

1 **A nonlinear multi-proxy model based on manifold learning to**  
2 **reconstruct water temperature from high resolution trace**  
3 **element profiles in biogenic carbonates.**

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14  
15 **Abstract**

16 A long standing problem in paleoceanography concerns the reconstruction of water temperature  
17 from  $\delta^{18}\text{O}$  carbonate, which is problematic in the case of freshwater influenced environments  
18 because the  $\delta^{18}\text{O}$  isotopic composition of the ambient water (related to salinity) needs to be  
19 known. In this paper we argue for the use of a nonlinear multi-proxy method called Weight  
20 Determination by Manifold Regularization to develop a temperature reconstruction model that is  
21 less sensitive to salinity variations. The motivation for using this type of model is twofold:  
22 Firstly, observed nonlinear relations between specific proxies and water temperature motivate the  
23 use of nonlinear models. Secondly, the use of multi-proxy models enables salinity related  
24 variations of a given temperature proxy to be explained by salinity-related information carried by  
25 a separate proxy. Our findings confirm that Mg/Ca is a powerful paleothermometer and highlight  
26 that reconstruction performance based on this proxy is improved significantly by combining its

1 information with the information for other trace elements in multi-proxy models. Although the  
2 models presented here are black-box models that do not use any prior knowledge about the  
3 proxies, the comparison of model reconstruction performances based on different proxy  
4 combinations do yield useful information about proxy characteristics. Using Mg/Ca, Sr/Ca,  
5 Ba/Ca and Pb/Ca the WDMR model enables a temperature reconstruction with a root mean  
6 squared error of  $\pm 2.19^{\circ}\text{C}$  for a salinity range between 15 and 32.

7 **Keywords:**

8 Sclerochronology, Temperature reconstruction, Multi-proxy, Trace elements, Bivalves, Manifold  
9 learning

10  
11 **1 Introduction**

12 To improve our understanding of global change and assess human impact on global warming,  
13 reconstructions of past temperatures are essential. Such reconstructions are mostly based on the  
14 analysis of trace elements and isotopes in accreting biogenic or abiogenic substrates, called  
15 archives. The choice of the parameters (called proxies) to be analysed is based on prior  
16 knowledge of their relationship with an environmental variable as derived by observing such  
17 relationship in the present-day situation (Kucera et al., 2005). Several natural archives in the  
18 terrestrial and the marine environment record environmental information in their trace element  
19 and isotope profiles. Bivalve shells, in particular, represent a suitable archive for reconstructing  
20 seasonal and long term variations of ambient water conditions and many elemental and isotopic  
21 temperature proxies have been proposed and discussed for these archives (e.g., Epstein et al.,  
22 1953a, b; Klein et al., 1996a, b; Wanamaker et al., 2006; Freitas et al., 2009). Indeed, bivalves  
23 are sensitive to environmental conditions, have a global distribution, and are commonly found in  
24 archaeological sites (Pearce and Mann 2006; Klunder et al. 2008; Butler et al. 2009). Bivalve  
25 shells thus offer the potential for reconstructing environmental conditions for a wide variety of  
26 aquatic environments, including fresh water systems (Versteegh, 2009), estuarine and marine  
27 environments from tropical (Aubert et al., 2009) to cold polar regions (Tada et al., 2006).

1 These and other studies reveal that though a given proxy may correlate well with an  
2 environmental parameter, the data usually show significant variation around the regression line,  
3 reflecting that the process of proxy-incorporation is much more complex than assumed originally  
4 (Wanamaker et al., 2007; Gillikin et al., 2005).

5  
6 Most water temperature reconstructions based on biogenic carbonates are based on  $\delta^{18}\text{O}$  records.  
7 For instance, for the common blue mussel (*Mytilus edulis*; the species studied in this paper) it  
8 has been shown that temperature reconstructions from shell  $\delta^{18}\text{O}$  records can achieve an  
9 excellent accuracy of 0.57°C in Root Mean Squared Error (RMSE) (Wanamaker et al., 2007).  
10 However, this paleothermometer equation requires that the  $\delta^{18}\text{O}$  value of the ambient water be  
11 known. This is obviously not possible for archeological specimens and given that the  $\delta^{18}\text{O}$  value  
12 of the ambient water strongly depends on salinity (a salinity variation of 1 can incorrectly be  
13 interpreted as a change of 1°C in water temperature), a proxy or model which is less sensitive to  
14 salinity variations may therefore significantly improve paleotemperature reconstructions (Faure,  
15 1986).

16  
17 Several alternative (salinity-robust) temperature proxies have been proposed (e.g., Mg/Ca-ratios,  
18 Klein et al., 1996b; Sr/Ca ratios, Foster et al., 2009). However, proxies mostly appear influenced  
19 by several environmental parameters (e.g. Elliot et al. 2009, Foster et al. 2009). Moreover, the  
20 fact that these potential temperature proxies are recorded in biogenic material, makes them  
21 subject to physiology-related biases such as kinetic effects (Lorrain et al., 2005), metabolic  
22 effects (Strasser et al., 2008) and ontogenetic effects (Elliot et al., 2009). It becomes more and  
23 more clear that biomineralisation is a complex process, whose adequate study ideally requires the  
24 involvement of several disciplines (Weiner and Dove 2003).

25  
26 In the present paper we investigate whether more complex, non-linear models are better suited  
27 for describing the integrated impact of environmental conditions, physiological state of the  
28 organism and a complex suit of biochemical and chemical processes, on proxy incorporation  
29 during bivalve shell growth. We propose to combine a suit of proxies, differentially influenced

1 by environmental and biological controls, into a multi-proxy model. Multi-proxy models offer  
2 the advantage that variation in the different proxies yields information that is useful to resolve  
3 environmental and biological interferences. The proposed multi-proxy model combines  
4 information on elemental ratios (in this case Mg/Ca, Sr/Ca, Ba/Ca and Pb/Ca) based on the two  
5 general (statistical) assumptions: (i) the proxies are influenced by the same environmental and  
6 intrinsic parameters, and therefore combining them may help explaining variation that was not  
7 understood before; (ii) the proxies are likely influenced to different degrees by temperature  
8 variation and, therefore, using temperature information derived from each of the proxies will  
9 yield more robust temperature reconstructions.

10  
11 The models presented in this paper are not based on a mechanistic understanding of the  
12 incorporation mechanisms of the proxies. However, along this paper it becomes clear that the  
13 studied proxies do not contribute equally to the final temperature reconstructions. The  
14 contribution of each proxy was calculated, though, from the temperature reconstruction  
15 performances of different proxy combinations.

## 16 **1.1 Why multi-proxy models?**

17 As mentioned in the introduction two reasons can be invoked for promoting the use of multi-  
18 proxy models:

19 The first and most important reason (i, above) is synthesized by the set of equations (1),  
20 representing a linear multiple regression model with a limited number of parameters. These  
21 equations express how a number of environmental parameters (e.g., temperature, salinity,  
22 chlorophyll concentration, etc.) all contribute to the final trace element signature of the archive.  
23 Solving this set of equations for the environmental parameters involves a new set of equations in  
24 which all environmental parameters can be described by multi-proxy equations, implying that all  
25 proxies add some information to the final paleo-temperature equation. For example: by  
26 combining an element that is mainly influenced by salinity with another element influenced by  
27 both, temperature and salinity, it is possible to construct a model that is more robust across a  
28 range of salinities.

1

$$2 \left\{ \begin{array}{l} Mg = a_1.Temp + a_2.Sal + a_3.chla + \dots + C_a \\ Sr = b_1.Temp + b_2.Sal + b_3.chla + \dots + C_b \\ Ba = c_1.Temp + c_2.Sal + c_3.chla + \dots + C_c \\ \dots \end{array} \right\} \Leftrightarrow \left\{ \begin{array}{l} Temp = \alpha_1.Mg + \alpha_2.Sr + \alpha_3.Ba + \dots + C_\alpha \\ Sal = \beta_1.Mg + \beta_2.Sr + \beta_3.Ba + \dots + C_\beta \\ chla = \gamma_1.Mg + \gamma_2.Sr + \gamma_3.Ba + \dots + C_\gamma \\ \dots \end{array} \right\} (1)$$

3

4 Though equations (1) as shown include only environmental parameters (Temp., Sal.,  
5 Chlorophyll) it is clear that other, organism-related parameters such as shell growth, spawning  
6 events, metabolic activity, etc.... may be included as well. Such multi-proxy equations would  
7 resolve part of the ‘vital effect’ commonly invoked to explain a chemical response that is not  
8 understood.

9 Note that solving a non-linear model with a large number of parameters is much more complex,  
10 but the idea behind it would be the same. Although it is algebraically possible to reverse such  
11 multiple regression equations when there are as many proxies as environmental parameters, this  
12 would induce large errors on the estimated parameters. Therefore the multi-proxy models  
13 obtained in this paper are considered as black-box models that cannot be reversed to obtain a  
14 mechanistic understanding in the proxy incorporation.

