



## CONTRIBUTION TO CHARACTERISTICS OF URANIUM OXIDES

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### Abstract

Uranium oxides from pegmatitic, metamorphic and metasomatic uranium occurrences were investigated with the objective to check for differences in their physico-chemical properties and, whether such properties are sufficiently distinct to be applied as an exploration tool. Research methods included microscopy, electron microprobe and X-ray diffractometry amended by determinations of reflectance, Vickers hardness, unit-cell dimension and oxidation grade. Tentative research results are as follows:

- (a) U-oxides (uraninites) of pegmatites always contain significant amounts of Th (1,5–10 wt.% ThO<sub>2</sub>).
- (b) U-oxides from metasomatic environments have high, but variable contents of Fe, Ca, Ti, Si and Th (around 10 wt.%), Th being low.
- (c) U-oxides crystallised during metamorphism contain minor impurities of the above listed elements (total of oxides < 2 wt.%).
- (d) Redistributed U-oxides have elevated amounts of these elements.
- (e) Unit-cell dimensions of U-oxides tend to reflect a complex function of formation temperature, oxidation grade and the influence of incorporated elements caused by their radius and electro-negativity.
- (f) A global negative correlation of unit-cell dimension and oxidation grade of uranium oxides is indicated but based on widely varying ratios of the two parameters.
- (g) Colloform U-oxide (pitchblende) is characterised by elevated Ca-contents (1–5 wt.% CaO) and an almost complete lack of Th (< 1 wt.% ThO<sub>2</sub>).
- (h) Idiomorphic U-oxide (uraninite) is commonly low in Ca (< 1.5 wt.% CaO) but contains relatively high Th values.
- (i) The reflectance of U-oxides generally correlates positively with Vickers hardness and unit-cell dimension, but the incorporation of other elements in the lattice of U-oxides may cause strong interference.

### 1. INTRODUCTION

The research programme was primed (a) to define uranium oxides by means of physico-chemical parameters which (b) may help to decipher, together with other criteria, the behavior of uranium in geological environments. Beside microscopy and auto-radiographic methods the following investigations were performed:

- (a) Reflectance (RV) was measured between 436 and 644 nm with a Leitz photometer using SiC and a glassprisma as standard (analytical error: 0,5% RV).
- (b) Vickers hardness (VH) was determined with a Leitz micro-hardness tester and a weight of 100 p.
- (c) Electron microprobe analyses were carried out with a measurement time of 20 and 60 seconds, operating voltage of 25 kV, and a sample current of 10 namps. Standards were Al, Ca, Ti, Si and Fe bound to minerals, synthetic PbS, metallic Th, Ce and U.
- (d) X-ray diffractometry: Gandolfi and powder method.
- (e) The unit-cell was found on material separated directly from the polished section by drilling to obtain homogeneous mineral fractions and examined with a Guinier-Jagodzinski Camera using sodalite as internal standard (see JCPDS 41–1422).
- (f) The oxidation grade respectively U(VI) and U(total) were analysed polarographically and determined by the standard addition method [1, 2].

## 2. GEOLOGY, MINERALOGY AND ORE PARAGENESIS OF INVESTIGATED OCCURRENCES

A summary of physico-chemical data of the investigated U-oxides and the corresponding occurrences is provided in Table I.

### 2.1. Pegmatite

*Madavaska*, formerly Faraday mine, Bancroft district, Ontario, Canada. Uranium ore bodies occur in late tectonic pegmatitic and granitic dikes located in a metagabbro-amphibolite belt [12]. The origin of the pegmatites is considered of partial melting during the Grenvillian Orogeny [13]. Principal ore minerals are Th-rich uraninite and uranothorite dated 1100 to 800 m.y. old [5]. Other uraniferous minerals are sphene, cryolithe, zircon, uranophane and REE-minerals. Uraninite is euhedral to subhedral, weakly corroded and broken due to growth of isotropic zircon. The autobrecciation shattered the host rocks, intense hematitization overprinted the rocks.

*Hagendorf*, NE — Bavaria, Germany. Granites and pegmatites of late Hercynian age form intrusions within Proterozoic rocks. The Hagendorf pegmatite is considered a derivation of the Flossenbürger Granite [4, 14]. The pegmatite contains a number of irregularly distributed ore minerals including uraninite, columbite, hematite, sulfides and rare minerals [3, 15, 16]. Two varieties of uranium oxides are noticed: up to 0,2 mm large uraninite octahedrons and cubes occur peripheral within and upon columbite (uraninite 1). The other variety consists of irregular shaped aggregates which commonly occur suspended along the long axis of columbite (uraninite 2). The latter were interpreted as exsolutions [17]. The chemical composition of both is similar. Host rock alteration is restricted to hematite along cracks, hematite halos around uraninite hosting columbite, and corrosion of columbite.

*Way Lake*, Wollaston Domain, Saskatchewan, Canada. Uraniferous pegmatite cutting Aphebian quartz-feldspar gneiss is overprinted by albitization caused by Na-metasomatism [6]. Mineralization occurs as massive uranium lenses emplaced in a shear zone which is cut off at both ends by faults. Two U-oxides are distinguished:

- (a) Massive Pb-rich U-oxide with high reflectance. A minimum age of 1735 to 1765 [6] corresponds to the Hudsonian Orogeny (Pitchblende 1).
- (b) Ca-rich U-oxide strongly pitted, cracked, corroded and patchy oxidized. Where fresh, RV is relatively high (Pitchblende 2). Partly euhedral looking U-oxides within the pitchblende are interpreted as relics of pegmatitic uraninite.

