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SYNTHESIS, PHASE TRANSITIONS, DEGASSING BEHAVIOUR OF MELANOPHLOGITE (TYPE I CLATHRATE)

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INTRODUCTION

The name "melanophlogite" derives from the Greek words "*melanos*" and "*flogos*", with the meaning of "black" and "fire" respectively, indicating the tendency of the mineral to change its colour, *i.e.*, blackening if subjected to thermal treatment, which promotes the decomposition of the organic compounds, occurring as guest species in the structural cavities or included organic material. Melanophlogite (MEP) is a tectosilicate belonging to SiO_2 type I clathrate compounds, zeolite–like materials with microporous framework of corner sharing [SiO_4] tetrahedra. It is a low–density polymorph of silica, with an average value of the specific gravity of 2.04 and characterized by a framework density (FD) of 17.9 (Momma, 2014). In melanophlogite, there are two types of structural isolated cages: pentagondodecahedral [5^{12}] and tetrakaidecahedral [$5^{12}6^2$]. The superscripts 12 and 2, above 5 and 6 respectively, are the number of pentagonal and hexagonal faces of each kind of cavities inside the silica framework: pentagondodecahedral [5^{12}] voids are formed by 12 pentagonal faces, and 20 vertices, and tetrakaidecahedral [$5^{12}6^2$] voids are made up of 12 pentagonal faces and 2 hexagonal faces, with 24 vertices.

Melanophlogite chemical formula, including potential fillers of the cavities, is $46SiO_2•2M^{12}•6M^{14}$, where M stands for the guest molecules inside the structural voids, and M^{12} and M^{14} denote the 12 and 14 coordinated pentagondodecahedral [5^{12}] and tetrakaidecahedral [$5^{12}6^2$] voids, with volume of 97 $Å^3$ and 136 $Å^3$ respectively, occurring in the unit cell with a ratio of 2:6 (Gies, 1983; Kolesov & Geiger, 2003; Nakagawa *et al.*, 2005). In both types of cage, weakly bonded guest molecules occur (Gies, 1983; van Koningsveld & Gies, 2004). CH_4, CO_2, H_2S, N_2 and recently S_2 have been reported as guest species in the cages; H_2O has never been found, revealing the mineral hydrophobicity (Tribaudino *et al.*, 2010; Momma, 2014). Guest–free melanophlogite is simply a silica polymorph, but it does not exist in nature: indeed, the formation of melanophlogite requires a template, so that different peculiar guest molecules mixtures occur in the structural cavities, depending on the geological setting of the occurrence sites.

In nature, melanophlogite is related to low temperature hydrothermal processes in connection with gas venting (Tribaudino *et al.*, 2008), so that a critical issue is melanophlogite synthesis. The formation enthalpy of melanophlogite is very similar to that of amorphous silica (Navrotsky *et al.*, 2003) and its crystallization is likely due to the templating action of guest phases, which enables the mineral nucleation process (Gunawardane *et al.*, 1987; Kolesov & Geiger, 2003; Navrotsky *et al.*, 2003).

OPEN PROBLEMS AND GOALS OF THIS STUDY

The aim of this work is the crystallographic and mineralogical characterization of one of the silica clathrate compounds: melanophlogite. The characteristic structure consisting of a three–dimensional network in which the four vertices of the tetrahedra [SiO_4] are shared to arrange a framework hosting polyhedral cages, populated by guest molecules, could make melanophlogite interesting for the gas storage, with potential environmental applications in greenhouse gases sequestration. For this purpose, the determination of sorption and desorption conditions and kinetics are the major problems, but at present very few information are available to describe the release of guest molecules with increasing temperature. From a practical point of view, gas storage presents two crucial problems concerning energy and technological aspects: 1) clarifying the conditions in which absorption and desorption phenomena take place; 2) defining the methods to store/extract molecules in/from absorbing materials, respectively.