15 (ii) A second drive for using multi-proxy models is rather intuitive. Assuming that different  
16 proxies each carry some temperature information it seems reasonable that a model based on the  
17 information of several proxies will yield more robust and accurate reconstructions, though this  
18 requires proper weighing of each proxy. The weight given to a proxy depends on the quality of  
19 the proxy environmental relationship in the calibration or training set and less importance is  
20 given to proxies that show a less clear or noisy relationship with the environmental condition  
21 (temperature). Noise may result from the large influence of an additional environmental or  
22 biological condition or from measurement uncertainty. This means that proxies that have a large  
23 load of environmental information have the largest influence on the final reconstruction, even  
24 though other proxies are used to explain or confirm parts of the signal.

25 Despite these clear advantages, applications of multi-proxy models are scarce in bivalve  
26 sclerochronology literature. Some steps in this direction are made by Klein et al. (1996b) and

1 Schöne et al. (2006), though these authors rather use a secondary proxy to confirm a signal that  
2 is revealed by a primary proxy. Gentry et al. (2009) and Bice et al. (2006) discuss two  
3 approaches in which the influence of salinity on  $\delta^{18}\text{O}_{\text{carbonate}}$  is eliminated by formulating an  
4 initial guess of the  $\delta^{18}\text{O}_{\text{water}}$  using information from a secondary proxy. However, to the best of  
5 our knowledge multi-proxy models in which a given environmental parameter is described by a  
6 combination of several proxies have not been published yet, one exception being the work of  
7 Freitas et al. (2006) who demonstrate that a linear multiple regression analysis using Sr and Mg,  
8 significantly improves temperature estimates.

## 9 **1.2 Why nonlinear multi-proxy models?**

10 Considering that physiological processes are nonlinearly influenced by environmental  
11 conditions, as is the case for instance for temperature, plankton blooms (Cloern et al., 1995),  
12 optimal feeding temperature (Yukihira et al., 2000), the occurrence of nonlinear relationships  
13 between proxies and environmental conditions does not come as a surprise. Figure 2 shows an  
14 example of a substantially nonlinear relationship between bivalve shell proxies and water  
15 temperature (Vander Putten et al., 2000), highlighting a direct but complex influence of  
16 temperature on trace element uptake. However, such relationships have been traditionally  
17 described using linear equations (Klein et al., 1996b; Wanamaker et al., 2008), though some  
18 recent publications describe or advocate the use of inverse exponentials (Clarke et al., 2009),  
19 exponentials (Freitas et al., 2005) and even dynamical (Klunder et al., 2008) relationships.

20 Nonlinear relationships between proxies and environmental conditions are difficult to describe in  
21 a single mathematical equation but they can be modeled by several modern multivariate  
22 statistical techniques (Izenman, 2008). Most scientists are familiar with the classical linear  
23 multiple regression and dimensionality reduction methods, such as Principle Component  
24 Analysis (PCA), Cluster Analysis, etc. These methods, however, are developed to detect linear  
25 relationships and are not applicable to datasets that behave substantially nonlinear. To detect  
26 nonlinear relationships in a multi-dimensional space, recently developed multivariate statistical  
27 tools are needed (Izenman, 2008). The best known nonlinear multivariate statistical techniques  
28 in paleoclimatology are Artificial Neural Networks which are being used for reconstructing  
29 ENSO events from coral records (Juillet-Leclerc et al., 2006) and in dendrochronology to

1 reconstruct precipitation rates (Woodhouse, 1999) and temperature (Guiot et al., 2005).  
2 However, other techniques such as Support Vector Machines and Manifold Learning can be used  
3 for the same purpose (Bauwens et al., 2010).

4

5 Different nonlinear multivariate statistical techniques are thus available to analyze  
6 multidimensional datasets, but the choice of a specific technique will depend on characteristics  
7 of the dataset such as number of data, intrinsic variance, smoothness, periodicity. As a  
8 consequence, each dataset has its own 'best method'. Bauwens et al. (2010) compared three  
9 nonlinear multiple regression methods: Two of the three nonlinear regression methods explored  
10 in that paper reduce the multi-proxy problem into a single dimensional problem by observing  
11 that the proxies lie on a one-dimensional manifold. One of the two is based on intuition and  
12 tailored for temperature reconstruction using bivalve shells. The other is a new system  
13 identification approach, *Weight Determination by Manifold Learning* (WDMR), and based on  
14 *manifold learning*. The third approach, *Support Vector Regression* (SVR), does not rely on an  
15 assumption of a manifold in the proxy space; it rather increases the dimensionality of the  
16 problem by creating 'new proxies' from nonlinear combinations of the original proxy data. In  
17 Bauwens et al. (2010) it is concluded that manifold based methods are the most powerful tools  
18 for reconstructing paleo-environmental conditions based on proxy records in shells of short-lived  
19 bivalves, suggesting that the proxy-environmental relationships are straightforward and no extra  
20 information is gained by using a more complex SVR model.

21 In the present paper we use the manifold based method called Weight Determination Manifold  
22 Regularization (WDMR) (Ohlsson et al., 2008; Ohlsson H. and L., 2009; Ohlsson et al., 2009) to  
23 build a salinity-robust model for reconstructing temperature using shells of the common blue  
24 mussel *Mytilus edulis*.

25

## 1   **2   Data**

### 2   **2.1   Raw data**

3   The trace element datasets used in this paper were originally published by Vander Putten et al.  
4   (2000) and Gillikin et al. (2006a; 2006b). Both datasets consist of spatially well resolved  
5   measurements of Mg/Ca, Sr/Ca, Ba/Ca and Pb/Ca ratios along the shell's main growth axis for  
6   approximately two years old *M. edulis* specimens. For both studies laser ablation craters (from  
7   LA-ICP-MS analyses) were produced in the calcitic layer of the shell. The ablation craters were  
8   approximately 50 µm in diameter and were spaced every 250 µm. For each shell 45 to 65  
9   ablations were performed over the shell section that grew during the period of monitoring. All  
10   specimens were sampled in the Scheldt Estuary (The Netherlands, Belgium); the exact  
11   geographical position of the four study sites is shown in Figure 1. The reader interested in more  
12   details about these data sets is referred to the papers by Vander Putten et al. (2000) and Gillikin  
13   et al., (2006a; 2006b).

14

15   The Gillikin et al. dataset consists of proxy profiles for a single shell sampled at the Knokke site  
16   and monitored from February to September 2002. Since the blue mussel stops growing when  
17   temperature drops below 8°C (usually in autumn; Gillikin et al., 2009), the analyzed Feb. to  
18   Sept. period closely corresponds to a complete growth season. The Vander Putten et al. data set  
19   concerns seven blue mussel shells from Terneuzen, four shells from Ossensisse and four shells  
20   from Breskens (Figure 1 and Figure 3). These data cover the period from April to June 1996, and  
21   do not cover the full growth season of the mussel, though it includes the spring period when shell  
22   accretion is fastest and variations in trace element concentrations largest. The total dataset covers  
23   a salinity range from 15 to 31 and a temperature range from 6.8°C to 18.6°C for 1996 and from  
24   8.7 °C to 19.3°C for 2002.



## 1 2.2 Data preprocessing

### 2 2.2.1 Linking proxy data to environmental information

3 The proxies were measured along the largest growth axis (i.e., along a distance scale) starting at  
4 the margin of the shell moving towards the umbo. Since temperature measurements are obtained  
5 on a time scale, linking proxy data to environmental information is not straightforward. For both  
6 data sets the link between spatial and temporal scales was established using the anchor point-  
7 method (Paillard et al., 1996), implying that between anchor points, growth is assumed linear.  
8 The anchor points for the Vander Putten et al. shells were  $T_0$  (marking on the shell),  $T_{\text{final}}$  (date of  
9 collection) and recognizable patterns in trace-elemental chemistry, such as a conspicuous Ba-  
10 peak associated with the spring bloom. The anchor points for the Gillikin dataset were obtained  
11 from pattern similarities between the  $\delta^{18}\text{O}$  profile of shell carbonate and the water temperature  
12 profile monitored at the study site. The assumption of subsequent linear growth events, however,  
13 is an approximation since shell growth is variable (Schöne et al., 2005). Other methods to  
14 reconstruct the shell growth, as reviewed in de Brauwere et al. (2008), could not be applied to the  
15 datasets used in the present study, since these methods are designed for periodic signals and are  
16 not applicable to records covering only a single season, as is the case here.

