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Evolution of air bubble and air hydrate ensembles: statistical analysis of the EPICA-DML ice core

Introduction

Air inclusions in ice from the large ice sheets are the most direct source to reconstruct the concentration of trace gases in the paleo atmosphere. Between 600 and 1300 m depth air bubbles convert into air hydrates. In this zone air bubbles and clathrates coexist. After conversion many air hydrates seem to change shape, they may subdivide into smaller fragments or smaller hydrates may coalesce to larger ones (Fig.5). One possible explanation for splintering is mechanical instability of rigid spherical inclusions in a power law plastic material under load (Levy, 2003). Grigoriev et al. (subm. 2004) considered the evolution of air hydrate shapes as an instability behaviour of rigid inclusions in visco-plastic ice. Theory predicts that air hydrates, mostly spherical and about 10 times harder than the surrounding ice matrix, should become instable in ice sheets below about 200 m depth (2 MPa) and transform to elliptical or more complex shapes (Fig.3-6). We performed a statistical analysis of air bubbles and hydrates in the transition zone of the EPICA-DML ice core currently drilled in Dronning Maudland, Antarctica, to find supporting evidence either for splintering or for coalescence.

Evolution of shapes of hydrates - Microscopical observations

Just after nucleation clathrates assume the shape of the pre-existing bubbles (primary hydrates, graupel-like shape with rough and irregular surfaces), then clathrates change their shape (metamorphosis) with occurrence of more complex shapes (multi-branched). At least rod-like air hydrates are observed to be splintered by intracrystalline deformation (Fig.7).

