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## U-Pb, U-Xe and U-Kr systematics of a greenschist facies metamorphic uranium mineralization of the Siviez-Mischabel nappe (Valais, Switzerland)

par J. Eikenberg<sup>1\*</sup>, V. Köppel<sup>1</sup>, T. Labhart<sup>2</sup>, P. Signer<sup>1</sup>

### Abstract

In the frontal part of the Siviez-Mischabel nappe uranium occurrences are widespread between Isérables and Verbier. They occur together with a copper dominated, complex sulfide assemblage in deformed carbonate veinlets hosted in Permo-Carboniferous basement rocks (metasediments and metavolcanics) as well as in Permo-Triassic cover rocks (metasediments) where the mineralizations also occur as stratiform, discontinuous layers. The last metamorphism to affect all rocks occurred during the Tertiary orogeny when greenschist facies conditions were attained. Fission U/Xe and U/Kr ages are compared to isotopic U-Pb ages. Coarse and fine grained pitchblades yield a U-Pb discordia which indicate a primary crystallization age of about 255 Ma and 40 Ma as a time of lead loss, which varied in intensity from virtually 0 to 90%. However, the straight forward interpretation of the discordia is only partly supported by the U/Xe and U/Kr ages. Coarse grained pitchblende with concordant U/Pb ages around 255 Ma also yields similar and concordant U/Xe and U/Kr ages. Discordant U-Pb ages of coarse grained pitchblende correlate with discordant U/Xe > U/Kr ages. Fine grained (< 10 micron) pitchblende samples, however, on which no mineral separation was performed, yield highly discordant U-Pb ages but concordant U/Xe and U/Kr ages which agree with the lower intercept age of about 40 Ma of the U-Pb discordia. This indicates that the fine grained pitchblende represents a new generation which was formed during a period of fluid activity which was related to the Tertiary metamorphism. Electron microprobe analyses of U and Pb confirm the young crystallization age of 40 Ma. The higher but discordant isotopic U-Pb ages are thus attributed to the presence of old radiogenic lead which now resides in accompanying carbonate or phosphate bearing phases. The microprobe analyses furthermore reveal distinct chemical differences between the Permian and the Tertiary pitchblende generations, the former having distinctly higher Ca and Cl concentrations than the latter. The study demonstrates the high retentivity of Kr and Xe in pitchblende even during low grade metamorphic conditions. It also demonstrates the advantages of combining U-Xe and U-Kr fission age with isotopic U-Pb age studies: The inherent ambiguities in interpreting U-Pb discordias can be resolved with the aid of U-Xe and U/Kr ages. The presence of two coexisting pitchblende generations attests for the mobility of uranium in a non-oxydising environment.

**Keywords:** Uranium mineralization, U/Xe-U/Kr-U/Pb ages, metamorphism, Siviez-Mischabel nappe, Switzerland.

### 1. Introduction

A fundamental problem in the interpretation of discordant U-Pb ages with  $t_{206/238} < t_{207/235} < t_{207/206}$  is the fact that this age pattern can be produced by (I) lead loss, (II) uranium gain, (III) mixing of minerals with different ages or (IV) inherited radiogenic lead. Loss of radiogenic daughter elements can be induced experimentally in many minerals, whereas gain of radioactive parent elements is more difficult to prove. There-

fore, lead loss from uranium bearing minerals is commonly presumed to explain discordant age patterns rather than U or Th gain. Most investigators also dismiss the third explanation, especially when analyzing small quantities (> 1 mg) of uranium minerals obtained, for example, from polished sections and processed without further mineral separations. Case (IV) occurs frequently in zircons and normally the old radiogenic lead resides in cores (GEBAUER and GRÜNENFELDER, 1979; KÖPPEL et al., 1980). However, significant

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incorporation of lead in uranium oxides is not expected to occur (BERMAN, 1957). Therefore discordant pitchblende ages are usually attributed to Pb loss.

Our first attempt to determine the age of pitchblende mineralizations at Isérables indicated that all samples crystallized about 260 Ma ago and suffered a lead loss 40 Ma ago. These ages agree partly with the conclusions of HÜGI et al. (1965) who, based on geological and petrographic evidence, favored a Permian age of the mineralization; however, they also concluded that considerable remobilization occurred during the Alpidic metamorphism. Although at least one of the analysed samples was considered to represent a remobilized pitchblende and was therefore expected to yield a Tertiary age, the results did not support this view. Therefore, to clarify the apparent contradiction between field observations and U-Pb isotope data we investigated in addition to the two U-Pb also the U-Xe and U-Kr systems of pitchblendes from Isérables.

In this paper we present the comparison of the ages deduced from all four decay systems and demonstrate that ambiguities arising from U-Pb ages can be resolved by a combined study of these U-decay systems.

## 2. Geological and mineralogical descriptions

### 2.1. GEOLOGICAL SETTING OF THE URANIUM OCCURRENCES

Although none of the uranium mineralizations of the Swiss Alps is of any economic significance conspicuous concentrations of this metal nevertheless occur. One of the areas containing noteworthy uranium mineralizations is the north-western front of the Penninic Siviez-Mischabel nappe which forms part of the Bernhard nappe. A geological overview is given in Fig. 1. The U-occurrences are located between Nendaz and Verbier in a band of 6 km length and several 100 m width running parallel to two lithologically distinct series which were inverted during the Alpidic orogeny (Fig. 2). The tectonically upper se-

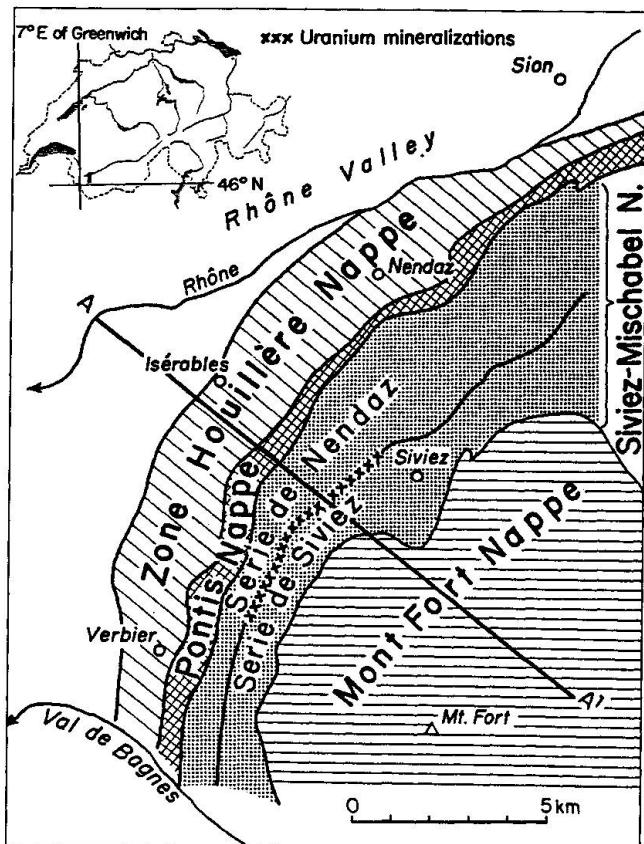


Fig. 1 Tectonic sketch map indicating the zone at the boundary between the Série de Siviez and the Série de Nendaz with numerous U-mineralizations. The sample location of I-7 is about 40 km ENE of Siviez.

ries (série de Siviez) consists of muscovite-albite schists, greenschists (metabasalts) and amphibolites and forms a crystalline basement. The tectonically lower series (série de Nendaz) comprises conglomerates, sandstones and schists. The lithology is typical for sequences which are considered to represent Permo-Carboniferous sediments (Verrucano s.l.). They rest discordantly with a deformed contact on the basement rocks. Both were overprinted by an Alpidic greenschist facies metamorphism and plunge with 45° towards S.

