

Migration of sharks into freshwater systems during the Miocene and implications for Alpine paleoelevation

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ABSTRACT

Trace-element and isotopic compositions of fossilized shark teeth sampled from Miocene marine sediments of the north Alpine Molasse Basin, the Vienna Basin, and the Pannonian Basin generally show evidence of formation in a marine environment under conditions geochemically equivalent to the open ocean. In contrast, two of eight shark teeth from the Swiss Upper Marine Molasse locality of La Molière have extremely low $\delta^{18}\text{O}$ values (10.3‰ and 11.3‰) and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.707840 and 0.707812) compared to other teeth from this locality (21.1‰–22.4‰ and 0.708421–0.708630). The rare earth element (REE) abundances and patterns from La Molière not only differ between dentine and enameloid of the same tooth, but also between different teeth, supporting variable conditions of diagenesis at this site. However, the REE patterns of enameloid from the “exotic” teeth analyzed for O and Sr isotopic compositions are similar to those of teeth that have O and Sr isotopic compositions typical of a marine setting at this site. Collectively, this suggests that the two “exotic” teeth were formed while the sharks frequented a freshwater environment with very low ^{18}O -content and Sr isotopic composition controlled by Mesozoic calcareous rocks. This is consistent with a paleogeography of high-elevation (~2300 m) Miocene Alps adjacent to a marginal sea.

Keywords: shark, isotope, oxygen, strontium, rare earth elements, Miocene Alps.

INTRODUCTION

A number of studies have shown that the trace-element and isotopic composition of mineralized phosphatic tissue of shark teeth, particularly that of the fluorapatite of enameloid, represents a useful tool for interpreting both present and past environmental, as well as thermal or climatic, conditions (e.g., Longinelli, 1966; Staudigel et al., 1985; Kolodny and Luz, 1991; Schmitz et al., 1997; Vennemann and Hegner, 1998; Kohn and Cerling, 2002; Vennemann et al., 2001a, 2001b). This, combined with an abundance of shark teeth in the largely sandy sediments of the Upper Marine Molasse, has made them the focus of a research project aimed at characterization of past oceanographic and climatic changes during the Miocene within sedimentary basins surrounding the tectonically active Alps.

The Swiss Molasse Basin represents the western end of the North Alpine foreland basin, situated between the Jura Mountains and the Alps. Sedimentation of the Molasse started in the late Eocene to early Oligocene and ended in the late Miocene. The Molasse deposits are subdivided into four main stratigraphic units (Fig. 1), from which the Upper Marine Molasse is of interest to this study. The Upper Marine Molasse shelly sandstone of La Molière is exposed in a number of quarries from which numerous fossils have been collected and described during the last two centuries (Weidmann and Ginsburg, 1999). The sedimentation occurred under a strong tidal influence in a proximal marine setting (Berger, 1985). The age of the sediments is estimated as early Burdigalian on the basis of mammalian fossils (MN3 zone, 17.6–20.3 Ma; Becker, 2003). At this time the region represented a shallow, narrow seaway between the Tethys and Paratethys, marginal to large delta fans of the southwestern Alpine foreland (Berger et al., 2005b). Other Upper Marine Molasse sampling

localities, Auberson and Tavannes, are early Burdigalian in age, while the quartz-sands of Benken (MN3–4) were deposited during the late Burdigalian (Becker, 2003).

METHODS

The shark teeth analyzed in this study are part of the collection of the Geological Museum of Lausanne (MGL 90032–90061). The oxygen isotope compositions were measured from biogenic phosphate (PO_4^{3-} , $\delta^{18}\text{O}_p$) of the enameloid and structural carbonate within phosphate (CO_3^{2-} , $\delta^{18}\text{O}_c$) of whole teeth separately. Sample preparation was adapted after a method described by Dettman et al. (2001), and the $\delta^{18}\text{O}_p$ was analyzed via reduction with graphite in a TC/EA (high-temperature conversion elemental analyzer) (Vennemann et al., 2002) coupled to a Finnigan MAT Delta Plus XL mass spectrometer. Oxygen isotope compositions are expressed in delta notation relative to Vienna standard mean ocean water (VSMOW). The NBS120c standard measured during the same period gave an average value of $21.2 \pm 0.5\text{‰}$. $\delta^{18}\text{O}_c$ was obtained using a Gasbench II according to a method adapted after Spötl and Vennemann (2003). The analytical precision for this method was better than $\pm 0.1\text{‰}$.

