

## Strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) dating of marine shells from Pliocene and Pleistocene shallow marine deposits in The Netherlands

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### Abstract

$^{87}\text{Sr}/^{86}\text{Sr}$  (Strontium) ratio analyses of shell material (mainly *Arctica islandica*) from 24 levels in the Maassluis Formation of boreholes Noordwijk, Zegveld and Terschelling suggest that the age of the formation ranges from 0.82 to 2.34 Ma ( $\pm$  0.5 Ma), and that the Oosterhout Formation at Noordwijk could be as much as 2.5 Ma older than hitherto assumed.

**Keywords:** Maassluis Formation, Oosterhout Formation, Strontium isotopes

### Introduction

The TNO-NITG funded 'Process model Lower Pleistocene' project aims to decipher the subsurface stratal patterns of the shallow marine and deltaic Maassluis Formation in order to reconstruct the Late Pliocene and Early Pleistocene depositional history of the Netherlands. A coherent lithological facies model of the Lower Pleistocene marine deposits in The Netherlands is lacking. However, such a model is of great importance both to the geological mapping of The Netherlands and the understanding of the geo-hydrological properties of these deposits that form the base of the shallow groundwater system.

The Maassluis Formation was deposited at the southern margin of the North Sea Basin, with the coastline shifting rapidly in response to climatic events (Laban, 1995). Figs 1 and 2 show the depositional limits, directions of main sediment supply and lithostratigraphic position of the Maassluis Formation. By definition (Doppert et al., 1975), its top is marked by the top occurrence of marine shells and its

base is marked by the top occurrence of glauconite. Several biostratigraphical studies of this interval are available, mainly on foraminifera and molluscs (see Zagwijn & Van Staalduin, 1975, for a summary). The foraminiferal content of the Maassluis Formation generally fits in the FA1 biozone and partly in the FA2 biozone of Doppert (1975), which correlate with the Early Pleistocene and the Late Pliocene sensu Zagwijn (1975, 1998) respectively. The Maassluis Formation pollen content is generally of Tigian nature, its top is usually in the TC4c pollen zone (Van Montfrans, 1975) but can be as high as TC5 in the Brielle area (Gibbard et al., 1991). These pollen zones are generally used to indicate the age of this formation, even in cases where the palynological analysis was on dinoflagellates using British dinoflagellate events (Van Kolfschoten & De Boer, 1988). Up to now, only numeric ages derived from magnetostratigraphy were available for these sediments (Van Montfrans, 1971).

To obtain additional numeric age estimates, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of shell material from the Maassluis

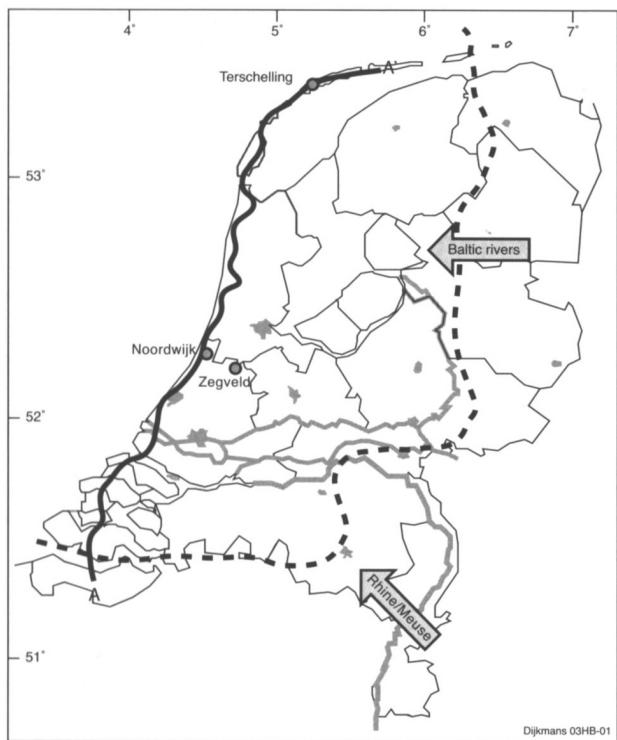


Fig. 1. Map of The Netherlands with location of boreholes used in this paper, southern and eastern boundary of Maassluis Formation occurrence (dashed line, from Zagwijn, 1975) and directions of river sediment transport during Praetiglian and Tiglian. Line A-A' marks location of profile in Fig. 2.

