



Article

Minasgeraisite-(Y) discredited as an ordered intermediate between datolite and hingganite-(Y)

Daniel Atencio

Instituto de Geociências, Universidade de São Paulo, Brazil

Abstract

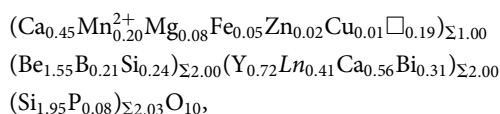
Minasgeraisite-(Y) is discredited on the basis of it being an ordered intermediate between datolite and hingganite-(Y) (IMA-CNMNC Proposal 23-F). An idealised formula is $(\text{Ca}_2\text{Y}_2)\square_2(\text{Be}_2\text{B}_2)\text{Si}_4\text{O}_{16}(\text{OH})_4$, which corresponds to $\text{Ca}_2\square\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$ (datolite) + $\text{Y}_2\square\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$ (hingganite-(Y)). The type material is rich in Bi, the Bi-richest portion yet discovered from the type locality is shown to be an intermediate member between datolite, hingganite-(Y) and a hypothetical end-member phase yet to be found of composition $\text{Bi}_2\square\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$. Minasgeraisite-(Y) has a different space group to datolite and hingganite-(Y). This lowering of symmetry to an acentric triclinic system is caused by different element occupancies on the A site of the gadolinite supergroup structure, which for minasgeraisite-(Y) becomes four individual sites. Such an order–disorder of elements is not considered as species-defining criteria despite the change in space group. Therefore, minasgeraisite-(Y) is discredited.

Keywords: minasgeraisite-(Y); datolite; hingganite-(Y); gadolinite supergroup; order–disorder; discreditation

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Introduction

Foord *et al.* (1986) described minasgeraisite [changed to minasgeraisite-(Y) to conform to the International Mineralogical Association (IMA) rules of nomenclature for rare-earth minerals (Bayliss and Levinson 1988)] as a new member of the gadolinite group, from the zoned complex of the Jaguarapu granitic pegmatite, in the Mr. José Pinto quarry, Jaguarapu, Minas Gerais, Brazil (IMA1983-90a). Using Inductive Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption Spectroscopy (AAS) and electron microprobe analyses, the empirical formula was given as:



where Ln expresses lanthanoids, La–Lu.

Their presented end-member formula was $\text{CaBe}_2\text{Y}_2\text{Si}_2\text{O}_{10}$ and their data suggested monoclinic symmetry. Since this time, a gadolinite-group mineral with this formula has been regarded as unlikely (Demartin *et al.*, 2001, Bačík *et al.*, 2014, 2017). The gadolinite supergroup (Bačík *et al.*, 2017) includes mineral species with the general chemical formula $A_2MQ_2T_2O_8\Phi_2$, they can be silicates, phosphates or arsenates. They have monoclinic symmetry, space group $P2_1/c$. The currently recognised gadolinite-supergroup minerals are given in Table 1.

Corresponding author: Daniel Atencio; Email: datencio@usp.br

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The structure of gadolinite-supergroup minerals can be described as composed of two different layers parallel to (100) and alternating along the [100] direction (in the $P2_1/c$ space group). One layer consists of TO_4 and QO_4 tetrahedra, and the other of $\text{AO}_6\Phi_2$ polyhedra and $\text{MO}_4\Phi_2$ octahedra.

At that time, the crystal structure of minasgeraisite-(Y) had not been determined, but to many, it seemed unlikely that the [6]-coordinated M-site would be dominantly occupied by Ca, which is assigned to the larger [8]-coordinated A-site in all other members of the supergroup.

A complicating factor in the ongoing discussion on the validity of minasgeraisite-(Y) as a mineral species, were several analyses performed in the original paper that indicated a high Bi content (Foord *et al.*, 1986).