Sr was isolated on quartz columns by conventional ion-exchange chromatography, and its isotope composition was measured at the University of Geneva on a Finnigan MAT 262 mass spectrometer. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured in semidynamic mode, corrected for mass fractionation with $^{88}\text{Sr}/^{86}\text{Sr}$ of 8.375209, and normalized to the SRM987 standard with $^{87}\text{Sr}/^{86}\text{Sr} = 0.710240$ using an average of 0.710233 ± 12 (2σ , $n = 31$).

Rare earth element (REE) concentrations were determined by laser-ablation–inductively coupled plasma–mass spectrometry at the University of Lausanne, following the method of Günther et al. (1997). Results are expressed as REE patterns normalized to post-Archean Australian Shale (PAAS).

RESULTS

$\delta^{18}\text{O}_p$ and $^{87}\text{Sr}/^{86}\text{Sr}$ Values of Enameloid

The O and Sr isotope compositions, if preserved, represent those obtained in-vivo because both elements are incorporated into the biogenic apatite structure during growth of the teeth (Longinelli, 1966; Kohn and Cerling, 2002; Staudigel et al., 1985; Schmitz et al., 1997; Vennemann et al., 2001a).

Average $\delta^{18}\text{O}_p$ values of $21.5 \pm 0.6\text{‰}$ ($n = 6$; excluding two) were measured for La Molière, $21.5 \pm 0.8\text{‰}$ ($n = 9$) for Auberson, $22.5 \pm 0.7\text{‰}$ ($n = 6$) for Tavannes, and $21.2 \pm 0.8\text{‰}$ ($n = 7$) for Benken. These values are similar to those for shark teeth both from modern subtropical environments (Vennemann et al., 2001a) and fossilized teeth of other Miocene marine deposits (e.g., Lécuyer et al., 1996; Vennemann and Hegner, 1998; Vennemann et al., 2001b). Most samples from the Swiss Molasse localities, as well as localities from the North Alpine sedimentary basins, have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios expected for teeth formed in Lower Miocene seawater (Fig. 2). However, two teeth from La Molière (Mol-5 and Mol-6) have unusually low $\delta^{18}\text{O}_p$ (10.3‰ and 11.3‰), as well as $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 2). Given that they have been preserved, these compositions of Mol-5 and Mol-6 indicate formation in low- ^{18}O freshwater with a large input of Sr from Mesozoic marine carbonate rocks of the fluvial drainage basin. Carbonates of this type are common in the Alps and the Jura Mountains, which are known to