### 17 2.2.2 Normalized data

18 Proxy signals in different specimens from the same species sampled at the same location are  
19 often similar but seldom identical. Since environmental variability is unlikely over the small  
20 spatial scale of a mussel bank, the variation can be seen as an intrinsic and unexplained variation  
21 that we shall call ‘noise’. Besides noise, site- and year- specific variation can occur. By  
22 normalizing the data the reconstructed environmental parameter will become dependent on the  
23 overall shape of the proxy record. Normalization was done by dividing the data by the standard  
24 deviation and subtracting the mean. This offers the advantage of the data becoming less sensitive  
25 to site and year specific variability as well as concentration shifts [see Figure 3; and also Stecher  
26 et al., 1996; Gillikin et al., 2008)] since these effects will be filtered out. The disadvantages,  
27 however, are that (1) some potential useful information may be lost and (2) temperature  
28 reconstructions are not possible from individual measurements since the model extracts its  
29 information out of the overall shape of the proxy record, and not out of discrete data.

### 1 2.2.3 Training and validation data

2 The data were divided into two parts: a training dataset consisting of 6 shells from the Terneuzen  
3 site in the Scheldt Estuary and a validation dataset consisting of shells from all 4 sites along the  
4 Scheldt Estuary, i.e., one shell from Knokke sampled in 2002, four shells from Breskens, one  
5 shell from Terneuzen and four shells from Ossensisse, all sampled in 1996 (Figures 1 and 3). The  
6 fact that the Knokke specimen is from a different year than the other shells provides the  
7 possibility to check whether the model is sensitive to year to year variability. The training dataset  
8 was used to construct a model and the validation dataset to evaluate the computed model's  
9 performance.

10

## 11 3 The methods

### 12 3.1 Linear multiple regression

13 Linear multiple regression is the most commonly used multivariate model to describe the linear  
14 relationship between two or more explanatory variables (here proxies) and a response variable  
15 (here temperature). This is done by fitting a linear equation to observed data. An equation similar  
16 to the equations in equation 1 describes how temperature co-varies with the proxies. A limited  
17 number of parameters  $\alpha_1, \alpha_2, \dots, \alpha_n$  define the slope of the regression line and a coefficient  $C$   
18 defines the offset.

19 The main advantages of linear multiple regressions are that appropriate toolboxes are available  
20 on all statistical software packages and that models have a limited number of parameters and  
21 model outputs which renders interpretation easier. A large disadvantage, however, is that linear  
22 models are not able to fit nonlinear relationships which are likely to occur in biogenic archives.

### 23 3.2 Weight Determination by Manifold Regularization (WDMR)

24 The mathematical details of the method called Weight Determination by Manifold  
25 Regularization (WDMR) are beyond the scope of the present paper and the interested reader is  
26 referred to (Ohlsson et al., 2008; Ohlsson et al., 2009). Interested users can also download a

1 Matlab WDMR toolbox that is added as supplementary material to this paper, although we  
2 recommend contacting the corresponding author to ensure correct use of the WDMR toolbox.

3 In the following we briefly describe the concept of the WDMR approach. Manifold learning is an  
4 umbrella term for algorithms or methods for describing low-dimensional structures in data. A  
5 manifold can be defined as a low-dimensional structure which underlies a collection of high  
6 dimensional data, for example a curve in the space of Mg, Sr, Ba and Pb concentrations. An  
7 algorithm that builds on concepts from manifold learning is the nonlinear semi-supervised  
8 regression method called Weight Determination by Manifold Regularization (WDMR) (Ohlsson  
9 et al., 2008). WDMR, like a manifold learning algorithm, finds descriptions of manifolds but  
10 unlike most manifold learning methods WDMR can utilize a training set for the description. If  
11 the temperature associated with a specific measurement of Mg, Sr, Ba and Pb in the training set  
12 is known, that information can be used in WDMR to impose a one-dimensional description of  
13 the curve imitating the temperature. In the case that proxy composition are controlled solely by  
14 water temperature, concentrations of Mg, Sr, Ba and Pb would be restricted to a one-dimensional  
15 curve in the four-dimensional measurement space with each position on the curve having a  
16 temperature value associated with it. As a result the curve can be parameterized by the water  
17 temperature. The computed WDMR-model can then be used to estimate the water temperature  
18 for any other dataset of Mg, Sr, Ba and Pb. As in all real-world problems there is of course noise  
19 associated with the measurements. **And more importantly, it is unlikely that the concentrations of**  
20 **Mg, Sr, Ba and Pb will only depend on water temperature. Rather, they will depend also on other**  
21 **conditions such as salinity, food availability, shell growth or metabolism) and therefore the data**  
22 **will scatter around a one-dimensional curve in the Mg, Sr, Ba and Pb space.**

23 The assumption of a one-dimensional manifold is therefore only an approximation, but the  
24 performance of the computed model shows that this approximation is appropriate.

25

## 1 **4 Comparing linear multiple regression to WDMR**

### 2 **4.1 Method**

3 To investigate the benefit of using nonlinear methods rather than linear methods we compared  
4 the reconstruction performance of models generated using WDMR with models obtained by  
5 classical linear multiple regression. Six shells from Terneuzen were used to train both the linear  
6 model and the WDMR model. The linear multiple regression analysis where don on not  
7 normalized data, since these analysis are traditionally done on raw data. The model performances  
8 were calculated for the four validation sets consisting of shells from the 4 study sites, including  
9 one additional shell from the training site (see Figure 1).

10 To calculate the model performance the Root Mean Squared Error (RMSE) between measured  
11 and reconstructed temperatures for each data point was used. The reconstructed temperatures for  
12 the nonlinear WDMR model and the linear multiple regression model were compared and the  
13 differences between their RMSE used to verify whether some proxy combinations benefited  
14 more than others from the nonlinear model.

### 15 **4.2 Results**

16 The RMSE are smaller for the WDMR than for the linear approaches . The nonlinear WDMR  
17 model results in a better reconstruction of the seasonal temperature pattern for the Knokke site,  
18 as shown in Figure 4. Also for the three other sites and for most proxy combinations the  
19 nonlinear WDMR model performs better than the linear multiple regression models in RMSE-  
20 sense (Figure 5). This is true, in particular for the temperature reconstructions at Terneuzen and  
21 Knokke where only the Sr-only and the combined SrPb proxies do better with a linear model.  
22 The reconstruction performance of the nonlinear WDMR model is up to 1.5 °C better than the  
23 one for the linear model. Furthermore, the performance of nonlinear models is increasing when  
24 more proxies are included. This result confirms that relationships between a proxy and the  
25 controlling environmental condition can indeed be nonlinear. However, the weaker  
26 reconstruction performances of the nonlinear model for the Breskens and Ossensisse sites indicate  
27 that the nonlinear model over-fits the training data for some proxy combinations, such that in  
28 these cases linear models result in better reconstruction (Figure 6). This is in particular true for

1 Ba at the Breskens site, showing a distinct site-specific behavior which results in the linear  
2 model performing better.

### 3 **4.3 Discussion**

4 For most proxy combinations Figure 4 clearly shows for the Knokke site that the nonlinear  
5 WDMR model results in more accurate temperature reconstructions than the linear multiple  
6 regressions. The reconstruction performance of the nonlinear model is up to 1.5°C better than for  
7 the linear model. However, Figure 5 also shows that some proxy combinations do not benefit  
8 from the nonlinear model. A linear model is less sensitive to model errors related to over-fitting.  
9 The temperature reconstructions from the Breskens shell, for instance, are improved when using  
10 a linear model based on proxy combinations containing Ba information. The site specificity of  
11 Ba that can be observed in Figures 3 and 5 is discussed later in ‘section 5.2.3 Barium’. Several  
12 relationships between proxy and environmental control factors reported in literature, behave  
13 linearly (Wanamaker et al., 2008; Carre et al., 2006) and in these cases a linear model with a  
14 lower number of parameters is still preferable. However, this should not be a reason for not using  
15 nonlinear methods since nonlinear methods can fit linear data, while nonlinear data cannot be  
16 described by linear regression methods: a linear model is, generally spoken, a special case of a  
17 nonlinear one. So, by applying a model selection criterion, the optimal model complexity could  
18 be selected.

19

## 20 **5 Evaluation of proxy combinations**

### 21 **5.1 Method**

22 To investigate the benefit of a multi-proxy approach using the WDMR method and to examine  
23 the contribution of the different proxies, different models were constructed based on a limited  
24 number of proxies. In total 15 combinations of proxies were investigated. The RMSE values  
25 obtained on the validation data were used to quantify the model performances. For the nonlinear  
26 models seven unique contribution factors were defined in order to quantify the contribution of  
27 each proxy. Every contribution factor quantifies how much a specific proxy contributes to a

1 specific model; in other words the contribution factor informs on how much the RMSE decreases  
2 by including the information of the investigated proxy into a specific model. For example one of  
3 the seven contribution factors for Mg is 1.62. This means that the RMSE of a MgSr model was  
4 1.62 lower than the RMSE of a Sr-only model. Negative contribution factors, on the other hand,  
5 reflect that including a specific proxy in the model has a negative influence the on model  
6 reconstruction performance. All contribution factors are defined as the difference between the  
7 RMSE between two model configurations (i.e. models run with different combinations of  
8 elemental ratios) (Table 1). This enables evaluating model performance change due to inclusion  
9 of additional proxies. All trace element combinations were tested for their robustness to salinity  
10 by using the different models to reconstruct the temperature based on the validation shells from  
11 the four sites along the estuarine salinity gradient.

