

Uranium distribution and speciation in Greek Tethyan limestones by μ -XRF and μ -XANES spectroscopy

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The average abundance of U in carbonate sedimentary rocks is 2.2 ppm while the concentration of U in relevant Tethyan rocks from SE Europe and the Middle East is reported to be in the range 1–10 ppm (e.g. [1]). Uranium is removed from the oceanic water due to chemical processes at the interface of organic-rich sediments whereas the reduction of U(VI) to U(IV) occurs relatively late in the diagenetic sequence [2]. However, additional diagenetic processes as well as further tectonic and weathering processes may modify the primary distribution and speciation of U in marine sediments. Here we demonstrate the first Synchrotron-based investigation, performed in the SUL-X beamline of ANKA (Germany), of typical marine carbonates originating in the Tethys paleo-ocean. The samples represent stratified organic-rich calcitic limestone and tectonized/weathered dolomitic limestone of Triassic age from Mt. Kithaeron, central Greece, exhibiting unusually elevated U concentrations (up to ca. 53 ppm). The SR μ -XRF study revealed that U is not particularly enclosed into Fe and/or Mn phases (containing V, Cr, Zn and As) but it is accumulated (together with Y and potential REEs) in certain areas of the surrounding Ca-rich –carbonate- matrix which includes, according to supplementary microscopic data, minor phosphate and aluminosilicate compounds. The corresponding μ -XANES spectra indicated the presence of U(IV) in Ca-rich regions around distinct Mn phases. This is the second mention for U(IV) in carbonate geologic materials, after a similar study of a 35 Ma-old spar calcite (5-35 ppm U) from a Mississippi Valley-type zinc ore deposit [3].

[1] Ehrenberg, Svånå & Swart (2008) *AAPG Bull.* **92**, 691-707. [2] Klinkhammer & Palmer (1991) *Geochim. Cosmochim. Acta* **55**, 1799-1806. [3] Sturchio *et al.* (1998) *Science* **281**, 971-973.

Metal and sulfide origin in Eucrite and Diogenite

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Metal and sulfide phases are common accessory mineral in Eucrite and diogenites. We have investigated the occurrence, mineralogy and composition of these phases in 4 eucrites (EET-92023, Petersboug, Stanern, Camel Donga) and in two diogenites (Johnstown and Tatahouine). Highly siderophile elements (HSE) abundances of sulfides and Fe-Ni metal were determined using LA-ICP-MS techniques [1, 2]

Except for Camel Donga, Fe-Ni Metal (kamacite- taenite \pm taenite) is associated with troilite. In the diogenites, troilite is associated with pentlandite and Cu-rih sulfide as described by Lauretta [3].

HSE abundances are extremely variable from sample to sample and between phases. For instance Fe-Ni metals have high Os and Ir abundances ($(Os)_N \approx 15$; N, Chondrite CI1 normalised) in EET-92023. The normalised HSE pattern show a slight negative slope toward Pd and Re ($(Re)_N \approx 10$), Au and Ag are much more depleted relative to Ir ($(Au/Ir)_N < 0.5$, $(Ag/Ir)_N < 0.01$). The coexisting troilite show an inverse HSE pattern, with low Os and Ir content (e.g. $(Os)_N < 0.1$), positive slope toward Pd ($(Pd)_N > 0.1$) and extreme Au and Ag enrichment ($(Au/Ir)_N > 10$). These two types of complementary patterns are found in all eucrite and diogenites (except Stanern) even in Camel Donga which show only Ni-poor metal. This suggests that as proposed by Palme and coworkers, part of the metal grains are due to desulfidation of preexisting troilite in Camel Donga.

Overall the high abundance of HSE in metal (\pm sulfide) suggest that metal was not formed by reduction of silicate-Fe. Similarly, petrographic observation and metal/sulfide compositions (major elements and HSE) indicate that metal was not formed by S-loss of sulfide due to thermal event(s) - except for Ni-free metal grains in Camel Donga- and inversely troilite was not formed by sulfurization of metal to troilite [3]. Our observations rather suggest the evolution (common to Diogenites and Eucrites) of a HSE-rich Fe-Ni-S magmatic liquid, with sequential crystallisation of Fe-Ni-metal, followed by the crystallisation of an immiscible sulfide melt.

[1] Alard *et al.* (2000) *Nature* **407**, 891-894. [2] Mullane *et al.* (2004) *Chem. Geol.* **208**, 5-28. [3] Lauretta *et al.* (2004) *Lunar Planet. Sci.* **XXXV**, A#1752. [4] Palme *et al.* (1988) *Meteoritics* **23**, 49-57.