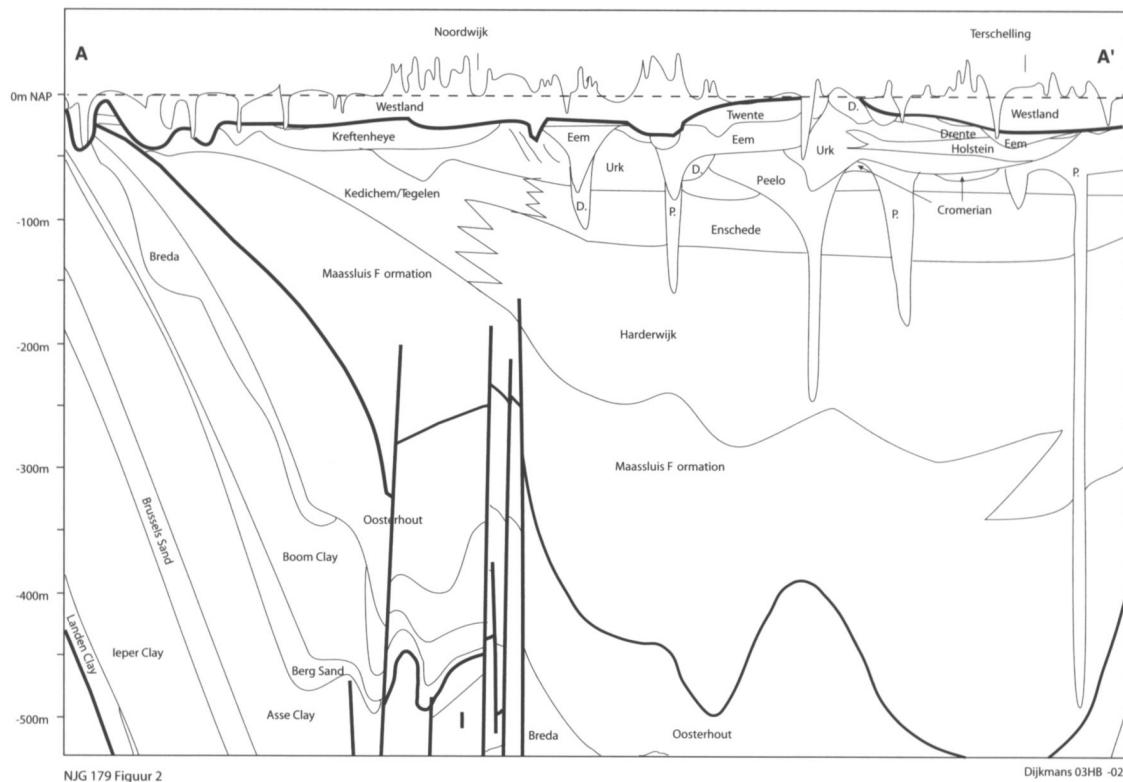


Fig. 2. Schematic profile showing the relation of the Maassluis Formation with other formations in the Dutch subsurface. After a profile compiled by De Gans, Parker-Witmans & Zwaan (TNO-NITG) for a 1995 exhibition to commemorate the 750 year existence of the city of Haarlem (lithostratigraphy cf. Zagwijn & Van Staalduin, 1975). The location is indicated on Fig. 1. NAP = Normaal Amsterdams Peil. Note the fault block position of the Noordwijk borehole.

Formation was determined, to improve on positioning the Maassluis Formation in the numeric time scale, to date the litho- and biostratigraphic units of the boreholes used in this paper, and to test the time-stratigraphic value of traditional correlation.

For consistency with Beets' (1992, Chapter 2) earlier study on dutch material, the shell material has been dated using his calculation method on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. This provides age estimates with a 0.5 Ma uncertainty for the 0.0 - 2.34 Ma age interval. The numeric ages refer to the timescale of Berggren et al. (1985), as used by Beets (1992). More modern compilations of Sr-isotope stratigraphy data (Howarth & McArthur, 1997; McArthur et al., 2001) are usually based on the timescale of Shackleton et al. (1995) for the 0 - 6.4 Ma interval.

