Introduction to innovative nano Electro Application Technique (nEAT) to improve the performance of alcoholic nanolime

MAUCOURANT, Cyril and O'FLAHERTY, Fin <http://orcid.org/0000-0003-3121-0492>

This document is the Published Version [VoR]

Citation:

MAUCOURANT, Cyril and O'FLAHERTY, Fin (2026). Introduction to innovative nano Electro Application Technique (nEAT) to improve the performance of alcoholic nanolime. In: Stone 2025: proceedings of the 15th international congress on the deterioration and conservation of stone. ICOMOS, 928-934. [Book Section]

INTRODUCTION TO INNOVATIVE PROTOTYPE NANO ELECTRO APPLICATION TECHNIQUE (*nEAT*) TO IMPROVE THE CONSOLIDATION PERFORMANCE OF ALCOHOLIC NANOLIME

C. Maucourant[1]* and F. O'Flaherty[2]

Abstract

Nanolime (i.e. colloidal hydro-alcoholic dispersion of $CaOH_2$ nanoparticles) was first introduced in the early 2000's with the aim of consolidating carbonate substrates such as wall paintings and built heritage limestones. Despite its extensive use over decades, commercialised nanolimes show limited in-depth consolidation performance on low-porosity substrates (i.e. open porosity Φ below 20%) and instead accumulate near to the surface. Although previous work aimed to address this issue by assessing the impact of the application methods and solvent properties on the penetration process, the problem persists as alcoholic nanolimes penetrate fine-grained and low-porosity substrates by only a couple of millimetres at best. To solve this problem, extensive research was conducted at Sheffield Hallam University (UK) to develop innovative *nano Electro Application Technique* (nEAT), with the aim to improve the performance of commercialised alcoholic nanolime treatments. nEATgives better mass (i.e. in-depth) consolidation efficiency and is based on the principle of electrophoresis to increase the penetration of the nanolime from the deteriorated surface through the porous mineral matrix. During its development, this international patent-pending technique was tested on various types of fine-and coarse-grained limestones with different open porosities ranging from 11% to 30%. In this paper, laboratory tests conducted on different *Caen* limestone samples affected by powdering and treated with a commercialised nanolime will be presented. Results of consolidation tests confirmed that after only one application of nEAT, the penetration of the nanolime and the mineral cohesion in-depth increases dramatically.

Keywords: DRMS, nEAT; nanolime; limestone; stone consolidation, phenolphthalein.

1. Introduction

The consolidation of porous calcareous substrates with nanolime is a conservation treatment that first appeared around 2000 (Otero *et al.,* 2017 and Baglioni *et al.,* 2015). Alcoholic commercialised nanolimes proved to be efficient in the consolidation of wall paintings, frescoes, plasters, renders and lime-mortars. The distinct advantage of using nanolime is that it is entirely chemically compatible with limestone and restores the cohesion loss by regenerating mineral bridges with new calcite. However, the penetration of nanolime into fine-grained substrates is hugely challenging and can be limited to no more than a few millimetres at best, yielding ineffective consolidation. Quick evaporation of the solvent used for the alcoholic nanolime dispersion and the low substrate porosity (i.e $\Phi < 20$ %) are amongst the main factors responsible for the observed insufficient penetration and consolidation efficiency. During the absorption of the nanolime a few millimetres into the treated limestone, the calcium hydroxide nanoparticles tend to migrate back towards the surface as the solvent evaporates. This phenomenon is known as "back-migration" and, in addition to limiting the penetration of nanolime in-depth, it also contributes to the formation of a white haze over the treated surface. To tackle this issue and improve the penetration of the nanolime, previous work investigated the use of several solvents characterised by different physical properties (Borsoi *et al.,* 2016a). In addition to the solvent properties, different work demonstrated that the penetration of alcoholic nanolime can be affected by different environmental factors such as the RH (López-Arce *et al.,* 2011), the CO2 level and the air temperature (Camerini *et al.,* 2019) but also by the type and porosity of the limestone (Otero *et al.,* 2019), the application methodology (Borsoi *et al.,* 2016b) and the properties of the nanolime dispersion (Arizzi *et al.,* 2015). The focus of this work is to develop a prototype application technique named nano Electro Application Technique ($nEAT$) to enhance the penetration and consolidation efficiency of a commercialised alcoholic nanolime with the view of improving its performance when applied on a fine-grained compact limestone characterised by a low porosity. This innovative and patent-pending technique entails the application of an electric current applied on a dampened limestone and is based on the evidence that applying an energy to a solid material can modify its surface energy, roughness, and charge density (Pozo-Antonio *et al.,* 2019; Cui and Cui 2015; and Hosseini and Karapanagiotis 2018). nEAT was developed at Sheffield Hallam

