



Fate of trace elements during alteration of uraninite in a hydrothermal vein-type U-deposit from Marshall Pass, Colorado, USA

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Abstract

Alteration of uraninite from a hydrothermal vein-type U-deposit in Marshall Pass, Colorado, has been examined by electron microprobe analysis in order to investigate the release and migration of trace elements W, As, Mo, Zr, Pb, Ba, Ce, Y, Ca, Ti, P, Th, Fe, Si, Al, during alteration, under both reducing and oxidizing conditions. The release of trace elements from uraninite is used to establish constraints on the release of fission product elements from the UO_2 in spent nuclear fuels. Uraninite occurs with two different textures: (1) colloform uraninite and (2) fine-grained uraninite. The colloform uraninite contains 1.04–1.75 wt% of WO_3 , 0.16–1.70 wt% of As_2O_3 , 0.06–0.88 wt% of MoO_3 ; whereas, the fine-grained uraninite retains 2.25–4.93 wt% of WO_3 , up to 5.76 wt% of MoO_3 , and 0.26–0.60 wt% of As_2O_3 . The near constant concentration of incompatible W in the colloform uraninite suggests W-incorporation into the uraninite structure or homogeneous distribution of W-rich nano-domains. Incorporation of W and Mo into the uraninite and subsequent precipitation of uranyl phases bearing these elements are critically important to understanding the release and migration of Cs during the corrosion of spent nuclear fuel, as there is a strong affinity of Cs with W and Mo. Zoning in the colloform texture is attributed to variation in the amount of impurities in uraninite. For unaltered zones, the calculated amount of oxygen ranges from 2.08 to 2.32 [apfu, (atom per formula unit)] and defines the stoichiometry as UO_{2+x} and U_4O_9 ; whereas, for the altered zones of the colloform texture, the oxygen content is 2.37–2.48 [apfu], which is probably due to the inclusion of secondary uranyl phases, mainly schoepite. The supergene alteration resulted in precipitation of secondary uranyl minerals at the expense of uraninite. Four stages of colloform uraninite alteration are proposed: (i) formation of an oxidized layer at the rim, (ii) corrosion of the oxidized layer, (iii) precipitation of U^{6+} -phases with well-defined cleavage, and (iv) fracture of the uraninite surface along the cleavage planes of the U^{6+} -phases.

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1. INTRODUCTION

During the last two decades, a number of studies of uraninite (UO_{2+x} ; space group $Fm\bar{3}m$; $Z = 4$; number of units per one unit cell) in natural U-deposits have been used to establish constraints on the corrosion of used nuclear fuel and the subsequent release of fission product and trans-uranium elements (e.g., [Grandstaff, 1976](#); [Langmuir, 1978](#);

[Parks and Pohl, 1988](#); [Finch and Ewing, 1992](#); [Janeczek and Ewing, 1992a,b](#); [Percy et al., 1994](#); [Fayek et al., 1997a](#); [Jensen et al., 1997](#); [Finch and Murakami, 1999](#); [Jensen and Ewing, 2001](#); [Bruno and Ewing, 2006](#)). The migration of U and other trace metals during corrosion (i.e., dissolution) of natural uraninite is of particular interest, because it provides information that can be used to understand the alteration of used nuclear fuel, mainly UO_2 , over long periods in geologic repositories. Previous studies have shown the importance of the trace element geochemistry of uraninite in determining the alteration phases that form ([Finch and Ewing, 1992](#)). Impurities, such

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as Pb, in the interstitial sites of UO_{2+x} , have an important effect on the secondary U-phases that form. Lead in uraninite has been described in sedimentary U-deposits at Oklo, Gabon, and unconformable U-deposits within Athabasca Basin, Canada (e.g., Kotzer and Kyser, 1993; Janeczek and Ewing, 1995; Evins et al., 2005). The interest in Pb was prompted by its use in “chemical dating” of uraninite, especially the variations that occur within the oscillatory zoning that can be used to infer the composition of altering fluids (e.g., Kempe, 2003; Alexandre and Kyser, 2005). Most commonly, uraninite with this oscillatory zoning is formed in the vein-type hydrothermal deposits that also include W, Ag–Co–Ni–Bi, Cu, Pb–Zn, and Ba–F mineralization (Plant et al., 1999; and references therein). Hence, these types of uraninite have high-impurity contents with a number of trace elements that are chemically similar to those of fission product elements, such as ^{137}Cs and ^{90}Sr .

The uraninite from vein-type hydrothermal deposits commonly contains trace elements such as Ni, Co, As, Bi, Cu, Pb, Zn, Mn, Se, V, Mo, Fe, and Ag (Ruzicka, 1993). The formation of this type of ore is related to high-fluid activity of late-stage orogenic cycles in which uranium fluoride complexes dominate at high temperatures, whereas at low-temperatures uranyl-carbonate is dominant (Ruzicka, 1993). In those cases for which the impurity concentration is high, the presence of the impurities can significantly affect the dissolution and reprecipitation of uraninite under both reducing and oxidizing conditions (Finch and Ewing, 1992; Janeczek and Ewing, 1992b; Fayek et al., 1997b). The vein-type uranium deposits formed under reducing conditions are commonly altered by oxidizing surface waters. The alteration of uraninite in this type of U-deposit is an ideal “analogue” for inferring the influence of these impurities on the dissolution of primary and secondary uraninite formed under reducing conditions. One can also determine the paragenesis of U-alteration phases under reducing and oxidizing conditions, as well as the release and mobilization of trace elements.

In order to understand the evolution of the chemical composition of uraninite and its properties, previous studies (e.g., Finch and Ewing, 1992; Percy et al., 1994; Fayek et al., 1997a) have focused on U^{6+} -phases. Typically, common impurities, such as Ca and Pb, and elements characteristic of supergene processes, such as Si, Fe, and Al, are studied. In general, As, W, Mo, and Sb are considered as highly incompatible with the UO_2 structure and only minor amounts ~ 1.0 wt% can be accommodated into the uraninite structure. As for the concentration of trace elements in uraninites in previous studies, Hofmann and Eikenberg (1991) reported up to 3.65 wt% of As_2O_3 and 0.90 wt% of WO_3 ; Leroy and Holliger (1984) measured 0.28 wt% of MnO. The concentrations of MoO_3 , SeO_2 , ReO_2 , and MgO were 0.32 wt%, 0.22 wt%, 0.32 wt%, and 0.21 wt%, respectively, (Min et al., 2005); 0.24 wt% of V_2O_5 and 0.12 wt% of TiO_2 (Bros et al., 2003). Fayek et al. (1997a) reported 0.19 wt% of As_2O_3 ; 0.39 wt% of CuO; and 0.4 wt% of MnO. Percy et al. (1994) measured 0.2 atomic % of As in uraninite from the widely cited Nopal I mine (Janeczek et al., 1996; Finch and Murakami, 1999). Percy et al. (1994) characterized this Tertiary uraninite in detail

and found that the stoichiometry is close to UO_2 , a good analogue for the UO_2 in used nuclear fuel.

Uranium deposits in Marshall Pass, Colorado, were chosen for the present study because the uraninite from this locality contains a large amount of impurities that are seldom reported, such as W, As, Ba, and Cu. This locality is a hydrothermal vein-type deposit with polymetallic mineralization and exhibits both reducing and oxidizing alteration. The uranium ore in the Marshall Pass deposit has been described mainly from the perspective of mining (e.g., Malan and Ranspot, 1959). The only recent study of the Colorado uranium mines, including the Marshall Pass deposit, provided some indication of the loss of trace elements during alteration (Zhao and Ewing, 2000). However, the fate of other trace elements, such as W, Mo, As, Ba, was not included in their analyses. Our preliminary studies have shown differences in the sequence of uranyl phases caused by incorporation of W, Mo, As, and Ba (Deditius et al., 2007). The influence of these impurities on the alteration of uraninite and on the formation of secondary uranyl-phases containing As and W was not discussed. The complex evolution of the U-deposits at Marshall Pass includes tectonic processes that lead to uraninite brecciation. Thus, the effect of fracture on the oxidation and water infiltration into the uraninite can also be evaluated in samples from this locality.

The objective of this paper is to understand the influence of trace element impurities on the process of uraninite alteration and corrosion, here defined as dissolution of the early formed crystals under a range of geochemical conditions. The results are discussed in the context of the alteration of used nuclear fuel under oxidizing conditions, similar to the geochemical conditions expected at the proposed geological repository at Yucca Mountain, Nevada.

2. SAMPLES AND METHODS

Detailed petrographic and mineralogical studies of thin sections of uraninite samples from vein-type uranium deposits at Marshall Pass, Saguache Co., Colorado, USA, were completed by optical and analytical electron microscopy. The back-scattered electron (BSE) images were obtained by scanning electron microscopy (SEM, Hitachi S3200N) equipped with energy-dispersive X-ray spectroscopy (EDS). The chemical composition of uraninite and its alteration products were determined by electron microprobe analysis (EMPA, a Cameca SX100) at the University of Michigan's Electron Microbeam Analysis Laboratory (EMAL). The trace elements, As, W, and Mo, were determined in addition to the common elements, U, Pb, Si, and Ca. Analysis was completed using an accelerating voltage of 20 kV and beam current of 40 nA with wave-length dispersive X-ray spectrometers (WDS) and counting times of 120 s in order to improve the statistics of the count rates. A beam spot of ~ 1 μm in diameter was used for the analysis. The standards and detection limits (in ppm) were: zircon (ZrSiO_4) for Zr (L_α) (108), scheelite (CaWO_4) for W (M_β) (255), andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) for Si (K_α) (37), Ca (K_α) (116) and Fe (K_α) (140), albite ($\text{NaAlSi}_3\text{O}_8$) for Al (K_α and K_β) (52 and 1833, respectively), benitoite

(BaTiSi₃O₉) for Ba (L_α) (550), synthetic UO₂ for U (M_β) (1137), synthetic KTaO₃ for K (K_α) (97), synthetic YPO₄ for Y (L_α) (288), synthetic KTiO₃ for Ti (K_α) (78), thorinite (ThSiO₄) for Th (M_α) (243), cerussite (PbCO₃) for Pb (M_α) (350), synthetic CaMoO₄ for Mo (L_α) (218), synthetic YPO₄, LaPO₄ or CePO₄ for P (K_α) (140), synthetic CuS for Cu (K_α) (197), and FeAsS for As (L_α) (204). Aluminum, K_α and K_β, were selected to avoid interference from As lines. Because the Al K_β line has a very low intensity, we repeated the Al analysis at the same points using the K_α line. There was no correlation between As and Al in the data, which confirms that interference was not significant. In order to avoid contamination from associated sulfide, sulfosalt, wulfenite, and various uranyl minerals the analytical procedure excluded the analyses of the fractured and/or near grain-boundary (<3 μm) areas.

3. GEOLOGICAL SETTING

The hydrothermal vein-type uranium deposit at Marshall Pass, Colorado, is in the Rocky Mountain and Intermountain Basin Uranium Province, USA (Dahlkamp, 1993; Finch, 1996) (Fig. 1). The main uranium ore is concentrated along the pre-Tertiary 60–100 m wide Chester reverse fault, which is the most prominent structural feature of the area. This fault thrusts crystalline Proterozoic rocks westward over Paleozoic sequences (Olson, 1988) (Fig. 1).

Field studies, as well as petrographic and geochemical observations, of the host rocks (Gross, 1965; Olson, 1988; Zhao and Ewing, 2000) demonstrate that the uranium deposit formed as a result of interactions between migrating fluids and a variety of host rocks. The host rocks are typically intensively deformed. The age of the host rocks ranges from Precambrian to Pennsylvanian. The oldest basement rock consists of gneiss, schist, migmatite, pegmatitic granite, and quartz monzonite, which is unconformably adjacent to a Paleozoic sedimentary sequence of quartzite, dolomite, limestone and shale. The Proterozoic and Paleozoic assemblages are uncomfortably overlain by Tertiary volcanic rocks. The Tertiary andesite and tuffs were dated by the K–Ar method to be 35 My (Lipman et al., 1970). This is the time of closure of the K–Ar window at 350 °C, which reflects post-depositional migration of the high-temperature hydrothermal fluids. The Tertiary volcanic rocks are proposed to be the main source of uranium, which was leached by migrating fluids and subsequently reduced to U(IV) within the dolomite and quartzite containing carbonaceous matter and asphaltic pellets (Olson, 1988). Gross (1965) determined three different ages for the rock units at the Lookout Mine: 94, 99, and 203 Ma using the U–Pb method, and suggested that these inconsistent ages are due to the presence of non-radiogenic lead.

The internal structure of the main fault zone is complicated. The uranium deposit occurs mainly in the shale of the Carboniferous Belden Formation and middle Ordovician Harding Quartzite; there are minor deposits of U located in Precambrian rocks in the sheared and extensively brecciated zones (Fig. 1).

