.5}\square_{0.5})LnM3^{3+}\mathrm{Al}_2(\mathrm{Si}_2\mathrm{O}_7)(\mathrm{SiO}_4)\mathrm{O(OH)}$] can be estimated from *A*2-site contents by $^{A2}\mathrm{Ca}$ (epidote–clinozoisite component), $2\,{}^{A1}\square$ [*Ln* associated with $(\mathrm{Ca}_{0.5}\square_{0.5})LnM3^{3+}\mathrm{Al}_2(\mathrm{Si}_2\mathrm{O}_7)(\mathrm{SiO}_4)\mathrm{O(OH)}$ end-members], and $Ln - 2\,{}^{A1}\square$ [*Ln* associated with allanite-(Ce), allanite-(La) and allanite-(Y) end-members]. Similarly, the proportions can be estimated from *M*3-site contents by $M3^{3+} - 2^{A1}\square$ (trivalent *M*3-site cations attributable to epidote–clinozoisite end-members), $2^{A1}\square$ [trivalent *M*3-site cations attributable to $(\mathrm{Ca}_{0.5}\square_{0.5})LnM3^{3+}\mathrm{Al}_2(\mathrm{Si}_2\mathrm{O}_7)(\mathrm{SiO}_4)\mathrm{O(OH)}$ end-members], and $M3^{2+}$ [allanite-(Ce), allanite-(La) and allanite-(Y) end-members]. The best estimate is obtained by combining expressions for both the *A*2 and *M*3 sites. Hence Figure 5 is a useful plot for assessing species affiliation and the relative degree of significance of each of the three groups of end-members.

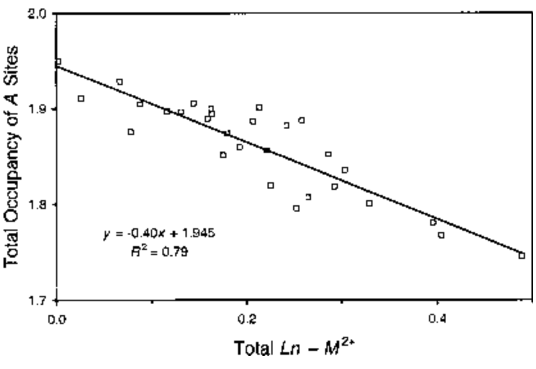

FIG. 3. Variation of total occupancy of *A* sites with "excess" *Ln* (= $Ln - M^{2+}$). After Peterson & MacFarlane (1993), without data for altered samples (R1006, R1008, R1024, R1041 to R1043, R1048 and R1054).

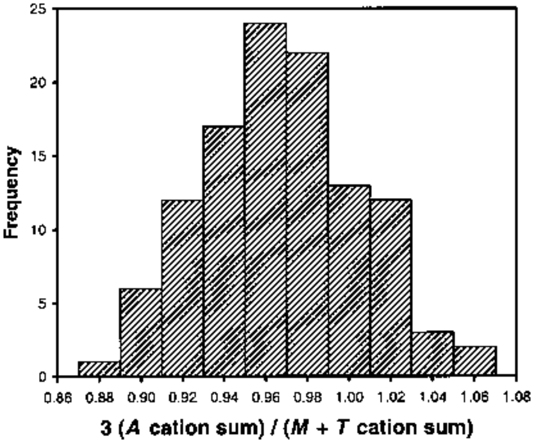

FIG. 4. Sum of *A* cations normalized to the sum of (*M* + *T*) cations. In the absence of *A*1-site vacancies, the normalized sum should be 1. Data sources are: Campbell & Ethier (1984), Carcangiu *et al.* (1997), Chesner & Ettlinger (1989), Finger *et al.* (1998), Gieré (1986), Peterson & MacFarlane (1993), Pan & Fleet (1990), Treloar & Charnley (1987), Wood & Ricketts (2000), Zakrzewski *et al.* (1992), and unpublished data of the author for granitic pegmatites from the Grenville Province, Canada.

