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New constraints on the Eastern Mediterranean δ^{18}O:δD relationship

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Abstract

Previous work on oxygen and hydrogen isotope data from Eastern Mediterranean water samples has defined a mixing relationship in this region that is different from the world surface ocean. This prompted speculations about the hydrological processes in the Mediterranean region. We present new δ^{18}O and δD data from the Eastern Mediterranean region and the East Greenland Current system, spanning a wide salinity range. These data define δ^{18}O:δD relationships for both regions that are consistent with the world surface ocean δ^{18}O:δD relationship, despite the highly evaporative conditions that prevail in the Mediterranean region. These new geochemical data have suggested that the world surface ocean δ^{18}O:δD relationship holds throughout almost the entire global salinity range.

1 Introduction

The relationship between oxygen and hydrogen isotope ratios in the hydrological cycle is governed by the fractionation processes associated with evaporation and precipitation. Using data from a global survey of precipitation, continental runoff and polar meltwater, Craig (1961) defined a global meteoric water line (GMWL) as:

$$\delta\mathrm{D} = 8\delta^{18}\mathrm{O} + 10 \quad (1)$$

where δD and δ^{18}O are the conventional delta-notations for the ratios of D to ^{1}H and ^{18}O to ^{16}O, expressed as a per mil (‰) deviation from the international Vienna Standard Mean Ocean Water (VSMOW) reference standard.

Equilibrium fractionation of oxygen and hydrogen isotopes during evaporation and precipitation occurs proportionally with a factor of 8. The deuterium excess (d-excess), defined by $\delta\mathrm{D} - 8\delta^{18}\mathrm{O}$, occurs as a result of kinetic fractionation occurring in addition to equilibrium fractionation during evaporation. Kinetic fractionation, sometimes referred to as vapour-diffusion fractionation, occurs as a result of the differences between the

OSD
8, 39–53, 2011

molecular diffusivities of each of the isotope water species in air (e.g., Craig, 1961). The diffusion fractionation factor (and therefore the kinetic effect) for $H_2^{16}O$ relative to $HD^{16}O$ is not 8 times greater than that for $H_2^{16}O$ relative to $H_2^{18}O$, resulting in a relative excess of D, outside the factor of 8 relationship (e.g., Craig, 1961). Increased evaporation rates at higher atmospheric vapour pressures (high temperature or low relative humidity) will therefore result in a greater kinetic versus equilibrium fractionation and thus, higher *d*-excess values.

2 Oxygen and hydrogen isotopes in the surface ocean

In sea surface waters, the relationship between δD and δ^{18}O is similar to that of the meteoric water line:

$$\delta D = s\delta^{18}O + i \quad (2)$$

where s is the slope of the line (7.37 ± 0.17 based on a linear regression through world surface (upper 250 m) ocean data, Rohling, (2007); grey circles in Fig. 1), and i is the intercept. In the majority of the world surface ocean, i is much smaller than in the GMWL (-0.72 ± 0.97‰, Rohling, 2007; see also Schmidt et al., 1999; data originally reported by Duplessy, 1970; Weiss et al., 1979; Aharon and Chappell, 1986; Östlund et al., 1987; Yobbi, 1992; and Delaygue et al., 2001) (grey circles in Fig. 1). This world surface ocean δ^{18}O:δD relationship is isotopically shifted to heavier values relative to the GMWL (in that it lies to the right of the GMWL in δ^{18}O:δD space; see Fig. 1). Generally, the water input to the sea surface lies on the meteoric water line, however, evaporation from surface waters preferentially extracts the lighter isotopes leaving the sea surface isotopically heavy relative to the GMWL. The higher evaporation rates at low latitudes (Gat, 1996) results in a greater difference between the GMWL and the world surface ocean δ^{18}O:δD relationship at low latitudes relative to higher latitudes. This therefore accounts for the slightly shallower slope of the world surface ocean δ^{18}O:δD relationship relative to the GMWL. Laboratory experiments have shown that

OSD
8, 39–53, 2011

at 20 °C and varying humidity levels, the evaporation line has a slope of 4.34 (Cappa et al., 2003). Specifically, across the Mediterranean basin, the evaporation line ranges from 3.94 to 4.24 (Gat et al., 1996; hereafter G96).

