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K/Ar AGE OF MANGANESE OXIDE ORES OF ÚRKÚT, HUNGARY: Ar RETENTION IN K-BEARING Mn MINERALS

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Abstract: The black shale-hosted Mn-carbonate deposits of Úrkút (Bakony Mts., Hungary) are Toarcian in age (Falciferum Ammonite zone). Subsequent to burial, during the Late Cimmerian orogeny erosion nearly uncovered the bedded Mn-carbonate ores where they were oxidized, thereby forming laminated noduliferous Mn-oxide ores with a clay mineral-bearing ferruginous crust. The clay mineral-bearing samples of the primary Mn-carbonate deposit yielded scattered K/Ar apparent ages of 293 to 110 Ma, indicating that associated detrital minerals partly retained radiogenic ^{40}Ar during transportation, deposition, and diagenetic changes. In contrast, more than half of the Mn-oxide ores gave K/Ar ages of 105 to 91 Ma. The other Mn-oxides yield ages older than 105 Ma. Selective dissolution of cryptomelane demonstrates that older K/Ar ages of Mn-oxides are caused mostly by incorporated clastic minerals. It has been shown by comparing the Ar retention of Mn-oxide ores and the clay mineral rich host rock that the uniform K/Ar ages of the Mn-oxide ores correspond to the real ages of oxidation, which occurred during the Austrian and Subhercynian phases of the Alpine orogeny.

Key words: Hungary, Úrkút, Mn-ores, K/Ar age.

Introduction

Radiometric dating of Mn ore mineralization was first attempted by Chukhrov et al. (1965) who determined the K/Ar age of cryptomelane. K/Ar ages were interpreted in terms of the time of supergene mineralization and it was noted that detrital contamination may result in apparent ages older than actual ages of oxidation. To correct for this bias Chukhrov et al. (1965) dissolved the Mn ore, measured the K content of the residue, determined the provenance and estimated the age of clastic material, and calculated the age of dissolved manganese minerals. The calculated values agreed fairly well with the ages expected from geological evidence. Yashvili & Gukasian (1973) also dated cryptomelane using the K/Ar method and obtained values in good agreement with the stratigraphy. Segev & Steinitz (1986) dated Mn nodules from the Timna Formation, Israel, which contained illite as a contaminating clastic mineral. These authors dated the whole rock and insoluble residue after selective dissolution of the Mn minerals. They did not describe the dissolution process, but the agreement of ages of the clastic illite residue and the illite from the host rocks indicate that the illite was unaffected by the chemical treatment. The ages determined by Segev & Steinitz (1986) for the Mn minerals were consistent with geological evidence. Segev et al. (1991) dated Mn minerals and clastic contaminating minerals after selective dissolution of Mn ores from the Eisenbach Region, Black Forest, Germany. The reliability of the Mn mineral ages was supported by their excellent agreement with the chronology of magmatism and mineralization of that area.

The results noted above demonstrate that the K/Ar ages determined for cryptomelane probably represent the ages of mineralization and that the presence of older detrital material will result in apparent ages that are too old.

In Hungary, different phases of the Alpine orogeny frequently reset the K/Ar system of minerals (Árva-Sós & Balogh 1979; Balogh 1984). Since the Ar retention in Mn minerals is still uncertain, their K/Ar ages may reflect the time of mineralization, or that of any secondary process that reset the K/Ar clock. In the present study the agreement of cryptomelane K/Ar ages with the time of oxidation has been supported by a direct comparison of Ar retention in cryptomelane and that of the host rock.

Geological setting

The Mn ore deposits of Úrkút (Transdanubian Central Range, Bakony Mts., Hungary) (Fig. 1) are geologically well studied (Cseh-Németh et al. 1980; Szabó et al. 1981; Kaeding et al. 1983; Varentsov et al. 1988; Simoncsics & Kedves 1961; Kedves & Simoncsics 1964; Konda 1970; Galácz & Vörös 1972; Géczy 1968; Géczy 1972; Polgári et al. 1991; Polgári et al. 1992). Geological, sedimentological, palynological, faunal, and facies investigations demonstrated that the black shale-hosted Mn-carbonate was deposited within the Upper Liassic Toarcian Falciferum Ammonite zone.

In the Úrkút Basin, the Upper Liassic Mn ore sequence averages about 40 m thick, and consists of dark-gray radiolarian marlstone (black shale) with alternating layers of finely to coarsely banded Mn-carbonate ore. In the central part of the basin, the Middle Liassic beds are overlain by finely laminated, organic carbon-rich pyritiferous radiolarian marlstone in the lower intervals, whereas upwards Mn-carbonate bands are increasingly more frequent. This black shale is overlain by the main Mn-carbonate bed, with a thickness of 5 - 12 m. The lower part of the main bed consists of green-gray, Mn-carbonate-bearing, finely laminated marlstone, followed upward by brown Mn-carbonate ore. The upper part of the main ore bed consists of alternating layers of green (celadonite rich, Kaeding et al. 1983) and gray Mn-carbonate ores. The uppermost gray rhodochrosite bed of the main ore bed is overlain again by black shale 20 - 25 m thick, with a second Mn-carbonate ore bed occurring near the top. The manganiferous section is overlain by Toarcian ammonite-bearing marlstone.

