

**PAST pH VARIATION OF A FRESHWATER LAKE KUSSHARO, JAPAN,
INFERRED FROM VERTICAL VARIATIONS OF LONG-CHAIN
ANTEISO COMPOUNDS IN SEDIMENTS**

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Lake Kussharo is located in the large Kussharo caldera in Hokkaido, Japan. The volcanism is still active and has been considerably influencing the lake water chemistry through a supply of strongly acidic hot spring water. The pH of the Kussharo water, however, abruptly increased from 4.7 to 7 in the late 1980s, the reason of which is not known. In the lake sediments, series of long-chain branched compounds ($\geq C_{23}$ alkanes, alkenes, alcohols and alkanolic acids) with a methyl group at the *anteiso* position are identified, as is known to be unique and ubiquitous in moderately acidic (pH=3-5) freshwater lake environments in Japan (Fukushima et al., 1996, 2005). In the present work, abundances of the *anteiso* compounds in the short sediment cores were determined, in order to trace back the history of the Lake Kussharo water chemistry, by assuming the *anteiso* compounds as markers of low pH conditions. In addition, compound specific carbon isotopic compositions of the *anteiso* (*ai*-) and *normal* (*n*-) alkanes were determined to provide evidence on their source organisms.

The sediment cores were taken in 1993, 1995 and 2003 and sectioned immediately after sampling at every 1 cm, considering that the sedimentation rate is reported to be 1.3 mm/y (Tanaka et al., 1994). The *anteiso* compounds were found in every sediment core and most sediment sections. Their abundances obviously tend to decrease in the uppermost layers, in well accordance with the neutralization during the last two decades. Figure 1 represents the typical vertical variations of *n*- and *ai*-alkanes in the sediment core taken in 2003. It strengthened the hypothesis that the *anteiso* compounds should be promising biomarkers of low pH conditions.

The second point to be remarked in Fig. 1 is the vertical variation of *n*-alkanes, varying significantly in parallel with *ai*-alkanes. The abundances of both *ai*- and *n*-alkanes are

high in the surface, decrease in the middle and again increase slightly in the bottom horizons. Together with the increase in abundance, the odd-to-even carbon number predominance of *n*-alkanes decreased to almost unity. It implies that the occurrence of the *ai*-alkanes was accompanied by the occurrence of a huge amount of *n*-alkanes with little odd-even carbon number preference.

The third point to be noticed is the increases in the bottom layers. This is in contrast to the findings in L.Tazawa (Fukushima et al., 1996) and L.Inawasiro (Fukushima et al., 2005), where the *anteiso* compounds decrease monotonously with increasing depth to disappear completely in the bottom horizons. It suggests that L.Kussharo may have experienced the acidification-neutralization excursion at least twice during the last 150-200 years.

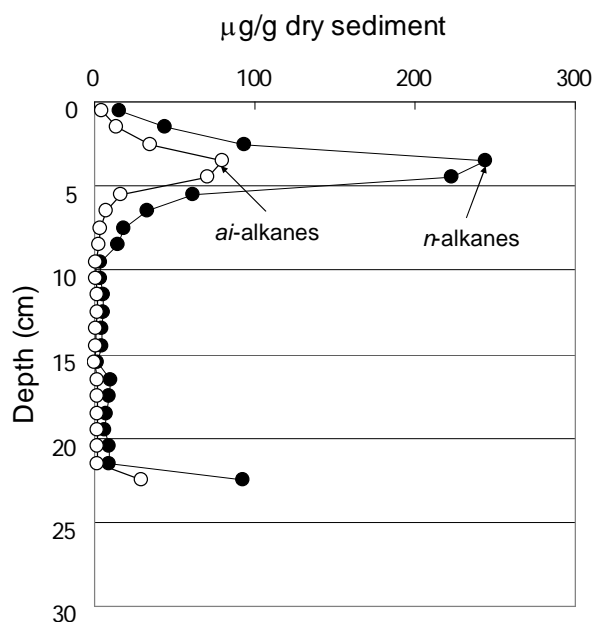


Figure 1. Vertical variation of *n*- and *ai*-alkanes in the sediment core taken in 2003.

The compound specific carbon isotopic compositions of *ai*-alkanes (C₂₅-C₃₁) ranged from -28 to -30‰, being slightly heavier than usual C3 plants. On the other hand, those of *n*-alkanes in the sections (11-12cm) with a minimal amount of *ai*-alkanes ranged from -30 to -34 ‰(odd) and from -35 to -37 ‰(even). In the upper sections concomitant with abundant *ai*-alkanes, they (both odd and even) decreased down to -38 - -39 ‰. These facts suggest different source organisms or different synthetic pathways between *n*- and *ai*-alkanes.

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