Samples were collected from the Lookout Mine No. 22, where a high-grade ore formed by complete replacement of

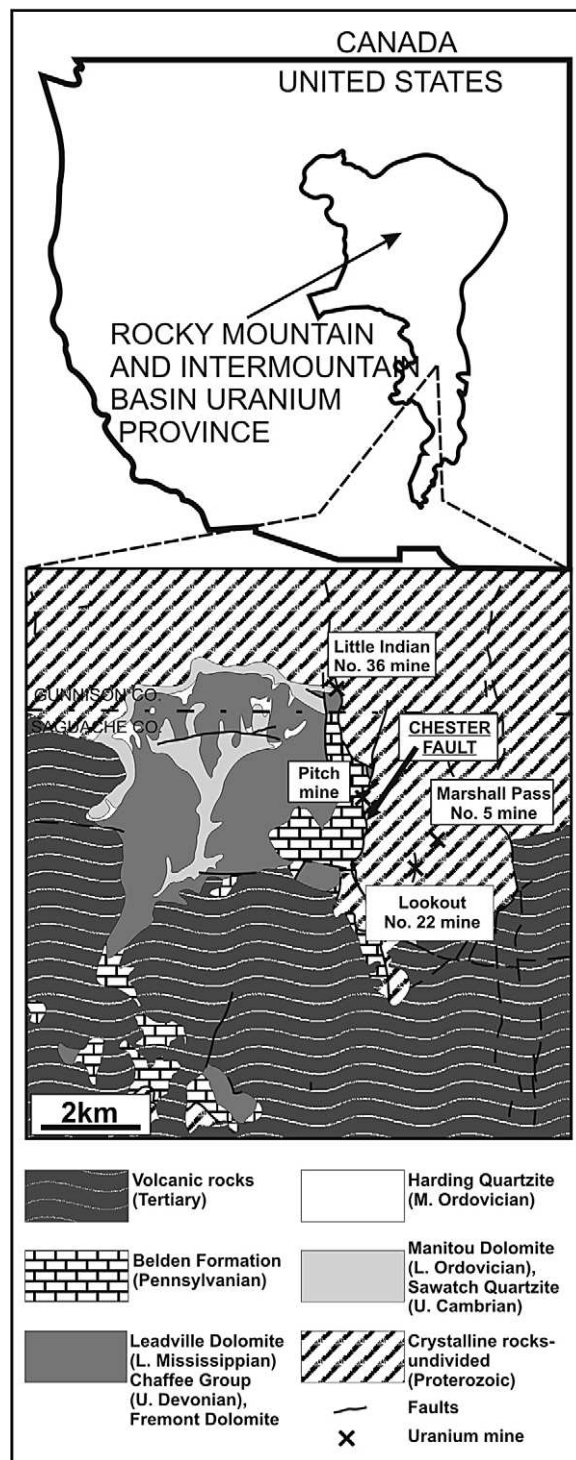


Fig. 1. Schematic geologic map of Marshall Pass district, Colorado, USA, with the localities of the uranium mines. Modified after Finch (1996) and Olson (1988).

the quartz–feldspar–biotite schist along the fault zone adjacent to a pegmatite (Gross, 1965; Olson, 1988) (Fig. 1). The host rock shows intensive kaolinitization and silicification in the form of fine-grained chalcedony transecting the host rock. The U has migrated and formed secondary uranium

minerals within only a few meters of the primary ore. Gross (1965) has described that the uraninite breccia is cemented by sulfide minerals. Elements, such as Ag, Cu, Pb, and Sb, are concentrated in the “black” ore, whereas the Mo, Y, Yb, and W were reported to occur in the pitchblende. Gross (1965) also pointed out that the colloform overgrowth of uraninite might have formed continuously with the precipitation of cementing sulfides. Other uranium-bearing solutions resulted in precipitation of banded ~0.2 mm thick colloform pitchblende overgrowths. Tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), chalcopyrite (CuFeS_2), sphalerite (ZnS), and galena (PbS) are the primary minerals of the polymetallic ore, whereas chalcocite (Cu_2S) and covellite (CuS) have been described as secondary minerals (Gross, 1965). The primary and secondary sulfide and sulfosalt are considered as the source of As, Sb, Ag, Mo, Y, Yb, Ni, Cu, S, Pb, and W (Gross, 1965). The main uranium minerals and phases previously reported by Gross (1965) are uraninite (UO_{2+x}), schoepite [$(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}$], ianthinite [$\text{U}^{4+}(\text{UO}_2)_4(\text{OH})_6(\text{H}_2\text{O})_9$], bequerelite [$\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8$], soddyite [$(\text{UO}_2)_2\text{SiO}_4(\text{H}_2\text{O})_2$], boltwoodite [$\text{K}(\text{UO}_2)(\text{SiO}_3\text{OH})(\text{H}_2\text{O})_{1.5}$], uranophane [$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2(\text{H}_2\text{O})_5$], zeunerite [$\text{Cu}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{16}$], and metazeunerite [$\text{Cu}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$] (chemical formulae after Finch and Murakami, 1999). The uraninite occurs as intergrowths with tetrahedrite, chalcopyrite, and sphalerite.

4. RESULTS

4.1. Petrography of the uranium ore

The samples of U-ore from Marshall Pass consist mainly of massive, black uraninite with a mantle of bright yellow alteration products that are uranyl minerals such as: schoepite, “dehydrated schoepite”, trögerite [$(\text{UO}_2)_3(\text{AsO}_4)_2(\text{H}_2\text{O})_{12}$], uranophane, soddyite, swamboite [$\text{U}^{6+}(\text{UO}_2)_6(\text{SiO}_3\text{OH})_6(\text{H}_2\text{O})_{30}$], U–W–Mo–Ba phase and a U–Sb phase. The uranyl phases were identified by high-resolution transmission electron microscopy (HRTEM) and tentatively by EMPA analyses (Deditius et al., 2007). Based on reflected-light microscopy and SEM analysis of uraninite, two types of uraninite were recognized that differ in the size and form of individual crystals. The first type is colloform uraninite, which varied in size from 0.1 to 15 mm, and the second type is fine-grained uraninite, which has crystals with diameters of ~5 μm (Fig. 2).

The central core of rounded colloform uraninite is rarely preserved and appears to be homogeneous in back-scattered electrons (BSE) contrast, reflecting a homogeneous chemical composition (Fig. 2a). In most of the massive uraninite grains, a patchy dark BSE contrast was present, indicating some variation in chemical composition (Fig. 2b). The rarely preserved cores most likely correspond to the primary euhedral uraninite, but relicts of terminating crystal surfaces were not preserved. The outer part of colloform uraninite grains shows complex oscillatory zoning and alteration structures. These areas show a large variation in BSE contrast, indicating a large variation in the chemical composition. The alternating zones of colloform uraninite appear to have precipitated on partly dissolved rounded

surfaces of primary uraninite. In the case of extensive alteration under oxidizing conditions, uraninite cores were completely replaced by uranyl minerals forming atoll-like structures with rims of alternating zones (Fig. 2d).

In Fig. 3a, the core of colloform uraninite is fractured into an irregular shape; and the grain boundaries are filled with alteration products appearing dark in BSE contrast. In most of the samples, the uraninite cores are subdivided into polygonal fragments, 10–50 μm (Figs. 2a and 3b–f). These micro-blocks also show zoning similar to the colloform uraninite, which is relatively unaltered uraninite core and bright rims. These micro-blocks are surrounded mainly by “dehydrated schoepite” and uranyl arsenates, which precipitated as a result of uraninite alteration under oxidizing conditions (Figs. 3b, d, and e). These bright rims are partially dissolved, and microfractures have been created perpendicular to their surfaces. Two different genetic types of fractures were observed. Some were created during brecciation (Fig. 2a), and others result from dissolution and precipitation of uranyl phases, subsequently creating the additional fractures probably related to their sheet-like structures (Figs. 2c and 3e). As this microfracturing proceeds into the bright rim, the fractures then develop along the boundary of the bright rims parallel to the zoning as revealed in Figs. 3d and e. The second type of fracture preferentially developed in altered zones of colloform uraninite with gray BSE contrast (Figs. 2a and c). Large fractures in colloform uraninite are filled with alteration products, such as schoepite and “dehydrated schoepite” (Figs. 2a, c and 3c). The colloform uraninite also shows many fractures filled with quartz, secondary U-alteration products, wulfenite (PbMoO_4) and very rare relicts of primary ore minerals, such as tetrahedrite, chalcopyrite, and sphalerite, and secondary chalcocite and covellite. The breccia also contains fragments of partially kaolinitized K-feldspar, which is the only non-ore primary mineral. Brecciated fragments of colloform uraninite have been moved at distances ranging from micrometers to several centimeters, which clearly occurred during the formation of the zoning (Figs. 2a–c and e).

Fine-grained uraninite occurs outside the colloform uraninite and is one of the most abundant phases in the matrix (Figs. 2f and g). Rectangular crystals of the fine-grained uraninite formed radial concentrations, which were subsequently replaced pseudomorphically by uranyl arsenates (Fig. 2g). The generation of remobilized uraninite co-precipitates with sulfides and sulfosalts is evidenced by numerous intergrowths with tetrahedrite and chalcopyrite (Fig. 2g). The grain boundaries between rectangular crystals of fine-grained uraninite are filled mainly with quartz and kaolinite. The matrix of fine-grained, radial uraninite is filled with alteration products with the dark rim enriched in tungsten (Fig. 2f). In some cases, fine-grained uraninite is also concentrated at a distance of 10–50 μm from the colloform uraninite (Fig. 2c). Fine-grained uraninite is also found as narrow, ~5 μm , bright, continuous layers surrounding the areas that contain different minerals, such as colloform uraninite, altered K-feldspar, and various uranyl alteration phases (Fig. 2h). The mineral paragenetic sequence is illustrated in Fig. 4. The sequence of uranyl

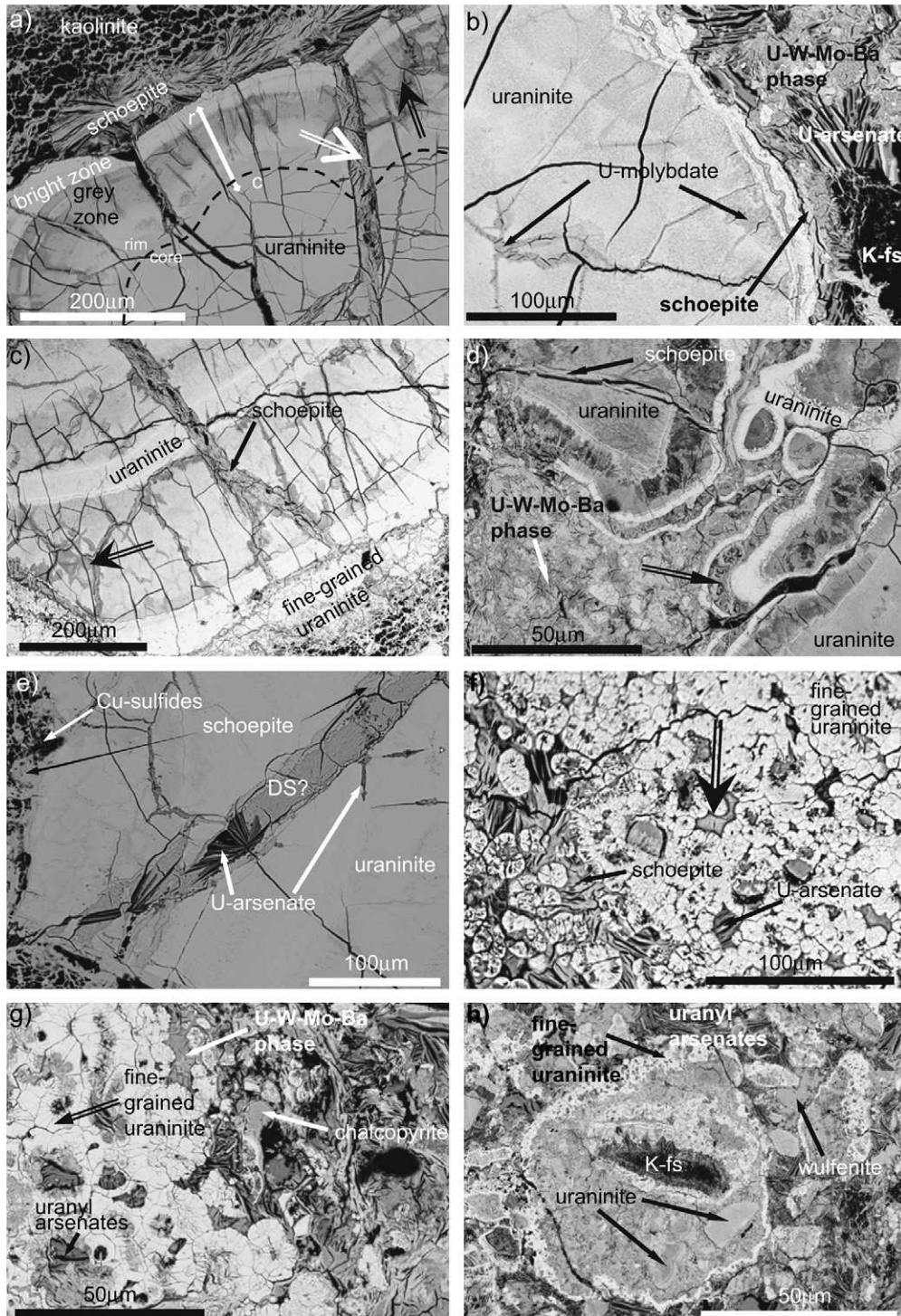


Fig. 2. BSE images of uraninite from the Marshall Pass vein-type deposit. (a) Brecciated colloform uraninite with schoepite occurring within the fractures and at the outermost part of the zoned area. Note the homogeneous contrast of uraninite core separated from the zoned rim (dashed black line). The white line (r–c) indicates the location of line scan analysis (r—beginning, point 1; c—end, point 28 on the Fig. 5a–d). The double white arrow and the double black arrow point to a tectonic fracture and a fracture originating from dissolution, respectively. (b) Patchy core of colloform uraninite is replaced by uranyl molybdates and uranyl arsenates adjacent to K-feldspar (K-fs). (c) Colloform uraninite grain with well-defined zoning altered along fractures. (d) “Atoll”-like structures in colloform uraninite with bright layers and almost complete alteration of the cores and the gray zones (double black arrow). (e) Fractured core of colloform uraninite filled with secondary alteration products schoepite and probably “dehydrated schoepite” (DS?). (f) Spherical concentrations of fine-grained uraninite associated with schoepite and uranyl arsenates in the matrix. Double black arrow indicates the dark W-rich zone between fine-grained uraninite and schoepite. (g) Chalcopyrite and radial concentration of rectangular crystals of fine-grained uraninite indicated by the double black arrow. The cores are filled with uranyl arsenates and schoepite. (h) “Mega-grain” of uraninite associated with the fine-grained uraninite at the rim. Relict of partially dissolved K-feldspar (K-fs) with uranyl arsenates; altered fine-grained uraninite replacing the K-feldspar.

