Dynamic adsorption of Pb by Fe-Mg clay-quartz beds using micro-column testing

Z. Kypritidou[1*], M-A. Gatou[2], A. Argyraki[1], V. Zotiadis[3]

[1] Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, Athens 157 84, Greece

[2] School of Chemical Engineering, National Technical University of Athens, Zografou, Athens 15780, Greece

[3]Edafomichaniki S.A.., 14121 Athens, Greece

SUPPLEMENTARY MATERIAL

Characteristics of the clay samples

The tested samples consist mainly of palygorskite and Fe-smectite (>70%). The palygorskite content was calculated following the approach proposed by (Gionis *et al.*, 2007), whereas the Fe-smectite content was estimated by the XRD patterns.

The palygorskite phase of the samples PCM and MCM was identified by the basal (011) reflection at ~10.5Å (Fig. S1). NIR spectra showed the stretching Mg_3OH, Al_2OH, AlFeOH, Fe_2OH overtones at 7213, 7059, 6995 and 6928 cm^{-1} respectively (Fig. S2), which were assigned to palygorskites with both dioctrahedral and trioctahedral character by Gionis *et al.*, (2006, 2007) and Stathopoulou *et al.* (2011). Specifically, the palygorskite in PCM sample has mainly a dioctrahedral character, whereas in MCM sample has mainly a trioctahedral character (Fig. S2).

The Fe-smectite phase was characterized by a basal reflection at ~15Å in the air-dried oriented samples which shifted to ~16.5-17Å upon treatment with ethylene glycol (Fig. S.1). The d_{060} at ~1.51Å and the presence of the FeFeOH combination band at 4366 cm^{-1} respectively, confirmed the dioctrahedral nature of the phase (nontronite), as also noted by Frost *et al.* (2002) and Christidis *et al.* (2010). However, the samples also exhibit stretching Mg_3OH overtones at 7184 and 7153 cm^{-1} which according to Gionis *et al.*, (2006) were assigned to trioctrahedral smectite (saponite). It should be noted that the overtone at 7240 cm^{-1} belongs to serpentine (Fig. S2). Extensive study of Fe-smectite by Kaufhold *et al.*, (2019), revealed the rather complex nature of this phase, which could not be separated by the accompanying trioctahedral minerals (serpentine, talc, and palygorskite). Due to the presence of both dioctrahedral and trioctahedral components in its structure, the name Fe-smectite was used to describe this phase.

