High magnitude MIF-S due to increased atmospheric $p(O_2)$

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Earth's atmosphere experienced several profound changes in the geological past. Among these was the Great Oxidation Event (GOE) at ~2.4 Ga as indicated by the subsequent absence of mass independently fractionated sulphur isotopes (MIF-S). The temporal evolution in MIF-S from low towards high magnitude was recently suggested to reflect changes in the total atmospheric composition and not exclusively resulting from variations in $p(O_2)$. [1] proposed that a rise in the atmospheric SO_2/H_2S ratio enlarged the magnitude of MIF-S.

Black shales from the Superior craton (2.71 Ga) record a high magnitude MIF-S signal ($\Delta^{33}S$ up to 4‰) following a period with greatly attenuated MIF-S between 3.2 and 2.7 Ga. Their $\Delta^{33}S$ vs. $\Delta^{36}S$ relationship shows a slope of -1, which appears to be a typical signature of rocks younger than 2.7 Ga. We interpret this shift towards high magnitude MIF-S and the concomitant change in the slope of $\Delta^{33}S$ vs. $\Delta^{36}S$ at 2.71 Ga as a consequence of a rise in atmospheric SO_2/H_2S. However, we suggest that a rise in atmospheric O_2 ultimately caused this increase, not variations in volcanic outgassing [1]. An increase in atmospheric $p(O_2)$ would have strengthened the conversion of H_2S to SO_2 resulting in a higher SO_2/H_2S ratio. Such a scenario would be consistent with a proposed onset of oxidative weathering already at 2.7 Ga [2]. Still, a generally reducing atmosphere kept oxygen levels below 10^{-5} PAL, low enough to allow for MIF-S until the GOE at ~2.4 Ga.

[1] Halevy *et al*. (2010) *Science* **329**, 204–207. [2] Frei *et al*. (2009) *Nature* **461**, 250–254.

Internal structure of icy satellites of Jupiter and Saturn and subsurface oceans

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Models of the internal structure of icy satellites have been constructed on the basis of the mass and moment of inertia constraints, geochemical constraints on composition of silicate fractions of ordinary and carbonaceous chondrites, and thermodynamic data on the equations of state of minerals and high-pressure ices [1, 2]. The mass and moment of inertia values are used as input data for determination of the thickness of an outer water-ice shell, the density distribution with depth, and the core sizes and masses. The equilibrium phase assemblages in the system Na_2O-TiO_2-CaO-FeO-MgO-Al_2O_3-SiO_2 were calculated using the technique of free energy minimization combined with the Mie-Grüneisen equation of state. The density variations in the mantle and Fe-S core radii are found by the Monte-Carlo method. The allowed thickness of Europa's H_2O layer (whether liquid or ice) ranges from 115 to 135 km (6-8% of total mass) for a L/LL-type chondritic mantle [2]. Two alternative models of Ganymede's outer shell composed of the high-pressure ice phases or of water and ice are considered. The thickness of the shell is in the range 800-900 km. The content of H_2O in Ganymede's outer shell is 46-48% [1]. We show that Callisto must only be partially differentiated into an outer ice-I layer, a water ocean, a rock-ice mantle, and a rock-iron core. The maximum thickness of the outer water-ice shell is up to ~300 km and that of the internal ocean is about 150 km. The total amount of H_2O in Callisto is found to be 48-55 wt%. The results of modelling support the hypothesis that Callisto may have an internal liquid-water ocean [2, 3]. The correspondence between the density and moment of inertia values for the Galilean satellites shows that their bulk compositions may be, in general, similar and may be described by the composition close to a material of the L/LL type chondrites [1-3]. Planetesimals composed of these types of ordinary chondrites could be considered as analogues of building material for the rock-iron cores of the Galilean satellites. A comparison of the internal structure of Ganymede and Callisto with that of Titan has been made.

[1] Kuskov O.L. & Kronrod V.A. (2001) *Icarus* **151**, 204–227. [2] Kuskov O.L. & Kronrod V.A. (2005) *Icarus* **177**, 550–569. [3] Kuskov O.L. & Kronrod V.A. (2005) *Solar Syst. Res*. **39**, 283–301.