

Enrichments of heavy sulfur (^{34}S) in sulfide minerals: Gas hydrates, methane delivery, and anaerobic methane oxidation

W.S. BOROWSKI,^{1*} N.M. RODRIGUEZ,² C.K. PAULL,³
AND W. USSLER III³

¹Eastern Kentucky University, Richmond, KY 40475, USA

(*correspondence: w.borowski@eku.edu)

²Shell, Houston, TX 77079, USA

³MBARI, Moss Landing, CA 95039, USA

The sulfur isotopic composition of authigenic, sedimentary sulfide minerals is largely controlled by sulfate reduction and related processes. Histograms show that $\delta^{34}\text{S}$ values of sulfide minerals are most often negative ($\delta^{34}\text{S} < 0\text{‰}$ CDT) reflecting the original isotopic composition of seawater sulfate (now 21‰), microbially-mediated fractions of ~-8 to -40‰ ($\alpha = 1.029-1.059$) during sulfate reduction, and more extreme fractionations caused by sulfur disproportionation. Enrichments of heavy sulfur ($\delta^{34}\text{S} > 0\text{‰}$) represent about 18% of measured $\delta^{34}\text{S}$ values worldwide. Excluding seafloor seepage sites, most (~59%) ^{34}S enrichments are associated with anaerobic methane oxidation (AMO) occurring at the sulfate-methane interface (SMI).

Blake Ridge (offshore southeastern USA) sediments associated with methane gas hydrates experience higher rates of upward methane diffusion than sediments in similar depositional environments not coincident with gas hydrates. Methane delivery to the SMI fuels AMO and results in $\delta^{34}\text{S}$ values of sulfide minerals of up to +23.6‰. $\delta^{34}\text{S}$ values in the sulfate reduction zone are negative (-46.6 to -8.4‰) but become more positive approaching the SMI, where maximum enrichments of heavy sulfur in interstitial sulfate and authigenic sulfide minerals generally occur. ^{34}S enrichments below the SMI likely reflect the positions of earlier SMIs. Heavy ^{34}S values in the sedimentary record with appropriate depositional and diagenetic settings may indicate the presence of ancient gas hydrate deposits. Such ^{34}S enrichments are not diagnostic but should be distinguished by their depositional environments and differing diagenetic signals.

Regularities of luminescence variations of substance of different geospheres of the Earth

N.N. BOROZNOVSKAYA¹, T.S. NEBERA¹, A.V. KLIMKIN²,
V.M. KLIMKIN² AND P.A. TISHIN¹

¹Tomsk State University, Tomsk, Russia

²Institute of Atmospheric Optics SB RAS, Tomsk, Russia

Luminescence (L) of the following geospheres is examined: atmosphere, hydrosphere, the earth's crust, the upper mantle. In the atmosphere the L agents are free atoms and molecules of gaseous admixtures, as well as aerosol of mineral and organic origin. In lower atmosphere the excited states of atoms and molecules are liable to quenching in atomic-molecular collisions, and only components with minor radiation lifetimes of excited states, such as NO, OH. In the upper atmosphere the molecular quenching does not have such significance. Here, under influence of solar radiation, electron and ion flows, one can observe fluorescence (FL) of a great number of free atoms, molecules and radicals.

Admixtures in natural waters are characterized by intensive FL. These are admixtures of mineral and organic origins (phyto- and bioplankton and their decomposition products). FL spectrum of phytoplankton has a dual line in the region 680-740 nm, which is typical for chlorophyll.

Basic luminogens within the earth's crust, 92 % of which is formed of silicates, are defects in silicon-aluminum-oxygen tetrahedron (O^-) and isomorphous admixtures instead of K, Na, Ca, Mg, Al, Si (Ti^+ , Pb^{2+} , Mn^{2+} , Fe^{3+} , Cr^{3+} and rare earths). L of O^- defects may be regarded as background. Its intensity is often determined by presence of decay structures and cooling rate. L of impurity defects in the earth's crust minerals depends on formation conditions (depth, crystallization temperature and cooling rate). X-ray luminescence (RL) of garnets, zoisites and omphacites from crust and mantle rocks, and RL of pyroxenes from low-temperature metasomatic jadeites are studied. L of Mn^{2+} (570-590 nm), Cr^{3+} (680-700 nm) and Fe^{3+} (700-730 nm) in the lower earth's crust levels and upper mantle minerals correlates with vicissitude of metamorphic processes.

Thus, L peculiarities of substance of different geospheres is greatly determined by its density, internal structure and environment. FL of a great number of free atoms, molecules, radicals in the atmosphere gives place to L of dotted defects in a structure of lithosphere minerals, concentration of which is determined by disturbance of stoichiometry and unsoundness of crystal lattices of the minerals, by availability of polymorphous and phase transformations that is connected with depth, crystallization rate and rate of metamorphous transformations, oxidation-reduction and temperature regime.