APPENDIX

COMPARISON OF SHIPBOARD POROSITY VALUES USING OVEN- AND FREEZE-DRYING TECHNIQUES: SITES 1039, 1040, AND 1043[1, 2, 3, 4]

ABSTRACT

Shipboard porosity measurement is routinely carried out by drying small masses of core sediment for 24 hr at an oven temperature of 105°C. This drying procedure is used even though oven heating can drive off interlayered water from clay minerals, in particular smectite. Oven heating can thus result in a weight-loss–based calculation of intergranular porosity that is both incorrect and higher than in situ values.

An alternative drying method is to desiccate discrete sediment samples by freeze drying. Freeze drying involves placing a water-saturated sediment sample in a vacuum chamber. Exceptionally low vapor pressure (5–10 µm of Hg) maintained over the samples evaporates intergranular pore water at freezing temperatures. Evaporative drying can also liberate interlayered water. An experiment was therefore run to determine whether similar or different porosity values resulted from oven and freeze drying of closely adjacent (1–2 cm) samples of sediment collected from cores recovered at Ocean Drilling Program Leg 170 Sites 1039 and 1040, and also the upper part of Site 1043, all of which cored continental margin terrigenous and oceanic pelagic deposits. This report only considers experimental results from Sites 1039 and 1040 core samples.

Porosity data were gathered for 137 pairs of sediment samples, 85% of which (117) record an oven-dried porosity value exceeding that of the companion freeze-dried sample. The mean porosity of oven-dried samples is 1.9 porosity units greater than the freeze-dried pair (67.1% vs. 65.2%, respectively). For deposits rich in terrigenous debris (upper sections at both Sites 1039 and 1040), the mean porosity contrast increases to 2.4 porosity units. The terrigenous slope sequence drilled at Site 1040 is characterized by a porosity contrast of 2.8 porosity units. Larger samples of sediment judged to be enriched in clay minerals also display high contrast in porosity values. Conversely, oceanic pelagic and hemipelagic beds recovered at both Sites 1039 and 1040 exhibit a porosity contrast of oven dried vs. freeze dried of only ~0.75 porosity units. No differences were recorded between oven- and freeze-dried samples of artificial sediment (glass beads and seawater) that lack a clay mineral content.

From a comparison of porosity contrast with sample size (water-saturated mass) and sediment composition, greater water release was recorded by oven drying of larger samples of terrigenous-rich deposits, and by terrigenous-rich sediment with respect to pelagic deposits of biogenic debris. Most likely, the difference is tied to both the presence and abundance of clay minerals.

A remaining issue is the removal of interlayered water by the low vapor-pressure environment of freeze-drying cambers. With respect to freeze drying, data gathered on Leg 170 sediment establish that oven drying more aggressively (i.e., completely) evaporates interlayered water. Additional experimentation is needed (or perhaps exists) to thoroughly address this matter and explore the nature and magnitude of incorrect high-porosity measurements that result from rapid drying of ocean-floor–sediment samples by practical laboratory procedures, including by microwave radiation.

Based on Leg 170 shipboard findings, it is recommended that (1) Leg 170 experimental results be compared with the clay mineral compositions of Site 1039 and 1040 sediment; (2) companion oven- and freeze-drying experiments be carried out during other ODP legs where sediment types differ from those collected during Leg 170; (3) companion shore-based laboratory and theoretical studies of sediment desiccation be initiated; and (4) a modern, relatively large-capacity, freeze-drying apparatus that can sustain an operating vacuum of at least 10 µm Hg be placed in the Core Lab to continue shipboard experimentation for the purpose of providing a method that may more accurately and speedily measure intergranular porosity, in particular for sediment that is rich in clay minerals.

INTRODUCTION

During shipboard planning for the collection of Ocean Drilling Program Leg 170 data, concerns were raised that oven drying of sediment samples, which is routinely employed to measure index physical properties, would result in the calculation of incorrect porosity values. Oven drying of sediment samples for 24 hr at 105°C is known to liberate weakly bound interlayered water from clay minerals. Because the weight loss through sediment drying is converted to the volume of pore water originally present, the vaporization of interlayered water results in a calculated porosity that is higher than the correct values. Other index property values are also affected, for example grain density. Brown and Ransom (1996) discuss this matter and link the measurement of incorrectly high-porosity values to the abundance of smectite.

A major goal of Leg 170 science was the quantitative determination of the volume of interstitial water expelled by sediment compaction, both caused by gravitational loading and subhorizontal tectonic stresses arising from accretionary processes. Because sediments recovered at Leg 170 sites were expected to be relatively rich in clay minerals, an experiment was designed to contrast porosity measurements determined by oven desiccation with those derived from freeze drying, a technique thought to be less extractive of interlayered water.

The experiment addressed three questions:

1. Does oven-drying desiccation of sediment samples lead to higher porosity values than those resulting from freeze drying?
2. Are the oven- and freeze-drying techniques equally effective in removing available interstitial moisture from water-saturated sediment samples?
3. Can observed porosity differences be linked to the likely presence and abundance of clay minerals?

EXPERIMENTAL APPROACH

Five procedural and measurement components were involved in the drying porosity experiment: (1) selection of closely adjacent samples of core sediment for separate determination of porosity via oven- and freeze-drying desiccation; (2) determination of time/weight-loss drying curves for oven- and freeze-dried samples; (3) determination of the sensitivity of porosity change to incomplete or excessive (i.e., extraction of interlayered water) drying; (4) measurement by both drying methods of the physical properties of water-saturated samples of artificial sediment lacking clay minerals; and (5) analysis of results.

SAMPLING STRATEGY AND SITE STRATIGRAPHY

Site 1039

Routinely, closely adjacent (~1–2 cm apart) samples of core sediment, ~8–10 g in wet bulk mass, were collected from split core sections. One of the paired samples (Sample 1) was oven dried, and the other (Sample 2) was desiccated by freeze drying.

Two sample pairs were collected for each core section for the 28-m-thick sequence of trench-floor deposits penetrated at Site 1039A. At adjacent Hole 1039B, two sample pairs were gathered per section only above the middle of Core 170-1039B-5H (40 mbsf). Because of a limited through-put capacity of the freeze-drying equipment (mainly used by the chemistry lab), below this depth the sampling density was reduced to one pair per core. Sediments from Hole 1039A and the upper part of Hole 1039B were thus the most densely sampled of all Leg 170 cores.

Hole 1039A recovered a sequence of diatom ooze and interbedded ash that, in the upper 5 m, included turbidite beds. The upper part of Hole 1039B consists of diatom ooze and ash to ~85 mbsf, silty clay with ash to ~133 mbsf, siliceous and calcareous clay to ~180 mbsf, calcareous ooze (nannofossils) to ~350 mbsf, and calcareous ooze and microbreccia to ~424 mbsf, the base of the stratigraphic section overlying a gabbro sill. The porosity of the section drilled at Hole 1039B is generally high, 75%–70% in diatom ooze and silty clay above the calcareous section (180 mbsf), and ~65% within the chalk section below this depth.

Sampling positions and oven- and freeze-dried porosity values for the entire stratigraphic sequence sampled at Site 1039 are displayed in Figure 1. Data for the more densely sampled upper 50 m of Holes 1039A and 1039B are placed in Figure 2. Tabulated data (Appendix Tables 2–4) for Site 1039 are found on CD-ROM (back pocket, this volume).

Site 1040

The sedimentary sequence cored at Site 1040 is a 371-m-thick section of terrigenous silty clay and clayey silt that structurally overlies the stratigraphically equivalent section of pelagic and hemipelagic deposits penetrated at Site 1039. The structural contact, a décollement, separates continental slope deposits of the upper plate from an underthrusting oceanic section.

Sampling for porosity comparison was limited, typically, to the collection of one closely adjacent pair from each core. Porosity values for the silt and

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Previous Chapter Table of Contents

clay sediment of the slope deposits range from about 40% to 60%. Porosity in the underlying ocean pelagic beds is higher, ranging from 55% to 70%.

Sampling positions and oven- and freeze-dried porosity pairs for the stratigraphic sequence penetrated at Site 1040 are presented in Figure 3. The full data set for Sites 1039 and 1040 are displayed in Figure 4. Tabulated data (Appendix Tables 5–7) for Site 1040 are found on CD-ROM (back pocket, this volume).

DRYING CURVES

Comparative analyses of porosity values require that water extraction by oven and freeze drying is carried out to completion. To assess the thoroughness of moisture extraction, weight change with progressive drying time at 105°C was monitored. Low-temperature drying, at 60°C, of Site 1039 and 1040 sediments was also monitored. Weight stability was not reached after 41 hr of oven drying. These samples continued to lose weight, as much as 0.5 g, when subjected to freeze drying for an additional 18 hr. Low-temperature drying, perhaps not a time-practical method for shipboard operations, may nonetheless remove less interlayered water and thus provide a more accurate determination of intergranular porosity. Corresponding time/weight-loss curves for oven- and freeze-dried control samples are displayed in Figures 5 and 6.