The lithological and mineralogical associations and the chemical and isotopic (C) compositions of the Úrkút manganese deposit indicate that manganese may have been concentrated at oxidation-reduction boundaries with the initial formation of manganese oxides and oxyhydroxides. Rhodochrosite formation probably took place as a very early diagenetic process in pore waters of the sediment pile (Polgári et al. 1991). Reduction of manganese oxyhydroxides to manganese carbonates took place as a byproduct of organic matter oxidation. Low pyrite contents in parts of the mineralized zone suggest that an additional reaction involving the oxidation of iron monosulphide via manganese oxide reduction may also have been important (Polgári et al. 1991).

The Late Cimmerian orogeny played an important role in development of Mn deposits of the Úrkút Basin. Some units were uplifted, and denudation of the Upper Jurassic rocks took

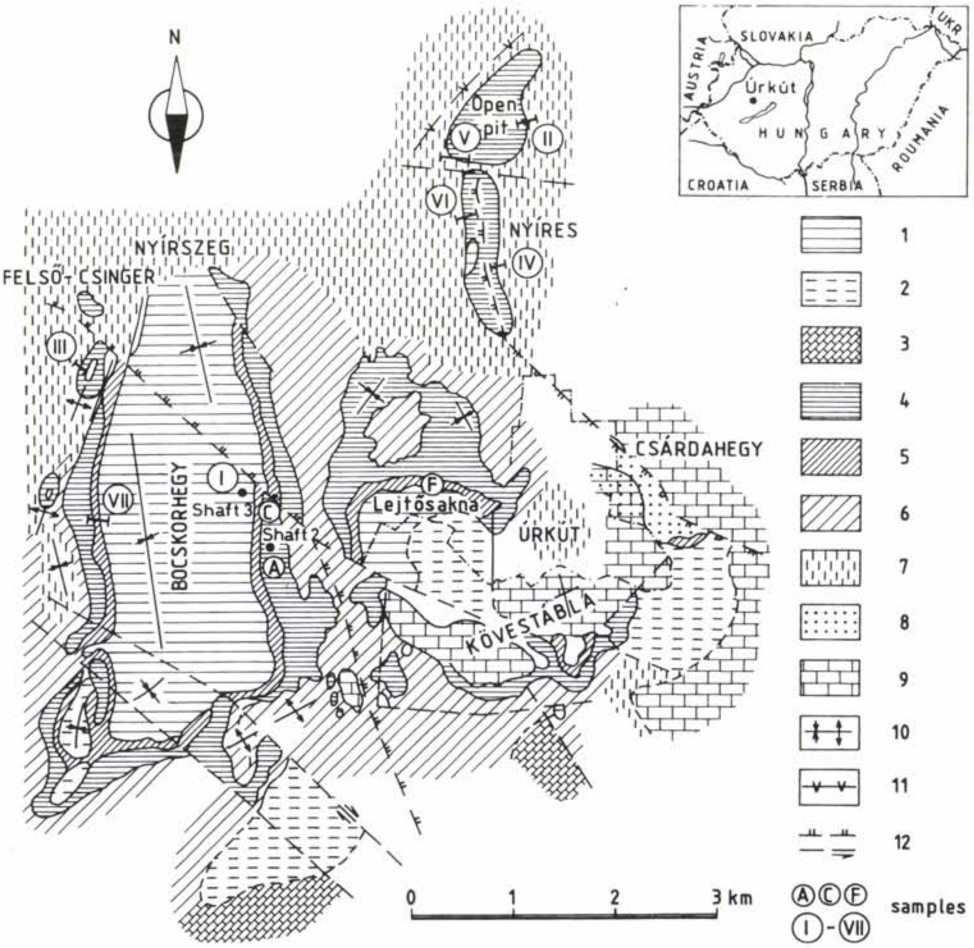

Fig. 1. Location map, geological sketch map of the Úrkút area, Hungary (after Cseh-Németh et al. 1980) and locations of the samples. The main ore bed and ore bed No. 2 are the thickest where indicated as fully developed; both bed are present, but are thinner where indicated as less developed. The denuded areas are predominantly, but not completely, eroded to the basement. Key: 1 - fully developed manganese carbonate ore; 2 - less-developed manganese carbonate ore; 3 - limestone; 4 - oxidized manganese ore; 5 - transitional zone between manganese carbonate and manganese oxide deposits; 6 - redeposited manganese ore; 7 - denuded area; 8 - iron-manganese ore bed at Csárdahegy; 9 - limestone bedrock cropping out at the surface; 10 - anticline; syncline, 11 - flexure; 12 - fault. Samples: Groups are defined by their mineralogical compositions, which are described in the text. **I.** Group 1. U-1; U-2; U-4; U-6; U-10; U-17; U-19; Samples from the Mn-carbonate deposit, shaft 3, W-field, N-part. Group 2. U-Cel; U-Cel5; Celadonite-rich samples from the different parts of Mn-carbonate bed, shaft 3, W-field, N-part. **II.** Group 3. Ksl-8; Ksl-12a; Ksl-12b; Mn-oxide ore samples formed by oxidation of Mn-carbonate ore bed, shaft 3, Kislöd mine field, N-part. **III.** Group 3. U3-21; U3-27b1; U3-27b2; U3-28; U3-29; Mn-oxide ore samples formed by oxidation, shaft 3, W-field, N-part. **IV.** Group 3. Ksl-39a; Ksl-39b1; Ksl-39b2; Ksl-49a; Ksl-49b; Mn-oxide ore samples formed by oxidation (transitional zone), shaft 2, Kislöd mine field. **V.** Group 3. Ksl-52; Ksl-60a; Ksl-60b1; Ksl-60b2; Mn-oxide ore samples formed by oxidation of black type, fine-laminated Mn-carbonate ore, shaft 2, Kislöd mine field. **VI.** Group 3. Ksl-68; Ksl-72a; Ksl-72b; Ksl-88; Mn-oxide ore samples formed by oxidation of green- (Ksl-68; Ksl-72a,b) and brown-black type laminated (Ksl-88) Mn-carbonate ore, Kislöd, open pit, N-part. **VII.** Group 3. U3-94; U3-95; U3-100; Mn-oxide ore samples formed by oxidation of black-type, fine-laminated Mn-carbonate ore (transitional zone), shaft 3, W-field, S-part. **A, C, F.** Group 4. Mn-oxide concretions embedded in the oxidized beds. **A** - shaft 2, S-part, **C** - shaft 3, W-field, **F** - shaft 1.