A particularly interesting aspect concerns the possibility of synthesizing melanophlogite, trying to reproduce the same conditions of natural genesis in laboratory. To be able to carry out the most complete possible characterization of the synthesized material, it is necessary to have an adequate quantity to conduct the required experimental analyses and, consequently, it is fundamental to define synthesis procedures, which allow to obtain material as pure as possible and in appropriate quantities, *i.e.*, hundreds of milligrams. This goal seems to have never been achieved before, as there are no references in the literature.

Samples of natural and synthesized melanophlogite have been studied, using a multi–analytical approach. The choice of the experimental analyses to be used has been strongly influenced by the characteristics of natural and synthesized melanophlogite samples to be investigated. On account of this, it has been not possible to carry out the same experimental analyses on all the natural and synthesized samples of melanophlogite, steered towards this study.

XRD (X–Ray Diffraction) analyses, using conventional and unconventional X–Ray sources, on powders and single crystals, at room and varying temperature, have been carried out in order to define: 1) how pure and crystalline the natural and synthesized samples are, in terms of possible presence of accessory mineralogical phases and of the amorphous fraction, respectively; 2) the structure characterizing the natural and synthesized samples, with the thermal ranges of stability and the possible phase transitions, specifying the temperatures at which they take place and the symmetries involved.

Raman spectroscopy analyses have been carried out in order to: 1) ascertain the presence of characteristic guest molecules, and to estimate whether they occur in [5^{12}] and [$5^{12}6^{2}$] structural cavities on samples of natural melanophlogite from different Italian localities; 2) identify the guest species occurring within the structural cavities on synthesized melanophlogite.

TGA (Thermal Gravimetric Analysis) has been done to define the behaviour of natural and synthesized melanophlogite samples as function of increasing temperature, in terms of release of guest molecules and consequent mass variation. Till now, TGA has been never done to detail the guest molecules release process: for instance, it is not clear if degassing takes place with a steady rate or if it is different with varying temperature or if there are some differences in degassing due to the kind of guest molecules enclathrated in the structural cavities.

DSC (Differential Scanning Calorimetry) has been carried out on natural and synthesized melanophlogite in order to identify possible phase transitions, specifying the temperature at which they occur and the type of these, for instance, if they are reversible or not reversible processes.

An INS (Inelastic Neutron Spectroscopy) study is currently in progress on synthesized melanophlogite in order to clarify the interactions between the guest molecules into the structural voids and the silicate framework, which host them, in particular in order to gain a deeper insight into the dynamical properties of the host framework, as well as onto the diffusion mechanism of the guest molecules.

STRUCTURE, PHASE TRANSITIONS AND DEGASSING BEHAVIOUR OF NATURAL SAMPLES OF MELANOPHLOGITE

In this study, three samples of Italian melanophlogite, coming from different geological settings, and consequently characterized by different guest molecules, have been considered, and named with their own localities of finding, namely: melanophlogite from Fortullino (near Livorno), melanophlogite from Racalmuto (near Agrigento), and melanophlogite from Varano Marchesi (near Parma).

Melanophlogite from Fortullino is in the form of spheroidal aggregates, scattered like dewdrops on the surface of ophiolitic breccias. Images collected using a SEM (Scanning Electron Microscope) have shown that these clusters are actually constituted by single cubic microcrystals, which are very difficult to isolate. Melanophlogite from Fortullino derives from the precipitation of silica in the form of clathrate, in the presence of CO_2 acting as a templating agent, during the processes of carbonate alteration of serpentinites. The Raman spectrum has shown the presence of accessory mineralogical phases, such as dolomite and quartz. The CO_2

peaks show the characteristic Fermi doublet. A quite large peak of CH_4 is at high frequency, and related to small amounts of methane. At frequencies lower than 1000 cm^{-1}, the silica pattern, which is peculiar of melanophlogite, is the same in all samples, not only in the natural ones, but also in synthesized melanophlogite, as explained in the following.

