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Change in CO_2 concentration and O_2/N_2 ratio in ice cores due to molecular diffusion

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[1] Polar ice cores are unique archives for ancient air. However, a loss of air due to molecular diffusion during storage could affect the composition of the remaining air. We formulate a model with a high spatial resolution (1 mm) calculating the loss of N_2, O_2 and CO_2 in pure clathrate ice in order to determine which layers of an ice core are affected by significant changes in the CO_2 concentration and the $\delta(O_2/N_2)$ ratio for storage durations up to 38 years. The results agree with experimental $\delta(O_2/N_2)$ measurements at ice core pieces performed after different storage durations. Additionally, the calculations confirm the importance of the storage temperature and show that the CO_2 concentration is less affected than that of $\delta(O_2/N_2)$. Furthermore, guidelines for ice core sample preparation are provided in dependence of storage duration and temperature. **Citation:** Bereiter, B., J. Schwander, D. Lüthi, and T. F. Stocker (2009), Change in CO_2 concentration and O_2/N_2 ratio in ice cores due to molecular diffusion, *Geophys. Res. Lett.*, *36*, L05703, doi:10.1029/2008GL036737.

1. Introduction

[2] Antarctic ice cores are well established paleoclimatic archives containing unique information about the history back to 800,000 years before present (a B.P.) [*Jouzel et al.*, 2007; *Loulergue et al.*, 2008; *Lüthi et al.*, 2008]. Even though the ice in an ice core is subject to strong ambient changes during drilling (pressure decreases up to a factor of 200), most analyzed tracers in the enclosed air do not show noticeable fractionation effects, even after several years of storage in cold rooms. However, *Ikeda-Fukazawa et al.* [2005] found a drift in the O_2/N_2 ratio, which correlated with the duration of storage within the first two years after drilling. The underlying mechanism is thought to be outgassing driven by molecular diffusion through the ice matrix due to the large gas pressure difference between the inside and outside of the core together with different diffusion characteristics of the two molecules. With a two-box model they estimated a thickness of the permeation layer of N_2 and O_2 of 12 mm and 7 mm, respectively.

[3] Here, we investigate the exchange of gas between clathrates and ice and the gas loss by diffusion using a more realistic model with higher spatial resolution. We implement the diffusion characteristics of CO_2 using information from *Ahn et al.* [2008], whereas for O_2 and N_2 we use the same parameters as *Ikeda-Fukazawa et al.* [2005]. This allows us to provide more precise information about the penetration depth of gas fractionation (Δr_p) and to estimate the thickness of the surface layer that needs to be removed when preparing the ice samples for O_2/N_2 or for CO_2 measurements.

[4] We focus on pure clathrate ice as this part of deep Antarctic ice cores covers a wider range of climate history than pure bubble ice. Also the brittle zone (depth interval in ice sheets where bubbles and clathrates coexist) is not considered in this study, because the air is anyway highly fractionated due to the transformation process of bubbles to clathrates [*Ikeda et al.*, 1999].

2. Model Construction

[5] The typical shape of an ice core after drilling is a cylinder of 1 m length and 10 cm diameter. The diffusion process is driven by the different concentrations of dissolved gas inside the core and near its surface. Accordingly, the diffusion mainly takes place in the radial direction. This allows us to simplify the problem to a one-dimensional model where only the radial component of the axially symmetric diffusion equation is considered:

$$\frac{\partial C}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right), \tag{1}$$

where C represents a gas concentration in the ice, t the time, D a constant and isotropic diffusion coefficient and r the radial variable. Equation (1) governs solely the part of the gas that is dissolved in the ice which corresponds to less than 1% of the total air content (over 99% are kept in inclusions, either in air bubbles or clathrates). The two reservoirs (gas dissolved in ice and kept in inclusions) are assumed to be locally in equilibrium at all times (i.e., for the numerical case within each layer). The concentration of dissolved molecules of gas m (m = N_2, O_2 or CO_2) inside pure clathrate ice, C_m, which is initially distributed homogenously, is calculated as follows:

$$C_m = Z_m \cdot P_m^d \cdot S_m. \tag{2}$$

Z_m represents the molar fraction of gas m of the air enclosed in the clathrates, P_m^d the dissociation pressure (pressure at which clathrates are formed) of pure gas m clathrates and S_m the solubility of m-molecules in ice. In contrast to *Ikeda-Fukazawa et al.* [2005], we use in equation (2) (equivalent to equation (1) of *Ikeda-Fukazawa et al.* [2005]) the dissociation pressure of pure gas instead of mixed air clathrates, since we assume that the ice, which surrounds a clathrate, is in equilibrium with the air in gas phase in equilibrium with the clathrates [*Salamatin et al.*, 1998].

