

Transforming waste into resource: Synthesis of tobermorite from crystalline silica

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RESEARCH AIM

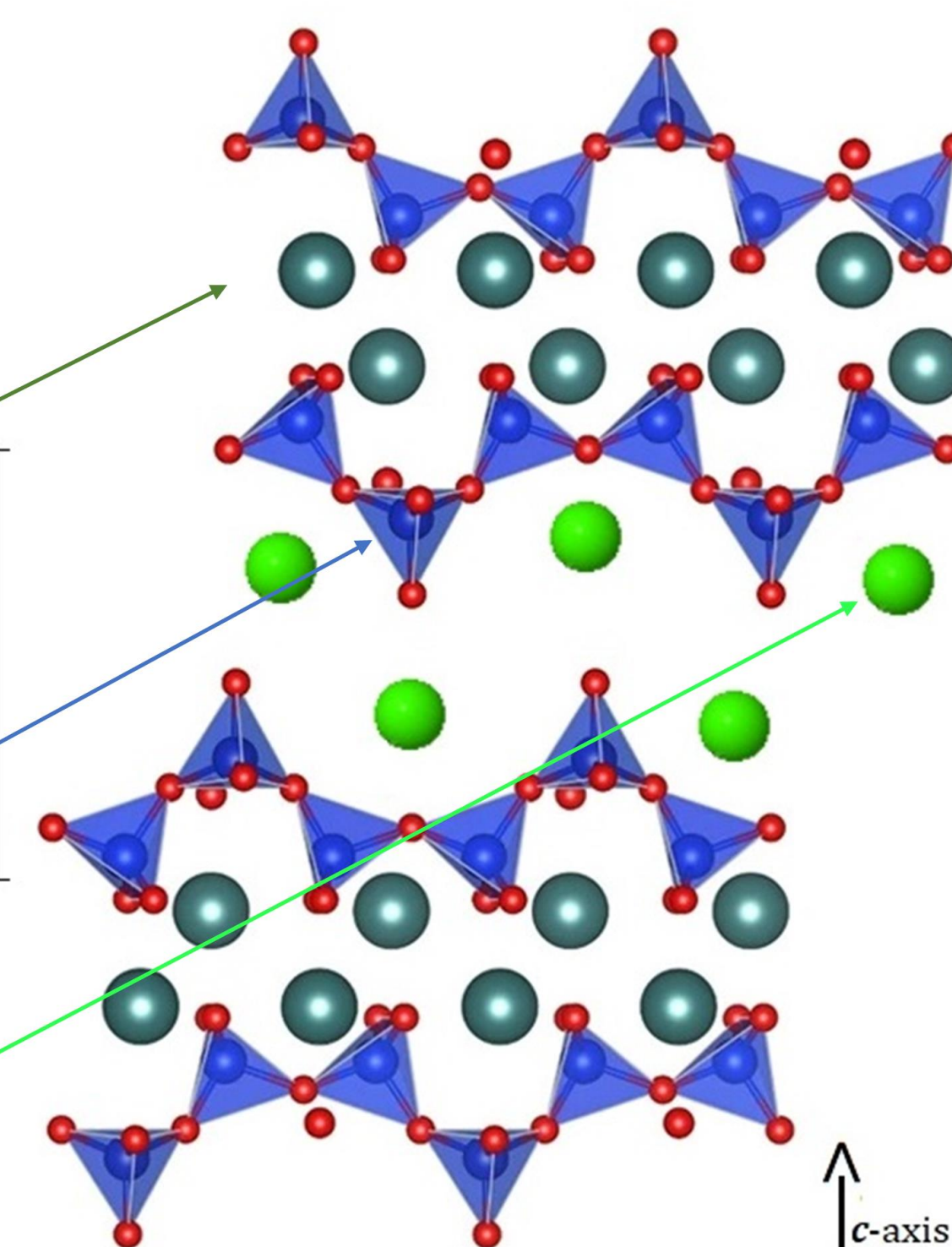
Substituted tobermorites (ST) are nanoporous phases with properties comparable to those of smectites and zeolites. ST can be synthesized from materials whose composition falls within the molar ratios $0.80 < \text{Ca}/[\text{Si} + \text{Al} + \text{Fe}] < 0.85$ and $0.00 < [\text{Al} + \text{Fe}]/[\text{Al} + \text{Si} + \text{Fe}] < 0.17$. Having achieved encouraging results using adequate amounts of glass (from recycling collection) and KRY·AS (i.e., thermally processed cement asbestos), we explored the possibility of recovering **crystalline silica (CS)**. In addition to being naturally present in sediments and raw materials, CS dust can be released during the processing of various geomaterials. In the latter case, it is waste, which encourages research into options for recovering these materials. In fact, long-term exposure to CS particulate can be harmful to humans and pose significant health risks (e.g. silicosis, lung cancer, chronic obstructive pulmonary disease and other respiratory disorders).

