

# Bibliography of Hibschite, a Hydrogarnet of Grossular Type

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**ABSTRACT:** Crystalline representatives of an isomorphous series from  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$  (grossular) to  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  (katoite) are widespread natural phases described from a lot of mineral localities. Members of this series with a substitution of  $(\text{SiO}_4)$ -tetrahedra <50 % by  $(\text{OH})$ -groups and formula  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$  and  $x$  within the range  $0 < x < 1.5$  are specified as hibschite, while members with a substitution of 50 % to 100 % are specified as katoite. A substitution of Al by  $\text{Fe}^{3+}$  up to 50 % does not change the nomenclature.

The atomic arrangement, determined by X-ray and neutron diffraction data as well as IR-spectroscopic investigations confirmed the position of the  $(\text{OH})$ -groups substituting the  $(\text{SiO}_4)$ -tetrahedra. In addition to the substitution of  $(\text{SiO}_4)$ -tetrahedra by  $(\text{OH})$  groups, the presence of hydroxyl groups in other positions of the crystal structure was presumed in some hydrogarnets derived from metamorphic rocks and described as „defective garnet structures“.

Various reasons for anomalous optical behaviour of „cubic“ garnets are discussed in literature [e.g., the presence of  $(\text{OH})$ -groups distributed in a noncubic manner]. Annealing experiments indicate that the incorporation of hydroxyl groups is not the primary reason for this behaviour: cation ordering on octahedral positions may play an important role, too.

Hydrothermal syntheses revealed crystalline compounds within the whole range from grossular to katoite in dependence to the proportion of the inserted elements. These formations are in accordance with the widespread occurrences of minerals of the whole hydrogrossular series as hydrothermal formations in calcareous environments.

**KEY WORDS:** hydrogarnet, hibschite, katoite, bibliography.

## Introduction

Garnet is a general name applied to a group of specific silicate minerals with a characteristic crystal structure. The name is derived from the latin word “granatum” (pomegranate) alluding to the resemblance of some red varieties to the seeds of this fruit in color and shape. Garnets show great diversity of colour, ranging from colourless to black, except for bluish tints for natural specimens. In their crystallization, garnets are cubic, or apparently pseudocubic for some compositions, and commonly exhibit the crystallographic forms dodecahedron, trapezohedron or both.

A simple classification suggested by Shigley and Manson (1993), a.o., is a subdivision into three groups defined on the basis of the end-member species with idealized chemical composition:

- A) Pyrospite group (aluminum garnets with pyrope, almandine and spessartine)
- B) Ugrandite group (calcium garnets with uvarovite, grossular and andradite)
- C) rare garnets containing elements such as V, Y, Ti or Zr.

This classification was insignificantly completed by Strunz and Nickel (2001) with the nomenclature of the “Schorlomite Series” for rare Ti garnets and of the hydroxygarnet series.

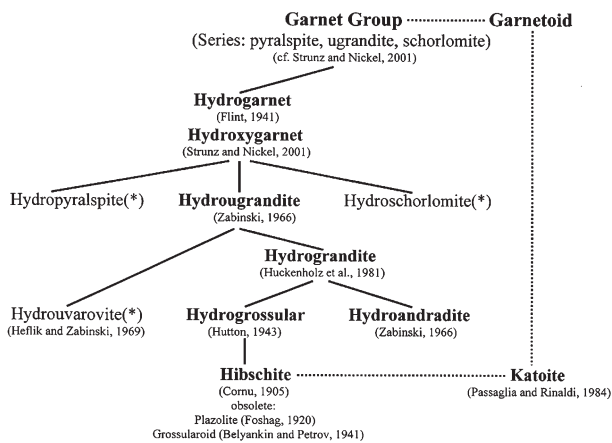
The atomic arrangement of the garnet structural type was determined in a calcium-aluminum variety (grossular) from Xalostoc, Mexico, already in the first days of X-ray crystallography (Menzer 1926, 1928). Further structural investigations performed on natural (or synthetic) crystals, completed with discussions of crystal chemical aspects, have been reported by (in alphabetical order): Allen and Busek (1988), Armbruster et al. (1992), Armbruster and Geiger (1993), Artioli et al. (1997), Carda et al. (1994), Geiger and Armbruster (1997), Griffen et al. (1992), Lager et al. (1987, 1989), Meagher (1975), Merli et al. (1995), Novak and Gibbs (1971), Pavese et al. (1995), Sawada (1993, 1997, 1999), Takeuchi et al. (1982), Zemann (1962).