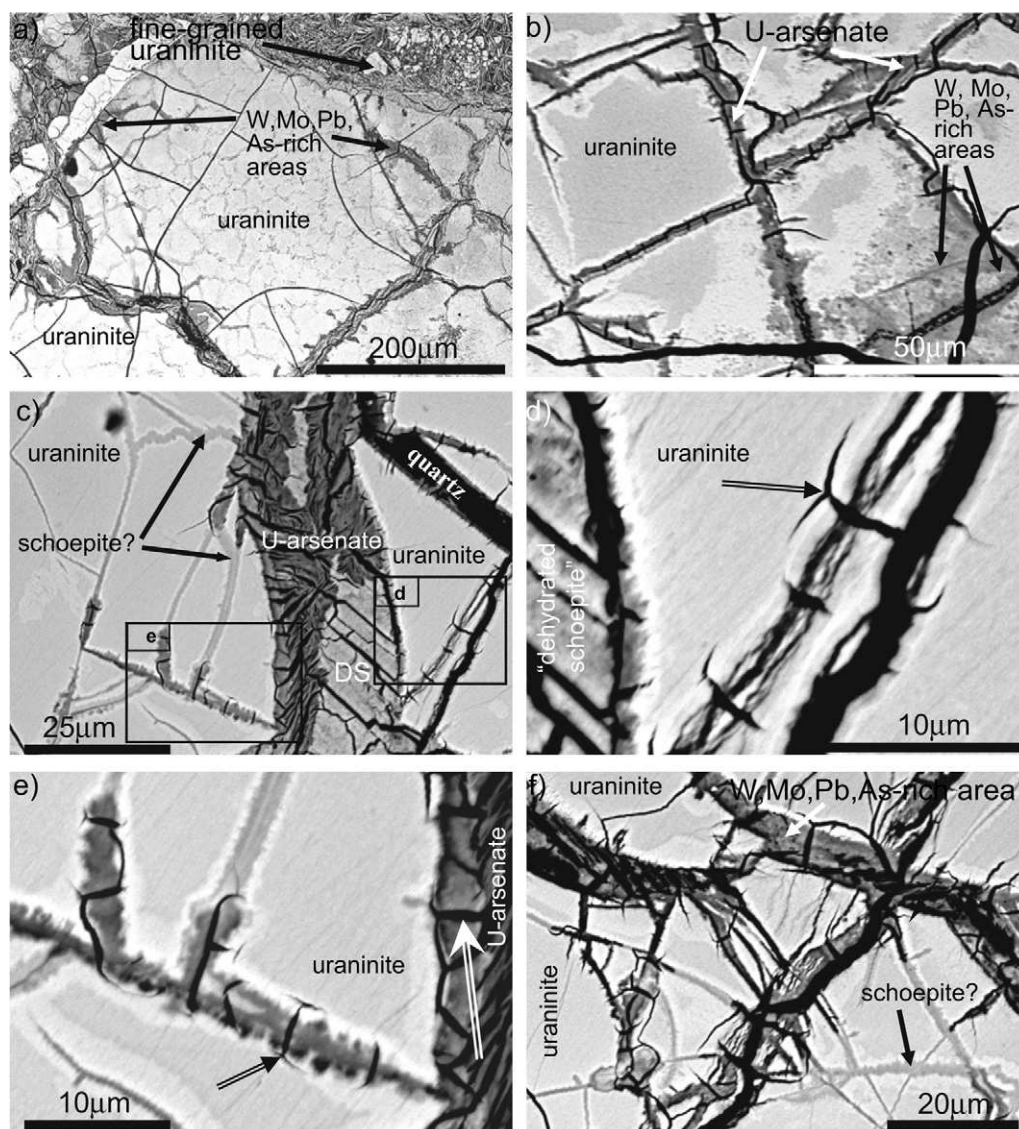


Fig. 3. BSE images of colloform uraninite from the Marshall Pass vein-type deposit. (a) Brecciated uraninite with alteration products concentrated along the grain boundaries (dark areas) and schoepite fills the fracture. The darkest areas are enriched in W, Mo, Pb, and As. (b) Fragments of deformed uraninite with alteration along the fractures. Note the bright rim around the relatively unaltered cores. (c–e) Uraninite grain altered along fractures and grain boundaries with alteration products and quartz. Note the microcracks caused by penetration of the cleavage planes of alteration phases (double white arrow) and their subsequent splitting along the boundary between gray and white areas (double black arrows). Separate fragments reveal extensively altered bright rim. (f) Heavily deformed uraninite with fractures filled with quartz and a secondary uranyl phase enriched in W, Mo, Pb, and As.

minerals is complex, however it is possible to distinguish two stages: (1) dominated by uranyl oxide hydrates, uranyl arsenates and a U–W–Mo–Ba-phase with very rare uranophane; the U–Sb phase precipitated within the fractured and dissolved tetrahedrite; and (2) a second generation of uranyl oxide hydrates, mainly “dehydrated schoepite” replaced by uranyl silicates such as swamboite and soddyite (Fig. 4).

4.2. Chemical composition of uraninite

The changes in BSE contrast of the colloform texture of uraninite grains correspond to a significant variation in

trace element content. Based on the chemical composition and paragenetic relations, the Marshall Pass uraninite can be divided into three groups; (i) the bright zone and core of colloform uraninite in (BSE), which correspond to the areas of higher values of average atomic weight, (ii) the gray zones in colloform uraninite which correspond to the lower reflectivity in BSE-image (Fig. 2), and (iii) a fine-grained uraninite. Colloform uraninite of groups (i) and (ii) and fine-grained uraninite, group (iii), contain relatively large amounts of impurities, 7.76–9.67 wt% (as oxide) and 7.13–12.13 wt% (as oxide), respectively, which, in turn, results in the variation of UO_2 content; 85.20–89.00 wt% and 77.97–89.00 wt%, respectively (Tables 1–3). The Pb

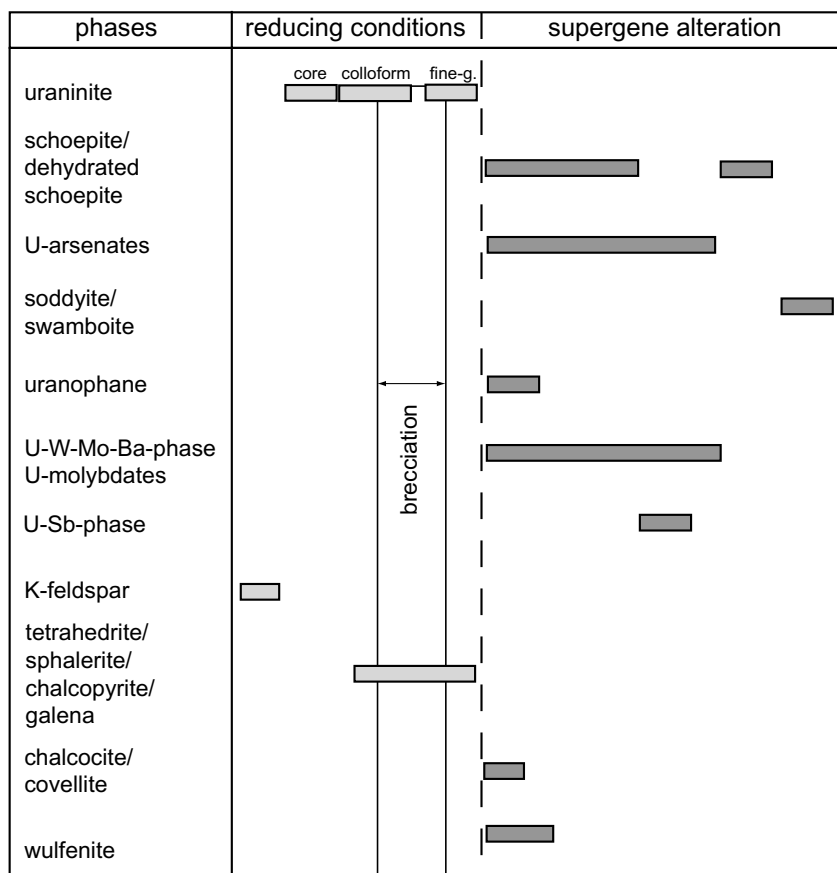


Fig. 4. Paragenetic sequence of minerals from Marshall Pass.

concentration in uraninite of group (i) and (ii) varies over a range of 0.97–2.51 wt% and 1.59–4.79 wt%, respectively. The PbO in uraninite group (i) shows a negative correlation with UO_2 ($R^2 = 0.42$) (Fig. 5a). In the uraninite of groups (i) and (ii), PbO correlates positively with MoO_3 characterized by the two different trends; $R^2 = 0.57$ and $R^2 = 0.85$ (Fig. 5b). Potentially, there are two sources of Pb; (1) dissolution of galena and tetrahedrite and (2) release of radiogenic Pb from uraninite. Molybdenum was probably introduced by migrating fluids and varies in the range 0.06–0.88 wt% of MoO_3 . However, based on the available sample, we are not able to define precisely the source of these fluids, for example an unstable Mo-rich sulfide. There is a weak positive relation of CaO with UO_2 ($R^2 = 0.31$) in uraninite group (i) and a negative correlation of CaO with PbO ($R^2 = 0.39$), suggesting Pb substitution for Ca in the uraninite structure (Fig. 5c and d). In group (i) uraninite, there is a weak positive correlation between UO_2 and Y_2O_3 ($R^2 = 0.35$), whereas there is a weak negative correlation between Ce_2O_3 and UO_2 ($R^2 = 0.34$) (Fig. 5e and f). This suggests different behaviors of Y and Ce in the group (i) uraninite structures. The other impurities in uraninite groups (i) and (ii) are: WO_3 (1.04–1.75 wt%), As_2O_3 (0.16–1.70 wt%), ZrO_2 (0.32–1.30 wt%), SiO_2 (0.30–0.84 wt%), K_2O (0.35–0.63 wt%), Fe_2O_3 (0.10–0.53 wt%), TiO_2 (0.17–0.34 wt%), and P_2O_5 (0.05–0.18 wt%) (Tables 1 and 2). Thorium is below the detection limit (0.05 wt%).

The chemical composition of fine-grained uraninite, group (iii), is substantially different from those of groups (i) and (ii) (Fig. 6). The groups (i) and (iii) of uraninite contain larger amounts of UO_2 than the altered uraninite group (ii). The group (iii) uraninite does not contain K, but has the highest concentrations of ThO_2 (0.07–0.65 wt%) and is the only one to have higher concentrations of BaO. The PbO concentration in uraninite group (iii) is smaller than in uraninite group (i) and (ii), and varies over a much smaller range, 1.00–1.58 wt%, with only two points below this range (Table 3 and Fig. 5a). A limited range of composition is also noted for As_2O_3 (0.26–0.60 wt%), and ZrO_2 (0.11–0.45 wt%), of which the highest concentrations were found in uraninite group (ii). The lowest concentration of Fe_2O_3 (0.07–0.46 wt%) was found in uraninite group (ii) (Table 3 and Fig. 6). The CaO and SiO_2 contents in uraninite group (iii) vary in the ranges of 0.68–2.25 wt%, and 0.10–0.37 wt%, respectively, and are slightly lower than that in the uraninite of groups (i) and (ii). The concentrations of WO_3 , MoO_3 , TiO_2 , and P_2O_5 in uraninite group (iii) are: 2.25–4.93 wt%, 0–5.76 wt%, 0.17–0.89 wt%, 0.15–0.32 wt%, respectively, and are higher than the concentrations in the uraninite of group (i) and (ii) (Fig. 6).