place, at which time oxidation of the Mn-carbonate beds on the surface began. Further oxidation may also have occurred whenever the carbonate beds were moved into oxic diagenetic zones either by erosion or tectonic activity. The autochthonous, in situ-oxidized Mn ores mostly preserved the lamination of the original Mn-carbonate ores.

Samples analyzed

Nine samples were collected for K/Ar dating from the Mn-carbonate bed (drift section) of shaft 3, W field, N part (Groups 1 and 2, Tab. 1) and 25 samples from different sections of the oxidized deposit, partly from the western margin of shaft 3, and partly from the Kislőd field (Nyíres), NE of Úrkút (Groups 3 and 4, Tab. 1).

The mineral compositions of the samples were measured by means of X-ray diffraction. The main characteristics of the different groups follow.

Group 1: the predominant minerals of the Mn-carbonate bed are rhodochrosite, calcite, 1 nm phyllosilicate, smectite, goethite, siderite, quartz, pyrite, with smaller amounts of K-feldspar, plagioclase, dolomite, anatase, gypsum, chlorite, and zeolite in some samples. In samples U-1 and U-10 the 1 nm phyllosilicate proved to be sericite-illite, whereas in the other samples it is celadonite. The smectite is dioctahedral Ca-Mg-montmorillonite in each sample. Beside the dominance of Ca-Mg-montmorillonite, the samples also contain trace amounts of nontronite. The smectite fraction is 20 percent of the interstratification 1 nm phyllosilicate/smectite mixed-layer clay mineral; celadonite/nontronite interstratified clay mineral occur only in sample U-2.

Group 2: the celadonite content of the samples is more than 95 percent; quartz and sericite-illite compose the remainder of the samples.

Group 3: the main Mn-oxide minerals are cryptomelane, pyrolusite and manganite; other minerals include goethite, quartz, calcite, siderite, 1 nm phyllosilicate, smectite, 1 nm phyllosilicate/smectite mixed-layer clay minerals with traces of todorokite and perhaps groutite in some rocks. The clay minerals are represented by sericite/illite and Ca-Mg-montmorillonite with kaolinite in some samples. The amounts of celadonite and nontronite, which are characteristic of the Mn mineralized rocks from Úrkút, are minor in group 3 samples.

Group 4: the predominant minerals of Mn-oxide concretions collected from different places in the oxidized bed are composed of cryptomelane and goethite, with calcite and sericite-illite as accessories.

Experimental methods

Measurement of K/Ar ages was performed in the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary. The samples were first crushed to 0.1 - 0.3 mm for Ar determination, than a part of the crushed samples was selected and pulverized for K determination.

An argon extraction line and a mass spectrometer, both designed and built in the ATOMKI, were used to determine the Ar content. The rock was degassed by high frequency induction heating, the usual absorbents (titanium sponge, CuO, zeolite and cold traps) were used for cleaning the Ar. The ^{38}Ar spike was introduced to the system from a gas-pipette before the degassing started. The cleaned Ar was directly introduced into the mass spectrometer. The mass spectrometer was a magnetic sector type of 150 mm radius and 90° deflection and was operated in the static mode. Recording and evaluation of the Ar spectra were controlled by a microcomputer.