SUBSTITUTED TOBERMORITE

CaO-like polyhedra coupled on both side with wollastonite-like tetrahedral chains running along the *b*-axis

Si tetrahedral chain with $\text{Al}^{3+} / \text{Fe}^{3+}$ for Si^{4+} substitutions (up to 15%)
↓
Substituted tobermorites (high CEC)

Ca^{2+} , but also Na^{+} and K^{+} exchangeable cations in amount depending on Si substitutions

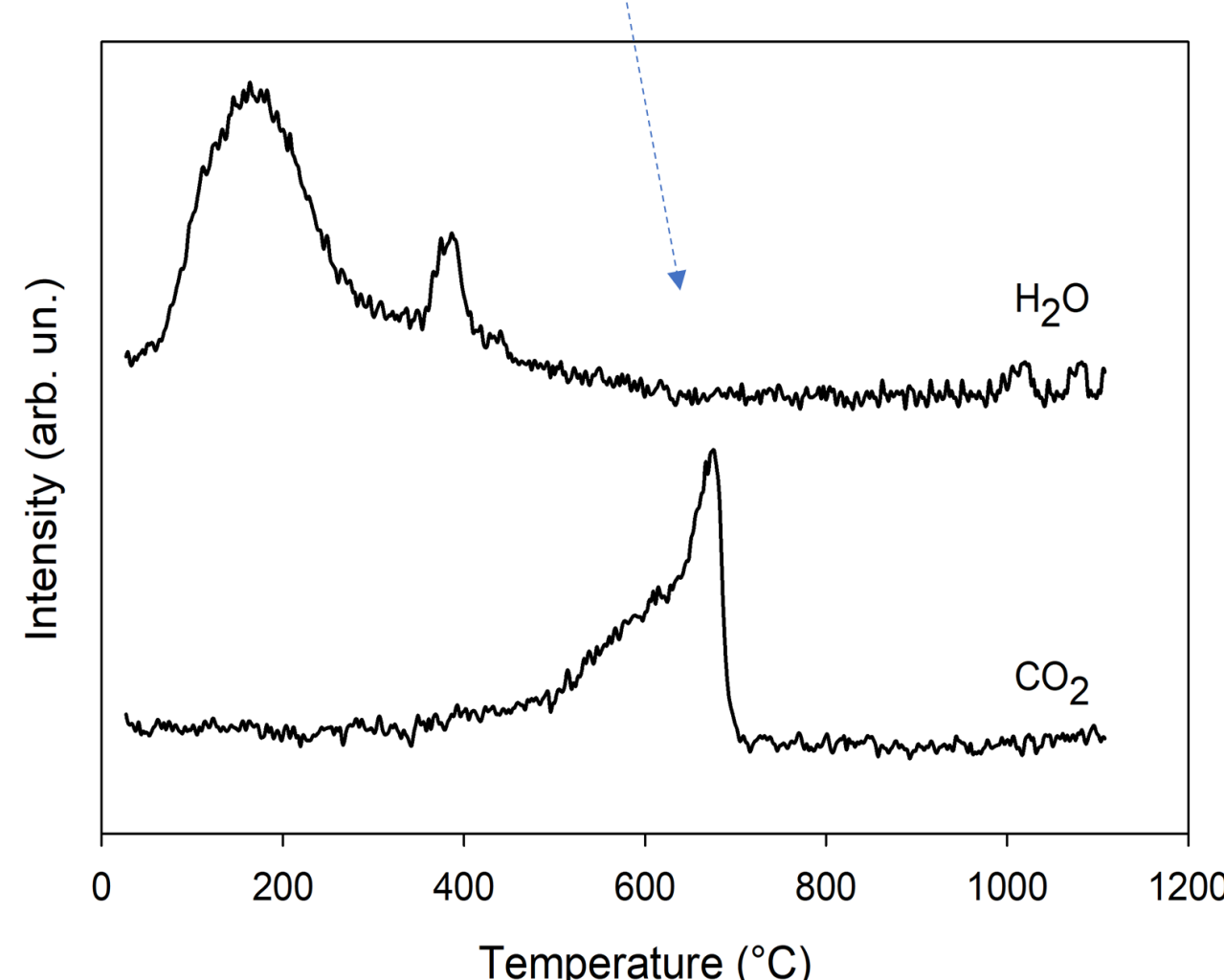
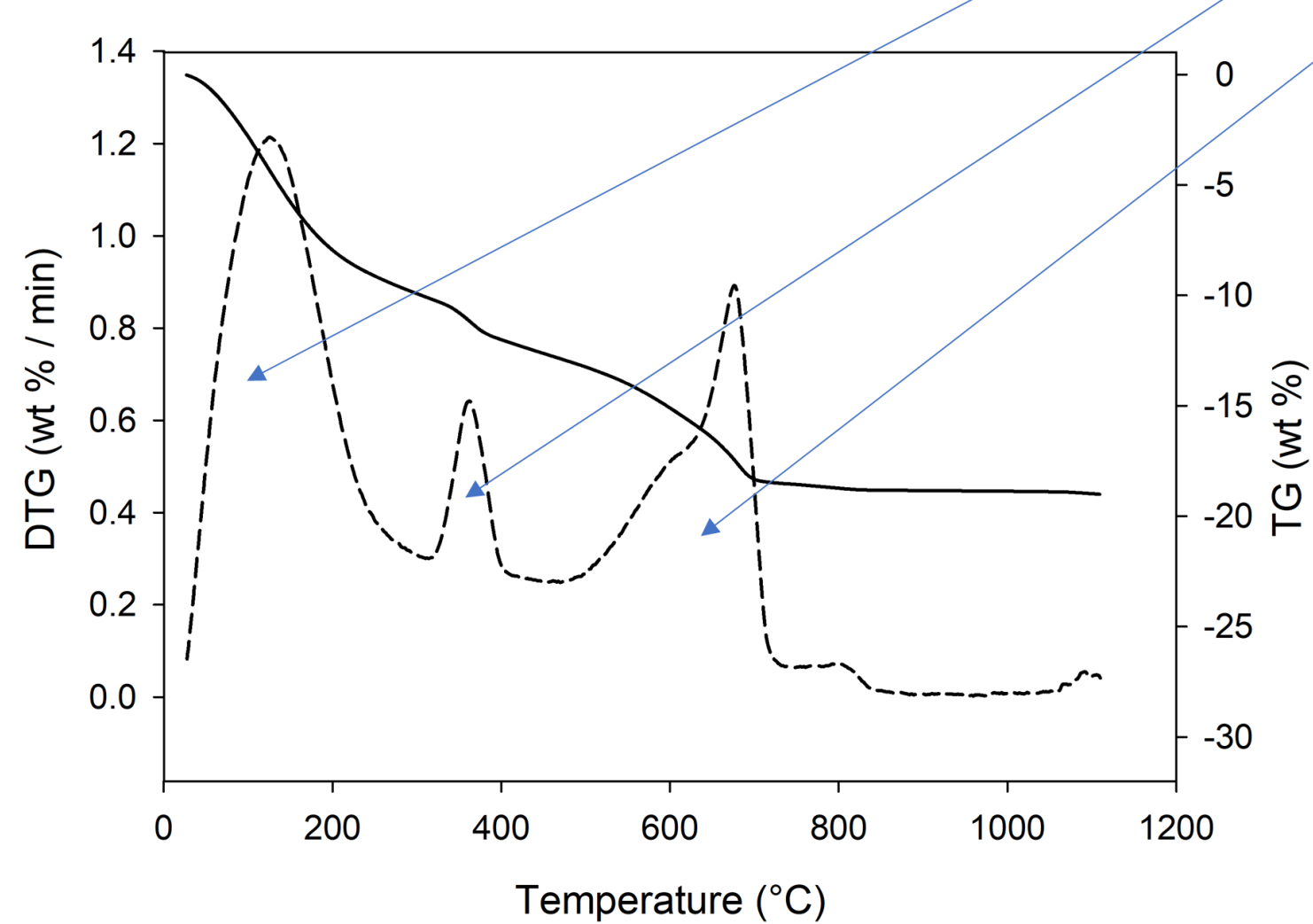