## 12 **5.2 Results**

13 Figure 6 demonstrates that the four-proxy model generated with the WDMR method is relatively  
14 insensitive to changes in salinity, since the model is able to reconstruct the temperature for all  
15 study sites along the estuarine salinity gradient, without systematic errors due to differences in  
16 salinity. The overall trend of reconstructed temperatures is very similar to the measured  
17 temperature, but the reconstructed temperature profiles show more variability. Though the best  
18 reconstruction is obtained for the validation shell from the same study site and collected at the  
19 same time as the training shells (RMSE = $\pm 1.29$  °C), the temperature reconstructions for the three  
20 other study sites are still better than  $\pm 2.19$  °C. The validation shell from Knokke, sampled in a  
21 different year than the training set, has a similar RMSE as the validation shells sampled in  
22 Ossenisse and Breskens, the same period as the training set. Therefore we can conclude that the  
23 model correctly resolves possible inter-annual variability in the proxies-temperature relationship.

24

25 The reconstruction performance of models trained for different proxy combinations is shown in  
26 Figure 7. In general RMSE decreases with an increasing number of proxies. This trend is also  
27 observed in Table 1 where it is demonstrated that the use of an additional proxy in a multi-proxy  
28 model greatly improves reconstruction performance since most contribution factors (i.e. RMSE  
29 with proxy - RMSE without proxy) are positive. The benefit of using a multi-proxy model is thus

1 significant, although it is clear that not all proxies contribute equally to the final reconstruction  
2 and the four-proxy model is not necessarily the best model.

3 Table 1 shows that on average all proxies contribute positively to the final reconstruction. Mg  
4 can improve the RMSE of a temperature reconstruction with 0.72, on average. Ba improves the  
5 RMSE of a temperature reconstruction with 0.42. Pb and Sr, however, show lower contribution  
6 factors of 0.20 and 0.04, respectively. The average contribution factors shown in Table 1 thus  
7 suggest that Mg and Ba contribute the most to an accurate temperature reconstruction. Ba,  
8 however, shows several negative contribution factors for the Breskens site, revealing site specific  
9 effects. However, information stored in the Sr-signature of the shell almost completely  
10 compensates for these site specific effects. This can clearly be seen by comparing the performance  
11 of the MgBa-model with the one of the MgSrBa-model in Figure 7, with the latter yielding fairly  
12 accurate and salinity robust temperature reconstructions. Adding Pb to this MgSrBa-model does  
13 slightly improve the reconstruction, although by not more than 0.2 °C.

### 14 **5.3 Discussion**

15 Using the WDMR-method to construct paleo-thermometer models yields accurate temperature  
16 reconstructions for shells from Terneuzen where the training set was sampled. This  
17 reconstruction shows that it is possible to reconstruct the temperature based on Mg, Sr, Ba and  
18 Pb. The reconstruction performance is slightly poorer for shells from the other sites suggesting  
19 that the model is sensitive to site-specific variations. However, considering the salinity range  
20 from 32 (Knokke) to 15 (Ossensisse), the reconstruction performance (RMSE lower than 2.19 °C)  
21 for shells from a different site (and salinity) than the training set, is promising. Compared to  
22 other approaches for reconstructing water temperature based on the blue mussel archive (Epstein  
23 et al., 1953b; Wanamaker et al., 2006; Klein et al., 1996b) the performance of the method  
24 proposed here is of similar standard, if not better.

25 The multi-proxy model presented in this paper is built on four proxies of which two (Ba and Pb)  
26 were previously not considered to have potential as paleo-thermometers. It is thus probable that  
27 this method will provide even better reconstructions when trained on a set of well known  
28 temperature sensitive proxies or when combined with another paleothermometry method [*e.g.*  
29  $\delta^{18}\text{O}$ , Epstein et al., 1953b]. Nevertheless, the use of nonlinear methods in general allows

1 discovering less obvious (nonlinear) relationships between proxies and temperature.  
2 Consequently, it is possible that the use of modern nonlinear multivariate statistics (among which  
3 the WDMR method) will help to find new proxies with hidden paleothermometer potential. The  
4 use of nonlinear models in general will probably open new research paths in paleoclimatology.  
5 Figure 7 clearly shows that models based on a combination of proxies perform better than single  
6 proxy models. But it is also clear that not all proxy combination perform as well. Table 1 gives  
7 an objective overview of the contributions of Mg/Ca, Ba/Ca, Sr/Ca and Pb/Ca to  
8 paleotemperature models. It thus appears that Mg, already known as a temperature proxy (Klein  
9 et al., 1996b; Wanamaker et al., 2006), shows the highest contribution to the temperature  
10 reconstruction. More surprising is that Ba and Pb, which have not been proposed as temperature  
11 proxies, seem to contribute more to the temperature reconstruction than Sr which has been  
12 suggested as paleothermometer (Wanamaker et al., 2008).

### 13 5.3.1 Magnesium

14 Our results confirm the paleothermometry capacity of the Mg/Ca ratio as reported for several  
15 bivalve species by others (e.g. Klein et al., 1996b; Wanamaker et al., 2006).

16 However, Figure 2 clearly shows that the Mg-temperature relationship is not linear. The Mg-  
17 temperature relationship seems to reflect that Mg incorporation in *M. edulis* is driven by a  
18 physiological response to temperature, with a maximal Mg incorporation around 16 °C. Except  
19 for the work of Vander Putten et al. (2000), which is based on the same dataset, a similar Mg/Ca-  
20 temperature relationship showing maximal Mg uptake at an intermediate temperature has not  
21 been reported in literature. Most published papers propose linear Mg-temperature relations for  
22 bivalves (e.g. Richardson et al., 2004; Pearce and Mann, 2006; Klein et al., 1996b; Klein et al.,  
23 1996a). Freitas et al. (2006) observe an exponential Mg-temperature relationship for different  
24 bivalve species. That relationship is similar to the abiogenic Mg/Ca-temperature relationship  
25 reported by Oomori et al. (1987) and the temperature dependent Mg-incorporation in  
26 foraminifera reported by Barker et al., (2005).

27 On the other hand, it has been shown that Mg/Ca ratios in shells are influenced by growth rate  
28 (Ford et al., 2008) and by metabolic activity (Strasser et al., 2008). Moreover, Mg is shown to be  
29 incorporated majorly in shell organic matrix (Foster et al., 2009). Such biological controls on



1 Mg may explain why combining Mg with other proxies results in better reconstructions (see  
2 Figure 7). For instance if Mg incorporation in the shell indeed depends on physiology it is  
3 reasonable to assume that Mg incorporation will also be influenced by other vital factors, since  
4 the animal's physiological condition will be influenced by metabolic activity, growth rate, food  
5 availability and/or ontogenetic stage. Therefore, Sr (being a potential proxy for metabolic  
6 activity and growth rate), Ba (being a potential proxy for food availability) and Pb (also being  
7 influenced by ontogenetic stage) may explain some of the variation in the Mg/Ca profile of a  
8 shell.

### 10 5.3.2 Barium

11 Except for the specimens from Breskens, the nonlinear Ba-model results in fairly good SST  
12 reconstructions, indicating that Ba uptake in the shell of *M. edulis* is partly driven by  
13 temperature. It is probable that the Ba-temperature relationship is indirect and rather reflects  
14 temperature driven plankton blooming or water mixing events (Lazareth et al., 2003; Barats et  
15 al., 2009). These indirect relationships can be informative but one should be aware of the model  
16 errors that could be created, possibly biasing the temperature reconstruction. Indeed bloom  
17 events are quite complex and are influenced by many environmental parameters such as river  
18 discharge, wind speed, insulation etc (Cloern et al., 1995). The failure of the Ba-model at the  
19 Breskens site is probably due to these model errors. Indeed Figure 3 shows that Breskens is the  
20 only site where a second Ba-peak is observed, although the temperature profiles at the three  
21 study sites monitored in 1996 are very similar. The model trained on shells of Terneuzen  
22 incorrectly couples the barium peak to temperature increase since all training shells  
23 independently showed a Ba peak coinciding with temperature increase in spring. As a result the  
24 model provides a similar interpretation for the second Ba peak observed for the Breskens shells  
25 although the origin of this second Ba peak is probably different. To avoid this kind of model  
26 errors it is not recommended to use Ba/Ca ratios as stand alone temperature proxy.

27 However, this does not mean that Ba/Ca ratios can not add information into a multi-proxy  
28 model. Several studies report that phytoplankton bloom events can influence the metabolism of  
29 the filter feeding bivalve, thereby inducing variation in shell growth rate (Versteegh, 2009;

1 Schöne et al., 2006; Gillikin et al., 2008). Therefore, it can be expected that the combination of  
2 Ba and Sr (a potential proxy for shell growth and metabolism) in a multi-proxy model will  
3 contribute to resolving variations in other proxies which are due to shell growth.