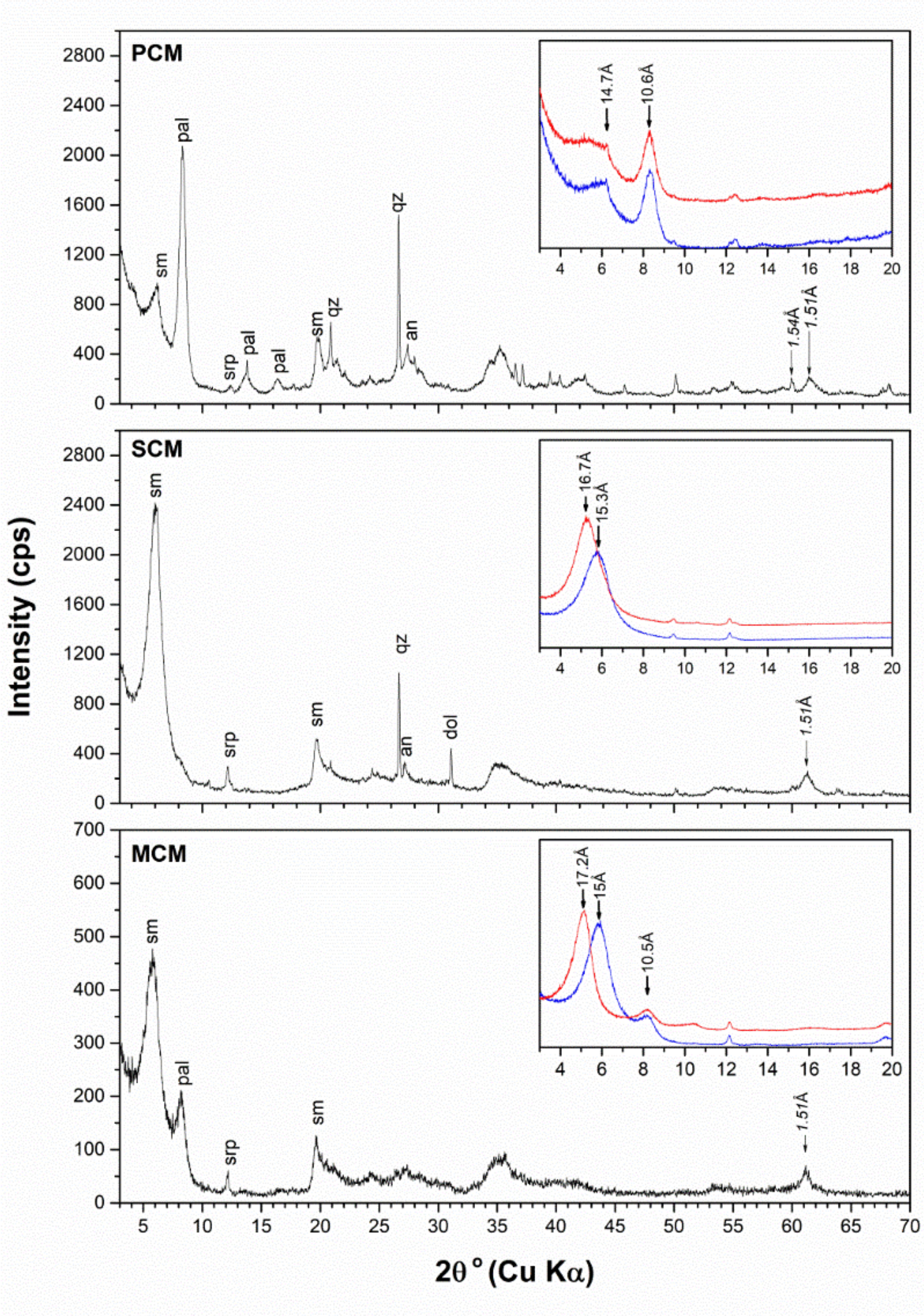

Fig. S1: Mineralogical characterization and assignments of the main peaks (sm=Fe-smectite, pal=palygorskite, srp=serpentine, qz=quartz, dol=dolomite). Black line=bulk sample, blue line=air-dried oriented sample, red line=ethylene glycol saturated sample.