Substituted tobermorite structure. To a first approximation and without considering disorder and polytypism, the structure of tobermorite is given by a sequence of Ca–Si layers stacked along the *c*-axis. Hetero-valent substitutions may be neutralized by cations in the interlayer as well as by hydroxyl for oxygen substitution in the CaO polyhedra.

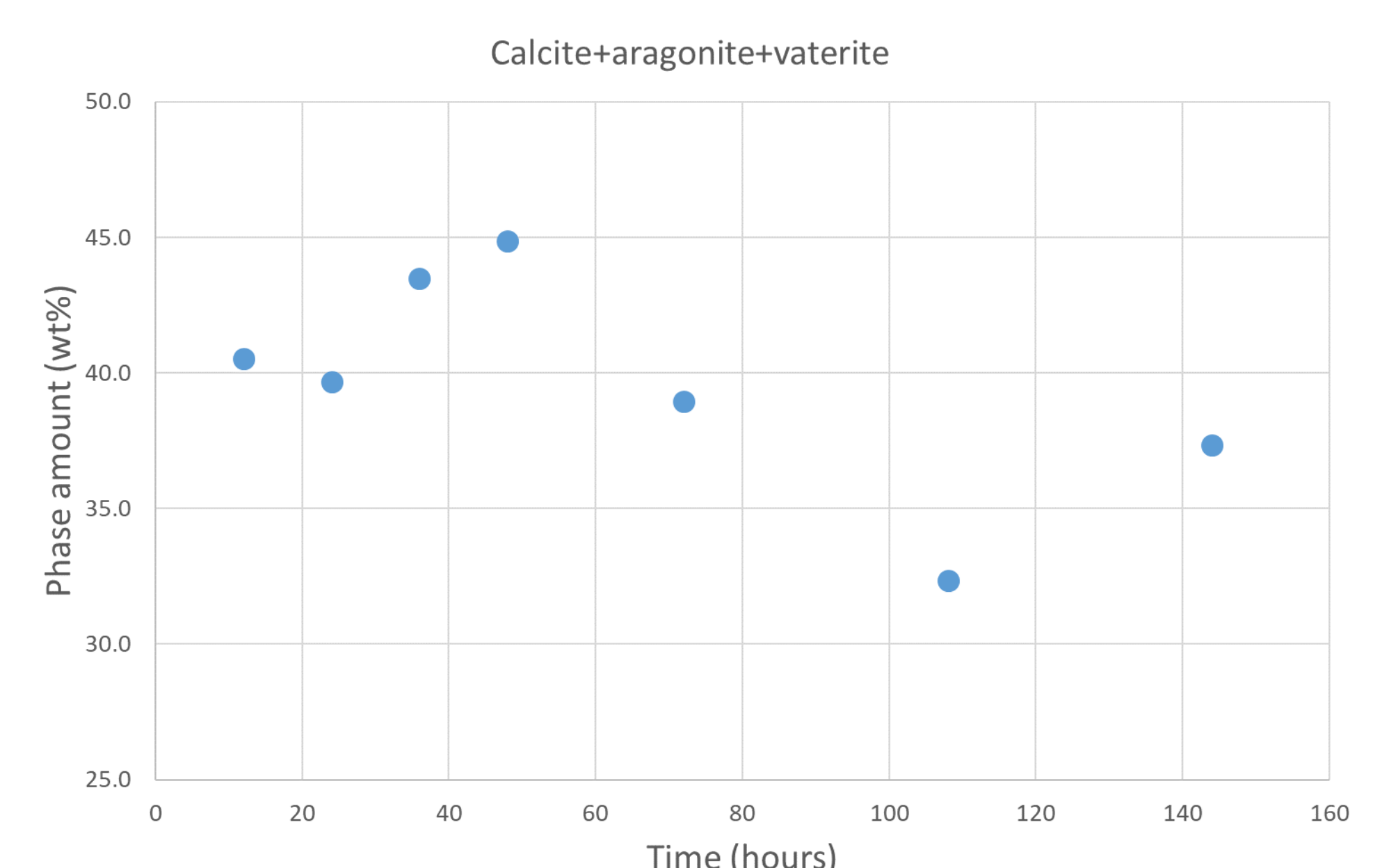
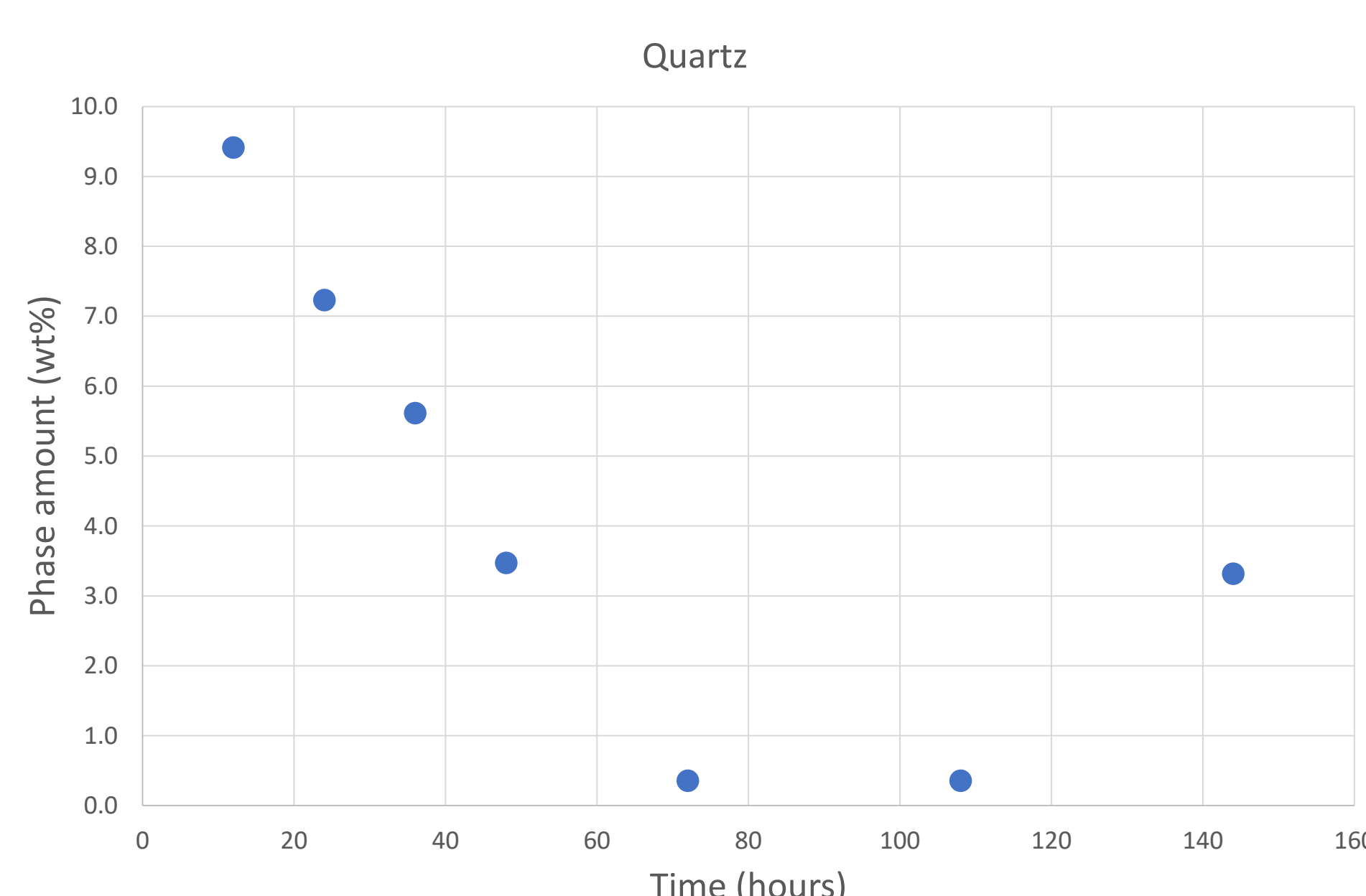
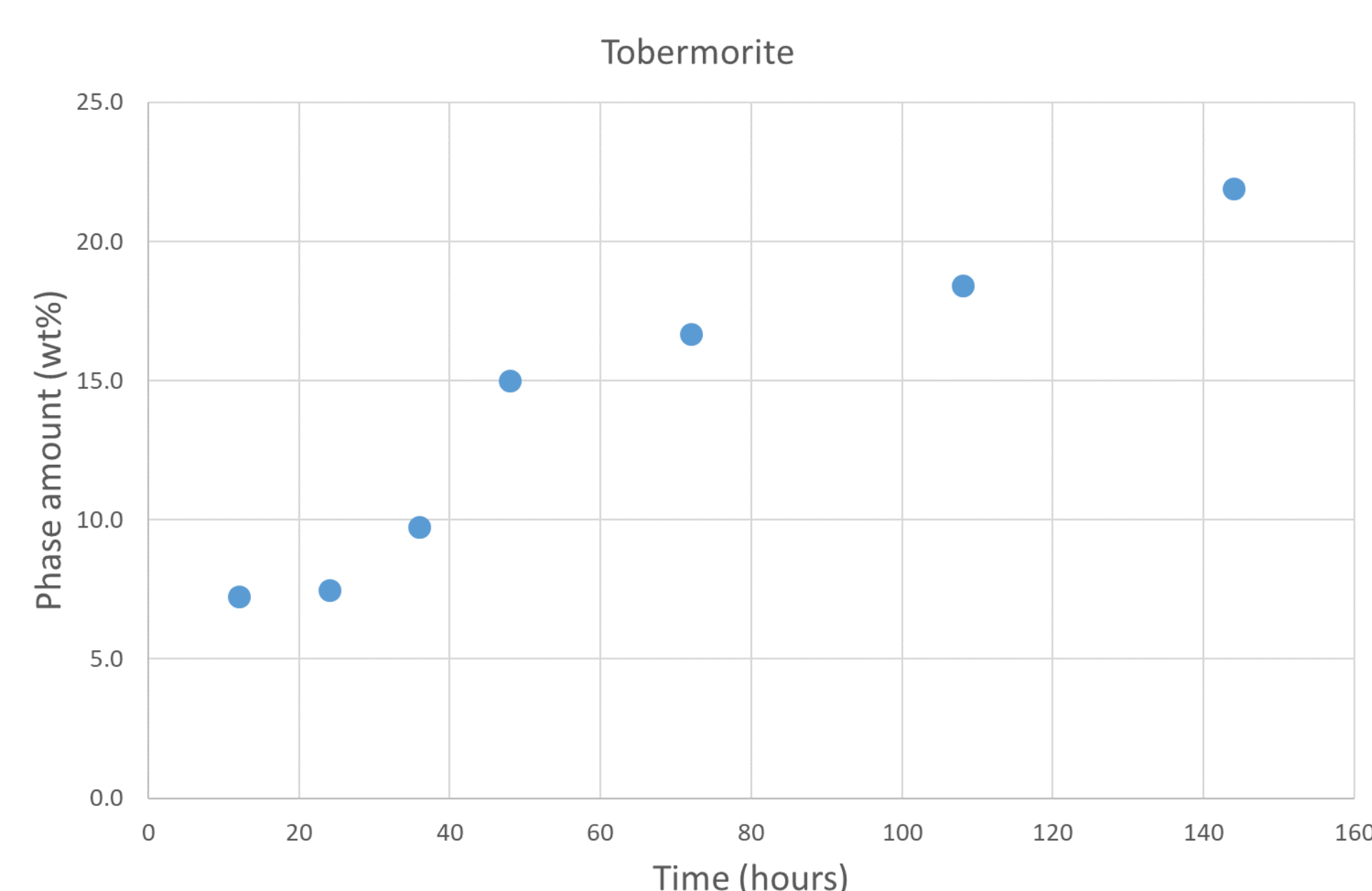
SUBSTITUTED TOBERMORITE RICH MATERIAL