Figure 5 compares oven drying with freeze drying carried out in a large drying chamber holding as many as 30–40 samples. A similar number of samples were simultaneously dried in the oven. Under these conditions weight stability (+0.02 g about a mean value) for oven-drying samples is reached in about 12 hr, whereas freezing drying of multiple samples in a large vacuum chamber requires at least 22 hr. However, because of degraded equipment performance, a drying vacuum of only 100 µm (Hg) could be sustained, whereas the optimal vacuum for freeze-drying samples is nearly 15 times lower (i.e., 5–10 µm Hg). This circumstance contributed to the longer time required to desiccate sediment samples by freeze drying. Under the same pressure conditions (100 µm Hg), samples placed in small freeze-drying chambers, which can hold only three, 10-cm^3 volume beakers, achieved weight stability within 8 hr (Fig. 6).

Theoretical considerations predict that drying pressures of 100 µm can never remove the same amount of water as can be achieved at 5–10 µm. It was presumed, based on the results of freeze-drying non–clay-bearing artificial sediment (see below), that the bulk of potentially remaining moisture from core sediment was interlayered water rather than aqueous pore fluid. The degraded performance of the vacuum pump leaves open the question as to whether freeze drying at 5–10 µm Hg would have removed a mass of interlayered water equivalent to that liberated by oven drying.

SENSITIVITY OF POROSITY VALUES TO INCOMPLETE OR EXCESSIVE DRYING

Sediment cored at Sites 1039 and 1040 range in porosity from ~42% to 81%. The mean porosity of the sample pairs for oven and freeze drying is 67%. If water available for evaporation is not fully removed by either of the drying processes, then the calculated porosity will be commensurably lower. For example, sediment with a mean porosity of 73% will have mean porosity errors of 0.4, 1.7, and 3.2 porosity units, respectively, for water retention of 0.2, 0.5, and 1.0 g (Fig. 7). The mean mass of water evaporated from all dried samples is 5.7 g (range = 2.8–7.1 g). Hence, with respect to this value, the mass of water retained for the porosity errors noted above is, respectively 3.5%, 8.7%, and 17.5% of that originally available. Similar relations attend excessively dried samples that lost interlayered water.

PHYSICAL PROPERTIES OF ARTIFICIAL SEDIMENT

An attempt was made to eliminate the potential contribution of interlayered water in clay minerals to oven- and freeze-dried–based porosity calculations. Three paired samples of artificial sediment were prepared by inoculating 10.00 g of small glass beads (each ~1 mm in diameter and 3–4 mg in weight) with 3 cm^3 of seawater (measured salinity of 38). The pairs were oven and freeze dried, and their corresponding porosity and grain density calculated with the same equations used to determined these properties for "natural" sediment samples. The experimentally determined results are listed below in Table 1, including the expected values based on the measured volume and mass of the components combined to make the artificial sediment:

ANALYSIS OF RESULTS

Figures 1–3 graphically demonstrate that porosity values based on oven-drying weight loss are characteristically higher (117 examples out of 137 pairs) than those based on freeze drying at a vacuum pressure of ~100-µm Hg. The histogram of Figure 8 shows that for the 137 pairs measured, the mean porosity of oven-dried samples exceeds the mean of freeze-dried specimens by 1.9%. If this difference is a function of incomplete water extraction from freeze-dried samples, excessive desiccation of oven-dried samples, or a combination of these possibilities, then the relations plotted in Figure 7 identifies the amount of water as roughly 0.55 g, which is ~10% of the mean mass of water (5.7 g) actually extracted. Based on the drying curves of Figures 5 and 6, retention of 0.25–0.5 g of available pore water is unlikely for the freeze-dried samples.

The virtual identical laboratory-measured and predicted values of porosity and grain density of artificial sediment (Table 1) document that accurate measurement of the index properties of sediment lacking clay minerals is not affected by contrasting oven- and freeze-drying desiccation procedures in themselves. This assessment bolsters the notion that the nearly 2% higher porosity values for oven-dried samples does not reflect a systematic incomplete evaporation of interstitial water by freeze drying, despite the less than ideal drying vacuum (100 actual vs. 5–10 µm Hg preferred). This statement does not apply to a potential differential retention of oven- vs. freeze-dried interlayered water.

The issue of water retention was also addressed by inspecting porosity contrast with respect to sample size. Samples of wet mass less than about 12 g show little difference in the distribution of positive (i.e. oven-dried > freeze-dried porosity) and negative porosity contrast (Fig. 9). However, for larger samples, only porosity pairs with higher oven-dried values were recorded. Most of these larger samples are from the slope-mantling deposits penetrated at Site 1040, beds that are dominantly terrigenous silty clay and clayey silt and presumably have an enriched clay-mineral content (see Group 1 sediment, below, and Fig. 10). The relatively higher oven-dried porosity of these larger sediment samples may reflect the presence of larger amounts of interlayered water available for evaporation. Preliminary analysis of shipboard XRD records imply that the clay mineral component is dominantly a mixed chlorite/smectite assemblage.

The determined porosity contrast was also analyzed with respect to lithotype. Figure 11 displays the depth distribution of porosity contrast for Site 1039 and 1040 sample pairs. Higher porosity contrasts of oven-dried samples over freeze-dried samples are more characteristic of the upper ~380 m of the combined sections than below this depth. The upper ~180 m of section at Site 1039 and the upper ~425 m of Site 1040 contain common to abundant clay-size material of probable terrigenous origin, whereas the sections below these respective depths are dominantly hemipelagic and biogenic ooze and, in particular, chalk. The magnitude of the porosity difference and the concentration of higher amplitude differences in the upper sections of both sites are consistent with a suspected upsection enrichment in clay mineral content.

A further test of this possibility was made by plotting the porosity contrast of sample pairs with respect to their basic lithology, which also serves to group them according to depositional environment. Group 1 deposits are terrigenous silty clay and clayey silt deposits of the slope mantling unit drilled at Site 1040 (0–371 mbsf, Unit P1). Sediment assembled into Group 2 are silty, clayey, and diatom ooze that underlie the upper 85 m of the trench-floor section drilled at Site 1039 (Unit U1), and the upper ~50 m (371–422 mbsf, Unit U1) of the underthrusting oceanic section at Site 1040. The underlying clayey and silty beds (Unit U2 at Sites 1039 and 1040) are assembled into Group 3. Older Group 4 sediment are Unit U3 deposits of siliceous nannofossil-rich carbonate or chalk beds and underlying calcareous diatomaceous ooze sequences cored at Sites 1039 and 1040.

With respect to depositional environment,

1. Group 1 sediment is ashy continental slope deposits of terrigenous nature.
2. Group 2 sediment is ash-bearing oceanic pelagic and terrigenous to hemipelagic beds deposited in a trench-proximal setting at the base of the continental slope.
3. Group 3 sediment is hemipelagic to pelagic beds that accumulated in a oceanic setting at some distant seaward of the trench.
4. Group 4 sediment is pelagic biogenic debris that accumulated in an open oceanic environment.

Figure 10 plots these lithostratigraphic depositional groups with respect to the porosity contrast (difference) of oven-dried and freeze-dried pairs. The ashy terrigenous beds of the slope deposits of Group 1 exhibit the highest contrast and the greatest spread in porosity values. The diatom-rich, ash-bearing,

clayey and silty beds of Group 2 are only slightly less contrasting in porosity difference and range. Group 3 and 4 deposits of the oceanic realm are much less contrasting in porosity values.

When grouped as explained above, the mean porosity difference between oven- and freeze-dried pairs is

Group 1 = +2.8% porosity units,
Group 2 = +2.2% porosity units,
Group 3 = +0.8% porosity units, and
Group 4 = +0.7% porosity units.

Taken together, the mean porosity difference for the more clay-mineral– and ash-rich deposits of Groups 1 and 2 is +2.4% porosity units, a value ~25% higher than the mean +1.9 greater porosity value for all oven-dried samples with respect to their freeze-dried pair.

A FINAL EXPERIMENT AT SITE 1043

Group 1 sediments were also cored at Site 1043, positioned at the base of the landward trench slope, which penetrated the clayey slope mantling unit (Group 1) and pelagic-rich oceanic section underthrusting the margin. Cores were collected to a depth of 282 mbsf, but 34 sample pairs for oven- and freeze-drying comparison were only gathered from the slope mantling unit of ashy silty clay and breccia (Unit T1), which extends to a depth of ~151 mbsf.