Melanophlogite from Racalmuto is the first finding of the mineral. It crystallizes in sulphur deposits, and found together with cristobalite, quartz, sulphur, celestine, calcite and dolomite. H_2S and, in smaller quantities, CH_4, are the templating agents. The Raman peaks of H_2S and CH_4 are doubled, and the Raman peaks of CO_2, occurring in small quantities, show the characteristic Fermi doublet. The double peaks indicate a distribution of the guest compound, associated to them, in the two structural cavities: tetrakaidecahedral, at lower frequency, and pentagondodecahedral, at higher frequency, with an intensity ratio of 3:1, respectively.

Melanophlogite from Varano Marchesi shows crystals with a cubic shape, often grown around opal seeds, and transformed into pseudomorphic quartz, and occurs in small veins and pockets, along fractures in siliceous marls, invariably separated from the host rock by a thin crust of opal–CT, which represents the result of a low temperature hydrothermal activity. CH_4 is the templating agent, and its Raman peak is doubled. Moreover, it should be observed that the positions of the Raman peaks of the guest molecules within the structural cavities of melanophlogite is slightly lower than the ones of the same molecules, calculated in the free state, and at room temperature. This aspect is due to the weak interactions, which are Van der Walls interactions, developed between the guest species and the silica host framework. Contrary to melanophlogite from Fortullino and Racalmuto, it was not possible to isolate the adequate quantity necessary for the experimental analyses of melanophlogite from Varano Marchesi, since it was always closely associated with other silica polymorphs.

Preliminary DSC analyses carried out on the samples of melanophlogite from Fortullino and Racalmuto have shown significant peaks related to the decomposition of the carbonate phases naturally associated with melanophlogite, namely dolomite between 475 and 575 °C and between 650 and 725 °C in the sample from Fortullino, and calcite between 600 and 700 °C in the sample from Racalmuto. Consequently, a purification procedure from the associated carbonate phases appeared to be required, in order to investigate exclusively the behaviour of melanophlogite. The sample from Fortullino used for the experimental analyses was constituted by almost pure melanophlogite, since it was possible to carry out purification procedures by chemical attack with HCl and manual separation. The purification by chemical attack has been done by immersion in HCl, with a concentration of 37 %, at room temperature for about forty–five days. In both purification methods, the starting material has been obtained by grinding roughly the spheroidal aggregates peculiar of melanophlogite from Fortullino. On the contrary, the sample from Racalmuto has not been purified, due to a very small quantity available, and contains calcite: consequently, the maximum temperature reached during the experimental analyses was 500 °C, *i.e.*, before the decomposition of the calcite.

XRPD (X–Ray Powder Diffraction) analyses, carried out employing a conventional X–Ray source from room temperature up to 400 °C on the sample from Fortullino, showed a resolution which allowed the Rietveld refinement exclusively using the cubic symmetry proposed by Gies (1983). A discontinuity observed in the unit cell parameters at about 60 °C, identified by a change in the slope of the unit cell volume curve against temperature, suggested a phase transition, as previously reported for melanophlogite from Mt. Hamilton (Santa Clara County, California), which shows a phase transition from a cubic symmetry, characteristic of high temperature, to a room temperature tetragonal symmetry, at about 60 °C (Nakagawa *et al.*, 2005), as illustrated in Figure 1.

XRPD measurements have been done with the high resolution powder diffractometer at ID22 beamline of ESRF (European Synchrotron Radiation Facility), in Grenoble (France), in the thermal range between –163 and 107 °C (Fig. 2). Thanks to the high resolution characteristic of the diffractometer of ID22 beamline and the synchrotron radiation, it has been possible to observe the splitting of the diffraction peaks, testifying the phase transition from a lower symmetry, typical of low temperature, with split peaks, to a high temperature cubic symmetry, with unsplit peaks.

