Mazzite: history of a new mineral and its crystal structure determination

A tribute to the memory of Professor Fiorenzo Mazzi

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Romano Rinaldi
Ex Chair of Mineralogy, University of Perugia, Italy (Retired)

Abstract

The history of the discovery of the mineral Mazzite, named in honour of Professor Fiorenzo Mazzi, and its crystal structure determination in the dehydrated and natural forms, lends itself to the description of several interesting aspects of mineralogical and crystallographic research, such as was carried out in the early 1970’s, but with implications still valid to this day. The main issues described have bearings on the mineralogical nomenclature, the crystallography and crystal chemistry of natural and synthetic zeolites and some intriguing aspects of experimental research and scientific discoveries.

Introduction

This story begins in the early 1970’s, when the “Modena Group” working on Zeolites was forming under the inspiring guidance of Professor Glauco Gottardi (Fig. 1). As part of the ongoing quest for zeolite samples from various localities, which had become a constant in the summers of the Group, a trip to the Massif Central, and Puy de Dome, in France was organized in 1972 and subsequently repeated in 1973. Unfortunately I could not participate in either as, at that time, I was still manoeuvring my life among several commitments. Having left Modena as soon as I graduated, in the summer of 1969, to pursue a scholarship at the University of Manitoba which allowed me to obtain a Master’s degree in Mineralogy and Crystallography in the Fall of 1970, I was then offered another scholarship at the University of Chicago towards a PhD degree, a totally unknown degree in Italy at that time. As a matter of fact, my life history was about to take a number of unexpected twists, but this is not the place to go into this. Suffice to say that, in the summer of 1972 I was serving my compulsory military duty in the Italian Army, and you can imagine how much I would have preferred a field trip to France that summer, instead. In any case the timing was such that, when I was ready to resume my position at the University of Chicago, in the Autumn of 1972, Glauco, Ermanno, Elio and Daria were bursting with excitement having identified, in one of the samples from that summer’s expedition, what had all the appearance of a new zeolite mineral.

Work soon started on the definition of all the physical and chemical properties of the tiny needles from the few bundles available, while trying to preserve one of particular beauty to be used for the photos taken at the stereomicroscope (Fig. 2). The differential thermal analysis and X-Ray powder pattern soon confirmed the mineral was not one of the known natural zeolites. There remained the density determination and the refractive index for which Ermanno set himself to work with his proverbial precision and care. A similarity with the powder pattern of the synthetic zeolite Omega was soon discovered and this added to the interest for this new species.

As to the chemical properties, the decision was the most obvious; as I was about to return to Chicago to resume my study and research scholarship (having been blessed by the newly established American Law for conscripts, which reinstated me in my position), it would be my task to perform the electron probe microanalysis with one of the very first instruments dedicated to mineralogy, under the guidance of my tutor, prof. Joseph V. Smith. Incidentally, that was one of the instruments purchased in view of the planned analyses of some of the lunar samples brought back to Earth by the Apollo missions, starting with Apollo 11 exactly 50 years ago.

This was the time when Glauco decided to name the mineral in honour of Professor Fiorenzo Mazzi of Pavia University, a revered older colleague and a constant reference in crystallographic matters for Italian mineralogists. In fact, the collaboration of his research team with other groups was later formalized with the establishment of one of the very first PhD programmes in Italy in the form of a consortium between the Universities of Modena, Pavia and Turin, starting in 1984. Anyhow, coming back to Glauco's decision, he was well aware that the mere mention of his plan to his colleague (and friend) Mazzi, would almost certainly obtain a firm refusal with words that he himself had used against similar proposals on the same subject. The anticipated answer would have been something along the lines of: "No way, I'm not dead yet and I do not intend to die soon in order to deserve such an honour!". So Glauco decided to keep the naming of the new mineral quiet until the mineral and its name had been approved by the appropriate International Mineralogical Association (IMA) Commission on New Minerals and Mineral Names (CNMMN) and therefore put Mazzi in front of the accomplished fact so that there could be no refusal on his part. And this is how it went as can be read between the lines of the paper describing the mineral and its discovery (Galli et al.,1974).