The mean difference in oven-dried vs freeze-dried porosity of closely adjacent sediment pairs was determined to be +1.6% units (i.e., the mean oven-dried porosity is 1.6 units greater than mean freeze-dried porosity). However, Figure 12 demonstrates that the bulk of sample pairs establishing this differential were recovered in the upper 70–80 mbsf. Magnetic susceptibility (MST) measurements and visual descriptions (see "Site 1043" chapter text and Fig. 1, this volume) establish that the upper 75 m of Unit T1 is rich in ash deposits. Presumably, the upper part of Unit T1, which is dominated by higher porosity readings for oven-dried samples, may be a manifestation of the abundance of ash. Ash debris is generally abundant in Group 1 and Group 2 sediment, a circumstance that probably contributes to the characteristically higher oven-dried–based porosity values from these sediment types (Fig. 10). Tabulated data (Appendix Table 8) for Site 1043 are found on CD-ROM (back pocket, this volume).

CONCLUSIONS AND RECOMMENDATIONS

The mean laboratory measured porosity of oven-dried samples from Site 1039 and 1040 cores are nearly 2 percentage units higher than the mean of freeze-dried samples. For supposedly clay-rich deposits of Group 1 and 2 sediments, the contrast is 2.4%, and for the terrigenous slope sediment of Group 1 strata, the porosity contrast increases to 2.8%. No difference was found in the ability of oven and freeze drying to completely evaporate intergranular water. The tendency for higher porosity contrasts to be linked to suspected clay-rich deposits and also to higher mass weight samples, supports the notion that higher oven-dried porosity values can be attributed to the release of interlayered clay water (Brown and Ransom, 1996), provided the less than ideal vacuum-drying pressure was not a significant factor.

The results of the porosity experiment run on Leg 170 samples brings forward the following recommendations with respect to follow-up shore-based laboratory studies and shipboard equipment installation and procedures:

1. Shore-based laboratory work should be carried out to determine the clay-mineral composition, ash content, and composition of Leg 170 samples. It would be ideal to measure these components on the freeze-dried sample pair.
2. Shore-based laboratory work should be undertaken to determine the clay-size particle fraction of Leg 170 samples. It would be ideal to use one of the sample pairs for this purpose.
3. Oven- and freeze-drying experiments should be conducted on a variety of "pure" clay mineral types or groups, and also on types of ash (perhaps these experiments have already been done).

The purpose of the above measurements is to relate, as quantitatively as possible, oven- and freeze-dried experimental results to the clay fraction, clay mineral composition, ash fraction, and ash composition, of Site 1039, 1040, and 1043 sediment samples. A number of other experiments should be carried out, such as (1) step-heating weight-loss studies from 50° to 120°C, (2) controlled relative humidity drying environments, (3) controlled vacuum conditions, (4) theoretical work on drying, and (5) microwave drying.

Follow-Up Shipboard Experiments

Results gleaned from the oven- and freeze-drying experiment on Leg 170 samples should be continued during other legs, and in particular those legs where sediment types are different from those cored at Sites 1039 and 1040.

This will gather additional information bearing on the issue raised by Brown and Ransom (1996), and, as quickly as possible, begin the measurement and tabulation of porosity values that, within the practical realities of shipboard operations, most accurately represent in situ conditions.

An issue remains, however, about how to effect the most accurate shipboard determination of porosity because low-humidity conditions inherent in freeze drying also remove interlayered water (Brown and Ramsom, 1996). Leg 170 experimental results with Site 1039, 1040, and 1043 deposits indicate that oven drying may more aggressively (completely) remove interlayered water from terrigenous and pelagic sediment.

Follow-Up Shipboard Equipment and Drying-Option Additions

A modern freeze-drying apparatus capable of sustaining vacuum pressures of 5–10 µm Hg when drying at least 100, 10-cm^3 beaker-size samples of wet sediment (equivalent to about 1 kg of wet sediment containing about 0.6 kg of water), should be placed in the Core Lab. The ideal location would be on the starboard-side physical properties counter top or perhaps beneath this counter.

The purpose for installing the freeze-drying apparatus is to

1. Provide an efficient sediment-desiccation option to oven drying;
2. Possibly provide a more accurate method for determining the porosity of discrete sediment samples, and in particular those containing clay minerals and volcanic ash;
3. Significantly reduce (by about 50%) the amount of time needed to measure the index physical properties of porosity, moisture content, bulk density, and grain density.

A modern, properly functioning freeze-drying apparatus is capable of desiccating large groups (50–100) of sediment samples in about 12 hr, and perhaps in as little as 8 hr. This practical drying method thus has the potential of at least halving the time presently recommended for sample desiccation by oven drying.

REFERENCES

Brown, K.M., and Ransom, B., 1996. Porosity corrections for smectite-rich sediments: impact on studies of compaction, fluid generation, and tectonic history. *Geology*, 24: 843–846.

Appendix Table 1. Porosity and density measurements on artificial sediment.

Drying method	Porosity (%)	Grain density (g/cm^3)
Oven dried		
Sample 1	42.9	2.54
Sample 3	42.5	2.49
Sample 5	42.9	2.52
Average:	42.8	2.51
Freeze dried		
Sample 2	42.7	2.51
Sample 4	43.1	2.53
Sample 6	43.2	2.51
Average:	43.0	2.52
Expected values		
Oven dried:	43.4	2.52
Freeze dried:	43.4	2.52

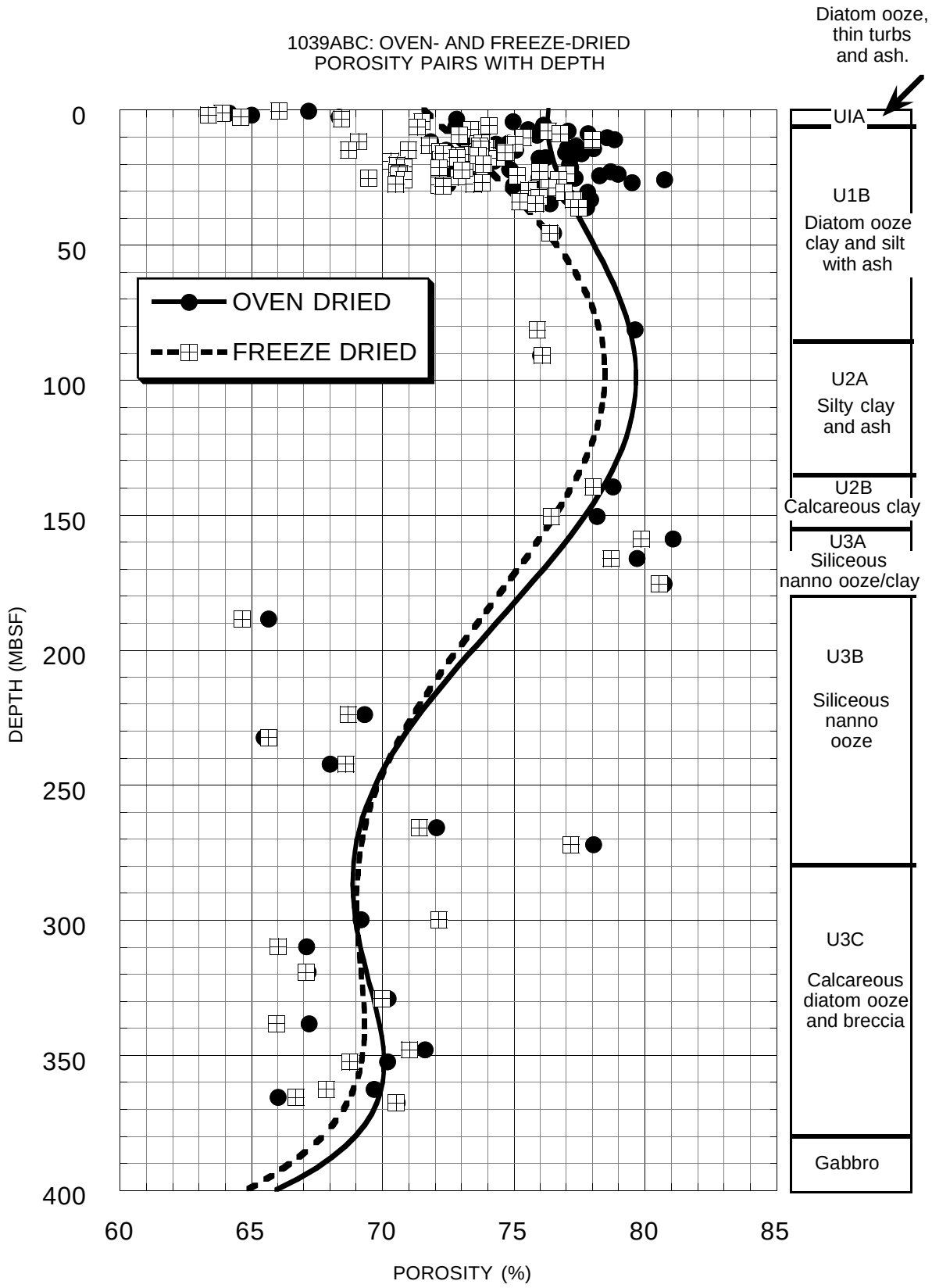


Figure 1. Sampling positions and oven- and freeze-dried porosity values for the stratigraphic sequence of Site 1039.

