Mineralogical and geochemical properties of a water dam receiving historic AMD contamination by sulfide tailings in the Riotinto Mine SW Spain

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The present study was performed in the Marismillas water dam, in the Iberian Pyrite Belt, SW Spain. This reservoir receives water from the Tinto River, known by its historical high levels of contamination by AMD. Additionally to soluble pollutants, sulfates and metals in the form of particulate matter have been transported for decades. Consequently, today, Marismillas is clogged by the accumulation of sulfide-rich material from the RioTinto mines.

An integrated sampling campaign was accomplished with the following objectives: i) to characterize the input waters; ii) to reveal horizons for preferential accumulation of metals, and iii) to propose a model of the clogging process.

The samples were collected in three drill cores, from the surface to the bottom. Geochemical and mineralogical analyses were performed each 10 cm.

The results indicate high average concentrations of metals and metaloids (Cu, Zn, Pb, and As > 1200 ppm). A strong accumulation of these elements (> 2000 ppm) was detected at depth 1-2 m. Geochemical trends indicate strong correlation between major elements mobilized from the source materials (sulfides and felsic host rocks). So, Fe and Al, as well as Cu and Zn are clearly associated in the sediments. Regarding mineralogy, in addition to clay minerals, the finest fraction (<2μm) is dominated by jarosite and goethite. Therefore, combining geochemistry and mineralogy allowed mapping the properties of dam, identifying major mineralogical hosts of environmental, but also economic relevant elements, such as REE.

A Second Lunar Magma Ocean?

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The Lunar Magma Ocean (LMO) model is one of the key concepts in the current understanding of lunar evolution. It is used to explain a range of geological, mineralogical and chemical characteristics of the Moon, such as the presence of anorthositic crust, a reservoir enriched in incompatible elements and mare basalts. The LMO model suggests that the lunar crust, made up of Ferroan-Anorthosite (FAN), formed by segregation and floatation of plagioclase from the magma ocean, after ~75% of the initial liquid has crystallised as mafic cumulates. After ~95% solidification, the remaining liquid is enriched in incompatible elements (e.g. K, REE, P, U, Th, Zr…) and constitutes the KREEP reservoir. Although this reservoir has never been sampled as such, its existence is indicated by incompatible elements enrichment in some plutonic rocks, which are interpreted to be emplaced into the FAN crust. These rocks are also enriched in Mg and are referred to as Mg-suite. The presence of a KREEP component in this suite and the associated enrichment in incompatible elements also results in a widespread crystallisation of zircon in these rocks.

Very specific sequence of crystallisation predicted by the LMO model demands particular timing relationships between FAN, KREEP reservoir and Mg-suite rocks. However, absolute dating of FAN and Mg-suite samples reveals a significant overlap in ages that is inconsistent with the LMO model. In particular, the contradiction is highlighted by the recently obtained precise ages of (i) the oldest lunar zircon at 4417 ± 6 Ma [1], which must represent the youngest possible limit for the formation of KREEP reservoir and (ii) a sample of FAN at 4360 ± 3 Ma [2], which suggests the oldest limit for the lunar crust crystallisation.

The only way to resolve the controversy posed by chronological data is to accept the possibility of a second magma ocean on the Moon at ~4360 Ma, resulting from a massive impact and probably restricted to the near site of the Moon.

[1] Nemchin *et al.* (2009) *Nature Geosc.* **2**, 133-136. [2] Borg *et al.* (2011), *Nature* **477**, 70-73.

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