The mineralizations occur in both series and they are concentrated towards the contact zone.



Fig. 2 Profile A - A' (Fig. 1). Note that the Série de Siviez forms the basement to the Série de Nendaz.

Apart from secondary U-minerals which result from recent weathering processes pitchblende is the only important primary U-mineral. Two types of pitchblende can be distinguished. The majority consists of botryoidal grains ranging in size from mm to cm. Pitchblende with grain sizes of a few microns occur quite commonly in stratiform layers. Both types of pitchblende are accompanied by a complex sulfide paragenesis comprising about 35 ore minerals. The principal element association is U and Cu followed in varying amounts and proportions by As, Sb, Bi, Ni, Co, Pb, Zn and Ag. The paragenesis includes minerals of the host rocks, i.e. quartz, albite, calcite, chlorite and sericite. Mineralogy and trace chemistry of the ores are similar in both rock units, except that As is more abundant in occurrences of the Permo-Carboniferous sediments where tennantite dominates in contrast to the basement series where chalcopyrite is the principal Cu-mineral. Within the basement rocks the mineralizations occur mostly in carbonate rich veinlets which are oriented both discordantly and concordantly to the layering of the host rock. Some veinlets are free of pitchblende. They were deformed by Alpidic movements and transected and boudinaged by an Alpidic schistosity. Within the Permo-Carboniferous sediments the mineralization is mainly stratiform to strata-bound. Three later tectonic phases deformed these rocks and produced schistosities. Most of the coarse grained pitchblende suffered cataclasis. The origin of the fine grained pitchblende cannot be deduced from macro- and microscopic evidence. This type may either result from deformation or remobilization processes or it may even be of primary origin. Textural evidence for Alpidic remobilization and recrystallization is reported by

HÜGI et al. (1965). They observed parallel intergrowths of pitchblende and Alpidic chlorite, tennantite as interstitial fillings between idiomorphic albite and idioblasts of pyrite with oriented inclusions of silicates.

Field evidence and microscopic observations indicate that the primary U mineralization which is related to an unconformity is best explained by hydrothermal activity in the basement causing an epigenetic mineralization within the upper parts of the basements and a syn- to diagenetic mineralization in the overlying Permo-Carboniferous clastic sediments.

## 2.2. SAMPLE DESCRIPTIONS

For the initial U-Pb study most of the samples were collected from surface outcrops of the series de Nendaz and de Siviez near Isérables. The combined study used coarse grained pitchblende from occurrences between Col des Mines and Le Fou and from the mineralization observed in a tunnel of a hydroelectric power plant. An additional seventh sample consisting also of fine grained material was collected near Törbel (compare sample description in Tab. 1).

Three samples from Isérables (I-1, I-2 and I-3) consisted of coarse grained, variably cataclastic pitchblende which were virtually free of other mineral phases. Sample I-2 corresponds to LhU 103, also a coarse grained pitchblende from an Alpidic cleft. These four samples will be denoted as type A pitchblende (Fig. 3). The two others and the one from Törbel were fine grained pitchblende with grain diameters of 1 - 10 microns. They form disseminated clusters. They will be referred to as type B pitchblende (Fig. 4). No mineral separation was performed

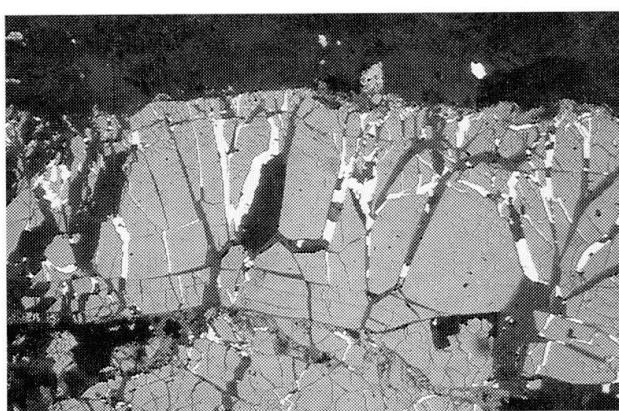


Fig. 3 Coarse grained pitchblende (type A) of Permian age. The slightly cataclastic pitchblende is banded and the cracks are cemented by chalcopyrite, quartz and carbonate. Dimensions 2 x 3 mm.

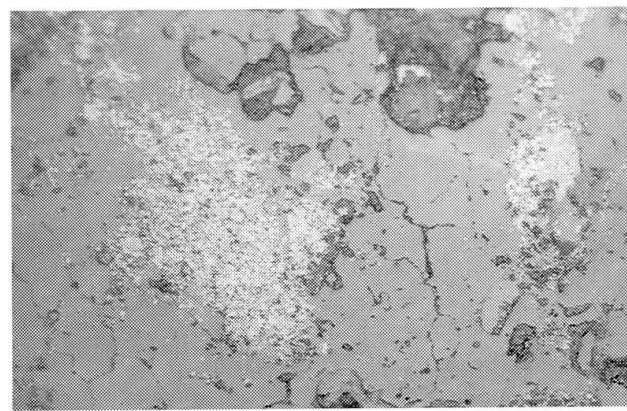


Fig. 4 Cluster of fine grained, disseminated pitchblende (type B), 37-39 Ma old. Dimensions 0.33 x 0.22 mm.

*Tab. 1 Sample description*

680722.48, Le Fou N 17, (No. 9.1, I-3, I-5)

Série de Siviez, Le Fou.

Discordant, deformed veinlet with carbonate, pitchblende, chalcopyrite, tennanite, pyrite, galena, magnetite and ilmenite. Slightly cataclastic pitchblende with chalcopyrite in cracks, fine grained (1-10  $\mu$ ) pitchblende disseminated in quartz, sericite and chlorite.

690715.94, (No. 25)

Série de Siviez, Col des Mines.

Slightly deformed cleft filling. Banded pitchblende with layers of differing reflectivities, pyrite and chalcopyrite.

25: Optically homogeneous pitchblende grain, slightly cataclastic free of sulfides.

25.1: Kidney-shaped, banded pitchblende with layers of varying reflectivity.

LhU 103 (No. I-2)

Série de Siviez, Col des Mines.

Cleft filling with pitchblende, some chalcopyrite and pyrite. Pitchblende forms coarse grained (mm), botryoidal fragments which are cemented by undeformed carbonate.

690811.135 (No. 18)

Série de Siviez, Le Fou.

Boudinaged carbonate veinlet with pitchblende, chalcopyrite, pyrite and cobaltite.

18.1 Massive, cataclastic pitchblende.

18.2 Fine grained pitchblende forms a network surrounding quartz grains.

670711.15 (No.4)

Série de Nendaz, Grand Alou.

Deformed stratiform ore-layer of massive to cataclastic pitchblende with tennantite and pyrite.

