Windows of metamorphic sulfur generation

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The source of metamorphic sulfur, critical in understanding ore-forming processes, has been hypothesised for some time to be largely derived from breakdown of pyrite (FeS_2) to pyrrhotite ($Fe_{1-x}S$) during regional metamorphism. Previous field-based studies of sulfur production focused on graphitic schists or massive sulfide deposits because these are typically pyrite-rich and thus easy to study. In these rocks pyrite has been found to break down over a broad range of temperatures from the lower amphibolite facies up to lower granulite facies. However, in many regions carbonaceous rocks and massive sulfides are volumetrically insignificant, so these studies are not broadly applicable to understanding regional sulfur generation. Pyrite is also found in trace quantities in common metamorphic lithologies that may, through their greater volumes, be more important as source rocks on a regional scale.

In this study a mass balance approach and the thermodynamic computer programs THERMOCALC and PerpleX were used to constrain the P-T range of pyrite breakdown in common metamorphic lithologies. The results suggest that most of the continental crust's metamorphic sulfur is produced in a relatively narrow temperature window corresponding to the terminal breakdown of chlorite. This is because pyrite stability is controlled partly by temperature, and partly by the amount of H_2O present. As T increases, more sulfur is required to maintain equilibrium proportions of H_2O, H_2S and SO_2 in the fluid. At low T, little sulfur is required by metamorphic fluid released during initial chlorite breakdown, whereas at higher T coinciding with the terminal breakdown of chlorite, not only is more fluid present, but the fluid's sulfur requirement has also increased dramatically. Beyond the chlorite stability field there is minimal metamorphic fluid production, except at low P and high T where muscovite can break down without causing melting; conditions that are a long way from typical crustal geotherms.

However, the role of deformation must also be considered. Without deformation, small amounts of fluid in chemical communication with individual pyrite grains will quickly aquire equilibrium concentrations of the sulfur species. But during deformation, there may be a continuous fluid flux past pyrite grains, promoting continual sulfur liberation. In this way, periods of deformation may be the major sulfur-generating episodes during a metamorphic cycle.

He characterisation near the active methane seepage offshore the eastern edge of New Zealand

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Different geochemical He components can be distinguished by their typical $^3He/^4He$ isotope ratios ($\sim10^{-5}$ for mantle-type He, $\sim10^{-8}$ for crustal He and $1.36\cdot10^{-8}$ for atmospheric He). Therefore the $^3He/^4He$ isotope ratio gradients measured in lacustrine sediments allow to characterize the underlying geochemical reservoir from where terrestrial He and simultaneously other transient fluids originate (e.g. CH_4) at a local scale.

The routine measurement of noble gases in the pore waters of ocean sediments was up to now limited by textural problems which allowed only a partial degassing of the sediment/water mixture.

A new extraction method to determine routinely noble gas concentrations in unconsolidated sediment was developed in the last years with the goal to extend the application of dissolved noble gases to the pore water of oceanic sediments. The method applies high speed centrifugation to separate the liquid from the solid phase and allows to use standard protocols for noble gas analysis in water.

The cold seeps offshore the eastern edge of New Zealand have been invstigated on recent cruises with RV TANGAROA in 2006 and RV SONNE in 2007. During the SO191-3 expedition ocean sediment samples intended for noble gas analysis were collected along the Hikurangi margin at three sites (two located at Omakere Ridge and one at Rock Garden).

Our noble gas measurements show that at Omakere Ridge mainly crustal He emanates ($^3He/^4He$ $\sim3.7\text{-}4.2\cdot10^{-7}$). This finding is in line with the $\delta^{13}C$ signature of the water samples collected over the bubble plumes indicating a biogenic CH_4 source.

The seeps at Rock Garden are characterized by the (weak) release of He from a depleted mantle source ($^3He/^4He$ $\sim 3.8\cdot10^{-6}$). The vicinity of the Pacific-Australian subduction plate boundary near the northern part of New Zealand may foster the release of such mantle fluids into the sediment column.