

## Supporting Online Information

### **Al-substituted tobermorites: an effective cation exchanger synthesized from “End-Of-Waste” materials**

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The Supporting Information file contains:

- Further details about sample preparation before measurements, analytical methods, instruments, experimental conditions and data analyses
- Figure S1: a sketch of the tobermorite structure
- Figure S2: the graphical results of the Rietveld refinement of TRM
- Figure S3: time dependent metal cations removal reported as weight %.
- Table S1: chemical analyses of TRM considering the repartition of Ca between tobermorite and the sum of calcite and aragonite
- A list of the cited references.

## **Details about sample preparation before measurements, analytical methods, instruments, experimental conditions and data analyses**

### ***X-ray powder diffraction measurements***

X-ray powder diffraction (XRPD) patterns were recorded from air dried randomly oriented powdered samples. Measurements were carried out at room temperature using a Philips X'Pert PRO diffractometer equipped with first generation Real Time Multiple Strip (RTMS) X'Celerator detector. Experimental conditions were: Incident beam, Cu  $K\alpha$  radiation at 40 kV and 40 mA; filter, nickel; Soller slits, 0.02 rad; anti-scatter mask, 20 mm; anti-scatter slit,  $1/4^\circ$ ; divergence slit,  $1/4^\circ$ . Diffracted beam: anti-scatter mask, 5.0 mm; Soller slits, 0.02 rad; integration time, 240 s in continuous scanning (PSD length of  $2.12^\circ 2\theta$ ). Measurements were collected in the  $5\text{--}120^\circ 2\theta$  range and NIST SRM 676a (alumina powder, corundum structure) was used as internal standard (10% w/w)

### **Qualitative and quantitative phase analyses**

A preliminary qualitative analysis was carried out through the X'Pert HighScore Plus software and the PDF-4 database to identify the phases that will be after quantitatively determined. The quantitative mineralogical analysis was performed by the Rietveld method using the General Structure Analysis System (GSAS) software package,<sup>1</sup> EXPGUI as user graphical interface,<sup>2</sup> and the analytical schemes and protocols proposed in Gualtieri et al. (2008, 2019).<sup>3,4</sup> More in detail, raw data were smoothed with low pass filtering (convolution range equal to 5) before quantitative refinement and background was modelled using function 1 within GSAS, a Chebyshev polynomial of the first kind; peak shapes were modelled using the Thompson–Cox–Hastings pseudo-Voigt function (function 2) and March-Dollase function was chosen as intensity correction factor for preferred orientations and applied to the reflections (002) of tobermorite and (104) of calcite. The starting structural models used for the refinement are defined in the main text.

### **Thermogravimetric measurement coupled with evolved gas mass spectrometry**

The thermogravimetric analyses were carried out with a Seiko SSC 5200 thermal analyzer coupled with a quadrupole mass spectrometer (ESS, GeneSys Quadstar 422) to simultaneously detect the gas evolved during thermal reactions applying the method described in Bernini et al. (2017).<sup>5</sup> Gas sampling by the spectrometer is through an inert, fused silicon capillary heated to prevent gas condensing. Experimental conditions were: heating rate:  $20^\circ\text{C}/\text{min}$ ; heating range:  $25\text{--}1150^\circ\text{C}$ ; data measurement: every 0.5 s; purging gas: ultrapure helium, flow rate:  $100\ \mu\text{L}/\text{min}$ . Mass analyses were carried out in multiple ion detection mode measuring the  $m/z$  ratios (i.e., the dimensionless ratio between the mass number  $m$  and the charge  $z$  of an ion) 18, 30, 44, 64 to detect the emission of  $\text{H}_2\text{O}$ , NO,  $\text{CO}_2$ , and  $\text{SO}_2$ , respectively; a secondary electron multiplier detector set at 900 V was employed with 1 s of integration time on each measured mass. As specified in the text in the considered thermal range did not occur reactions that involve the release of NO ( $m/z=30$ ) and  $\text{SO}_2$  ( $m/z=64$ ); therefore, these data were not reported. Measurements were carried out in a Pt crucible on about 25mg of TRM prepared as described in paragraph 2.2 (main text) without any other additional pre-treatment.

## Chemical analyses

Major elements determination on solid sample was achieved through a wavelength dispersive Philips PW 1480 X-ray fluorescence (XRF) spectrometer (Philips, Almelo, The Netherlands) on powder pressed pellets obtained pressing at 7 tons 300mg of powdered sample on a boric acid support. To facilitate the adhesion of the powder to the boric acid support, about 10 mg of organic glue are added and after removed by evaporation, leaving the pressed pellets in air for 24 hours before measurement. The fluorescence intensity  $I_j$  of the element  $j$  in a sample containing  $N$  elements is related to the mass absorption coefficients of the sample by the formula

$$I_j = \frac{C_j}{\sum_{i=1}^N K_{j,i} C_i}$$

where  $C_j$  and  $N$  are the concentrations of the elements and the number of elements in the sample, respectively, and  $K_{j,i}$  are absorption coefficients. Loss on ignition (LOI) was obtained from thermogravimetric measurements.

