

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

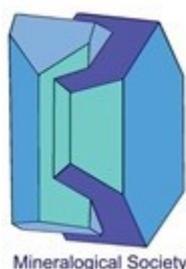
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Abstract

Minasgeraisite-(Y) is discredited based on it being an ordered intermediate between datolite and hingganite-(Y) (IMA-CNMNC Proposal 23-F). An idealized 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 $\text{Ca}_2\square\text{B}_2\text{Si}_2\text{O}_8(\text{OH})_2$ (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 gadolinite supergroup *A*-site, which for minasgeraisite-(Y) becomes four individual sites. Such 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.



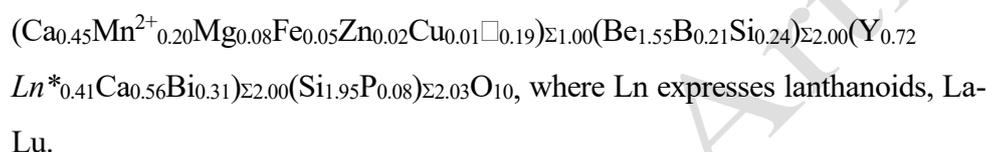
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Introduction

Foord et al. (1986) described minasgeraisite [changed to minasgeraisite-(Y) to conform to the IMA's rules of nomenclature for rare-earth minerals (Bayliss and Levinson 1988)] as a new member of the gadolinite group, in the zoned complex of the Jaguarapu granitic pegmatite, in the Mr. José Pinto quarry, Jaguarapu, Minas Gerais, Brazil (IMA 1983-90a). Using Inductive Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption Spectroscopy (AAS) and electron microprobe analyses, the empirical formula was given as:



Their presented end-member formula was $CaBe_2Y_2Si_2O_{10}$ 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, Bačík et al. 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 $P2_1/c$. Table 1 includes the currently recognized gadolinite-supergroup minerals.

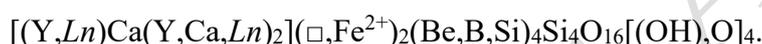
The structure of gadolinite-supergroup minerals can be described as composed of two different layers parallel to (100) and alternating along the [100] direction (in the $P2_1/c$ space group). One layer consists of TO_4 and QO_4 tetrahedra, and the other of $AO_6\phi_2$ polyhedra and $MO_4\phi_2$ octahedra.

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.

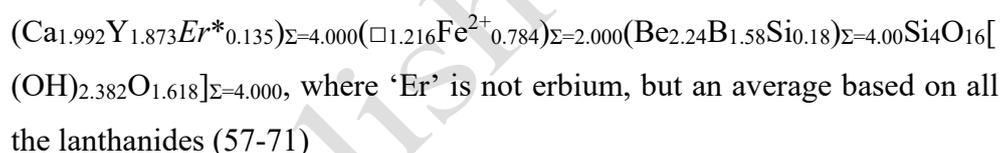
A complicating factor in the ongoing discussion on the validity of minasgeraisite-(Y) as a mineral species, were several analyses performed in the original paper that indicated a high Bi content (Foord et al. 1986).

Crystal structure data

Based on an observation that minasgeraisite-(Y) might be a calcium rich hingganite-(Y) (Cooper & Hawthorne 2018), Cooper et al. (2019) determined the crystal structure of a ‘*Ca-hingganite-(Y)*’ sample from the Heftetjern granitic pegmatite, located in southern Norway. They obtained a triclinic *P1* unit cell, *a* 9.863(4), *b* 7.602(3), *c* 4.762(2) Å, α 90.002(15), β 90.073(7), γ 90.020(5)°, *V* 357.1(5) Å³, *Z*=1, and expanded the general formula of gadolinite to 20 anions to show a *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, and no Ca was assigned to the *M* site. The presented structural formula was:



The refined formula was:

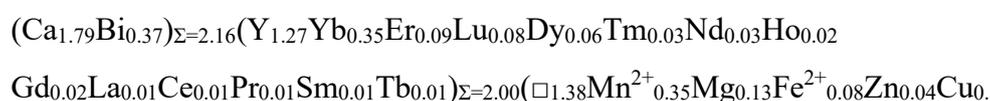


The simplified ideal formula reduces best to:



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:





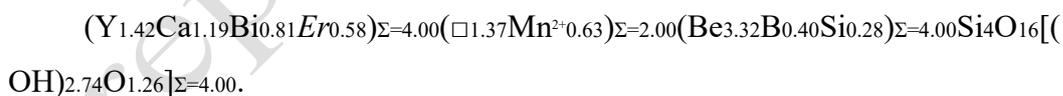
The significant visual difference between the Brazilian and Norwegian minasgeraisite-(Y) is the color, the lilac coloration of the Brazilian samples being likely due to Mn^{2+} and the brown-orange of the Norwegian due to the presence of Fe^{2+} at the *M* site.