690729.105 (No. 20.1)

Série de Siviez, Le Fou

Slightly deformed carbonate veinlet with pitchblende, chalcopyrite pyrite, cobaltite and galena. Coarse grained, zoned and botryoidal pitchblende with varying reflectivity.

670802.12 (No.3)

Série de Siviez, Col des Mines.

Massive pitchblende layers with chalcopyrite and pyrrhotite in strongly deformed muscovite schist. The pitchblende is coarse grained, slightly cataclastic and accompanied by some chalcopyrite.

670802.11a (No. 11a, I-1)

Série de Siviez, Col des Mines.

Deformed and brecciated cleft filling with pitchblende, chalcopyrite and pyrite. Coarse grained, botryoidal pitchblende.

No. Iser 3

Série de Nendaz, hydroelectric gallery near Isérables.

Fine grained, sponge-like network of pitchblende with quartz and carbonate, in a highly deformed (alpidic) chlorite schist.

I-4

Série de Siviez, Col des Mines.

Fine grained (1 - 10  $\mu$ ) disseminated pitchblende intergrown with quartz, sericite and chlorite. The assemblage is contained in a strongly folded schist and oriented parallel to an Alpidic schistosity.

I-5

Similar to I-4.

I-6

Série de Siviez, Col des Mines.

Cluster of fine grained (1 - 10  $\mu$ ) pitchblende, intergrown with quartz, carbonate and sericite. The cluster may replace an old, Permian pitchblende.

I-7

Série de Siviez, Embd (Mattertal, appr. 40 km. to the E of the other sample locations).

The mineralizations consists of a stratiform layer of fine grained, disseminated pitchblende in quartz together with sericite and xenotime. (Feldmann, 1986, Bearth, 1978, 1980)

on them in order to prevent loss of part of fissionogenic Xe and Kr which recoiled into neighbouring U-free material.

### 3. Analytical techniques

The first set of U-Pb data listed in table 2 was obtained from pitchblends which were removed from polished sections using drills with diameters of 0.2 and 0.3 mm. The coarse grained samples (type A) used for the combined U-Pb and U-Xe-Kr investigations (Tab. 3) were purified by quantitative mineral separation, whereas mineral separation of the type B pitchblende was not possible. From this material  $\text{cm}^3$  small pieces

were ground to a fine powder. Aliquots of both types were prepared for the U-Pb and noble gas analyses.

For the U-Pb analysis the material was dissolved in a few drops of perchloric acid. The solution was diluted and one aliquot was spiked with a mixed  $208\text{Pb}$ - $235\text{U}$  spike. Lead was separated from the solution by electrodeposition at 1.85V on a Pt-Anode from where it was stripped with a 2% mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ . The solution of the spiked aliquot was evaporated and the uranium was analysed without additional chemical treatment. Pb blanks amounted to about 200 picograms.

The U and Pb isotope analyses were carried out on a Finnigan-MAT 261 mass-spectrometer

Tab. 2 Analytical data

Sample	206Pb 204Pb	+/-	207Pb 204Pb	+/-	208Pb 204Pb	207Pb 206Pb	+/-
9.1 (=I-3)	307.5 411.4	1.5 1.0	29.96 35.34	0.05 0.02	38.26 38.51	0.09745 0.08589	0.00001 0.00001
25	1106 1285	22 8	71.13 80.42	1.40 0.45	37.70 37.82	0.06432 0.06249	0.00006 0.00002
25.1	1538 2257	9 13	93.46 130.8	0.46 0.7	37.28 38.31	0.06078 0.05793	0.00001 0.00002
LhU 103 (=I-2)	2163 1849	12 2	125.4 109.9	0.5 0.2	38.27 38.67	0.05801 0.05941	0.00002 0.00001
18.1 18.2	1289 1290	10 20	80.50 81.05	0.4 1.0	37.02 38.23	0.06241 0.06283	0.00007 0.00002
4	860.7	4	58.81	0.3	38.65	0.06833	0.00001
20	1709	20	102.9	1.0	38.06	0.05996	0.00002
3 11a	588.6 1869	2 4	44.44 110.9	0.15 0.2	38.13 38.86	0.07548 0.05936	0.00003 0.00004
Iser 3	534.7	2	40.49	0.14	38.14	0.07572	0.00002

#### Isotopic composition of galena

##### Col des Mines

19.093	15.671	38.599
18.383	15.632	38.404
18.337	15.590	38.309

##### Siviez

18.420	15.637	38.447
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equipped for simultaneous recording of all Pb isotopes. Kr and Xe were extracted from aliquots of the samples used for the U and Pb analyses by heating them up to 1800°C in an ultra-high vacuum furnace. After separation of Ar, Kr and Xe from the large quantities of radiogenic  $^4\text{He}$ , the amounts and isotopic compositions of Kr and Xe were determined in an all-metall, 15 cm radius, 60° magnetic sector mass-spectrometer. The whole system, consisting of the extraction furnace, the gas separation and purification line and the spectrometer is operated statically. Because of the large quantities of He, Kr and Xe in pitchblende subsequent analyses of small amounts of these gases with different isotopic compositions, e.g. meteorite samples, are hampered by memory effects. The gas amounts were determined by calibration of the spectrometer with precisely known amounts of atmospheric Kr and Xe. The time required for a Kr and Xe analyses is about 4 hours, including calibrations and data reduction. Details of the techniques are de-

scribed by EIKENBERG, (1988), WIELER et al. (1989) and GRAF (1989). In addition to the mass spectrometric investigations, we prepared samples electron microprobe analyses of major and minor elements (EIKENBERG, 1988).

## 4. Results

### 4.1. THE INITIAL U-Pb STUDY

The results of our first set of U-Pb isotope analyses will be discussed before presenting the combined U-Pb, U-Xe and U-Kr data. Table 2 contains the analytical data which is plotted in Fig. 5. The data points form a linear array which is, however, considerably disturbed at the upper end towards the concordia. Different samples of the same type of pitchblende from one polished section yielded U-Pb ratios which scatter beyond the analytical uncertainties. This demonstrates that their U-Pb system was disturbed to different

Tab. 2 (cont.)

U nanom.	Pb tot. nanom.	206Pb 238U	207Pb 235U	207Pb 206Pb	+/-	t6/8	t7/5	t7/6	+/-
81.79	1.323	0.01248	0.08553	0.04970 0.05023	0.00043 0.00030	80	83	181 206	25 15
91.74	2.476	0.02431	0.1712	0.05108 0.05118	0.00029	155	161	244 249	13
39.58	1.448	0.03355	0.2370	0.05123	0.00009	213	216	251	5
91.83	3.557	0.03605	0.2558	0.05145	0.00007	228	231	261	3
234.4 19191	14.21 932.2	0.05631 0.04481	0.3976 0.3182	0.05120 0.05149	0.00005 0.00010	353 283	340 281	250 263	4
89.40	3.119	0.03031	0.2133	0.05107	0.00023	193	196	244	11
109.8	4.077	0.03378	0.2398	0.05147	0.00015	214	218	262	7
170.8	5.1313	0.02666	0.1886	0.05131	0.00016	170	175	255	7
94.72	4.794	0.04669	0.3303	0.05131	0.00013	294	290	255	3
237.2 27366	4.945 848.9	0.01781 0.03494	0.1242 0.2482	0.05054 0.05150	0.00021 0.00009	114 222	119 225	220 263	5
79.38	0.7780	0.008266	0.05496	0.04821	0.00022	53	54	110	10