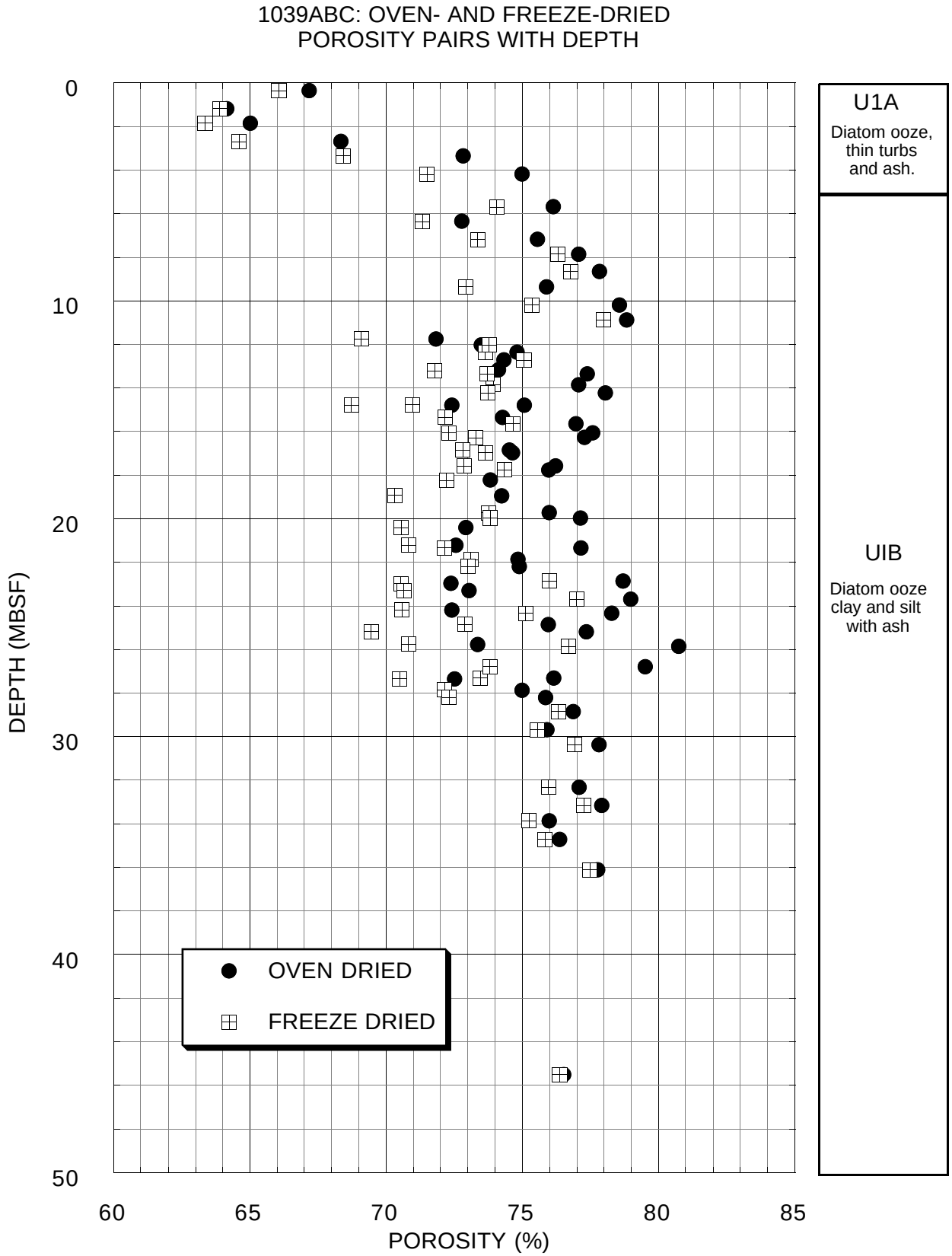


Figure 2. Sampling positions and oven- and freeze-dried porosity values for the more densely sampled upper 50 m of Holes 1039A and 1039B.

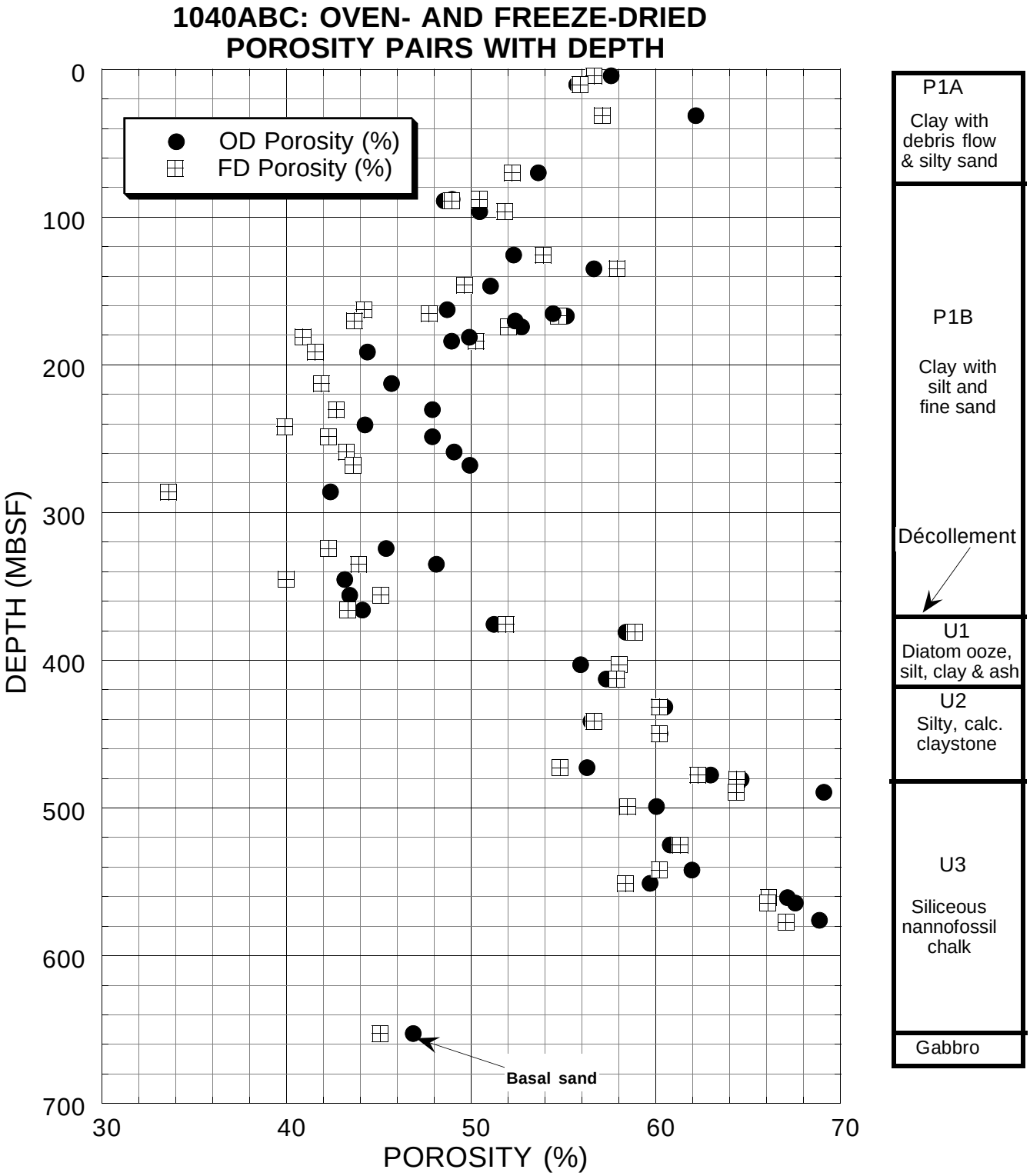


Figure 3. Sampling positions and oven- and freeze-dried porosity values for the stratigraphic sequence of Site 1040.

