UDC: 621.039.553

REVIEW: THE ROLE OF RADIATION, Fe(III) OXIDES AND MONTMORILLONITE IN ORGANIC METAMORPHISM

I.I. Mustafayev, M.K. Ismayilova
Institute of Radiation Problems of ANAS
ismayilovamehpara@gmail.com

Abstract: This paper aimed to investigate the variation of preserving organic matter bound in the interlayer space of montmorillonite under radiation. Interactions between organic matter and mineral matrices are critical to the preservation of soil and sediment organic matter. In addition to clay minerals, Fe(III) oxides particles have recently been shown to be responsible for the protection and burial of a large fraction of sedimentary organic carbon.

Keywords: radiation, uranium, organic matter, montmorillonite, clay, iron oxides, metamorphism

Though many questions remain about the origin of oil, the generally accepted scenario is that organic matter buried underground underwent organic metamorphism under appropriate temperature and pressure conditions and thus formed the hydrocarbon molecules constituting petroleum. The hydrocarbon molecules produced at this time and the quality of the petroleum itself vary depending on differences in the extent of organic metamorphism.

Preservation of organic matter in sediments promoted by iron (based on NASA materials)

The biogeochemical cycles of iron and organic carbon are strongly interlinked. In oceanic waters, organic ligands have been shown to control the concentration of dissolved iron. In soils, solid iron phases shelter and preserve organic carbon, but the role of iron in the preservation of organic matter in sediments has not been clearly established. It was used an iron reduction method previously applied to soils to determine the amount of organic carbon associated with reactive iron phases in sediments of various mineralogies collected from a wide range of depositional environments. The findings suggest that 21,5 per cent of the organic carbon in sediments is directly bound to reactive iron phases. Further estimated that a global mass of (19-45)%grams of organic carbon is preserved in surface marine sediments as a result of its association with iron. Lalonde and his collegues propose that these associations between organic carbon and iron, which are formed primarily through co-precipitation and/or direct chelation, promote the preservation of organic carbon in sediments [1]. Because reactive iron phases are metastable over geological timescales, suggested that they serve as an efficient 'rusty sink' for organic carbon, acting as a key factor in the long-term storage of organic carbon and thus contributing to the global cycles of carbon, oxygen and sulphur.

Preservation of organic matter on Mars by sulfur(based on NASA materials)

Based on NASA Astrophysics Data System (ADS) reported that Deltaic-lacustrine mudstones at Pahrump Hills, Gale Crater, Mars yielded a variety of sulfur-containing volatiles upon heating to 500-860°C, as detected by the Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover. The detection of organosulfur compounds comprising thiophenes, dimethylsulfide and thiols by gas chromatography-mass spectrometry and evolved gas analyses, together with aromatic and other hydrocarbon molecules with distributions specific to the sample (i.e., not from the SAM background) indicate that some or all of these organic fragments released at high temperatures are indigenous to the mudstones. The organosulfur compounds are most likely derived from sulfur organics in the sediments. However, there is a possibility that sulfurization of some organic fragments occurred in the oven. On Earth, sulfurization of organic matter is a key process that aids preservation over geological time-scales. This is because it reduces reactive functional groups and adds cross links between small unstable molecules thereby converting them into recalcitrant macromolecules. Sulfurization of organic materials prior to deposition and during early diagenesis may have been a key mechanism responsible for organic matter preservation in the Murray formation mudstones. Sulfur-bearing organics have also been observed in carbonaceous meteorites and there is indication of their presence in the Tissint martian meteorite. A quantitative assessment of organosulfur compounds relative to their non-organic counterparts will be presented for the Murray formation mudstones analyzed by SAM and meteorites analyzed in the laboratory under similar analytical conditions [2].