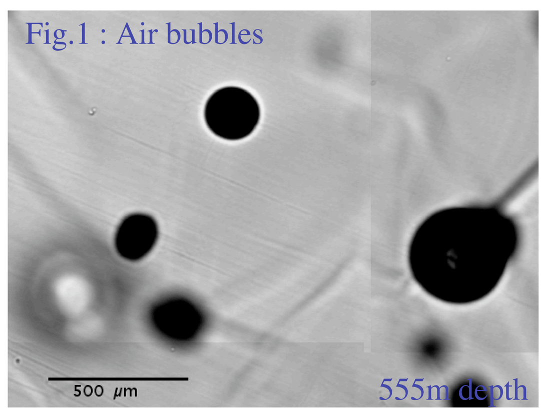


Fig.1 : Air bubbles

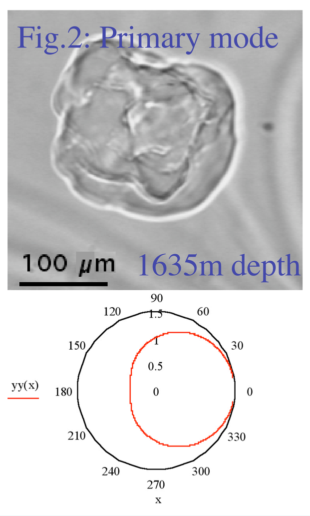


Fig.2: Primary mode

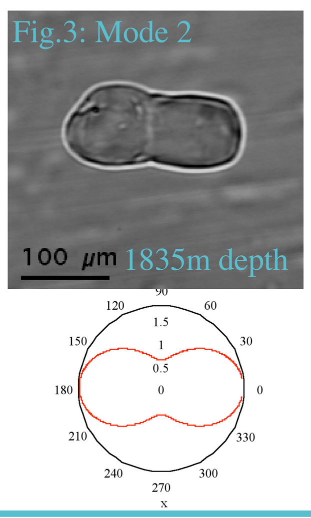


Fig.3: Mode 2

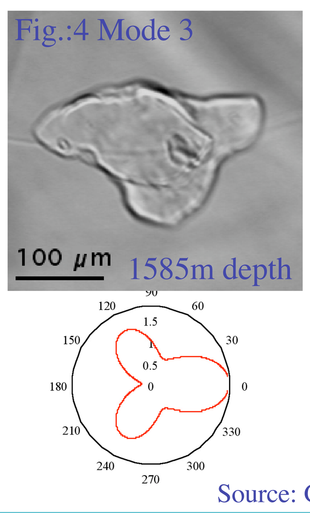


Fig.:4 Mode 3

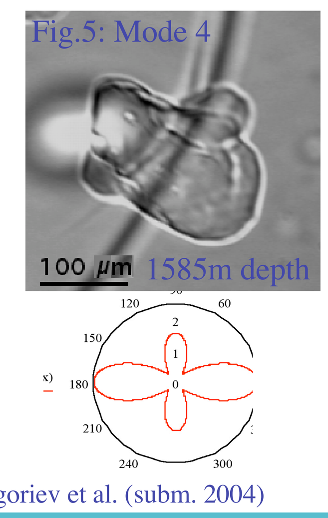


Fig.5: Mode 4

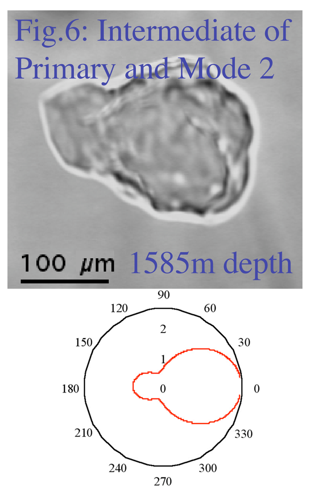


Fig.6: Intermediate of Primary and Mode 2

Source: Grigoriev et al. (subm. 2004)

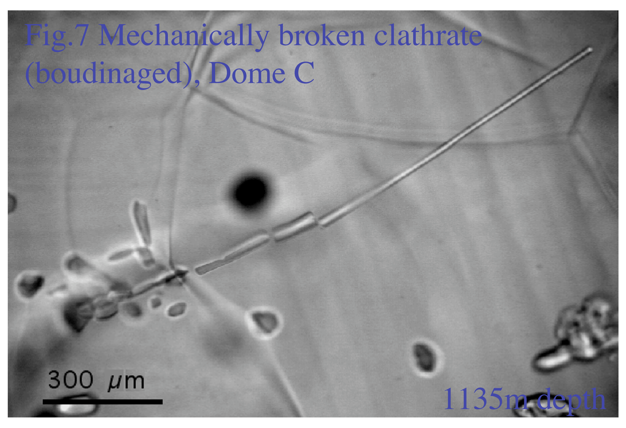


Fig.7 Mechanically broken clathrate (boudinaged), Dome C

Size distributions

Fig.8: Half normalized air bubble radii distributions (histogram of the hydrate sizes *f(R)* normalised by total number of inclusion per unit area N [$P_p = f(R)/N$]). The maxima of the distributions are shifted towards smaller radii (except depth 945 and 1054 m). A skewness towards small radii develops with depth into a small single maximum on the side of larger radii (depth 1156 m). The majority of bubbles in 855 m depth show radii between ~40 and 110 μm.