Application of strontium isotope chronostratigraphy to shallow marine deposits, such as beach to upper shelf, can be hampered by being positioned too far away from the world oceanic circulation of water masses, or by a dominant input of river source with deviating Strontium signature. The North Sea Basin had an open connection to the Atlantic Ocean during the Pliocene and Early Pleistocene, so restriction from world oceanic water masses should not be a problem in this area. The river Rhine precursor (in-

cluding Meuse), which flowed to the West through northern Belgium (Kasse, 1988), and of the Baltic river system from the East-northeast, however, may have been of influence on the isotopic ratios in their delta areas.

## Materials and methods

For this study 23 samples were analysed, 10 from borehole Noordwijk (RD Coordinates X: 91520, Y: 471800), 8 from hole Zegveld (X: 115382, Y: 460157) and 6 from hole Terschelling (X: 143820, Y: 598430), see Fig. 1 and Table 1. The position of the Maassluis Formation in the boreholes was established using TNO-NITG's sediment-petrological (Burger, 1998) and geological interpretations of airlifted samples. In hole Noordwijk, where the location of the base of the Maassluis Formation was uncertain at the time of sampling, the interval of uncertainty was also sampled.

From the airlifted samples of shell bearing sands and clays, the 24 shell samples were picked, mostly of the bivalve *Arctica islandica*. The specimens were selected after visual inspection for their pristine appearance by NITG malacologists T.Meijer (Noordwijk) and R.Pouwer (Zegveld and Terschelling), to avoid measurements on specimens that are either reworked or show alteration of their shell material. No SEM photography, cathode-luminescence or trace element analysis to further assess the diagenetic state of the studied material was done.

The shells were cleaned, pulverised, dissolved in 5N acetic acid (HOAc) and centrifuged, after which the Strontium-bearing "supernatant" could be siphoned off with a pipette. The Strontium was separated in a set of chromatography columns, filled with the Strontium retaining resin "Sr-spec". The resulting samples were dried down on a hot plate. The Strontium preparations were loaded onto outgassed zone-refined Rhenium filaments. For each ca. 10 samples a Standard Reference Material NBS 987 standard as well as a modern seawater standard was loaded, to control the quality of the measurements.

The filaments were measured in a thermal ionisation solid source mass-spectrometer (either Finnigan MAT 261 or 262). The data were corrected for Rb interference and normalized to a  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194 and a NBS 987 standard value of 0.710255 (see Vonhof, 1998, p. 19, for an ample discussion of these methods).

On the Noordwijk hole  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotopic analyses were done on the same shells as those used for the Strontium measurements. These measurements can provide information about the depositional environment of the assemblages.

Table 1. Strontium isotope ratio measurements on 24 samples from three boreholes in The Netherlands.  $^{87}\text{Sr}/^{86}\text{Sr}$  values are corrected to a NBS 987 standard value of 0.710257 or to a coral standard value of 0.709178. SE is Standard Error.

Hole Depth (m)	$^{87}\text{Sr}/^{86}\text{Sr}$	2xSE	Species
Noordwijk			
132.75	0.709081	11	<i>Arctica islandica</i>
133.75	0.709087	11	<i>Arctica islandica</i>
157.25	0.709059	9	<i>Arctica islandica</i>
179.25	0.709050	7	<i>Arctica islandica</i>
200.25	0.709053	8	<i>Macoma praetenuis</i>
218.25	0.709045	6	<i>Arctica islandica</i>
239.25	0.709079	13	<i>Arctica islandica</i>
255.25	0.709010	8	indet.
275.25	0.709035	10	<i>Arctica islandica</i>
304.60	0.709005	10	<i>Arctica islandica</i>
Zegveld			
165.50	0.709099	8	<i>Arctica islandica</i>
205.50	0.709086	6	<i>Arctica islandica</i>
220.50	0.709092	9	<i>Arctica islandica</i>
226.50	0.709084	6	<i>Arctica islandica</i>
256.50	0.709088	9	<i>Arctica islandica</i>
266.50	0.709190	11	<i>Arctica islandica</i>
271.50	0.709092	11	<i>Arctica islandica</i>
285.50	0.709123	10	<i>Arctica islandica</i>
Terschelling			
282.20	0.709176	7	<i>Arctica islandica</i>
318.70	0.709174	7	<i>Arctica islandica</i>
353.20	0.709221	5	<i>Arctica islandica</i>
383.70	0.709132	9	<i>Arctica islandica</i>
403.70	0.709146	8	<i>Arctica islandica</i>
427.30	0.709128	6	<i>Arctica islandica</i>

## Results

Figs 3-6 show the measured intervals of the three boreholes. Some of the ages calculated for the samples fall within the Strontium isotopic ratio 'platform' as defined by Beets (1992), Farrel et al. (1995) and others, which is a region in the Strontium isotope curve where the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is more or less constant. Beets (1992) defines this platform between ratios 0.709080 and 0.709050, which covers the period from 2.34 Ma to 4.43 Ma. These measurements are therefore considered less reliable for age dating, although they may still be used to provide a minimum age for the sample.

