



FIGURE 4.17. Secular changes in seawater. (A) Variation in the  $Mg^{2+}/Ca^{2+}$  ratio calculated by Demicco *et al.* (2005). At  $Mg^{2+}/Ca^{2+}$  ratios  $>2$ , high-magnesium calcite and aragonite precipitate, whereas below this value calcite precipitates. Compare this with the distribution of calcite seas and aragonite seas. (B) The  $Ca^{2+}$  molality (asterisks) and  $SO_4^{2-}$  molality (circles) back-calculated from brine compositions measured in fluid inclusions in marine halite (Lowenstein *et al.*, 2001; Demicco *et al.*, 2005). Curves are calculated changes in molalities of these ions in seawater (Demicco *et al.*, 2005). Where the curves cross, ancient seawater passes back and forth over the gypsum divide (Figure 4.14). When  $Ca^{2+} > SO_4^{2-}$ , all the sulfate is used up in the precipitation of gypsum and magnesium sulfate bitters do not form. These times correspond to KCl evaporites and calcite seas. When  $Ca^{2+} < SO_4^{2-}$ , all the calcium is used up in the precipitation of gypsum and sulfate builds up in the brine, leading to magnesium sulfate bitters.