---

[1]*C. Maucourant, Researcher, School of Engineering and Built Environment – Sheffield Hallam University, England (UK), c.maucourant@shu.ac.uk

[2] F. O'Flaherty, Professor, School of Engineering and Built Environment – Sheffield Hallam University, England (UK), f.j.oflaherty@shu.ac.uk

*Corresponding author

University and tested in the laboratories on different limestone samples. Based on the process of electrophoresis (i.e. the motion of electrically charged particles under the influence of an electric field), it was assumed that if the penetration of alcoholic nanolime through a damp limestone could be influenced by an induced electric field, the electrical conductivity of the substrate would be one of the main controlling factors. This study presents some of the laboratory experiments realised on Caen limestone and test results obtained with the phenolphthalein and the Drilling Resistance Measurement System. Experimental data showed that a deeper and more homogeneous penetration as well as a higher consolidation efficiency were obtained when dampened samples were subjected to an optimised electric current during the application of the nanolime.

2. Research significance

Limestone has been widely used throughout history for buildings, monuments, and sculptures. To be preserved for future generations, consolidation is often required to restore their strength and improve their durability after years of exposure to harsh climatic environments. One of the treatment options widely adopted by stone conservators is the use of nanolime. However, despite its chemical compatibility, the nanolime struggles to penetrate low-porosity limestone, thus leading in most cases to ineffective consolidation. nEAT is a prototype application technique which offers the possibility to address this issue by increasing both the penetrability and consolidation efficiency of commercialised nanolime. This new stone consolidation technique will be tested in due course worldwide on 8 historical buildings and monuments during an onsite test campaign which will allow its performance to be assessed against different environmental conditions and on different types and conditions of limestone.

3. Materials and methods

3.1 Nanolime dispersion

The commercially available nanolime CaLoSiL® E5 (5 g/L in ethanol) provided by *IBZ Salzchemie GmbH* was used in this work for the consolidation experiments. This alcoholic dispersion is composed of plate-like hexagonal nanoparticles of calcium hydroxide ranging in size between 50 nm and 250 nm (Ziegenbalg *et al.,* 2018). CaLoSiL® E5 is characterised by a density of 0.79 g/cm^3, a dynamic viscosity of 1.3 mPa.s and a zeta potential (i.e. the potential difference existing between the surface of the nanolime particle immersed in ethanol and the bulk of ethanol) of 57.8 mV (Ziegenbalg *et al.,* 2018).

3.2 Limestone samples

Experiments were carried out on ten Caen limestone blocks of prismatic shapes (3 x 3 x 3 cm to 5 x 5 x 5 cm) provided by Canterbury Cathedral (UK). The samples were affected by powdering (Figure 1) and were stored in the laboratory at 20 °C ± 1 °C and 40 % RH ± 5 % before treatment. Observations with Polarised Light Microscopy showed that the Caen limestone used was of clastic sedimentary origin and composed mainly of intraclasts, bioclasts and peloids, bound together by a micrite matrix. The mineralogical composition (determined using X-ray diffraction and fluorescence) revealed that the samples were mainly composed of calcite ($CaCO_3$, ICSD #01-078-4614, # 01-072-4582) with traces (1 % < Wt.%) of Mg, Fe, Al and Si. Mercury Intrusion Porosimetry established that the samples were characterised by a unimodal pore-size distribution ($0.007 \mu m$ – $5 \mu m$) with average porosities from 16 % to 18 %.

Figure 1: Example of Caen limestone sample used in this study.

3.3 nEAT and control treatments

3.3.1 Conditioning of sample

For the first step, the whole sample was dampened with tap water to increase its conductivity, this can be done by spraying or brushing if the surface can endure applied pressure (Figure 2 a & b). It will be noted that this humidification step should be discarded if the building or sculpture is exposed to a damp environment, thus likely to have a high humidity content in its mineral matrix. After humidification, the sample was covered with dampened Japanese tissue layers (2-7 gr/m2) applied by brushing (Figure 2, c & d). Following the conditioning, a thin layer of hydrous Laponite RD® gel in tap water (Figure 2, e) was spread over the Japanese tissue layers covering the whole sample apart from the surface to be consolidated (Figure 2, f), and an aluminum kitchen foil sheet was applied over it (Figure 2, g).