[6] P_m^d is a species-specific, temperature-dependent property and has been experimentally determined by *Kuhs et al.*

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[2000] for N_2 and O_2 and by *Miller* [1961] for CO_2 (see Table S1 in the auxiliary material for the parameter values)[1]

$$\log_{10} P_m^d = a_m - \frac{b_m}{T}. \quad (3)$$

T represents the temperature (in K) and the unit of P_m^d is Pa. The concentration of dissolved molecules of gas m near the ice core surface C_m^S is derived from the air pressure P^S outside the core (1 atm) and the molar fraction of gas m in the surrounding air Y_m as:

$$C_m^S = Y_m \cdot P^S \cdot S_m. \quad (4)$$

In our numerical model any disturbance caused by diffusion in the dissolved reservoir is assumed to be instantly balanced by an exchange flow of gas from the clathrates to the ice. We use an FTCS-scheme (forward in time, centered in space) for the discretization and an iterative method to calculate the exchanged gas amount, taking into account mass conservation. At the core surface we put one additional layer where the concentration conditions are kept constant at air levels according to equation (4). The innermost layer can exchange dissolved gas only with its neighboring layer radially outward.

[7] The clathrate reservoir looses gases until there is no air left. Thereby, we assume that (i) clathrates are spherical containers with an equilibrium gas pressure which is not affected by the falling air content and (ii) clathrates do not transform back to bubbles but simply disappear. Furthermore, based on investigations by *Salamatin et al.* [2001, 2003], we implement (iii) a radius-dependent solubility with an average initial radius for all clathrates. The radius is supposed to be shrinking with decreasing air content and consequently accelerating the outgassing. With the assumptions (i) and (ii) two effects of how the equilibrium gas pressure in the ice could be lowered and hence, of slowing down the outgassing are neglected. Especially the decay of clathrates to bubbles, (ii), is thought to have considerable influence on the outgassing, because restored bubbles expand after drilling and hence, the inner gas pressure is reduced. The third effect, (iii), is negligibly small. Therefore, our results likely provide the upper bound of the diffusion rate.

3. Model Input

[8] The main parameters for our calculations are the solubility and the diffusion coefficients in ice for the three components N_2, O_2 and CO_2. Due to the difficulty in assessing these parameters data are sparse and we only have knowledge about two sets of estimates: One is calculated by extrapolating established data of other gases [*Hondoh*, 1996] (set A: Table S1, column A), the other is based on data from ice core analysis and on molecular dynamic simulations [*Ahn et al.*, 2008; *Ikeda-Fukazawa et al.*, 2004, 2005] (set B: Table S1, column B). Both methods result in the following temperature dependence:

$$S_m^e(T) = S_m^0 \exp\left(-\frac{E_m}{R \cdot T}\right), \quad (5)$$

$$D_m(T) = D_m^0 \exp\left(-\frac{Q_m}{R \cdot T}\right), \quad (6)$$

where E_m and Q_m are activation energies for the temperature-dependent solubility $S_m^e(T)$ and for the diffusion coefficient of molecules of gas m in ice $D_m(T)$, respectively. R is the ideal gas constant, T the temperature and S_m^0 and D_m^0 are specific constants (values shown in Table S1 of the auxiliary material). Details about the numerical convergence of our model are noted in the auxiliary material.

[9] Gas diffusion in ice is smaller along the c-axis of the ice crystal compared to its rectangular direction for the gases used in our model [*Ikeda-Fukazawa et al.*, 2004]. Assuming the crystals are orientated isotropically, we use the weighted average for all calculations, although this does not apply for the bottom part of deep ice cores, where the c-axis preferentially orientates parallel to the core axis.