### 4 5.3.3 Strontium

5 Contrasting with the studies that report a relation between Sr/Ca ratios and water temperature in  
6 calcitic bivalve shells (Carre et al., 2006; Freitas et al., 2005; Wanamaker et al., 2008) our results  
7 indicate that Sr/Ca ratios do not carry much temperature information. The Sr/Ca-model  
8 computed in this paper does not result in satisfactory temperature reconstructions, neither for  
9 shells from the Terneuzen training site nor for the other sites. Moreover, when Sr is added to a  
10 multi-proxy model often a negative impact is seen, indicating that Sr uptake is poorly influenced  
11 by temperature and also that the variations in Sr/Ca ratios do not contain significant information  
12 that assists in resolving the variation in other proxies. Nevertheless, Sr/Ca seems to have a  
13 positive influence on the site specificity of Ba/Ca, suggesting that Ba/Ca ratios and Sr/Ca ratios  
14 are influenced by a common environmental factor. Lazareth et al. (2003) also observed some  
15 Sr/Ca maxima to coincidence with Ba/Ca-peaks. It is possible that the incorporation of both  
16 elements is influenced by shell growth rate as suggested at least for Sr/Ca by Carré et al. (2005),  
17 Gillikin et al. (2005) and Foster et al. (2009). Therefore, considering that Mg/Ca is a potential  
18 temperature proxy, even though it appears affected by variable shell growth rate and metabolic  
19 activity (Takesue et al., 2008), the combination of Mg/Ca with Sr/Ca and Ba/Ca can help explain  
20 a considerable fraction of the Mg/Ca signal noise. This is indeed observed in our dataset where  
21 the RMSE of the MgSrBa model is a significantly lower than the RMSE of the Mg/Ca model  
22 ( $\text{RMSE}_{(\text{MgSrBa-model})} - \text{RMSE}_{(\text{Mg-model})} = 1.28; 0.30; 0.40$  and  $0.34$  for Terneuzen, Breskens,  
23 Ossenisse and Knokke, respectively).

### 24 5.3.4 Lead

25 The Pb/Ca-model does not result in accurate temperature reconstructions (Figure 4) and when  
26 adding Pb to a multi-proxy model, low or negative impacts are observed. This means that Pb  
27 uptake is poorly influenced by temperature and also that the variation in Pb/Ca ratios do not  
28 contain much information helping to explain variation in other proxies. Nevertheless, when  
29 Pb/Ca is added to the MgBa model, contribution factors increase (Table 1). This suggests that

1 Pb/Ca and Ba/Ca are influenced by a common parameter. A common forcing for Pb/Ca and  
2 Ba/Ca, however, has not been reported in literature. However, it has been shown that Pb  
3 incorporation in a bivalve shell is influenced by temperature (Strasser et. al., 2008) and Pb/Ca  
4 profiles sometimes show ontogenetic trends (Dick et al., 2007). These facts may explain the  
5 positive contribution factors of Pb in the multi-proxy models.

6 However, Pb/Ca ratios in shells have been shown to be strongly influenced by anthropogenic  
7 activities (Gillikin et al., 2005; Richardson, 2001) rather than natural climate related changes. So,  
8 we do not recommend including Pb in a multi-proxy model.

9

## 10 **6 General discussion**

### 11 **6.1 Year to year and site specific variations**

12 Several studies reveal that trace element profiles in shells may vary significantly between  
13 successive years (Barats et al. 2009) and between different study sites (Gillikin et al. 2006a). Our  
14 study as well reveals year to year and site specific variations (see Figure 3). However, the  
15 accurate temperature reconstruction based on the shell from Knokke sampled during a different  
16 year , at a different site relative to the training site suggests that the models are relatively robust  
17 against year to year and site specific variations in trace element composition. Moreover, even  
18 though the distance between Terneuzen and Knokke is not more than 40 km the two sites  
19 strongly differ in environmental conditions: the Terneuzen site is an estuarine environment with  
20 a lower salinity compared to the Knokke site which is a more saline coastal environment,  
21 therefore the model is probably fit for application to a wider environment than studied here.

22 However, we did observe differences in site specificity for different proxy combinations (e.g. the  
23 Ba/Ca problem that is observed for the Breskens site) and therefore the site specificity of every  
24 proxy has to be investigated. This needs to be done independently and in combination with other  
25 proxies before a model based on a specific proxy combination can be extrapolated to a broader  
26 environment.

## 1 **6.2 Species specificity**

2 The model presented in this paper is trained on *M. edulis* shells. Although we do not expect this  
3 model to be directly applicable to other species because Mg/Ca (the main player in the  
4 temperature reconstruction) is assumed to be driven by a physiological temperature response that  
5 is probably species specific, some preliminary tests suggest that the models may be extrapolated  
6 to other bivalves with calcitic shells. Moreover it should be possible to generate a specific  
7 WDMR model for other substrates such also corals, trees, sediments ...

8 Thus WDRM method could be used to develop nonlinear models to reconstruct the  
9 paleoenvironment for all different types of natural climate archives.

## 10 **6.3 Building new models using the WDMR method**

11 As mentioned before, the model presented in this paper is species specific, implying that a  
12 different model needs to be constructed for other species. Furthermore, we believe that the  
13 WDMR method could also be used to build a stronger model for *M. edulis* shells. The model  
14 presented in this paper is based on trace elements of which some have never been linked to  
15 temperature before (i.e. Ba/Ca and Pb/Ca). Although Ba/Ca has clearly been shown to improve  
16 temperature reconstructions, a multi-proxy model that uses even more proxies with  
17 paleothermometry capacity would significantly improve the temperature reconstructions.  
18 Therefore, we encourage the construction of a WDMR model using high resolution  
19 measurements of Li/Ca ratios (Thebault et al., 2009), deuterium (Carroll et al., 2006) and oxygen  
20 isotopes (Epstein et al., 1953b). On the other hand we also encourage exploring other elemental  
21 and isotopic measurements using the WDMR-method since this method is able to detect less  
22 straightforward relationships between a potential proxy and its environment. The WDMR  
23 toolbox for Matlab is added as supplementary material to this paper.

24

## 1 **7 Conclusions**

### 2 **7.1 The benefit of nonlinear methods**

3 In this paper we show that using a nonlinear model to describe a proxy data set can improve  
4 temperature reconstruction performance with more than 1°C compared to classical multiple  
5 regression techniques.

### 6 **7.2 The benefit of combining proxies**

7 Furthermore, we demonstrate that combining different proxies results in better temperature  
8 reconstructions. However, it is clear that not all proxies contribute equally to the final result. Our  
9 tests confirm that the Mg/Ca ratio in bivalve shells is a successful paleothermometer. We suggest  
10 that the Mg biomineralization is driven by a physiological response to changing temperature,  
11 which is possibly perturbed by metabolic activity and variable growth rate of the bivalve. The  
12 Combination of Mg, Ba and Sr into a multi-proxy model was successful because Ba and Sr  
13 reduce interfering effects due to metabolism and growth rate variation, thereby reducing the  
14 variance of the temperature prediction based on Mg.

### 15 **7.3 The robustness of the WDMR method**

16 The nonlinear multi-proxy model obtained by the WDMR is able to reconstruct temperature with  
17 a RMSE of less than 2.19°C for a salinity ranging from 32 to 15. In comparison with other  
18 paleothermometry methods the performance using WDMR is good, if not better. This stresses  
19 that there is indeed a significant underlying low-dimensional structure in the proxy space.  
20 Although WDMR is a complex and sophisticated method, its success and robustness relies on its  
21 capability to nonlinearly combine proxy measurements into a multi-proxy model. One of the  
22 main messages of this contribution is therefore to encourage other researchers to combine their  
23 proxy measurements in one nonlinear multi-proxy model, since this will allow identifying new  
24 proxies with paleothermometer potential.

25

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9

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1 Table 1. Seven unique contribution factors are defined per proxy. Every contribution factor is  
 2 defined by the difference between the RMSE of a model based on a proxy combination with the  
 3 investigated proxy and the RMSE of a model based on a proxy combination without the  
 4 investigated proxy. The average contribution of each proxy is given per study site and for the  
 5 total validation set. Negative contribution factors are marked in red and mean that the  
 6 corresponding proxy does not contribute to a better reconstruction.