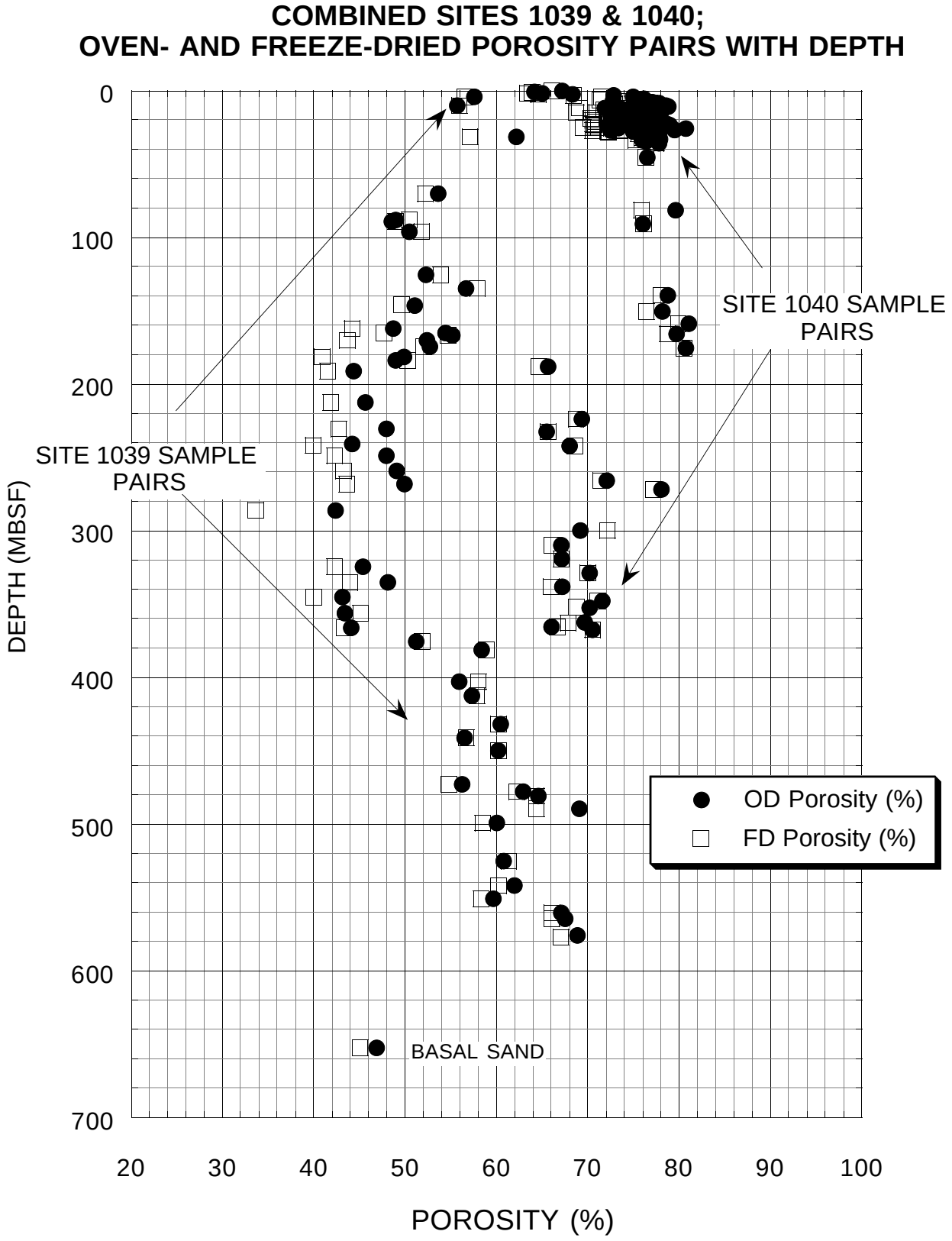


Figure 4. Combined sampling positions and oven- and freeze-dried porosity values for Sites 1039 and 1040.

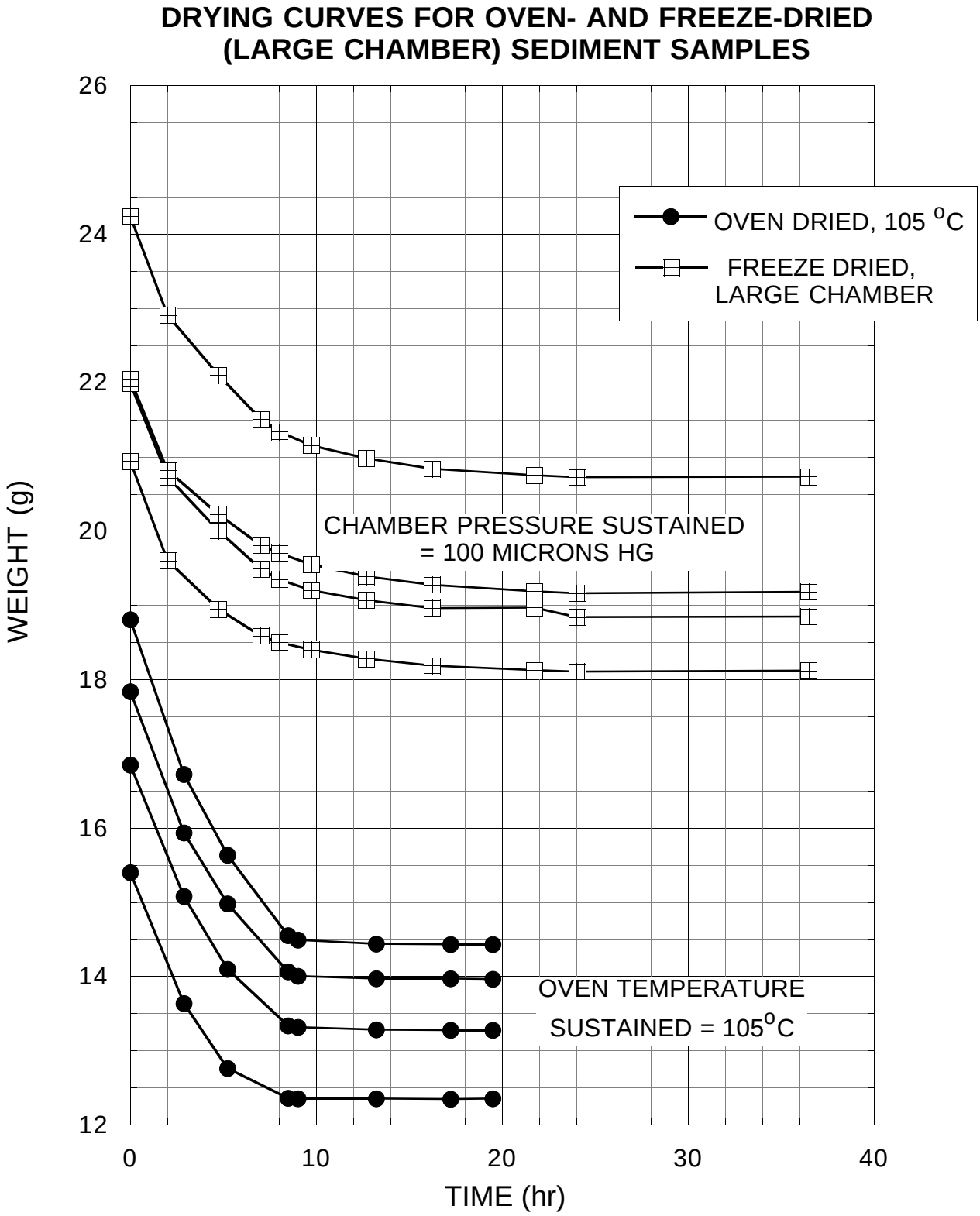


Figure 5. Drying curves for oven- and freeze-dried (large chambers) control samples, Sites 1039 and 1040 samples.