[10] We ran our model for storage durations of up to 38 years at temperatures of −25°C and −50°C with an ice core radius of 5 cm using both sets of diffusion and solubility coefficients. For every run, we calculated the CO_2 concentration (ppmv, initially enclosed concentration is 200 ppmv) and the $\delta(O_2/N_2)$ ratio (‰, enclosed ratio: 1/3.77 [*Kawamura et al.*, 2007], used standard for δ-notation: 1/3.73 [*Brasseur et al.*, 1999]) in the outermost 20 mm after 2, 4, 6 and 38 years of storage.

4. Results

[11] The model shows increased CO_2 concentrations and decreased $\delta(O_2/N_2)$ ratios in the layers toward the ice core surface (Figure 1). Since all gases diffuse to the core surface, the relative ratios between the permeation coefficients (product of diffusion and solubility coefficient) multiplied by the corresponding dissociation pressures (P_m^d), quantifying the outgassing of the single air elements, govern the changes of the mixing ratios inside the clathrates. Accordingly, the high loss of O_2 in the clathrates compared to the other gases is mainly responsible for the drifts in the O_2/N_2 ratio mentioned above.

[12] We use the uncertainties in the experimental measurements, i.e. 1.5 ppmv for actual CO_2 concentration [*Lüthi et al.*, 2008] and 0.2‰ for $\delta(O_2/N_2)$ measurements [*Kawamura et al.*, 2007] (the dotted area in Figure 1), to define the penetration depth of fractionation (Δr_p) for these simulations. We define this depth as the deepest layer below the ice core surface, where the difference between the value of the layer and the base line (value at the undisturbed part of the ice) is bigger than the actual measurement uncertainty. The results show that Δr_p for $\delta(O_2/N_2)$ is about three times higher than for CO_2 (Figure 1). This is due to the combination of a lower uncertainty in $\delta(O_2/N_2)$ measurements and the high loss rate of O_2 which changes the O_2/N_2 ratio more strongly than the CO_2 concentration.

[13] There is a conspicuous difference in the base lines between the two different storage temperatures using the parameter values as calculated by *Hondoh* [1996] (Figures 1a and 1b; 1.4 ppmv, 1.6‰). This is due to the relatively high solubility used which allows the temperature-dependent dissociation pressure to substantially change the equilibrium condition. Even if real, such an effect would most likely have remained hidden in $\delta(O_2/N_2)$ as well as in CO_2 measurements, since part of the dissolved gas in the ice also gets extracted eliminating this difference. This is the case especially for wet extraction systems which are used

[1]Auxiliary materials are available in the HTML. doi:10.1029/2008GL036737.