A 0.1 g split of each pulverized sample was digested in HF with the addition of some sulphuric and perchloric acids. The digested sample was dissolved in 100 ml of 0.25 mol.l^{-1} HCl and, after a fivefold dilution, 100 ppm Na and 100 ppm Li were added as buffer and internal standard, respectively. K concentration was measured with a digitized flame photometer of OE-85 type manufactured in Hungary.

The interlaboratory standards Asia 1/65 and GL-O and atmospheric Ar were used for calibrating the measurements. Reproducibility of K measurements was < 1.5 % and values obtained for the standards were within these limits too (6.60 ± 0.1 % for GL-O and 4.12 ± 0.06 % for Asia 1/65). However, an additional 1.5% error was added as a maximum possible bias for the K concentrations of the standards. Thus, 3 % total error was accepted for the K concentrations. Reproducibility of Ar isotopic ratio measurements was 0.2 - 0.3 %. Considering the possibility of fractionation during baking the Ar extraction line, 1 % total error was accepted for the Ar isotopic ratios. Details of the instruments, the applied methods and results of calibration have been described elsewhere (Balogh 1985; Odin et al. 1982).

Results and discussion

The apparent ages determined for the fine-grained host rocks and Mn-carbonates mostly predate the age of deposition (Tab. 1., Fig. 2). Because Mn-carbonates are free of K, these ages reflect the associated detrital minerals (mostly clay minerals) that retained at least partly their radiogenic Ar content during transport, deposition, and diagenetic changes. No correlation was found between the age and mineral composition of the host rock, but the younger age of sample U3-27b2 indicates that at some locations the phyllosilicates lost their radiogenic Ar some time after deposition.

The K/Ar ages of the Mn-oxide ores group mostly in the time interval from 126 to 91 Ma. During oxidation of Mn-carbonate, K is incorporated and cryptomelane is formed. The source of K is most likely clay minerals in the host rocks. If radiogenic Ar was not lost from the K-bearing Mn minerals, the K/Ar ages will reflect the time of K incorporation, i. e. the time of oxidation of Mn-carbonate. If any secondary event (e.g. additional supergene processes, recrystallization, heating, etc.) allowed for the release of radiogenic Ar from the Mn minerals, then the K/Ar ages would reflect the age of the youngest secondary event. The old K/Ar ages of the clay mineral-bearing host rocks show that secondary events were not strong enough to release Ar from the clay minerals. Several pre-depositional ages determined for K-bearing Mn ores are probably due to older clastic minerals (e.g. the 256 - 254 Ma age of sample U3-100 is older than the age of deposition).

In order to better understand the age distribution, we first tried to decide, if the possible secondary events that allowed for the release of radiogenic Ar were related to certain zones of the study area, or these events, because they were too weak to release radiogenic Ar from the clay mineral-bearing host rock, affected only the Mn-oxide ores. Both the oxide nodules and their clay mineral-bearing crusts were dated from some locations (e.g. samples: U3-27b(1 and 2); U3-(28 and 29); Ksl-39(a and b1); Ksl-49(a and b); Ksl-60(a and b1)). Identical post-oxidation

Table 1: Sample descriptions K/Ar ages.

Sample	Description and mineral composition of samples	K (wt %)	^{40}Ar(rad) (10^5cc STP/g)	^{40}Ar(rad) (%)	K/Ar age(Ma ± σ)	
					Mn-oxides	carbonates and host rocks
Group 1. Samples from the Mn-carbonate deposit, Shaft 3, W-field, N-part						
U-1	reddish-brown, green, marlstone (Rh>1 nm>Q>G>K)	2.38	2.184	78		222±9
U-2	dark gray radiolarian marlstone underlying the main Mn-carbonate bed (1 nm/Sm>Q>K>Sm>Py>D>Gy>Ze>Ch(tr))	3.35	2.826	82		205±8
U-4	green/gray Mn-carbonate ore, lower level of the main bed (1 nm>Rh>G>K(tr))	0.83	0.744	40		217±10
U-6	brown, finely laminated Mn-carbonate ore, middle level of the main bed (Rh>1 nm≥G>Sm)	1.33	1.036	47		190±9
U-10	gray Mn-carbonate ore, upper level of the main bed (Rh>Sm>Py>1 nm>A>Pl(tr))	0.20	0.232	18		270±28
U-17	radiolarian marlstone overlying the main bed (Q>Cal>Sm>Py>D>Ze)	1.94	1.578	12		198±23
U-19	second Mn-carbonate bed in the upper level of the radiolarian marlstone (Sid>Rh> Cal>Py>Q>1 nm (tr))	0.24	0.290	23		293±30
Group 2: Celadonite rich samples from the Mn-carbonate bed						
U-Cel	average celadonite sample collected from different parts of the main Mn-carbonate bed (Cel>>Q>1 nm)	7.13	4.356	97		151±6
U-Cel5	"green clay" (celadonite) from the level underlying the main carbonate bed (Cel>>1 nm>Q)	5.34	3.564	91		166±7
Group 3: Mn-oxide ore samples formed by oxidation of the different sections of the oxidized bed						
Ksl-8	radiolarian marlstone (Ka≥Cr>Q>G>1 nm>Tod)	1.23	0.946	78		188±8
Ksl-12a	lumpy, laminated Mn-oxide ore (Cr>Q>G>Ka>1 nm)	1.28	0.648	91	126±5	
Ksl-12b	lumpy, laminated Mn-oxide ore (Cr>Ka>Q>G>Tod>P(tr))	1.35	0.935	87	170±7	
U3-21	reddish-brown sediment underlying the oxidized bed (Q>1 nm/Sm>Cr)	3.35	2.801	83		203±8
U3-27b1	laminated Mn-oxide ore with clay mineral-bearing interstratification (Cr>G>Cal)	0.73	0.353	46	120±5	
U3-27b2	clay mineral rich host rock from beside of U3-27b1 (G>Sm>1 nm>Cal>Sid)	1.14	0.501	77		110±3
U3-28	hard Mn-oxide layer (Cr>G>Cal)	1.65	0.616	86	94±4	
U3-29	clay mineral rich crust of sample U3-28 (G>Sm>1 nm>Cal>Sid)	1.89	1.511	82		195±8
Ksl-39a	clay mineral-bearing crust of sample Ksl-39b1 (Cr>G>1 nm≥M)	0.46	0.458	90		240±14
Ksl-39b1	hard, nodular Mn-oxide 15*40 cm (M>Cr>G>1 nm)	1.47	0.532	74	91±4	
Ksl-39b2	hard, nodular Mn-oxide (Cr>M>G>1 nm)	1.64	0.597	81	91±4	

