

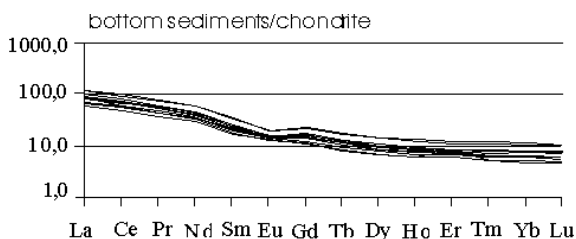
## Geochemical features of the Amur River sediments in its middle reaches

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The Amur River is one of the largest rivers of the East Asia. The main channel and tributaries of the Amur River cross the geological units of different ages.

A distribution of rare earth elements in the studied samples of the bottom sediments of the Amur River is moderately differentiated ([La/Yb]  $n=9.6-14.9$ ). A characteristic feature of their distribution is also an enrichment in LREE relatively to MREE and comparatively gentle graph in the in the field of MREE and heavy HREE which is supported by the ratios of [La/Sm] $n=3.3-4.1$  and [Gd/Yb]=1.1-2.2. All spectra of rare earth elements have moderately expressed negative Eu anomaly (Eu/Eu\* $=0.7-0.9$ ) (Fig.1).



**Figure 1:** The rare earth elements' distribution in the bottom sediments of the Amur river. The composition of chondrite is used according to [1].

In comparison with the composition of the upper continental crust the bottom sediments under study are at a definite degree depleted in such elements as Sc (3.7 – 9.0 ppm), Cu (8-22ppm), Nb (9-13 ppm), Ta (0.21-0.37 ppm), Y (9-17 ppm). The concentration of Zn (50-75 ppm), Rb (82-109 ppm), Sr (290-350 ppm), Pb (15-24 ppm), W (1.1-2.2 ppm), Th (5.2-11.9 ppm), U (1.0-5.4 ppm), REE correspond to the level of those in the upper continental crust while the concentrations of Ba (550-840 ppm), V (63 – 81 ppm), Cr (63-80 ppm), Co (12-14 ppm), Ni (31-43 ppm), Zr (190-309 ppm) a bit higher than their crust values.

It was established that the most probable sources of the bottom sediments in the studied section of the Amur River were siliceous acid magmatic or metasedimentary rocks.

[1] McDonough, Sun S-s. (1995) *Chemical Geology*. **120**, 223–253.

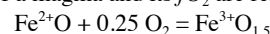
## Systematic underestimation of the oxidation state of MORB glasses

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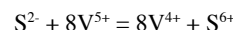
The  $Fe^{3+}/\Sigma Fe$  of a magma and its  $fO_2$  are related by:



This dependence has been calibrated using a wide range of silicate melt compositions equilibrated at known  $fO_2$  and analysed by wet chemistry ([1], [2]) and Mössbauer. Analyses of large sets of natural MORB glasses by wet chemistry (e.g. [3], [4]) report tight distributions around  $Fe^{3+}/\Sigma Fe \approx 0.1$ , corresponding to the relative oxidation state  $\Delta QFM \approx -0.5$ . However, recent determinations of  $Fe^{3+}/\Sigma Fe$  on MORB glasses by XANES ([5], [6]) consistently return more oxidised values, about 0.16, corresponding to  $\Delta QFM \approx +0.5$ .

The wet chemistry method [7] relies on the complete oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  by reduction of  $V^{5+}$  to  $V^{4+}$ . However, it does not discriminate between  $Fe^{2+}$  and other reduced species. One such species,  $S^{2-}$ , is present in MORB glasses at  $\sim 10^3$  ppm, but not in the glasses used to establish the  $Fe^{3+}/\Sigma Fe - fO_2$  relationship.

To test the effect of  $S^{2-}$  during wet chemistry, a series of Fe-free glasses with the An-Di eutectic composition were prepared using  $CO_2-CO-SO_2$  gas mixtures to produce  $S^{2-}$  ranging from 0 to 4500 ppm [8]. These glasses were subjected to the procedure of ref. [7]. The results establish that  $S^{2-}$  is fully oxidised during dissolution to  $S^{6+}$  (i.e. sulfate) according to the reaction:



From the reaction stoichiometry, 1000 ppm  $S^{2-}$  is equal to 2 wt%  $Fe_2O_3$ , which is more than enough to account for the discrepancy in the  $Fe^{3+}/\Sigma Fe$  of MORB between wet chemistry and XANES. Determination of S and its speciation in basalts is essential to understanding their redox state, since degassing of S as  $SO_2$  will tend to further reduce basalts with  $S^{2-}$  but oxidise basalts with  $S^{6+}$  [9].

[1] Kilinc *et al.* (1983) *Contrib. Min. Pet.* **83**, 136–140.  
[2] Kress & Carmichael (1991) *Contrib. Min. Pet.* **108**, 82–92.  
[3] Christie *et al.* (1986) *EPSL* **79**, 397–411. [4] Bézou & Humler (2005) *GCA*, **69**, 711–725. [5] Berry *et al.* (2003) *Am. Min.* **88**, 967–977. [6] Kelley & Cottrell (2009) *Science*, **325**, 605–607. [7] Wilson (1960) *Anal.* **85**, 823–827. [8] O'Neill & Mavrogenes (2002) *J. Pet.* **43**, 1049–1087. [9] Metrich & Clochiatti (1996) *GCA* **60**, 4151–4160