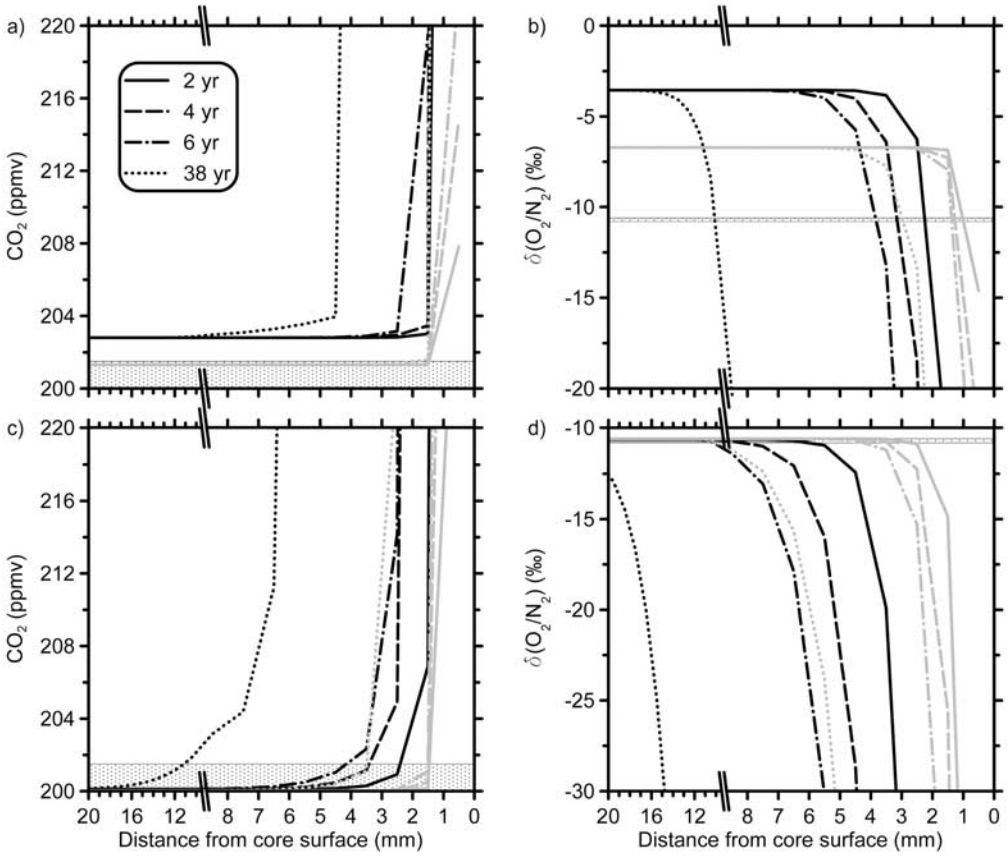

Figure 1. Composition of simulated (a and c) CO_2 concentrations and (b and d) $\delta(O_2/N_2)$ values in the clathrates of a specific layer of the outermost 20 mm of an ice core with a radius of 50 mm, calculated according to the input values of Table S1, column A (Figures 1a and 1b), column B (Figures 1c and 1d) and Table S2 shown in the auxiliary material. The black lines show the simulation results with a storage temperature of −25°C and the gray lines of −50°C. The different types of lines represent storage durations as follows: solid line: 2 years; dashed line: 4 years; dashed-dotted line: 6 years; dotted line: 38 years. The dotted area denotes the uncertainty of the corresponding measurements.

for $\delta(O_2/N_2)$ measurements. Anyway, the calculation of solubility and diffusion coefficients by *Hondoh* [1996] is strongly dependent on the choice of the Van De Waals radius and, therefore, afflicted with large uncertainties. Hence, we concentrate further discussions on the results based on the parameterizations of *Ikeda-Fukazawa et al.* [2004, 2005] and *Ahn et al.* [2008] (set B; Figures 1c and 1d).

[14] Our results in Figure 1 show the fractionation within a specific layer of an ice core with 5 cm radius. Measurements on real samples, however, provide values of air

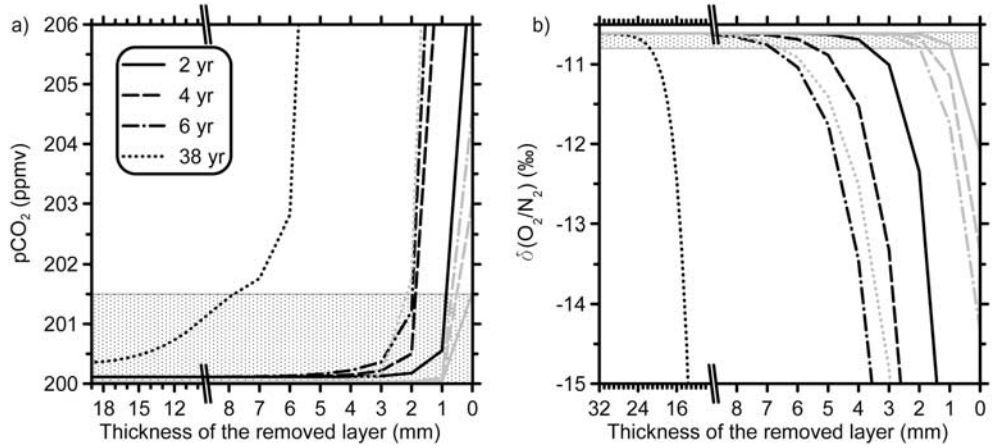

Figure 2. Composition of simulated (a) CO_2 concentration and (b) $\delta(O_2/N_2)$ measurements (input values: Tables S1 and S2 of the auxiliary material) considering the thickness of the removed layer y on the ice core surface (calculated after formula (8) and (9), respectively), using ice core radii of 20 mm (Figure 2a) and 33 mm (Figure 2b). The colors and types of the lines follow the same key as in Figure 1.