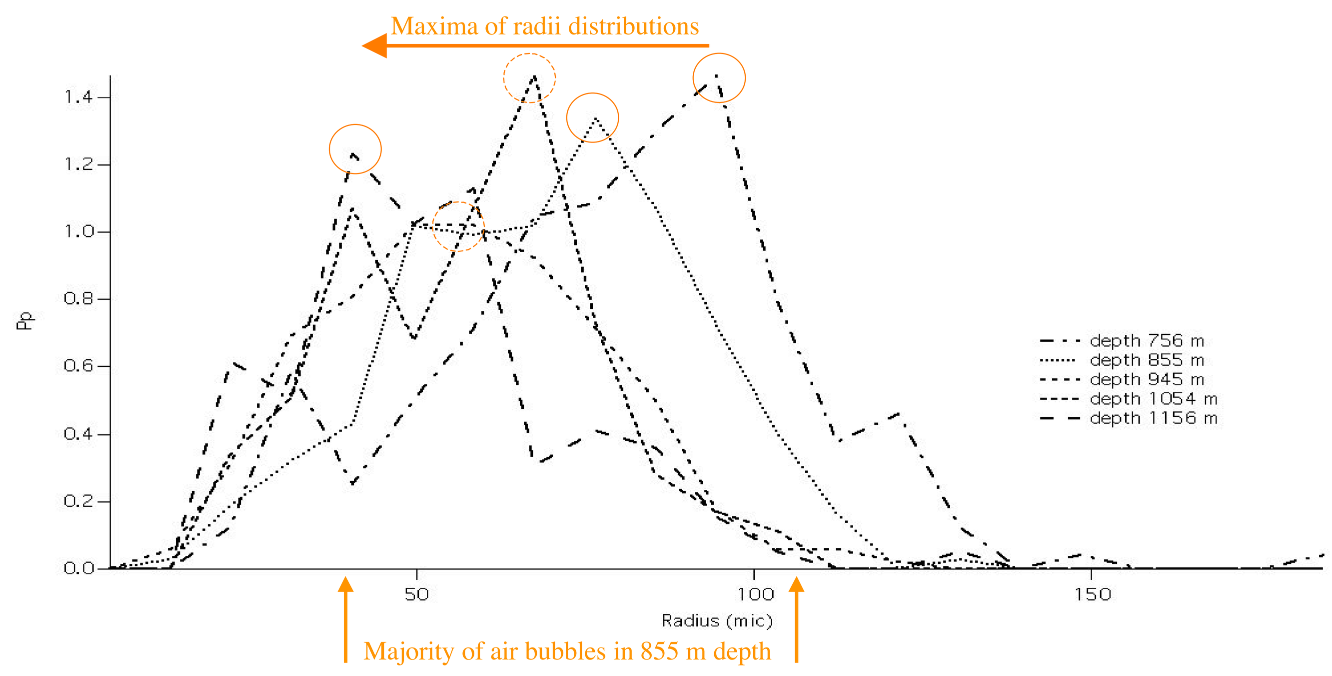
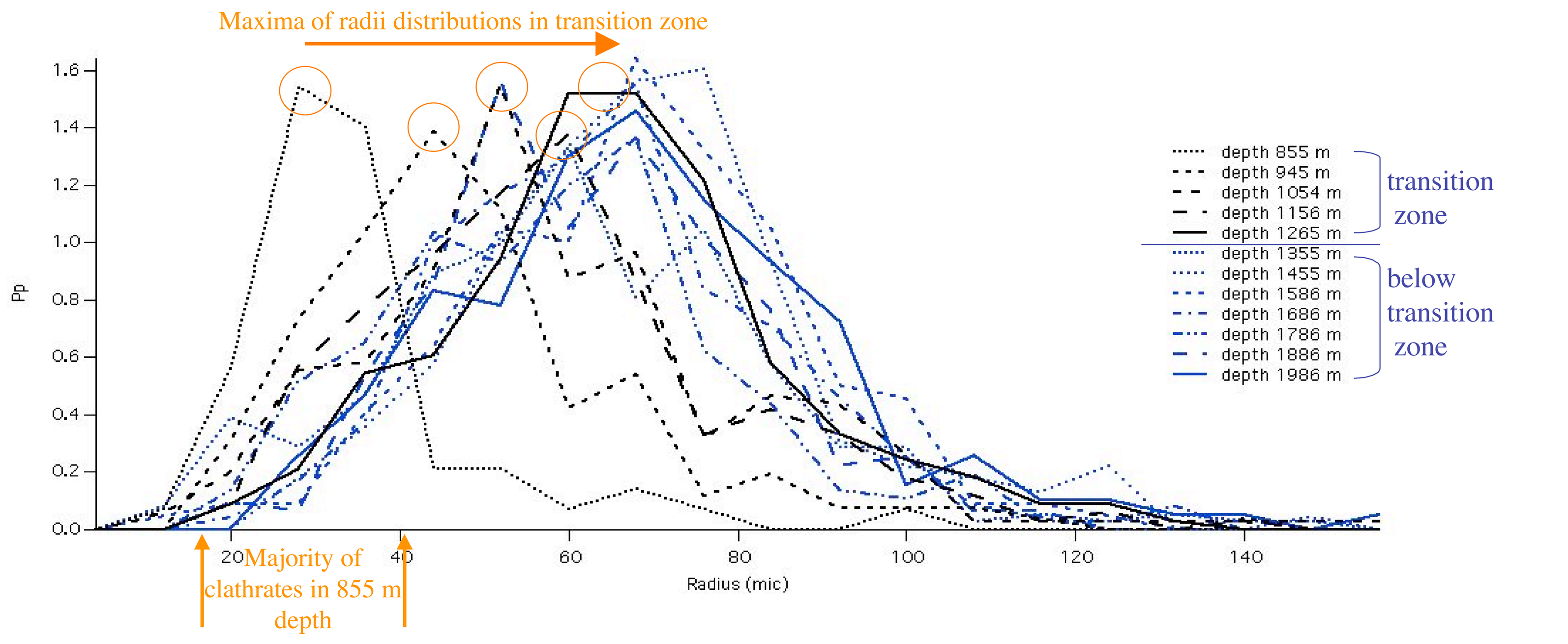