The garnet structure is a 3D framework built of  $\text{YO}_6$  octahedra and  $\text{ZO}_4$  tetrahedra joined to each other by common oxygen atom corners. The resulting framework is of the composition  $\{\text{Y}_2\text{Z}_3\text{O}_{12}\}$ . A position in the interstices of this framework with an [8]-coordination completes the structure, revealing the final formula  $\text{X}_3\text{Y}_2\text{Z}_3\text{O}_{12}$  for this family of orthosilicates. Crystal chemistry of various oxide garnets was summarized by Geller (1967), a common systematics of the garnets was worked out by Hawthorne (1981). Surveys of crystal chemistry were reported by Meagher (1980) and Griffen (1992).

A hydrous component has been determined in natural and synthetic garnets of various compositions. Prefix “hydro” or “hydroxy” was used in the nomenclature: hydrogarnet (Flint et al. 1941) with a subdivision into the species hydropyrospite, hydrougrandite (Zabinski 1966, Shigley and Manson 1993) or hydroxygarnet (Strunz and Nickel 2001).

A very informative compilation of the history of investigations on hydrogarnets with reinvestigations of a lot of specimens and suggestions on the terminology of hydrogarnets was given by Zabinski (1966). The present article is therefore only a compilation of literature data on the members of the mineral family hydrougrandites and their nomenclature within the last three decades. Of course, a special object of view is the mineral “hibschite” with occurrences and analyses leading to its crystal chemical characterization. Fig. 1 represents a compilation of notations from literature for the hydrogarnets in a simple family tree. Table 1 gives an overview of fundamental contributions to hydrogarnets.

Garnetoids are compounds with an atomic arrangement showing features of the garnet structural type, but with a nonmetallic atom in substitution for silicon: berzeliite (Machatschki 1930, Hawthorne 1976) and griphite (McConnel 1942, Rinaldi 1978), an arsenate and a phosphate mineral, or cryolithionite, a fluoride with formula  $\text{Na}_3\text{Al}_2(\text{LiF}_4)_3$ , respectively (Menzer 1930).

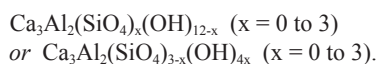


**Fig. 1.** A simplified family tree with the nomenclature of hydrogarnets. The notations with an (\*) are neoterized by the author.

Worth mentioning are further the garnet-related structures of mayenite,  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (Büssom and Eitel 1936, Hentschel 1964) and yafsoanite,  $\text{Ca}_3\text{Te}_2(\text{ZnO}_4)_3$  (Jarosch and Zemann 1989).