Fig. 3 ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measurements plotted against depth) shows that a linear trend in the measurements is only clearly present in Noordwijk, where Terschelling has a two-step trend. We ignored values that either obviously deviated from the trend or are outside the seawater range. For values within the ratio

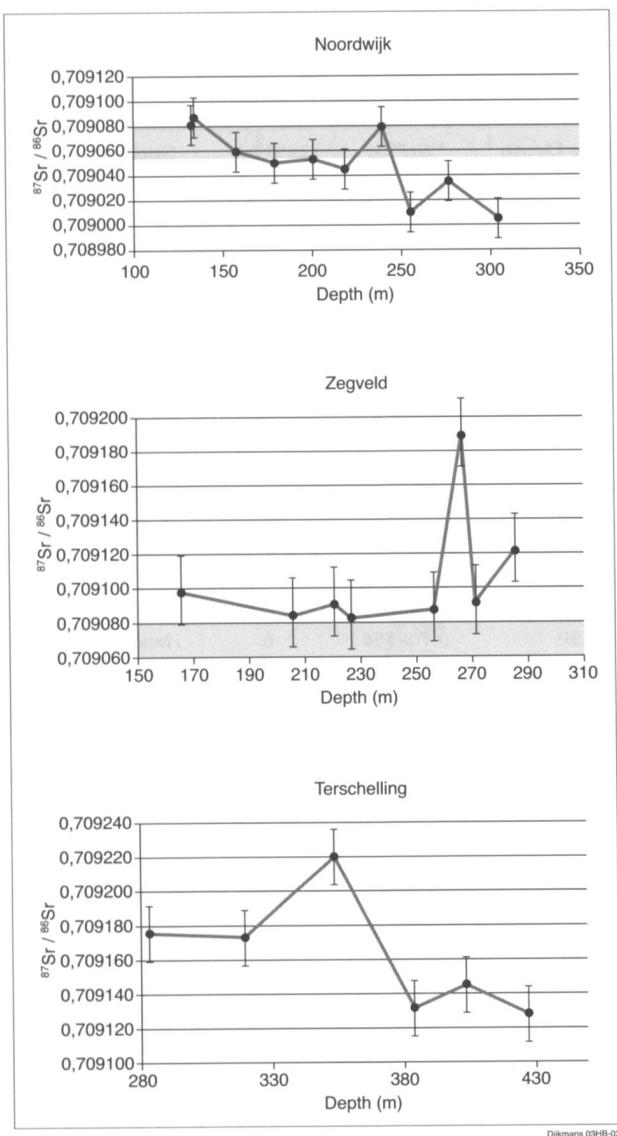


Fig. 3.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios versus depth of the three holes. The grey area represents Strontium ratio ‘platform’ values (see text). Note lack of downward trend in Zegveld and two-step trend in Terschelling. Also note differences in vertical scale.

platform the minimum value can be used.

#### Noordwijk

In borehole Noordwijk (Fig. 4) the lithostratigraphy left some doubt about the position of the base of the Maassluis Formation (Burger, 1998), so the sampling interval included the zone of uncertainty (222–283 m). Currently, NITG places the base at 239.75 m, based on the first downhole occurrence of glauconite in the sediment.

As shown in Fig. 3 and Fig. 4, the Strontium isotope ratios decrease gradually, if irregularly, downwards. The calculated Strontium ages at the top of the formation are around 2.0 Ma. Near the base of the

Maassluis Formation (239.25 m) the estimated Sr-isotope age is in the 2.34 to 4.43 Ma ‘platform’ age range, which gives a minimum age of 2.34 Ma ( $\pm 0.5$  Ma). However, at 218.25 m the Sr-isotope ratios suggest an age of 4.7 Ma, which would extend the age range of the Maassluis Formation well into the Early Pliocene.