Fig.9: Half normalized clathrate-radii distribution (histogram of the hydrate sizes *f(R)* normalised by total number of inclusion per unit area N [$P_p = f(R)/N$]). Radii of majority of clathrates in 855 m depth lay between ~15 and 40 μm.
1) In the transition zone the radii of the maxima of the distributions continuously increases, probably due to the onset of conversion of bigger bubbles. Below the transition zone the radii of the maxima of the distributions remain stable.
2) A secondary maximum/tail on the side of larger radii slightly grows in the transition zone (855 to 1054 m depth), but shrinks in the lowest transition zone (1145-1265 m depth) and finally disappears below the transition zone. This secondary maximum also appears in the air bubble distribution close to the transition zone (1156 m depth). The distribution type develops from a log-normal type (in transition zone) to a gaussian type with a slight tendency to a skew distribution with a translation to smaller radii (below transition zone).



- The size distributions (Fig.8 & 9) show clearly that in the beginning of the transition zone first small air bubbles start to convert, later size of converting bubbles increases.
- The disappearance of the secondary maxima in the transition zone may indicate splintering of larger primary hydrates, but may also be due to the relocation of the distribution towards larger radii, which fills the "gap". The size distributions do not allow to draw firm conclusions of the role of splintering or coalescence.

More statistical data

Fig.10: Mean and maximum radii of bubbles and clathrates with depth. The mean radius of bubbles decreases in the first part of the transition zone and increases at its end. Below the transition zone the average clathrate radius adopts a relatively constant value around 70 μm with a slightly increasing tendency. The evolution of the maxima radii assumes the same shape with a more rough character.