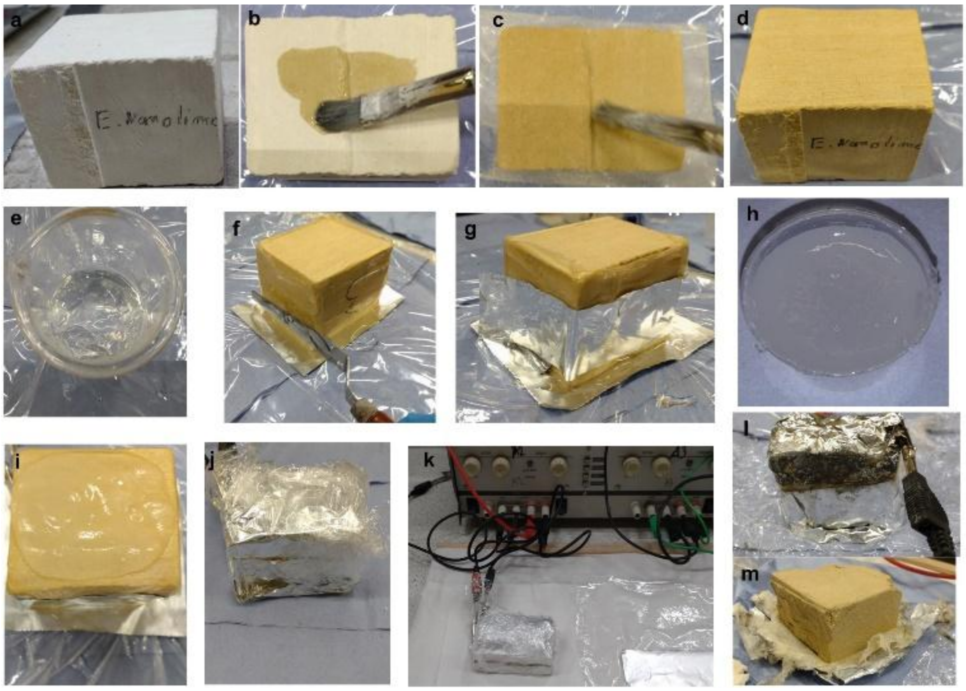


Figure 2: Illustration of the application of the nEAT on a Caen sample: (a) sample before treatment; (b-c) during conditioning by brushing with water and application of dampened Japanese tissue layers and (d) sample after pre-wetting; (e) aqueous Laponite gel (f) applied over the sample with a spatula and (g) sample after application of Laponite and Aluminium kitchen foil applied over it; (h) alcoholic nanolime mixed in Laponite and (i) applied over the surface to be consolidated; (j) sample with treated surface covered with another aluminium sheet and wrapped in Cling® Film; (k) application of power using crocodile cable clipped onto the aluminium foils, and (l & m) sample after treatment with nEAT technique.

This last conditioning step maintains surface conductivity throughout the treatment period, given the fact that the water introduced during the conditioning migrates through the mineral matrix by capillarity, thus reducing the surface conductivity over time.

3.3.2 Application of nanolime

Upon completion of the conditioning, undiluted CaLoSiL® E5 was mixed with Laponite RD® aqueous gel (Figure 2, h) and applied over the dampened Japanese tissue layer covering the surface to be consolidated as shown in Figure 2, i. Laponite was used as a reservoir delivering gradually the nanolime through the treated surface, secondly, as an aqueous gel, it provides a constant humidity level required to make the surface conductive enough to ensure the electrophoresis process, thus the desired motion of the nanolime. Upon the application of the nanolime-based Laponite gel, the treated surface was covered with another sheet of aluminum kitchen foil to maintain electrical conductivity, and the sample was then covered with Cling Film® to prevent the evaporation of moisture (Figure 2, j). In addition to the sample treated with nEAT control sample was also treated with undiluted CaLoSiL® E5 until surface refusal following the application procedure as advised by the literature.