The 207Pb/206Pb error comprises the mass spectrometric errors of the 207Pb/206Pb and 206Pb/204Pb measurements and the uncertainty of the common lead correction resulting thereof plus an uncertainty of +/-0.1 of the 207Pb/204Pb ratio which was applied for the common lead correction: 206Pb/204Pb = 18.4, 207Pb/204Pb = 15.6

Tab. 3 Analytical Xe-, Kr-, U- and Pb-data

Sample weight		$^{136}\text{Xe}$	$^{86}\text{Kr}$				
	g		$(10^{-8}\text{cc/g})$				
I-1	0.035317	6.952	1.103				
I-2	0.030564	5.508	0.852				
I-3	0.039301	5.021	0.698				
I-4	0.055245	0.148	0.028				
I-5	0.069665	0.169	0.043				
I-6	0.060563	0.391	0.066				
Xe isotope composition normalized to $^{136}\text{Xe}$							
I-1	134	132	131	130	129	84	83
I-1	0.828	0.574	0.093	0.0003	0.0029	0.182	0.054
I-2	0.831	0.575	0.094	0.0002	0.0024	0.171	0.052
I-3	0.831	0.574	0.096	0.0002	0.0028	0.167	0.053
I-4	0.823	0.570	0.085	0.0000	0.0000	0.406	0.098
I-5	0.830	0.621	0.139	0.0097	0.0639	1.264	0.268
I-6	0.822	0.570	0.088	0.0001	0.0000	0.284	0.070
Kr isotope composition normalized to $^{86}\text{Kr}$							
U weight% Pb							
			$^{208}_{\text{Pb}}$	$^{207}_{\text{Pb}}$	$^{206}_{\text{Pb}}$	$^{204}_{\text{Pb}}$	
				atomic %			
I-1	50.61	1.831	1.907	5.487	92.556	0.050	
I-2	69.65	2.360	1.621	5.395	92.940	0.044	
I-3	69.87	0.9380	9.658	7.772	82.320	0.250	
I-4	7.671	0.3347	42.372	17.861	38.683	1.084	
I-5	7.992	0.2490	40.799	17.328	40.382	1.041	
I-6	16.10	0.3953	38.782	16.718	43.507	0.992	
I-7	26.40	0.3184	25.886	12.648	60.804	0.662	

degrees on a mm to cm scale. The best fit through all data points intercepts the concordia curve at  $257 \pm 12$  and  $39 \pm 9$  Ma. A higher intercept age of  $273 \pm 2$  Ma is obtained by a concordia defined by eight samples; the lower intercept age of  $40 \pm 1$  Ma remains the same.

#### 4.1.1. Discussion of the initial U-Pb data

The upper intercept of  $257 \pm 12$  Ma indicates a Permian age of the uranium mineralization which is not surprising in view of the widespread occurrences of uranium mineralization in Permian sandstones in the Eastern and Southern Alps as well as in the Alpes Maritimes (CEVALES, 1961; KRAMERS, 1973; PETRASCHEK et al., 1975, PECHMANN and BIANCONI, 1982; GILLERON, 1988). The data at the upper end of the array scatter and may thus indicate an early (Permian to Triassic) disturbance of the pitchblende cau-

sing some Pb-losses and/or renewed pitchblende deposition between 250 and 275 Ma. Although remobilization of sandstone hosted uranium deposits during a renewed influx of oxygenated waters seems quite feasible, isotope evidence of multiple U-deposition in such deposits is scarce. LUDWIG et al., (1984) reported a redistribution of an early Cretaceous uranium deposit during the late-Tertiary in New Mexico. They furthermore found evidence for diffusive loss of  $^{222}\text{Rn}$  which leads to a  $^{206}\text{Pb}$  deficit and thereby to abnormally high radiogenic  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios. We did not, however, observe in any sample excessively high  $^{207}\text{Pb}/^{206}\text{Pb}$  ages which would argue for a continuous Rn-loss. However, the possibility cannot be dismissed that such a process operated at an early stage of the history of these occurrences, e.g. until an advanced stage of diagenesis and compaction was reached. Therefore, the question of the age of pitchblende deposition cannot be answered with the desired precision; the best estimate in our view is  $257 \pm 12$  Ma.

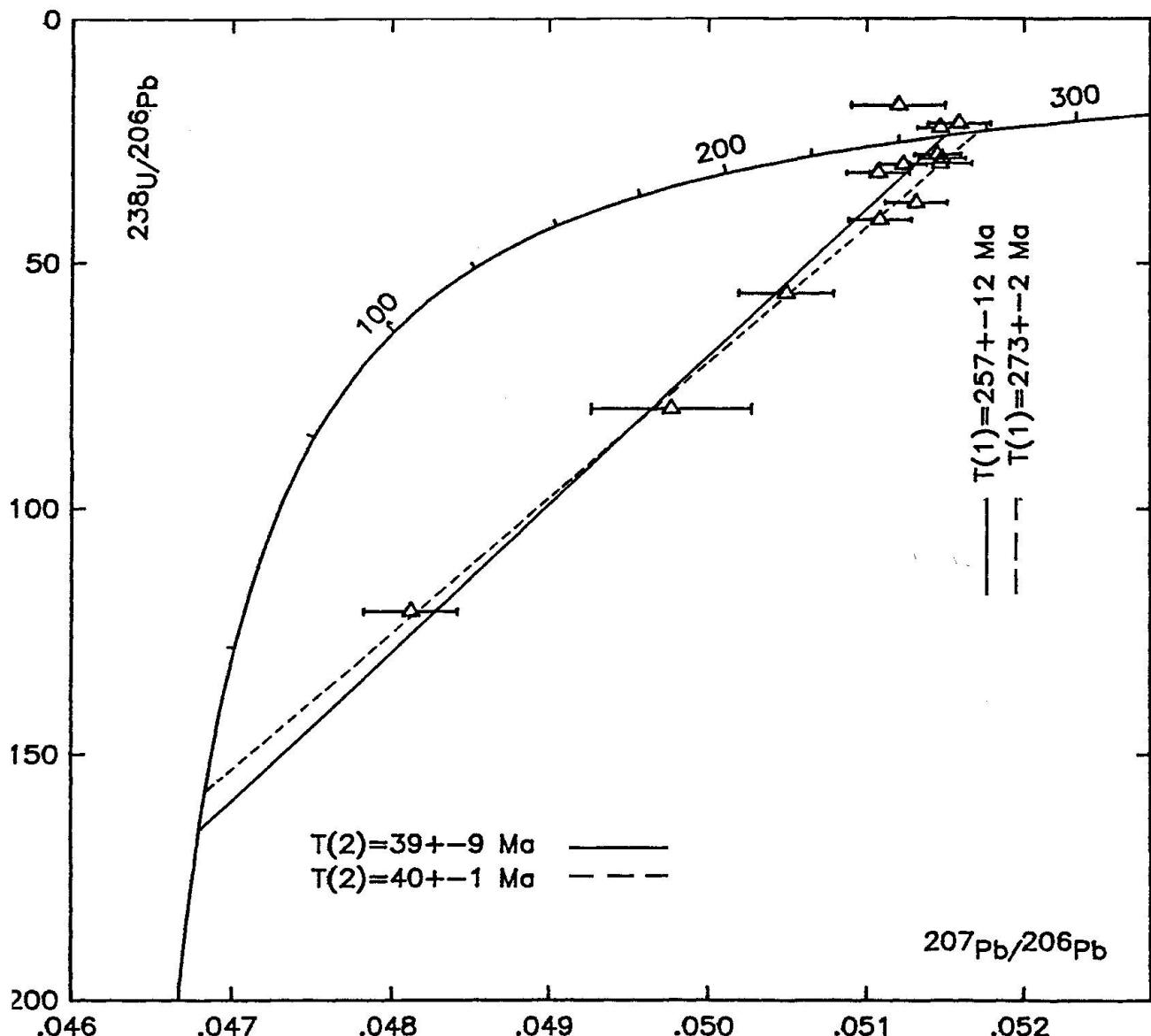


Fig. 5  $^{206}\text{Pb}/^{207}\text{Pb}$ - $^{238}\text{U}/^{206}\text{Pb}$  diagram showing the concordia curve, the discordia through all data points (solid line) and a best fit defined by 8 data points which form within the analytical uncertainty a linear array (broken line).