The major issue in the composition of group (i) uraninite is the existence of relatively high and almost constant concentration of WO_3 (1.04–1.75 wt%) (Fig. 7a). This constant amount of WO_3 means that there is almost no correlation

Table 1

Representative analyses of chemical composition of colloform uraninite group (i), in wt%

Points	1	2	3	4	5	6	7	8	9	10
Al ₂ O ₃	0.21	0.15	0.29	0.16	0.16	nd.	0.18	0.16	0.09	0.30
SiO ₂	0.44	0.39	0.63	0.45	0.44	0.36	0.53	0.48	0.53	0.48
P ₂ O ₅	0.08	0.12	0.14	0.08	0.08	0.10	0.08	0.07	0.14	0.10
K ₂ O	0.55	0.36	0.35	0.63	0.57	0.42	0.39	0.37	0.41	0.42
CaO	1.32	2.58	2.01	1.26	1.29	2.06	1.67	1.66	1.94	1.78
BaO	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
TiO ₂	0.29	0.29	0.26	0.29	0.30	0.22	0.33	0.30	0.27	0.23
Fe ₂ O ₃	0.24	0.21	0.43	0.19	0.22	0.27	0.31	0.30	0.45	0.39
As ₂ O ₃	0.82	0.36	0.27	0.94	0.94	0.48	0.44	0.40	0.27	0.26
Y ₂ O ₃	0.10	0.15	0.15	0.08	0.08	0.13	0.12	0.12	0.16	0.14
ZrO ₂	0.34	0.55	0.59	0.32	0.32	0.39	0.43	0.45	0.71	0.60
MoO ₃	0.61	0.42	0.24	0.66	0.65	0.30	0.61	0.47	0.08	0.11
Ce ₂ O ₃	0.10	0.12	0.10	0.11	0.12	0.08	0.15	0.16	0.04	0.06
WO ₃	1.12	1.36	1.68	1.18	1.18	1.18	1.54	1.57	1.75	1.55
PbO	2.11	1.95	1.38	2.16	2.15	2.51	2.42	1.94	1.22	1.85
ThO ₂	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
UO ₂	86.73	86.85	87.66	86.14	86.59	86.91	86.13	85.82	88.55	87.41
Total	95.06	95.86	96.18	94.65	95.09	95.41	95.33	94.27	96.61	95.68

Number of cations based on 2 O

Al	0.008	0.006	0.011	0.006	0.006	nd.	0.006	0.005	0.003	0.011
Si	0.014	0.013	0.020	0.014	0.014	0.012	0.017	0.014	0.018	0.015
P	0.002	0.003	0.004	0.002	0.002	0.003	0.002	0.002	0.004	0.003
K	0.021	0.015	0.014	0.022	0.023	0.017	0.015	0.014	0.017	0.017
Ca	0.044	0.089	0.070	0.050	0.042	0.070	0.055	0.053	0.069	0.061
Ba	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Ti	0.007	0.007	0.006	0.007	0.007	0.005	0.008	0.007	0.007	0.005
Fe ³⁺	0.005	0.005	0.011	0.005	0.005	0.006	0.007	0.007	0.011	0.009
As	0.025	0.011	0.008	0.025	0.028	0.015	0.013	0.012	0.009	0.008
Y	0.002	0.003	0.003	0.002	0.001	0.002	0.002	0.002	0.003	0.002
Zr	0.005	0.009	0.009	0.005	0.005	0.006	0.007	0.006	0.012	0.009
Mo	0.008	0.006	0.003	0.008	0.008	0.004	0.008	0.006	0.001	0.001
Ce	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001
W	0.009	0.011	0.014	0.010	0.009	0.010	0.012	0.012	0.015	0.013
Pb	0.018	0.017	0.012	0.017	0.018	0.022	0.020	0.015	0.011	0.016
Th	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
U	0.833	0.823	0.822	0.829	0.830	0.839	0.822	0.832	0.835	0.837
Total	1.067	1.081	1.066	1.067	1.067	1.079	1.064	1.062	1.064	1.069

Calculated U⁴⁺, U⁶⁺ and total excess oxygen

U ⁴⁺	0.625	0.629	0.659	0.611	0.628	0.626	0.625	0.581	0.681	0.640
U ⁶⁺	0.301	0.252	0.242	0.320	0.300	0.272	0.285	0.331	0.221	0.268
O	2.234	2.143	2.154	2.257	2.236	2.177	2.205	2.258	2.136	2.186

Points	11	12	13	14	15	16	17	18	19	20
Al ₂ O ₃	0.09	0.27	0.13	0.13	0.13	0.11	0.16	0.19	0.09	0.16
SiO ₂	0.84	0.72	0.44	0.53	0.44	0.31	0.32	0.51	0.38	0.44
P ₂ O ₅	0.14	0.14	0.07	0.08	0.09	n.a.	n.a.	0.11	0.05	0.07
K ₂ O	0.36	0.36	0.36	0.37	0.35	0.43	0.46	0.35	0.40	0.57
CaO	2.25	0.82	2.87	1.70	2.41	1.89	1.67	2.24	1.96	1.51
BaO	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
TiO ₂	0.25	0.17	0.25	0.34	0.24	0.25	0.25	0.22	0.22	0.30
Fe ₂ O ₃	0.53	0.10	0.34	0.29	0.22	0.27	0.22	0.14	0.24	0.23
As ₂ O ₃	0.16	1.70	0.32	0.47	0.18	1.20	1.06	1.20	0.47	0.82
Y ₂ O ₃	0.17	0.09	0.14	0.14	0.16	0.12	0.10	0.12	0.12	0.10
ZrO ₂	0.52	0.92	0.41	0.57	0.36	1.21	1.30	1.19	0.40	0.32
MoO ₃	0.06	0.88	0.22	0.59	0.26	0.76	0.77	0.47	0.30	0.63
Ce ₂ O ₃	0.05	0.11	0.08	0.15	0.06	0.07	0.07	0.09	0.07	0.12
WO ₃	1.53	1.18	1.23	1.58	1.30	1.10	1.04	1.23	1.14	1.19
PbO	0.97	2.20	1.33	2.28	2.17	1.56	1.74	1.59	2.39	2.09
ThO ₂	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
UO ₂	89.0	85.8	88.3	85.2	86.5	85.2	85.4	85.9	87.0	86.6

(continued on next page)

Table 1 (continued)

Points	11	12	13	14	15	16	17	18	19	20
Total	96.92	95.4	96.49	94.42	94.87	94.48	94.56	95.55	95.23	95.15
<i>Number of cations based on 2 O</i>										
Al	0.003	0.010	0.005	0.005	0.005	0.004	0.006	0.007	0.003	0.006
Si	0.028	0.022	0.015	0.016	0.013	0.009	0.009	0.016	0.012	0.014
P	0.004	0.004	0.002	0.002	0.002	n.a.	n.a.	0.003	0.001	0.002
K	0.016	0.014	0.015	0.014	0.014	0.016	0.017	0.014	0.016	0.022
Ca	0.081	0.027	0.102	0.054	0.079	0.060	0.053	0.074	0.066	0.050
Ba	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Ti	0.006	0.004	0.006	0.008	0.005	0.006	0.006	0.005	0.005	0.007
Fe ³⁺	0.013	0.002	0.008	0.006	0.005	0.006	0.005	0.003	0.006	0.005
As	0.005	0.051	0.010	0.014	0.005	0.035	0.031	0.036	0.014	0.025
Y	0.003	0.001	0.002	0.002	0.003	0.002	0.002	0.002	0.002	0.002
Zr	0.008	0.014	0.007	0.008	0.005	0.017	0.019	0.018	0.006	0.005
Mo	0.001	0.011	0.003	0.007	0.003	0.009	0.010	0.006	0.004	0.008
Ce	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001
W	0.013	0.009	0.011	0.012	0.010	0.008	0.008	0.010	0.009	0.010
Pb	0.009	0.018	0.012	0.018	0.018	0.012	0.014	0.013	0.020	0.017
Th	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
U	0.829	0.795	0.832	0.819	0.839	0.807	0.812	0.797	0.845	0.829
Total	1.068	1.052	1.087	1.063	1.079	1.074	1.070	1.078	1.076	1.071
<i>Calculated U⁴⁺, U⁶⁺ and total excess oxygen</i>										
U ⁴⁺	0.692	0.644	0.656	0.588	0.598	0.583	0.590	0.618	0.636	0.625
U ⁶⁺	0.202	0.288	0.219	0.325	0.295	0.320	0.318	0.267	0.282	0.296
O	2.107	2.237	2.102	2.248	2.195	2.242	2.246	2.177	2.197	2.225

between WO₃ and UO₂ ($R^2 = 0.05$, positive slope) in the group (i) uraninite, but the correlation is better expressed in the group (ii) uraninite ($R^2 = 0.31$, negative slope) (Fig. 7a). In uraninite of group (iii), WO₃ correlates positively with ThO₂ on two different trends ($R^2 = 0.76$ and $R^2 = 0.62$) (Fig. 7b). The elevated concentration of BaO may indicate the presence of W in the form of uranotungstite [(Ba,Pb,Fe²⁺)(UO₂)₂(WO₄)(OH)₄(H₂O)₁₂; after Walenta, 1985].

Because these samples have been altered under oxidizing conditions by supergene fluids, it is necessary to estimate the variation of the amount of excess oxygen during the formation of colloform and fine-grained uraninite. The excess amount of oxygen was calculated based on the chemical formula of uraninite proposed by Janeczek and Ewing (1992a). The zoning in the colloform uraninite is mostly caused by the variation of UO₂ and CaO concentrations. The line scan analysis from an outermost bright zone through a gray zone in the colloform uraninite reveals a significant variation in the composition within these zones (Figs. 2a and 8a–d). The excess oxygen varies over the range of 2.1–2.3 [apfu] (Fig. 8b). Based on this line-scan and point analyses, we attempted to reconstruct the evolution of the chemical composition of fluids that influenced the dissolution and precipitation of the colloform uraninite. The line scan reveals that in the first step of colloform uraninite formation, which is evidenced near the primary uraninite core (points 23–26 in Fig. 8c), the uraninite zone is enriched in Pb and Mo. There is also a slight increase in the Zr-content in this zone. Then the concentration of UO₂, CaO, and Y₂O₃ increases, Ce₂O₃ dramatically decreases, similar to the concentrations of

the other trace elements (points 16–22 in Figs. 8a–c). Subsequently, As-rich fluids penetrated the grains with relatively higher concentrations of oxygen and precipitated the zone enriched in Pb, Mo, As, Zr, Ce, and W with higher oxygen concentration, 2.2–2.3 [apfu], but lesser amounts of UO₂ and CaO than the other zone (points 5–15). This part of uraninite located between points 5 and 15 contains some thin bright layers (<1 µm), which reveal decreasing amounts of the trace elements in the line profile (points 8 and 11, Figs. 8a and c). The negative correlations of UO₂ with PbO and positive trends between PbO and MoO₃ in Figs. 4a and b suggest simultaneous incorporation of Pb and Mo, and U release from the colloform uraninite of group (i) and (ii). The bright zone adjacent to the uraninite core at points 23–24 reveals the amount of U and Ca decreases as Pb and Mo contents increase (Figs. 8a and c). Consequently, the As-rich fluids caused the dissolution of uraninite and reprecipitation of gray zones significantly enriched with impurities. Subsequently, granular, bright, fine-grained uraninite of group (iii) formed in the matrix, incorporating relatively higher amounts of Mo, W, Ti, Ba, and Th, but lower amounts of Pb, Zr, Ce, and Y, as compared with the other groups of uraninite (Fig. 6).