3.3.3 Application of power and curing

The final step of the technique is the application of power; in this case it was delivered by a *Thurlby Thandar Instrument PL320QMD* DC laboratory power supply. Referring to Figure 2, k, electrodes were plugged onto the aluminium foils with crocodile clips and cables, the anode (-) being attached onto the aluminium foil covering the treated surface and the cathode (+), being attached to the foil covering the rest of the sample. During the treatment, the power settings were adjusted to ensure the optimal electrical conductivity (σ), which is for a given voltage, the highest current level delivered by the power supply and flowing between the electrodes. It will be noted that Direct Current was preferred to Alternating Current (AC) because the former generates a unidirectional flow of electrons which should favour the migration of the nanolime from the treated surface to the core of the stone sample.

However, it should be noted that because of the reduction-oxidation reactions happening at the electrodes [Vasudevan *et al.,* 2010] during the treatment, the top and bottom surfaces of the sample become more alkaline and acidic, respectively. Therefore, alkaline corrosion occurs at the cathode due to the increase in alkalinity, thus promoting the formation of aluminium corrosion products which are transferred and trapped over the Japanese tissue layers, which in this case, are acting as protective layers (Figure 2, l). Upon treatments with nEAT, none of the samples were discoloured or affected by transfer of aluminium corrosion products (Figure 2, m).

At the end of the treatment (i.e. until the electrical conductivity was reduced to its minimum), the power was switched off and all the materials used in the application process were removed (i.e. the aluminium foils, Japanese tissue layers, and the laponite-nanolime gel). Then, to accelerate the carbonation of the nanolime, the treated samples were stored in a curing chamber for at least two months at RH at 70 % (± 5 %) and air temperature and CO_2 levels at 20 °C (±1 °C) and around 500 ppm, respectively.

3.4 Assessment of $nEAT$ efficiency

At the end of the treatment period, samples treated with nEAT were split apart with a chisel and tested by means of phenolphthalein GPR^{TM} (1 % W/V diluted in 60 % of ethanol and 40 % of H_2O) which was pipetted over the cross-sections to assess the penetration of the nanolime. Control samples which were also dampened (by spraying water over the treated surface) and wrapped with Cling Film$^{®}$ after the application of the nanolime, were tested by means of phenolphthalein at the same time. The mechanical properties of the Caen limestone used in this project were determined before and after the application of the treatment. Two months after treatments, all the treated samples (nEAT and Controls) were tested by means of a Drilling Resistance Measurement System (DRMS) from SINT-Technology, to assess their drilling resistance profiles.

The DRMS measures the drilling force Fd (N) required to drill a hole at constant rotational speed (ω in rpm) and a lateral feed rate (v in mm/min). Common technical features characterising the DRMS apparatus used in this study are the following: ω ranging from $20-1000$ rpm, v ranging from $1-80$ mm/min; specialist flat-tip drill bit supplied by the manufacturers (made of diamond cutters attached to a tungsten-carbide bed and bonded to a steel drill rod) with diameters of $3-10$ mm; maximum load cell of 100 N, and Force Threshold of one Newton. In this work, DRMS tests were conducted with a drill bit of 5 mm Ø, ω of 600 rpm, v of 3 mm/min, and a drilling depth of 20 mm. Drilling resistance values were calculated as a mean of six tests carried out on each sample.

4. Results and discussion

4.1 Phenolphthalein tests

The phenolphthalein tests show that the use of an applied voltage during the application of alcoholic nanolime greatly improves its penetration into the limestone (Table 1). Results show that a sample treated with the nEAT exhibits a deeper penetration of the nanolime which reaches a depth of about 2 cm to 4 cm, in comparison to the Control sample where almost no penetration of the nanolime is observed.

4.2 DRMS tests

DRMS results presented in Table 2 show that in addition to increasing the nanolime penetration, nEAT improves the consolidation performance too. Indeed, the comparison of data obtained before and after treatment reveals that in this case, one application of nEAT was sufficient to increase the drilling resistance F_d by $\sim$ 54 %. Conversely, Control sample (treated with the nanolime applied by brushing) show a limited increase of the drilling resistance with an average force of about 1.44 N ($\pm$ 0.18 N), which is a marginal increase in the as-received drilling resistance of 1.39 N or about 3.60 %. Drilling resistance profiles shown in Table 2 confirmed the phenolphthalein results which show that nEAT improved the nanolime performance in-depth. Indeed, in comparison with the Control and as-received (before treatment) samples, the sample treated with nEAT show a drilling resistance profile which is characterised by a higher and constant drilling resistance over the tested depth.