Below this, in the Oosterhout Formation, the Strontium isotope ratio values suggest ages in the 4.8–5.2 Ma (Early Pliocene) range. Since these are in line with that at the base of the Maassluis Formation as currently defined in this hole, the Sr-isotope ratios of these sediments actually suggest that the base of the Maassluis Formation should be placed higher, around 200 m rather than at 239.75 m, possibly with a hiatus between the Maassluis and Oosterhout formations spanning about 2.2 Ma. There is a clear log break around 202 m, which separates a blocky (sand) log pattern above from three sand-clay gradations (Fig. 4) below.

Below 202 m, the isotope ages are at odds with the dinoflagellate (Munsterman, 1999), foraminiferal (Van Leeuwen, 1999) and mollusc (Meijer, oral communication) stratigraphy of this borehole. These suggest a Praetiglian to Tiglian-A position for the sediments from 307.10 m to 251.75 m (2 to 2.5 Ma), and Tiglian-B and -C (1.6 to 2 Ma) for the sediments from 244.75 m to 131.25 m (Fig. 4).

Munsterman (1999) mentions that the sediments from 307 m to 210 m were deposited under neritic conditions (outer neritic between 251–257 m) and arctic influence (peaking at 258–259 m), with both arctic and oceanic influences decreasing between 245 m and 210 m. This is in line with the  $\delta^{18}\text{O}$  isotopic data that suggest cold-water conditions in this interval (Fig. 4). As there has been arctic water (North Atlantic Deep Water) since the Late Miocene (Kennett, 1982, p. 737), finding a ‘cold’ signal in open and deep marine deposits on the northern hemisphere therefore does not automatically imply that the sediments are of Praetiglian (or younger) age. Only if established chrono-species ranges are used one can be confident about the biostratigraphic age estimate. The Strontium ratios in the Oosterhout/Maassluis formations of more locations will have to be measured to establish if there is a systematic difference between the age estimates of biostratigraphy and Strontium isotopes in these sediments. The data from our study indicates that this only occurs in the Noordwijk area.

River input influence on Strontium isotope ratios in these sediments is a possible alternative cause for these deviating values. Indeed, Kasse (1988) describes how the Rhine/Meuse River deposits are the lateral equivalent of the marine Oosterhout deposits

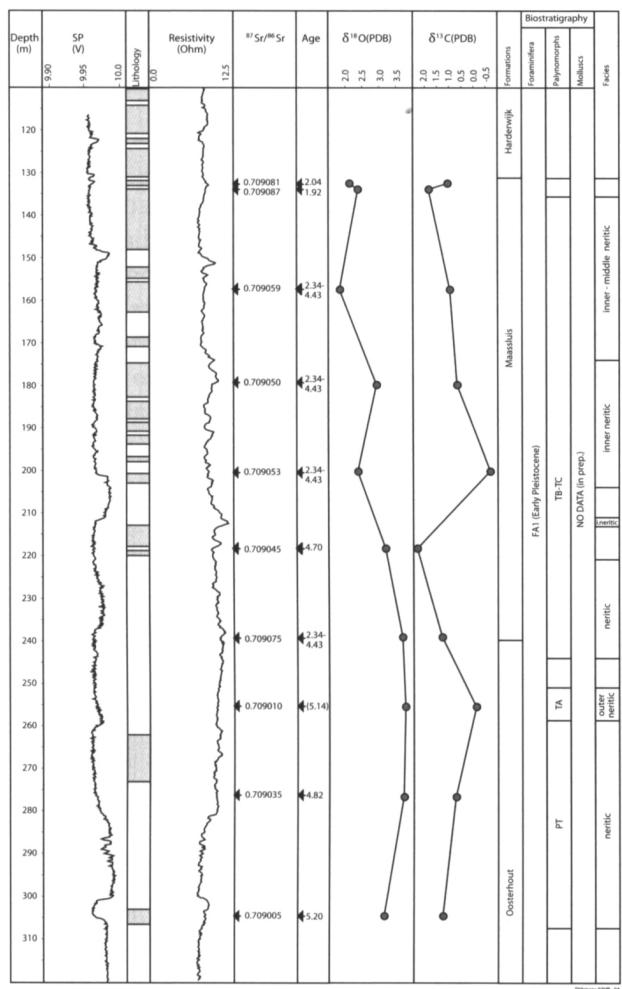


Fig. 4. Summary of the Noordwijk borehole data. Age estimates based on Strontium measurements calculated after Beets (1992). The schematic lithology is a summary of the detailed lithological description compiled by NITG: White intervals denote sandy and silty clay, grey intervals indicate sand.