The elemental analyses (C, N, S) were performed by a Carlo Erba Elemental Analyzer (Model 1106) on about 2 mg of sample without applying any specifically pre-treatment.

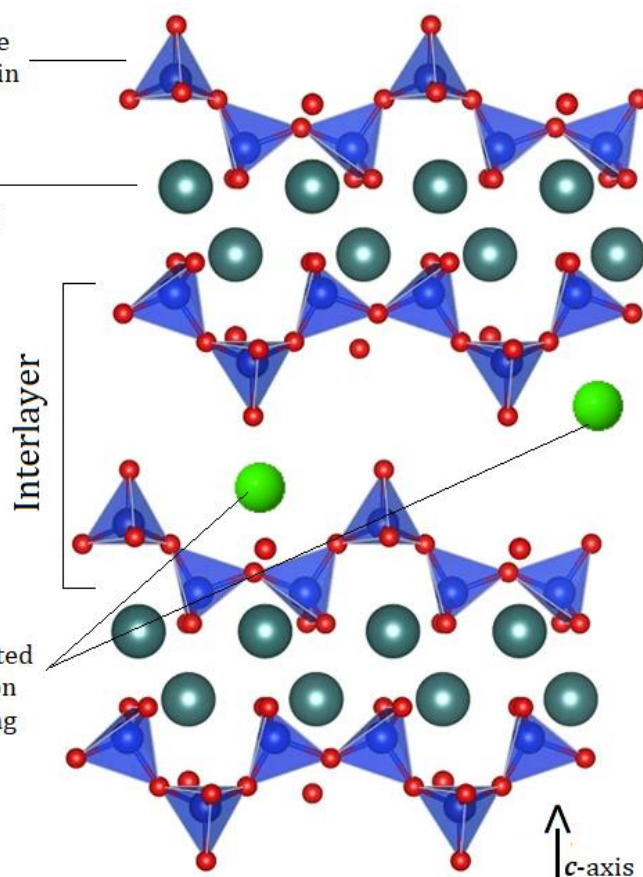
Metal cations ( $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ) removal was calculated measuring their residual concentration in solution through Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Perkin Elmer Optima 4200 DV (Perkin Elmer, Waltham, Massachusetts, U.S.A.) calibrated with certified standard solutions from Perkin Elmer. Element were determined in the solution after interacting with TRM. As indicated in the main text (paragraph 2.3), the supernatant liquors were recovered by centrifugation at 8000 rpm (Thermo mod. Espresso) for 5 min, acidified with 0.1ml of  $\text{HNO}_3$  to prevent possible salts precipitation and after analyzed.