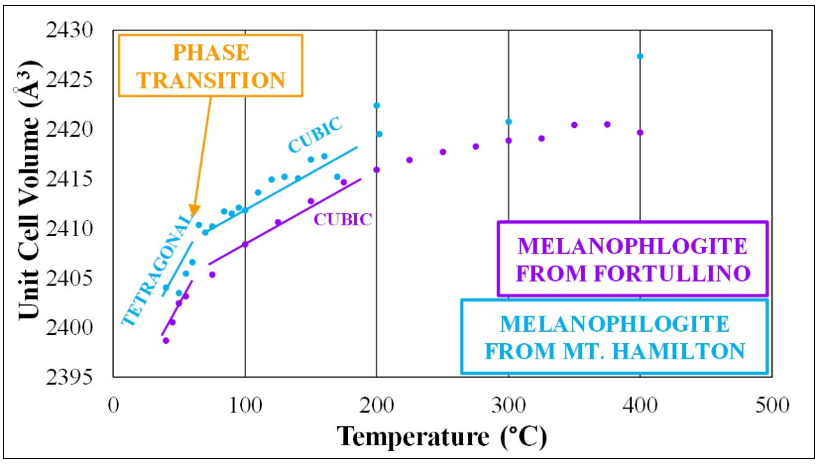

Fig. 1 - HT–XRPD on melanophlogite from Fortullino, from room temperature up to 400 °C, compared with results for melanophlogite from Mt. Hamilton (Nakagawa *et al.*, 2005).

Synchrotron radiation powder diffraction patterns have shown peaks already split at room temperature. The splitting of diffraction peaks is more apparent at lower temperature, and some peaks, which are single at the higher temperature, become a triplet with decreasing temperature. Peak splitting, hardly detectable at temperature higher than about 60 °C, is more evident at low temperature, with some of the main peaks becoming triple.

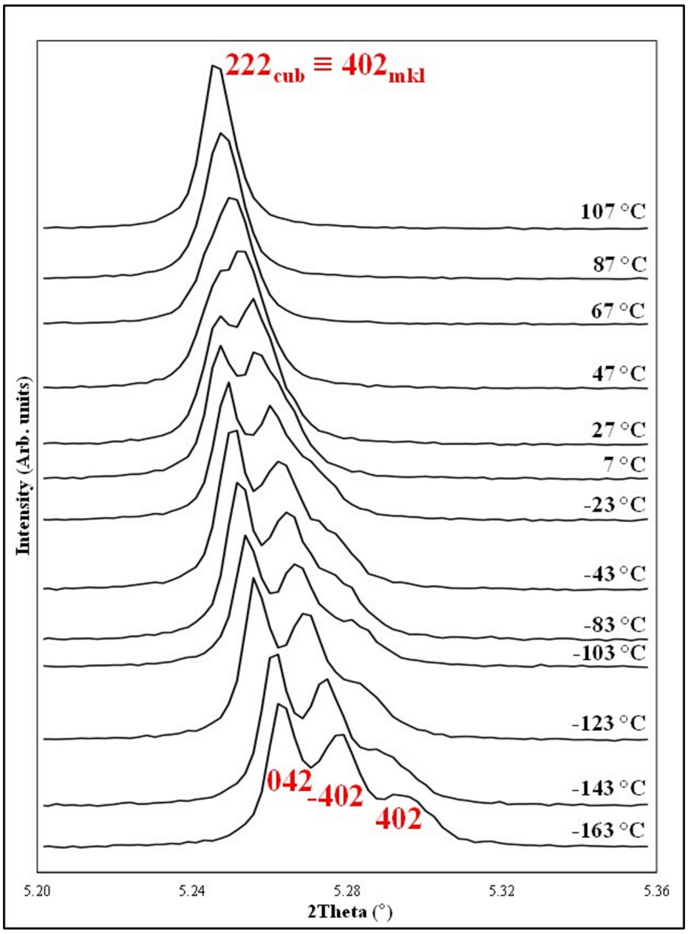

Fig. 2 - Peaks evolution in diffraction patterns taken for melanophlogite from Fortullino, in the thermal range between –163 and 107 °C investigated with XRPD carried out with synchrotron radiation at ID22 of ESRF (Grenoble, France).