Continuation Tab. 1

Sample	Description and mineral composition of samples	K (wt %)	^{40}Ar (rad) (10^{-5} cc STP/g)	^{40}Ar (rad) (%)	K/Ar age (Ma ± σ) Mn-oxides	K/Ar age (Ma ± σ) carbonates and host rocks
Ksl-49a	clay mineral-bearing crust of sample Ksl-49b (M>G>1 nm>Cr)	0.49	0.470	79		233±10
Ksl-49b	nodular Mn-oxide in the fissure manganite crystals (M>G>1 nm)	0.27	0.171	18	156±13	
Ksl-52	brown, manganiferrous host rock with chert debris (Q>Cr≥G>Tod>Sm)	1.40	0.706	65		125±6
Ksl-60a	clay mineral rich crust of sample Ksl-60b1 (Cr>G>1 nm)	0.85	0.715	83		205±9
Ksl-60b1	nodular Mn-oxide (Cr>G>1 nm (tr))	2.21	0.905	84	102±4	
Ksl-60b2	nodular Mn-oxide (Cr>G>1 nm (tr))	2.14	0.894	87	105±4	
Ksl-68	radiolarian marlstone from environment of Mn-oxide concretions (Q>>Sm>Cr>1 nm≈M)	2.24	2.231	78		240±10
Ksl-72a	nodular Mn-oxide (G>M>Cr>Q>1 nm (tr)≈Tod(tr)≈P(tr)) 0.5 - 0.63 mm size	0.76	0.354	58	116±5	
	<0.063 mm size	0.81	0.448	66	137±5	
Ksl-72b	clay mineral rich crust of Ksl-72a (G>1 nm>Q)	0.85	0.889	55		251±11
Ksl-88	nodular Mn-oxide (P>Cr>G>1 nm (tr))	1.30	0.981	94	187±7	
U3-94	nodular Mn-oxide (Cr>G>1 nm>M)	2.20	0.895	76	101±5	
U3-95	nodular Mn-oxide (Cr>G>1 nm≈M)	1.78	0.883	83	124±5	
U3-100	nodular Mn-oxide	1.08	1.145	76	254±11	
	(M>Cr>G)	1.10	1.176	68	256±11	
Group 4: Mn-oxide concretions embedded in the oxidized beds						
A	Mn-oxide concretion with shrinkage cracks, field of shaft 2 (Cr>G>P)	2.81	1.060	87	95±4	
C	flat, laminated Mn-oxide concretion, W-field of shaft 3 (Cr>G>Cal(tr)>1 nm (tr))	2.20	0.898	83	102±4	
F	Mn-oxide concretion, field of shaft 1, inclined adit (Cr>G>Cal(tr)>1 nm (tr))	1.21	0.501	69	104±4	

Ages calculated with constants after Steiger & Jäger (1977)
Abreviations of mineral names: Rh = rhodochrosite, Cal = calcite, 1 nm = 1 nm phyllosilicate, Sm = smectite, G = goethite, Sid = siderite, Q = quartz, Py = pyrite, K = K-feldspar, P1 = plagioclase; D = dolomite, A = anatase, G = gypsum, Ch = chlorite, Ze = zeolite, Cel = celadonite, Cr = cryptomelane, P = pyrolusite, M = manganite, Tod = todorokite, Gr = groutite, Ka = kaolinite, (tr) = traces