content mixed over several layers of a longitudinal section of the initial ice core with both flat and curved surfaces (prepared right after drilling). To approximate these conditions, we estimate the surface-to-volume ratio (S/V-ratio) for the used samples (60 m^{-1} for $\delta(O_2/N_2)$ samples [*Ikeda-Fukazawa et al.*, 2005]; 100 m^{-1} for CO_2 samples (see auxiliary material)) and perform the same simulations as discussed above but with the corresponding S/V-ratio (33 mm and 20 mm core radius, respectively). The difference in the geometry is assumed to have little influence, since less gas escapes through the flat areas which is largely compensated by more gas escape through the corners. The two runs (−25°C and −50°C) with the smaller radius (20 mm) were used to calculate the CO_2 concentration $pCO_2(y)$ after 2, 4, 6 and 38 years (Figure 2a), taking into account the thickness y (mm) of the removed layer at the sample surface as follows:

$$pCO_2(y) = \frac{\sum_{r=1}^{20-y} N_{CO_2}(r)}{\sum_{r=1}^{20-y} N_{CO_2}(r) + N_{O_2}(r) + N_{N_2}(r)}. \quad (7)$$

The two other runs were used to calculate the ratio $\delta(O_2/N_2)(y)$ as a function of removed layer y (Figure 2b) according to:

$$\delta(O_2/N_2)(y) = \left(\frac{1}{3.73} \cdot \frac{\sum_{r=1}^{33-y} N_{O_2}(r)}{\sum_{r=1}^{33-y} N_{N_2}(r)} - 1 \right) \cdot 1000\%. \quad (8)$$

Thereby, $N_m(r)$ represents the amount of gas m enclosed in the clathrates (ml/kg) in the ice core layer with radius r (resolution of r and y: 1 mm).

[15] The results in Figure 2 show that the fractionation in the $\delta(O_2/N_2)$ sample penetrates deeper than that in the CO_2 sample, despite the smaller S/V-ratio. For this specific case (S/V-ratio and uncertainty as described above), after four years of storage at −25°C, 6 mm of ice have to be removed at the surface for preparing $\delta(O_2/N_2)$ samples and only 2 mm for CO_2 samples. Similar to the results of Figure 1, this indicates that the fractionation of the O_2/N_2 ratio penetrates about three times deeper in the initial piece of the core than the fractionation of CO_2 concentration. After two years of storage, at least 4 mm have to be removed at the surface for $\delta(O_2/N_2)$ samples, which is thicker than the amount of ice removed during conventional preparation (0.7–4 mm) [*Ikeda-Fukazawa et al.*, 2005]. For longer storage durations (>6 years) at −25°C, it is necessary to remove more than a third of the ice mass of the initial ice core piece for $\delta(O_2/N_2)$ measurements. The fractionation of the CO_2 concentrations, however, only penetrates the outer 2 mm of the sample within 6 years, which corresponds to less than 20% of the initial ice mass.

[16] Comparing the different storage temperatures, there is significantly less fractionation in both tracers at colder temperature. Even after 38 years, our model predicts the possibility of measuring a fractionation-free $\delta(O_2/N_2)$ signal (removing 7 mm at the surface). Undisturbed CO_2 measurements would likely be possible up to 50 years after drilling, and within the first 6 years of storage it is necessary to remove only 1 mm of the surface. In general, the calculations (Figures 1 and 2) show that Δr_p is about three times smaller at −50°C (gray lines) than at −25°C (black lines).

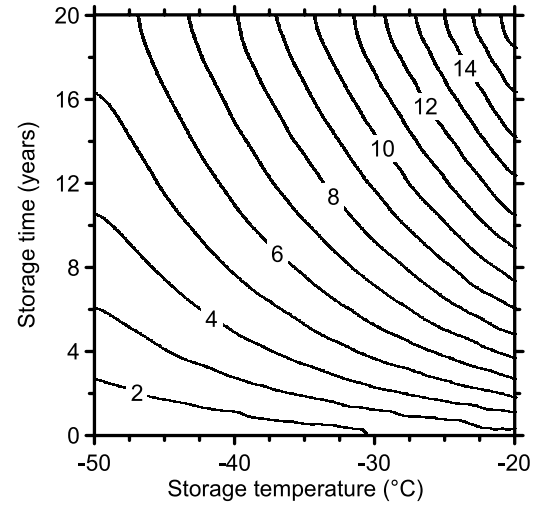

Figure 3. Depth of the layer beneath the ice core surface where the simulated fractionation of $\delta(O_2/N_2)$ is at −2‰. The contours represent the ice thickness of ice that must be removed for fractionation-free measurements (mm).