### 2.2. Metamorphite

*Orient*, Kettle Falls Gneiss Dome, NE Washington State, USA. The occurrence is situated in a belt of Proterozoic metasediments of upper amphibolite facies (Boulder Creek Formation) intruded by a variety of plutons. Country rocks are quartzite and quartz-feldspar-biotite gneiss. Mineralization is hosted by a schlieren augengneiss with bands of biotite accumulations. Principal uranium mineral is finely disseminated broken and corroded euhedral U-oxide (uraninite) arranged in bands and lenses together with magnetite and pyrite. The uraninite contains about 1 wt.% ThO<sub>2</sub>, PbO and SiO<sub>2</sub> each. The Vickers hardness is high. Alteration is very minor consisting of chloritization and bleaching of biotite.

TABLE 1: SUMMARY OF OUR CHEMICAL AND PHYSICAL DATA OF U-OXIDES FROM PEGMATITE, METAMORPHITE AND METASOMATITE ENVIRONMENTS

Occurrence U-oxide	n	Average microprobe analyses of uranium oxides															Age m.y.		
		UO <sub>2</sub>	ThO <sub>2</sub>	PbO	CaO	Ce <sub>2</sub> O <sub>3</sub>	FeO	TiO <sub>2</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Total	UO <sub>2</sub> / ThO <sub>2</sub>	CaO/ ThO <sub>2</sub>	UO <sub>2-x</sub> x =	VH 100 p	RV <sub>rad. am</sub> (%)	a, (Å)	Rock	U-oxide
<b>Pegmatite</b>																			
<b>Hagendorf</b>																			
Uraninite 1	23	94,29	2,22	3,55	0,04	0,01	0,09	0,01	0,08	---	100,29	42	<0,1	981	18,0	5,50 [3]	293 [4]		
Uraninite 2	3	94,30	1,57	3,32	0,07	---	0,16	---	0,13	0,03	99,58	60	<0,1		18,3				
<b>Mada-waska</b>																			
Uraninite	24	72,38	6,40	10,77	1,16	1,38	0,02	0,04	0,18	---	92,33	11	0,2	898	16,4	5,460		800- 1100 [5]	
Uranothorite	5	13,76	43,34	1,04	3,48	0,75	0,37	0,02	20,38	---	83,44	<1	0,1	266	5,8				
<b>Way Lake</b>																			
Pitchblende p1	8	67,48	2,59	17,79	1,43	2,15	---	---	0,16	---	91,60	26	0,6		16,4	5,494		1765 and	
Pitchblende p2	9	67,99	1,02	15,18	2,96	1,10	0,02	---	0,75	0,02	89,04	67	2,9	619	16,7	5,463		1735 [6]	
<b>Metamorphite</b>																			
<i>contact-met:</i>																			
<b>Alm Bos</b>																			
Uraninite	29	98,20	0,25	0,54	0,45	0,13	0,02	0,01	0,15	0,01	99,76	393	1,8	1394	17,4	5,467	Intrusion 52-19 [7]		
<i>med. grade:</i>																			
<b>Orient</b>																			
Uraninite	33	94,68	1,11	1,08	0,15	0,11	0,01	0,01	0,08	0,02	97,25	85	0,1	1333	17,8				
<b>Höhenstein</b>																			
Uraninite	23	90,59	0,10	2,73	0,60	0,22	0,12	0,36	0,51	0,02	95,25	906	6,0	980	16,5				
Pitchblende p1	23	86,81	0,20	1,65	2,49	0,52	0,17	0,20	0,44	0,01	92,79	434	12,5	1155	16,0	5,436		295 [8]	
Pitchblende p2	7	79,69	0,37	2,19	0,94	0,57	0,61	0,45	0,73	0,12	85,67	215	2,5	564	13,8				
Pbl. -schlieren (s)	6	81,83	0,42	2,89	1,89	0,85	2,18	0,51	1,15	0,02	91,74	195	4,5	524	15,7				
<b>Wäldel</b>																			
Uraninite	22	92,91	0,24	2,91	0,54	0,09	0,07	0,21	0,26	0,04	97,27	387	2,3	927	16,5		Granite 303 [9]		
<i>low-grade:</i>																			
<b>Niamtougou</b>																			
Pitchblende	5	90,77	0,18	7,12	0,73	0,01	0,08	---	0,29	0,05	99,23	504	4,1						
<b>Forstau</b>																			
Pitchblende	7	87,57	0,22	2,49	0,38	0,17	0,09	0,10	0,36	0,08	91,46	397	1,7						
<b>Metasomatite</b>																			
<b>Mosquito Gulch</b>																			
Uraninite (u) <sup>*</sup>	12	63,91	0,15	10,94	2,77	0,08	7,28	0,34	4,69	1,50	91,66	426	18						
Pbl veinlets (v)	15	73,07	0,07	18,37	2,66	0,28	0,03	0,06	0,42	0,03	94,99	1045	38		16,8			2200 [10]	
Pbl on grains (g)	9	85,55	0,21	4,18	2,33	0,11	0,02	0,02	3,82	0,09	96,33	407	20						
<b>Kitongo</b>																			
Uraninite (I) <sup>*</sup>	29	74,44	0,13	2,78	3,11	0,17	2,98	0,30	6,19	0,43	90,53	572	24	351	11,2			590 [11]	
U-Ti-oxide (II)	5	57,84	0,19	1,27	2,53	0,15	1,17	17,77	3,40	---	84,32	351	21		10,2				

\* Corroded/stained

Pbl: Pitchblende

pl: massive Pitchblende

p2: Spherulitic/oxidized Pitchblende

( ): see Fig. 1+2

*Höhenstein*/Poppenreuth and *Wäldel*/Mähring, NE-Bavaria, Germany. Moldanubian biotite-sillimanite-mica schist and gneiss of upper amphibolite facies contain granitoid bands and lenses parallel to the schistosity [18].

