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STUDY OF PHOSPHATIC NODULES AS A POSSIBLE SOURCE OF URANIUM MINERALIZATION IN WARCHA SANDSTONE OF NILAWAHAN GROUP, SALT RANGE USING SSNTD TECHNIQUE

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Abstract

The strong similarity in the sedimentary depositional characteristics between the Warcha Sandstone of Nilawahan Group in the Salt Range and the uranium bearing sandstones of Siwalik Group in the foot hills of Himalaya and Sulaiman Ranges tempted the geologists to investigate the former group for the occurrence of any uranium deposits in it. Like volcanic ash beds in Siwaliks, phosphatic nodules may be a possible source of uranium mineralization in Warcha Sandstone of Nilawahan Group. Samples of phosphatic nodules occurring in the Sandstone of Nilawahan Group Salt Range were analyzed using Solid State Nuclear Track Detention Technique (SSNTD) for the determination of their uranium concentration. The results obtained are quite encouraging and favour the idea of exploring the area in detail for any possible occurrence of uranium deposit. Uranium concentration in these samples ranges from (434 $\pm$39) ppm to (964 $\pm$81) ppm with an average concentration of (699 $\pm$62) ppm.

1. Introduction

The secondary ore minerals of the uranium metal occur frequently along with a large variety of other secondary uranium bearing minerals, such as phosphates, carbonates, sulphates, hydrous–oxides and silicates (Nininger, 1954). Phosphorus-rich sea water resulted in the booming of phosphate secreting marine organisms which led to the deposition of a large amount of phosphorous bearing organic matter, which periodically accumulated on the ocean bottom. Apatite formation in phosphate nodules is believed to take place in one of three different ways such as: (1) biogenesis, (2) carbonate epigenesis, and (3) precipitation (Slansky, 1986). Often organic matter is intimately associated with phosphate nodules suggesting that organic matter was the likely source of the phosphate in the nodules (Ece, 1990).

The presence of uranium mineralization in the Phosphatic nodules bearing Warcha Sandstone of Nilawahan Group has been reported in a limited number of recently written unpublished reports (Azizullah, et al, 2003; Nisar, 2003). As phosphatic nodules (one of the source materials for uranium mineralization) are recognized to be associated with secondary uranium mineralization in the world, therefore, we conducted some experimental work in order to judge its potential of being a possible source of any uranium mineralization of economic importance in the associated sandstones of Nilawahan Group. In the present investigation, some samples of phosphatic nodules occurring in Warcha Sandstone of Nilawahan Group were collected and analyzed for their uranium content determination and its spatial variation using the technique of Solid State Nuclear Track Detectors. The samples were collected from a shale bed occurring in the upper part of the Warcha Sandstone of Nilawahan Group in different localities including:

a) Warala area

Samples of phosphatic nodules of the Warala area are associated with the shale bed in the upper Warcha Sandstone. These nodules are grayish black, granules to pebble size, sub rounded with high density.

b) Malot Area

Samples of phosphatic nodules in Malot area occur in the two upper most shale beds of Warcha Sandstone. These nodules are pinkish brown to blackish grey, pebble size, sub rounded with high density.

c) Karuli area

The samples of phosphatic nodules were collected from a couple of places in the Karuli area. All these nodules are pebble size, and angular to sub angular to sub rounded. The color of these nodules ranges from dull red to brownish black.

d) Simbal area

Phosphatic nodules in this area are reddish black to dark maroon, pebble size, sub angular to sub rounded. These nodules also occur in the shale bed of the upper Warcha Sandstone.

e) Gahi area

Phosphatic nodules in Ghahi area Dhok Hani Bakash are similar to those found in Simbal area.

f) Nurpur area

In Nurpur area, the phosphatic nodules are restricted to a single stratigraphic horizon within shale bed of the upper part of Warcha Sandstone. These nodules are pinkish brown to blackish grey, pebble size, sub angular to sub rounded with high specific gravity.

g) Nawabi Kas area

Phosphatic nodules in this area are pinkish to grayish black, pebble size, and granular with high specific gravity.