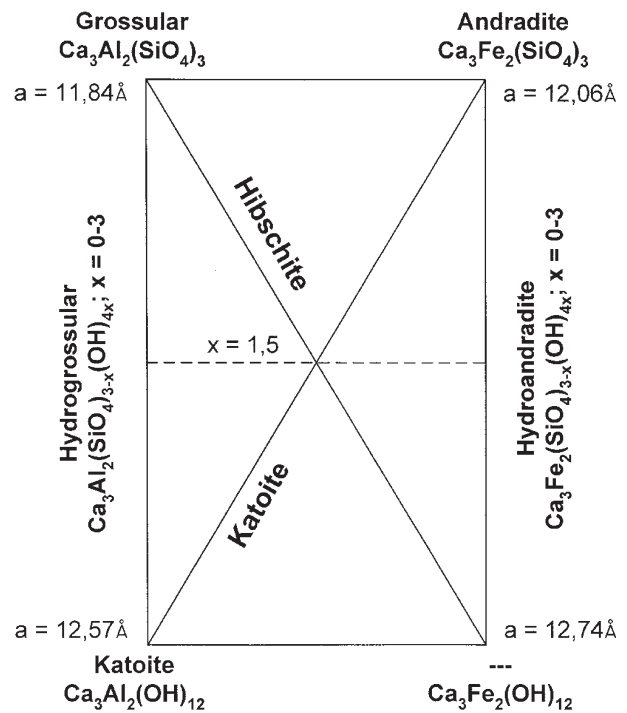
## Hydrograndites

Boeke (1914) reported an isomorphous series between grossular and andradite from natural occurrences without a gap. This was established by a compilation of physical and chemical parameters from literature and experiments performed by this author. The synonym “hydrograndite” for hydrated members of this series was used by Yun-Lung (1964) and Zabinski (1966). Hydrogrossular (first mentioned by Hutton 1943) and hydroandradite (Zabinski 1966) are most appropriate extended names for members of this series with an appreciable (OH)-content and with a variable ratio of  $(\text{SiO}_4)/(\text{OH})$ . The nomenclature proposed by Passaglia and Rinaldi (1984) together with mineral names and lattice constants for the end-members is drawn in Fig. 2. Two types of writing of the formulae of members of this isomorphous series with the end-members grossular,  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ , and katoite,  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , are common (Cohen-Addat et al. 1967, Cohen-Addat 1970):



The kind of substitution  $(\text{SiO}_4)$ -tetrahedra \* (OH)-groups implied in these formulae was presumed by McConnell (1942) and confirmed by X-ray studies by Cohen-Addat et al. (1963) for the first time. An open discussion on the real symmetry of hydrograndites is going on, since a significant birefringence for the members of the grossular – andradite series was reported by Akizuki (1984), Griffen (1992), Hofmeister et al. (1998) and Rossman and Aines (1986). For further information on this topic see Aines and Rossman (1984a, b, c), Geiger et al. (1991), Rossman and Aines (1991).

Modern physical and chemical investigations of natural hydrogrossulars confirm a more or less continuous substitution of  $\text{SiO}_4$  by OH from grossular to katoite. The reality of this substi-



**Fig. 2.** Nomenclature of minerals of the hydrograndite group recommended by Passaglia and Rinaldi (1984). The values for the lattice constants of the end-members are mean values adopted from the literature.

tion was supported by synthesizing experiments in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ , which gave no hints for a gap, also at moderate temperatures. As many nomenclatural problems arise from this transition, the majority of authors avoid discussions by using the term “hydrogrossular”.

The present article may therefore only be a compilation of articles from relevant literature, in which the definite indications “hibschite” and “katoite” were used.

## Hibschite

A mineral assemblage consisting of an outer clear octahedral shell grown over a dodecahedral dark core from the Mariánská hora Hill (Marienberg) phonolite at Ústí nad Labem (Aussig), Bohemia, was first mentioned by Cornu (1905). A detailed description, chemical analyses, physical constants and considerations about the formation of these two coexisting mineral phases were reported in a thesis performed under the auspices of F. Becke and G. Tschermak at the University of Vienna (Cornu 1906a) and in a true copy of this thesis (Cornu 1906b).

According to the composition, the dark core was denoted as “titanomelanite” for a pronounced Ti content. The mineral name “hibschite” was suggested by Cornu for the outer shell, a hydrogrossular. This name was chosen in honour of J. E. Hibschi, the most renowned geologist in the study of the České středohoří Mts. in northern Bohemia (Michel 1939/1940).

Besides the description of hibschite from Mariánská hora Hill, a second occurrence of this mineral was reported from the Mädistein, Bohemia (Cornu 1907). Two further occurrences from Ni-

korzminda (Republic of Georgia, formerly U.S.S.R.) with quantitative chemical analyses recalculated to  $3(\text{Ca},\text{Mg})\text{O} \cdot (\text{Al},\text{Fe})_2\text{O}_3 \cdot 2(\text{Si},\text{Ti})\text{O}_2 \cdot 2\text{H}_2\text{O}$  were mentioned in the following years (Belyankin and Petrov 1939, 1941a, b). These authors assumed more or less the identity of hibschite and plazolite. Plazolite was described by Foshag (1920) from the metamorphosed limestone at Crestmore, Riverside County, California; it was stated that this mineral seems to be most closely related to sodalite. Pabst (1937) disregarded the  $\text{CO}_2$  content and described the crystal structure as a defective grossular-type structure. Subsequently, Basso et al. (1983) confirmed the crystal structure suggested by Pabst (1937). Plazolite is a natural hydrogrossular with a pronounced  $(\text{SiO}_4)^*(\text{OH})$  substitution. Nowadays, the name is discredited and therefore obsolete.

The mineral assemblage including hibschite from the type locality was investigated by X-ray powder study by Pabst (1942). A modern chemical characteristic of toptype of hibschite was published by Rinaldi and Passaglia (1989). Worth mentioning in this respect is also an earlier article by these authors (Passaglia and Rinaldi 1984) with a summary of data on the topic of hydrogrossular.