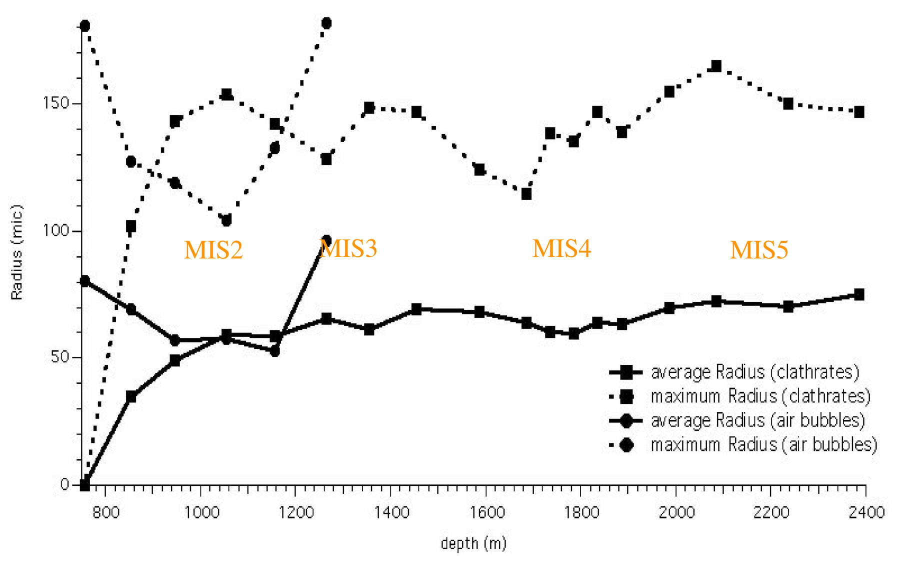


Fig.11: Mean radii of clathrate-classes with depth. Oval clathrates are in all depths the smallest ones. Clathrates of mode 2 and 3 are successively bigger than ovals. The evolution of mode-4 clathrates and primary clathrates are more irregular. But in principle it is visible that they are the biggest clathrates.

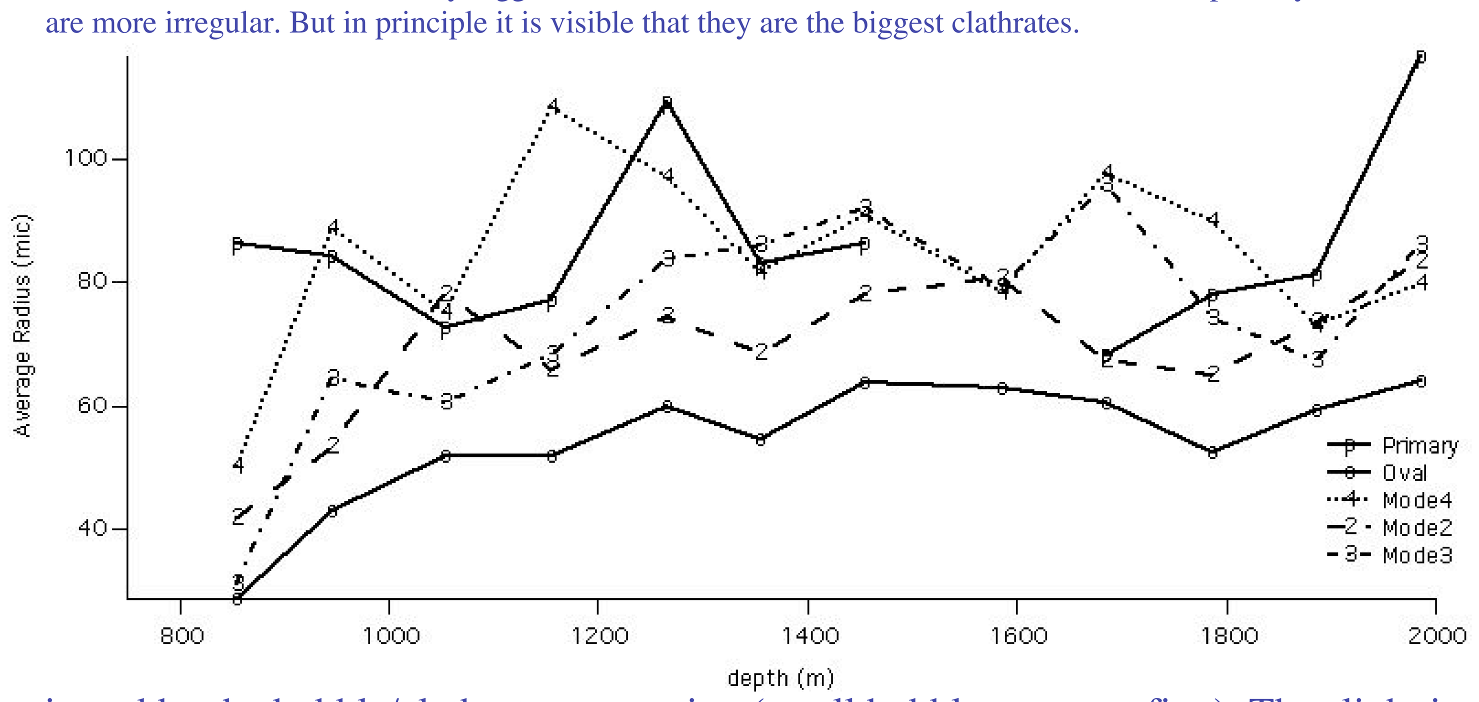
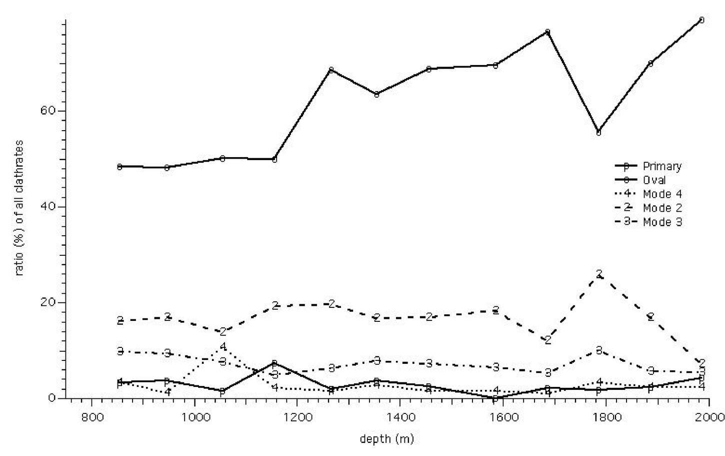