The uranium bearing phosphatic nodules are characteristic of the Warcha Sandstone of Nilawahan Group of Salt Range. Preliminary studies show that these nodules are scavenger of heavy metals, particularly, rare earth elements and uranium. Earlier, it was recommended that the geology of eastern part of the Salt Range is favorable for concentrating uranium to form deposits (Azizullah, et al, 2003). In 1992-93, geological and radiometric surveys were carried out in the Salt Range, which resulted in the discovery of several uranium and thorium anomalies in the eastern part (Azizullah, et al, 2003). Further geological studies delineated more promising areas for hosting significant uranium resources in the Salt Range (Azizullah et al. 2003).

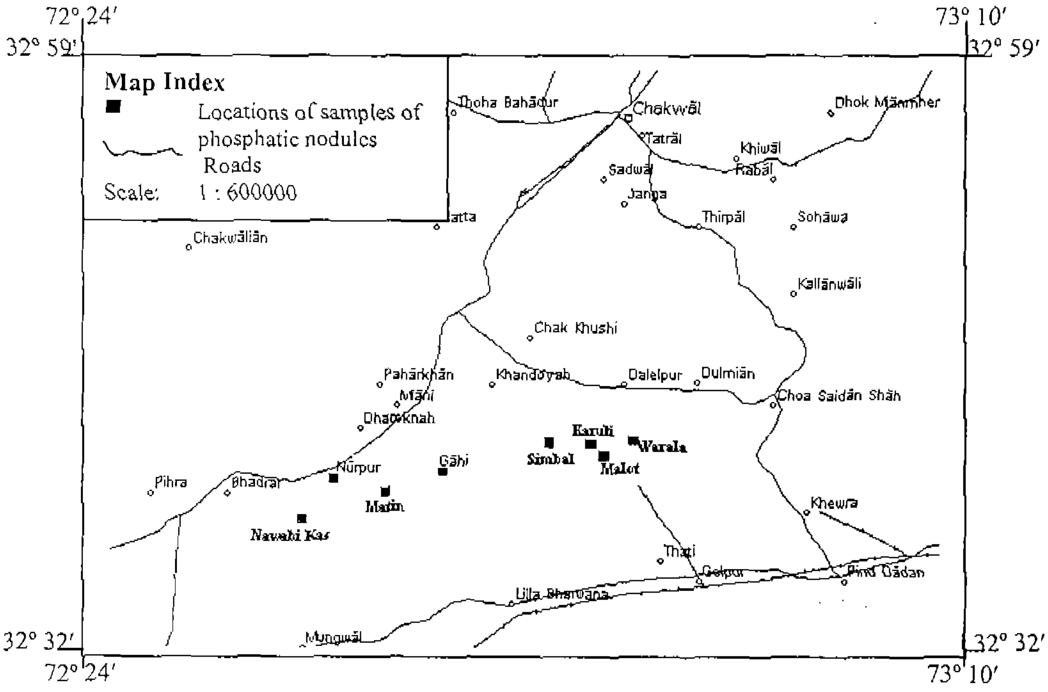

Fig.1. Map showing locations from where the samples were collected from Warcha Sandstone of Nilawahan Group, Salt Range for the determination of uranium concentration using SSNTD-technique.

2. Uranium

Uranium has an average concentration of about 4 ppm by weight in the earth crust. Among the naturally occurring elements, it ranks 48th in natural abundance in crustal rocks, and is more common than boron and zinc. Uranium occurs as a significant constituent of more than 150 different minerals and as a minor component of another 50 minerals. The important uranium ore minerals in phosphatic group of minerals are torbernite ($CuO*2UO_3*P_2O_5*nH_2O$; 60% U_3O_8), meta-torbernite, autunite ($CaO*2UO_3*P_2O_5*nH_2O$; 60% U_3O_8) and meta-autunite. Torbernite, meta-torbernite are hydrous copper uranium phosphates, the only difference between the two being the number of water molecules. Physical properties of torbernite and meta-torbernite are identical e.g; both have bright emerald color, a pearly luster, hardness of 2-2.5 and specific gravity of about 3.5 (R. D. Nininger, 1954).

Due to its property to get dissolved in aqueous solution in hexavalent (U^{+6}) state and to precipitate as a discrete mineral in tetravalent (U^{+4}) state; uranium forms deposits in the earth's crust where the geological conditions become favorable. Chemical behavior of uranium in solution is controlled by redox reactions. In a reducing environment, the dominant U ion in solution is U^{+4} and is relatively insoluble. In an oxidizing environment, the dominant U ion in solution is U^{+6} and is relatively soluble. So uranium-bearing oxidizing solutions precipitate uranium upon reduction.

