Linking the MIF-S record of sedimentary rocks to biological evolution

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The presence of mass-independently-fractionated sulfur isotopes (MIF-S) in pre-2.45 Ga sedimentary rocks, but the general absence in post-2.45 Ga rocks, have been linked to atmospheric oxgen evolution [1, 2]. However, recent studies have revealed that: (1) Archean sedimentary rocks with no MIF-S signatures are common, particularly during the mid-Archean era [3, 4]; (2) the magnitude of MIF-S may vary greatly within short (<10 m) stratigraphic intervals (e.g., 2.5 Ga Mt. McRae Fm) [5].; (3) Antarctic snow that accumulated during violent (stratospheric) volcanic eruptions trapped sulfates with small but distict MIF-S [6]; (4) Archean sedimentary rocks with MIF-S are more common in organic carbon-rich black shales with hydrothermal alteration effects than in organic carbon-poor sandstones/carbonates [3]; (5) Pyrites in a Jurrasic ammonite show small but distict MIF-S [7]; and (6) H_2S that generated from the thermochemical reduction of sulfate by organic compounds (amino acids) at 150-200°C exhibit distinct MIF-S ($\Delta^{33}S$ as high as 0.6‰ and $\Delta^{36}S$ as low as -1.8‰) [our study]. These new discoveries question a simple linkage between the MIF-S record and an atmospheric O_2 evolution model. Here we suggest that thermochemical sulfate reduction (i.e., TSR) by organic matter during sediment diagenesis may have been the primary cause of MIF-S in sedimentary rocks.

The extrapolation of the observed relationships between $\Delta^{33}S$ values and sulfate reduction rates suggests that, at 100°C, TSR occurs within ~10,000 years and the single-step $\Delta^{33}S$ values are ~1‰. If recycling and Rayleigh fractionation processes are also considered, the entire ranges (i.e., -4 to +10‰) of $\Delta^{33}S$ that were observed in pre-2.4 Ga sedimentary rocks are easily accounted for. Furthermore, the $\Delta^{33}S$ and $\Delta^{36}S$ relationships of the experimental products are essentially identical of those in pre-2.45 Ga rocks with MIF-S. Therefore, the MIF-S record of sedimentary rocks may be linked to the thermal and biological evolution of the Earth, rather than to its atmospheric evolution.

References

[1] Farquhar J. and Wing B. (2003) *EPSL* **213.** 1-13.
[2] Bekker A. *et al*. (2004) *Nature* **427.** 117-120.
[3] Ohmoto *et al*. (2006) *Nature 442.* 980-911.
[4] Ono *et al*. (2006) *S. A. J. Geol.* **109.** 97-108.
[5] Kaufman A.J. *et al*. (2006) *Astrobiol*. **6.** 136-137.
[6] Baroni M. *et al*. (2007) *Science* **315.** 84-87.
[7] Ono S. *et al*. (2006) *GCA* **70.** 2238-2252.

Configurational heat capacity and structure of aluminosilicate melts

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The Na^+- and Ca^{2+}-aluminosilicate melt systems are used as analogs for the more complex natural magmatic systems of the Earth in studies of the physical properties, structure and flow mechanisms of silicate melts. Although the description of flow in binary alkali-silicate melts is clear; that for multi-oxide melt compositions quickly becomes very complex. The presence of aluminium in silicate melts creates the need for a charge-balancing cation for the tetrahedrally co-ordinated Al^{3+}. The presence of both mono- and di-valent ions in aluminosilicate melts raises questions about which atom is preferred as the charge balancer and which will create the non-bridging oxygens. This study addresses the change in structure of peraluminous and peralkaline/metaluminous Na_2O-CaO-Al_2O_3-SiO_2 melts with composition, based on shear viscosity and heat capacity data; and calculation of configurational entropy and configurational heat capacity.

Viscosity has been determined using the micropenetration technique; the heat capacity and configurational heat capacity have been determined by differential scanning calorimetry. The viscosity of these melts indicates there are structural changes at the condition where there is no longer enough Na^+ or Ca^{2+} to charge balance all of the Al^{3+} in tetrahedral co-ordination. The heat capacity data, however, provide more information about the energy required for flow to occur in the melts as the structure changes due to changing composition.

The configurational heat capacity is determined from the difference between the liquid and the glass heat capacity at the glass transition temperature. Configurational entropy $S_{conf}(T_g)$ has been calculated from the viscosity data using the Adam-Gibbs equation for viscosity as a function of configuration entropy and temperature. If there are no anomalous changes in melt structure, the heat capacities of the glasses and melts may be described by a linear sum of the contributions of the component oxides. The configurational entropies and configurational heat capacities determined for the melts in this study can not be described by such a linear summation. For all physical properties determined for these melts, there is one trend for the peraluminous melts and another trend for the peralkaline/metaluminous composition melts. In addition to the change in structure implied from changes in the trends of the viscosity and heat capacity data when there are no longer enough charge balancers for all of the Al^{3+} in tetrahedral co-ordination, there appears to be a further change in structure at the composition where there are no longer enough Ca^{2+} in the melt that each Al^{3+} tetrahedron has its own charge balancer – that is the composition at which pairs of Al^{3+} tetrahedra must share a Ca^{2+} as charge balancer