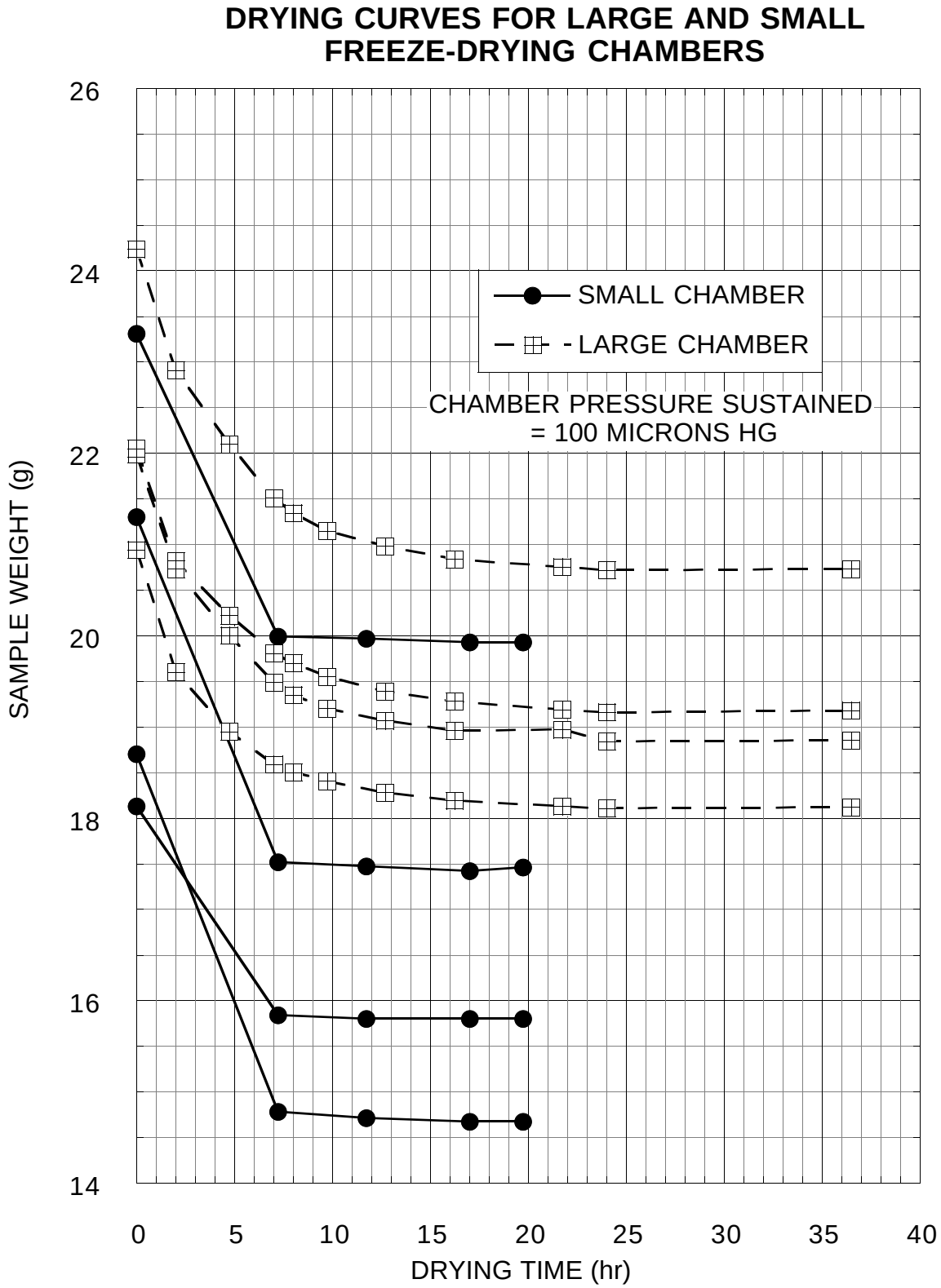


Figure 6. Drying curves for large and small freeze-drying chambers, Sites 1039 and 1040 samples.

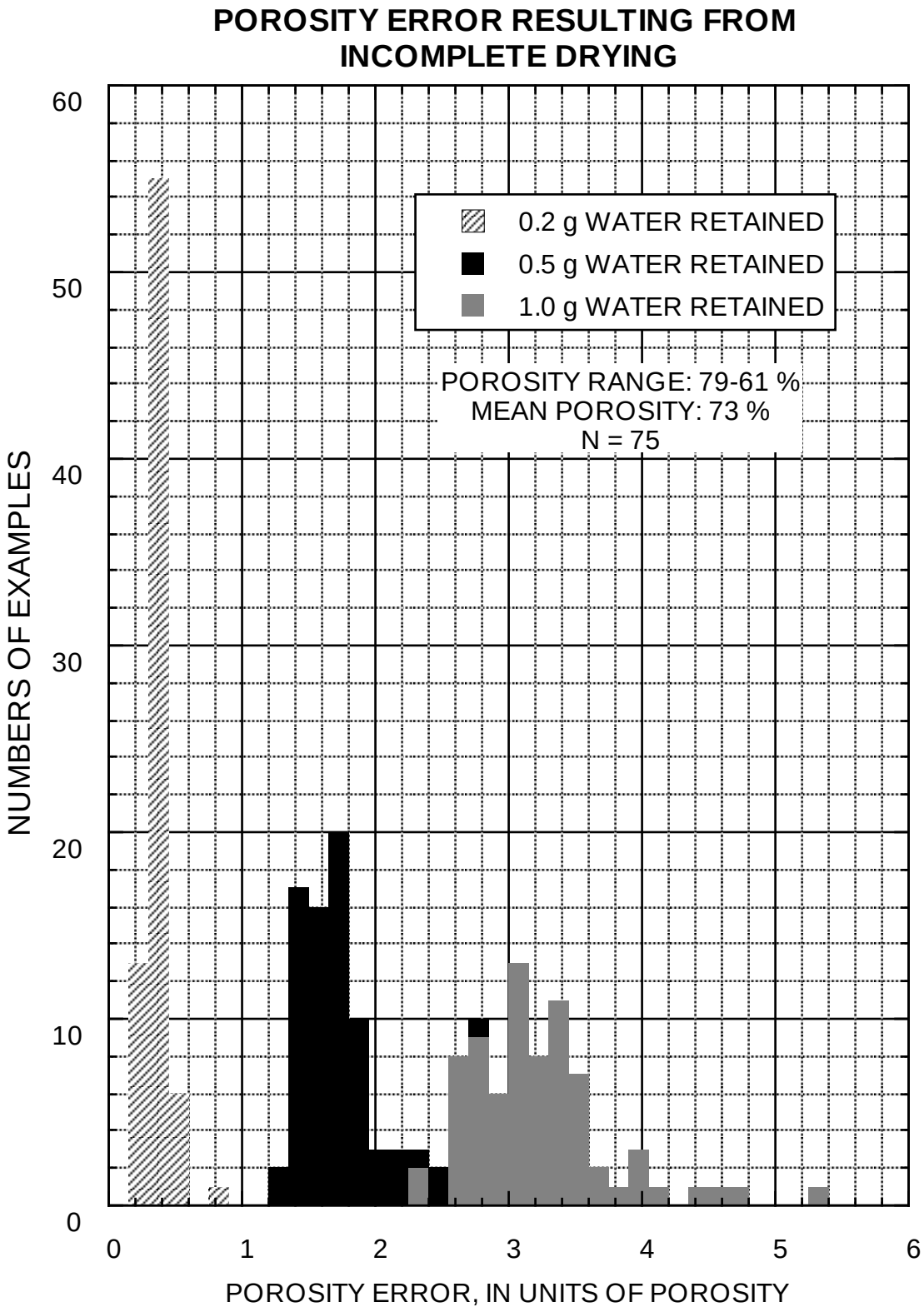


Figure 7. Sensitivity of porosity errors to incomplete sediment drying.