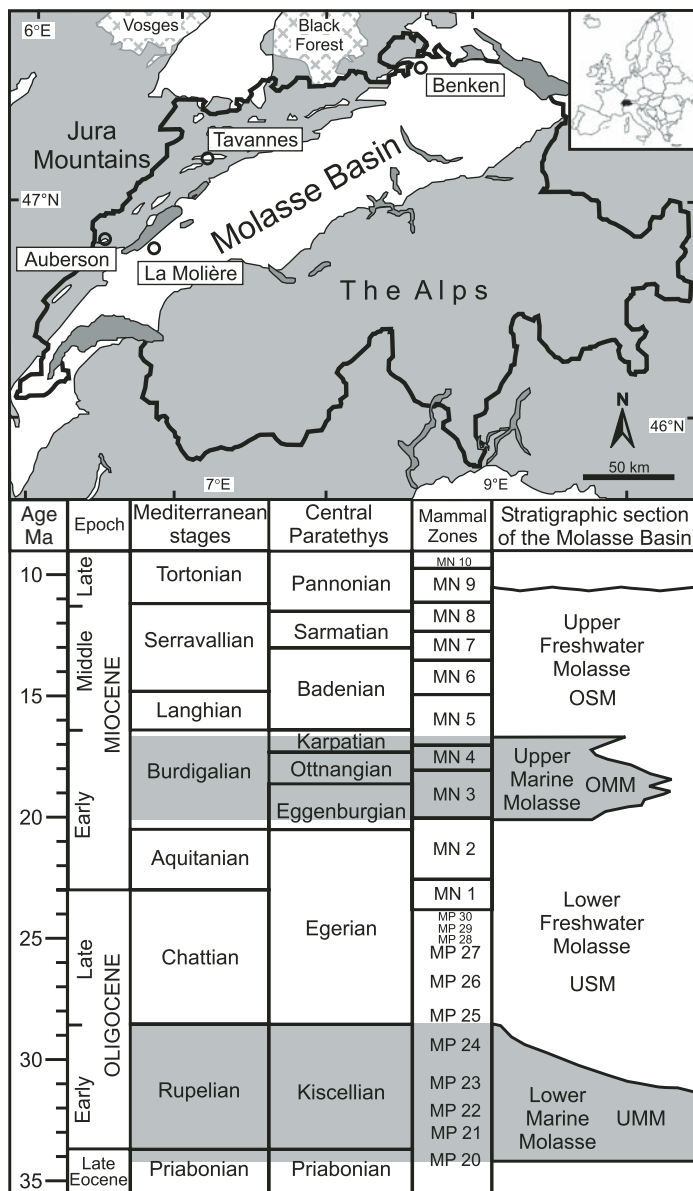


Figure 1. Stratigraphy of Swiss Molasse Basin (after Berger et al., 2005a) and geographical position of sampled Upper Marine Molasse (OMM) localities.

have been exposed in the hinterland of La Molière (Weidmann and Ginsburg, 1999; Schlunegger et al., 2001; Kuhlemann and Kempf, 2002). Other exceptions for $^{87}\text{Sr}/^{86}\text{Sr}$, but not for the $\delta^{18}\text{O}_p$ values, are given by teeth from Benken, which have $^{87}\text{Sr}/^{86}\text{Sr}$ values that are higher than expected for open-ocean conditions, suggesting a local source of rocks enriched in ^{87}Sr . This is compatible with the proximity of crystalline rocks of the Black Forest area and the Aar massif (cf. Liew and Hofmann, 1988), which are also known to have had an influence on the sediment budget at this locality (Schlunegger et al., 2001; Kuhlemann and Kempf, 2002). In contrast to the study of Barrat et al. (2000), which suggested that Sr isotopic compositions may be reset by diagenesis, those measured for the teeth of this study are considered to reflect primary compositions, because we exclusively measured the enameloid, which is known to be more robust to alteration (cf. Kohn and Cerling, 2002), and because teeth from the same sedimentary unit have different compositions that are unlike those of the surrounding sediment ($^{87}\text{Sr}/^{86}\text{Sr} = 0.717899$ and 0.719197).

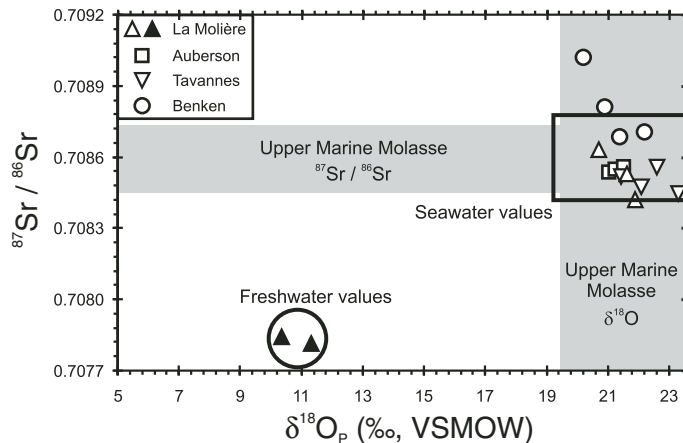


Figure 2. $\delta^{18}\text{O}_p$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for shark teeth from Upper Marine Molasse. Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ for Upper Marine Molasse samples is similar to that typical of the Miocene open ocean (after Hodell et al., 1991) (see Table DR1, see text footnote 1). VSMOW—Vienna standard mean ocean water.