## Additional figures

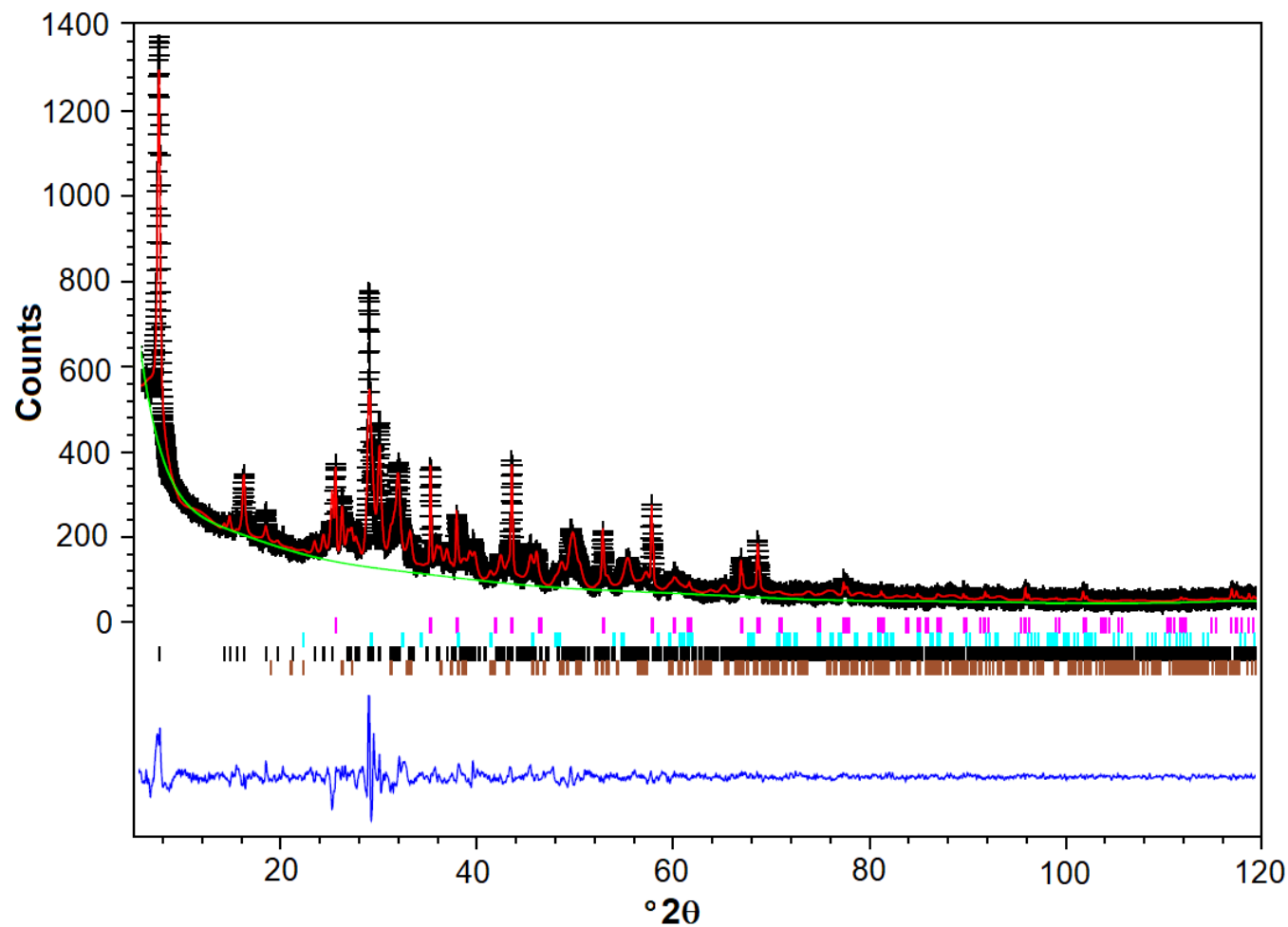
Si tetrahedral chains (dreierketten) which could be partially replaced (up to 15%) by  $\text{Al}^{3+}$  and/or  $\text{Fe}^{3+}$  in substituted tobermorites.

CaO-like polyhedra coupled on both sides to wollastonite-like tetrahedral chains running along the  $b$ -axis.

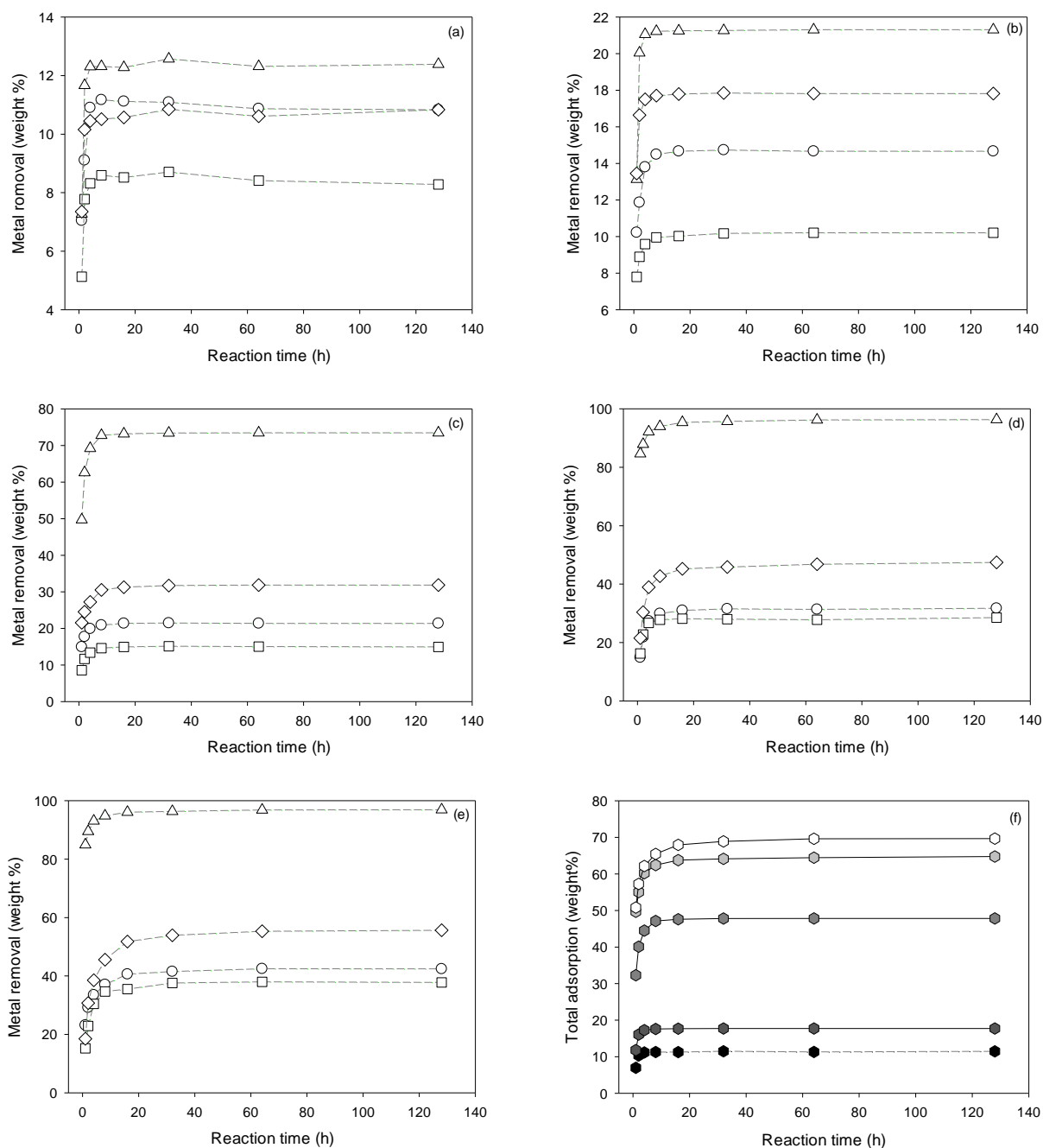
$\text{Ca}^{2+}$ , but also  $\text{Na}^+$  and  $\text{K}^+$ , zeolitic cations intercalated between the Ca-Si units in an amount depending on the  $\text{Al}^{3+}$  and/or  $\text{Fe}^{3+}$  for  $\text{Si}^{4+}$  substitutions. Solvating water molecules are omitted for sake of clarity.