At *Höhenstein* uranium occurs in a variety of minerals disseminated in schists and granitoids [8, 19, 20, 21]. Our studies yielded the following results:

- (a) U-oxide with high reflectance (uraninite) predating pyrite,
- (b) U-oxide with low reflectance (tetragonal  $U_3O_7$ , [20]),
- (c) U-oxide massive or colloform (pitchblende) present in several generations and oxidation grades with partly high reflectance,
- (d) Mostly concentrically zoned globules of U-oxide and U-oxides coating quartz grains (pitchblende),
- (e) Coffinite as individual grains or coating quartz and brannerite.

The reflectance decreases from the euhedral uraninite to the pitchblende globules with higher CaO and FeO content. Uraninite supposedly formed by metamorphism from sedimentary uranium. Subsequent U redistribution resulted in uraninite accumulation in veinlets. Repeated cataclasis remobilized and redistributed this material again.

At *Wäldel* U-oxides are associated with quartz-filled structures [9]. Three U-minerals are distinguished:

- (a) Euhedral crystals often dissolved from the core outwards (uraninite),
- (b) Globular, concentric U-oxide with very low reflectance values (pitchblende),
- (c) Coffinite coating quartz grains, filling voids and concentrated in aggregates paralleling the schistosity.

*Niamtougou*, Lama Kara, northern Togo. Country rock is quartz-mica-amphibol gneiss and calcite-quartz-mica gneiss of greenschist facies. The Pb-rich U-oxide forms 5 to 10  $\mu$  large globules irregularly shaped and partly colloform aggregates (pitchblende) disseminated on schistosity planes as well as in minifractures. Locally the aggregates indicate euhedral habits. Biotite and hornblende are chloritized adjacent to the U-oxides. Other ore minerals are mainly ilmenite, magnetite and pyrite.

*Forstau*, Land Salzburg, Austria. Spotty U showings occur in the Permo-Triassic phyllite series originated from lacustrine sediments by greenschist facies grade metamorphism during the Alpine Orogeny. Host rock is a banded ankerite-sericite-quartz schist [22] stratigraphically underlain by graphitic horizons [23, 24]. Host rock alteration is very minor consisting of hematitisation, limonitization and chloritization. U-oxides are present as pitchblende and minor uraninite. The U-oxides occur parallel to the schistosity in dark quartz laminae, in sericitic parts or in fold saddles of microfolds, and along irregular joints which trend more or less perpendicular to the schistosity. U-oxides also occur at the interface between carbonate lenses and quartz-muscovite layers. These U-oxides are interpreted as replacements of algae or other organic substances. Pyrite is present in fine grained anhedral partly, framboidal aggregates associated with U-oxides and in euhedral crystals which do not show any relationship with the uranium mineralization.

*Alm Bos*, Adamello Massif, northern Italy. Intrusions of igneous rocks, 52 to 19 m.y. old [7] have contact-metamorphosed uraniferous arkoses and sandstones of Permian age to

quartz-feldspar hornfels and quartzite. In sediments unaffected by metamorphism the Uranium is present as pitchblende and amorphous material commonly associated with organic substances. With approach to the Adamello intrusion, the U-oxides are gradationally recrystallized, ultimately to euhedral uraninites in the inner contact-metamorphosed aureole [25]. Well crystallized uraninite is distinctly anisotrop, partly porous and intergrown with silicates. The uraninite is very pure. It has a high uranium content and very low contents of the other compounds [26]. Principal associated sulfides are pyrite, pyrrhotite and chalcopyrite. The Alm Bos mineralization illustrates the spaciouly transitional impact along a thermal gradient on a sedimentary, sandstone-type uranium mineralization.

### 2.3. Metasomatite

*Mosquito Gulch*, Nonacho Basin, NWT, Canada. Na-metasomatism along a cataclastic zone at the contact of the granitic basement and the overlying late Aphebian Nonacho Formation transformed the granite into albitite. Where mineralized, the albitite is massive and pink coloured due to hematitization. In strongly albitized rocks [10] U-oxides are present in several varieties/generations.

- (a) Finely disseminated strongly corroded U-oxides in chloritic intervals within breccias (uraninite).
- (b) Anhedral U-oxides along grain boundaries (pitchblende).
- (c) Anhedral U-oxides in fractures and as veinlets (pitchblende).

Compared with (a) the varieties (b) and (c) have a relatively high reflectance and significant lower Fe content. Type (c) has a relatively high Ca content. All varieties are low in Ti.

*Kitongo*, Poli area, Cameroon. Metasediments of the Upper Precambrian Série de Poli (greenschist to amphibolite facies [27]) are intruded by Panafrican plutons including the Kitongo granite [11]. The U occurrence is situated at the northwestern cataclastically overprinted intrusive contact of the Kitongo granite with schists and gneisses. Intense Na-metasomatism affected the biotite-hornblende granite. U-oxides are hosted by an albitization zone in which the granite is partly transformed to Na amphibole albitite or aegerine albitite. Si and K are removed and Na is added [28, 29]. Additional alteration includes hematitization and limonitization. The U-oxides are more or less decomposed and "oxidized". The style of "oxidation" is caused by increasing incorporation of Ti. Reflectance is decreasing with increasing Ti and Si content. Paragenetic minerals are magnetite and subordinate pyrite, galena, chalcopyrite and alteration products thereof.