Table 1: Examples of phenolphthalein results obtained for sample treated with $nEAT$ and Control treatments.

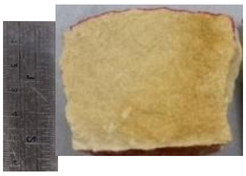
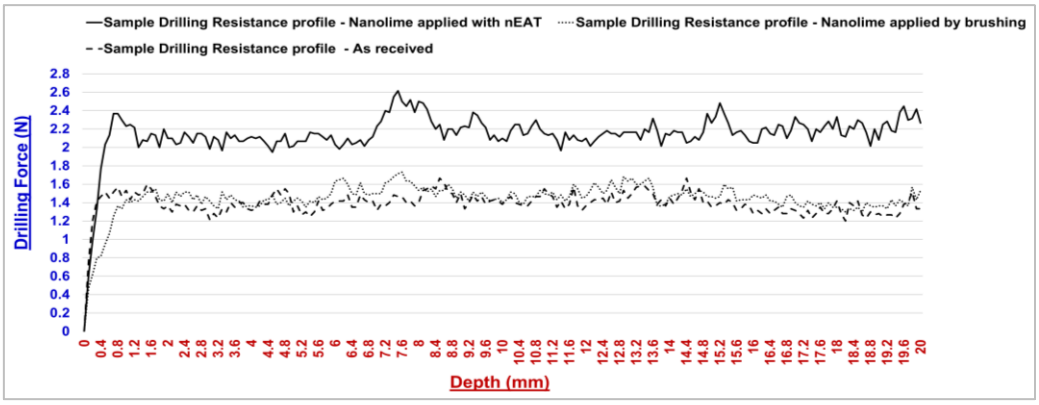
Samples ID	Type/condition	Treatment details	Phenolphthalein results
nEAT	Caen limestone Powdering	One application of CaLoSiL® E5 (8 ml) mixed in laponite gel (3 % W/V in H_2O) and applied with $nEAT$	
Control	Caen limestone Powdering	One application of CaLoSiL® E5 (8 ml) applied by brushing over the surface	

Table 2: Examples of DRMS results obtained for samples treated with $nEAT$ and Control treatments.

Samples ID	Average F_d (N)	Average F_d (N) as-received
$nEAT$	2.14 (± 0.25)	1.39 N (± 0.14 N)
Control	1.44 (± 0.18)	



5. Conclusions

5.1 Summary of findings

An innovative way to improve the performance of alcoholic commercialised nanolime by the action of an applied voltage has been investigated. The prototype technique named nEAT and developed in the laboratory at Sheffield Hallam University, proved to be effective in increasing both the penetration of the nanolime and its consolidation efficiency, when applied on a fine-grained compact Caen limestone characterised by a low porosity (Φ <20 %). The effectiveness of nEAT is due to a synergetic action involving the interaction of the following factors: **(1)** The action of an applied electric field on a wet limestone matrix generates electrophoresis and electrowetting phenomena which together affect the wetting properties of the surface of the treated sample, thus the migration process of the nanolime through the limestone; **(2)** The redox reactions happening at the electrodes during the treatment application increase the exchange of surface charges and develop alkaline corrosion of the aluminium kitchen foil present at the cathode. Therefore, changes are also evident on the conductivity of the limestone sample favoured by the deprotonation/protonation of basic surface group (from the nanolime), the preferential dissolution of ions (i.e. Ca^{2+}, CO_3^{2-} and HCO_3^-) from the carbonated crystal lattice, the differential adsorption of ionic species (H^+ and OH^-) from the electrolytes (i.e. nanolime and water present at the surface and in the porous matrix of the sample); **(3)** The induced Faradaic current generated nearby the electrodes during the electrowetting process favours the penetration of electrically charged nanolime particles through the wet stone matrix. **(4)** The variation of pH at the interface solid liquid during the electrolysis cause a preferential ionic absorption of the nanolime, thus its migration through the electrically charged sample matrix.