3. General Geology of the Area

Siwaliks sandstones are the major source of uranium in Pakistan. Siwaliks occur along the southern flanks of the Himalayas and consist predominantly of molasse sediments comprising sandstones, siltstones, mudstones and conglomerates. The characteristic sedimentary features of Siwaliks such as frequent occurrence of cross-bedding, ripple marks, vertebrate fossils and wood logs, and the association of pebble- and cobble-sized fragments with sand size detritus are suggestive of shallow water deposition for these rocks. These lithological characteristics favor braided stream deposition under swampy conditions (Abid *et al.*, 1983).

The Salt Range has been referred to as the southern slope of Potwar Plateau as well as that of Surghar Range, extending from Jogi Tilla area Jhelum in the east to Makarwal near Isa Khel in the west, covering a distance of more than 250 km. The Salt Range stratigraphic units range in age from Pre-Cambrian to Tertiary with the marked absence of rocks of Ordovician, Silurian, Devonian and Carboniferous ages throughout the region. The Permian sequence of the Salt Range is composed of two groups namely; i) the Nilawahan and ii) the Zaluch groups. The Nilawahan Group is well developed in the Salt Range and represents mostly non-marine rocks with only a small transitory marine transgression during Asselian. The Group includes Tobra Formation, Dandot Formation, Warcha Sandstone and Sardhai Formation (Table 1). Lithologically this group consists of boulders, conglomerates, sandstones, siltstones and shales. The Nilawahan Group is consistently exposed all over the Salt Range with some representative formations thinning out laterally. The age of the Group is Asselian to Sakmarian. While the Zaluch Group is mainly marine in origin (Shah, 1977, 1980).

In Indus Basin Cambrian was followed by regional uplift and break in sedimentation, which prevailed until the end of Carboniferous. At the time of the onset of Permian; conditions were generally cold and mostly fluvio-glacial environment prevailed all over the Indus Basin. The Nilawahan Group in the Upper Indus Basin represents the continental environment with glacio-lacustrine conditions in Early Permian as indicated by Tobra Formation. Its lower contact is marked by the most significance unconformity in the region with Cambrian rocks. Similarly the overlying Dandot Formation also indicates an overall lacuna in the region. (Kadri, 1995).

Table 1. Lower Permian succession of the Salt Range (Shah, 1980)

Formation	Description	Environment	Stage
Sardhai	Shale and clays of lavender color, with interbedded sandstone of greenish color, well bedded and cross bedded; carbonaceous in part with copper minerals, jasper and gypsum.	The formation was mostly deposited in the lacustrine but laterally marine reducing environment has also been noted.	Sakmarian
Warcha Sandstone	Sandstone, shale, conglomeratic beds and some carbonaceous shale; the facies changes from predominantly sandstone in the Western salt Range to alternation of sand and shale in the Eastern Salt Range. Thin coal seams and copper minerals are locally present.	Mostly fluvial with localized lagoonal conditions.	Sakmarian
Dandot	Olive grayish green shale and coarse sandstone with localized carbonaceous shale.	Marine in the Eastern and Western Salt Range.	Asselian
Tobra	Boulder with claystone, sandstone and siltstone.	Glacial, glacio-fluviatile and fluviatile environment.	Asselian

The sedimentary features and lithological characteristics of the Nilawahan Group of the Salt Range strongly resemble to those of the Siwalik Group of Pakistan (Table 2). Due to this resemblance, we conducted fission track radiographic study for uranium content determination in the phosphatic nodules to locate a possible source of uranium in the Warcha Sandstone.

Table 2. Comparison of Siwalik Group with Nilawahan Group of the Salt Range

Siwalik Group	Nilawahan Group
1) The stratigraphic units comprising these sediments are mainly Chingi, Nagri, Dhok Pathan and Soan Formations, collectively known as Siwalik Group	1) The Nilawaham Group id composed of four formations namely; Tobra Formation, Dandot Formation, Warcha Sandstone and Sardhai Formation.
2) Lithologically the Siwalik sequence mainly comprises of alternate sandstone and shale with occasional thin beds of conglomerate	2) The Nilawahan Group represents a dominantly continental deposits consisting of arenaceous and argillaceous sediments
3) These channel lag deposits are most characteristic of high energy braided stream and the clasts are commonly extrabasinal	3) The Tobra Formation at the base of the group exhibits true tillite; probably deposited by local glaciations in the eastern Salt Range.
4) Several of the sedimentary features and lithological characteristics, e.g., frequent occurrence of cross-bedding, ripple marks, logs of vertebrate fossils and woods, and the association of pebble- and cobble-sized	4) The sandstone is red, purple or shows lighter shades of pink. It is medium to thick bedded, fine to coarse grained with gravels and pebbles of granite at places. Sedimentary feature like cross bedding in the sandstone