The tetragonal structural model proposed for melanophlogite from Mt. Hamilton by Nakagawa *et al.* (2001; 2005) has not been able to fit the splitting of diffraction peaks. The choice of the lower symmetry structural model has been a quite difficult task, because of the little changes involved in the phase transition, not detectable by a conventional X–Ray source. Although the tetragonal model fits quite well the room temperature patterns taken by a conventional X–Ray source, in the synchrotron diffraction data, the tetragonal symmetry has failed to fit the observed peak splitting. Therefore, it appears that the $P4_2/nbc$ tetragonal symmetry (Nakagawa *et al.*, 2001) is a wrong choice for the low temperature structure of melanophlogite from Fortullino. The failure to model the peak splitting in a $P4_2/nbc$ tetragonal lattice is apparent also at room temperature. This may be related to a symmetry characteristic of melanophlogite from Fortullino, and different from the one characteristic of samples from other localities. An orthorhombic structural model seems to fit quite well the synchrotron radiation diffraction data, in the thermal range between –25 and 60 °C. Le Bail powder diffraction patterns decomposition has suggested that the most suitable symmetry to refine the diffraction data is represented by a rotated unit cell, characterized by *a* and *b* unit cell parameters corresponding to the diagonal along [110] and [–110] of the cubic unit cell, which have unit cell parameters of 13 Å. The resulting unit cell is a monoclinic one, with *a* and *b*, different from each other, of about 18 Å, and *c* of about 13 Å, as illustrated in Figure 3 (D'Alessio *et al.*, 2019).

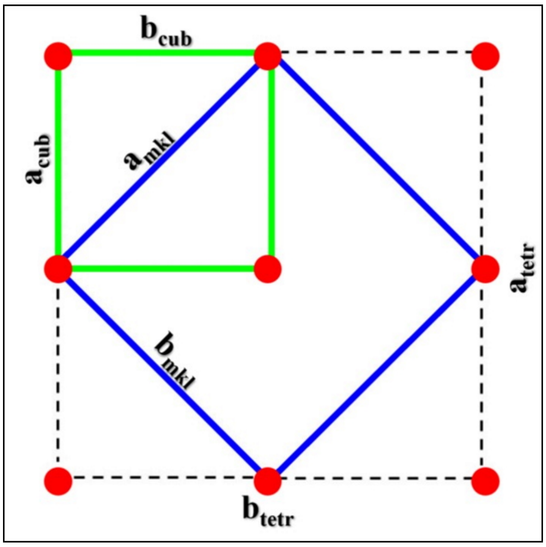

Fig. 3 - Relative setting of the monoclinic 18–18–13 Å (in blue), the cubic 13–13–13 Å (in green), and the tetragonal 25–25–13 Å (marked with black dashes) unit cells, viewed along [001] in a cubic structure.

In the thermal range between –23 and 97 °C, an orthorhombic symmetry has been used, but it has not been able to model adequately the splitting of diffraction peaks at low temperature. It is interesting to observe that the thermal expansion shows a decreasing trend for increasing temperature, and the unit cell volume remains constant for temperature higher than 200 °C. The unit cell parameters lose their equivalence, characteristic of the cubic symmetry, at about 100 °C, and this aspect marks the transition to the monoclinic symmetry, with *a* and *c* unit cell parameters very similar to each other, and with the ◘ angle slightly different from 90 ° (this difference is always less than 0.2 °). The slight deviation of the ◘ angle is such that the splitting of diffraction peaks cannot be modelled with a symmetry higher than the monoclinic. The phase transitions have been identified at about –23° C, within the monoclinic symmetry, and at about 97 °C, from cubic to monoclinic (D'Alessio *et al.*, 2019).

TGA has shown similar profiles for samples from Fortullino and Racalmuto, although with very different mass variations, since the guest molecules have different masses, and it is necessary to take into account the contribution of each guest to the mass variations indicated, which remain very limited up to 180 °C. At higher temperature, for the sample from Fortullino, the release of the guest molecules goes on, with different rate and without being complete, at the end of the thermal treatment, as evidenced by a second TGA, carried out on the already heated sample, which has shown a further mass variation. It is interesting to observe that the chemical purification procedure does not interact with the guest phases, and does not promote structural changes, and provides the same result obtained by the manually purified sample, in terms of thermogravimetric behaviour. The phase transition, detected by XRPD analyses at about 60 °C, is identified by a step in the calorimetric profiles of the melanophlogite samples from Fortullino and Racalmuto, which have shown an endothermic behaviour up to 200–250 °C, and a slightly exothermic behaviour at higher temperature, which begins in the same thermal range in which the onset of the release of the guest molecules is positioned.