during the Pliocene and Praetiglian without any substantial tidal deposits, characteristic of the rest of the Tiglian, between them. Burger (1998) mentions river influences in the interval from 213.75 m to 224.75 m, based on an increased proportion of ‘coarse-stable’ minerals. Thus river discharge might have directly influenced the marine realm, by providing Strontium to the system. However, the average modern rivers provide “high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio” Strontium (Beets, 1992). Since the Plio-/Pleistocene Rhine/Meuse had the same hinterland as the present system, we would expect this to lead to lower (‘younger’) age estimates for these sediments rather than the old ages we found. We would also expect a river discharge effect to be widespread, but actually it does not affect the nearby Zegveld location.

Diagenetic effects may have influenced our measurements through the upward movement of forma-

tion water, carrying ‘low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio’ Strontium to higher strata. This can lead to diagenetic alteration of the shell material in these higher strata to lower Sr-isotope ratios and consequently to age estimates which are too high. Since this effect is not recorded in the nearby Zegveld hole, it must be a local phenomenon, possibly related to fluid migration along a fault line.

### Zegveld

In Zegveld (Fig. 5), the age range for the Maassluis Formation suggested by the Sr-isotope ratios runs from about 1.70 Ma at the top to 1.90 Ma near the base, on average slightly younger than the Maassluis Formation in Noordwijk (2.0 to 2.34/4.43 Ma). The expected downward trend in the isotope ratio data is not very apparent (Fig. 3) and rather seems to hover around an average of 0.709090 (1.86 Ma). This suggests that these sediments have been deposited fairly rapidly in a short period of time, more rapidly than in the nearby Noordwijk hole.

The sampled interval lies in the FA1 foraminiferal zone (Van Leeuwen, 2000), which does not contradict the Strontium isotope ages. No palynological or mollusc data is available for this hole yet.

### Terschelling

In Terschelling (Fig. 3 and Fig. 6) the measurements near the top of the Maassluis Formation provide Strontium isotope ratios that are much too high. This has led to the two-step trend in the measurements, as shown in Fig. 3. The value at 353.20 m is even outside the range of Beets’ (1992) values for the 0 to 2.34 Ma age interval. The lower samples (383.7 m, 403.7 m and 427.3 m) suggest an age range between 0.82 Ma and 1.15 Ma for these sediments, which is in the Waalian to Menapian range (Fig. 7).

Herngreen (1997) correlated the dinoflagellate events in the interval from 355 to 435 m to the Tiglian A-C4b pollen zone (2 to 2.2 Ma) and from 467 to 552 m to the Praetiglian interval (2.2 to 2.5 Ma). Since he based his subdivision on well-dated dinoflagellate events, the Strontium isotope ratio values seem to be too young by at least 0.7 to 1.0 Ma.

These higher Strontium ratios in the samples may point to diagenesis in the shell material. Although river influence of the Baltic rivers could have contributed to the higher Sr-isotope ratios, unrealistically low salinities for the seawater would have to be assumed in order for binary mixing of river- and seawater to completely account for the deviating Sr-isotope ratios. Diagenesis of this type can occur through in-

