



## **Age constraints to sulfide weathering of black shale by $^{40}\text{Ar}/^{39}\text{Ar}$ dating of jarosite**

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Oxidative weathering of sulfide-containing black shales causes sulfide and organic matter degradation. Jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) is a product of acid oxidative sulfide weathering and can be dated by the  $^{40}\text{Ar}/^{39}\text{Ar}$  technique. Sulfide weathering forms the first step of oxidative weathering, followed by organic matter degradation. Assuming no Ar loss, the ages can be used as a maximum age constraint for the onset of black shale weathering.

In this study,  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of jarosite incrustations precipitated on oxidative weathered Paleozoic black shales from the Schwarzburg anticline (Thüringisches Schiefergebirge, Germany) were analyzed. The weathered shales are free of sulfides. Pseudomorphs of jarosite and goethite after sulfides were found in thin sections. The sampled incrustations have thicknesses of some hundreds of microns. Further, jarosite from ca. 1.5 mm thick veins was analyzed.

Four incrustations were scraped from handspecimen surfaces and two jarosite-veins were sampled. The total volume of each sample was some cubic millimeter.  $^{40}\text{Ar}/^{39}\text{Ar}$  analyses of the six jarosite samples were performed by stepwise heating experiments. The experiments were performed at the Argon Geochronology Laboratory at Vrije Universiteit Amsterdam.

$^{40}\text{Ar}/^{39}\text{Ar}$  data indicate two jarosite age groups. The younger age is approx. 8-9 Ma ( $8.2 \pm 2.7$  Ma;  $9.3 \pm 1.7$  Ma) and the older age is around 20-27 Ma ( $19.8 \pm 2.6$  Ma,  $19.9 \pm 6.3$  Ma,  $22.2 \pm 3.4$  Ma,  $27.4 \pm 3.8$  Ma). The data constrain the age of oxygen influence on sulfide-bearing Lower Devonian black shales of the Schwarzburg

anticline. The jarosite ages provide maximum ages of the onset of weathering, i.e., the age of exhumation of these rocks to oxic groundwater levels. Up to now little is known about the exhumation of the Thüringisches Schiefergebirge that is generally thought to have occurred in Late Mesozoic to Tertiary time. The new jarosite ages, however, give evidence about Late Tertiary weathering processes and, consequently, a minimum age for exhumation of these rocks to the surface. Furthermore, we conclude that sulfide weathering of black shales did start much earlier than the Pleistocene valley incision in the Schwarzburg anticline.