DSC analyses have been carried out on the sample from Fortullino in three consecutive steps, and it has been possible to identify a phase transition around –23 °C, and demonstrate its reversibility, thanks to the presence of endothermic and exothermic peaks, during the heating and the cooling, respectively. This phase transition is related to the discontinuity identified in the trends characteristic of the unit cell parameters at low temperature, with XRPD investigations. DSC measurements, repeated in narrow thermal ranges in order to better constrain the high temperature phase transition, have revealed that the passage to the cubic symmetry takes place at different temperatures in the two considered localities, *i.e.*, 95 °C for Fortullino, and 60 °C for Racalmuto, thus suggesting an influence of guest molecules on this phenomenon.

SYNTHESIS OF MELANOPHLOGITE

The syntheses of melanophlogite have been carried out at a temperature of about 170 °C, using the quartz vials and an autoclave as means of containment; a further synthesis test with the autoclave has been carried out at higher temperature (180–185 °C). Chemically purified water, TEOS (tetraethyl orthosilicate) and methylamine have been employed as medium, crosslinking agent and templating agent, respectively. The thermal treatments of about 12 and 16 weeks have been set for the quartz vials and the autoclave, respectively.

During the first attempts of synthesis, the vials have been chosen as mean of containment, created from quartz tubes worked with a flame. The preservation of the vials with increasing temperature is closely related to the pressures developed inside them. In order to achieve the vials integrity, quartz tubes with smaller diameters and greater thicknesses have been used, and the quantity of chemical reagents has been drastically reduced. Two sets of vials have been prepared, with increasing concentrations of methylamine and, for each of them, different ratios between chemically purified water and TEOS. It seems that higher methylamine concentrations and higher ratios between medium and crosslinking agent promote the melanophlogite crystallization. The vials with greater numbers of crystals of synthesized melanophlogite have been considered (even though just few crystals for each vial have been detected), and XRPD analyses at room temperature have shown the predominant presence of the amorphous fraction, as demonstrated by the quantitative analyses on the material recovered from the vials with more crystals of synthesized melanophlogite. Moreover, this is in agreement with what observed with the optical microscope, showing very few crystals dispersed in an amorphous matrix (Fig. 4a).

An "intensive production", namely a sort of upscaling in melanophlogite synthesis, has been possible with an autoclave as mean of containment, allowing to use greater quantities of chemical reagents with respect to the quartz vials. Consequently, it has been possible to obtain a greater quantity of synthesized material (hundreds of milligrams against a few crystals in the quartz vials), which appears almost completely crystalline, as shown by what observed with an optical microscope (Fig. 4b).

From Raman spectroscopy analyses, it appears that methylamine has entered only one type of structural cavities, which are the tetrakaidecahedral ones, taking into account what reported in the literature (During *et al.*, 1968; Gunawardane *et al.*, 1987; Fyfe & Gies, 1990), since the Raman peaks are single ones, even though with a structural configuration still to be clarified, through a multi–instrumental INS investigation, currently in progress at ILL (Institut Laue Langevin), in Grenoble (France).

With this information and using a cubic symmetry (Gies, 1983) in Rietveld refinement procedure, it has been possible to define the synthesized material as almost pure melanophlogite, with an amorphous fraction of less than 10 wt.%, in agreement with what observed with an optical microscope, *i.e.*, a synthesized material which is almost completely crystalline.