Crystal structure data

On the basis of an observation that minasgeraisite-(Y) might be a calcium rich hingganite-(Y) (Cooper and Hawthorne, 2018), Cooper *et al.* (2019) determined the crystal structure of a 'Ca-hingganite-(Y)' sample from the Heftejern granitic pegmatite, located in southern Norway. They obtained a triclinic $P1$ unit cell with $a = 9.863(4)$, $b = 7.602(3)$, $c = 4.762(2)$ Å, $\alpha = 90.002(15)$, $\beta = 90.073(7)$, $\gamma = 90.020(5)^\circ$, $V = 357.1(5)$ Å³ and $Z = 1$, and expanded the general formula of gadolinite to 20 anions to show A-site cation ordering, with Ca and Y(Ln) ordered over four A sites (Fig. 1). The dominant constituent at the M site was determined as a vacancy (\square), and no Ca was assigned to the M site. The structural formula presented was:

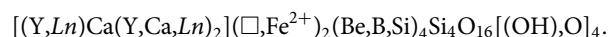
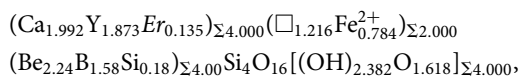


Table 1. Gadolinite-supergroup minerals.

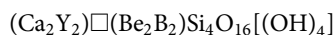
	A	M	Q	T	O	Φ
Gadolinite group (silicates)						
Datolite subgroup	A ²⁺		Q ³⁺			
Datolite	Ca ₂	□	B ₂	Si ₂	O ₈	(OH) ₂
Homilite	Ca ₂	Fe ²⁺	B ₂	Si ₂	O ₈	O ₂
Gadolinite subgroup	A ³⁺		Q ²⁺			
Gadolinite-(Y)	Y ₂	Fe ²⁺	Be ₂	Si ₂	O ₈	O ₂
Gadolinite-(Ce)	Ce ₂	Fe ²⁺	Be ₂	Si ₂	O ₈	O ₂
Gadolinite-(Nd)	Nd ₂	Fe ²⁺	Be ₂	Si ₂	O ₈	O ₂
Hingganite-(Y)	Y ₂	□	Be ₂	Si ₂	O ₈	(OH) ₂
Hingganite-(Ce)	Ce ₂	□	Be ₂	Si ₂	O ₈	(OH) ₂
Hingganite-(Yb)	Yb ₂	□	Be ₂	Si ₂	O ₈	(OH) ₂
Hingganite-(Nd)	Nd ₂	□	Be ₂	Si ₂	O ₈	(OH) ₂
Herderite group (phosphates and arsenates)						
Herderite subgroup	A ²⁺		Q ²⁺			
Herderite	Ca ₂	□	Be ₂	P ₂	O ₈	F ₂
Hydroxylherderite	Ca ₂	□	Be ₂	P ₂	O ₈	(OH) ₂
Bergslagite	Ca ₂	□	Be ₂	As ₂	O ₈	(OH) ₂
Unassigned member	A ²⁺		□			
Drugmanite	Pb ₂	Fe ³⁺	□ ₂	P ₂	O ₇ (OH)	(OH) ₂

The refined formula was:



where *Er* is not erbium, but an average based on all the lanthanides (57–71)

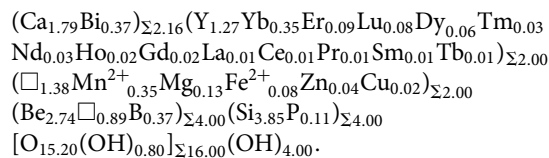
The simplified ideal formula reduces best to:



Cooper *et al.* (2019) did not address the discussion of defining a species name, but the ‘*Ca-hingganite-(Y)*’ studied corresponded to

what would have been a minasgeraisite-(Y) at the time, and therefore could be regarded as the second occurrence of the mineral.

The chemical formula of Brazilian minasgeraisite-(Y) as reported by Foord *et al.* (1986) based on the structural data obtained by Cooper *et al.* (2019) becomes:



The significant visual difference between the Brazilian and Norwegian minasgeraisite-(Y) is the colour, the lilac colouration of the Brazilian samples probably being due to Mn²⁺ and the brown–orange of the Norwegian due to the presence of Fe²⁺ at the *M* site.