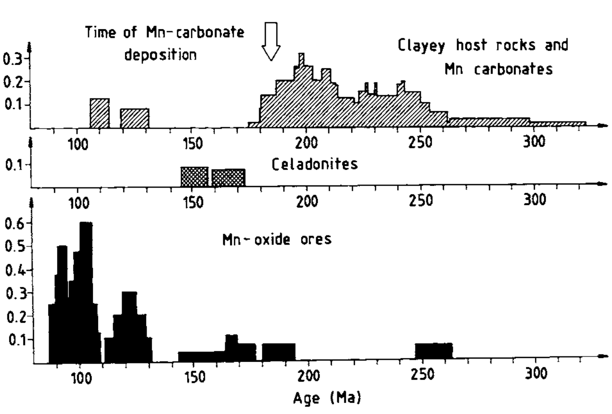

Fig. 2. Distribution diagram of K/Ar ages.

conditions are assumed to have affected both the nodules and their crusts. Except the sample pair of U3-27b(1 and 2) much older ages were obtained for the crusts than for the oxide nodules. This result may be interpreted to reflect either that oxide nodules formed under conditions that did not affect the K/Ar system of the surrounding fine-grained clastic rocks or, cryptomelane is more sensitive to secondary effects than the minerals of the surrounding sediments. In order to answer the question of Ar retention in cryptomelane, we determined the K/Ar ages of apparently pure K-bearing Mn-oxides, and calculated the K/Ar age of contaminated Mn-oxides by eliminating the effect of clastic minerals. The meaning of the ages was considered by comparing the Ar retention of the Mn-oxide and its fine-grained crust.

A surprisingly old age (254 ± 11 Ma) was determined for oxide nodule U3-100. Age precision was confirmed by repeated K and Ar determinations. This shows that the presence of clastic minerals in the Mn-oxides, in even minor amounts that cannot be detected by X-ray diffraction in the presence of Mn minerals, may cause large increases of the apparent K/Ar ages. Samples U3-27b1 and U3-28 represent two pieces of a single oxide nodule. In spite of their similar mineral composition as determined by X-ray diffraction their K/Ar ages and K concentrations showed significant differences, reflecting the heterogeneity of the nodule.

Since a small amount of detrital minerals may be suspected in each Mn-oxide nodule, measurement of the actual age of the cryptomelane was attempted by first dating the whole rock oxide ore, than dissolving the manganese oxides and dating the residue. A true age can be calculated for the dissolved oxides, if the K/Ar system of the residue was not altered during the solution process.

The dissolution of manganese oxide from nodule No. Ksl-88 was attempted, because the old K/Ar apparent age (187 ± 7 Ma) indicated a large amount of associated clastic debris. Manganese oxides were removed using 3 percent HCl with repeated addition of several drops of H_2O_2 so that continuous fizzling was maintained for 5 hours. According to Hunziker et al. (1986) and Árkai & Balogh (1989), 2 mol.l^{-1} HCl does not change the K/Ar age of illite and a detailed study by Clauer et al. (1993) confirmed this conclusion. Lippolt et al. (1986) used H_2O_2 for non-destructive disaggregation of volcanic tuff, but did not mention whether this treatment disturbed the K/Ar system of the mica. However, for sample No. Ksl-88 the residue yielded an age of 132 ± 6 Ma, which produces a calculated age for the dissolved Mn-oxide older than the age of sediment. This can be explained by Ar loss from the residue during leaching of the manganese by HCl and H_2O_2. Instead of identifying the exact cause of this Ar loss (HCl or H_2O_2 use, Ar loss from the undissolved part of Mn-oxide), less aggressive chemicals were used for dissolving the Mn oxides.

A second set of measurements was performed on Mn-oxide nodule No. Ksl-72a (Tab. 2). Here a K/Ar apparent age of 251 ± 11 Ma was determined for the surrounding clay mineral-bearing crust. Two different size fractions were measured from the oxide nodule in order to determine whether crushing leads to mineralogical fractionation of the sample. The size fractions of 0.5 - 0.63 mm and <0.063 mm resulted in ages of 116 ± 5 Ma and 137 ± 5 Ma respectively, which indicates remarkable fractionation. The older minerals of greater K content are enriched in the smaller size fraction.

An attempt was made to concentrate manganese oxides from the oxide nodules by making use of their high density. In order to facilitate separation the finest grains of the <0.063 mm fraction were rinsed away and the residue was centrifuged in methylene iodide of 3.32 g/cm^3 density. Although some enrichment of detrital minerals was observed in the lighter density fraction (deduced from the K concentration and age data), the small grain size of minerals precluded success of this technique.

The <0.063 mm fraction of oxide nodule No. Ksl-72a was treated using the technique of Chester & Hughes (1967), i.e. using a solution of 25 percent acetic acid and 1.0 mol.l^{-1} hydroxylamine hydrochloride. Use of the <0.063 mm fraction was necessary, because dissolution of manganese oxides from larger grains is a very slow process. In 3 hours 20.36 percent of the oxide nodule had been dissolved and 190 ± 8 Ma was determined for the age of the residue. From these data 2.05 percent K and 7.023×10^{-6} cc STP/g radiogenic ^{40}Ar was calculated for the manganese oxides, which produced a K/Ar age of 86.0 ± 15 Ma. This date is close to the youngest K/Ar age determined for bulk oxide manganese nodules (from 91 to 95 Ma).