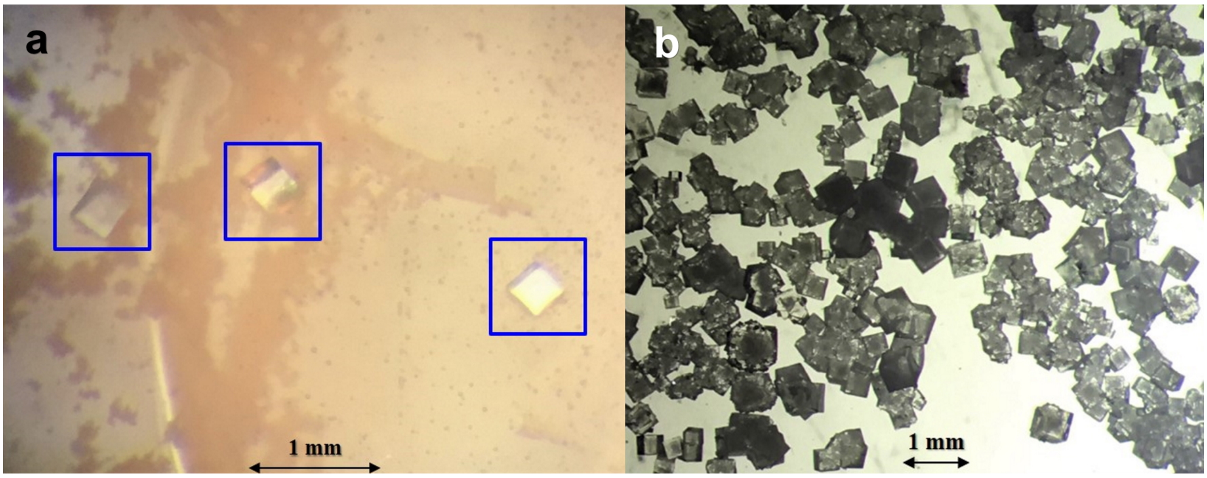

Fig. 4 - Images taken with an optical microscope of: a) cubic shape crystals of synthesized melanophlogite (in the quartz vials, at T = 170 °C for about 12 weeks), dispersed in an amorphous matrix; b) cubic shape crystals of synthesized melanophlogite (in autoclave, at T = 170 °C for about 16 weeks).

Two consecutive processes of mass loss can be identified by TGA: the first, located between 100 and 220 °C, and the second located between 220 and 880 °C, which is characterized by a higher loss rate between 600 and 800 °C, and resulting in a total mass variation less than 3 %, that is not even one third of the theoretical total mass variation of 9 %, calculated considering all the structural cavities occupied by methylamine. Nevertheless, this does not seem to take place, since methylamine is most likely exclusively in the tetrakaidecahedral cavities, as shown by Raman spectroscopy.

As done for the natural sample, the DSC investigations have been carried out in three consecutive steps, and it has been possible to identify a phase transition between –40 and –20 °C, and demonstrate its reversibility, thanks to endothermic and exothermic peaks during the heating and the cooling phases, respectively. The above mentioned peaks are split, and it means that the phase transition could occur through two consecutive steps.

A second test of synthesis in the autoclave, carried out at a temperature between 180 and 185 °C, has led to the crystallization of cristobalite and quartz, which are high temperature silica polymorphs: consequently, the temperature set for the thermal treatment resulted too high. This result is in contradiction with the experimental data reported in the literature, which extend the stability field of melanophlogite up to 200 °C (Gunawardane *et al.*, 1987).

Probably for the first time, since there are no references in the literature, it has been possible to synthesize melanophlogite in quantities of hundreds of milligrams, thanks to a hydrothermal synthesis procedure optimized with an autoclave, and make an upgrade from the synthesis carried out in the quartz vials, in terms of purity and quantity of the synthesized material.

GEOLOGICAL IMPLICATIONS

The onset of degassing is detected at about 200 °C for melanophlogite from Fortullino and Racalmuto. At high temperature, melanophlogite reacts to become cristobalite and quartz, which are high temperature silica polymorphs.

Degassing reduces structural stability of melanophlogite, since guest molecules act as templating agents. Consequently, in a sedimentary area, melanophlogite indicates local temperatures always lower than 200 °C, since, for higher temperatures, degassing and transformation of melanophlogite in high temperature silica polymorphs are promoted, as testified by melanophlogite cubic crystals transformed in pseudomorphic quartz, in rock samples found in Varano Marchesi quarries.

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