3 Oxygen and hydrogen isotopes in the Eastern Mediterranean

In semi-enclosed basins, regional meteoric water lines exist, where the slope remains close to 8 but the intercept may be higher. For example, in the Eastern Mediterranean the intercept of the meteoric water line is reported to be close to 22 (Gat, 1996; Matthews et al., 2000; McGarry et al., 2004). The δ^{18}O:δD relationship of surface waters in highly evaporative regions, like the Mediterranean basin, might differ from the world surface ocean as a result of the increased kinetic fractionation during evaporation into dry continental air masses. G96 reported oxygen and hydrogen isotope data from Eastern Mediterranean surface waters that define a δ^{18}O:δD relationship that is considerably different from that of the world surface ocean. Their reported mixing line in δ^{18}O:δD space is nearly flat, whereby the δD values are almost constant over a 1‰ range of δ^{18}O and i has a value of 7.44‰ (grey triangles in Fig. 1). G96 postulate that such a relationship may have developed as a result of continuous evaporation and precipitation cycles in a warm atmosphere with low relative humidity.

Schmidt et al. (2007) used a coupled ocean-atmosphere model (GISS) to simulate the oxygen and hydrogen isotope distributions in the world ocean. This model, as any global model, does not have the resolution that would allow all of the regional aspects of the relevant hydrological processes to be resolved. The data from the GISS model do however give a sound indication of the water isotope distribution in the global ocean basins. The GISS modelled annual average δ^{18}O:δD relationship results are also shown in Fig. 1 (in blue). The model reproduces the world surface ocean observations well with respect to δ^{18}O and δD. However, there is a distinct discrepancy between the GISS modelled and the G96 d-excess values in the Eastern Mediterranean. Schmidt et al. (2007) originally suggested that this discrepancy might indicate that the model

OSD
8, 39–53, 2011

incorporates insufficient evaporation or too much mixing with non-Mediterranean air over the Eastern Mediterranean.

Here, we present new oxygen and hydrogen isotope data from water samples collected in the Eastern Mediterranean and at Cape Farewell, East Greenland (Fig. 2) Using these data compared to previously recorded data from the Eastern Mediterranean (G96) and the rest of the world surface ocean, we investigate the discrepancy between the observed and simulated δ^{18}O:δD relationship in the Eastern Mediterranean.

4 Data and methods

A total of 98 surface water samples were analyzed from the two cruises; 40 of the surface water samples were collected during the November–December 2001 RV *Meteor M51-3* cruise in the Eastern Mediterranean, and the remaining 58 were collected from across the East Greenland Current system during the August–September 2005 RRS Discovery D298 cruise at Cape Farewell (Fig. 2). Together, these sample sets cover a salinity range of 29.97 to 39.38 allowing the assessment of the δ^{18}O:δD relationship across a very wide oceanic salinity range. This allows us to verify internal consistencies in the δ^{18}O:δD relationships found, as well as relative to previously reported global data. Oxygen isotope ratios were analyzed on the samples using a dual inlet Finnigan MAT 251 light stable isotope ratio mass spectrometer following equilibration of 5 ml of sample with CO_2 for 10 h at 18.1 °C. The external precision for the oxygen isotope analyses is ± 0.10‰ (2σ). Hydrogen isotope ratios were analyzed on the samples by means of Cr-based pyrolysis of 0.2 µl of sample in a Eurovector 3000 elemental analyzer feeding into a continuous-flow GV Instruments Isoprime mass spectrometer. The external precision for the hydrogen isotope analyses is ± 1.25‰ (2σ). Three in-house water standards, which were previously calibrated against VSMOW2 (Vienna Mean Standard Ocean Water 2), SLAP2 (Standard Light Antarctic Precipitation 2) and GISP (Greenland Ice Sheet Precipitation) (IAEA, 2009), were analyzed in duplicate during each sample run in order to produce an offset correction regression to shift the

OSD
8, 39–53, 2011

isotope data to the VSMOW scale. All analyses were performed at the University of California, Davis and we have performed an inter-laboratory calibration between the National Oceanography Centre, Southampton and the University of California, Davis.