These results suggest that the K/Ar age of the contamination free cryptomelane falls at the time of the Austrian and/or Subhercynian phases of Alpine orogeny and that the scatter of radiometric ages is caused mostly by the variable amounts of contaminating clastic minerals.

In lack of facilities for ^{40}Ar/^{39}Ar dating and considering the difficulties caused by the partial loss of recoiled ^{39}Ar atoms from fine-grained minerals (e.g. Hunziker et al. 1986), the Ar retention was checked by recording the Ar release spectra of a Mn-oxide nodule and that of the clastic sediment from its vicinity. The sample pair Ksl-60(a and b1) was selected because of the apparent minor detrital content of the oxide nodule and the relatively high K contents and old age of the crust. The Ar release spectra show (Fig. 3) that Ar is liberated from the crust at lower temperatures than from the oxide nodule. Stronger evidence for Ar retention in the Mn-oxide comes from the Arrhenius plot of the Ar release experiment (Fig. 4). According to Fechtig & Kalbitzer (1966), the D/a^2 diffusion parameters (D: diffusion coefficient, a: size of the grains) can be calculated from the fractional argon loss. Plotting the ln(D/a^2) values against 1/T, where T is the absolute temperature of argon release, the slope of the fitted line will be defined by the activation energy. For the oxide nodule, 15.0 ± 2.4 Kcal/mole activation energy was calculated for the 200 - 600 °C temperature range. The distribution of points does not indicate argon loss. The two points at 700 and 800 °C, which do not fit the straight line, correspond only to about 5 and 1 percent of released radiogenic Ar (see Fig. 3).

Table 2: K/Ar ages of clastic mineral contaminated Mn-oxide ores and their different fractions.

No.	Sample	K	^{40}Ar(rad)		Age
		%	10^{6}cc STP/g	%	Ma±σ
Ksl-88	nodular Mn-oxide	1.30	9.808	94	187±7
	undissolved residue	1.22	6.476	68	132±6
Ksl-72b	crust of Ksl-72a	0.85	8.892	55	251±11
Ksl-72a	nodular Mn-oxide				
	0.5- 0.63 mm whole rock	0.76	3.536	58	116±5
	< 0.063 mm whole rock	0.81	4.480	66	137±5
	density >3.32 g/cm^3	0.80	3.941	73	123±5
	density < 3.32 g/cm^3	0.78	4.100	76	130± 5
	undissolved residue	0.49	3.830	52	190±8
	calculated values for the dissolved oxide ore	2.05	7.023		86±15

A lower activation energy (8.9 ± 1.1 Kcal/mole) was obtained for the clay mineral-bearing sample Ksl-60a, forming the crust of sample Ksl-60b1, in the 300 - 800 °C temperature range. The lower diffusion parameter and higher activation energy at 200 °C, according to Fechtig & Kalbitzer (1966), indicates some radiogenic argon loss from the crust. Assuming greater Ar release at 200 °C, this point can be aligned with the straight line defined in the temperature range 300 - 800 °C, if about 8 percent Ar loss characterized the crust.

These results indicate greater Ar retention for the Mn-oxides than for the sedimentary host rock. Therefore the youngest ages measured on the Mn-oxides and calculated for sample Ksl-72a are regarded as the age of oxidation of the Mn-carbonates.

The isotopic age of deposition of manganese ores might be obtained by dating the authigenic celadonite, if it formed, similar to glauconite, soon after deposition. The ages of two samples were determined and the difference of ages (151 ± 6 Ma and 166 ± 7 Ma) is greater than the analytical uncertainty and both ages are younger than the Toarcian age of deposition. If celadonite loses Ar easily, similar to glauconite (Hurley 1966; Odin & Rex 1982), and if reworked clastic clay minerals occur with the celadonite, then definitive meaning cannot be attributed to the age data. Since sample U-Cel5 with a greater amount of contaminating phyllosilicates resulted in the older apparent age, a younger actual age has to be assumed for the celadonite. In addition, from the diffusion parameter data (Fig. 4) of sample

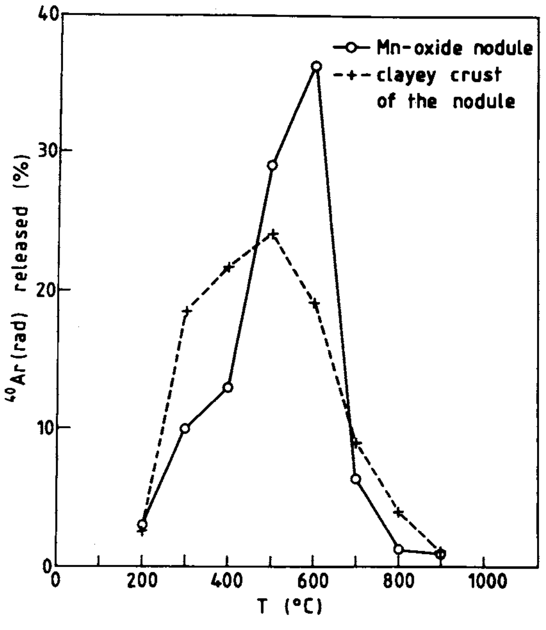

Fig. 3. Release of radiogenic Ar from the oxide nodule No. Ksl-60b1 and from its fine-grained crust (Ksl-60a) with detrital clay minerals.