fragments with sand size detritus are suggestive of shallow nature of the basin of deposition for the Siwalik rocks.	is suggestive of fluvial depositional environment. The formation was deposited probably in the near shore/fluviatile environments.
5) Thin beds of conglomerate in the sandstone and thinly laminated black shale in the middle part of the sequence also indicate the depositional environment.	5) The Warcha Sandstone consists of sandstone, conglomeratic in places and has interbeds of shale. The formation contains some carbonaceous shale with impersistent coal seams in the western Salt Range.
6) These lithological characteristics favor braided stream deposition under swampy conditions. The huge thickness of Siwalik can only be explained if considered that deposition took place in a shallow, fast sinking basin under the condition of rapid erosion, short transportation and quick deposition	6) The Nilawahan Group is well developed in the Salt Range represents mostly non-marine rocks with only a small transitory marine transgression during Asselian.

4. Solid State Nuclear Track Detection Technique

Solid State Nuclear Track Detectors (SSNTDs) are widely used in a number of fields such as nuclear physics, elementary particle physics, chemistry/geochemistry, geology and geophysics etc. The basic principle is that when an ionized nuclear particle passes through the SSNTDs it results in the formation of an intense damage ranging in size from 3-10 μm. These damages can not be observed under an ordinary optical microscope. However they become visible after "Chemical Etching", during which the damaged region of the detector is dissolved at faster rate than the remaining region and the damaged portion, the track, becomes enlarged (Durrani & Bull, 1987).

The Solid State Nuclear Track Detection Technique (SSNTD) is being used for measuring concentration and spatial distribution of certain elements which emit heavy nuclear particles either directly or as a result of specific nuclear reaction in different fields of science and technology (Fleischer et al., 1964). In this connection, this technique is a suitable choice and is selected to observe the uranium distribution pattern in the phosphatic nodules. The technique is here used for determination of uranium concentration in samples of phosphatic nodules with 235U (n,f) nuclear reaction under thermal neutrons conditions in order to search for uranium source in Warcha Sandstone. Samples of phosphatic nodules occurring in Warcha Sandstone, Nilawahan Group were collected from Nawabi Kas, Nurpur, Matin, Gahi, Simbal, Karuli, Malot and Warala areas as shown in Fig. 1.

5. Experimental Procedure

Twelve samples of phosphatic nodules taken from the studied area were cut into rectangular pieces and polished with automatic lapping and polishing machine to get smooth surfaces. Lexan detectors were placed in contact with all samples and Standard Reference Material (SRM-612) of known uranium content as shown in figure 2. Both the samples and Standard Reference Material were irradiated with thermal neutrons in the Pakistan Research Reactor-1 (PARR-1). After irradiation the lexan detectors were removed from samples and standard and etched in 6.5 M

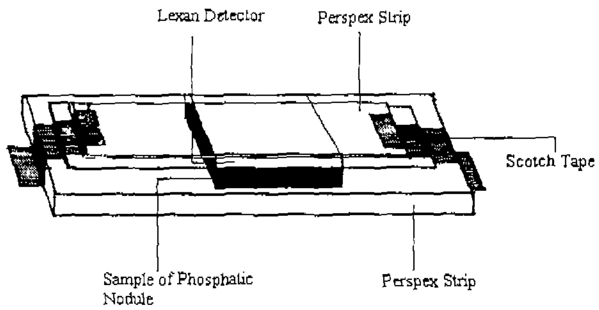

Fig. 2. Diagrammatic sketch showing packing assembly for irradiation of phosphatic nodules at Pakistan Research Reactor – I through a rabbit station at 10 MW power.