The discovery of this new zeolite mineral was going to have several implications, some of which reverberate to this day in various fields such as, the nomenclature of minerals, the crystal structure determination of zeolites and other related subjects which I will try and address in the following paragraphs.

The name

Just after the name Mazzite was approved, it became evident that the English speaking mineralogical community was losing the origin of the name (Mazzi) when pronouncing "Masait", as if the mineral was named in honour of a person named "Massa" (an Italian name meaning "mass" and the name of a City in Italy famous for white marble!). This I kept pointing out to my colleagues in Chicago and it must have contributed to convincing the IMA Commission for nomenclature to review the rules for the attribution of mineral names. It was then stated that, when the original name ends with an "i", the suffix "ite" should be added to the full name, without contraction. Therefore the proper name with the new rule would be "Mazziite" (pronunciation: "Mazzi-ait") but being the rule not retroactive, Mazzite has remained as such. The same name was in fact used when another mazzite was later discovered (Arletti et al., 2005), with Na in place of Mg, making the mineral ascend to the rank of Mineral Group and assigning the names of Mazzite-Mg and Mazzite-Na to the two minerals so far known within the Group (see chemical formulae here below).

Mazzite Group:

Mazzite-Mg: $|(Mg_{2.5}K_2Ca_{1.5})\ (H_2O)_{30}|\ [Al_{10}Si_{26}O_{72}]$

Mazzite-Na: $|Na_4(H_2O)_{30}|\ [Al_{10}Si_{26}O_{72}]$

The single crystal diffraction data collection; not a trivial experiment

Immediately after the discovery of the new mineral, a phase of intense research followed, in the autumn of 1973 for the determination of the crystal structure by the two working groups, in Modena, Italy and in Chicago, USA where I had, by then, taken up a position of Research Associate. By mutual agreement and in view of the communication difficulties at that time (no internet or e-mail), the solution of the structure was to be carried out independently by the two groups. The Modena group, mainly in the person of Ermanno Galli, was to work on single crystal diffraction data collected at ambient conditions, whereas the Chicago group had the task of working on data collected in the dehydrated form at high temperature, having verified, in the preliminary study of the mineral, an unusually high temperature stability for this zeolite, in excess of 600°C.

Both groups actually encountered unexpected experimental difficulties for reasons which gradually surfaced as the work went on in the following months. But they were both unaware of their respective problems and the total silence on the progress was seeding some mutual diffidence. The agreement was in fact to carry out the work independently but to eventually communicate the results obtained prior to any publication. However the results were hard to get …

The difficulties at room temperature were due to the large number of structural water molecules with a high degree of mobility in the 12-ring channels of the framework structure, giving rise to strong variations in some key reflections during data collection, yielding residual R factors in the range of 10-12% therefore too high to be acceptable. The high temperature Chicago group in the meantime was experiencing quite a number of problems with the initial experimental set-up consisting of a hot Nitrogen blow-gun mounted on a brand-new automated four-circle diffractometer. In this case, the combined instabilities of the instrumental set-up and the intrinsic ability of the crystal to change its hydration state within minutes (if not seconds) in response to temperature, humidity and instrumental fluctuations, was enough to discourage the most determined experimentalist. This eventually convinced us at Chicago, to switch to a totally different approach consisting of the dehydration of the single crystal in a capillary tube under vacuum at high temperature. We therefore went to work and built all the necessary apparatus; a glass vacuum line with a mechanical rotary pump and a mercury diffusion pump, vacuum gauges, a thermocouple-controlled furnace and all the glass blowing and cutting tools, including a hydrogen torch for instant sealing of the quartz capillary containing the crystal. After dehydration at high temperature, data collection was carried out at room conditions on the crystal sealed inside the quartz capillary tube. And this finally yielded some consistent diffraction data on the four circle automated diffractometer.