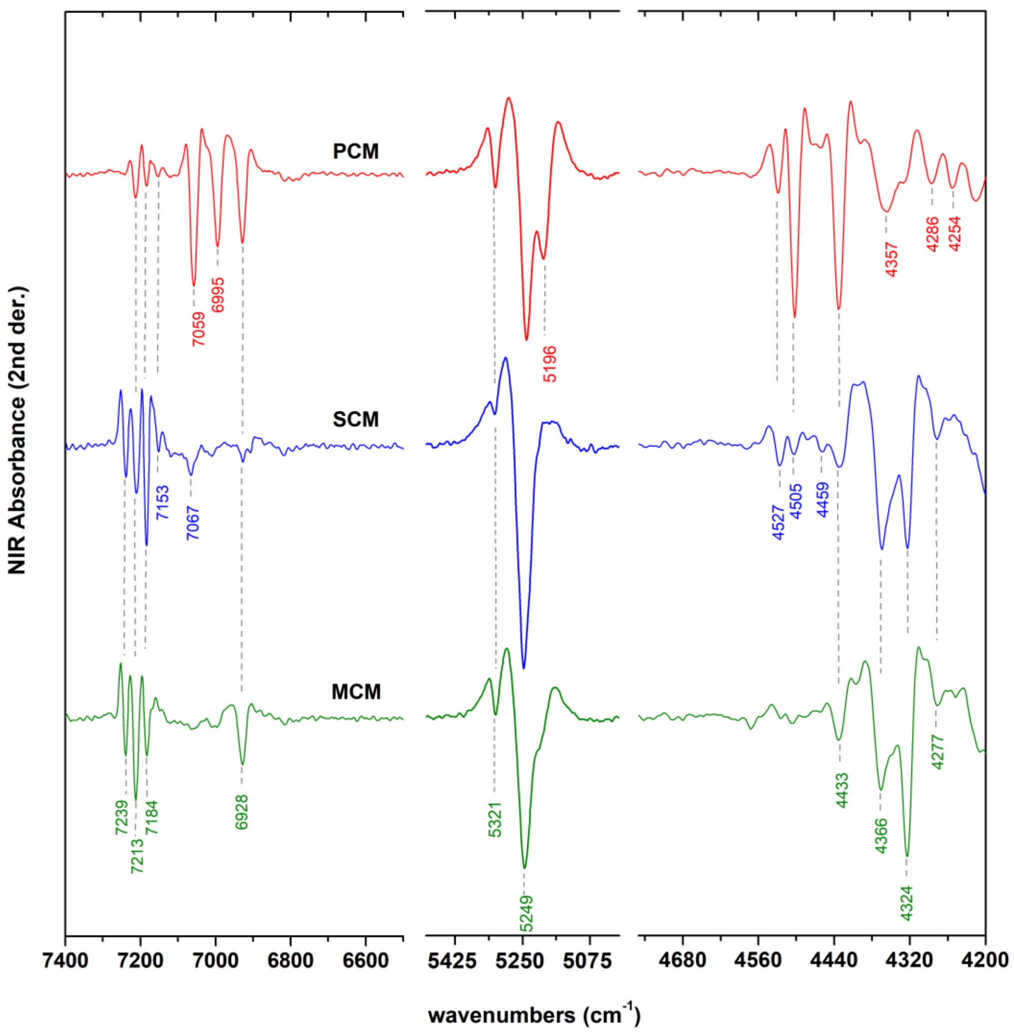

Fig. S2: NIR spectra (2nd derivative mode) of the three studied clays.