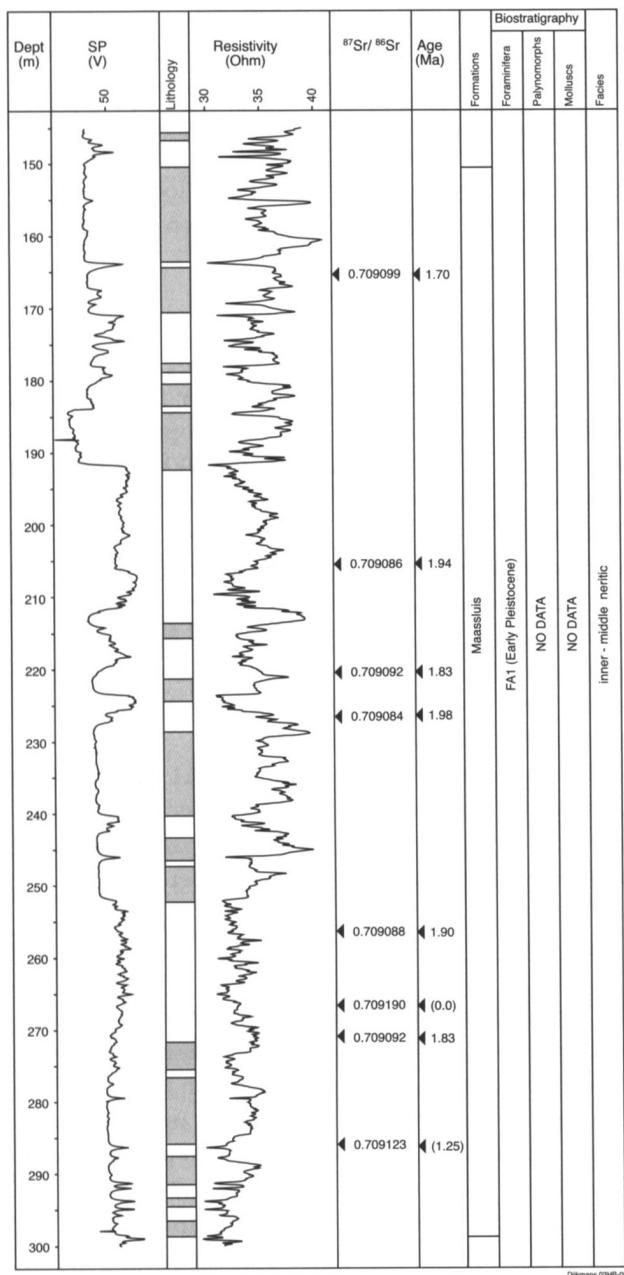


Fig. 5. Summary of the Zegveld borehole data. See Fig. 4 for explanation of lithology column.

roduction of fresh water down into older sediments under non-marine conditions.

## Conclusions

The ages obtained from the Strontium ratios of the Maassluis Formation in Noordwijk (RD X: 91520, Y: 471800) and Zegveld (X: 115382, Y: 460157) are consistent with the age estimates previously given for the formation on other locations (Van Montfrans, 1971). Most ages lie within the Tiglian and Praetigian intervals, the expected range.

The Sr-isotope age estimates for the base Maassluis

Formation and Oosterhout Formation in borehole Noordwijk indicate that these sediments are considerably older than earlier estimates based on biostratigraphic and environmental interpretations. The study of more locations will establish whether or not this is due to a local diagenetic effect.

At the Terschelling location, Sr-age estimates are consistently too young, which suggests diagenesis of the material and possibly introduction of high  $^{87}\text{Sr}/^{86}\text{Sr}$  into the system by the Baltic rivers.

The age discrepancies at the Terschelling and Noordwijk locations highlight the need to rigorously test for diagenetic changes in shell material with various methods in addition to visual inspection.