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.

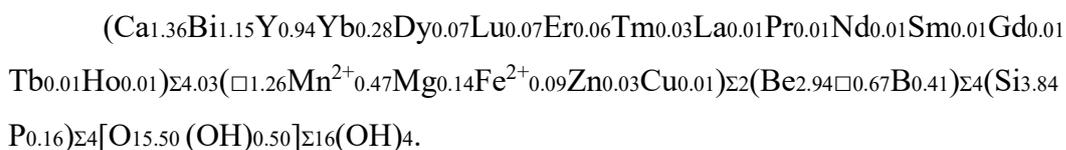
They obtained a triclinic *P1* unit cell (Fig. 5), *a* 9.994(4), *b* 7.705(3), *c* 4.764(2) Å, α 90.042(9), β 90.218(14), γ 90.034(9)°, *V* 366.8(5) Å³, *Z* = 1, and again expanded the general formula of gadolinite to 20 anions. They showed that Bi, Ca and REE were ordered over four different *A* sites,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



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 of the IMA-CNMNC proposal relevant to deciding if *minasgeraisite-(Y)* required mineral species status. That study (Vereshchagin et al. 2023) confirmed much of the data of Cooper & Hawthorne, but was unable to determine the lower symmetry due to lack of sample. 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

Based on the crystal structure and structural formula determined by Cooper et al. (2019) for '*Ca-hingganite-(Y)*' and on 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)*).

Based on the crystal structure determined by Cooper and Hawthorne (2018) for '*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-super group minerals with non-endmember compositions. 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-super group minerals with non-endmember compositions were analyzed 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 $\text{Bi}_2\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$, be discovered it would class as a new species.

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

Acknowledgements

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References

- Allaz, J.M., Smyth, J.R., Henry, R.E., Stern, C.R., Persson, P., Ma, J.J., Raschke, M.B. (2020) Beryllium-silicon disorder and rare earth crystal chemistry in gadolinite from the White Cloud pegmatite, Colorado, USA. *Canadian Mineralogist*, **58**(6), 829-845.
- Bačík, P., Fridrichová, J., Uher, P., Pršek, J., Ondrejka, M. (2014) Crystal chemistry of gadolinite-datolite group silicates. *Canadian Mineralogist*, **51**, 625-642.
- Bačík, P., Miyawaki, R., Atencio, D., Cámara, F., and Fridrichová, J. (2017) Nomenclature of the gadolinite supergroup. *European Journal of Mineralogy*, **29**, 1067-1082.
- Bayliss, P. and Levinson, A.A. (1988) A system of nomenclature for rare-earth mineral species: Revision and extension. *American Mineralogist*, **73**, 422-423.
- Cooper, M.A. and Hawthorne, F.C. (2018) Cation order in the crystal structure of 'minasgeraisite-(Y)'. *Mineralogical Magazine*, **82**, 301-312.

- Cooper, M.A, Hawthorne, F.C., Miyawaki, R., Kristiansen, R. (2019) Cation order in the crystal structure of 'Ca-Hingganite-(Y)', *Canadian Mineralogist*, **57**, 371-382.
- Demartin, F., Minaglia, A., and Gramaccioli, C.M. (2001) Characterization of gadolinite- group minerals using crystallographic data only: the case of hingganite-(Y) from Cuasso al Monte, Italy. *Canadian Mineralogist*, **39**, 1105-1114.
- Foord, E.E., Gaines, R.V., Crock, J.G., Simmons, W.B., Jr., and Barbosa, C.P. (1986) Minasgeraisite, a new member of the gadolinite group from Minas Gerais, Brazil. *American Mineralogist*, **71**, 603-607.
- Momma, K. and Izumi, F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, **44**, 1272- 1276.
- Nickel, E. H. and Grice, J. D. (1998) The IMA Commission on New Minerals and Mineral Names: Procedure and guideline on mineral nomenclature, 1998. *Canadian Mineralogist*, **36**, 913-926.
- Vereshchagin, O., Gorelova, L., Shagova, A., Kasatkin, A., Škoda, R., Bocharov, V., Galiová, M. (2023). Re-investigation of 'minasgeraisite-(Y)' from the Jaguaraçu pegmatite, Brazil and high-temperature crystal chemistry of gadolinite supergroup minerals. *Mineralogical Magazine*, 1-26. doi:10.1180/mgm.2023.19