The saddle-shape trends of Fe₂O₃ and SiO₂ in Fig. 8d are similar to each other, but do not correlate with the other elements in the line profile. The increase in Fe- and Si-content is probably due to hematitization and contemporaneous silicification, respectively (point 1–5 in Fig. 8d). These processes appear to cause the decrease in the other impurities, such as PbO, MoO₃, As₂O₃, ZrO₂, and TiO₂. The Al₂O₃ concentrations are almost constant with a

Table 2

Representative analyses of uraninite group (ii) (gray layers) in the colloform structures

Points	1	2	3	4	5	6	7	8	9	10
Al ₂ O ₃	0.14	0.07	0.24	0.18	0.17	0.29	0.31	0.27	0.13	0.26
SiO ₂	0.44	0.28	0.48	0.63	0.32	0.49	0.47	0.61	0.63	0.44
P ₂ O ₅	0.09	0.09	0.07	0.11	0.11	0.10	0.10	0.10	0.10	0.12
K ₂ O	0.51	0.46	0.64	0.55	0.51	0.37	0.38	0.37	0.43	0.38
CaO	1.14	2.19	0.65	1.32	1.55	1.72	1.89	1.85	1.59	1.69
BaO	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
TiO ₂	0.39	0.26	0.21	0.54	0.18	0.39	0.37	0.25	0.32	0.41
Fe ₂ O ₃	0.20	0.15	0.08	0.21	0.20	0.20	0.22	0.23	0.22	0.17
As ₂ O ₃	0.14	0.94	1.79	0.41	1.10	0.99	1.15	0.26	0.19	1.27
Y ₂ O ₃	0.07	0.10	0.04	0.08	0.10	0.14	0.16	0.11	0.09	0.13
ZrO ₂	0.51	0.34	0.88	1.26	0.97	1.95	1.97	1.24	0.78	1.89
MoO ₃	0.62	0.35	0.66	1.13	0.43	0.66	0.56	0.56	0.66	0.71
Ce ₂ O ₃	0.07	0.06	0.06	0.12	0.09	0.20	0.17	0.10	0.09	0.19
WO ₃	1.71	1.38	1.39	2.91	1.14	2.14	1.78	1.59	1.62	1.73
PbO	2.14	2.69	4.79	2.33	2.94	2.00	1.93	3.31	2.86	2.33
ThO ₂	nd.	nd.	nd.	nd.	nd.	nd.	0.05	nd.	0.05	0.06
UO ₂	83.9	85.0	80.8	82.0	84.2	81.6	83.0	82.7	85.0	81.7
Total	92.07	94.36	92.78	93.78	94.01	93.24	94.51	93.55	94.76	93.48
<i>Number of cations based on 2 O</i>										
Al	0.005	0.002	0.008	0.006	0.006	0.009	0.011	0.009	0.003	0.009
Si	0.012	0.008	0.013	0.018	0.009	0.013	0.014	0.017	0.018	0.012
P	0.002	0.002	0.002	0.003	0.003	0.002	0.002	0.002	0.004	0.003
K	0.017	0.017	0.022	0.020	0.019	0.013	0.014	0.013	0.017	0.013
Ca	0.033	0.070	0.019	0.040	0.048	0.051	0.059	0.056	0.069	0.050
Ba	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Ti	0.008	0.006	0.004	0.011	0.004	0.008	0.008	0.005	0.007	0.009
Fe ³⁺	0.004	0.003	0.002	0.004	0.004	0.004	0.005	0.005	0.011	0.004
As	0.004	0.027	0.048	0.011	0.031	0.026	0.033	0.007	0.009	0.034
Y	0.001	0.002	0.001	0.001	0.002	0.002	0.002	0.002	0.003	0.002
Zr	0.007	0.005	0.012	0.017	0.014	0.026	0.028	0.017	0.012	0.026
Mo	0.007	0.004	0.008	0.013	0.005	0.008	0.007	0.007	0.001	0.008
Ce	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.002
W	0.012	0.011	0.010	0.021	0.009	0.015	0.013	0.012	0.015	0.012
Pb	0.016	0.022	0.035	0.018	0.023	0.015	0.015	0.025	0.011	0.017
Th	nd.	nd.	nd.	nd.	nd.	nd.	0.000	nd.	0.000	0.000
U	0.840	0.823	0.786	0.770	0.814	0.764	0.767	0.798	0.818	0.764
Total	1.051	1.087	1.079	1.047	1.080	1.064	1.071	1.072	1.062	1.069
<i>Calculated U⁴⁺, U⁶⁺ and total excess oxygen</i>										
U ⁴⁺	0.524	0.577	0.528	0.557	0.569	0.527	0.571	0.539	0.598	0.537
U ⁶⁺	0.416	0.222	0.400	0.358	0.340	0.369	0.317	0.356	0.309	0.359
O	2.364	2.226	2.340	2.296	2.268	2.297	2.236	2.270	2.230	2.286

decrease near point 16 in Fig. 8d. The lower Al-concentration at points 16–28 is due to precipitation of the first bright layer, excluding Al³⁺ from the uraninite structure (group (i) uraninite), whereas the higher Al-concentration at points 1–15 is correlated with higher concentration of impurities, probably because uraninite with high impurities can have more defects (e.g., Janeczek and Ewing, 1992a) and is capable of incorporating some Al into the structure.

The WO₃ content is almost constant except for one higher concentration at point 6 in Fig. 8a. Thus, an almost higher constant concentration of W was retained in the fluids, and the uraninite group (i) and (ii) incorporated a relatively constant amount of W (1.23–1.80 wt%) into its structure. The line scan also reveals almost constant concentrations of P₂O₅. There is some deviation in this trend, an increase at point 7 (0.15 wt%) and subsequent decrease

in point 5 (0.08 wt%). This part of the P₂O₅ line scan overlaps with the increase in the content of oxygen, Ce₂O₃ and WO₃, and observed decrease in the amount of UO₂ (Figs. 8a, b, and d). The relatively constant concentration of phosphorous suggests that it was present during the precipitation of the primary uraninite and formed uranyl complexes during subsequent dissolution and reprecipitation events.

The calculated amount of oxygen [apfu] for all types of uraninite is summarized in Fig. 9. The data are plotted vs. Ca [apfu] associated with the stability fields of UO_{2+x}, $x = 0, 0.25, 0.33$, and 0.66 . In general, the calculated amount of U⁶⁺ in the analyzed colloform uraninite including group (i) varies over a wide range from 0.201 to 0.333 [apfu] corresponding to the amount of excess oxygen from 0.09 to 0.26 [apfu] (Table 1). These data plot in the stability

Table 3
Representative analyses of fine-grained bright granular uraninite group (iii)

Points	1	2	3	4	5	6	7	8	9	10
Al ₂ O ₃	0.18	0.08	0.05	0.15	0.13	0.09	0.18	0.02	0.10	nd.
SiO ₂	0.37	0.27	0.16	0.33	0.33	0.31	0.23	0.11	0.19	0.11
P ₂ O ₅	0.20	0.25	0.24	0.18	0.20	0.17	0.21	0.17	0.24	0.18
K ₂ O	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
CaO	2.25	1.56	1.51	1.65	1.66	1.91	1.63	0.68	1.11	0.82
BaO	1.10	1.08	1.37	1.22	1.54	1.32	1.11	0.89	1.14	0.96
CuO	nd.	0.04	nd.	0.03	nd.	nd.	nd.	nd.	0.03	nd.
TiO ₂	0.48	0.49	0.59	0.55	0.82	0.58	0.42	0.38	0.53	0.37
Fe ₂ O ₃	0.46	0.24	0.31	0.38	0.45	0.45	0.15	0.07	0.21	0.08
As ₂ O ₃	0.28	0.28	0.48	0.41	0.33	0.38	0.60	0.33	0.28	0.31
Y ₂ O ₃	0.07	0.07	0.05	0.07	0.04	0.08	nd.	0.05	0.05	nd.
ZrO ₂	0.26	0.35	0.29	0.45	0.39	0.34	0.38	0.27	0.30	0.30
MoO ₃	1.77	0.18	0.21	0.36	0.66	0.19	4.36	0.04	0.22	nd.
Ce ₂ O ₃	0.04	0.08	0.08	0.08	0.06	0.08	0.04	0.05	0.09	0.06
WO ₃	3.32	2.68	4.93	3.98	3.93	4.43	2.25	3.20	2.73	3.18
PbO	1.13	1.59	1.46	1.47	1.27	1.24	0.80	1.57	1.47	1.37
ThO ₂	0.56	0.23	0.23	0.26	0.22	0.21	0.15	0.65	0.24	0.35
UO ₂	85.0	87.1	84.7	83.3	78.0	83.9	81.5	88.1	85.6	89.0
Total	97.47	96.57	96.66	94.87	90.03	95.68	94.01	96.58	94.53	97.09
<i>Number of cations based on 2 O</i>										
Al	0.008	0.004	0.002	0.007	0.007	0.004	0.008	0.001	0.005	0.000
Si	0.015	0.011	0.006	0.014	0.015	0.013	0.009	0.005	0.008	0.005
P ⁵⁺	0.007	0.009	0.008	0.006	0.007	0.006	0.007	0.006	0.009	0.007
K	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Ca	0.097	0.071	0.067	0.074	0.077	0.085	0.070	0.032	0.052	0.038
Ba	0.017	0.018	0.022	0.020	0.026	0.021	0.018	0.015	0.019	0.016
Cu	nd.	0.001	nd.	0.001	nd.	nd.	nd.	nd.	0.001	nd.
Ti	0.014	0.016	0.018	0.017	0.027	0.018	0.013	0.012	0.017	0.012
Fe ³⁺	0.014	0.008	0.010	0.012	0.015	0.014	0.004	0.002	0.007	0.003
As ³⁺	0.011	0.011	0.019	0.017	0.014	0.015	0.024	0.014	0.012	0.013
Y	0.001	0.001	0.001	0.002	0.001	0.002	nd.	0.001	0.001	nd.
Zr	0.005	0.007	0.006	0.009	0.008	0.007	0.008	0.006	0.006	0.006
Mo ⁶⁺	0.030	0.003	0.004	0.006	0.012	0.003	0.073	0.001	0.004	0.000
Ce ³⁺	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
W ⁶⁺	0.034	0.029	0.053	0.043	0.044	0.048	0.023	0.036	0.031	0.036
Pb	0.012	0.018	0.016	0.017	0.015	0.014	0.009	0.018	0.017	0.016
Th	0.005	0.002	0.002	0.002	0.002	0.002	0.001	0.006	0.002	0.003
U ⁴⁺	0.758	0.821	0.782	0.779	0.754	0.777	0.730	0.853	0.828	0.855
Total	1.029	1.032	1.020	1.029	1.025	1.032	0.998	1.010	1.021	1.011
<i>Calculated U⁴⁺, U⁶⁺ and total excess oxygen</i>										
U ⁴⁺	0.710	0.686	0.687	0.602	0.450	0.634	0.574	0.714	0.609	0.741
U ⁶⁺	0.176	0.230	0.231	0.317	0.487	0.276	0.357	0.233	0.332	0.202
O	2.074	2.155	2.157	2.245	2.431	2.194	2.295	2.190	2.280	2.154

field of cubic uraninite. The majority of points in group (ii) of analyzed uraninite plot in the range from 2.2 to 2.36 of oxygen [apfu]; only three points deviate significantly: 2.46, 2.47, and 2.64 oxygen [apfu]. The calculated amount of U⁶⁺ and excess oxygen in the fine-grained uraninite, group (iii), are plotted as scattered triangles. However, these data can be divided into three different populations; uraninite with 2.08–2.32 [apfu] of oxygen; uraninite with 2.37–2.48 [apfu]; and uraninite with 2.11–2.22 [apfu] and lower values of Ca [apfu] (0.02–0.04). The negative correlations between the amount of oxygen and Ca [apfu] in all groups of uraninite are evidence that Ca incorporation into the uraninite structure creates oxygen vacancies in order to maintain charge balance (Janeczek et al., 1993).

5. DISCUSSION

5.1. The age of uraninite from Marshall Pass

For the calculation of chemical age, Cameron–Schiman's Eq. (1) (Bowles, 1990) was used.

$$t(y) = \text{Pb} \cdot 10^{10} / (1.612\text{U} + 4.95\text{Th}) \quad (1)$$

In this expression, the amounts of U, Th, and Pb are given in atomic percentage and the resultant age is in years. The age of ~35 Ma (Lipman et al., 1970) was considered to be the oldest limit for the chemical age of young Tertiary uraninite. This is the age of the local tuffaceous rock, which is believed to be the source of U. Because of this young age,