Interstellar and Solar System organic matter preserved in interplanetary dust (based on NASA materials)

NASA Technical Reports Server (NTRS) presents that interplanetary dust particles (IDPs) collected in the Earths stratosphere derive from collisions among asteroids and by the disruption and outgassing of short-period comets. Chondritic porous (CP) IDPs are among the most primitive Solar System materials. CP-IDPs have been linked to cometary parent bodies by their mineralogy, textures, C-content, and dynamical histories. CP-IDPs are fragile, fine-grained assemblages of anhydrous amorphous and crystalline silicates, oxides and sulfides bound together by abundant carbonaceous material. Ancient silicate, oxide, and SiC stardust grains exhibiting highly anomalous isotopic compositions are abundant in CP-IDPs, constituting 0.01-1% of the mass of the particles. The organic matter in CP-IDPs is isotopically anomalous, with enrichments in D/H reaching 50x the terrestrial SMOW value and 15N/14N ratios up to 3x terrestrial standard compositions. These anomalies are indicative of low T (10-100 K) mass fractionation in cold molecular cloud or the outermost reaches of the protosolar disk. The organic matter shows distinct morphologies, including sub-um globules, bubbly textures, featureless, and with mineral inclusions. Infrared spectroscopy and mass spectrometry studies of organic matter in IDPs reveals diverse species including aliphatic and aromatic compounds. The organic matter with the highest isotopic anomalies appears to be richer in aliphatic compounds. These materials also bear similarities and differences with primitive, isotopically anomalous organic matter in carbonaceous chondrite meteorites. The diversity of the organic chemistry, morphology, and isotopic properties in IDPs and meteorites reflects variable preservation of interstellar/primordial components and Solar System processing. One unifying feature is the presence of sub-um isotopically anomalous organic globules among all primitive materials, including IDPs, meteorites, and comet Wild-2 samples returned by the Stardust mission [3].

Variation of preserving organic matter bound in interlayer of montmorillonite induced by microbial metabolic process

Zhao Yulian and his collegues investigate the variation of preserving organic matter bound in the interlayer space of montmorillonite (Mt) induced by a microbe metabolic process [4-23]. They selected Bacillus pumilus as the common soil native bacteria. The alteration of d 001 value, functional group, and C,N organic matter contents caused by bacteria were analyzed by XRD, FTIR, and elementary analyzer, respectively. XRD results showed that the d 001 value of montmorillonite increased with the concentration decreasing and decreased with the culture time increasing after interacting with bacteria indicating the interlayer space of montmorillonite was connected with the organic matter. The findings of long-term interaction by resetting culture conditions implied that the montmorillonite buffered the organic matter when the nutrition was enough and released again when the nutrition was lacking. The results of the elementary analyzer declared the content of organic matter was according to the d 001 value of montmorillonite and N organic matter which played a major impact. FTIR results confirmed that the Si-O stretching vibrations of Mt were affected by the functional group of organic matter. The results showed that the montmorillonite under the influence of soil bacteria has a strong buffering capacity for preserving organic matter into the interlayer space in a short-term. It might provide critical implications for understanding the evolution process and the preservation of fertilization which was in the over-fertilization or less-fertilization conditions on farmland.

Where is DNA preserved in soil organic matter? (based on NASA materials)

Zaccone Claudio and co-authors defined that Deoxyribonucleic acid (DNA) consists of long chains of alternating sugar and phosphate residues twisted in the form of a helix. Upon decomposition of plant and animal debris, this nucleic acid is released into the soil, where its fate is still not completely understood. In fact, although DNA is one of the organic compounds from living cells that is apparently broken down rapidly in soils, it is also potentially capable of being incorporated in (or interact with) the precursors of humic molecules. In order to track DNA occurrence in soil organic matter (SOM) fractions, an experiment was set up as a randomized complete block design with two factors, namely biochar addition and organic amendment. In particular, biochar (BC), applied at a rate of 20 t/ha, was combined with municipal solid waste compost (BC+MC) at a rate equivalent to 75 kg/ha of potentially available N, and with sewage sludge (BC+SS) at a rate equivalent to 75 kg/ha of potentially available N. Using a physical fractionation method, free SOM located between aggregates (unprotected C pool; FR), SOM occluded within macroaggregates (C pool weakly protected by physical mechanisms; MA), SOM occluded within microaggregates (C pool strongly protected by physical mechanisms; MI), and SOM associated with the mineral fractions (chemically-protected C pool; MIN) were separated from soil samples. DNA was then isolated from each fraction of the two series, as well as from the unamended soil (C) and from the bulk soils (WS), using Powersoil DNA isolation kit (MoBio, CA, USA) with a modified protocol. Data clearly show that the DNA survived the SOM fractionation, thus suggesting that physical fractionation methods create less artifacts compared to the chemical ones. Moreover, in both BC+MC and BC+SS series, most of the isolated DNA was present in the FR fraction, followed by the MA and the MI fractions. No DNA was recovered from the MIN fraction. This finding supports the idea that most of the DNA occurring in the SOM [24].