Sorption of Pb onto clay-quartz columns

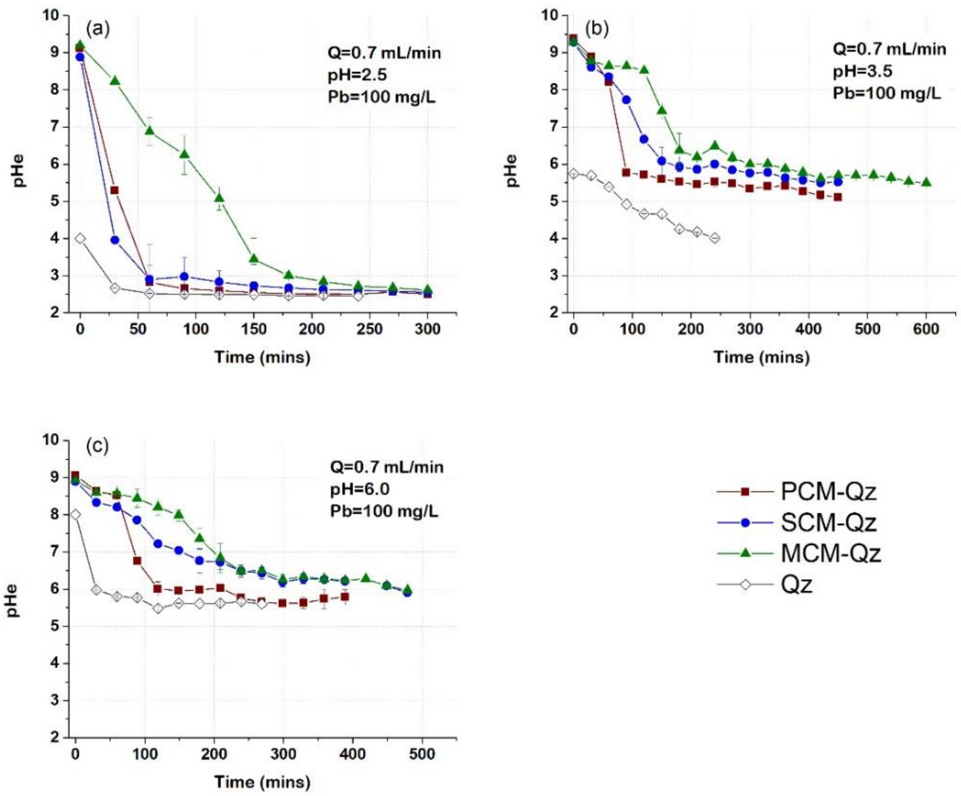

Fig. S3: Effluent pH (pHe) as a function of time for PCM-Qz, SCM-Qz and MCM-Qz clay beds and quartz sand (Qz), at inlet solution pH (a) 2.5, (b) 3.5 and (c) 6.0.

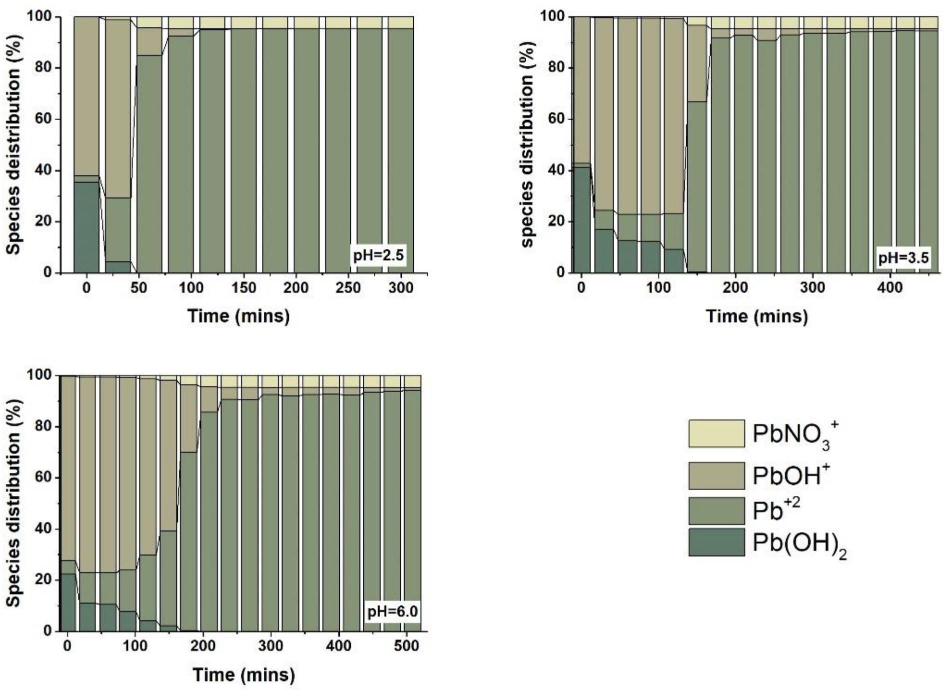

Fig. S4: Distribution of Pb species in the effluent solutions collected from MCM-Qz beds versus time at different inlet pH (2.5, 3.5 and 6.0). Speciation calculations were carried out with PHREEQC geochemical code using as input the effluent Pb concentrations and pHe.