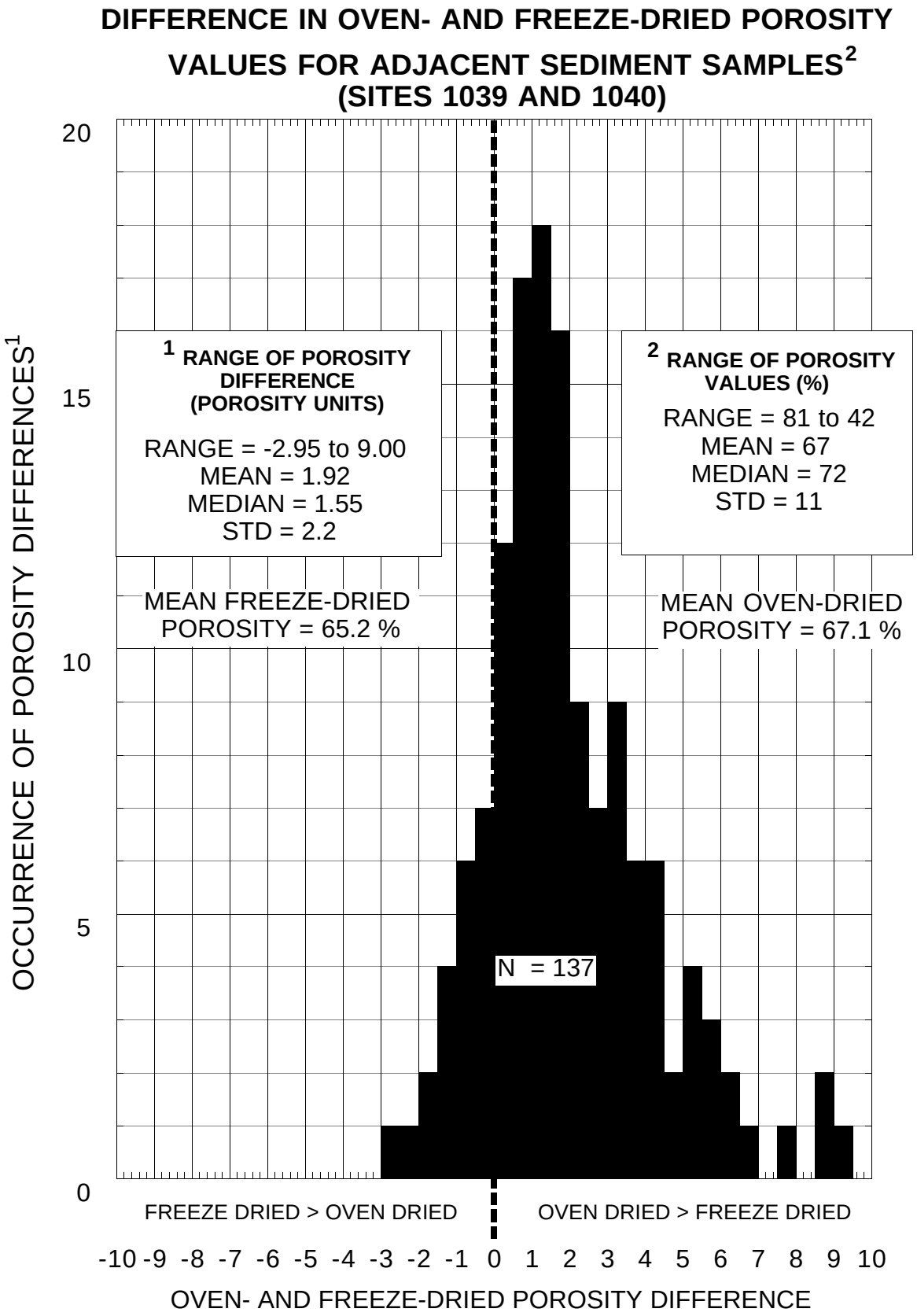


Figure 8. Histogram and statistical parameters of porosity difference of oven- and freeze-dried sediment samples, Sites 1039 and 1040.

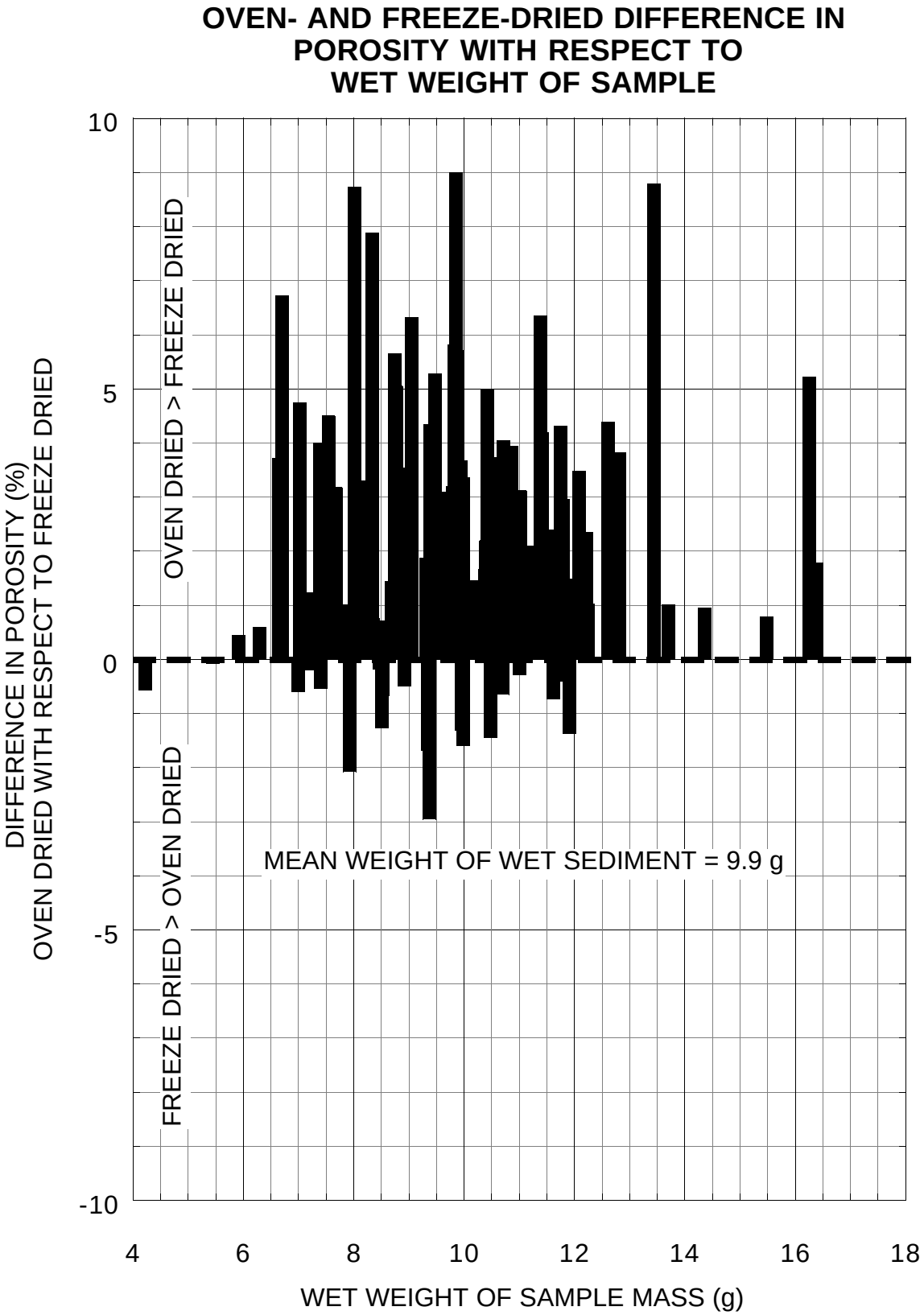


Figure 9. Oven- and freeze-dried porosity difference as function of wet mass of sediment sample, Sites 1039 and 1040.

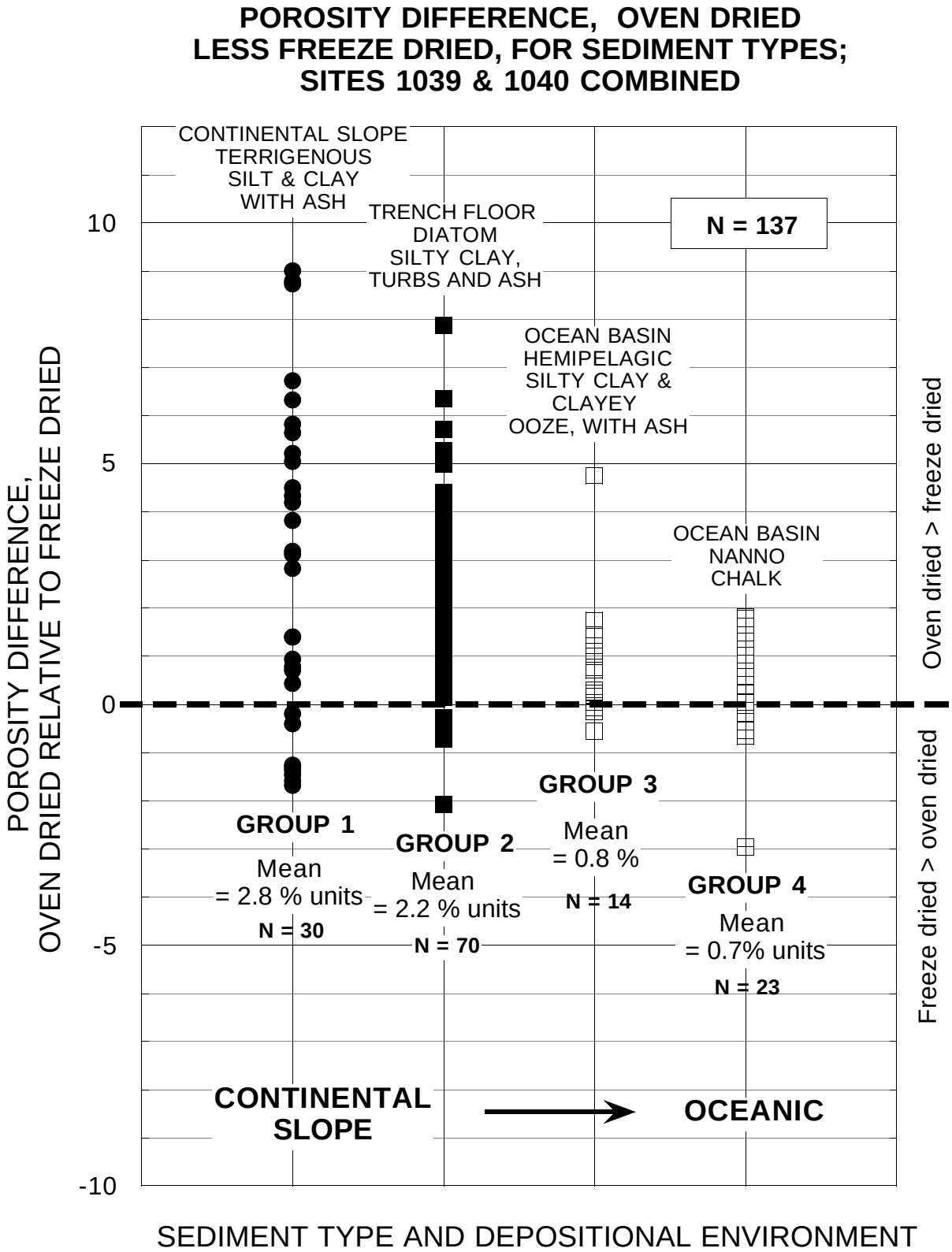


Figure 10. Oven- and freeze-dried porosity difference as a function of lithology and depositional environment, Sites 1039 and 1040.