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Table 1. Gadolinite-supergroup minerals

	<i>A</i>	<i>M</i>	<i>Q</i>	<i>T</i>	O	φ
Gadolinite group (silicates)						
<i>Datolite subgroup</i>	<i>A</i> ²⁺		<i>Q</i> 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
<i>Gadolinite subgroup</i>	<i>A</i> ³⁺		<i>Q</i> 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) ^a	Nd ₂	□	Be ₂	Si ₂	O ₈	(OH) ₂
Herderite group (phosphates and arsenates)						
<i>Herderite subgroup</i>	<i>A</i> ²⁺		<i>Q</i> 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
<i>Unassigned member</i>	<i>A</i> ²⁺		□			
Drugmanite	Pb ₂	Fe ³⁺	□ ₂	P ₂	O ₇ (OH)	(OH) ₂

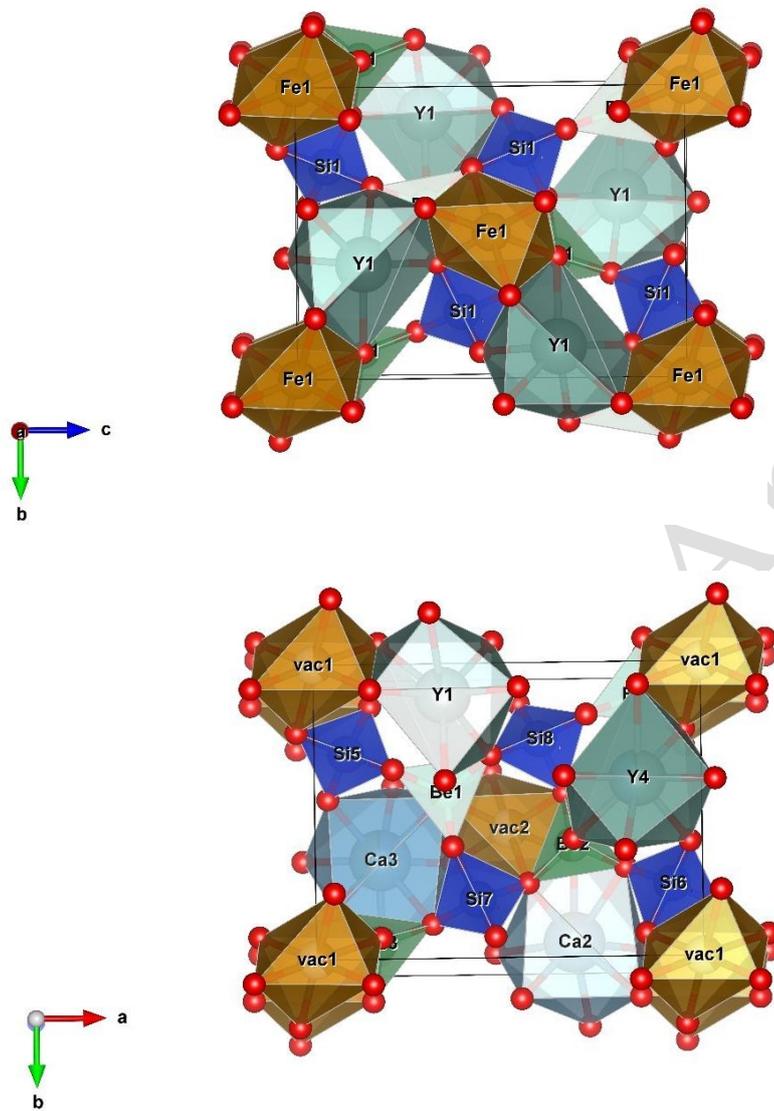


Figure 1. Views of the two types of space groups. Above gadolinite-(Y) from the White Cloud pegmatite, Colorado, USA (Allaz et al. 2020). Below minasgeraisite-(Y) from Heftetjern granitic pegmatite, southern Norway (Cooper et al. 2019). Drawn using VESTA 3 (Momma and Izumi 2011).