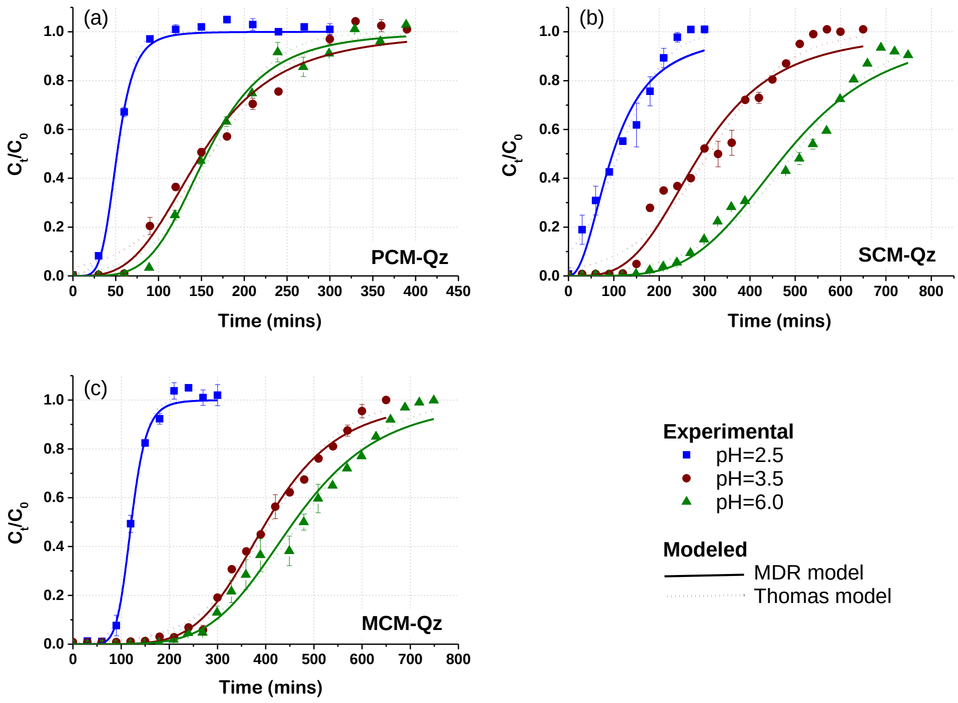

Fig. S5: Fitted curves of Thomas and MDR models in the experimental data for C_0=100 mg/L Pb, Q=0.7 ml/min and pH=2.5, 3.5 and 6.0 respectively, for (a) PCM-Qz, (b) SCM_Qz and (c) MCM-Qz beds.

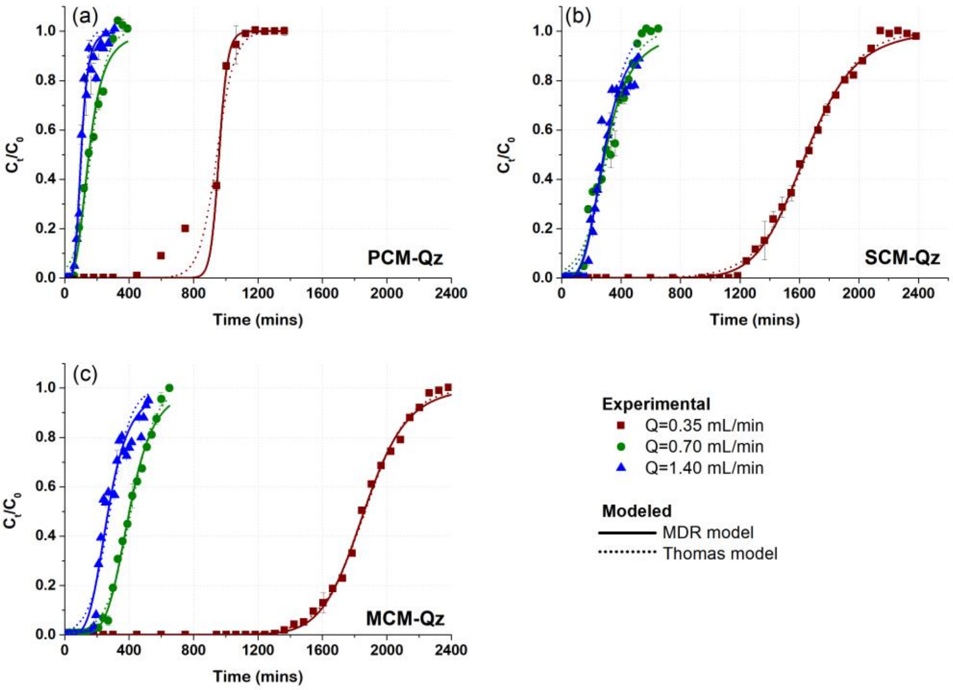

Fig. S6: Fitted curves of Thomas and MDR models in the experimental data for C_0=100 mg/L Pb, pH=3.5 and Q=0.35, 0.7 and 1.4 ml/min respectively.