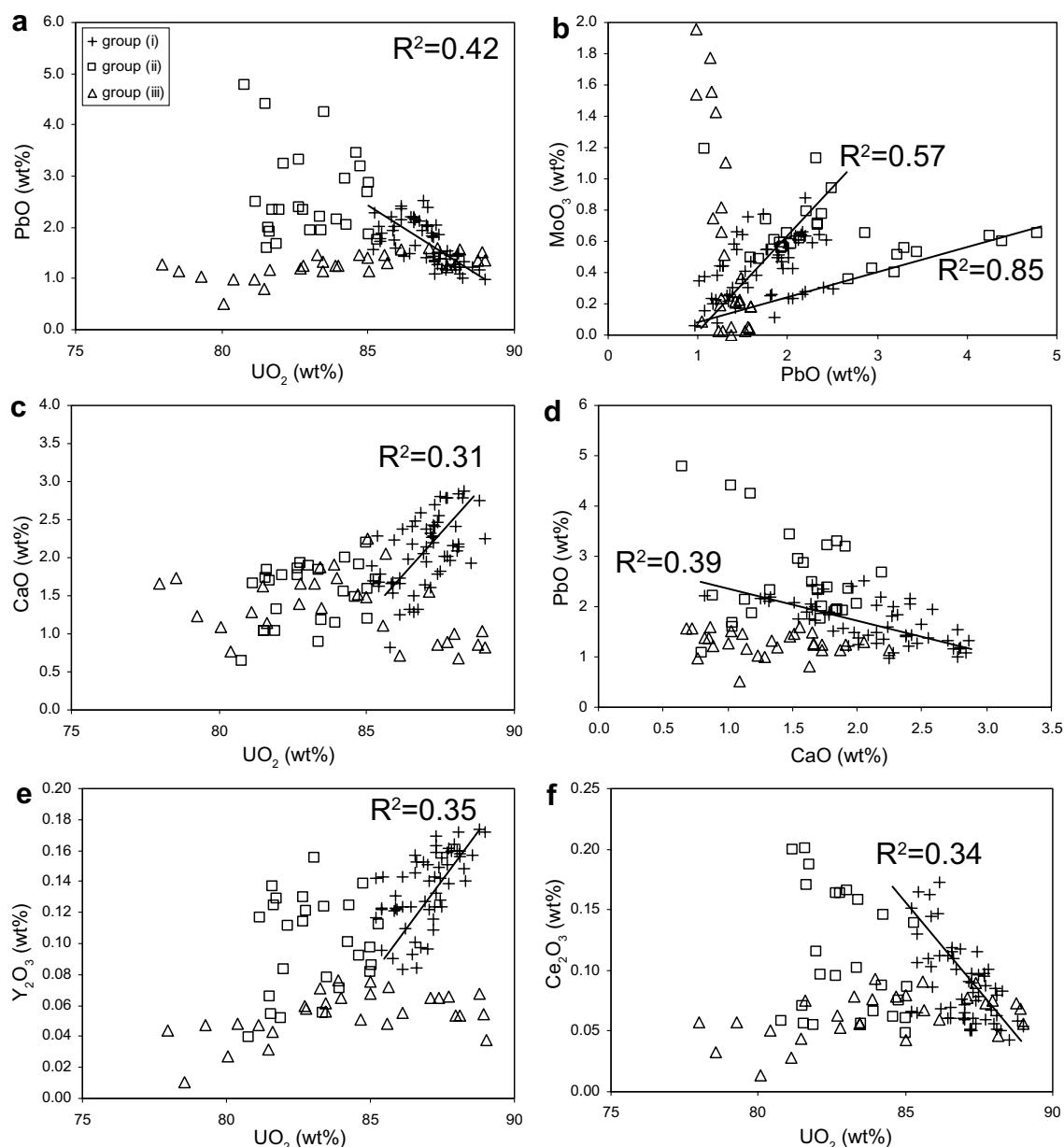


Fig. 5. Chemical variation plots of uraninite compositions for groups (i) (crosses), (ii) (squares), and (iii) (triangles). (a) UO_2 and PbO ; (b) PbO and MoO_3 , the two trends show a positive correlation for uraninite group (i) and (ii); (c) UO_2 and CaO ; (d) CaO and PbO ; (e) UO_2 and Y_2O_3 ; (f) UO_2 and Ce_2O_3 . All analyses of uraninite are plotted; group (i) and (ii)—colloform uraninite—(i) bright zones and core; (ii) gray zones; group (iii)—fine-grained uraninite.

the maximum amount of radiogenic Pb in the Marshall Pass uraninite should be in the range from 0.134 to 0.175 atomic % of Pb. However, the amount of Pb in analyses varies in the range from 0.369 to 1.894 atomic %, giving ages of 44.0–444.7 Ma (Figs. 10a and b). These calculated ages are much older than 35 Ma due to the incorporation of non-radiogenic Pb into the uraninite, which originated from the fluids carrying Pb derived from dissolved galena and tetrahedrite. The local supersaturation with respect to Pb and Mo caused precipitation of PbMoO_4 . This is evident because the gray zone, uraninite group (ii), which recrystallized after the uraninite core group (i), was calculated to be

older than the core. There are consistent data: the ages of fine-grain uraninite, group (iii), are younger than ~143 Ma and generally older than ~80 Ma, which is also the upper limit for uraninite of group (i) (Fig. 10b). However, none of the data for the uraninite, even data for the core, give a calculated chemical age of less than 35 Ma. This raises the question of the actual source of uranium in uraninite in the Marshall Pass District and the age of its formation.

Based on these results, a source for the U can be assigned to different type rocks. One of the most probable scenarios is that granitic rocks of the crystalline basement

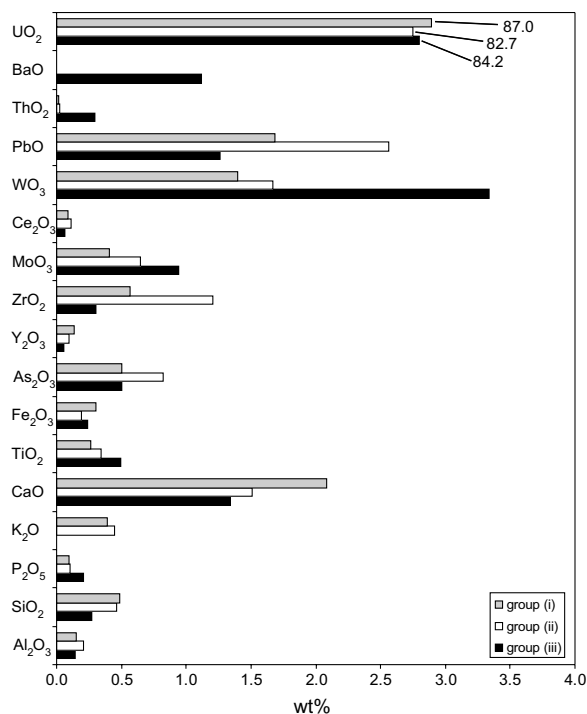


Fig. 6. Diagram showing relations among averaged concentrations of the analyzed elements in uraninite groups (i), (ii), and (iii).

were penetrated by ascending fluids during a Laramide tectonic event causing mineralization along the main discontinuity created by the Chester fault. We propose that uranium was transported by oxidizing brines and subsequently crystallized in the form of uraninite on contact with overlying layers of carbonaceous matter. Tertiary volcanic rocks were probably the source of sulfide and sulfosalt mineralization that precipitated in the matrix of the brecciated uraninite. Hydrothermal fluids from the volcanic rocks penetrated the already deposited U-ore and probably caused partial remobilization of uranium. The Pitch mine in the Marshall Pass area, approximately 2 km NNW from Look-

out Mine, also formed by the interaction of hydrothermal fluids in the tectonic zone. Here U-ore is found along the contacts between sedimentary rocks and Precambrian (schist and granite) bedrock units (Fig. 1). These sedimentary rocks contain a large amount of organic matter, which probably reduced the U(VI) in the ascending fluids to U(IV).

5.2. Mechanism and condition of trace element incorporation into uraninite

The chemical composition of uraninite depends largely on the fluid chemistry from which uraninite precipitated and the fluids that caused the alteration of UO_{2+x} under both reducing and oxidizing conditions (e.g., Finch and Ewing, 1992; Janeczek and Ewing, 1992b). The colloform texture of uraninite groups (i), (ii), and (iii) is likely the result of events of multiple periods of dissolution and re-precipitation under nominally reducing conditions with high concentration of impurities: W, Pb, Mo, As, Zr, Ca, Ti, Fe, Si, and Al; uraninite group (iii) contains Ba and trace amounts of Cu. These impurities have been previously reported as incompatible with the uraninite structure (Finch and Ewing, 1992; Janeczek and Ewing, 1992a; Janeczek and Ewing, 1995; Bros et al., 2003). Although the current chemical system contains Sb derived from tetrahedrite, Sb was not detected in the uraninite.

These results show that W is homogeneously distributed in uraninite groups (i) and (ii), including their cores that based on the petrographic observations are presumed to be the oldest part of uraninite. Thus, the most likely process is the precipitation of the primary uraninite from fluids that contain W and incorporation of W into the interstitial positions in the uraninite structure. Janeczek et al. (1996) have suggested that the incorporation of W^{6+} into the uraninite structure is very unlikely based on crystal-chemical considerations, since W is, in most cases, octahedrally coordinated (Burns, 2005; and references therein). Based on the similarities in crystal-chemistry between W and Mo, and the previous studies reporting the occurrence of Mo and the

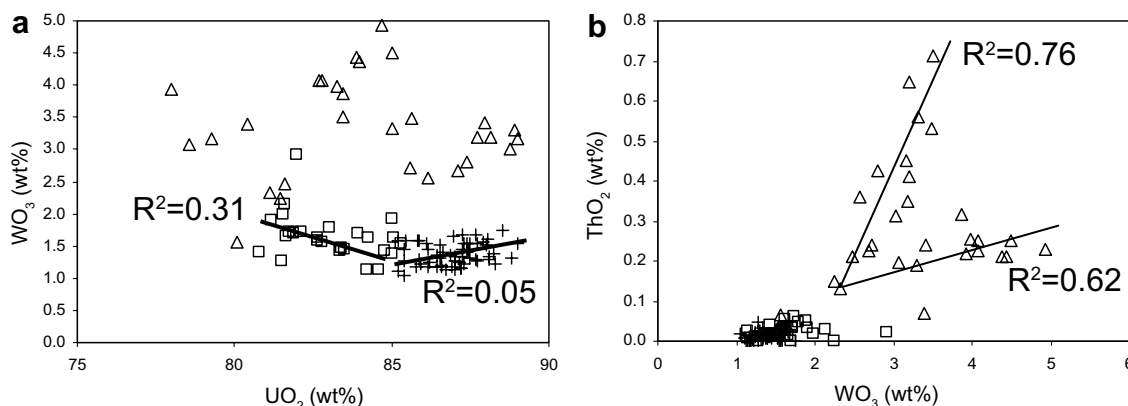


Fig. 7. Chemical variation plots of uraninite compositions for groups (i) (crosses), (ii) (squares), and (iii) (triangles). (a) UO_2 and WO_3 ; (b) WO_3 and ThO_2 with two different correlation trends for uraninite group (iii); all analyses of uraninite are plotted; group (i) and (ii)—colloform uraninite—(i) bright zones and core; (ii) gray zones; group (iii)—fine-grained uraninite.

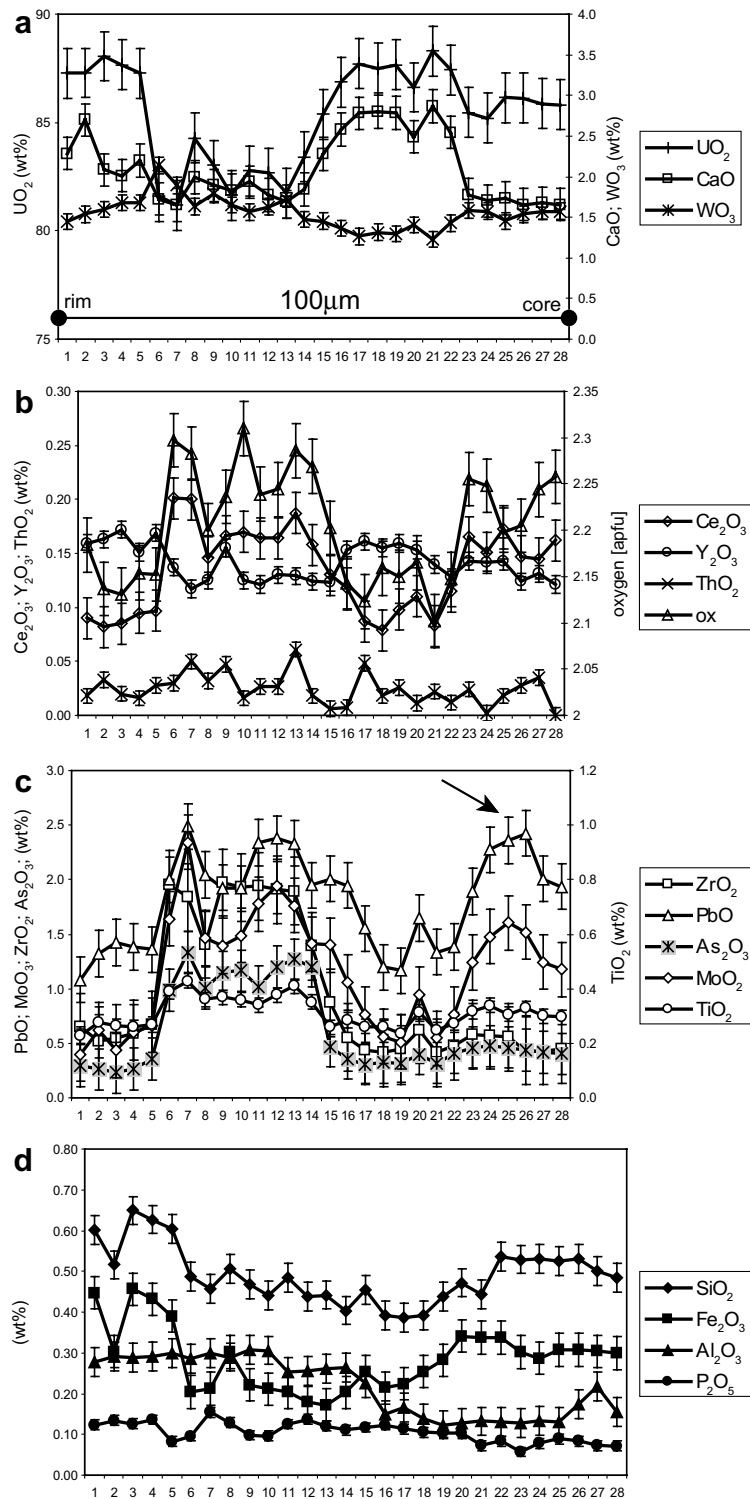


Fig. 8. Representative line scan analysis of colloform uraninite group (i) and (ii) from r—rim to c—core as marked in Fig. 2. (a) UO_2 (—+—), CaO (—□—), and WO_3 (—*—) with the highest concentration of WO_3 marked at the end of gray zone. (b) Trend of Ce_2O_3 (—◇—), Y_2O_3 (—○—), ThO_2 (—×—), and oxygen (—△—). Ce_2O_3 increases with the amount of oxygen, whereas Y_2O_3 decreases. (c) PbO (—△—), MoO_3 (—◇—), ZrO_2 (—□—), As_2O_3 (—×—), and TiO_2 . PbO behaves similar to MoO_3 showing a peak next to uraninite core indicated by the arrow. (d) Trend of SiO_2 (—◇—), Fe_2O_3 (—■—), Al_2O_3 (—▲—), and P_2O_5 (—●—). Note the similar behavior of SiO_2 to Fe_2O_3 .