Fig.12: Frequency of clathrate-classes with depth. This graphic shows that oval clathrates are the most frequent ones and their frequency even increases. Modes 2, 3 and 4 are in each case less frequent.



- The average radius (Fig.10) in the transition zone is dominated by the bubble/clathrate conversion (small bubbles convert first). The slight increase of clathrate radii below the transition zone might be caused by crystal growth or by transition into warmer climate (Eem). Maximum radii show a clear dependence on climate variations. The mean radius development of air bubble indicates that in the lower part of this zone only very view, large bubbles are left, whereas in the upper part the climate transition (into LGM) controls the evolution.
- Division or coalescence of clathrates influence the sizes of single clathrate-classes (Fig.11). The oval clathrates as a potential product of shape instability and splintering are the smallest inclusions. They seem to determine a minimum size, so that successively larger clathrates adopt mode 2, 3 resp. 4. The irregularity of mode-4 and primary clathrates may be due to problems of distinguishing between these two types.

Conclusions

Our statistical analysis shows that in shallower depths smaller bubbles convert first. There is some evidence that mechanical instability occurs and leads to subdivision of air hydrates in the size of the different shape classes, but neither the coalescence of small clathrates nor the subdivision of air hydrates due to mechanical instability can be identified in the number and size distributions of hydrates in the transition zone. Other processes influence size and number of hydrates in the EDML core: 1. increasing pressure reduces bubble size and 2. the conversion of bubbles into hydrates in depths between 700 and 1300 m may both affect porosity and occupancy of hydrates and so size; 3. the climatic change from glacial to interglacial (Holocene) between 1000 and 700 m depth produces much more, but smaller bubbles in glacial ice; 4. diffusion of air molecules into ice matrix is unknown. On the basis of size distributions these processes are not easily distinguishable.

References

Levy, A. J. 2003. Bifurcation phenomena in the rigid inclusion power law matrix composite sphere. Int. J. Solids Struct., 40, 2535-2561
Grigoriev, D., Kipfstuhl, S., Sammonds, P. R., Hamann, I., Faria, S. 2004. Bifurcation instability of Polar air hydrate clathrates under ice sheet pressure. Submitted 2004