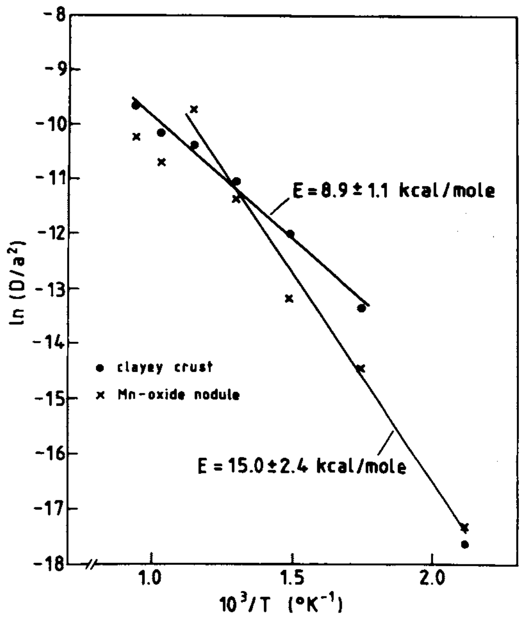

Fig. 4. Arrhenius plot and activation energies of Ar(rad) release for the oxide nodule No. Ksl-60b1 and its crust No. Ksl-60a.

Ksl-60a with fine-grained clay minerals, ≈ 8 percent argon loss was estimated and similarly Ar loss from the phyllosilicate clastic contamination with the celadonite cannot be excluded. According to the work of Odin (1982), K/Ar ages for samples from the mineral family glaucony frequently give the time of sedimentation. However, for the Mn-bearing sediments of the Úrkút area, celadonite dates are clearly younger than the age of deposition. Because the phyllosilicate contamination with the celadonite is small, the actual age of the pure celadonite is probably only a little younger than the apparent K/Ar age of 151 ± 6 Ma. This suggests that celadonite formation took place towards the end of a very prolonged diagenetic history.

Conclusions

1 - K/Ar ages measured on the sedimentary host rocks and on Mn carbonates in the Úrkút Basin mostly predate the Lower Toarcian age of Mn-carbonate deposition. This shows that part of the radiogenic Ar was retained by the associated detrital minerals during transportation, deposition, diagenetic changes, and oxidation of the Mn carbonates. On the other hand, a few ages younger than the age of deposition suggest that for some samples radiogenic Ar was lost during or after deposition.

2 - More than half of the oxidized samples gave ages in the 105 - 91 Ma age range. This cannot be attributed to rejuvenating effects acting only at certain places of the study area, since the clay mineral-bearing crusts of the oxide nodules resulted in older K/Ar ages than the oxide nodules.

Ages older than depositional ages obtained for part of the oxide nodules are caused mostly by their detrital contamination. By partial dissolution of the cryptomelane and dating the residue, a 86.0 ± 15 Ma age could be calculated for the dissolved cryptomelane. This was in accordance with the youngest ages measured on whole-rock oxide nodules (95 - 91 Ma). These K/Ar ages of K-bearing Mn-oxides are coeval with the time of the Austrian and Subhercynian phases of the Alpine orogeny.

The percentage, age, and K content of detrital contamination is variable and their measurement by X-ray diffraction is difficult in the presence of Mn minerals. This explains the lack of correlation between the age increase and the amount of detected contamination.

3 - Through recording the Ar release spectrum of Mn-oxide nodules and their fine-grained crust with clastic clay minerals, it was demonstrated that Ar is released at lower temperatures from the crust than from the oxide nodule and the activation energy of Ar removal is higher for the oxide than for the crust surrounding it. An Arrhenius plot of the diffusion parameter against $1/T$ revealed that Ar was not lost from the oxide nodule, but an Ar loss of about 8 percent was estimated for the crust. This strongly supports the conclusion that the Austrian - Subhercynian tectonic events are coeval with the time of the oxidation and not with some later secondary process.

4 - Ages measured on 2 celadonite samples post date the time of deposition. A younger age (151 ± 6 Ma) was obtained on the celadonite with less clastic phyllosilicate contamination. This indicates that the contamination may be older and the celadonite younger than the measured age. In view of the relatively good Ar retention of glaucony minerals (Odin et al. 1982), the 151 ± 6 Ma age value can be only a little older than the actual age of celadonite formation. This suggests that celadonite formation took place towards the end of a very prolonged diagenetic history.

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