5 Results and discussion

Our data from Cape Farewell (hereafter D298) define a low salinity, high latitude mixing line with a slope and intercept of 7.59 ± 0.27 and -0.48 ± 0.27‰, respectively (where uncertainty limits represent 95% confidence intervals; r^2=0.98), which are consistent with the rest of the world surface ocean data (black squares in Fig. 1). Our new data from the Eastern Mediterranean (hereafter M51-3) do not reproduce the unusual δ^{18}O:δD relationship reported by G96. Instead, we find a high-salinity mixing line with a slope and intercept of 6.99 ± 0.82 and 0.31 ± 1.11‰, respectively (r^2=0.89), which agree well with the rest of the world surface ocean data (black crosses in Fig. 1). Our new data from both low salinity and high salinity regions indicate that the previously observed world surface ocean δ^{18}O:δD relationship holds well throughout this salinity range. The G96 mixing line for Eastern Mediterranean surface waters therefore stands out as a distinct anomaly relative to both the new data presented here, and the previously published data from the rest of the world (Fig. 1). Direct comparison of the annual average GISS data from East Greenland and the Mediterranean with our data from these regions shows that the mixing relationships are similar, however, the modelled isotope ratios are more enriched in ^{18}O and D than is observed in both regions (Fig. 1). Therefore, the anomalous, nearly flat δ^{18}O:δD relationship found in the Mediterranean (G96) has not been reproduced in either our new isotope data or in the GISS model data from that region. Our new data from the Mediterranean, therefore, suggest that the GISS model is in much better agreement with waters from this region than was previously thought, and that the discrepancy may be with the G96 dataset.

OSD
8, 39–53, 2011

The spatial distributions of salinity, δ^{18}O and δD values from the G96 and M51-3 datasets across the Eastern Mediterranean are shown in Fig. 3. The salinity values from the M51-3 dataset increase from 38 in the west to 39 in the east. The M51-3 δ^{18}O and δD data also increase from west to east, similar to the salinity distribution over the basin. This is as expected because these parameters in the surface waters are determined by the same processes. The G96 salinity values are at a maximum northeast of Crete and decrease northwards and eastwards. The G96 δ^{18}O values broadly increase eastwards with a maximum north of Crete. However the G96 δD values decrease eastwards to a minimum in the Easternmost Mediterranean. Therefore, the G96 salinity and isotope distributions are very different from that found in the M51-3 data and the Schmidt et al. (2007) model data. The M51-3 water samples were collected at similar depths and locations to the G96 samples (Fig. 2). The M51-3 samples were collected in autumn 2001, while the G96 samples were collected in both summer-winter 1988/89. These spatial and temporal similarities in sample collection indicate that depth, location and seasonal difference cannot explain the disparity between the two datasets in a straightforward manner. Furthermore, the similarity in salinities indicates that the disparity cannot be explained in terms of a difference in overall evaporation and precipitation either.

We infer that the drivers of the Mediterranean δ^{18}O:δD relationship are similar to those controlling the global surface ocean δ^{18}O:δD relationship. However, the Mediterranean meteoric water line has a slope and intercept of 8 and 22‰, respectively (Gat, 1996; Matthews et al., 2000; McGarry et al., 2004). Therefore, evaporation from the Mediterranean surface water will shift the surface water mixing line, along the local evaporation line (that has a slope of approximately 4; see Fig. 1; G96), to higher δ^{18}O and δD values while retaining the same slope. The slightly shallower slope of 6.80 that we observe in the Mediterranean surface waters likely results from higher evaporation rates in the Eastern Mediterranean relative to the west, thereby, shifting the higher salinity watermasses to slightly higher isotopic values.

OSD
8, 39–53, 2011

6 Conclusions

We conclude that, in light of the new Eastern Mediterranean data, there would seem to be no anomalous behaviour of the δ^{18}O:δD relationship for Mediterranean surface waters, contrary to the findings of G96. The Mediterranean surface water δ^{18}O:δD mixing line instead remains consistent with the world surface ocean mixing line at the higher salinity end and our understanding of isotopic processes, despite the highly evaporative nature of the region. The new Eastern Mediterranean δ^{18}O data presented here have very slightly lower values than the previously obtained values, suggesting that the Eastern Mediterranean Transient (EMT) of the late 80s to early 90s impacted the distribution of δ^{18}O in the Eastern Mediterranean basin (see appendix).

We have added 98 new δ^{18}O:δD data points to the original world total of 244 (Schmidt et al., 1999) and the new Mediterranean δ^{18}O:δD data together with that from the East Greenland Current verifies that the world surface ocean relationship holds throughout most of the global oceanic salinity range, therefore affirming this as the global surface ocean δ^{18}O:δD relationship. Given the agreement of our new data across the salinity range with previous global data, as well as with the GISS model output, we contend that there may have been issues with the isotope measurements of G96.