In modern literature, the occurrences of hibschite (mentioned by name) have been reported from contact-metamorphic rocks in New Mexico (Homme and Rosenzweig 1970), from Mont Saint-Hilaire (Horvath and Gault 1990) and from melilite-bearing skarns of the Carpathians in Romania (Marincea et al. 2001, Pascal et al. 2001).

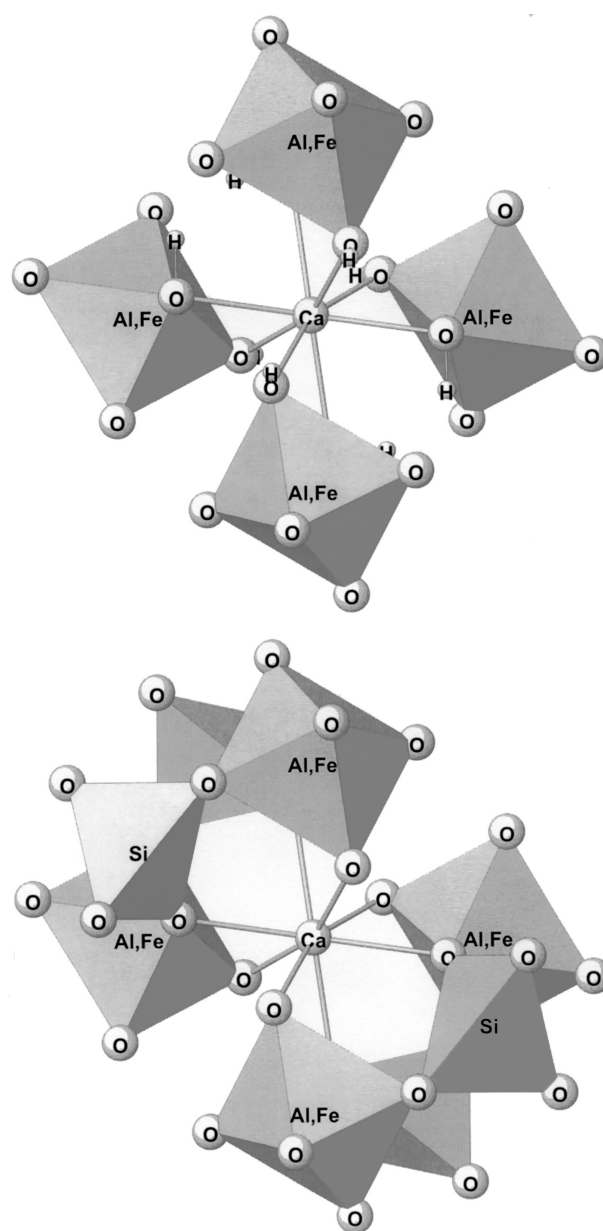
### Katoite

A mineral with chemical formula  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$  was described by Passaglia and Rinaldi (1984). This mineral occurs in vugs of phonolite associated with hydrated calcium silicates and aluminates in Pietramassa near Montalto di Castro (Viterbo, Italy). By the name katoite the mineralogist A. Kato was honoured in recognition of his activity in mineralogy, especially of his productive chairmanship of the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Besides chemical and thermal analyses, powder and single crystal X-ray studies for the definition of the new mineral, a compilation of data on the topic hydrogrossular from literature is given by these authors. A new nomenclature for the hydrogrossular group of minerals is another part of this paper. In an article about katoite by Sacerdoti and Passaglia (1985), confirmation of the first structural determination as well as implications within the hydrogrossular group of minerals were described.

### Crystal chemistry of the $(\text{SiO}_4)^*(\text{OH})$ substitution

The "starting points" for the crystal chemical explanation of this substitution are the structures of garnet s.s. (Menzer 1928) and of the synthetic compound  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , crystallizing in a structural type analogous to garnet but with vacant Si positions. A complete series of solid solution between these two more or less isotypic structures was already presumed by Flint et al. (1941), but without a confirmation by X-ray or neutron diffraction for a member of this series.