## 3. CHEMICAL AND PHYSICAL PROPERTIES OF U-OXIDES

The  $\text{TiO}_2\text{-SiO}_2\text{-CaO}$  triangles presentation (Fig. 1) illustrate the wide range of these compounds in U-oxides. Most samples group in the CaO sector. But samples of metamorphites contain higher amounts of Ti and Si compared to those of pegmatites (Fig. 1a). U-oxides of metasomatites are relatively enriched in Si and Ti (Fig. 1b). The  $\text{SiO}_2\text{-CaO}$  correlation diagram (Fig. 2) shows that the U-oxides of metasomatites plot above about 1 wt.%  $\text{SiO}_2$  whereas those of pegmatites and metamorphites are below this level. In the latter field two distribution groupings are obvious: all uraninites analysed contain less than 1,5 wt.% CaO whereas the CaO content of pitchblende ranges from 0,5 to 4 wt.%.

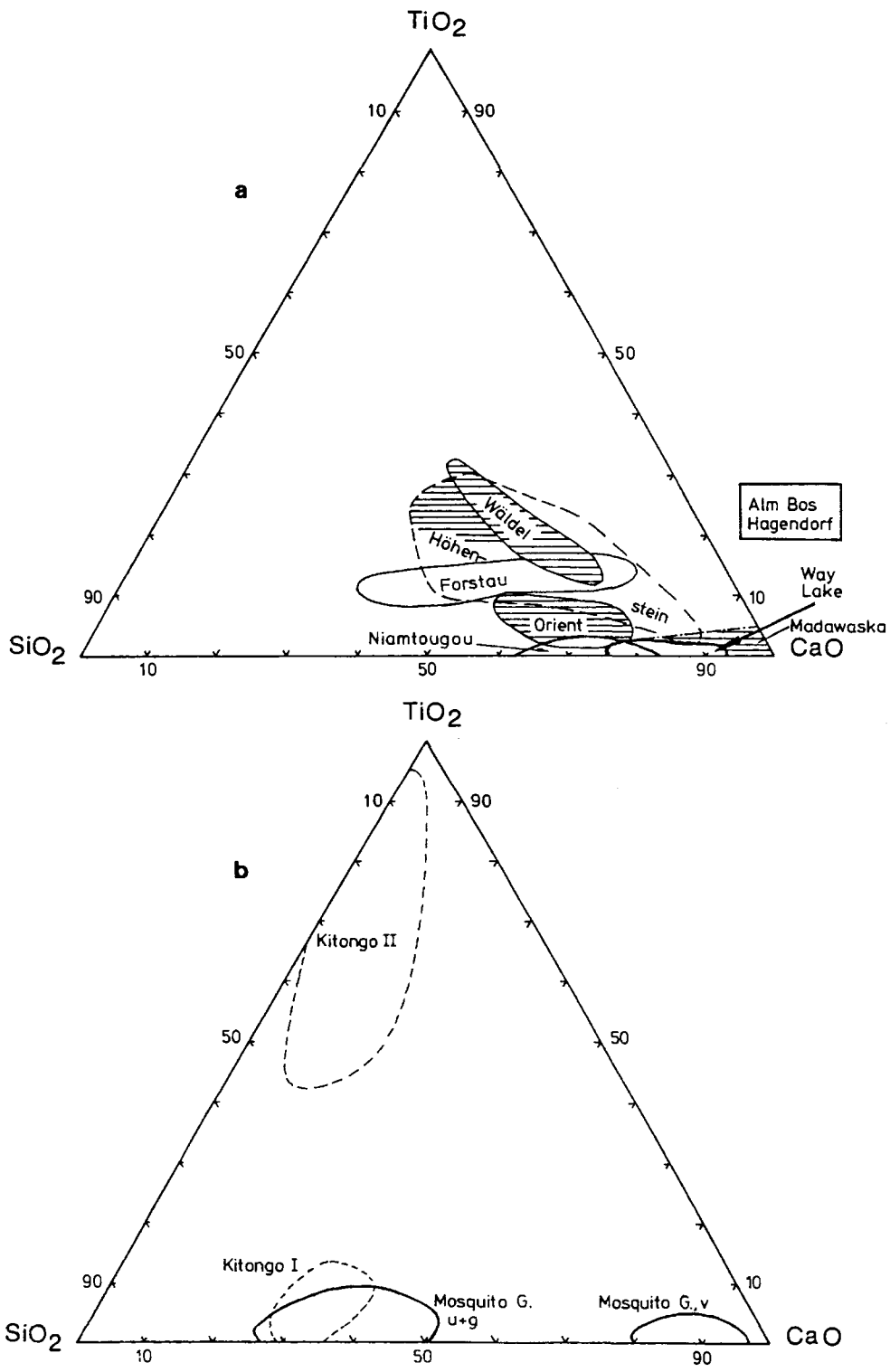


FIG. 1. Triangle diagrams for U-oxides of the investigated occurrences.

(1a) Pegmatites and Metamorphites.

Hatched sections: uraninite, white sections: pitchblende

(1b) Metasomatites. u = uraninite, v = U-oxide in veins, g = U-oxide on grains, Kitongo I = uraninite, Kitongo II = "oxidized" uraninite.

Solid line: Mosquito Gulch, dotted line: Kitongo

Alm Bos and Hagendorf do not plot in this type of diagram.