other fission products as discrete metallic particles in UO_2 and uraninite matrix (e.g. Kleykamp, 1985; Gauthier-La-

faye et al., 1996; Utsunomiya and Ewing, 2006), it is expected that W is not compatible with uraninite structure

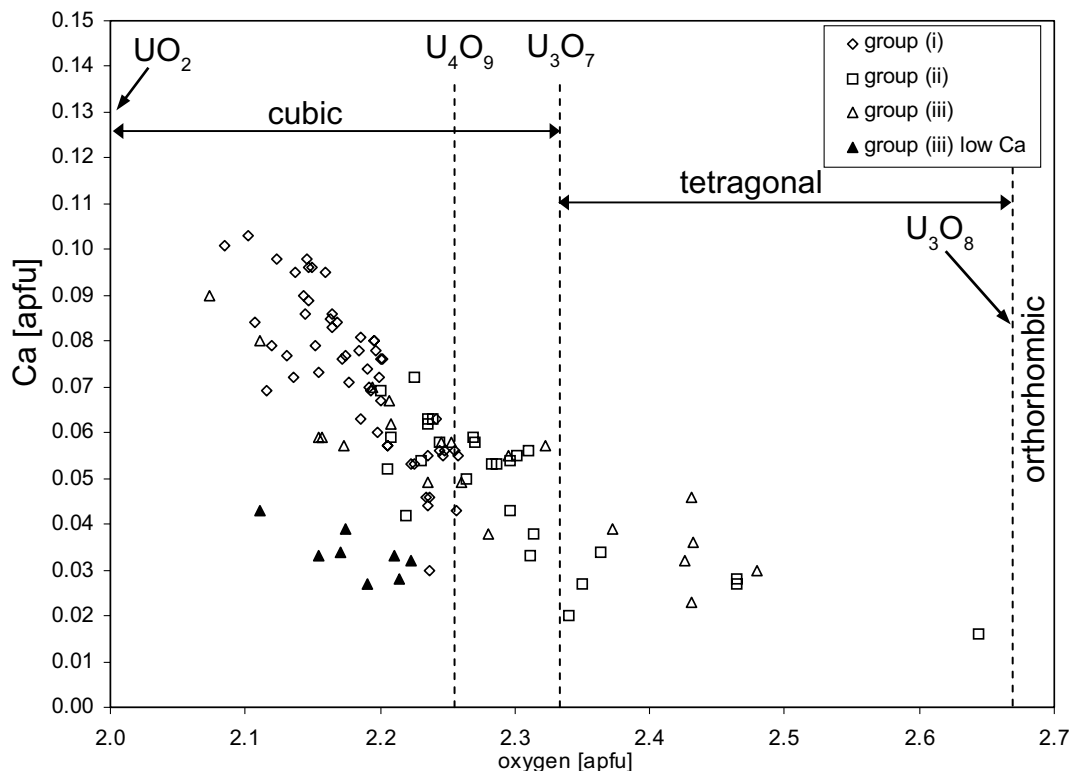


Fig. 9. Diagram presenting the amount of calculated excess oxygen [apfu] in analyzed uraninite vs. Ca [apfu]; group (i) and (ii)—colloform uraninite—(i) bright zones and core (ii) gray zones; group (iii)—fine-grained uraninite.

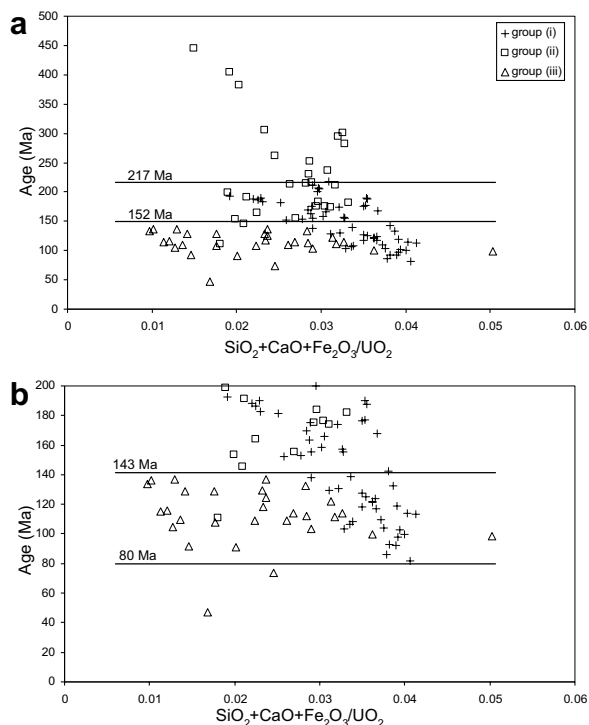


Fig. 10. (a and b). Relation between the calculated U–Pb chemical ages (Ma) and the content of $\text{SiO}_2 + \text{CaO} + \text{Fe}_2\text{O}_3/\text{UO}_2$ in different uraninite groups: groups (i) and (ii)—colloform uraninite—(i) bright zones and core, (ii)—gray zones; group (iii)—fine-grained uraninite.

and may form W-rich nano-domains. The precipitation of W-rich nano-domains may be responsible for elevated concentrations of incompatible W in uraninite group (ii) with decreases in U concentration (Fig. 7a). Uraninite group (ii) is more oxidized and contains a higher average concentration of WO_3 , which may be preferentially released from uraninite group (i) during alteration. Both W and Mo are considered to behave similarly to each other geochemically, such that both, W^{6+} and Mo^{6+} , have a high affinity for oxygen (Wood and Samson, 2000). For example, Buck et al. (1997) characterized a Mo–Cs uranyl oxide during spent nuclear fuel corrosion, and a W–Cs uranyl hydroxide has been reported by Burns (2005). Because of the radiotoxicity of Cs, the association of Cs with W and Mo suggests an important role for those elements in retarding the migration of Cs. However, thermodynamic properties of aqueous UO_2WO_4^0 and $\text{UO}_2\text{MoO}_4^0$ complexes have not been reported; thus, it is not possible to predict the stability of these Mo–Cs uranyl oxides and the W–Cs uranyl hydroxide.

Calcium and lead are key impurities that affect the physico-chemical properties of uraninite (e.g., Finch and Ewing, 1992; Janeczko and Ewing, 1992b). Besides the negative correlation between Ca and oxygen vacancies in uraninite groups (i) and (ii) (Fig. 9), a negative relation between Ca and Pb was also found in group (i) uraninite (Fig. 5d). This suggests a competition between Ca and Pb for structural positions during precipitation of the primary uraninite. Because their ionic radii are close to each other; 0.112

and 0.129 nm for Ca and Pb, respectively, there should be Pb substitution for Ca in the uraninite structure (ionic radii after [Shannon, 1976](#)). However, there is an additional discrepancy between Ca and Pb in these analyses as mentioned in Section 5.1, that Pb could have been introduced from at least two different sources: radiogenic Pb and liberated from sulfide, as indicated by the two different correlations between PbO and MoO₃ ([Fig. 5b](#)). The line scans of colloform uraninite reveal an almost identical distribution of UO₂ and CaO (wt%). This is in good agreement with the documented incorporation of Ca into the uraninite structure and limited solid solution between synthetic UO₂ and CaO ([Janeczek et al., 1996](#); and references therein) and shows that Ca can be preferentially incorporated into the structure of uraninite groups (i) and (ii), rather than Pb.

Another interesting point is the different behaviors of Ce (ionic radius 0.1143 nm) and Y (ionic radius 0.1019 nm), both of which are compatible with the uraninite structure (e.g., [Janeczek and Ewing, 1992a](#)). There is a negative correlation between UO₂ and Ce₂O₃ in [Figs. 5e and f](#), and a positive correlation between UO₂ and Y₂O₃ in group (i) uraninite. A similar behavior for Y and Ca was observed in uraninite groups (i) and (ii), which negatively correlate with the amount of calculated oxygen. These relations suggest a more complex substitution involving Ca²⁺, Y³⁺, REE³⁺, and U⁴⁺ and U⁶⁺. In uraninite group (i), Y³⁺ and Ca²⁺ probably occupy the interstitial positions; whereas, Ce³⁺ is located in the U⁴⁺ position. The oxidation of U⁴⁺ to U⁶⁺, requires that O²⁻ enter the interstitial sites for charge balance, which would reduce the concentrations of Ca and Y in these sites. However, the partial oxidation of uraninite could also change the oxidation state of Ce to 4+, which has smaller ionic radius 0.097 nm. This may influence the incorporation of Ce into the uraninite of group (ii), as Ce⁴⁺ fits better into the uraninite structure than Ce³⁺ according to the charge and ionic radius. The chemical fractionation of Ce due to the change of oxidation state has also been observed at natural reactors in Oklo, Gabon ([Hidaka et al., 2005](#)).

Uraninite group (ii) contains a ZrO₂, TiO₂, and As₂O₃. Zirconium appears to have been released from the uraninite of group (i) during dissolution and subsequently co-precipitated in uraninite because of its compatibility with the uraninite structure; the ionic radius of Zr is 0.084 nm ([Janeczek and Ewing, 1992b](#)). Zirconium does not have any correlation with other elements. Titanium is incompatible with the uraninite structure and increased amounts of Ti were observed from uraninite groups (i) to (iii), suggesting Ti incorporation during the alteration events as sub-micron scale impurities, as reported by [Janeczek and Ewing \(1995\)](#). It is difficult to determine the extent of the incompatibility of As with the uraninite structure because As has multiple oxidation states. For the purpose of this study, we nominally assigned As as As³⁺. The constant concentration of As₂O₃, ~0.3–0.5 wt%, in uraninite group (i) may reflect the presence of As in the mineralizing fluids. The arsenic could occur as submicron inclusions of tetrahedrite, which precipitated during the brecciation event. However, Cu and S were not detected in the zones of uraninite group (ii) enriched with As; thus, this excludes the possibility of

tetrahedrite micro-inclusions. The As concentration is the highest in uraninite group (ii), which also contains high concentrations of calculated oxygen ([Figs. 8b, c and 9](#)). This may indicate that As is in the higher oxidation state, 5+.

In summary, the precipitation of uraninite group (i) resulted in incorporation of Ca and Y (1.26–2.87 wt% and 0.08–0.17 wt%, respectively) and depletion of Pb, Zr, Mo, As, Ti, Ce, and W. The elements which were not incorporated into the uraninite group (i) concentrated in the gray zone ([Figs. 2a; 8b and c](#)) of group (ii) uraninite with higher amounts (2.2–2.31 [apfu]) of total oxygen than group (i) uraninite.

Regarding the calculated amount of oxygen in [Fig. 9](#), some data plotted above the line for the composition of U₃O₇, which has a tetragonal structure. However, the tetragonal-structure for uraninite has never been reported in nature, the data set with the high oxygen content must be ascribed to the presence of U⁶⁺ alteration phases, rather than tetragonal uraninite at a higher oxidation state (e.g., [Janeczek et al., 1993; Fayek et al., 1997b](#)).