$\delta^{18}\text{O}_c$ and Rare Earth Element Compositions

The alternative explanation, that the O and Sr isotopic compositions of Mol-5 and Mol-6 were reset during diagenesis, is intuitively considered unlikely because none of the other teeth from this same locality has these unusual compositions. However, to address this possibility in more detail, the $\delta^{18}\text{O}_c$ values, considered to be more readily reset relative to $\delta^{18}\text{O}_p$ values (cf. Kolodny and Luz, 1991; Iacumin et al., 1996; Kohn and Cerling, 2002; Showers et al., 2002), and the REE abundances and patterns were measured.

Unlike O and Sr (latter replacing Ca), the REEs are not important for the metabolism of sharks, and hence their content is very low in recent teeth (e.g., Elderfield and Pagett, 1986; Vennemann et al., 2001a). REEs do, however, have an affinity for the apatite lattice and strongly partition into phosphate during postmortem, early diagenetic recrystallization (Staudigel et al., 1985; Shaw and Wasserburg, 1985; Reynard et al., 1999; Trueman and Tuross, 2002). As a function of the abundance of REE in the ambient fluid and their respective partitioning into newly formed crystals, the teeth may thus record patterns characteristic of the local depositional environment.

The REE abundances measured for five teeth from La Molière (Fig. 3) are always higher in dentine compared to enameloid in the same tooth. This is typical for recrystallized phosphates (e.g., Picard et al., 2002) and reflects originally smaller crystallites, higher content of organic matter, and, after destruction of organic matter, higher porosity of the dentine compared to enameloid during diagenesis, which implies that dentine is more susceptible to recrystallization and REE uptake (Kohn and Cerling, 2002). The REE patterns measured for enameloid and dentine can be quite different from one tooth to another, however, as well as within any one tooth. This variability is interpreted to reflect changing environmental conditions during diagenetic recrystallization of the teeth (e.g., Trueman and Tuross, 2002; Haley et al., 2004), where dentine and enameloid recrystallize at different rates and times. Frequently alternating coastal conditions in the Swiss Molasse Basin, and particularly for La Molière (Berger, 1985; Weidmann and Ginsburg, 1999; Berger et al., 2005b), are compatible with this interpretation. Thus, while some teeth, such as those for the enameloid of Mol-3, Mol-6, Mol-8 and dentine of Mol-5 and Mol-6, have patterns not unlike those typical for seawater, even including a weak Ce-anomaly, others tend toward a slight middle rare earth element (MREE) enrichment (enameloid of Mol-2 and Mol-5; dentine of Mol-2 and Mol-3), typical of pore fluid, sediment-dominated