5. Discussion

[17] *Ahn and Brook* [2007] reconstructed CO_2 concentrations between 46,000 and 64,000 a B.P. using samples from the Byrd ice core by removing 1 cm at the surface after a storage duration of 38 years at −25°C. Our model predicts an offset of 1 ppmv for these conditions. This is probably overestimated, since part of the contaminated ice of *Ahn and Brook* [2007] was removed during the ice sample preparation of *Blunier and Brook* [2001] (J. Ahn, personal communication, 2008), and because we neglect relaxation processes such as the decay of clathrates to bubbles, which is very advanced in the Byrd ice core [*Ahn and Brook*, 2007].

[18] The decay rate of clathrates to bubbles strongly depends on the storage temperature. *Uchida et al.* [1994] estimated this rate to be decreased by a factor of 50 at storage temperatures of −50°C compared to −25°C. For instance, under the storage conditions of the Byrd ice core (−25°C, 38 years) more than 50% of all clathrates are predicted to be transformed back to bubbles. At −50°C less than 10% of all clathrates should decay to bubbles within 60 years of storage. Since we neglect this decay, our simulations are likely more realistic for colder temperatures.

[19] *Ikeda-Fukazawa et al.* [2005] presented $\delta(O_2/N_2)$ measurements in dependence of the storage duration up to 2.5 years, showing the drift of the $\delta(O_2/N_2)$ values. The result of our model is in agreement with their data. A quantitative comparison, however, is limited due to the relatively large variability (5‰) of the measurements.

[20] We have calculated the thickness of the layer that must be removed as a function of storage time (up to 20 years) and temperature (between −20°C and −50°C), assuming one would like to exclude layers with a $\delta(O_2/$

N_2)-fractionation above 2‰ (Figure 3) (compare Figure 1d with 2b). In general, the results show that lowering the storage temperature by 20°C halves the affected ice thickness. The change in CO_2 is less than 0.1 ppmv for the storage times and temperatures depicted in Figure 3.

6. Conclusion

[21] Our gas diffusion simulations in ice cores are in good agreement with the measurements of *Ikeda-Fukazawa et al.* [2005] for short term storage durations (~2 years). With rising storage durations, however, our model is expected to slightly overestimate the diffusion effect, since the decay of clathrates to bubbles (lowers the outgassing) in ice cores [*Uchida et al.*, 1994] is not included in our calculations. This overestimation should be smaller at low storage temperatures, where clathrates are much more stable. Only in the case of crystals with their c-axis preferentially parallel to the sample axis our model underestimates the diffusion effect by up to 50%, since the diffusion is higher rectangular to the c-axis.

[22] We have shown that the outgassing affects the CO_2 concentration and $\delta(O_2/N_2)$ values differently. CO_2 is not affected by our sample preparation standards (cutting away about 2–3 mm at the surface) and storage conditions (temperature: −25°C; duration: up to 4 years), which is similar to the standards of most other labs. In contrast to that, the O_2/N_2 ratio is fractionated between −0.4‰ and −7‰ under the same conditions (measurement uncertainty 0.2‰). Accordingly, we recommend either cutting away 4 to 6 mm ice at the surface for preparing O_2/N_2 ratio samples that have been stored 2 to 4 years, storing the samples at −40°C or below (see Figure 3), or at least recording strictly the storage history of the ice cores after drilling. Lower storage temperatures would strongly increase the long term stability of ice cores and, hence, would enable to measure an undisturbed $\delta(O_2/N_2)$ signal even after 38 years (CO_2 even >50 years). Similar improvements in ice quality could be reached by storing the cores under high pressure (> 10^6 Pa). In addition, longitudinally sliced ice core pieces undergo faster fractionation since they have a higher S/V-ratio than the original cylindrical core. Accordingly, we recommend avoiding immediate ice cutting after drilling. Cores that have been subject to strong sublimation during storage require special consideration.

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