Before the work on ‘*Ca-hingganite-(Y)*’, Cooper and Hawthorne (2018) had already determined the crystal structure of a ‘*minasgeraisite-(Y)*’ sample from the type locality. They used the name in single quotes because it was not the type specimen and, unfortunately, they were unable to chemically analyse it, choosing to apply the chemical data from Foord *et al.* (1986) instead.

They obtained a triclinic *P1* unit cell (their figure 5) with *a* = 9.994(4), *b* = 7.705(3), *c* = 4.764(2) Å, α = 90.042(9), β = 90.218(14), γ = 90.034(9)°, *V* = 366.8(5) Å³ and *Z* = 1, and again expanded the general formula of gadolinite to 20 anions. They showed that Bi, Ca and REE were ordered over four different *A* sites, the dominant constituent at the *M* sites was a vacancy and Ca did not occur at the *M* sites. The structural formula given was:

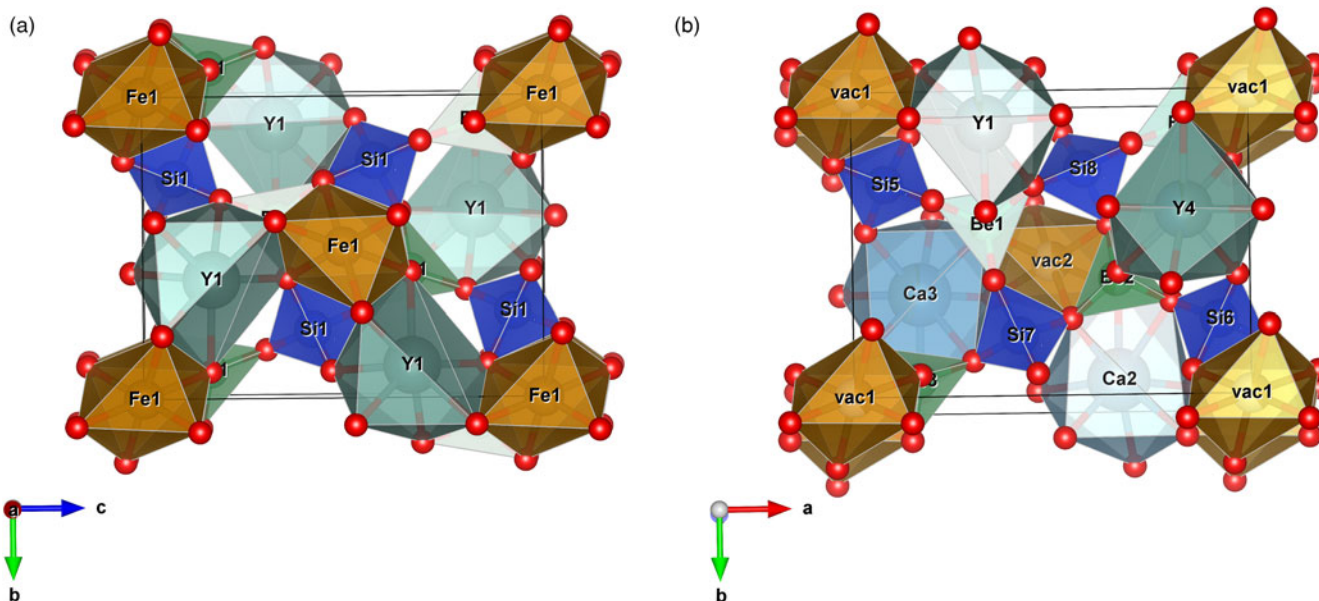
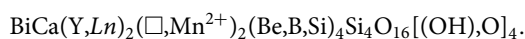
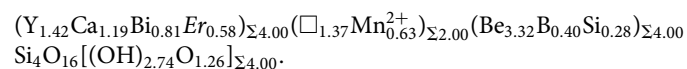
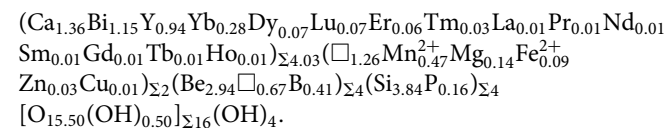


Figure 1. Views of the two types of space groups. (a) Gadolinite-(Y) from the White Cloud pegmatite, Colorado, USA (Allaz *et al.*, 2020). (b) Minasgeraisite-(Y) from Heftetjern granitic pegmatite, southern Norway (Cooper *et al.*, 2019). Drawn using VESTA 3 (Momma and Izumi, 2011).