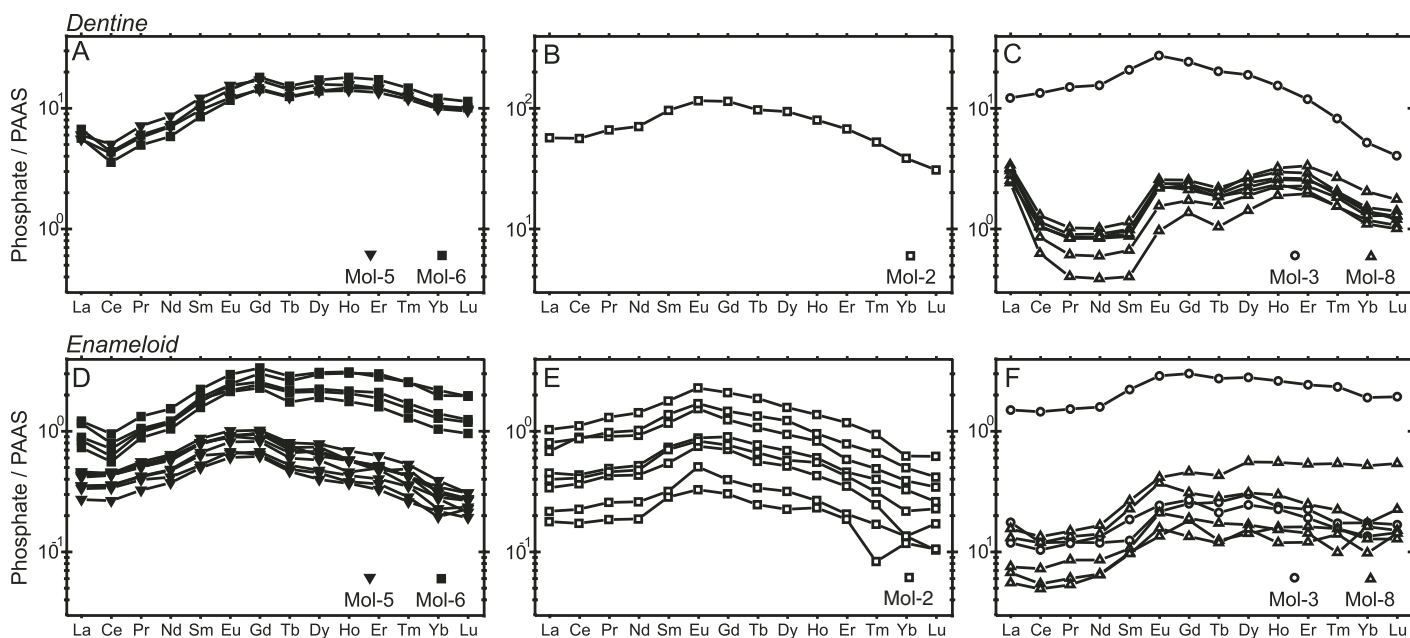


Figure 3. Rare earth element (REE) patterns of dentine (A–C) and enameloid (D–F) of shark teeth from La Molière (see Table DR2, see text footnote 1). Variability in REE distribution among teeth and between enameloid and dentine in teeth Mol-3 and Mol-5, reflects a changing diagenetic environment that corresponds well to strong tidal influence and high-energy setting of Swiss Molasse Basin during the early Miocene. Similarities between “freshwater” and normal marine teeth indicate that some teeth (e.g., Mol-5 [D] and Mol-2 [B and E]) experienced similar stages of diagenesis. PAAS—post-Archean Australian Shale.

REE patterns (Reynard et al., 1999; Trueman and Tuross, 2002; Haley et al., 2004; Lécuyer et al., 2004). Typical bell-shaped REE patterns characteristic of extensive recrystallization (Reynard et al., 1999) were not observed for any of the teeth.

The fact that the REE pattern of enameloid of Mol-5 is indistinguishable from that of Mol-2, while that of enameloid from Mol-6 is similar to that of enameloid from Mol-3 and Mol-8, reflects a similar diagenetic history, at least for these parts of the teeth. Because only Mol-5 and Mol-6 amongst these have truly exotic O and Sr isotope compositions, the possibility that diagenesis changed only the $\delta^{18}\text{O}$ value and $^{87}\text{Sr}/^{86}\text{Sr}$ of Mol-5 and Mol-6 is again considered unlikely.

The $\delta^{18}\text{O}_{\text{C}}$ values for the shark teeth are between 20.9‰ and 27.6‰. These values are higher than $\delta^{18}\text{O}_{\text{P}}$ values of the same samples, but they are all generally lower than values expected for equilibrium between these two oxygen-bearing sites in phosphate, which is estimated to have a $\Delta^{18}\text{O}_{\text{C-P}}$ of ~9‰ (Kolodny and Luz, 1991; Iacumin et al., 1996). Mol-5 and Mol-6 are exceptions because they have a $\Delta^{18}\text{O}_{\text{C-P}}$ value higher than 9‰. Although it is unclear whether $\Delta^{18}\text{O}_{\text{C-P}} \approx 9\%$ is even applicable to recent fish teeth (cf. Kolodny and Luz, 1991; Vennemann et al., 2001a), it is generally agreed that this value is applicable to completely recrystallized samples and inorganic phosphatic precipitates (e.g., Kolodny and Luz, 1991; Showers et al., 2002). A common explanation for deviations from $\Delta^{18}\text{O}_{\text{C-P}} \approx 9\%$ is partial oxygen isotope exchange of the carbonate site but not the phosphate site with an ambient fluid during diagenesis. The $\delta^{18}\text{O}_{\text{C}}$ values of phosphates formed in marine waters may hence be lowered if freshwater forms part of the ambient diagenetic fluid (and $\Delta^{18}\text{O}_{\text{C-P}} < 9\%$; Mol-1 to Mol-4, and Mol-7), while for those formed in freshwater but altered in brackish or marine waters, $\delta^{18}\text{O}_{\text{C}}$ values may become higher ($\Delta^{18}\text{O}_{\text{C-P}} > 9\%$; Mol-5, Mol-6; see Table DR1¹).