Dehydration of the interlayer
Thermal decomposition of amorphous
Decarbonation

NO tobermorite deoxydilation



structure and cannot form other phases. Thermo-gravimetric analyses coupled with evolved gas mass spectrometry show that the silica substitutions are compensated by Ca^{2+} (and also Na^{+}) entry into interlayer rather than by hydroxyl for oxygen substitutions in the CaO-like polyhedra. This represents a promising feature for the material's use as an ion exchanger.

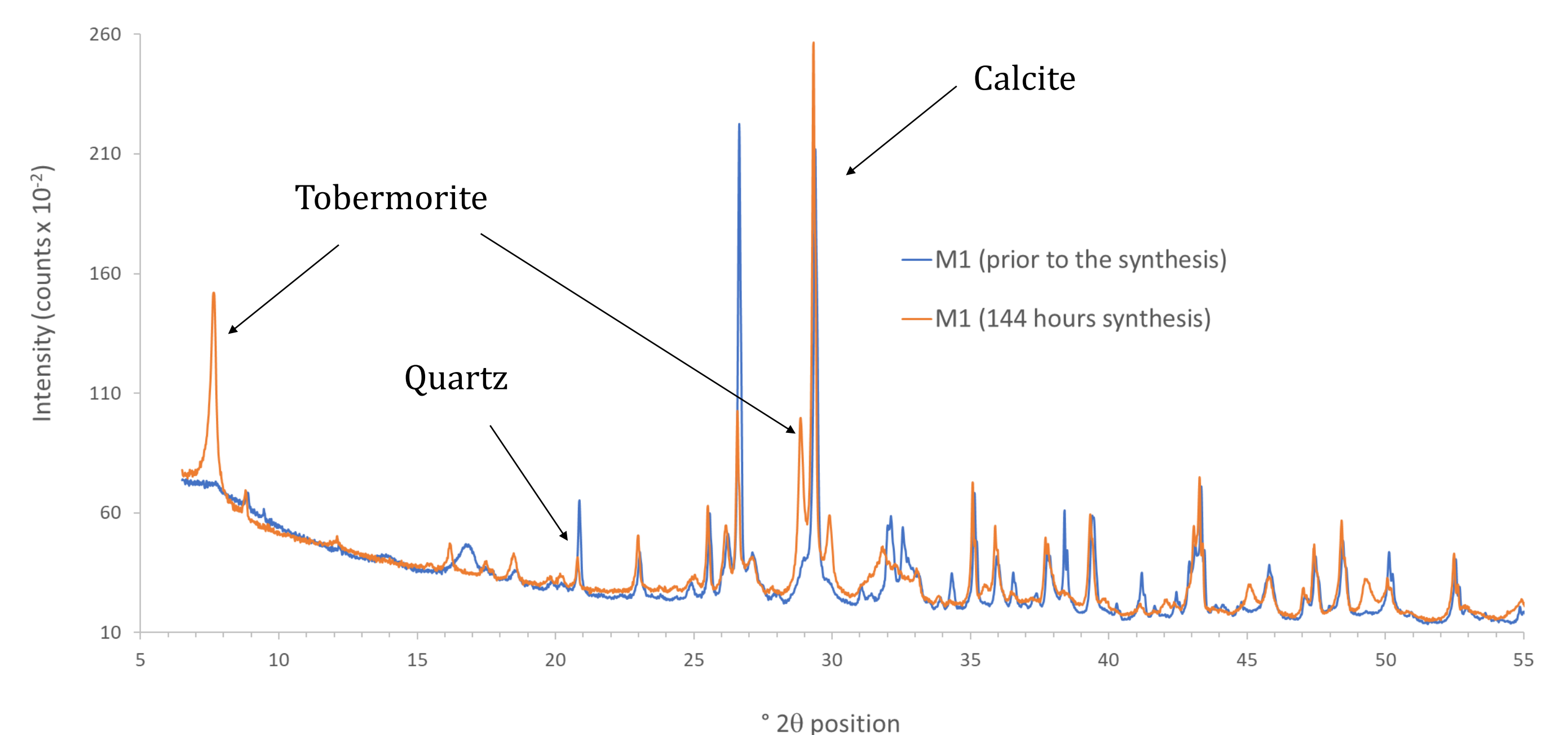


Kinetic and terpene adsorption. Preliminary results of the syntheses carried out at 120°C starting from M1 show a progressive increase in the amount of tobermorite as a function of time at the expense mainly of quartz and, after 48 hours, of the carbonate present in KRY·AS leading to its partial consumption and transformation into aragonite and vaterite. Initial alpha terpene uptake tests were also carried out with the intention of producing materials to be used as insect repellents; the results indicated uptake ranging from 0.75 to 2.16 mg/g depending on the terpene tested.

Materials and End-of-Waste method