NaOH solution at 50 °C for 45 minutes. The fission tracks registered in the lexan detectors (see figure 3) were counted using Zeiss binocular microscope at an overall magnification of 400X. The uranium content in the phosphatic nodules was determined by comparing track density of unknown and standard using the following relation (Fleischer et al., 1975);

$$C_{ux} = \frac{T_x}{T_s}\frac{I_s}{I_x}\frac{R_s}{R_x}C_{us}$$

Where C_{ux} and C_{us} are the uranium content in the unknown and standard samples, T_x and T_s are the track densities in lexan detectors for the unknown and standard samples, I_x and I_s are the isotopic abundance ratios of U^{235} to U^{238} in the unknown (0.71%) and standard (0.2392%) samples and R_x and R_s are the average etchable ranges of fission fragments in the unknown and standard samples, respectively. The ratio R_s/R_x was assumed to be unity, because the average etchable ranges of fission fragments in the SRM-612 and phosphatic material approximately the same.

6. Result and Discussion

Twelve samples of pinkish brown to dark brown phosphatic nodule were collected from Nawabi Kas, Nurpur, Matin, Gahi, Simbal, Karuli, Malot and Warala areas of Chakwal district, Punjab, Pakistan (Fig. 1). These nodules have high specific gravity and range in size from 1 to 15 mm. These nodules are mainly restricted to the shale in the upper part and are characteristic of the Warcha Sandstone. These nodules are present throughout along strike in a strip of 25 km length.

The uranium content in this study has been found to range from 434±32 ppm to 964±74 ppm with an average value of 699±16 ppm. The average uranium concentration in each nodule has also been given in table 2. It has been observed that some irregular pattern of calcite filled veins on the polished surfaces of the samples have negligible uranium content. Some clusters of fission tracks have also been noted showing a relatively high content of uranium at few places in these nodules. Generally, uranium distribution is uniform and no preferred control of increasing uranium content from core to periphery or vice versa has been noted in these phosphatic nodules.

The results of this study can be compared with the uranium concentration in these phosphatic nodules determined by Nisar (2003), ranging from 470±20 ppm to 786±25 ppm using gamma spectrometry (unpublished M. Sc. thesis). The results of uranium concentration in phosphatic nodules determined with SSNTD technique are in good agreement with uranium concentration determined with gamma spectrometry.

Strong bleaching and uraniferous solution movements are also present in Simbal and Matin areas, in the Eastern Salt Range. The presence of color bandings and bleaching within the sandstones strata due to uraniferous solution movements indicates that some uranium deposit was formed in the vicinity of Matin area, but has possibly been disturbed due to block faulting associated with Salt Range Thrust. Therefore, areas with high radioactivity, bleaching, color bandings and relatively higher values of uranium, both within the sandstone as well as in phosphatic nodules need attention for further exploration (Azizullah et al., 2004).

7. Conclusions

(1) Like volcanic ash beds in Siwaliks, phosphatic nodules may be a possible source of uranium mineralization from where uranium has been leached out and distributed in the Warcha Sandstone of Nilawahan Group, Eastern Salt Range.

(2) The presence of color bandings and bleaching within the sandstones strata due to uraniferous solution movements also support the idea that uranium has been leached from these nodules and possibly precipitated where the geological condition were favorable.

Keeping in view these encouraging results, it is suggested to carry out a comprehensive exploratory work in all other extensions of the Warcha Sandstone, especially in areas having phosphatic nodule beds. It is hoped that these studies would lead to the discovery of new uranium deposit in the Nilawahan Group, Eastern Salt Range.

