

$^{40}\text{Ar}/^{39}\text{Ar}$ dating of geological events of the Allchar deposit and its host rocks

F. NEUBAUER^{1*}, M.K. PAVIĆEVIĆ^{2,3}, J. GENSER¹,
R. JELENKOVIĆ⁴, B. BOEV⁴ AND G. AMTHAUER²

¹Div. Geology, University of Salzburg, Austria

(*correspondence: Franz.Neubauer@sbg.ac.at)

²Dept. Material Sciences, University of Salzburg, Austria

³Faculty of Mining and Geology, Belgrade, Serbia

⁴Fac. of Mining and Geology, University., Stip, Macedonia

Allchar is a Sb–As–Tl–Au deposit with an uncertain geodynamic setting located at the western part of the Vardar Zone, close to the border between Macedonia and Greece. Allchar is unique because of the abundant presence of the mineral lorandite (TlAsS₂). A total of 25 mineral concentrates from 18 samples has been measured with the $^{40}\text{Ar}/^{39}\text{Ar}$ method to examine the relationship between volcanism and secondary alteration associated with mineralization. Our results suggest that there is no relationship between volcanism and alteration/mineralization in the basement.

Experiments with amphibole from a subvolcanic latite body result in disturbed Ar release patterns and an age of 4.8 ± 0.2 Ma. Biotite yield slightly varying ages ranging between 4.6 ± 0.2 and 4.8 ± 0.2 Ma, K-feldspar disturbed, staircase patterns with ages increasing from 3.3 to 4.0 Ma. The mineral ages of the subvolcanic latite body are interpreted, therefore, to monitor rapid cooling from ca. 550–500°C (amphibole) through ca. ca. 300°C (biotite) to ca. 250 to 160°C (K-feldspar) between 4.8 and 3.3 Ma.

The biotite ages of 5.0 ± 0.1 and 5.1 ± 0.1 Ma from blocks of the Vitačovo tuff are geologically significant and interpreted to date the age of initial volcanism in the Allchar region. Overprint on amphibole may also date the age of a thermal partial thermal resetting during formation and emplacement of the tuff at ca. 1.7 Ma.

Dating of sericite and K-feldspar of sericite-quartz alteration zone from five different localities, considered to be associated with Tl-mineralization in the Allchar area, yield consistently ages between 119.8 ± 1.2 and 125.1 ± 1.8 Ma. The age of a thermal overprint in all Ar release patterns is younger than ca. 31 Ma. A hydromorphic K-feldspar from the locality Rudina resulted in an undisturbed age of 4.31 ± 0.02 Ma. Consequently, the age of sericite growth is between 120 and 125 Ma and not associated with volcanism as believed before. Interestingly, low-energy steps monitor a low thermal overprint, which is not higher than ca. 300°C, consistent with annealing effects on sericite seen in thin sections of the quartz breccia of the alteration zone. The K-feldspar of the alteration zone has been likely reset during reheating by the intruding subvolcanic latite.

Assessing the redox reactivity of nitroaromatic compounds and polychlorinated ethanes with structural iron in smectites

ANKE NEUMANN¹, THOMAS B. HOFSTETTER^{1*},
OLAF A. CIRPKA², SABINE PETIT³,
AND RENÉ P. SCHWARZENBACH¹

¹Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, CH-8092 Zurich, Switzerland

(*correspondence: thomas.hofstetter@env.ethz.ch),

²Center for Applied Geoscience, University of Tübingen, D-72076 Tübingen, Germany,

³Université de Poitiers, FRE 3114 CNRS – HydrASA, 86022 Poitiers Cedex, France

Structural ferrous iron species in clay minerals can be of great importance for the reductive transformation of organic contaminants under anoxic conditions. Owing to the dynamics of Fe(II)/Fe(III) cluster formation in the octahedral sheet of the minerals upon changes of Fe oxidation state, however, it has been difficult to assess the rates of contaminant reduction and thus the relevance of Fe(II) in clay minerals as reductants in the anoxic subsurface. To identify the factors governing the redox reactivity of organic compounds with Fe(II) in smectites, we combined the investigation of contaminant reaction kinetics and mechanisms by kinetic analyses and elucidation of C and N isotope effects with the characterization of structural Fe(II)/Fe(III) entities by infrared spectroscopy.

Based on evidence from studies with smectites of different total Fe content and Fe(II)/total Fe ratio we propose a conceptual kinetic model for quantifying the reactivity, abundance, and interconversion rates of two distinct Fe(II) sites in the minerals' octahedral sheet. Excellent agreement between observed biphasic reduction kinetics measured for nitroaromatic compounds and chlorohydrocarbons as well as model fits point towards the existence of two types of Fe(II) sites exhibiting reactivities that differ by three orders of magnitude in iron-rich ferruginous smectite (SWa-1), Ölberg montmorillonite, and synthetic Fe-nontronite. Low structural Fe content, as found in Wyoming montmorillonite (SWy-2), impedes the formation of highly reactive Fe sites and results in pseudo-first order kinetics of contaminant reduction that originate from the presence of a single type of Fe(II) species of even lower reactivity. Structure-reactivity correlations for nitroaromatic compounds further suggest that organic contaminant-Fe(II) interactions were identical in all smectite minerals. In contrast, the identity of the reactive structural Fe(II) entities observed by infrared spectroscopy varied between the different clay minerals.