Two mixtures were tested to synthesize TS. M1 composed of 75% KRY·AS (derived from thermal inerting of cement asbestos and source of Ca, Fe and Si), 22.5 wt% of CS (from quarry processing of quartzite and source of Si and Al) and 2.5 wt% of phillipsite rich-tuff (catalyst). M2 with 42 wt% of CaO, 55.5 wt% of CS and 2.5 wt% of tuff. M2 was prepared to estimate how much the absence of elements (present in KRI·AS) that do not enter the tobermorite structure affects the final product.

One gram of each mixture was reacted with 15 ml of 1M NaOH solution. The syntheses were carried out at different temperatures (100, 120 and 140 °C) and at different times (12, 24, 36, 48, 72, 108 and 144 hours).



Synthesis from M1 after 144 hours. The material synthesized from M1 is composed mainly of tobermorite (21.9 wt) and latterly of calcite (18.2 wt%), aragonite (11.2 wt%), vaterite (8.0 wt%) and katoite (5.1 wt%). Residual quartz is 3.4 wt%, compared with an initial amount of about 16 wt%. Little amount of larnite occurring in KRI·AS is still present as well as of illite (from quartzite). A considerable amount of amorphous material (likely Mg hydroxide) also occur as Mg does not enter the tobermorite structure.

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