7

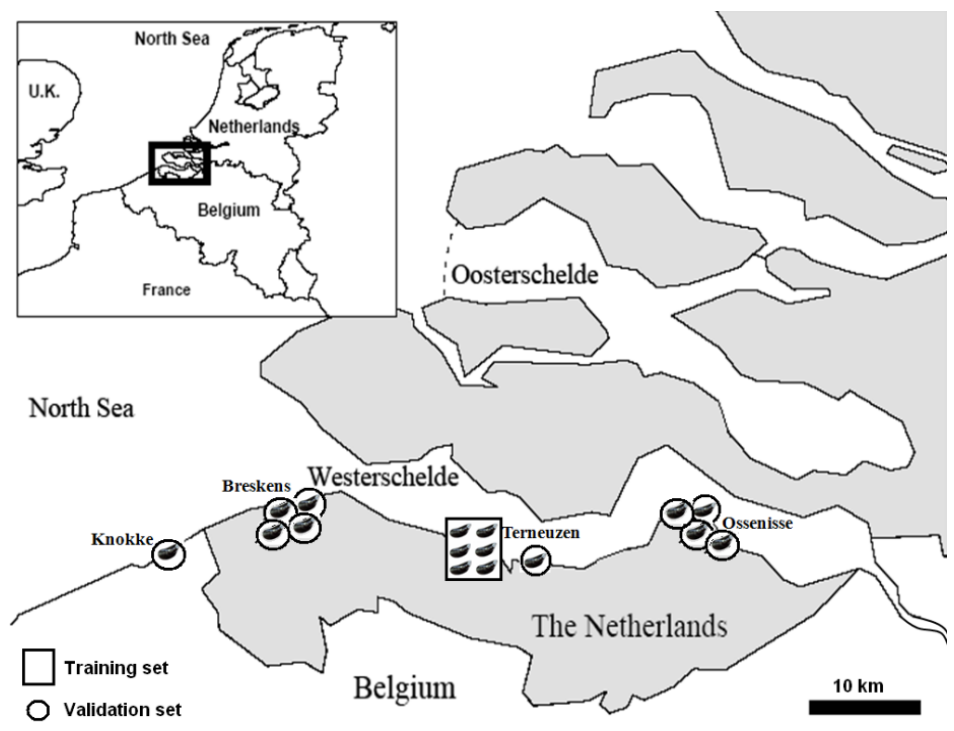
<i>Contribution of Mg</i>	<i>Terneuzen</i>	<i>Breskens</i>	<i>Ossensisse</i>	<i>Knokke</i>	<i>Average</i>
RMSE using MgSr-RMSE using Sr	1,62	0,47	0,43	0,78	
RMSE using MgBa- RMSE using Ba	0,47	0,04	0,30	0,20	
RMSE using MgPb- RMSE using Pb	1,46	0,59	1,11	0,79	
RMSE using MgSrBa- RMSE using SrBa	1,13	1,03	0,20	0,28	
RMSE using MgSrPb- RMSE using SrPb	1,86	0,54	1,02	0,75	
RMSE using MgBaPb- RMSE using BaPb	1,06	0,70	0,17	0,31	
RMSE using MgSrBaPb- RMSE using SrBaPb	1,07	1,00	0,21	0,58	
<b>Average</b>	1,24	0,62	0,49	0,53	0,72
<i>Contribution of Ba</i>	<i>Terneuzen</i>	<i>Breskens</i>	<i>Ossensisse</i>	<i>Knokke</i>	<i>Average</i>
RMSE using MgBa- RMSE using Mg	0,62	-0,83	0,28	0,16	
RMSE using SrBa- RMSE using Sr	1,08	-0,21	0,81	0,94	
RMSE using BaPb- RMSE using Pb	0,70	-0,32	1,26	0,58	
RMSE using SrBaPb- RMSE using SrPb	0,93	-0,08	1,40	0,55	
RMSE using MgBaPb- RMSE using MgPb	0,31	-0,21	0,32	0,09	
RMSE using MgSrBa- RMSE using MgSr	0,59	0,35	0,58	0,44	
RMSE using MgSrBaPb- RMSE using MgSrPb	0,13	0,38	0,59	0,38	
<b>Average</b>	0,62	-0,13	0,75	0,45	0,42
<i>Contribution of Sr</i>	<i>Terneuzen</i>	<i>Breskens</i>	<i>Ossensisse</i>	<i>Knokke</i>	<i>Average</i>
RMSE using MgSr- RMSE using Mg	0,69	-0,05	-0,18	-0,10	
RMSE using SrBa- RMSE using Ba	0,00	0,13	0,23	0,10	
RMSE using SrPb- RMSE using Pb	-0,31	-0,07	-0,48	-0,09	
RMSE using MgSrPb- RMSE using MgPb	0,09	-0,12	-0,57	-0,13	
RMSE using MgSrBa- RMSE using MgBa	0,65	1,12	0,12	0,18	
RMSE using SrBaPb- RMSE using BaPb	-0,09	0,17	-0,34	-0,12	
RMSE using MgSrBaPb- RMSE using MgBaPb	-0,08	0,47	-0,30	0,15	
<b>Average</b>	0,14	0,23	-0,22	0,00	0,04
<i>Contribution of Pb</i>	<i>Terneuzen</i>	<i>Breskens</i>	<i>Ossensisse</i>	<i>Knokke</i>	<i>Average</i>
RMSE using MgPb- RMSE using Mg	0,97	0,16	0,42	0,26	

RMSE using SrPb- RMSE using Sr	0,13	0,03	-0,56	0,26	
RMSE using BaPb- RMSE using Ba	0,06	0,11	0,58	0,09	
RMSE using SrBaPb- RMSE using SrBa	-0,02	0,15	0,02	-0,13	
RMSE using MgBaPb- RMSE using MgBa	0,66	0,78	0,45	0,20	
RMSE using MgSrPb- RMSE using MgSr	0,37	0,10	0,02	0,23	
RMSE using MgSrBaPb- RMSE using MgSrBa	-0,08	0,12	0,03	0,17	
<b>Average</b>	0,30	0,21	0,14	0,15	0,20

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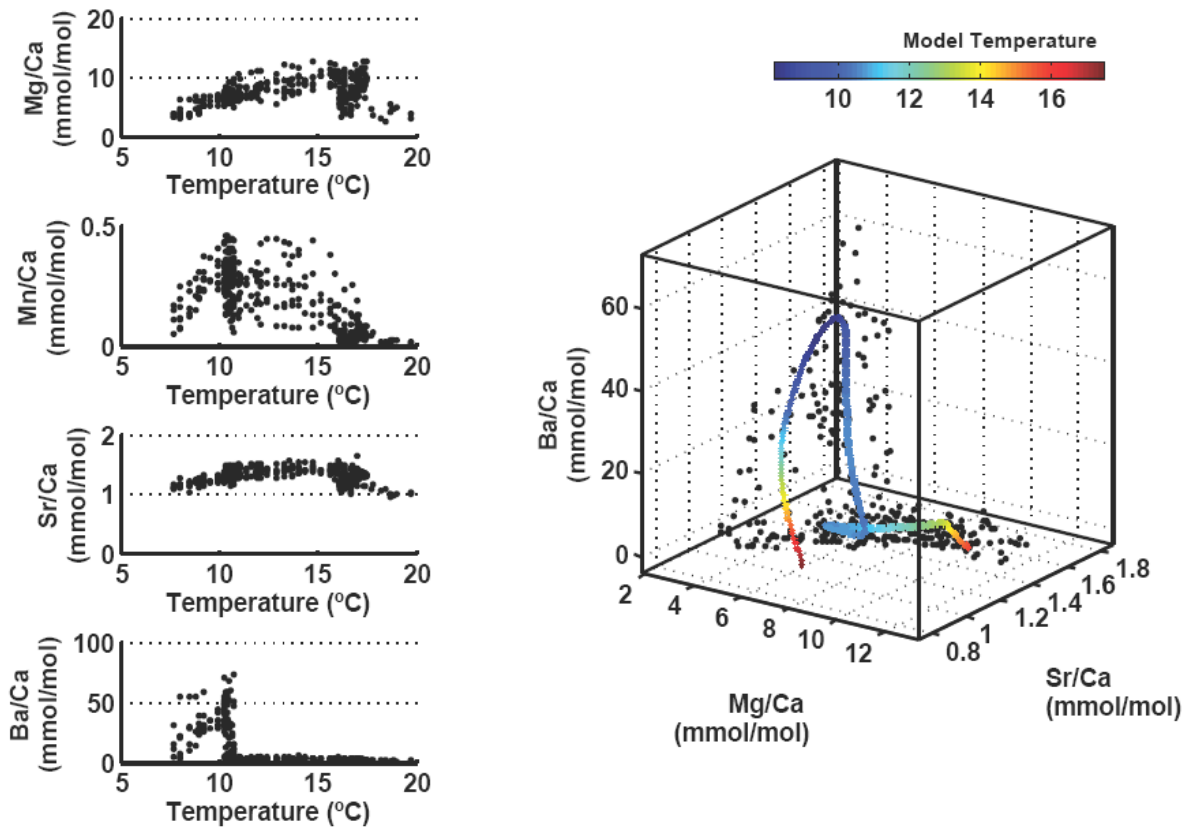
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Figure 1. Geographical position of the study sites in the Scheldt Estuary. Boxed: six shells from Terneuzen were used for training the models, Circled: the shells used for validation.