Applying this to the bulk sample chemical data presented in Foord *et al.* (1986), they acquired the empirical formula:



Applying the same methodology to the most Bi-rich analysis presented in Foord *et al.* (1986) gives:



A recent further study, the first which has studied both chemically and structurally a 'minasgeraisite-(Y)' sample from the type occurrence was published during review by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA of the proposal relevant to deciding if minasgeraisite-(Y) required mineral species status. That study (Vereshchagin *et al.*, 2023) confirmed much of the data of Cooper and Hawthorne (2018), but was unable to determine the lower symmetry due to lack of sample material. Their conclusion was that their sample, which was linked to the original description, but not confirmed as the type specimen was equivalent to a monoclinic Bi- and Mn-bearing hingganite-(Y). There was no additional discussion on the structural position of Ca other than noting excess Ca on the M site.

Conclusions

On the basis of the crystal structure and structural formula determined by Cooper *et al.* (2019) for 'Ca-hingganite-(Y)' and the chemical analysis determined by Foord *et al.* (1986) for the type specimen, the simplified ideal formula of minasgeraisite-(Y) is $(Ca_2Y_2)\square_2(Be_2B_2)Si_4O_{16}(OH)_4$, which corresponds to $Ca_2\square B_2Si_2O_8(OH)_2$ (datolite) + $Y_2\square Be_2Si_2O_8(OH)_2$ (hingganite-(Y)).

On the basis of the crystal structure determined by Cooper and Hawthorne (2018) for a 'minasgeraisite-(Y)' sample from the type occurrence and the chemical analysis determined by Foord *et al.* (1986) on their 'Bi-richest portion', the simplified ideal formula for the richest Bi composition thus far reported of minasgeraisite-(Y) is $(Y_2CaBi)\square_2(Be_3B)Si_4O_{16}(OH)_4$, which corresponds to $Y_2\square Be_2Si_2O_8(OH)_2$ (hingganite-(Y)) + 0.5 $Ca_2\square B_2Si_2O_8(OH)_2$ (datolite) + 0.5 $Bi_2\square Be_2Si_2O_8(OH)_2$ (unknown phase).

Both minasgeraisite-(Y) and the Bi-richest minasgeraisite-(Y) are gadolinite-supergroup minerals with non-end-member compositions. The solid solution of more than two elements in the A sites causes a lowering of their symmetry to acentric triclinic resulted from cation ordering of Ca, REE (and Bi) at the A site, which become non-equivalent sites A1–A4 (Cooper *et al.*, 2019). However, topologically similar polymorphs where such order–disorder relationships affect the symmetry of a mineral (different space group), without modifying the global topology do not define a new species (Nickel and Grice, 1998).

It is likely that, if the crystal structures of many gadolinite-supergroup minerals with non-end-member compositions were analysed accurately, P1 symmetry would be identified in the

strictest sense, yet they would have $P2_1/c$ average structures. As a consequence, minasgeraisite-(Y) should not be separately created based on its space group nor the presence of Bi. Should a Bi-dominant analysis overall on the A site(s), with ideal formula $Bi_2\square Be_2Si_2O_8(OH)_2$, be discovered it would classify as a new species.

In summary, minasgeraisite-(Y) is discredited as an ordered intermediate between datolite and hingganite-(Y) (IMA–CNMNC Proposal 23-F, Atencio, 2023). The Bi-richest portion is an intermediate member between datolite, hingganite-(Y), and a hypothetical phase yet to be found.

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Competing interests. The authors declare none.

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