Role of ionizing radiation in the natural history of the Earth

A role of ionizing radiation in some global processes and events in geological history of the Earth is considered by Byakov V.M.[25-30]. In particular, was discussed: (1) the influence of ionizing radiation from radioactive nuclei disseminated in sedimentary rocks on the transformation of terrestrial organic matter into stone coals and oil; (2) the effect of cosmic rays from Supernova stars as a common cause of quasi-regular global geological processes and biocatastrophes.

Taking a look back in time on the history of the Earth we would like to discuss two problems where the role of ionizing radiation was, probably, very significant: (1) the transformation of terrestrial organic matter (TOM) to stone coal and oil and (2) planetary biocatastrophes accompanied by global environmental changes. From a chemical point of view TOM is a complicated mixture of high-molecular-weight compounds composed mainly from four elements - C, H, O, N. With time TOM undergoes alterations accompanied by an increase of the carbon atom fraction. This process is often called carbonization or coalification. Only beds of organic matter (OM) form coals, while oil and natural gas are by-products of carbonization of dispersed OM. One usually attributes the formation of coal and oil to the action of heat flux from depth of the Earth. The effect of ionizing radiation from radioactive elements dispersed in small amounts (several g/ton) in matter itself, although discussed in the literature (Mazor et al., 1984), has never been considered as a basic factor in the carbonization of TOM. Byakov V.M. presents arguments in favor of the hypothesis that formation of the main power resources on the Earth is a radiation-chemical process. It should be mentioned that ionizing radiation plays an important role in the genesis of a remarkable physical property of oil, its optical activity. It has been suggested the following empirical relationship for the mean optical activity α (grad/dm) of oils formed in a deposit of the age t (Myr) and uranium content U (g/ton) in it (Byakov et al., 1991).

$$\alpha\ (t,U) = 0.85(t)\ /\ \sqrt{t}$$

This equation successfully predicts an extremely high optical activity of crude oils from uraniferous black shales as well (Byakov et al., 1991). Proportionality between α and U indicates on biogenetic origin of oil and could be of special importance for the problem of origin of life (Goldanskii, 1997).

Results:

- The role of iron in the preservation of organic matter in sediments has not been clearly established. It was suggested that they serve as an efficient 'rusty sink' for organic carbon, acting as a key factor in the long-term storage of organic carbon and thus contributing to the global cycles of carbon, oxygen and sulphur.
- On Earth, sulfurization of organic matter is a key process that aids preservation over geological time-scales. This is because it reduces reactive functional groups and adds cross links between small unstable molecules thereby converting them into recalcitrant macromolecules.
- The results showed that the montmorillonite under the influence of soil bacteria has a strong buffering capacity for preserving organic matter into the interlayer space in a short-term. It might provide critical implications for understanding the evolution process and the preservation of fertilization which was in the over-fertilization or less-fertilization conditions on farmland.
- The role of ionizing radiation in natural processes is still generally underestimated. The above data suggest a modification of the traditional view on formation mechanisms of main power resources, coal and oil, and indicates the important role of radiation from disseminated radioactive elements.
- It was discovered the role of uranium radiation in the formation of oil. It was found that intense separation of petroleum hydrocarbons from disseminated OM begins at a certain stage of its maturation, when the content of carbon in it increases to C=0.74g/g.