The determination of the crystal structure and the structural peculiarities of Mazzite

Working on the crystal structure determination of Mazzite revealed a number of unique structural properties for this uncommon zeolite and opened up some interesting aspects of scientific research which I deem worthy of mention.

1. It was the first natural zeolite discovered after a synthetic analogue (zeolite Omega) had already been synthesized. However, the tiny dimensions of the synthetic crystals (too early for synchrotron-based crystallography) and the unavailability of methods of structure determination by powder diffraction (i.e. the Rietweld method), prevented any data collection amenable to the correct structure determination. Some hypothetical models had been described (Barrer & Villiger, 1969) but none had actually provided definite clues. Furthermore, the existence of a natural compound with the same framework structure of a synthetic product, could jeopardize the right to hold an International Patent on the latter. And this question was further aggravated by the fact that, while I was working at the structure solution, I was being paid with funds coming (also) from the Company which had deposited the Patent! A clear case of conflict of interest, but in reverse! This rather delicate matter was resolved by Joe Smith with a subtle and careful wording of this point in the paper describing the structure of Mazzite in the dehydrated form (Rinaldi et al., 1975).

2. Another unique characteristic of this structure with large continuous channels, was revealed during the electron microprobe analyses. Besides the expected loss of water and mobilization of cations which one expects when zeolites undergo the “nondestructive” effects of a fierce electronic bombardment concentrated in a micrometer spot (Rinaldi, 1984), Mazzite gave rise to a new phenomenon which was observed through the optical microscope mounted in the electron probe, with the emission of cathodoluminescence (pale pink light) on the opposite end of the crystal prisms (embedded in epoxy glue) to that on which the electrons were impinging. This behavior can be attributed to a light pipe effect, a first example of the property nowadays exploited in the well-established optic fiber technology!

3. Mazzite was then the first known zeolite which preserved all of its structural properties, as regards the tetrahedral framework, upon dehydration at a relatively high temperature, and even maintained some of its structural water molecules (7 out of the original 28 in the natural form) up to 600°C. This gave rise to an all-time effort to investigate the detailed structural properties of zeolites at high temperature and eventually at non-ambient conditions, as we would say nowadays, with the extension to studies at high pressure as well.
Incidentally, upon returning to Italy a few years after these experiments, I put into use (among others) the know-how for the dehydration technique under vacuum at high temperature and successive data collection of single crystals sealed in quartz capillary tubes. So I replicated at Modena the experimental apparatus Joe Pluth and I had built at Chicago, and that was largely exploited for many more studies on natural zeolites, especially by Alberto Alberti and his collaborators (mainly M. Giovanna Vezzalini) starting from 1977-78 (i.e. Alberti et al., 1978, 1984, 1996, etc.), followed by data collections performed, to begin with, at the CNR Centre for Crystallography in Pavia, headed by Professor Mazzi.

A sad thought is due here to my colleague and old time friend Alberto who unexpectedly passed away only a couple of days before this celebration, which he was supposed to contribute to with his own memories about Fiorenzo Mazzi and those very profitable years of crystallographic research on zeolites.

4. The framework structure of Mazzite, with continuous channels delimited by 12-rings of silicate tetrahedra (Fig. 3), provides this mineral with some unique properties, especially as a result of the speed with which the water molecules (and cations) hosted in these channels can move, as opposed to the contents of the much tighter environment provided by the gmelinite cages which open up into these large channels via 8-membered rings of tetrahedra.

The ease of mobility along the continuous channels was what caused many of the problems during data collection as both groups experienced. We actually discovered that the crystal was faster at feeling the slightest variation of temperature than the thermocouple on which it was mounted for our attempts at collecting HT data with the hot nitrogen gun. The difficulties the Modena group had experienced are testified by the fact that a first publication on the solution of the structure (Galli, 1974) was followed by another one, in January the following year (Galli, 1975) where a refinement to a much more acceptable R factor was reported.