Appendix A

We note that our new Mediterranean δ^{18}O values are consistent with δ^{18}O values of surface water samples collected in this region in 1995 (Gat et al., 2003). However, these new data are ~ 0.3‰ lower than those of G96 and compared to the δ^{18}O data of Pierre et al. (1986) and Pierre (1999) (collected 1986–1990), our new Mediterranean data are also ~0.2‰ lower (see Fig. 4). We suggest that the shift to slightly lower δ^{18}O values in this region may have resulted from the EMT, which occurred between 1987 and 1995 (e.g., Roether et al., 1996; Klein et al., 1999). During the EMT, deep-water

OSD
8, 39–53, 2011

intrusion of Aegean waters, previously prevented by the admixture of lower density water during outflow, caused a basin-wide redistribution of salinity, temperature and nutrient concentrations (Roether et al., 1996; Klein et al., 1999; Malanotte-Rizzoli et al., 1999). These changes persisted for at least a decade (Theocharis et al., 2002). If the EMT also caused a shift in δ^{18}O values and not in salinity then that suggests a change in the freshwater source rather than a change in the amount of freshwater addition to the basin. The major rivers feeding the Black Sea, and therefore the Aegean surface waters, have higher latitude catchment areas (for example the river Danube that flows from Germany to the Black Sea) than the rivers that flow directly into the Eastern Mediterranean (for example from Turkey or Egypt). These higher latitude source rivers contribute freshwater with lower δ^{18}O values (e.g., Rank et al., 1999) to the Black Sea and the exchange of surface waters between the Black Sea and the Aegean Sea then results in a surface freshwater admixture with a relatively low δ^{18}O signature in the Aegean. Additionally, the M51-3 data points in Fig. 4 from a greater depth (100 m) indicate that these waters in the Eastern Mediterranean basin have the same salinity: δ^{18}O character as the surface waters. This is not true of the values portrayed by Pierre et al. (1986) and Pierre (1999) and G96, whereby the deeper water samples define a different salinity: δ^{18}O relationship relative to the surface samples (Fig. 4), supporting our hypothesis that the EMT has influenced δ^{18}O distribution in the Mediterranean Sea. Therefore, during the EMT, when these waters penetrated and filled the deep Mediterranean, there was, not only a redistribution of salinity, but also waters with a potentially lower δ^{18}O signature were introduced into the Eastern Mediterranean Basin.

