^{238,234}U, ^{232,230}Th, ^{226}Ra, and Ba in Holocene marine carbonate and its potential for age-dating

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In this study we investigate the system of ^{238},^{234}U, ^{232},^{230}Th, ^{226}Ra, and Ba in marine mollusc shells and explore the potential of dating Holocene marine mollusc shells using ^{226}Raexcess/Ba ratios as an alternative or complementary method to radiocarbon dating. Five modern and six Holocene specimens of the Antarctic scallop *Adamussium colbecki* from beach terraces of the Ross Sea region with radiocarbon ages of 700 to 6100 years cal. BP (assuming constant reservoir ^{14}C ages of 1300 years) have been analysed by isotope dilution for Ra (TIMS) and Ba, Th, and U (MC-ICP-MS). ^{226}Ra concentration and ^{226}Ra/Ba ratios in the calcite shells generally decrease with age, and suggest decay as a first order controlling mechanism. Diagenetic uptake of ^{226}Ra or Ba from the environment is not observed.

The two major problems with ^{226}Ra/Ba dating are detrital contamination and in-growth of ^{226}Ra from initial and secondary U present in the shell. Detrital Ba and ^{226}Ra can be accounted for using measured ^{232}Th. On graphs of ^{232}Th/Ba versus ^{232}Th/^{226}Ra subsamples of the same shell fall along mixing lines, which provide a detritally corrected ^{226}Ra/Ba ratio. For shells with a high U concentration or of an old age a correction for ^{226}Ra in-growth from ^{234}U is necessary. Such a correction is complicated by the general 'open system' behaviour of U in mollusc shells, which may lead to a *post mortem* increase of the U concentration by an order of magnitude or more. If this secondary uptake of U occurs at a significant time after the death of the mollusc, such a correction would be difficult or impossible to achieve, and ^{226}Ra in-growth would be the limiting factor in ^{226}Ra/Ba dating. For shells younger than ~ 3000 years in-growth appears to be of minor significance only, and ^{226}Ra/Ba ratios are a potentially useful chronometer. Its main application could be for paleoceanographic studies in regions where ^{14}C reservoir ages vary in space and time due to ocean upwelling or seasonal deep convection, such as the Southern Ocean or the eastern Pacific Ocean, and utilisation of ^{14}C as a paleo circulation proxy.

Structural environments for chloride and fluoride ions in aluminosilicate glasses: NMR results

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The local structural environment of chloride and fluoride ions in magmas, as recorded in their glassy, quenched equivalents, are critical in controlling the solubility of Cl- and F-containing volatiles such as HCl, HF, and volatile metal halides, their mobilities, and their effects on bulk magma properties such as viscosity and silica activity. High-resolution solid-state NMR on F-19 (enabled by super-fast magic angle spinning) and on Cl-35 (enabled by high magnetic fields of 14.1 and 18.8 T) are beginning to reveal a great deal of detail on halide bonding environments in anhydrous systems, and will soon be extended to hydrous glasses.

Synthetic glasses were prepared at 1 bar pressure in sealed Pt tubes and contained roughly 1 wt % F or Cl. In simple binary silicate glasses, almost all fluoride and chloride is coordinated by network modifier cations, although some Si-F bonding can be detected in Na-silicates. In Na-, Ca-, and Ba-aluminosilicates, most F is bonded to Al plus one or more charge-balancing cations, with minor amounts of coordination solely to the higher field strength modifier cations. An exception appears to be Mg aluminosilicates, where most F seems to be coordinated only by Mg. In contrast, chloride in aluminosilicate glasses is bonded only (or at least mostly) to modifier cations. (This conclusion relies on quantifying spectral intensities, as Cl bonded to Al probably will have a large enough quadrupolar coupling constant as to be unobservable in such concentrations.) This dramatic difference in behavior between Cl and F is reflected by the relative stability of Al-Cl (low) vs. Al-F (high) bonds in crystalline solids, and is probably the primary control on the difference in partitioning between magmas and fluid phase of the two halides.