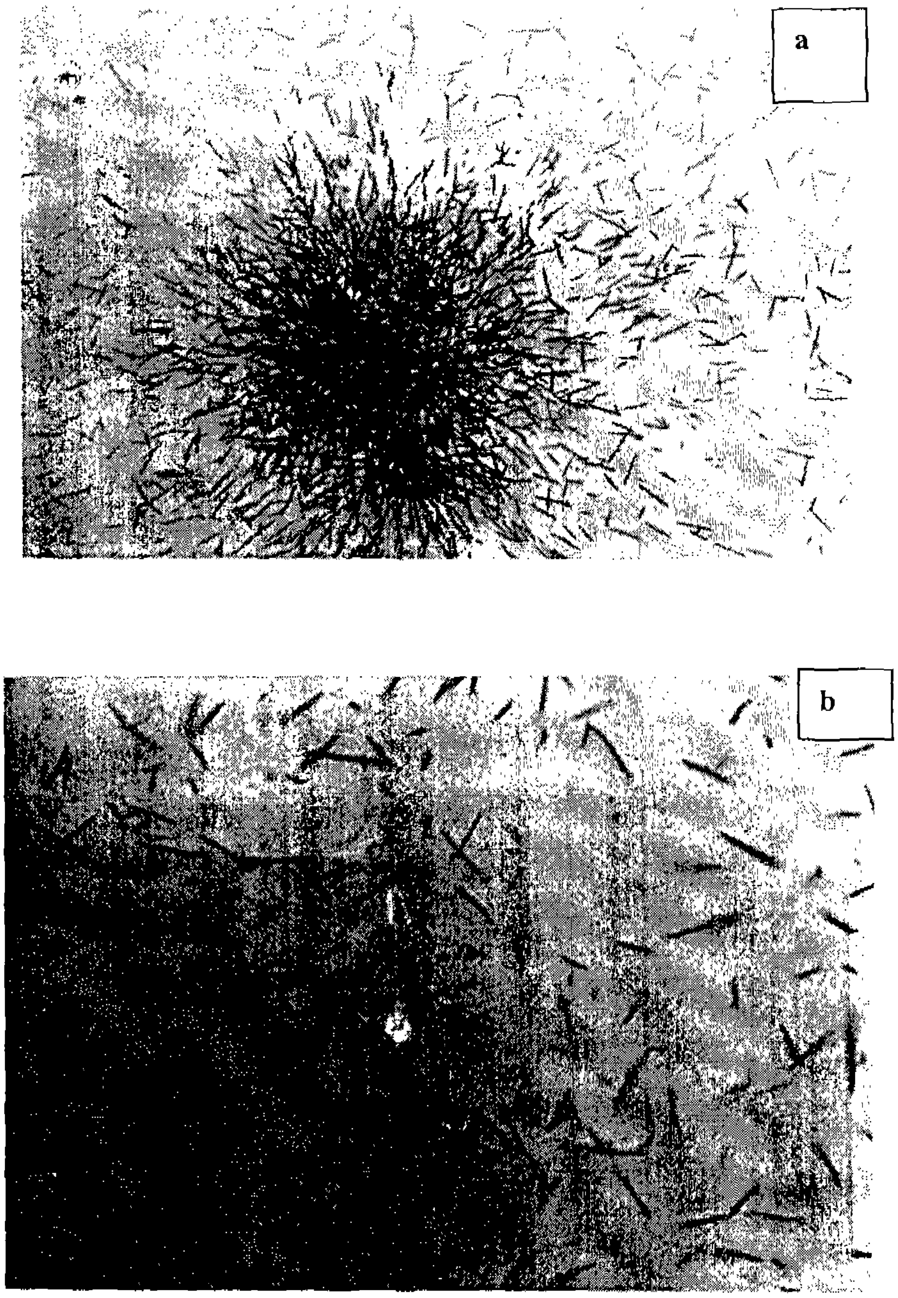

Fig. 3. Photomicrograph of uranium fission tracks in lexan; a) fission star due to localized uranium concentration at x 200 magnification, b) fission tracks showing uniform distribution of uranium in samples at x 400 magnification.

Table 3: Uranium concentration in samples of phosphatic nodules of Warcha Sandstone, Nilawahan group, Salt Range.

Sample No / uranium concentration unknown			***Standard SRM-612**		**Uranium Conc. in sample (in ppm)**
Sample No.	**Tracks per field of view**	**Track Density (tracks cm^{-2})**	**Tracks per field of view**	**Track Density (tracks cm^{-2})**	
KKW-2	423.7	707579	7.5	12525	711±60
KKW-3(a)	413.3	690211	7.5	12525	694±60
KKW-3(b)	332.3	554941	7.5	12525	558±49
KKW-4(a)	490.2	818634	7.5	12525	823±71
KKW-4(b)	552.2	922174	7.5	12525	927±79
KKW-5(a)	378.4	631928	7.5	12525	635±56
KKW-5(b)	362.6	605542	7.5	12525	609±54
KKW-6(a)	258.4	431528	7.5	12525	434±39
KKW-6(b)	306.5	511855	7.5	12525	515±46
KKW-7	395.2	659984	7.5	12525	664±58
KKW-8(a)	574	958580	7.5	12525	964±81
KKW-8(b)	508	848360	7.5	12525	853±72
Mean					**699±62**

*Standard Reference Material 612 was provided by National Bureau of Standards (NBS). It contains 37.38 ± 0.08 ppm ^{238}U with 0.2392 atom % ^{235}U.

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