As a matter of fact, the sequence of the first publications on the structure determination of Mazzite by both groups, reveals an aspect which came close to creating some embarrassment on the two sides of the Atlantic… Having agreed to communicate any significant progress on the structure solution on either side, the unexpected reciprocal long silence, had created some suspicion that one of the two was keeping the results from the other in order to have the advantage of the first publication. In actual fact the two bosses of the groups, Joe Smith and Glauco Gottardi must have been keeping some telephone contact since one day, in the Autumn of 1973, Joe came into my room and stated that, should we come up with the solution of the structure before them, we were not to keep the results in abeyance for the Modena group to come first. This came to me as a surprise having never thought, in my young innocence, that this sort of thing would matter. At that moment I could not see the point but in retrospect, knowing both characters well, I can imagine that the exchange between them must have been polite but firm. Worth noting here is the fact that phone calls at that time went through an overseas operator and they were impossible to activate from an unauthorized line (such as the ones within my reach). The truth of the matter is that, once we finally solved the structure, right before Christmas 1973, I sent a postcard to the Modena Institute, addressed to Ermanno Galli, with a drawing of the unit cell content of Mazzite consisting of two gmelinite cages staggered by a glide plane (Fig. 4) and I drew a stylized comet tail coming out of the "head" of the drawing, symbolizing the arrival of the solution, along with my best wishes for Christmas. Unfortunately I was never acknowledged as having shared the news with my postcard, although soon after that, the publication by Galli (1974) appeared. This gives me reason to believe that we, at Chicago, had come up with the structure solution first. In fact, the structure at room temperature still needed refinement but it was sent out, in its preliminary form, to a national Journal, certainly chosen for its speed of publication, trying to secure the primacy.

More or less at the same time I was presenting the results of the solution of the structures of two dehydrated minerals I had been working on: Mazzite and Cavansite at the American Crystallographic Association Meeting taking place in the spring of 1974 at Penn State University

(Rinaldi et al., 1974). And this is the proof that we already had the solution for the Mazzite structure early in 1974 and without having had any news from Modena.

This was also the very first time I experienced the intricacies of competition in scientific research!

5. The story of the structure solution of dehydrated Mazzite is also a good example of the saying “You can’t see the wood for the trees”.

While I was struggling with the N^th^ electron density map and it’s Patterson function (at the beginning of Dec. 1973), I was placing the Si/Al atoms in the model I was building with brass rods and cork balls (sticks and balls model) and I was playing with a whole array of gmelinite cages built with plastic tubing and metal tetrahedral links, in other words I was facing a very intricate world of sticks, balls and cages, when Joe Smith and Verner Schomaker (visiting from Seattle) came into my room. Verner took a look at my table full of all these implements and exclaimed: “Did you try to put a glide plane to alternately stagger the gmelinite cages?” And that’s how, the next day, the structure was solved!

It is worth noting here that Verner Schomaker (who passed away in 1997), had been a pupil of Linus Pauling, he was Joe Pluth’s advisor and was very similar in scientific character to prof. Fiorenzo Mazzi. He was well known for being quite happy to help colleagues with their crystallographic problems rather than occupying himself with writing his own papers. His name in fact appears in the literature some ten times more often in the acknowledgements than as an author.

Note:

A short version of these historical notes was presented by my ex pupil, now colleague and friend prof. Giacomo Diego Gatta (University of Milan; President of AIC) at the meeting held at the University of Pavia in memory of Prof. Fiorenzo Mazzi on June 14th, 2019. (www.mineralogylab.com/event/giornata-in-memoria-del-prof-mazzi/)

Acknowledgement

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Figures

Fig. 1. The Modena Zeolite Group. Circa 1980. Top row: Ermanno Galli, Romano Rinaldi, Daria Pongiluppi, Elio Passaglia; bottom row: Glauco Gottardi, Alberto Alberti, Giovanna Vezzalini.