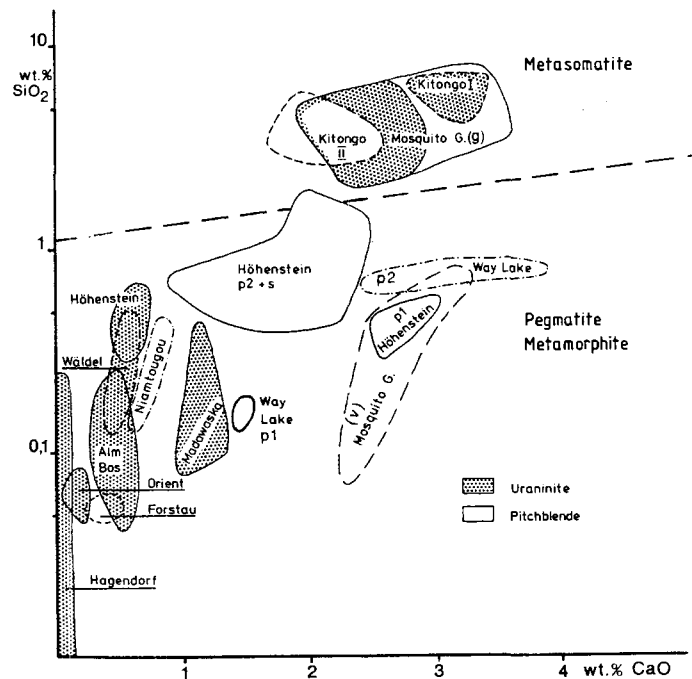


FIG. 2. Correlation diagram for U-oxides of the investigated occurrences.

*p1: massive pitchblende; p2: spherulitic or oxidized pitchblende; s: pitchblende schlieren, v: U-oxide in veins.*

Plotting our analytical data and literature data in a  $\text{TiO}_2\text{-SiO}_2\text{-CaO}$  triangle diagram (Fig. 3) permits in a general way the distribution of four segments. In Fig. 3a, segment 1 represents the relatively pure U-oxides (uraninite) but partly also U-oxides with high CaO content (pitchblende) of metamorphic, pegmatitic and contact-metamorphic origin. Segment 2 contains U-oxides with higher Si values (1 to 10 wt.%  $\text{SiO}_2$ ) relative to Ti (< 1 wt.%  $\text{TiO}_2$ ) and Ca (1–3 wt.% CaO). These are minerals from metasomatic deposits and redistributed U-oxides from metamorphites. Segment 3 and 4 includes Si-rich U-oxides (> 10 wt.%  $\text{SiO}_2$ ) or coffinite, and Ti-rich U-Oxides and brannerites formed in various environments. Transferring data of segment 1 from Fig. 3a into a  $\text{CaO-ThO}_2\text{-UO}_2$  diagram (Fig. 3b) two segments can be established representing Ca-rich U-oxides (pitchblende) and Ca-poor, partly Th-rich U-oxides (uraninite). The high Th uraninite tends to be typical for pegmatites and the low to zero Th uraninite for contact-metamorphite and metamorphite environments.

Figure 4 displays the interrelationship of lattice constants ( $a_0$ ), oxidation grade, reflectance (RV), and hardness (VH) for U-oxides. Diagram 4a shows no correlation of the two parameters  $a_0$  and VH. Diagram 4b displays a positive correlation of  $a_0$  and RV. Higher amounts of elements incorporated in U-oxides and/or  $\text{U}^{6+}$  are associated with a decrease in RV. Diagram 4c indicates a negative correlation of  $a_0$  and oxidation grade except for the Way Lake samples (WL). The open dots and the extrapolated line are taken from Brooker & Nuffield [43]. The differing  $a_0$  values of the Way Lake samples correspond to elevated Th contents. This illustrates that not only a change in oxidation grade provokes a variation in the unit-cell dimension. The same effect results also from the incorporation of other elements. The data imply that incorporation of certain elements in U-oxides causes unit-cell shrinking. The reason lies in the smaller ionic radius of the introduced element (Si, Ti etc.) compared to that of  $\text{U}^{4+}$  (1,01 Å in coordination 8). On the other hand, a  $\text{Th}^{4+}$  (1,06 Å) content in U-oxides causes a greater lattice constant. Replacing  $\text{U}^{6+}$  (0,80 Å) by  $\text{Ca}^{2+}$  (1,03 Å) would mean an increase of  $a_0$  but when  $\text{Ca}^{2+}$  replaces  $\text{U}^{4+}$  the lattice remains more or less constant.