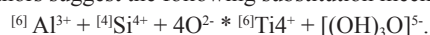
Nowadays, one possible mechanism of incorporation of (OH)-groups via the substitution  $(\text{SiO}_4)^*(\text{OH})$  has been well defined by X-ray and neutron diffraction analyses and by IR spectroscopy. This verification is primarily the merit of scientists from the Centre National de la Recherche Scientifique, Grenoble, reported in several papers: Cohen-Addad et al. (1963, 1964, 1967) and Cohen-Addad (1970). Further reports on X-ray and neutron diffraction studies on this topic were given by the following authors: Foreman (1968), Bartl (1969, 1986), Basso et al. (1983), Sacerdoti and Passaglia (1985), Lager et al. (1987), Smrcok (1987), Lager et al. (1989), Armbruster and Lager (1989), Chakoumakos et al. (1992), Kobayashi and Shoji (1984), Armbruster (1995). The described substitution of  $(\text{SiO}_4)$  tetrahedra by (OH)-groups in grossular and in katoite is drawn in Fig. 3.



**Fig. 3.** The coordination sphere of the Ca atoms in katoite by eight oxygens of OH-groups and in grossular by eight oxygens of  $\text{SiO}_4$ -tetrahedra.

Lager et al. (1989) investigated the tetrahedral-site occupation in titanian andradites. The main conclusion of this work seems to be of great importance for the  $(\text{SiO}_4)^- (\text{OH})$  substitution in garnets. Verbatim: “*The presence of OH in the structure suggests that charge balance can be achieved by the substitution  $(\text{O}_4\text{H}_4)^- = (\text{SiO}_4)^-$ . There is no evidence to support a multisite OH substitution*”.

Despite of this statement, a discussion continues on other mechanisms for the incorporation of OH-groups (Basso et al. 1984, Langer et al. 1993, Khomenko et al. 1994, Geiger et al. 2000). In Ti-bearing garnets, in particular, the last mentioned authors suggest the following substitution mechanism:



This substitution was presumed on the basis of optical absorption spectra.

### Syntheses and ab initio studies of hydrogarnets

Experimental syntheses in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  under hydrothermal conditions confirmed the existence of a complete isomorphous series between the end member  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$  and  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  (Flint et al. 1941). This system was chosen for many experiments because Ca, Al, and Si occur in nature in only one stable valence state over the whole range of hydrogen ion concentrations.

Hydrothermal experiments at modest temperatures and pressures, 450 °C and 750 °C, saturation vapour pressure, succeeded in preparation of hydrogrossular of variable composition (Yoder 1950). The region  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3 - \text{Ca}_3\text{Al}_2(\text{SiO}_4)_2(\text{OH})_4$  at elevated temperature and pressure was investigated in detail by Pistorius and Kennedy (1960), Amthauer and Rossman (1998). Experimental syntheses of hydrogrossular were described by Cohen-Addad et al. (1967), Cohen-Addad (1970), Harmon et al. (1982), Kobayashi and Shoji (1983, 1984, 1987), of a compound  $\text{Ca}_3\text{Al}_2(\text{O}_4\text{D}_4)_3$ , isotypic with katoite by Lager et al. (1987).

Comparable experiments in this system were performed by Ito and Frondel (1967) in teflon-coated autoclaves in the temperature range from ~85 °C to 105 °C and in aqueous acid (4N HCl) or alkaline (7N NaOH) solutions.

Syntheses of pyropes with low-water contents in the system  $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$  over a range of hydrothermal pressures from 20 to 50 kbar and temperatures from 800 °C to 1200 °C were performed by Ackermann et al. (1983) and Geiger et al. (1991). Syntheses of garnets and hydrogarnets melted glass of defined composition by a piston cylinder device were further described by Armbruster and Geiger (1993), Bosenik et al. (1995), Olijnyk et al. (1991). Comparable apparatus was used by Chakoumakos et al. (1992) for the synthesis of Sr-Al-hydrogarnets.

Of common interest are articles about syntheses, chemical and physical characteristics as well as thermodynamic calculations of garnet members with a composition between  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$  and  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  published by Brandenberger (1933), Büssem and Eitel (1936), Cohen-Addad et al. (1964), Weiss and Grandjean (1964), Foreman (1968), Bartl (1969), Lager et al. (1987), Olijnyk et al. (1991), Schoenitz and Navrotsky (1999).

The structural properties of katoite as a function of applied pressure were investigated by ab initio studies, too. These calculations were done for a static geometry and have been further used to predict the relative stability of hypothetical hydropyrope (Nobes et al. 2000a, b).

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