References

1. Lalonde, Karine; Mucci, Alfonso; Ouellet, Alexandre Gaolinas.Preservation of organic matter in sediments promoted by iron. Geochemistry: A rusty carbon sink. [Nature. 2012]
2. Eigenbrode, J. L.; Steele, A.; Summons, R. E.; McAdam, A.; Sutter, B.; Franz, H. B.; Freissinet, C.; Millan, M.; Glavin, D. P.; Szopa, C.; Conrad, P. G.; Mahaffy, P. R. .Preservation of organic matter on Mars by sulfur. American Geophysical Union, Fall General Assembly 2016, abstract id.P21D-082016.
3. Messenger Scott; Nakamura-Messenger Keiko. Interstellar and Solar System organic matter preserved in interplanetary dust. NASA Astrophysics Data System (ADS).2015.
4. Zhao, Yulian; Dong, Faqin; Dai, Qunwei; Li, Gang; Ma, Jie. Variation of preserving organic matter bound in interlayer of montmorillonite induced by microbial metabolic process., 2017. pp 1-8.pub.med. PubMed: 28744678 DOI: 10.1007/s11356-017-9806-7
5. Ehlmann BL, Mustard JF, Fassett CI, Schon SC, Head JW III, Des Marais DJ, Grant JA, Murchie SL (2008) Clay minerals in delta deposits and organic preservation potential on Mars. Nat Geosci 1(6):355–358
6. Huang PM, Bollag JM, Huang PM, Senesi N, Buffle J (1998) Minerals-organics-microorganisms interactions in the soil environment. Comput Chem Eng 23(1):1–9

7. Liu D, Dong HL, Bishop ME, Zhang J, Wang H, Xie S, Wang S, Huang L, Eberl DD (2012) Microbial reduction of structural iron in interstratified illite-smectite minerals by a sulfate-reducing bacterium. Geobiology 10(2):150–162
8. Mueller B (2015) Experimental interactions between clay minerals and bacteria: a review. Pedosphere 25(6):799–810
9. Pannirselvam M, Gupta RK, Bhattacharya SN, Shanks RA (2007) Intercalation of montmorillonite by interlayer adsorption and complex formation. Adv Mater Res 29-30:295–298
10. Parkes JR (1998) Geomicrobiology: interactions between microbes and minerals. Mineral Mag 62(5):725–726
11. Pearson VK, Sephton MA, Kearsley AT, Bland PA, Franchi IA, Gilmour I (2002) Clay mineral-organic matter relationships in the early solar system. Meteorit Planet Sci 37(12):1829–1833
12. Peinemann N, Amiotti NM, Zalba P, Villamil MB (2000) Effect of clay minerals and organic matter on the cation exchange capacity of silt fractions. J Plant Nutr Soil Sci 163(1):47–52
13. Spence A, Robinson C, Hanson RE (2014) The effects of microstructural changes on montmorillonite–microbial interactions. J Mol Struct 1056-1057:157–165
14. Thuc C-NH, Grillet A-C, Reinert L, Ohashi F, Thuc HH, Duclaux L (2010) Separation and purification of montmorillonite and polyethylene oxide modified montmorillonite from Vietnamese bentonites. Appl Clay Sci 49:229–238
15. Vorhies JS, Gaines RR (2009) Microbial dissolution of clay minerals as a source of iron and silica in marine sediments. Nat Geosci 2(3):221–225
16. Yesiltas M, Kebukawa Y (2016) Associations of organic matter with minerals in Tagish Lake meteorite via high spatial resolution synchrotron-based FTIR microspectroscopy. Meteorit Planet Sci 51(3):584–595
17. Yu BS, Dong HL, Han PY (2012) Experimental research on microbial degradation of organic matter adsorbed in smectite internal surface area in the interlayer of the structure. Acta Petrol Sin 28(3):949–960
18. Zeng Q, Dong HL, Zhao LD, Huang QY (2016a) Preservation of organic matter in nontronite against iron redox cycling. Am Mineral 101:120–133
19. Zeng LL, Hong ZS, Wang C, Yang ZZ (2016b) Experimental study on physical properties of clays with organic matter soluble and insoluble in water. Appl Clay Sci 132:660–667
20. Zhang J, Dong HL, Zeng Q, Agrawal A (2014) The role of Fe(III) bioreduction by methanogens in the preservation of organic matter in smectite. Chem Geol 389:16–28
21. Zhang G, Kim J, Dong HL, Sommer AJ (2016) Microbial effects in promoting the smectite to illite reaction: role of organic matter intercalated in the interlayer. Am Mineral 92(8–9):1401–1410
22. Zhao YL, Dai QW, Dong FQ, Han LB, Dang Z (2017) Microbially retention process of Sr(II) ions mediated by metabolite and putrefaction in montmorillonite-*Pseudomonas fluorescens* aqueous system. J Nanosci Nanotechnol 17:6597–6602
23. Zhu Y, Li Y, Lu AH, Wang HR, Yang XX, Wang CQ, Cao WZ, Wang QH, Zhang XL, Pan DM, Pan XH (2011) Study of the interaction between bentonite and a strain of *Bacillus Mucilaginosus*. Clay Clay Miner 59(5):538–545
24. Zaccone Claudio, Beneduce Luciano, Plaza Caosar. Where is DNA preserved in soil organic matter? NASA Astrophysics Data System (ADS).2015.
25. Byakov, V.M., 1983. The role of actinides fission in the formation of medium heavy elements in Nature. Radiochem. Radioanal. Lett. 57 (4), 233–240.
26. Byakov, V.M., Pimenov, G.G., Stepanova, O.P., 1987. Role of ionizing radiations in the coalification of organic matter in Nature. High Energy Chem. 21 (1), 34–38.
27. Byakov, V.M., Pimenov, G.G., Stepanova, O.P., 1990. To the estimation of the maximum paleotemparature in sedimentary rocks. Dok. Acad. Nauk SSSR 315 (5), 1184–1187.