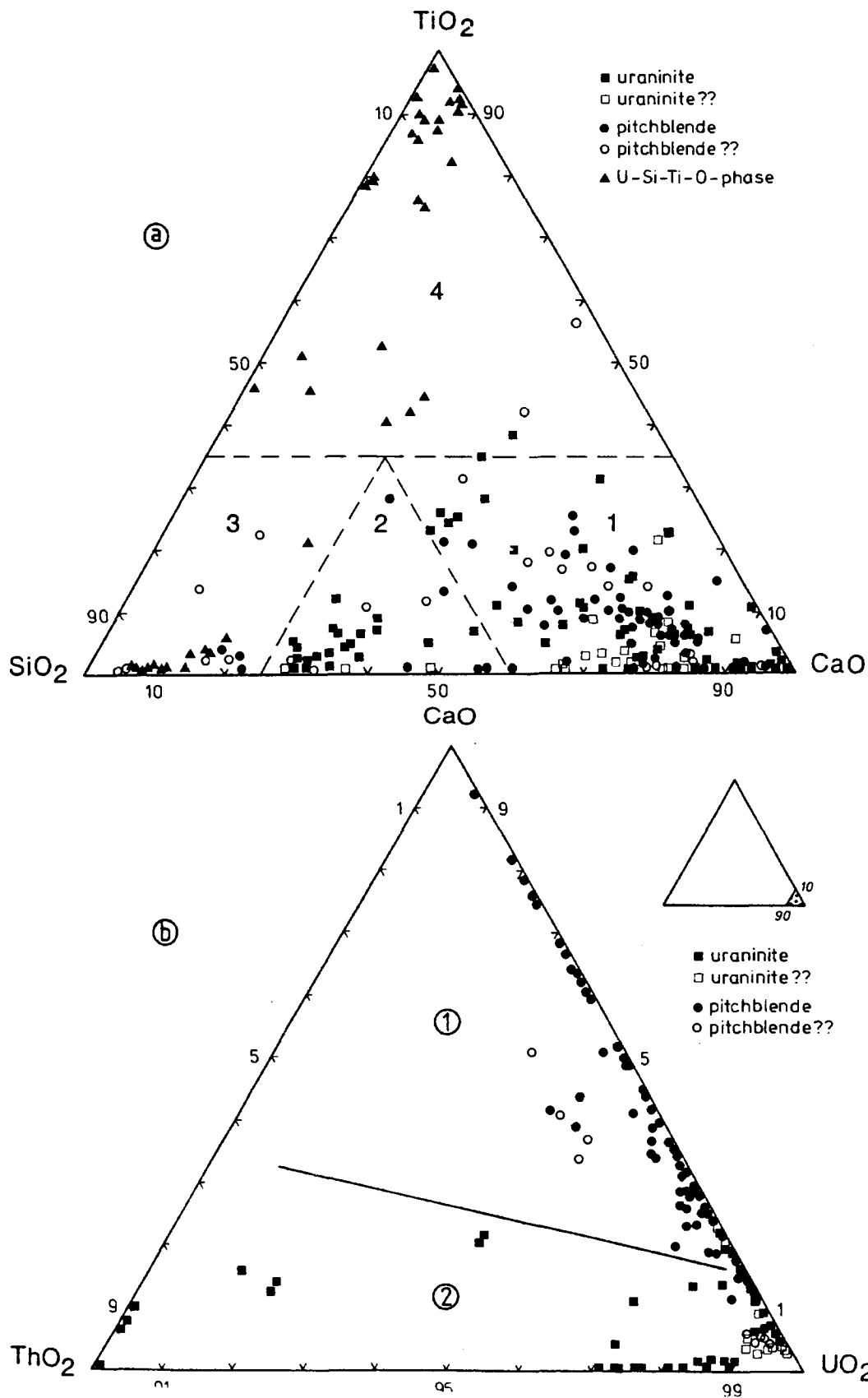


FIG. 3. Triangles for uranium mineral phases. (own data amended by data from [30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42]). Fig. (a) data of all samples (number analyses: 205). Fig. (b) data of samples from segment 1 of Fig. (a). Field 1 in Fig. (b) reflects the composition of pitchblende, field 2 that of uraninite.