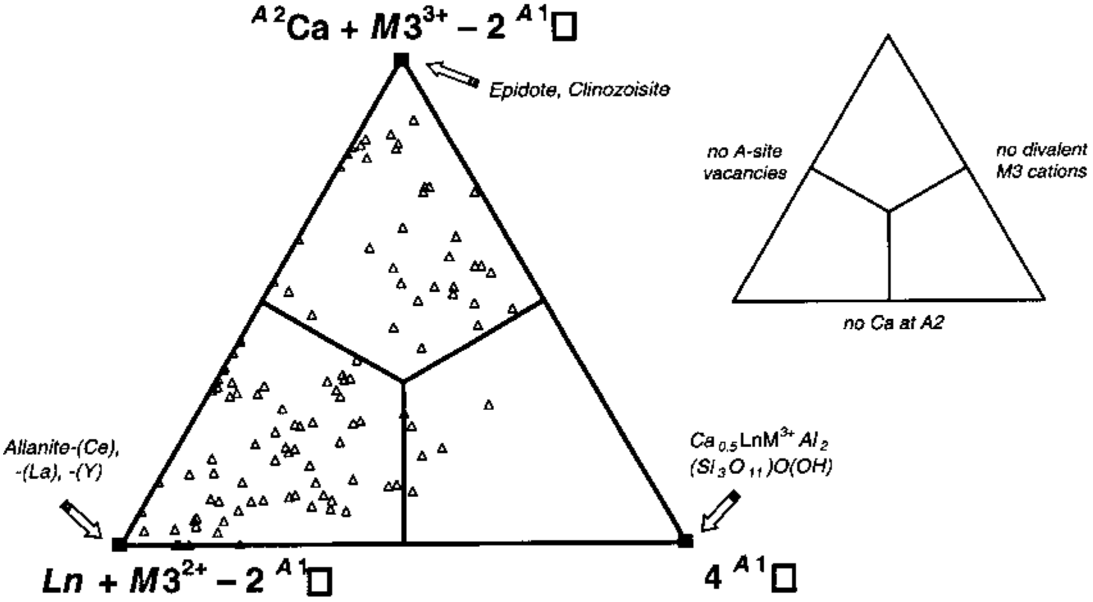

FIG. 5. Chemical variations in the lanthanon-bearing members of the epidote group. Inset: interpretation of the side-lines; data sources as in Figure 3.

Formula Calculation for *Ln*-bearing Members of the Epidote Group: Suggested Approach

The crystal structures of epidote-group minerals are highly susceptible to damage from alpha particles, and even low levels of actinide elements (predominantly Th) can induce considerable structural damage. Members of the allanite subgroup are commonly Th- or U-bearing; consequently, they may be metamict, and thus highly susceptible to alteration. If it is suspected that a sample of an allanite-subgroup mineral or a region within a crystal has undergone detectable alteration (*e.g.*, vermiform textures in BSE images, additional phases in XRD patterns, analytical totals below about 96%, including calculated H_2O), no attempt should be made to calculate formula contents from analytical results.

The following procedure for calculating the formulae of lanthanon-bearing members of the epidote group is based on published refinements of the structure, chemical data, and arguments presented in preceding sections; it applies only to unaltered samples. Attempts to use the procedure on samples that are known to have suffered post-metamictization alteration (*e.g.*, Campbell & Ethier 1984) can result in excessive Si contents (more than 3.09 *apfu*), uneven distribution of cations among the *M* sites, and deviant *A*-site sums.

1) *Unless otherwise indicated*, all Mn should be considered as Mn^{2+}. MnO is assigned equally between the *M* sites and the *A* sites. As such, only one-half of the total Mn^{2+} is used in the normalization scheme of step (2), below. (For ease of calculation, if Mn contents are low, *e.g.*, less than 0.10 Mn^{2+} *apfu*, it is acceptable to consider all Mn^{2+} as a *M* cation).

2) A tentative formula is calculated on a basis of 6 ($M + T$) cations and 12 (O,F,Cl) + 1 (OH). Fluorine and Cl should *not* be assumed to occupy the *O*10 site with OH. In some instances, it will not be possible to normalize on a fixed number of cations *and* anions. Rather than generate negative amounts of Fe^{2+} or Fe^{3+}, anion-site vacancies, or OH $\rightleftharpoons$ O disorder, formulae for these compositions should be calculated on a fixed number of anions only (*i.e.*, 12[O,F,Cl] + 1[OH]), and all Fe should be assumed to be either ferrous or ferric.

3) All Si is assigned to the *T* sites. If total Si is less than 3 *apfu*, $^{[IV]}$Al is calculated as 3 – Si.

4) The *M*2 site is fully occupied by Al; any minor deficit (1 – Al) is to be considered as Fe^{3+}.

5) Ti^{4+} is assigned to *M*1. For Mg-poor compositions, Cr^{3+} is assigned to *M*1. Aluminum is assigned as 1 – (Ti + ^{M1}Cr); if, after steps 3 and 4, there is insufficient Al, Fe^{3+} and then Mg are assigned to bring the *M*1-site total to 1. (Note: In the presence of abundant Mn^{2+} at *M*3, Mn^{3+} will order at *M*1; however, in most cases, Mn^{3+}, where present, orders at *M*3).