The calculated formulae of uraninite groups (i)–(iii) did not reveal a high U⁶⁺ (0.587–0.808 [apfu]), which is equivalent to 2.480–2.727 of oxygen [apfu], as has been reported from the same uraninite from Marshall Pass analyzed by [Zhao and Ewing \(2000\)](#). The highest value of U⁶⁺ in our data is 0.637, which corresponds to 2.644 of oxygen [apfu]. Except for this maximum value of U⁶⁺, all other data are less than 2.5 [apfu] of oxygen. [Zhao and Ewing \(2000\)](#) suggested that the bright zone of colloform uraninite [i.e., group (i) uraninite] formed by dissolution and reprecipitation. Our data also supports this process for group (i) uraninites. However, the bright zones of these uraninites still contain relatively high amounts of impurities, which was not noted by [Zhao and Ewing \(2000\)](#), owing to their incomplete list of analyzed elements ([Figs. 5a, c; Tables 1 and 2](#)). In addition, [Zhao and Ewing \(2000\)](#) characterized the gray zone ([Fig. 2a](#)) of the colloform texture as schoepite with high amounts of trace elements. However, such a high amount of impurities cannot be incorporated into the schoepite structure ([Burns, 1999](#)). Our results reveal that the gray zone [group (i)] of the colloform texture is uraninite with a formula close to U₄O₉ ([Fig. 9](#)).

The concentration of BaO, 0.68–2.36 wt%, in the group (iii) uraninite is probably derived from inclusions of uranotungstite, because Ba²⁺ is incompatible with uraninite structure owing to its large ionic radius, 0.142 nm in eight-fold coordination ([Bros et al., 2003](#)). The group (iii) uraninite appeared to be resistant to the alteration, which could be attributed to the elevated concentration of ThO₂ in this uraninite ([Grandstaff, 1976](#)). During the formation of U-ore deposits, the geochemical behavior of Th is different from that of U; lower amounts of Th can be incorporated into uraninite at lower temperatures ([Ruzicka, 1993](#)). The lower temperatures are characteristic of epigenetic deposits, such as at Marshall Pass. Thus, fine-grained uraninite of group (iii) with relatively higher concentrations of Th as compared with uraninite groups (i) and (ii) should precipitate at slightly higher temperatures that did not exceed the 200 °C reported by [Finch \(1996\)](#).

The elevated concentrations of SiO_2 and Fe_2O_3 at the outermost parts of colloform uraninite shown in Fig. 8d reflect the supergene alteration under oxidizing conditions. The saddle shape of the line scan implies that recrystallization of uraninite groups (i) and (ii) excluded the incompatible Si and Fe from the structure. This stage of the U-ore evolution causes intensive alteration of all groups of uraninite and precipitation of secondary uranyl minerals, as well as alteration of sulfide and sulfosalt to chalcocite and covellite. Uraninite group (ii) appeared to be altered most intensively to the secondary uranyl-phases, which is consistent with the previous studies (e.g., Janeczek and Ewing, 1992b) reporting that higher concentrations of the incompatible elements enhances the solubility of uraninite.

The almost constant W concentration in the core of the uraninite group (i) may indicate that U and W were derived from the same source, which may be from the surrounding granitoids. The genetic relationship between W-mineralization and granitoid plutons has been documented by Wood and Samson (2000). Our hypothesis assumes that the uranyl ion was transported in chloride brines. The chloride brines could increase the solubility of W-bearing minerals (Foster, 1977), such as scheelite (CaWO_4) and/or stolzite (PbWO_4). Thus, we suggest that a hydrothermal fluid with high Cl^- concentration possibly penetrated through the granitic rocks dissolving U- and some W-minerals and subsequently transported U and W at temperatures of 100–200 °C (Finch, 1996) as UCl_3^+ , UCl_4 , $\text{UO}_2(\text{aq})$ and H_2WO_4 , HWO_4^- , WO_4^{2-} , NaHWO_4^0 , and NaWO_4^- complexes, respectively. This is consistent with conditions of uraninite precipitation at ~200 °C at the depths of ~2–5 km for hydrothermal unconformity-type and vein-type U-deposits with a large range of salinity (e.g., Hofmann and Eikenberg, 1991; Fayek et al., 2002), and experimental studies

on uraninite and scheelite solubilities at elevated temperatures (e.g., Murphy and Shock, 1999; Wood and Samson, 2000; and references therein).

5.3. Implications for the corrosion of the UO_2 in used nuclear fuel

The dissolution of uraninite is enhanced by secondary uranyl phases forming on the surface of the uraninite in the present samples. The sequence of alteration is comparable to that of previous studies of the alteration of UO_2 in spent nuclear fuel under oxidizing conditions. Four different stages of alteration were recognized in the present samples (Fig. 11). During the first stage, the rim of uraninite grain (bright contrast in BSE images) is oxidized and enriched in U^{6+} (Fig. 11, stage B). Similarly, the aggregates of uraninite grains in spent nuclear fuel begin to be oxidized to U_4O_9 along grain boundaries (Thomas et al., 1991; Einziger et al., 1992; Wronkiewicz et al., 1996; Stroes-Gascoyne et al., 1997; Schoesmith, 2000). The second stage is corrosion of the oxidized rim (Figs. 3c and e) of uraninite (Fig. 11, stage C). At the third stage, alteration products of U(VI) phases precipitate onto the corroded surface, which may slow down the dissolution of uraninite by creating a “protective” or diffusion barrier to water reaching the surface. However, owing to the well-defined cleavage of U(VI)-phases, microfractures form even in the oxidized rims, reaching the boundary between oxidized rim and the uraninite core (Fig. 11, stage D). At the last stage, the microfractures split and continuously penetrate along the boundary between the unaltered uraninite core and the corroded bright rim of oxidized uraninite (Figs. 3d, e, and 11, stage E). The third and fourth stages of alteration clearly show the destructive role of uranyl phases on uraninite

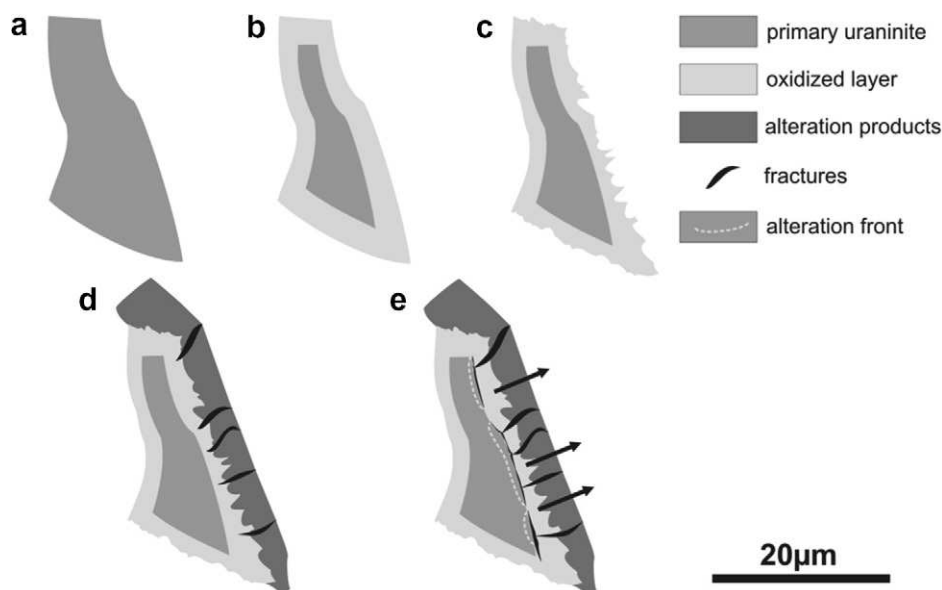


Fig. 11. Schematic diagrams illustrating alteration of brecciated colloform uraninite. (a) uncorroded fragment of primary uraninite; (b) fragment with bright oxidized rim; (c) preferential dissolution of the oxidized layer of uraninite with creation of corrosion rinds and microfractures; (d) precipitation of alteration phases and penetration of additional discontinuities connected by the perfect cleavage of the uranyl minerals; (e) fragmentation of separate “micro-blocks” of oxidized uraninite and exposure of fresh surfaces to further alteration.

grains. Physical fracturing of uraninite causes an increase in the surface area of unaltered and altered uraninite and exposed the UO_2 to further corrosion. Indeed, [Taylor et al. \(1995\)](#) have reported microfracturing and precipitation of dehydrated schoepite within fractures during leaching experiments of UO_2 fuel in a steam–air mixture at a temperature of 225 °C. Such fracture formation ([Fig. 11](#), stage E) may be caused by a slight shrinkage of the unit cell parameters in the oxidized uraninite, with a $\sim 0.5\%$, and $\sim 1.5\%$ decrease in density during the transformation from UO_2 to U_4O_9 ([Janeczek and Ewing, 1991](#); [Einziger et al., 1992](#)). As a result, nano- or atomic-sized defects or a slight misfit in the structure of the oxidized uraninite may be created during corrosion. This oxidation of uraninite does not involve crystallographic reorientation ([Janeczek and Ewing, 1991](#); [Einziger et al., 1992](#)). As indicated by the thickness of the oxidized uraninite rim, the oxidation rate of uraninite depends on the position of the grains. That is grains towards the outer edge of the aggregate were oxidized more quickly.

The preferential precipitation of the uranyl minerals in the gray zones of uraninite group (ii) and higher resistance of bright layers of uraninite group (i) to dissolution ([Figs. 2b–d and h](#)) suggests that the relatively large amounts of the incompatible impurities enhance the alteration of uraninite group (ii). Although it was noted that uraninite exposed to irradiation for periods as long as 1 By remains crystalline, the uraninite grains that contain high amounts of Si, Ca, and Pb exhibits subgrain formation and polygonization ([Fayek et al., 2000](#)). The polygonization was observed also in the present uraninite from Marshall Pass as well ([Figs. 3a–f](#)). The same effect was also reported for synthetic UO_2 , even though fluorite-related structures are generally not susceptible for radiation-induced amorphization (e.g., [Matzke, 1992](#); [Weber et al., 1998](#)). However, the incompatible elements in analyzed uraninite group (i) and (ii) moved to the grain boundaries of the uraninite grains ([Figs. 3c and e](#)). The higher concentration of the incompatible elements at the outermost parts of the uraninite grains may stabilize the damaged aperiodic areas and retard the recovery processes. The damaged aperiodic areas are more susceptible to dissolution than the crystalline domains ([Fletcher, 1982](#); [Fayek et al., 2000](#)) and result in preferential dissolution and precipitation of the uranyl minerals such as schoepite and/or “dehydrated schoepite” followed by uranyl arsenates.

6. CONCLUSIONS

1. Based on the detailed micro-analyses of colloform uraninite, the evolution of U- mineralization in the Marshall Pass district can be summarized as follows: (i) precipitation of primary uraninite from U- and W-rich fluids; (ii) formation of Pb–Mo-rich uraninite zones adjacent to the core of the uraninite due to later Pb–Mo-rich fluids; the Pb probably comes from the two different sources: (a) radiogenic Pb from the primary uraninite; (b) and Pb from the unstable sulfides; (iii) multiple alteration events of partial dissolution and reprecipitation of uraninite

groups (i) and (ii), with significant variation in the composition and the amount of structural oxygen; (iv) extensive brecciation of colloform uraninite, enhancing the migration of Cu–Zn–Ag–As–Sb–S-rich fluids and precipitation of ore sulfides and sulfosalts within the fractures (the brecciated uraninite core was oxidized from the rim inwards); (v) subsequent dissolution and reprecipitation processes formed the concentrations of fine-grained uraninite group (iii) in the matrix; (vi) U^{6+} -minerals, mainly “dehydrated schoepite”, uranyl arsenates and a U–W–Mo–Ba phase precipitated (this event coincides with extensive micro-dissolution along the grain boundaries and microfractures); (vii) extensive hematitization and silicification.

2. The homogenous distribution of W in the core of colloform uraninite indicates W incorporation into the uraninite structure in the interstitial sites. However, based on the suggested incompatibility of W with uraninite structure, W-rich nano- or micro-domains may exist in the cores.
3. Migration of Mo and W is important because of the potential precipitation of Mo–Cs- and W–Cs-phases during the alteration of spent nuclear fuel. These elements were retained in the recrystallized uraninite and subsequently precipitated as uranyl tungstates and uranyl molybdates at Marshall Pass.
4. The degree of uraninite alteration appears to depend on the chemical composition of the uraninite. Uraninite zones with lower concentrations of impurities are generally more resistant during the alteration processes under oxidizing conditions. There were four stages of uraninite alteration under oxidizing conditions: (1) formation of oxidized layer at the rim; (2) dissolution of the rim; (3) subsequent precipitation of U^{6+} -phases within cleavage; (4) fracturing in the uraninite enhanced by the cleavage parallel to the U^{6+} -sheet structures. This last process also increased the surface area of unaltered uraninite that was exposed to the ambient fluids.
5. Based on the calculation of U–Pb chemical ages for Marshall Pass uraninite, U-mineralization may be older than Tertiary. The source of U may be the granite–gneiss basement units, which were penetrated by ascending hydrothermal brines. However, further U–Pb isotopic studies are necessary to define the actual age and consequently the source of U-mineralization.
6. The typical distances of U, Ce, and Y migration appeared to depend on the local physico-chemical properties of the migrating fluids. In the studied samples, the U-migration did not exceed 5 mm, as migration was retarded by reprecipitation of fine-grained uraninite under reducing conditions and by secondary uranyl phases under oxidizing conditions.

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