Fig. 2. Bundle of mazzite needles associated with white rhombohedra of chabazite and white pseudotetragonal phillipsite twins (field of view approx. 1x1 cm). From Galli et al., 1974.

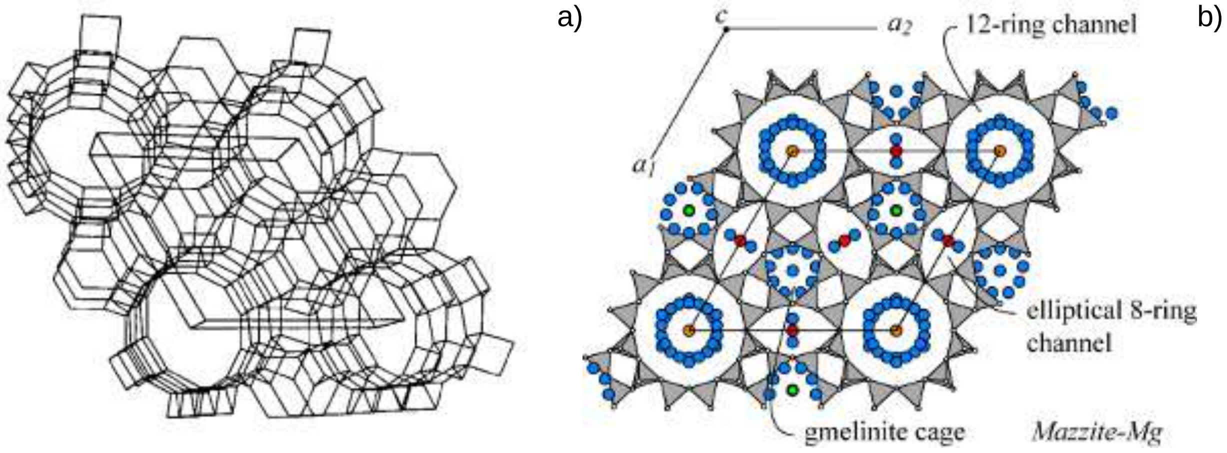

Fig. 3 a) The framework structure of Mazzite with its large 12-membered rings of tetrahedra and outline of the unit cell comprising alternately staggered gmelinite-type cages. From Rinaldi et al., 1975.

b) Projection onto the (0001) plane of the structure of Mazzite-Mg with its water molecules (blue) and cation contents (red = K, at the centre of the 8-rings; orange = Ca, at the centre of the 12-rings; green = Mg, at the centre of alternated gmelinite-type cages). From http://www.iza-online.org/natural/Datasheets/Mazzite/mazzite.htm

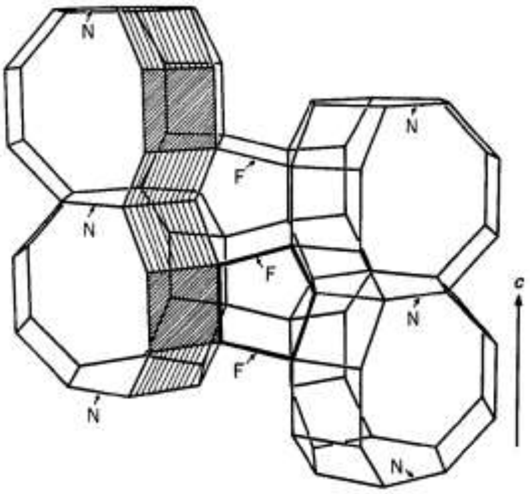

Fig. 4. Four staggered units of gmelinite-type cages alternating around the 12 rings of tetrahedra in Mazzite framework structure. From Rinaldi et al., 1975.

A similar drawing, with a comet tail, was heralding the solution of the structure in my Christmas postcard to Modena in 1973 (see text).

Romano Rinaldi

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