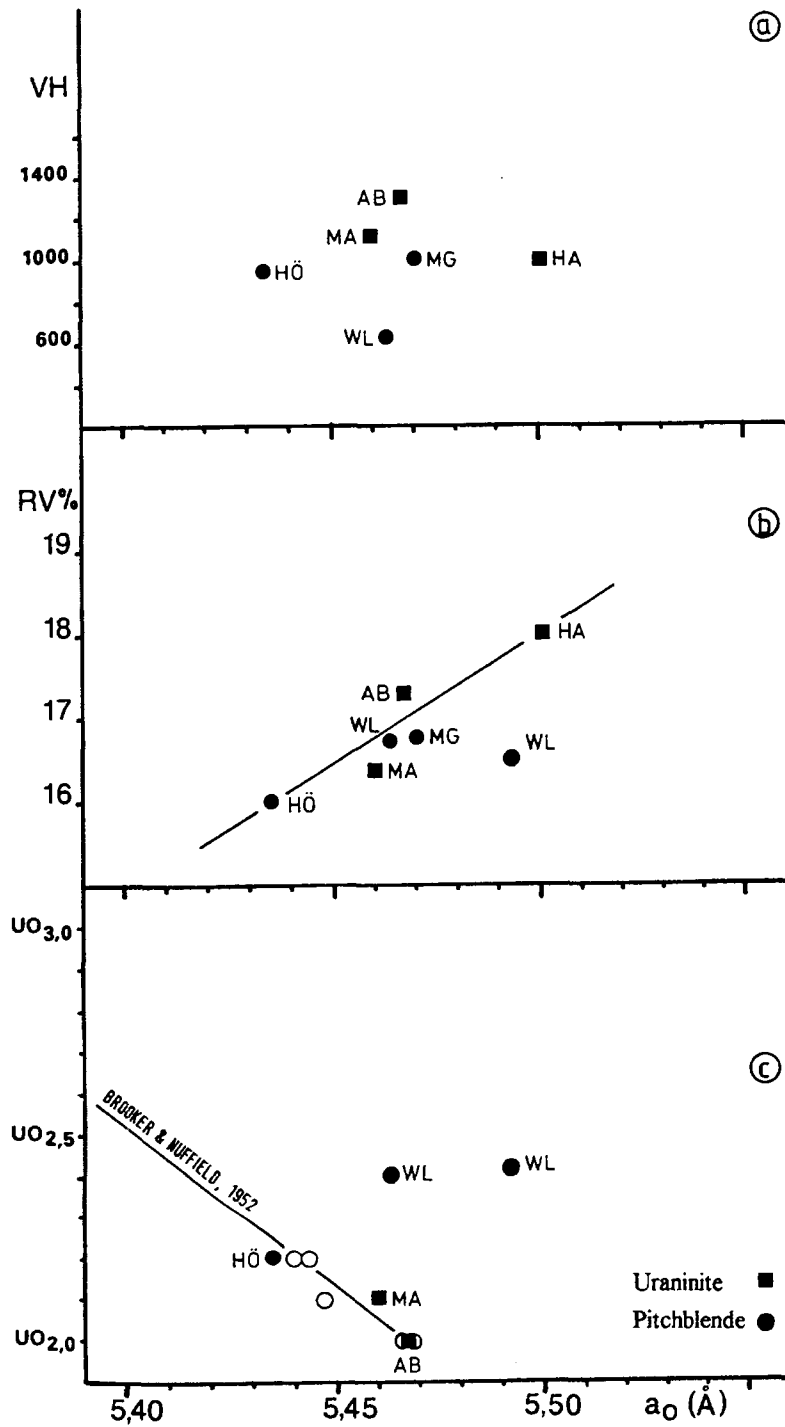


FIG. 4. Correlation diagram of unit-cell dimension versus Vickers hardness (VH), reflectance values (RV) and oxidation grade of pitchblende and uraninites. Open dots: [43]  
 AB: Alm Bos                      HA: Hagedorf                      HÖ: Höhenstein  
 MA: Madawaska                      MG: Mosquito Gulch                      WL: Way Lake  
 open dots:

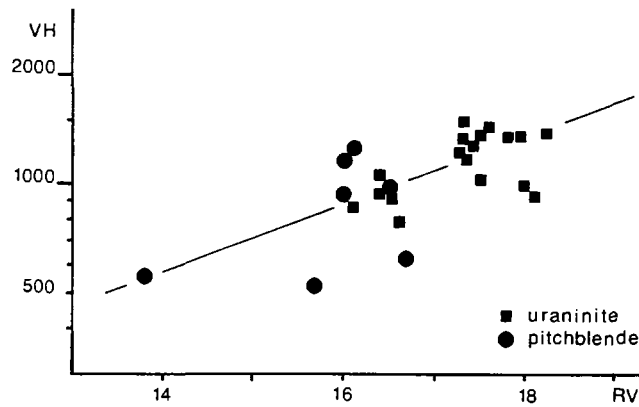


FIG. 5. Correlation diagram of reflectance (RV) versus Vickers hardness (VH) of U-oxides.

Figure 5 illustrates a positive correlation of reflectance and hardness of U-oxides. The uraninites tend to have higher values. Up to a certain amount ( $\text{ThO}_2$  ca. 2 wt.%,  $\text{PbO}$  ca. 4 wt.%,  $\text{SiO}_2$  ca. 0,5 wt.%,  $\text{CaO}$  ca. 1 wt.%) substitutes do not influence the reflectance of the U-oxides.

#### 4. COMPARISON WITH LITERATURE DATA AND DISCUSSION

Physico-chemical characteristics of U-oxides and related crystallographic variations and genetic implications have been researched by a number of geoscientists. Results from some of these authors be summarized as follows: Brooker & Nuffield [43] and other authors established a negative correlation between lattice constant and oxidation grade of U-oxides. Wasserstein [44] views a reduction of lattice constants with increasing age and explains this as a result of replacement of  $\text{U}^{4+}$  by  $\text{Pb}^{4+}$ . Morton & Sassano [36] demonstrate a positive relationship of Pb contents with hardness and reflectance but with some exceptions. The data also display a positive correlation of lattice constant and Pb tenor. Xu et al. [45] figured out that U-oxides with high Pb content have larger lattice constants than those with lower Pb tenors. They constitute further a positive correlation between lattice size and formation temperature as mentioned by other authors as well. Cathelineau et al. [32] document a correlation between radiogenic Pb loss and lattice reduction but without a change in the oxidation grade. These authors also noticed that old U-oxides (Proterozoic:  $a_0 > 5,44 \text{ \AA}$ ) have larger lattice sizes than younger ones (Hercynian:  $a_0 5,44\text{--}5,38 \text{ \AA}$ , Tertiary:  $a_0 < 5,38 \text{ \AA}$ ). Therefore they consider the size of U-oxide lattice being also a function of age. Nakhla [46] shows that both radius and electro-negativity of a cation influence the reflectance of a mineral. Increasing radius of a cation impose higher reflectance. That means, consigned to U-oxides, reflectance is positive correlated with the lattice size.

The above listed features would infer the following conclusions under the assumption that only almost pure U-oxides are involved.

- (1) Temperature — oxidation grade-unit-cell: The unit-cell dimension appears to be a function of formational temperature i.e. the higher the temperature the larger the  $a_0$  and the lower the oxidation grade.
- (2) Unit-cell dimension-Pb content: The postulated positive correlation of  $a_0$  and Pb content can be only valid if elementary Pb (ionic radius =  $1,75 \text{ \AA}$ ) is involved.  $\text{Pb}^{4+}$  has a radius of  $0,84 \text{ \AA}$  hence it is smaller than  $\text{U}^{4+}$  ( $1,01 \text{ \AA}$ ) and almost equals  $\text{U}^{6+}$  ( $0,8 \text{ \AA}$ ) and can therefore not cause expansion of the U-oxide lattice. Due to this a lattice reduction is postulated if  $\text{Pb}^{4+}$  replaces  $\text{U}^{4+}$  with increasing age [44].

- (3) Unit-cell dimension — age: Larger unit-cells related to older U-oxides [32] would imply that the often cited autooxidation of U-oxides plays only an insignificant role. On the other hand, a positive correlation of  $a_0$  and temperature exists. This would theoretically permit the deduction of a positive correlation of age and temperature what does not appear feasible. For these reasons the correlation of  $a_0$  and age can be only fictitious, or of secondary nature respectively.

This is supported by the Alm Bos occurrence of Tertiary age. Here temperature conditions from sandstone-type to contact-metamorphic U-oxides can be studied in the aureole of the Adamello intrusion. Sedimentary U-oxides have a composition of  $UO_{2,61}$  whereas U-oxides formed closest to the intrusive contact have a composition of  $UO_{2,06}$  and a unit-cell dimension of 5,467 Å [26] which compares with data of synthetic material and old samples e.g. from Mosquito Gulch (Table I). Lead content in the contact-metamorphic Alm Bos U-oxide is very low.