5.2 Synopsis of new concept and innovation

nEAT developed in this project is easy to implement and requires only the use of basic materials such as a DC power supply, kitchen aluminium foil, and conservation resources (i.e. nanolime and laponite gel). The effectiveness of the proposed technique relies on the electrical conductivity of the limestone sample treated. Upon completion of the treatment, the nanolime shows an impressive penetration of about 2 to 3 cm in-depth. According to the literature, it is believed that to date, no other known stone consolidation application technique can increase the penetration of alcoholic nanolime to such extent on fine-grained compact limestones characterised by open porosities lower than 20%.

5.3 Statement of future work

Further experiments are currently being planned in the laboratories to establish the performance of the new technique on different limestones of varied size, condition, and mineral compositions. nEAT will also be applied in various environmental conditions to assess its performance against freeze-thaw and salts weathering phenomena. Finally, during pilot projects to be scheduled in due course, the technique will be applied in real environmental conditions and its long-term performance assessed using non-destructive techniques, this to establish its reliability and efficiency for built heritage conservation.

References

Arizzi, A., Gomez-Villalba, L, S., Lopez-Arce, P., Cultrone, G., and Fort, R., 2015. Lime mortar consolidation with nano-structured calcium hydroxide dispersions: the efficacy of different consolidation products for Heritage conservation, European Journal of Mineralogy, 27 (3), 311-323.

Baglioni, P., Chelazzi, P., Giorgi Rodorico., (2015), Nanotechnologies in the Conservation of Cultural Heritage, Springer, Dordrecht, ISBN 978-94-017-9302-5, 144pp.

Borsoi, G., Lubelli, B., van Hees, R., Veiga, R., Silva Santos, A., Colla, L., Fedele, L., Tomasin, P., 2016a, Effect of solvent on nanolime transport within limestone: How to improve in-depth deposition, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 497, 171-181

Borsoi, G., Lubelli, B., van Hees, R., Veiga, R., and Silva Santos, A., 2016b, Application Protocol for the Consolidation of Calcareous Substrates by the Use of Nanolimes: From Laboratory Research to Practice, Construction and Building Materials, aop, 1-11.

Camerini, R., Poggi, G., Chelazzi, D., Ridi, F., Giorgi, R. and Baglioni, P., 2019, The carbonation kinetics of calcium hydroxide nanoparticles: A Boundary Nucleation and Growth Description, Journal of Colloidal and Interface Science, 547, 370-381.

Cui, J and Cui, Y., 2015, Effect of Surface Wettability and Roughness on the Heat Transfer Performance of Fluid Flowing through Microchannels, Energies, 8, 5704-5724.

Hosseini, M and Karapanagiotis, I., (2018), Advanced Materials for the Conservation of Stone, Springer Nature, Switzerland, ISBN 978-3-319-89163-7, 332pp.

López-Arce, P., Gómez-Villalba, L.S., Martínez-Ramírez, S., Álvarez de Buergo, M and Fort, R., 2011. Influence of relative humidity on the carbonation of calcium hydroxide nanoparticles and the formation of calcium carbonate polymorphs, Powder Technology, 205, 263-269.

Otero, J., Charola, A. E., Grissom, C. A., and Starinieri, V., 2017, An Overview of nanolime as consolidation method for calcareous substrates, Ge-Conservation, 1(11), 71-78.

Otero, J., Starinieri, V and Charola, A. E., 2019, Influence of substrate pore structure and nanolime particle size on the effectiveness of nanolime treatments., Construction and Building Materials, 209, 701-708.

Pozo-Antonio, J.S., Otero, J., Alonso, P and Mas I Barbera, X., 2019, Nanolimes and nanosilica-based consolidants applied on heated granite and limestone: effectiveness and durability, Construction and Building Materials, 201, 852-870.

Vasudevan, S., Suresh Kannan, B., Lakshmi, J., Mohanraj, S., and Sozhan, G., 2010, Effects of alternating and direct current in electrocoagulation process on the removal of fluoride from water, Journal of Chemical Technology Biotechnology, 86, 428-436.

Ziegenbalg, G., Dietze, C., and Ziegenbalg, G., 2018. Fundamentals of Nanolime, in Nanomaterials in Architecture and Art Conservation, Ziegenbalg, G., Drdácký, M., Dietze, C., and Schuch, D, Pan Stanford Publishing, Singapore, ISBN 9780429428753, pp. 131-166.