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OSD
8, 39–53, 2011

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OSD
8, 39–53, 2011

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OSD
8, 39–53, 2011

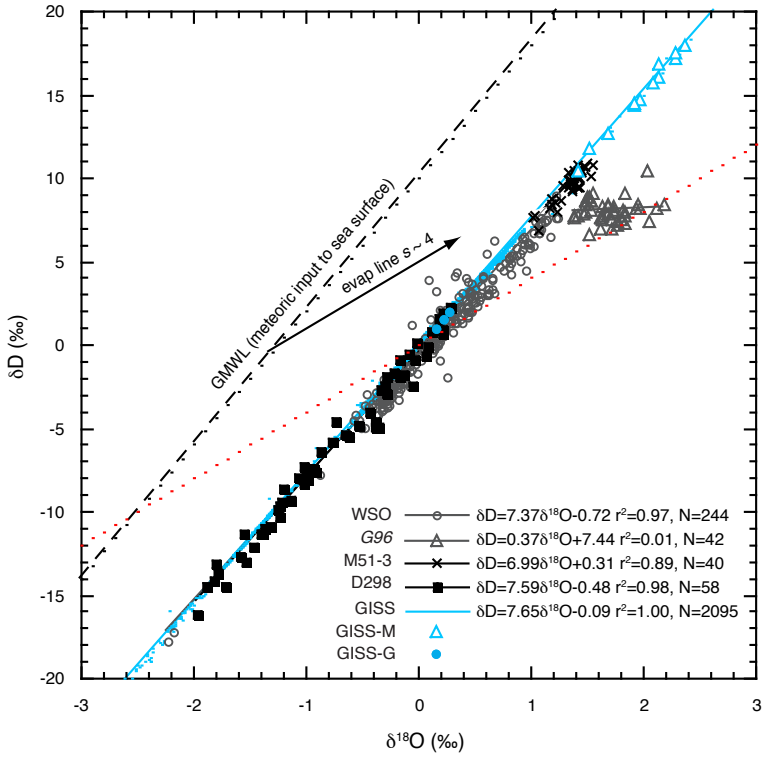

Fig. 1. The δ^{18}O:δD mixing relationships, from top to bottom in the legend: the modern world surface (upper 250 m) ocean (WSO) (from Schmidt et al., 1999, originally reported by Duplessy, 1970; Weiss et al., 1979; Aharon and Chappell, 1986; Östlund et al., 1987; Yobbi, 1992; and Delaygue et al., 2001), the G96 Mediterranean dataset, the M51-3 Mediterranean dataset, the D298 Cape Farewell dataset, the complete GISS model data mixing relationship (Schmidt et al., 2007), the GISS model results from the Mediterranean (GISS-M) (Schmidt et al., 2007) and the GISS model results from the East Greenland region (GISS-G) (Schmidt et al., 2007). The GMWL and an example evaporation line are also plotted.

OSD
8, 39–53, 2011

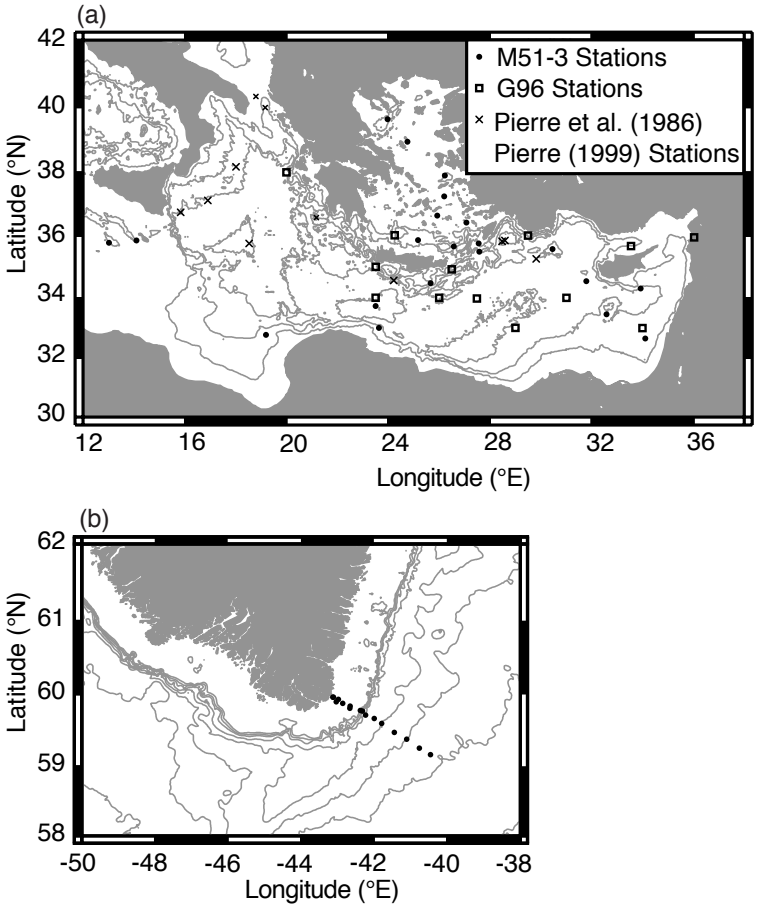

Fig. 2. Maps of the oxygen and hydrogen isotope data station locations for RV Meteor cruise M51-3, Pierre et al. (1986), Pierre (1999) and G96 **(a)** and the RRS Discovery cruise D298 **(b)**.