6) All Fe^{2+}, Cu^{2+}, *M*-site Mn^{2+} and V^{3+} is assigned to *M*3, together with the remainder of all Al, Mg, Cr,

TABLE 2. UNUSUAL COMPOSITIONS OF "ALLANITE"

Dominant Constituent					Reference	Analysis Number	Interpretation
*A*1	*A*2	*M*3	*M*1	*M*2			
Ca	Ce	Al	Al	Al	Carcangiu *et al.* (1997)	8	ceroan clinozoisite
Ca	Ca	Fe^{2+}	Al	Al	Pan & Fleet (1990)	core	ceroan clinozoisite
Ca	Ce	Fe^{3+}	Al	Al	Peterson & MacFarlane (1993)	R1005, 1014, 1015, 1018, 1020, 1023, 1025, 1027, 1028, 1032, 1044, 1052	mostly epidote – allanite-(Ce) solid solution
Ca	Y	Fe^{3+}	Al	Al	Peterson & MacFarlane (1993)	R1012	yttrian epidote
Ca	Ce	Fe^{3+}	Al	Al	Peterson & MacFarlane (1993)	R1002, 1011, 1019, 1035	*new end-member:*
					Chesner & Ettlinger (1989)	8-1	$(Ca_{0.5}\square_{0.5})CeFe^{3+}Al_2(Si_2O_7)(SiO_4)O(OH)$
Ca	La	V^{3+}	Al	Al	Pan & Fleet (1991)	4,6	*new end-member:* $CaLaV^{3+}Al_2(Si_2O_7)(SiO_4)O(OH)$
Ca	Ce	Fe^{2+}	Fe^{3+}	Al	Peterson & MacFarlane (1993)	R1026, 1045	*new end-member:*
					Wood & Ricketts (2000)	all *but* 12A-2, 12B-1, 12B-3	$CaCeFe^{2+}Fe^{3+}Al(Si_2O_7)(SiO_4)O(OH)$
Ca	La	Fe^{2+}	Fe^{3+}	Al	Peterson & MacFarlane (1993)	R1040	*new end-member:* $CaLaFe^{2+}Fe^{3+}Al(Si_2O_7)(SiO_4)O(OH)$
Ca	La	Mg	Al	Al	Treloar & Charnley (1987)	6, 8, 9, (11)	*new end-member:* $CaLaMgAl_2(Si_2O_7)(SiO_4)O(OH)$

Fe^{3+}. (Note: for Fe^{3+}-rich compositions, V will disorder over *M*1 and *M*3.)

7) All *Ln* is assigned to *A*2, together with Sr, Pb^{2+}, Cd, U^{4+} and Th^{4+}. Ca is assigned to bring the *A*2-site sum to 1.

8) All remaining Ca is assigned to *A*1, together with all Na and all *A*-site Mn^{2+} from step 1.

The above procedure necessarily generates the highest degree of order possible for lanthanon-bearing members of the epidote group. In reality, Fe^{3+} and Al^{3+} show variable degrees of disorder over *M*1 and *M*3 (Bonazzi & Menchetti 1995); at present, it is premature to attempt to model order–disorder relations involving the *M*1 and *M*3 sites.

UNUSUAL COMPOSITIONS

On the basis of the above procedure to calculate a formula, the results of a number of published studies were re-examined. Table 2 lists unusual compositions of allanite-subgroup minerals based on dominant constituents of the various sites, and on interpretation of these compositions. Many of these would seem to represent new species if interpreted on the basis of dominant-site constituent rather than dominant end-member components. For example, sample 8 of Carcangiu *et al.* (1997) would seem to represent a new species because of its unique composition, with Al dominant at *M*3 and *Ln* (Ce) dominant at *A*2. However, it is impossible to construct an end-member for such a composition without invoking a significant proportion of vacancies at *A*1, contrary to the observed full occupancy of *A*1 for sample 8. Instead, it is more correct to interpret sample 8 as an intermediate composition consisting mostly of a solid solution between clinozoisite and allanite-(Ce), with other less significant components. The same logic applies to the next three compositions in Table 2, which are more correctly interpreted as the products of solid solution between clinozoisite and allanite-(Ce), then epidote and allanite-(Ce), and epidote and allanite-(Y), respectively. However, the five remaining compositions feature significant amounts of components of as-of-yet unrecognized end-members. The proportions of these new components are sufficient to warrant descriptions of new species; however, to do so requires further work on these samples.

ACKNOWLEDGEMENTS

The author thanks F.C. Hawthorne, Associate Editor C.M. Gramaccioli, and R.F. Martin for their constructive reviews. Research was funded by a Canadian Museum of Nature RAC grant.

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Received October 17, 2001, revised manuscript accepted September 10, 2002.