The lower intercept at  $39+/-9$  Ma coincides in time with the main Alpidic thermal event  $38+/-2$  Ma ago in the area west of the Simplon fault zone (HUNZIKER, 1969). Thus, the conspicuous lead loss is related to this Tertiary thermal event.

It is noteworthy that samples which should have crystallised according to macro- and microscopic evidence after the last Alpidic deformation plot on the same discordia and thus indicate a Permian crystallisation age. Sample LhU 103, consisted of coarse grained, cataclastic fragments of botryoidal pitchblende cemented by undeformed calcite. This paragenesis fills a cleft of several cm length which is oriented perpendicular to the schistosity. Therefore the question arises

whether such pitchblendes are young and contain a component of old radiogenic lead, or whether the structures attributed to an Alpidic deformation in fact resulted from a Permian tectonism. Possibly, even mechanical reworking of old pitchblende at a late alpine stage with subsequent episodic Pb loss has to be considered, or opening of a cleft at the site of old pitchblende. The presence of old radiogenic lead seems to be rather unlikely because it is generally assumed that oxidizing conditions are necessary to mobilise pitchblendes. Furthermore, in the presence of carbonates and/or sulfates which both have been detected in our samples lead is immobile in the pH range between 2 and 12. Therefore, if preex-

isting pitchblendes were remobilized U and Pb should have been strongly fractionated. In a recent paper, however, GILBIN and APPLEYARD (1987) reported experimental results on the solubility of U in non-oxidizing conditions in pure water, dilute aqueous NaCl solutions and NaCl brines. They found that pitchblende is quite soluble in brines and therefore oxidizing conditions are not a prerequisite for the mobilization of U and a fractionation between U and Pb will not occur under such conditions.

Because the U-Pb method did not provide clear evidence of pitchblende crystallization during the Tertiary metamorphic event we attempted to further elucidate the nature of the Alpidic disturbance by analyzing their U-Xe and U-Kr systems. During dissolution, transport and redeposition of pitchblendes the fissogenic rare gases are separated from U. According to EIKENBERG (1988) episodic loss of lead is accompanied by systematic losses of Xe and Kr, and thus U-Xe and U-Kr ages are very helpful in interpreting discordant U-Pb ages.

#### 4.2. COMBINED U-Pb, U-Xe AND U-Kr STUDY

Before presenting our analytical data we briefly consider the systems U-Xe and U-Kr. Until now the U-Xe system was preferred to the U-Kr

system for dating minerals (SHUKOLYUKOV and MIRKINA, 1963; HEBEDA et al., 1987; SHUKOLYUKOV and MESHAK, 1988) because the yield of Xe from spontaneous fission of  $^{238}\text{U}$  is an order of magnitude larger than that of Kr (YOUNG & THODE, 1960; SABU, 1971; HEBEDA, 1987; EIKENBERG, 1988). In addition, the contamination of fission gases in pitchblende by noble gases from the atmosphere is about an order of magnitude higher for Kr than for Xe because of the high abundance of Kr compared to Xe. However, the use of both systems is of great advantage for the understanding and the interpretation of fission gas ages. EIKENBERG (1988) has shown that in undisturbed U-minerals with concordant U-Pb ages the ratio of spontaneous fission  $^{136}\text{Xe}/^{86}\text{Kr}$  is  $6.1 \pm 0.1$ . Using this ratio for the calculations the U-Xe and U-Kr ages agree with the concordant U-Pb ages. Rare gas loss by diffusion increases the  $^{136}\text{Xe}/^{86}\text{Kr}$  ratios because of larger losses of Kr than of the heavier Xe. Geologically disturbed pitchblendes are therefore characterized by a typical age pattern with  $T(\text{U-Kr}) < T(\text{U-Xe}) < T(\text{formation})$ . Thus, a geological event that causes discordant U-Pb ages in pitchblendes will also lead to discordant U-Xe and U-Kr ages. Note, however, that not all discordant U-Pb ages necessarily imply discordant U-Xe and U-Kr ages. For instance, a mixture of undisturbed pitchblendes of different ages will yield discord-

Tab. 4 Comparison of isotopic U-Pb, fission U-Xe and U-Kr and electron microprobe U-Pb ages

Sample	Isotopic U-Pb ages				Fission Xe und Kr ages				Microprobe ages			
	206/238	+/-	207/235	+/-	207/206	+/-	136/238	+/-	86/238	+/-	U/Pb	+/-
<b>Type A</b>												
I-1	245	3	246	4	257	8	246	11	233	18	250	15
I-2	230	3	232	4	245	8	141	9	131	12	220	20
I-3	77	2	81	11	178	28	127	9	106	11	90 <sup>a</sup>	30
											100 <sup>b</sup>	30
											130 <sup>c</sup>	20
<b>Type B</b>												
I-4	58	4	60	25	(120)	*	35	4	37	6	37	4
I-5	49	4	50	15	(110)	*	38	4	39	6	37	6
I-6	45	4	46	15	(80)	*	45	4	44	5	39 <sup>d</sup>	4
											200 <sup>e</sup>	15
I-7	43	4	43	10	(48)	*	—	—	—	—	—	—

Common lead correction for type A  
 $^{206}\text{Pb}/^{204}\text{Pb} = 18.40$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.60$ ,

For type B  
 $^{206}\text{Pb}/^{204}\text{Pb} = 18.80$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.66$ .

\* see text

a: slightly cataclastic grain

b: cataclastic grain

c: strongly cataclastic grain

d: fine grained pitchblende, type B

e: coarser grained, relicts of old pitchblende, type A

dant U-Pb ages but the U-Xe and U-Kr systems will agree with each other.

The results of our U-Pb and U-Xe-Kr isotope analyses of six pitchblende samples from Iséables are listed in Tab. 3 and 4, and the data points are plotted in a  $^{206}\text{Pb}/^{207}\text{Pb}$  -  $^{238}\text{U}/^{206}\text{Pb}$  diagram (Fig. 6) together with the U-Xe and U-Kr ages which are indicated on the concordia curve. All isotopic ages are summarized in Tab. 4.

