Mg-aenigmatite from the Tazheran massif (East Siberia, Russia)

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Aenigmatite ($NaFe^{2+}{}_5TiSi_6O_{20}$) occurs usually in high-Na magmatic rocks in association with nepheline, aegirine or augite, arfedsonite or riebeeckite, K-feldspar, sometimes fayalite. Variations of its composition are related mostly to the presence of Fe^{3+} whereas content of MnO and MgO is low (usually < 1 wt%). The Tazheran Massif of alkaline and nepheline syenites (East Siberia, Russia) [2] is the second occurrence of high-Mg aenigmatite (up to 10 wt% MgO, Mg/(Fe+Mg) – 0.3-0.4). The only high-Mg variety have been described before in Ne-syenite on Mount Kenia [1]. In the Tazheran massif both high-Mg and typical aenigmatites occur separately at the marginal part of the Ne-syenite veins with Mll-Wo-Cpx-Grt-Ne metasomatic rocks. Both aenigmatite varieties associate with aegirine-augite, nepheline, K-feldspar, sometimes with ilmenite, Fe-olivine and richterite (only with high-Mg aenigmatite) and have low content of CaO (less than 2 wt%) and Al_2O_3 (up to 5 wt%). In Mg-aenigmatite content of MgO varies from 8.5 to 10 wt%, whereas in aenigmatite – from 1 to 2 wt% There are no transition on composition between the minerals. In most cases aenigmatites as well as Cpx and Amp occur as symplectite with nepheline. According to composition high-Mg aenigmatite does not belong to aenigmatite-rhonite ($Ca_2(Mg,Fe^{2+},Fe^{3+})_5TiO_2[(Si,Al)_6O_{18}$) series, but is transitional veriety of series $Na_2Fe^{2+}{}_5TiO_2[Si_6O_{18}]$ (aenigmatite) - $Na_2Mg_5TiO_2[Si_6O_{18}]$ (unknown).

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[1] Price, R.C., Johnson, R.W., Gray, C.M. and Frey, F.A. (1985*) Contrib. Mineral. Petrol.,* **89**, 394-409. [2] Sklyarov E. V., Fedorovsky V. S., Kotov A. B. *et al.* (2009) *Russ. Geol. Geophys.* **50** (12), 1405–1423.

Fe isotopic composition of sequentially extracted reactive Fe from marine sediments

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The partitioning of Fe in sediments and soils has traditionally been studied by applying sequential leaching methods. These are based on reductive dissolution and exploit differences in dissolution rates between different reactive Fe (oxyhydr)oxide minerals. We used lab-made ferrihydrite, goethite, hematite and magnetite spiked with ^{58}Fe and leached two-mineral mixtures with both phases abundant in excess of the methods dissolution capacity. Leaching was performed with 1) hydroxylamine-HCl and 2) Na-dithionite as the reactive agent. Following Poulton & Canfield (2005) [1], the first dissolution is designed to selectively leach the most reactive Fe-phases, ferrihydrite and lepidocrocite, whereas the second dissolution is designed to leach goethite and hematite. Magnetite would then be dissolved in a third dissolution step with oxalic acid.

First results show that the hydroxylamine-HCl method for ferrihydrite dissolves only insignificant amounts of goethite and hematite. However, magnetite-Fe constitutes about 10% of the total dissolved Fe. The Na-dithionite dissolved Fe from goethite-magnetite and hematite-magnetite mixtures contain about 30% of magnetite-Fe.

We applied selective sequential leaching and Fe isotope analysis to fine-grained marine sediments from a depocenter in the North Sea, which contain abundant reactive Fe (oxyhydr)oxides and show evidence for Fe sulfide formation within the upper 10 cm. Fe isotopes of the hydroxylamine-HCl leach targeting ferrihydrite shows a downcore increase of $\delta^{56}Fe$ typical for sediments undergoing microbial reductive Fe dissolution, whereas Fe isotopes of the Na-dithionite leach (goethite and hematite) and oxalic acid leach (magnetite) are identical and show no downcore variation in $\delta^{56}Fe$. This means, that only the most reactive Fe phases participate in the Fe redox cycle in this location. The similar isotopic composition of goethite + hematite and magnetite suggests a detrital source, which is not utilized possibly due to the abundant ferrihydrite and lepidocrocite present.

[1] Poulton & Canfield (2005), *Chemical Geology 214*, 209–221

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