28. Byakov, V.M., 1991. Role of ionizing radiation in the chemical evolution of a substance in Nature. High Energy Chem. 25 (5), 325–336.
29. Byakov, V.M., Pimenov, G.G., Stepanova, O.P., 1991. Optical activity of crude oils: radio-chemical processes. High Energy Chem. 25 (1), 15–19.
30. Byakov, V.M., Stepanov, S.V., Stepanova, O.P., 1997. Quasiregular staying of solar system in supernova remnants and natural earth history. Radiat. Phys. Chem. 49 (3), 299–305.

ОБЗОР: РОЛЬ РАДИАЦИИ, Fe(III) ОКСИДА И МОНТМОРИЛЛОНИТА В ОРГАНИЧЕСКОЙ МЕТАМОРФИЗМЕ

И.И. Мустафаев, М.К. Исмаилова

Резюме: Эта статья предназначена для исследования изменений в органической материале в межслоевом пространстве монтмориллонита. Взаимодействие между органическим веществом и минеральными матрицами важно для сохранения органического вещества в почве и осадках. Было показано, что помимо глинистых минералов частицы, оксида железа (III) играет роль в преобразовании значительной части осадочного органического углерода.

Ключевые слова: радиация, уран, органический материал, монтмориллонит, глина, оксид железа, метаморфизм.

XÜLASƏ: ÜZVİ MADDƏLƏRİN METAMORFİZMİNDƏ RADİASİYA, Fe(III) OKSİD VƏ MONTMORİLLONİTİN ROLU

İ.İ. Mustafayev, M.K. İsmayılova

Xülasə: Bu məqalədə məgsəd radiasiyanın təsirilə montmorillonitin layları arasında baş verən üzvi maddələrin dəyişməsini araşdırmaqdır. Üzvi maddə və mineral matrislər arasındakı qarşılıqlı təsirlər üzvi maddənin torpaqda qalması və çökməsi üçün əhəmiyyət kəsb edir. Müəyyən edilmişdir ki, gil minerallarından əlavə, Fe (III) oksid hissəcikləri də üzvi karbon çöküntüsünün böyük bir hissəsinin yaranmasına səbəb olmuşdur.

Açar sözlər: radiasiya, uran, üzvi material, montmorillonit. gil, dəmir oksidləri, metamorfizm