The coarse grained sample I-1, I-2 and I-3 plot in the data field defined by the initial data set (compare Figs. 6 and 5). Sample I-1, a type A pitchblende yielded U-Pb, U-Xe and U-Kr ages which are, within analytical uncertainties, concordant at  $245 \pm 10$  Ma, whereas the U-Pb as

well as the U-Xe and U-Kr ages of the samples I-2 and I-3 are discordant.

The fine grained pitchblende samples all contain high common lead concentrations as can be seen by their low  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios. The uncertainty of their radiogenic  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios is therefore so high that no meaningful discordia can be calculated. When applying a common Pb correction with  $^{206}\text{Pb}/^{204}\text{Pb} < 20$  their discordant U-Pb age pattern suggests an extreme lead-loss 40 Ma ago. The uncorrected  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios are within their analytical errors linearly related and the slope of the line yields a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $40 \pm 40$  Ma. By applying lead corrections with  $^{206}\text{Pb}/^{204}\text{Pb}$  bet-

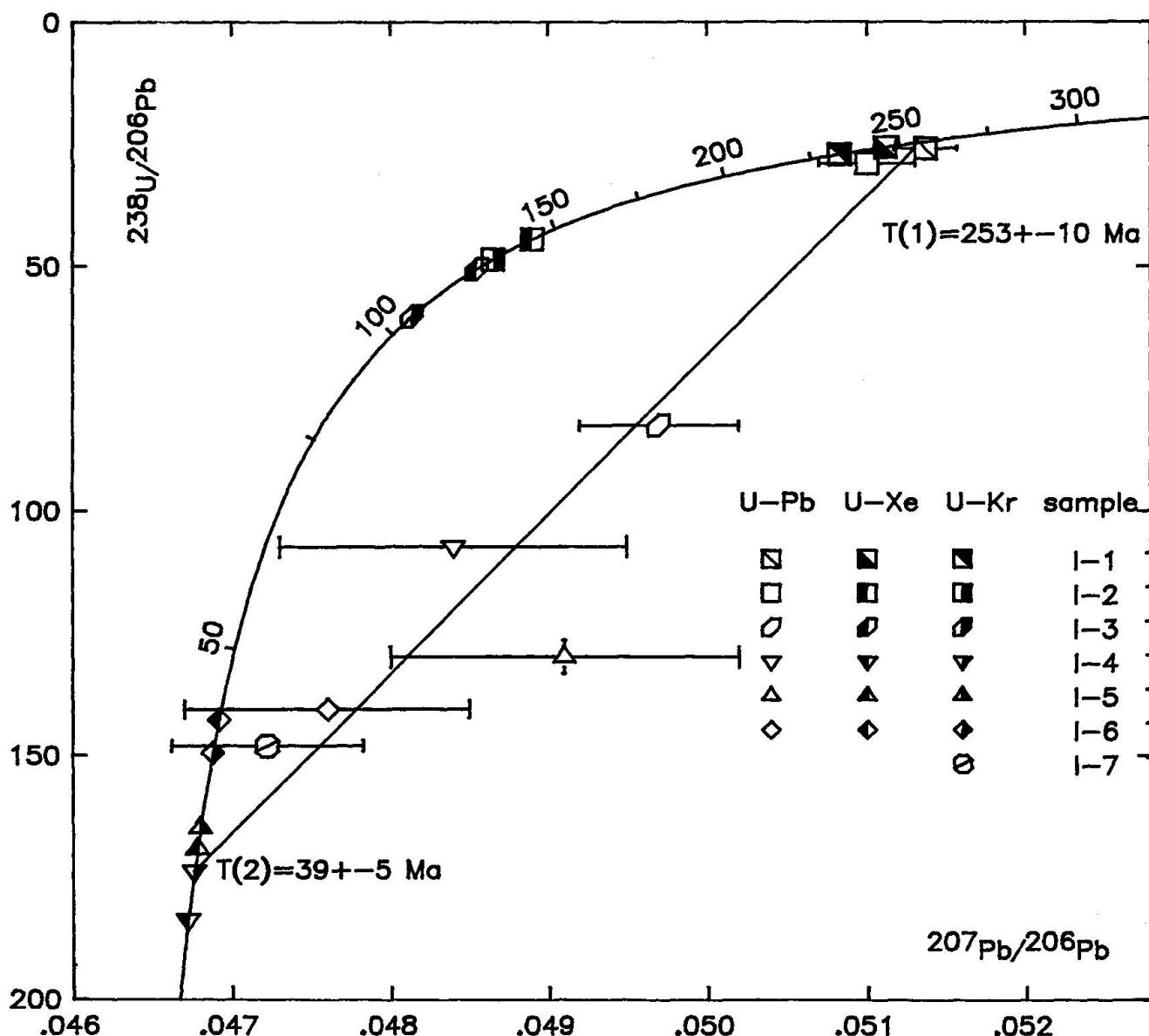


Fig. 6  $^{206}\text{Pb}/^{207}\text{Pb}$ - $^{238}\text{U}/^{206}\text{Pb}$  diagram showing the discordia of Fig. 5. The U-Xe and U-Kr ages are indicated on the the concordia curve.

ween 22 and 24.5 and  $^{207}\text{Pb}/^{204}\text{Pb}$  between 15.84 and 15.95 concordant U-Pb ages around 40 Ma can be obtained.

In contrast to the ambiguous U-Pb ages the U-Xe and U-Kr ages of the fine grained samples I-4, I-5 and I-6 were concordant. Those of samples I-4 and I-5 agree within error with the lower intercept age of 40 Ma (Fig. 6), whereas the concordant U-Xe and U-Kr ages of sample I-6 are slightly higher.

Microprobe investigations revealed significantly different Ca/U and Pb/U ratios of type A and B pitchblendes (Fig. 7). Pb and Ca concentrations are low in type B compared to type A. Furthermore type A pitchblende is characterized by Cl concentrations of 0.1 to 0.2 % versus 0.03 % in type B. On the other hand high REE concentrations were observed in type B, about 2% each of Sm, Gd and Dy versus 0.01 to 0.15 in type A (EIKENBERG, 1988).

Microprobe analyses of Th-free pitchblendes allow the calculation of U/Pb ages of areas of only a few microns in diameter. The microprobe analyses do not distinguish common from radiogenic lead. Therefore, U/Pb chemical ages are only meaningful if they are accompanied by Pb isotope analyses which allow an estimate of the different Pb-components to be made. The concentration of common Pb in type A pitchblende was assumed to be the same as that in the isotopically analysed samples. The common Pb content of type B pitchblende is probably not identical with the one observed in the isotopically analysed sample because the sample consisted of more than 50% gangue minerals.