Relevant information published by other authors have been compiled cumulatively with our values in a diagram showing lattice constants versus U oxidation grades (Fig. 6). There is globally a negative correlation of unit-cell dimension and oxidation grade but with wide deviations. Genetically founded distribution segments could be established. Particularly the segment of hydrothermal formed U-oxides is widespread and overlaps the fields of U-oxides in sediments and matasediments.

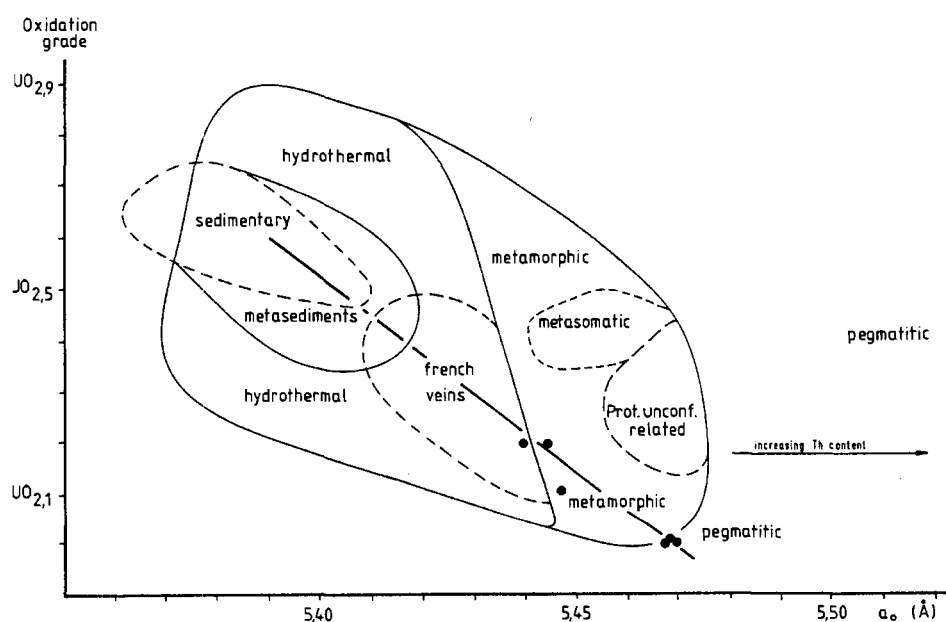


FIG. 6. Oxidation grade versus unit-cell dimension for uranium oxides, and their attribution to genetic fields (number of samples: 120) hydrothermal = vein type, french veins = granite related vein-type mineralization Own data and from [43] (dots and extrapolated line ), [32, 26, 47, 45, 39]. The terms e.g. metasediments or metamorphic are taken from the used literature.

## 5. CONCLUSIONS AND RESULTS

The above discussed features and relationships illustrate the complex influence of the various ingredients involved in the formation of U-oxides and their crystallographic properties. The following relationships for our samples can be outlined.

- (a) The chemical composition of U-oxides is different in each occurrence or group of occurrences respectively .
- (b) The content of Ti, Si, Ca, and Fe in U-oxides is variable.
- (c) The  $\text{UO}_2/\text{ThO}_2$  and  $\text{CaO}/\text{ThO}_2$  ratios of U-oxides permit the attribution of these oxides to formational environments (Table I).
- (d) It is possible to distinguish in a general way between euhedral U-oxide (uraninite) and colloform U-oxide (pitchblende) by means of their physico-chemical parameters as follows:

	<i>Uraninite</i>	<i>Pitchblende</i>
Habit	euhedral	colloform
Unit-cell dimension	> 5.46 Å	<5.46 Å
Oxidation grade	< $\text{UO}_{2.2}$	> $\text{UO}_{2.2}$
CaO content	< 1.5 wt.%	1–5 wt.%
ThO <sub>2</sub> content	up to several %	< 1 wt.%

- (e) U-oxides of pegmatites always contain significant amounts of Th (1,5 to 10 wt.%).
- (f) U-oxides of metamorphic and contact-metamorphic origin are relatively pure in composition containing only minor amounts of other elements (Fe, Ca, Ti, Si, Th less than 1,5 wt.% each, and < 2 wt.% combined). U-oxides of these environments tend to be chemically the purer the higher the grade of metamorphism.
- (g) Redistributed U-oxides derived from metamorphic and pegmatitic parent minerals are characterized by substitution of U by other elements.
- (h) U-oxides of metasomatic environments have high but variable contents of Si, Ti, Ca, Fe up to 10 wt.% each and ranging from 10 to 15wt.% combined. Thorium is low (< 0,3 wt.%).
- (i) The unit-cell dimensions of U-oxides is a function of formational temperature, oxidation grade, substitution of U by other elements and their radius and electro-negativity. U substituted by Th (and REE) results in enlargement of the lattice. Most other elements such as Si, Ti and Fe correlate with reduced lattice. Due to different ionic radius of  $\text{U}^{4+}$  and  $\text{U}^{6+}$  the replacement by Ca has different effects on the lattice size: the lattice remains more or less constant if  $\text{Ca}^{2+}$  replaces  $\text{U}^{4+}$  but by replacing  $\text{U}^{6+}$  the lattice would increase.
- (j) Reflectance and lattice constant of U-oxides correlate positively but incorporation of U substituting elements strongly interfere. Almost all elements except Th and Ca reduce RV.

Distinct U substituting elements and their ratios, and physico-chemical parameters of U-oxides seen as a whole may provide significant hints on the possible formation temperature and/or the formational environment.

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