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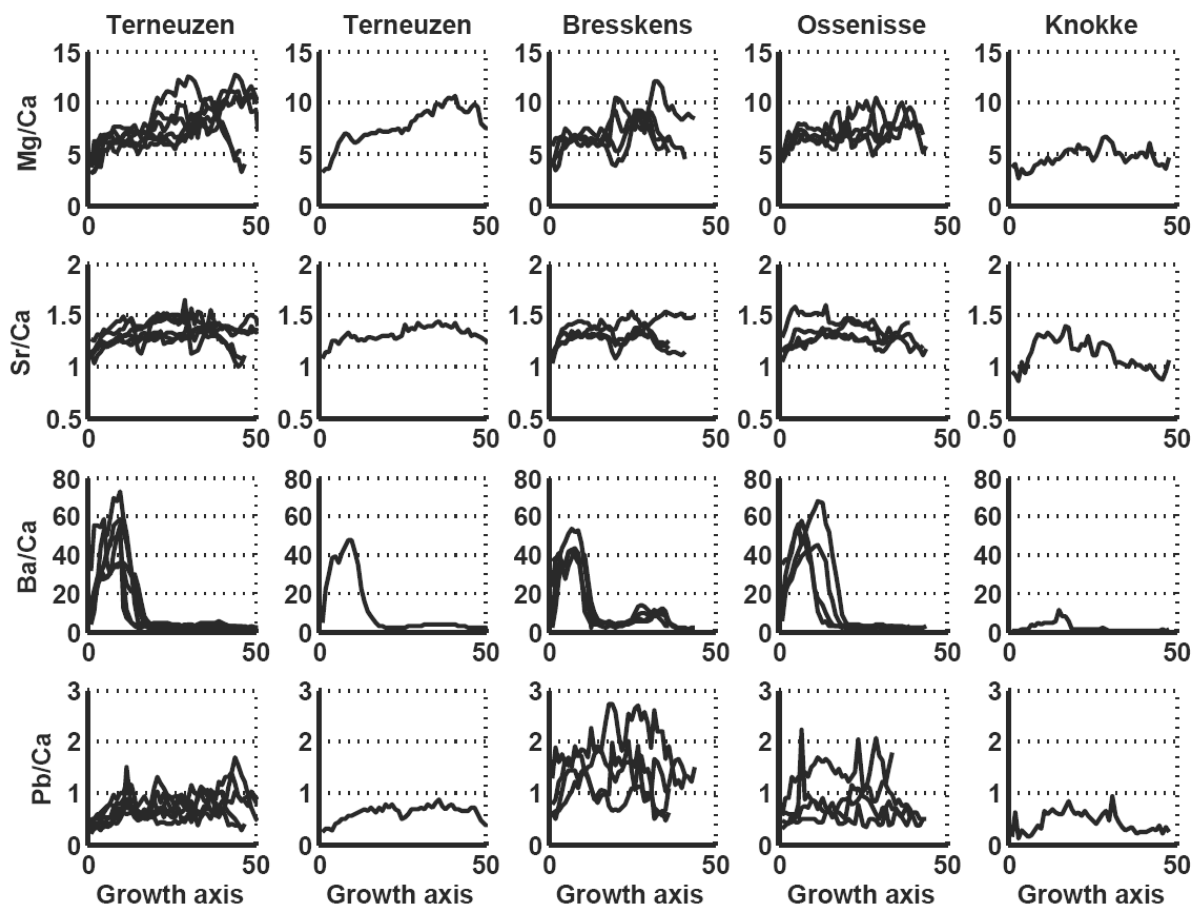


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3 Figure 2: Left: Ba/Ca, Sr/Ca, Mg/Ca and Pb/Ca ratios plotted against water temperature (Vander  
4 Putten et al. 2000). Right: Ba/Ca, Sr/Ca and Mg/Ca concentrations plotted against each other.  
5 The shown curve indicates how the concentrations are changing with water temperature (in  
6 colour).

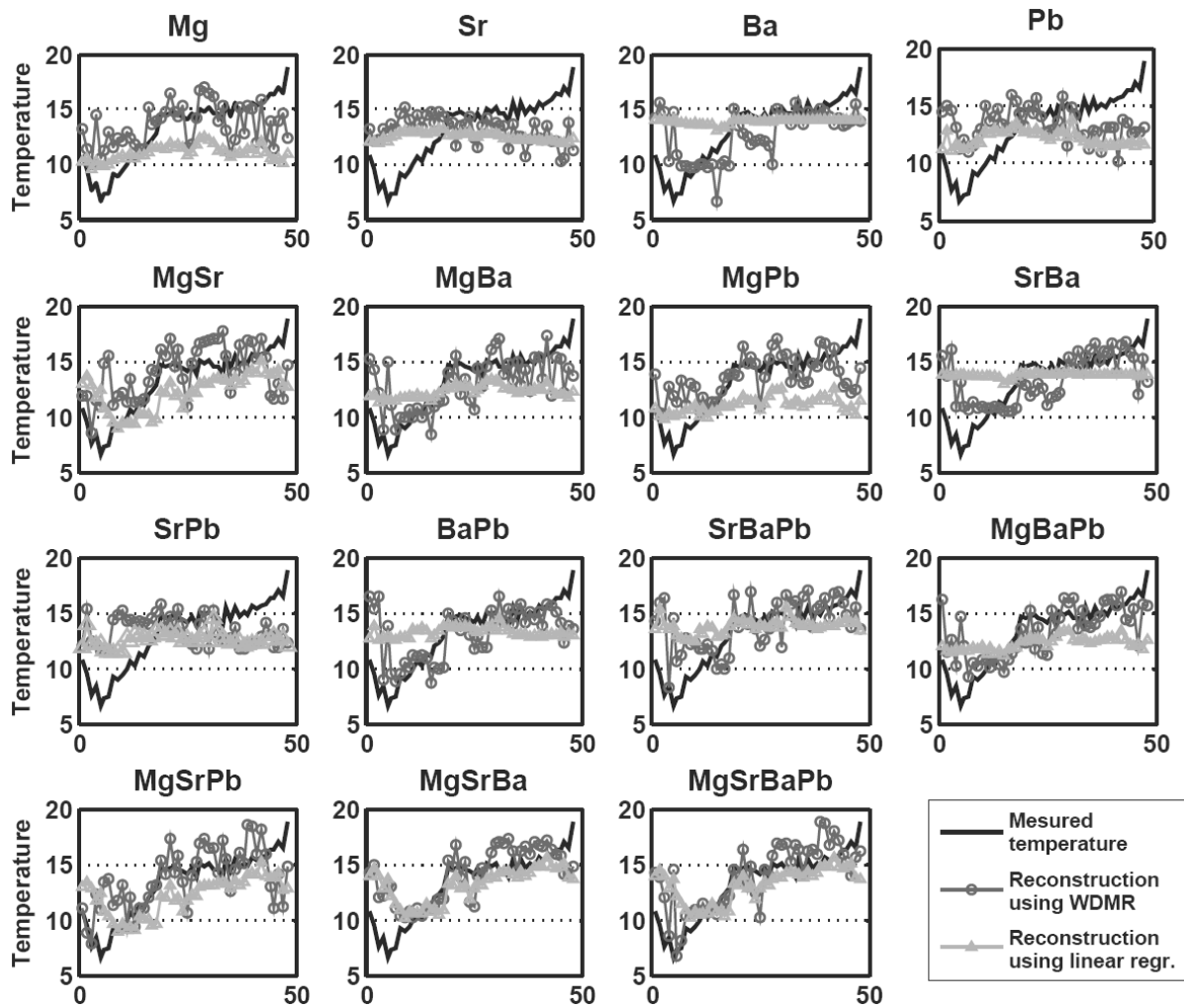
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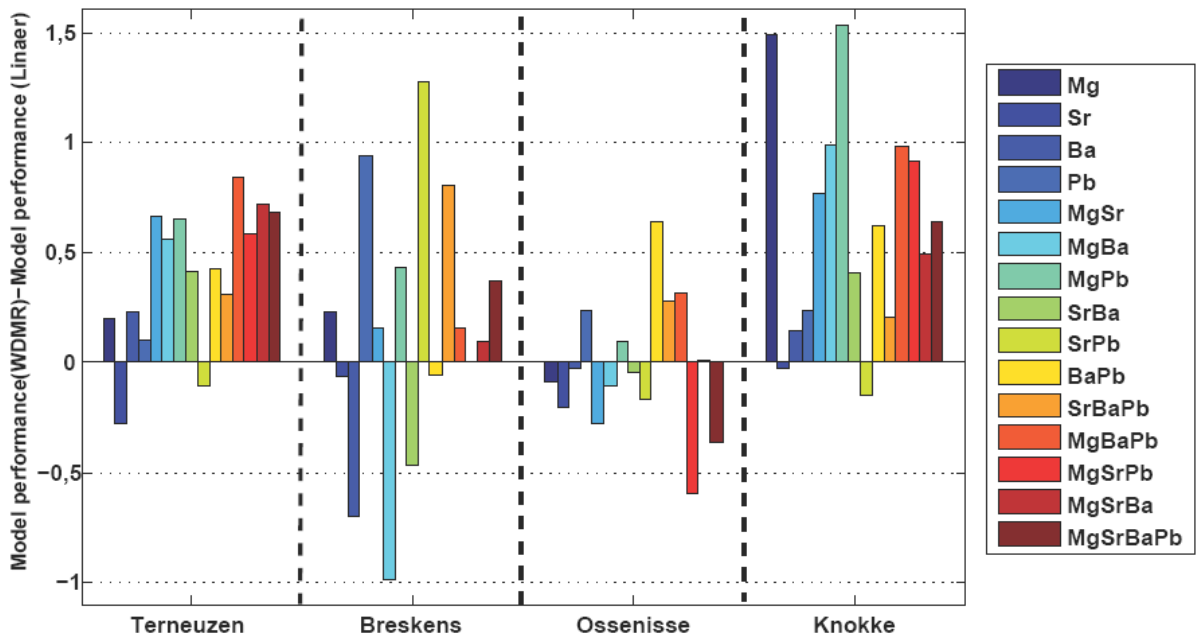
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 2 Figure 3. Chemical signature along the growth axis of the shells used to train (first column) and  
 3 to validate (columns 2 to 5) the models. The trace element/Ca ratios are in mmol/mol.  
 4