The homogeneous Pb/U ratio of sample I-1 corresponds, after correcting for common lead, to an age of 250+/-15 Ma. In contrast, the coarse grained pitchblendes I-2 and I-3 have more variable and significantly lower Pb/U ratios (Fig. 7). The type B pitchblendes of samples I-4, I-5 and I-6A have homogeneous and virtually identical Pb/U ratios. Due to very small grain size in sample I-5 uranium and lead could not be determined quantitatively; however, the Pb/U ratios are homogeneous. All three samples yield, without applying a common lead correction, ages between 37 and 39 Ma. They are essentially the same as the lower intercept age of the U-Pb discordia and agree also, within error, with the U-Xe and U-Kr ages of samples I-4 and I-5. Based on the lead isotope compositions the samples which contained very significant amounts of gangue minerals common lead corrections lead to ages of about 20 Ma. for which there is no supporting evidence. Therefore, only minor amounts

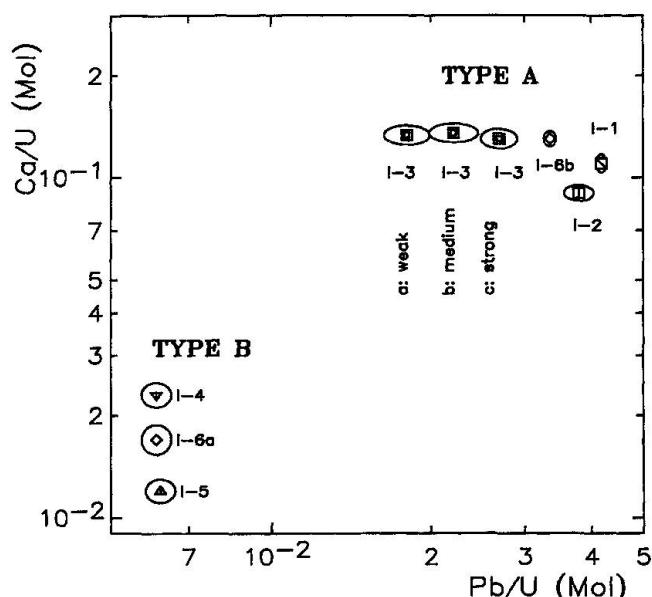


Fig. 7 Pb/U and Ca/U diagram illustrating the high Ca/U ratios of the Permian pitchblende (type A) and the contrasting low ratios of the Tertiary pitchblende (type B). Type B pitchblendes show uniform and low Pb/U ratios which correspond to an age of 37-39 Ma whereas the Pb/U ratios of type A are variable and reflect Pb-loss.

of common Pb are probably incorporated in type B pitchblende. Sample I-6 deserves special attention. Microprobe investigation revealed the presence of both types of pitchblende. The majority of grains had low Pb/U and Ca/U ratios similar to type B samples I-4 and I-5 but one slightly larger grain had high Ca/U and Pb/U ratios quite similar to those observed in type A pitchblendes. It is therefore likely that the «aliquots» used for determining the isotopic composition of the rare gases also consisted of these two types of pitchblendes. This would explain the somewhat high U-Xe and U-Kr ages of 45 Ma with respect to the lower intercept age of the discordia of 39 Ma.

## 5. Discussion

In the previous section we drew attention to the fact that the two types of pitchblendes exhibit different U-Pb and U-Xe-Kr systematics. A comparison and interpretation of the age patterns are summarized in Fig. 8.

Sample I-1 with the highest U-Pb chemical age of about 260 Ma, yielded concordant ages of 240-250 of all four uranogenic systems. This clearly indicates not only that uranium mineralization was formed during the Permian but also that the U-Xe and the U-Kr systems yield mea-

## Systematics between the U-Xe-Kr-Pb-Systems

case	U/Xe – U/Kr	U-Pb	sample: significance
A	concordant	concordant	I-1: crystallisation age
B	concordant	discordant	I-4,I-5: recrystallisation age I-6: mixing age
C	discordant	discordant	I-2,I-3: loss of daughter products
D	discordant	concordant	case not observed

Fig. 8 Comparison of age patterns. It should be noted that the discordant U-Pb ages in case B are most likely due to the presence of a somewhat radiogenic lead in the accompanying gangue minerals. Because of the small grain size of the pitchblende ( $> 10$  microns) no mineral separation was carried out. Microprobe U/Pb ages suggest an age similar to the rare gas ages.

ningful ages. It is important to note that the U-Pb as well as the U-Xe and U-Kr systems in this pitchblende survived a greenschist facies metamorphism without noticeable loss of radiogenic or fissionogenic daughter products.

We now turn our attention to the lower intercept age of about 40 Ma. of the U-Pb discordia (Fig. 5, 6) from which we conclude that the Tertiary event affected both the coarse and the fine grained pitchblendes. The concordant U-Xe and U-Kr ages of 40 Ma of the fine grained pitchblende show that the U-Xe and U-Kr systems were totally reset while the U-Pb systems of these two samples appears to have been severely disturbed. A comparison of the U-Pb isotope with the U-Pb microprobe analyses will help to clarify this puzzling difference.

The lead isotope analyses of samples which consisted besides pitchblende of substantial amounts of quartz, calcite, muscovite, apatite and sulfides revealed large amounts of common lead and yielded, after correction with a common lead ( $206\text{Pb}/204\text{Pb} > 19$ ), discordant U-Pb ages  $< 40$  Ma.. The uncorrected U/Pb ratios of the microprobe analyses yielded chemical U/Pb ages of  $37 \pm 5$  Ma for samples I-4 and I-5. Similar ages can

be calculated from the isotope analyses if one uses leads with  $206\text{Pb}/204\text{Pb}$  between 22 and 24 for correcting. These observations lead to the conclusion that the somewhat radiogenic lead resides in the accompanying phases rather than in the pitchblende. The concordant U-Xe and U-Kr ages, (2) the low and uniform U/Pb ratios, (3) the chemical U-Pb ages which are similar to the rare gas ages, (4) the agreement of all ages with the lower intercept of the U-Pb discordia and (4) their different Ca and Cl concentrations and their different REE-pattern preclude an origin from extremely cataclastic Permian pitchblende. These observations indicate that the fine grained samples I-4 and I-5 crystallized about 40 Ma ago as products of remobilization processes related to the meso-Alpine, thermal metamorphism.

On the basis of microscopic observations sample I-6A also belongs to type B pitchblende; its concordant U-Xe-Kr ages of  $45 \pm 4$  Ma are slightly higher than those of samples I-4 and I-5. The microprobe analyses revealed, however, besides the fine grained pitchblende of Tertiary age also the presence of an old relictic pitchblende grain of type A (I-6B in Fig. 7) It appears likely that the aliquots of I-6 used for isotope analyses

also contained both types of pitchblends. Therefore the U-Xe and U-Kr as well as the U-Pb ages are mixed ages of two pitchblende generations.

Finally, we have to discuss the results of the coarse grained samples I-2 and I-3 which yielded discordant ages, both of the U-Pb as well as the U-Xe and U-Kr systems. They range from 90 and 220 Ma (Tab. 4). The microprobe analyses show constant U but variable Pb concentrations. In sample I-3 we analysed three regions with different degrees of cataclasis (strong, medium and weak) and all have variable U/Pb ratios (Fig. 7) with ages lower than 260 Ma. These samples suffered different degrees of lead losses which were coupled with losses of fissionogenic Xe and Kr. The U-Kr age is always lower than the U-Xe age which reflects the preferential loss of the lighter and thus more mobile Kr. Such a behaviour was commonly observed in samples from other localities (EIKENBERG, 1988). However, no systematic relationship was found to exist of the degree of losses of the uranium daughter products.

Surprisingly, the electron microprobe analyses of different parts of sample I-3 (Fig. 7) revealed that the Pb/U ratios of the most cataclastic pitchblende are higher than those of apparently less affected, coarser grains. Thus, there is no relationship between cataclasis and degree of lead loss, possibly because the lead loss occurred prior to the cataclasis.