**Figure S1.** Schematics view nearly perpendicular to the  $c$  axes of tobermorite. Adapted with permission from Geng, G. *et al.* Aluminum-induced dreierketten chain cross-links increase the mechanical properties of nanocrystalline calcium aluminosilicate hydrate. *Sci. Rep.* 7, 44032; doi: 10.1038/srep44032 (2017).<sup>6</sup> Copyright © 2017, The Authors/Springer Nature.



**Figure S2.** Graphical results of the Rietveld refinement of TRM. Observed (crosses), modelled (solid green line) and difference curves (bottom blue line) of the Rietveld refined X-ray diffraction patterns of TRM sample with internal standard NIST SRM 676a. Graphical markers: black, 11Å-tobermorite; light-blue, calcite; brown, aragonite; pink, NIST SRM 676a. See Figure 1 in the main text for the detailed peak assignments.



**Figure S3.** Time dependent metal cations removal (weight %) from 100 (a), 50 (b), 10 (c), 5 (d) and 1 (e) mmol/L aqueous solutions. Triangle,  $Pb^{2+}$ ; diamond,  $Zn^{2+}$ ; circle,  $Cd^{2+}$ ; square,  $Ni^{2+}$ . (f) Total amount of metal cations removed (like in Figure 3); the gray scale of the symbols indicates the concentrations of the solutions from 100 (black) to 1 mmol/L (white).

**Table S1.** Chemical analyses of TRM considering the repartition of Ca between tobermorite and the sum of calcite and aragonite. For ease of reading, the chemical analysis of KGT is also reported as in Table 1.

	<b>KGT</b> <sup>(3)</sup>	<b>TRM</b> <sup>(3)</sup>	<b>TRM</b> <sup>(3)</sup>	<b>TRM</b> <sup>(3)</sup>
	mol/100g	mol/100g	mol/100g	Eq/100g
<b>Si</b>	0.6870	0.7065	0.7065	2.8261
<b>Al</b>	0.0786	0.0754	0.0754	0.2262
<b>Fe</b>	0.0271	0.0256	0.0256	0.0768
<b>Ti</b>	0.0026	0.0023	0.0023	0.0092
<b>P</b>	0.0001	0.0002	0.0002	0.0010
<b>Mn</b>	0.0012	0.0009	0.0009	0.0018
<b>Mg</b>	0.1840	0.1887	0.1887	0.3774
<b>Ca</b>	0.6444	0.6626	0.5522 (*)	1.1044 (*)
<b>Na</b>	0.1330	0.1967	0.1967	0.1967
<b>K</b>	0.0392	0.0121	0.0121	0.0121

<sup>(3)</sup> recalculated as anhydrous (see Table 1); (\*) Ca hosted in the tobermorite framework calculated assuming 11.05 wt% (average value between those from QPA and TGA) as the total amount of carbonates thus meaning that 0.1104 mol/100g of Ca are hosted in calcite and aragonite frameworks.

#### REFERENCE CITED

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