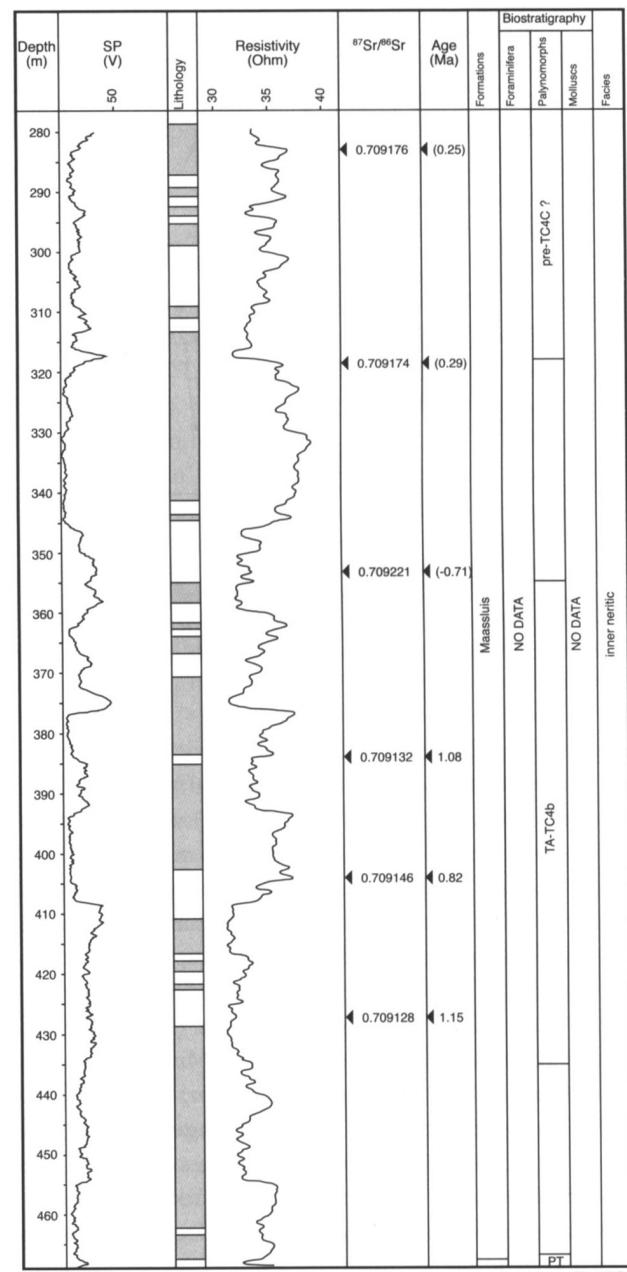


Fig. 6. Summary of the Terschelling borehole data. See Fig. 4 for explanation of lithology column.

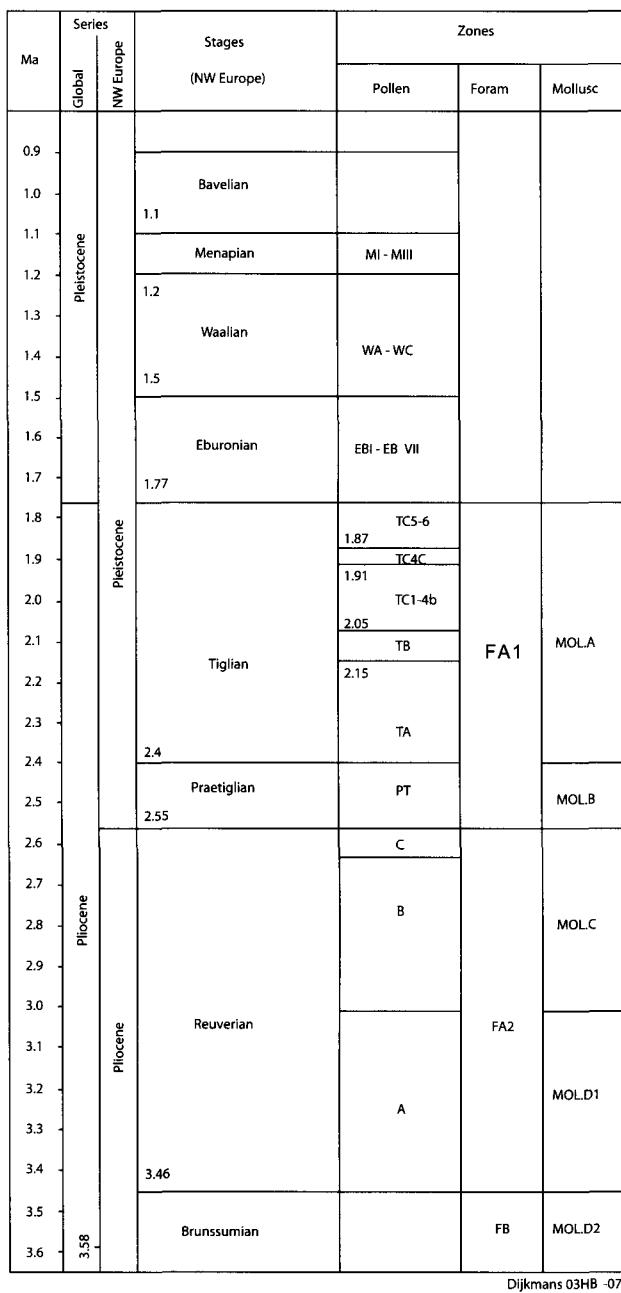


Fig. 7. Chronostratigraphy of the Pliocene/Pleistocene in The Netherlands (stages and zones after Zagwijn, 1975)

Strontium isotope ratios in the Pliocene and Lower Pleistocene shallow marine deposits of the Dutch onshore appear to be influenced by river discharge, and chronostratigraphy using these ratios should be undertaken with some trepidation in this type of sediments. As the discharge influence can be expected to lessen away from the coast it is advisable to extend the geographical spread of locations with Strontium isotope measurements on Maassluis Formation sediments (or equivalents) to the offshore Netherlands area.

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