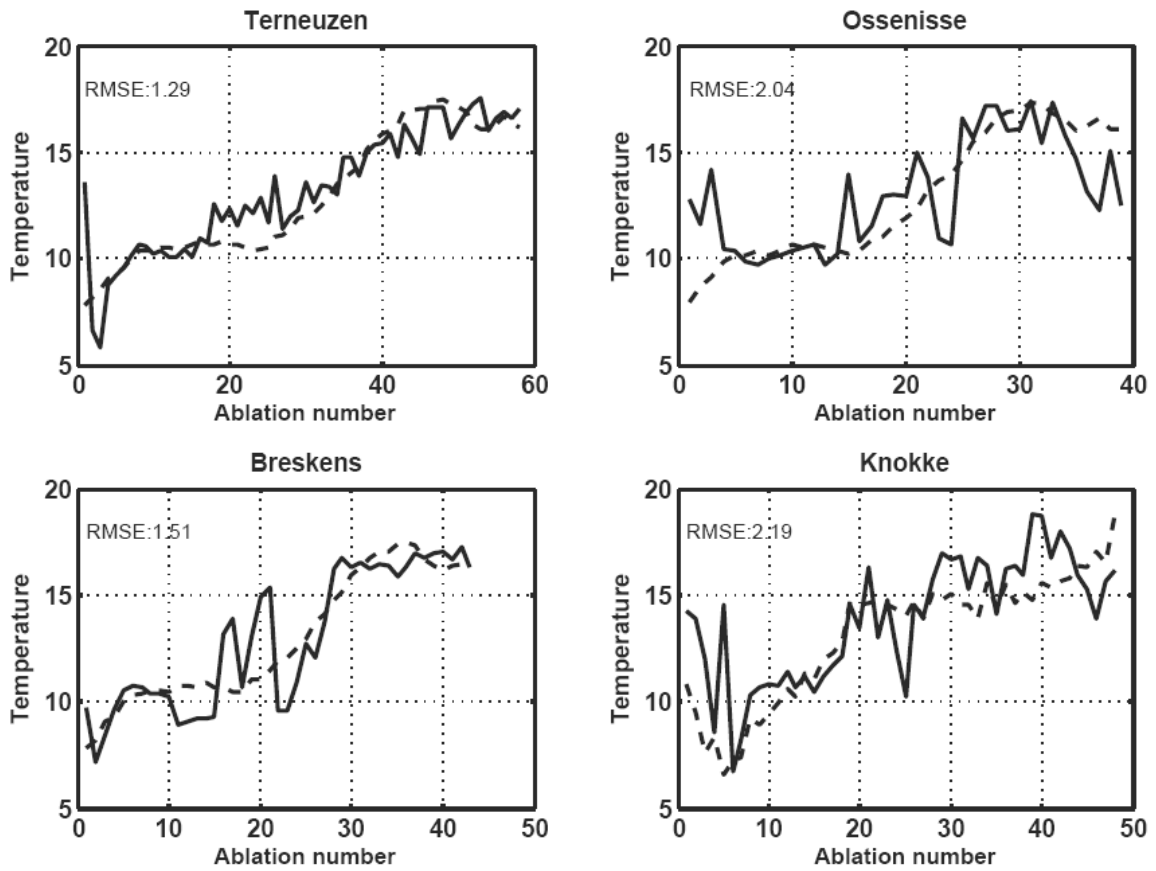
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 2 Figure 4. Detailed visualization of the temperature reconstructions for the shell from the Knokke  
 3 study site for all proxy combinations, the x-axis corresponds with sample number along the  
 4 along the shell's growth axis.

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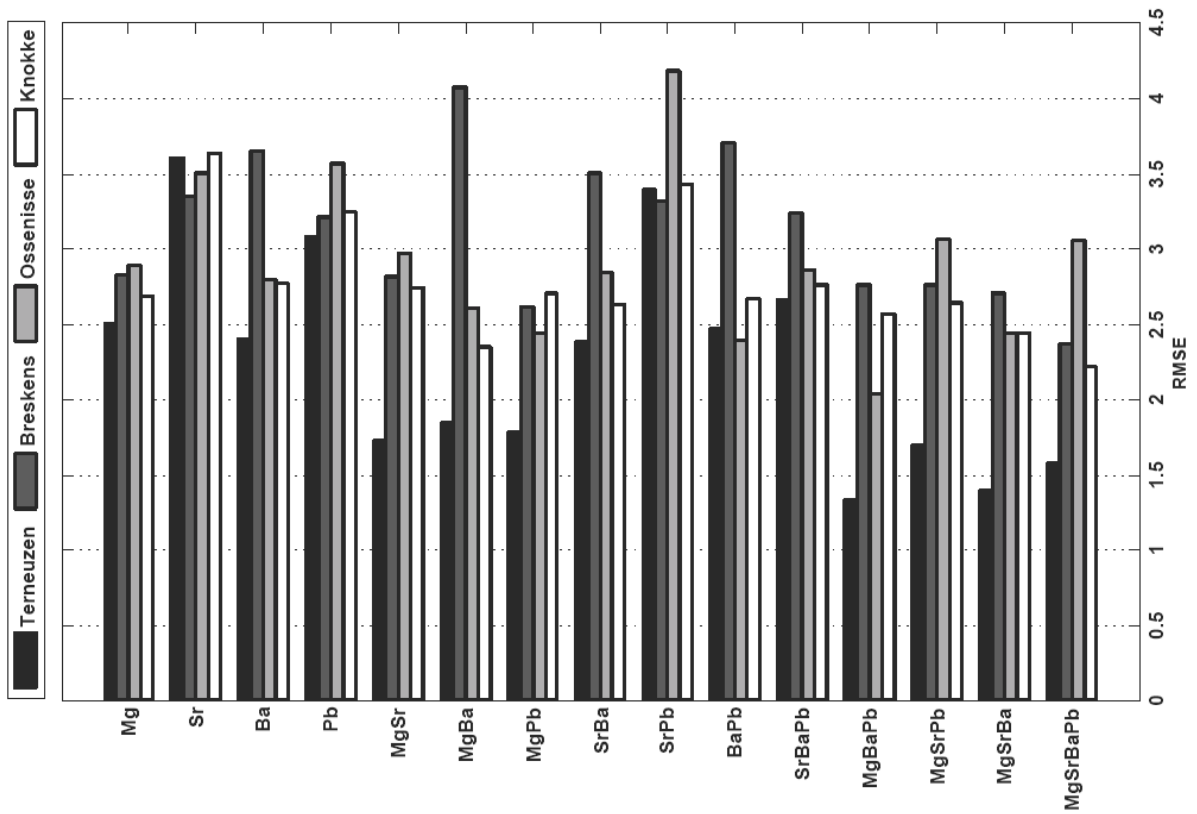
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Figure 5. Differences of model reconstruction performance obtained using the validation data between linear and non-linear multi-proxy models, for the 4 study sites. Positive differences indicate that the non-linear model performs better. The 15 different colors represent the 15 studied proxy combinations.



1  
 2 Figure 6. Measured water temperature (dashed line) and reconstructed water temperature (solid  
 3 line) obtained by the four-proxy WDMR model trained on Terneuzen data set and tested on a  
 4 single validation shell from Terneuzen, Breskens, Ossenisse and Knokke.

5



1

2 Figure 7. Model reconstruction performance expressed as RMSE obtained on the validation data  
 3 for the four sites, as based on the Terneuzen training dataset using different proxy combinations.

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