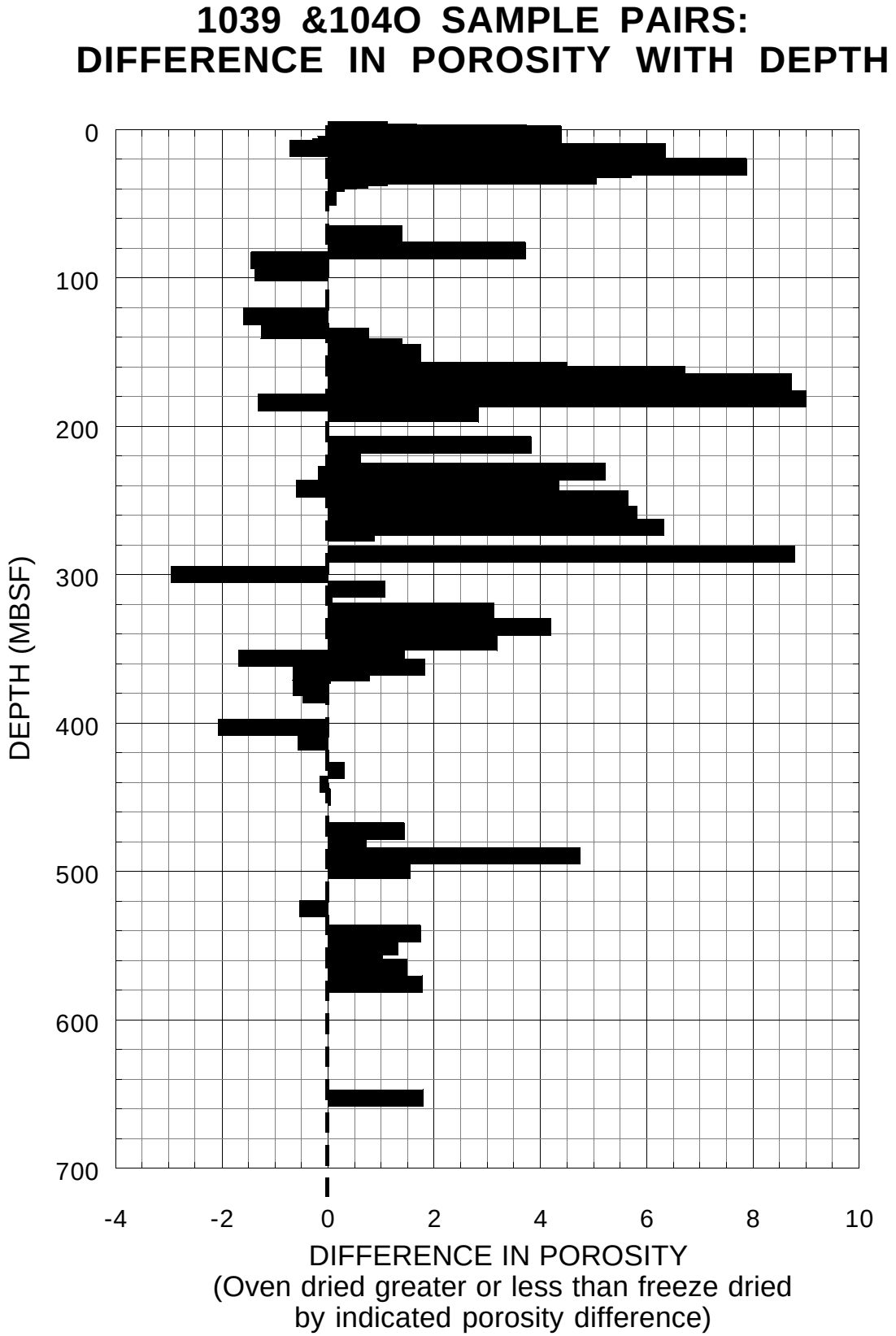
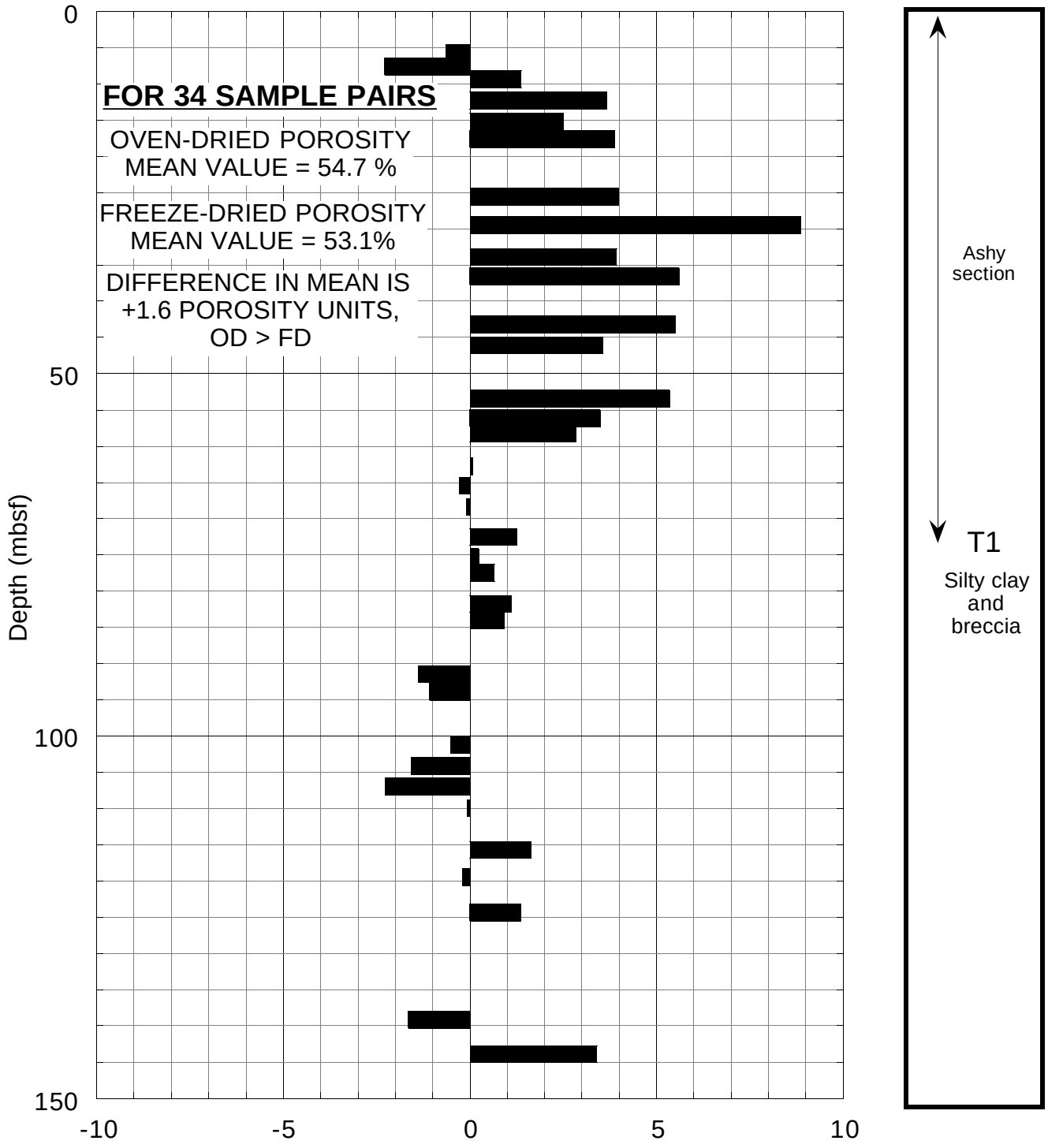


Figure 11. Oven- and freeze-dried porosity difference as a function of subsurface depth (mbsf), Sites 1039 and 1040.



SITE 1043A: DIFFERENCE IN MEASURED POROSITY WITH DEPTH
(Oven dried greater or less than freeze dried by indicated porosity difference)

Figure 12. Oven- and freeze-dried porosity difference as a function of subsurface depth (mbsf), Sites 1043A, Unit T1.

Previous Chapter Table of Contents