Sample I-2 (=LhU 103 of the first set of U-Pb isotope analyses) occurs in an Alpidic cleft. According to its discordant U-Pb, U-Xe and U-Kr ages as well as according to its trace element concentrations it clearly belongs to the Permian pitchblende generation. It either was mechanically transported into the cleft or the cleft developed around the pitchblende.

## 6. Conclusions

In summary, the lack of clearcut U-Pb isotope evidence for the existence of newly formed Alpidic pitchblende is explained: The fine grained samples where no mineral separation was possible contain excess radiogenic as well as common lead in coexisting mineral phases; consequently the U-Pb ages of such bulk samples are discordant, unless they are corrected with a somewhat radiogenic lead. Because all pitchblende samples plot on the same discordia one is tempted to invoke an episodic lead loss of old pitchblende rather than the presence newly crystallised pitchblende. If, however, the pitchblendes are really disturbed then fractionation between Xe and Kr occurs. Thus, concurrent studies of both the U-Xe-Kr and the U-Pb

systems are necessary to unambiguously interpret discordant U-Pb data of pitchblendes. Fission gas ages could become a valuable geochronological tool by complementing the conventional U-Pb isotope ages not only of pitchblende but possibly also of other U-bearing rock forming, accessory minerals. They help to interpret ambiguous discordias and they may eventually be applied to U-bearing minerals with high initial Pb concentrations.

Our study of pitchblendes from Isérables reveals the following history: The mineralization situated close to an unconformity of Permo-Carboniferous sediments was formed about 260 Ma ago presumably due to hydrothermal activities in the basement. During the meso-Alpidic, greenschist facies metamorphism some pitchblendes were mobilized and redeposited as fine grained, disseminated pitchblende about 40 Ma ago. At least part of the old radiogenic lead was incorporated in accompanying minerals. The newly formed pitchblende contains less Ca, Cl and F and exhibits a rare earth element pattern which differs from the one of the Permian pitchblende. The process of metamorphic mobilisation of uranium will be explored in detail in a forthcoming paper by J. Mullis on fluid inclusion studies of the mineralizations at Isérables. In contrast to the mobilized pitchblende the U-Pb as well as the U-Xe-Kr systems remained during the greenschist facies metamorphism undisturbed in some pitchblendes whereas others suffered losses of radiogenic and fissionogenic uranium daughter products.

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## References

- BEARTH, P. (1978): Geologischer Atlas der Schweiz 1:25000, 1308, St. Niklaus, Schweiz. Geol. Kommission
- BEARTH, P. (1980): Erläuterungen zu Blatt 1308, St. Niklaus, Schweiz. Geol. Kommission
- BERMAN, R.M. (1957): The role of Pb and excess O in uraninite. Am. Min. 42, 705-731.

CEVALES, G. (1961): Metamorphe Mobilisationsvorgänge in der Uranlagersätze des Preittals. *N. Jb. Mineral.* 96, 112-123.

EIKENBERG, J. (1988): Vergleichende Datierung von Uranmineralien mit den U-Xe, U-Kr und U-Pb Systemen sowie Untersuchungen der Produktion von nukleogenem Ar und Ne durch Kernprozesse. *Diss. No. 8522 ETH-Zürich.*

FELDMANN, M. (1986): Uran und Seltene Erden, Mineralisationen im Raum Embd-Törbel (Mulde von St. Niklaus), Matteringtal (Wallis). *Unveröff. Diplomarbeit, ETH-Zürich.*

GEBAUER, D. and GRÜNENFELDER, M. (1979): U-Th-Pb Dating of Minerals. In: *Lectures in Isotope Geology*; Springer-Verlag Berlin - Heidelberg - New York, 105-131.

GILBIN, A.M. and APPLEYARD E.C. (1987): Uranium mobility in non-oxidizing brines: field and experimental evidence. *Appl. Geochemistry* 2, 285-296.

GILLIERON, F. (1988): Zur Geologie der Uranmineralisation in den Schweizer Alpen. *Beitr. Geol. Schweiz, geotechn. Ser.* 77.

GRAF, TH., SIGNER, P., WIELER, R., HERPERS, U., SARAFIN, R., VOGT, S., FIENI, CH., PELLAS, P., BONANI, G., SUTER, M. and WÖLFLI, W. (1989): Cosmogenic nuclides and nuclear tracks in the chondrite Knyahinya. *Geochim. Cosmochim. Acta* (in press).

HEBEDA, E.H., FREUDEL, M., and SCHULTZ, L. (1987): Radiogenic, fissiogenic and nucleogenic noble gases in zircons. *Earth Plan. Sci. Lett.* 85, 79-90.

HÜGI, TH., KÖPPEL, V., DE QUERVAIN, F. and RICKENBACH, E. (1967): Die Uranverzerrungen bei Iséables (Wallis). *Beitr. Geol. Schweiz, geotech. Ser.* 42.

KÖPPEL, V., GÜNTHERT, A., and GRÜNENFELDER, M. (1980): Patterns of U-Pb zircon and monazite ages in polymetamorphic units of the Swiss Central Alps. *Schweiz. Mineral. Petrogr. Mitt.* 61, 97-119.

KRAMERS, J.D. (1973): Zur Mineralogie, Entstehung und alpinen Metamorphose der Uranvorkommen bei Trun, Graubünden. *Beitr. Geol. Schweiz, geotechn. Ser.* 52.

LUDWIG, K.R., SIMMONS, K.R., and WEBSTER, J.D. (1984): U/Pb isotope systematics and apparent ages of uranium ores, Ambrosia Lake and Smith Lake Districts, Grand Mineral Belt, New Mexico. *Economic Geology* 79, 322-337.

PECHMANN, E. VON and BIANCONI, F. (1982): Synmetamorphic uranium mineralisation from Tiraun, Graubünden, Switzerland. *Min. Mag.* 46, 173-180.

PETRASCHECK, W.E., ERKAN, E. and NEUWIRTH, K. (1975): Permo-Triassic uranium ore in the Austrian Alps - paleographic control as a guide for prospecting. *IAEA-SM-183/25*, 291-298.

RICH, R.A., HOLLAND, H.D. and PETTERSEN, U. (1977): Hydrothermal uranium deposits. *Developments in Economic Geology*. Elsevier scientific publishing company, 1-264.

SABU, D.D. (1971): On mass yield of xenon and krypton isotopes in the spontaneous fission of uranium. *J. Inorg. Nuc. Chem.* 33, 1509-1513.

SHUKOLYUKOV, YU. A. and MIRKINA, S.L. (1963): Determination of the age of Monazites by the xenon method. *Geochemistry* 7, 729-731.

SHUKOLYUKOV, YU. A. and MESHICK, A. P. (1987): Application of xenon isotopes for dating pitchblende. *Chem. Geol.* 66, 123-136.

STEIGER, R.H. and JÄGER, E. (1977): Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.* 36, 359-362.

WIELER, R., GRAF, TH., PEDRONO, A., SIGNER, P., PELLAS, P., FIENI, C., SUTER, M., VOGT, S., CLAYTON, R.N. and LAUL, J.C. (1989): Exposure ages of the regolithic chondrite Fayetteville: II. Solar-gas-free light inclusions. *Geochim. Cosmochim. Acta* 53, 1449-1459.

YOUNG, B.G. and THODE, H. G. (1960): Absolute yields of the xenon and krypton isotopes in  $^{238}\text{U}$  spontaneous fission. *Can. J. Phys.* 38, 1-10.

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