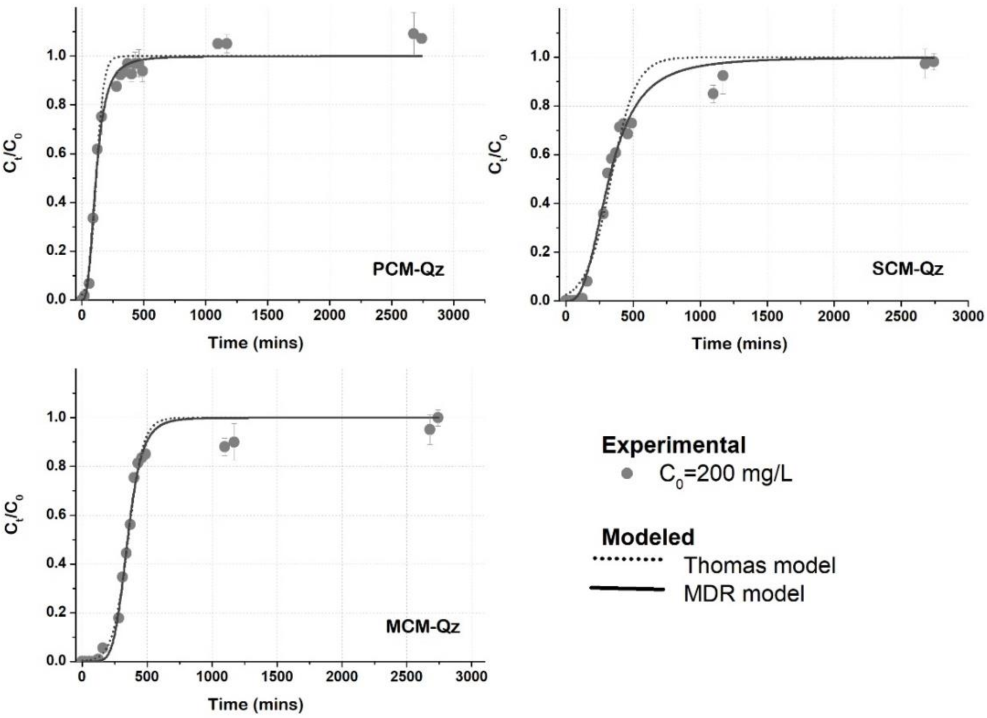

Fig. S7: Fitted curves of Thomas and MDR models in the experimental data for C_0=200 mg/L Pb, pH=3.5 and Q=0.7 ml/min.

REFERENCES

Christidis, G.E., Katsiki, P., Pratikakis, A. & Kacandes, G.H. (2010) Rheological properties of palygorskite-smectite suspensions from the Ventzia Basin, W. Macedonia, Greece. Pp. 2562–2569 in: *Bulletin of the Geological Society of Greece, Proceedings of the 12th International Congress, Patras, May, 2010*.

Frost, R.L., Kloprogge, J.T. & Ding, Z. (2002) Near-infrared spectroscopic study of nontronites and ferruginous smectite. *Spectrochimica Acta - Part A Molecular and Biomolecular Spectroscopy*, **58**, 1657–1668.

Gionis, V., Kacandes, G.H., Kastritis, I.D. & Chryssikos, G.D. (2006) On the structure of palygorskite by mid- and near-infrared spectroscopy. *American Mineralogist*, **91**, 1125–1133.

Gionis, V., Kacandes, G.H., Kastritis, I.D. & Chryssikos, G.D. (2007) Combined near-infrared and x-ray diffraction investigation of the octahedral sheet composition of palygorskite. *Clays and Clay Minerals*, **55**, 543–553.

Kaufhold, S., Chryssikos, G.D., Kacandes, G., Gionis, V., Ufer, K. & Dohrmann, R. (2019) Geochemical and mineralogical characterization of smectites from the Ventzia basin, western Macedonia, Greece. *Clay Minerals*, **54**, 95–107. Mineralogical Society.

Stathopoulou, E.T., Suarez, M., Garcia-Romero, E., Del Rio, M.S., Kacandes, G.H., Gionis, V. & Chryssikos, G.D. (2011) Trioctahedral entities in palygorskite: Near-infrared evidence for sepiolite-palygorskite polysomatism. *European Journal of Mineralogy*, **23**, 567–576.