¹GSA Data Repository item 2007106, Tables DR1 and DR2, oxygen and strontium isotopes and rare earth element compositions of the studied samples, is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

CONCLUSIONS

Our evidence shows that samples Mol-5 and Mol-6 had a diagenetic history that was as complex as that of other teeth of La Molière, and their unusual $\delta^{18}\text{O}_{\text{P}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values reflect formation of these two teeth while the sharks frequented a freshwater environment. Today, the phenomena of entering freshwater systems for extended periods of time is only known for bull sharks (*Carcharhinus leucas*) but not for sand-tiger sharks (*Carcharias taurus*; Compagno et al., 2005), which are considered to be the closest living relative of the La Molière sharks (*Carcharias cf. cuspidatus*). Sharks of La Molière may well have been forced into a freshwater system in order to survive in the rapidly changing environment exemplified by the Upper Marine Molasse sedimentation at this locality (Berger, 1985; Weidmann and Ginsburg, 1999; Becker, 2003; Berger et al., 2005b).

Since most of the teeth sampled are from the genus *Carcharias*, it is reasonable to assume that these sharks lived in habitats with temperatures that were roughly similar to recent habitats (cf. Vennemann et al., 2001a; Compagno et al., 2005). Hence, the difference of ~10‰ in $\delta^{18}\text{O}_{\text{P}}$ values between Mol-5 and Mol-6 and other teeth from the same locality can be related to a similar difference in the $\delta^{18}\text{O}$ of water in which the teeth were formed. Given a typical water temperature of 15–25 °C, approximated from closest living relatives (Compagno et al., 2005) and using the equation for oxygen isotope fractionation between phosphate and water ($T [^{\circ}\text{C}] = 113.3 - 4.38 \times [\delta^{18}\text{O}_{\text{P}} - \delta^{18}\text{O}_{\text{water}}]$) (Kolodny et al., 1983), calculated $\delta^{18}\text{O}$ values of water from the drainage basin are between -8.7‰ to -12.3‰. If we use an empirical relationship between elevation and $\delta^{18}\text{O}$ of precipitation similar to that derived by Garzzone et al. (2000), but regress the altitude- $\delta^{18}\text{O}$ data for the present Alps from nine stations of the Swiss National Network for the Observation of Isotopes in the Water Cycle (NISOT) (Schürch et al., 2003), we find $\delta^{18}\text{O}_h = (-1.425 \times 10^{-6})h^2 + 0.000656h - \delta^{18}\text{O}_{\text{SL}}$, where h represents the altitude (in m) above sea level (SL), and $\delta^{18}\text{O}_{\text{SL}}$ is the $\delta^{18}\text{O}$ value of precipitation at sea level (-3‰, typical for localities adjacent to the sea in subtropical areas). From this, we can calculate a paleoelevation of $\sim 2300 \pm 650$ m. The error is obviously quite large because it incorporates uncertainties in $\delta^{18}\text{O}$ of seawater (-1‰ to 0‰), hence also an uncertainty for $\delta^{18}\text{O}_{\text{SL}}$.

(−4‰ to −3‰) and the temperature range for water given previously. Collectively however, the analyses indicate a Lower Miocene paleogeographic situation with a high mountain belt adjacent to a marginal sea that generally had good connections to the open oceans for most of the time.

ACKNOWLEDGMENTS

This study was conducted with generous funding from the Swiss National Science Foundation (SNF #200021-100530/1). We would like to thank the Geological Museum of Lausanne for the supply of material and extend a special thanks to Thomas Tütken for help with the sample preparation and Y. Kolodny, J.P. Berger, C. Trueman, and C. Lécuyer for very constructive reviews.

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Manuscript received 29 September 2006

Revised manuscript received 3 January 2007

Manuscript accepted 9 January 2007

Printed in USA