OSD
8, 39–53, 2011

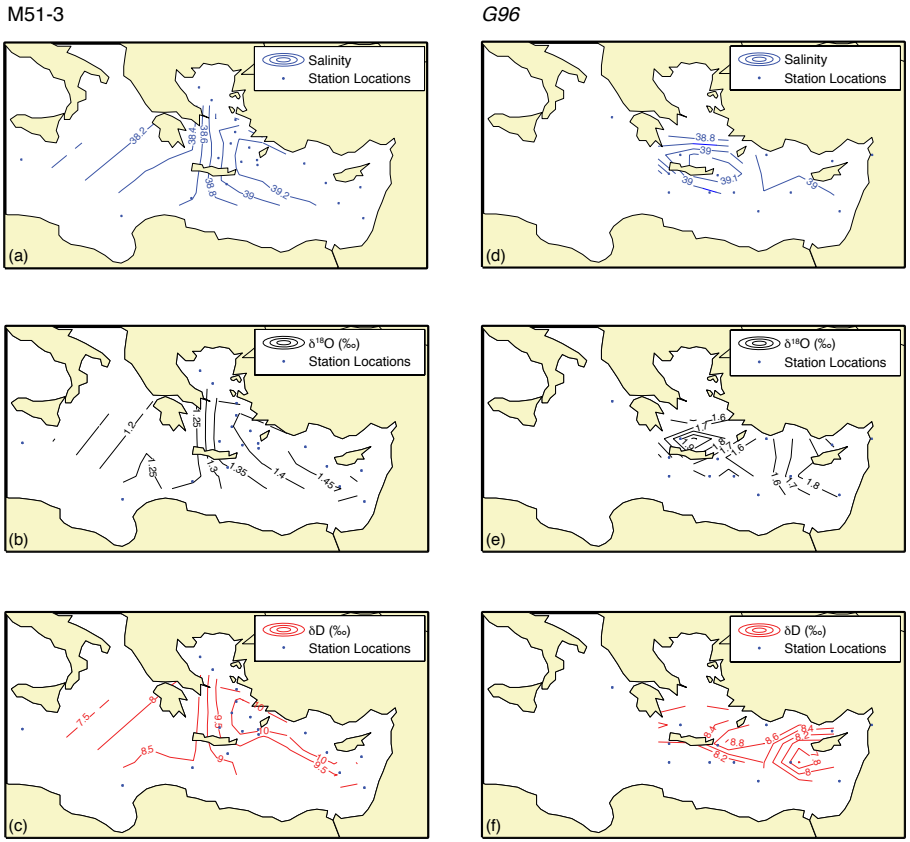

Fig. 3. Salinity, δ^{18}O and δD and distribution maps of the M51-3 data (**a**, **b**, and **c**) and the G96 data (**d**, **e** and **f**).

OSD
8, 39–53, 2011

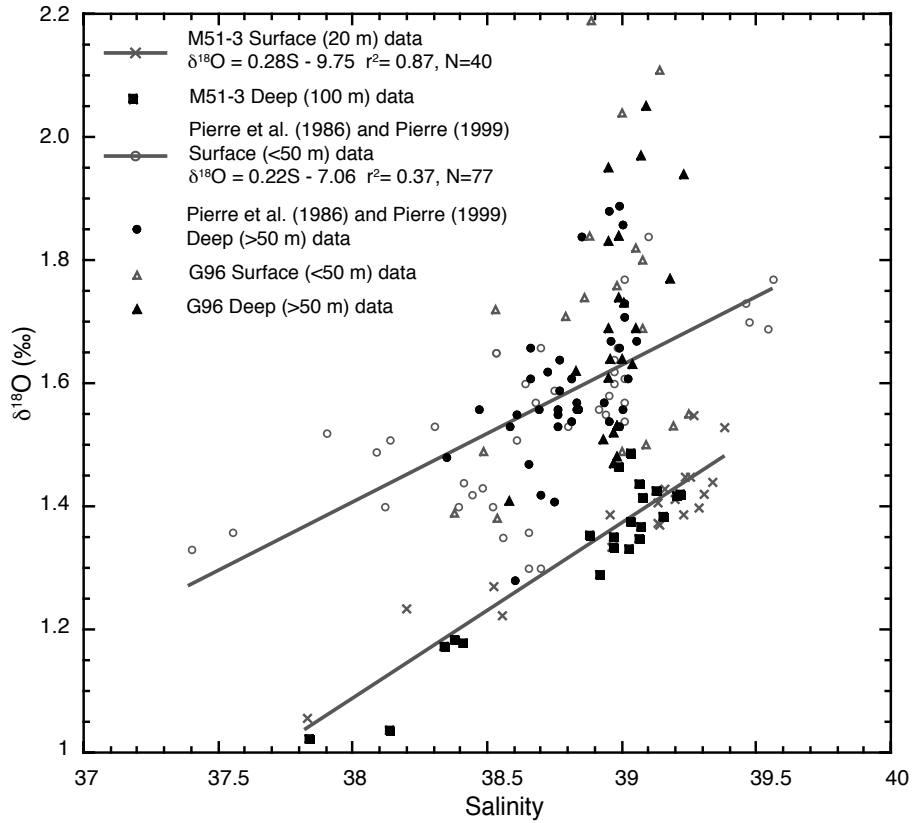

Fig. 4. Salinity:δ^{18}O plot of M51-3 data (crosses and squares) compared with Pierre et al. (1986), Pierre (1999) (circles) and G96 (triangles). Grey data points denote surface water samples and black data points denote deep water samples.

OSD
8, 39–53, 2011