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Potassium-Argon Ages of Glauconites from a biochronologically dated Upper Jurassic Sequence of Northern Switzerland

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ABSTRACT

Glauconites from two Upper Jurassic sections of northern Switzerland have been dated by the potassium-argon method. The samples were taken out of two marker beds biochronologically dated by ammonites, one bed at the base of the Oxfordian and the other at the base of the Kimmeridgian. The sampled strata are tectonically undisturbed and were never buried deeply. The glauconites are comparatively rich in potassium. The Oxfordian ages are 145, 145 and 146 ± 3 m.y., and the Kimmeridgian ages 137 and 134 ± 3 m.y. The Kimmeridgian glauconites may have been slightly affected by Late Cretaceous and Early Tertiary karst phenomena although no indications of this are evident.

(1) Introduction

Until 1961 many authors considered glauconite to be a promising material for absolute dating of sediments. Later J. D. OBRADOVICH (1965) compiled a large number of potassium-argon ages and found that only 40% of them were within 90–100% of the presumed real age. In his unpublished thesis OBRADOVICH was rather pessimistic about the value of glauconite for absolute dating.

Many of the earliest glauconite measurements apparently were made without much concern about the nature and geologic history of the mineral and therefore cannot be taken at face value.

However, many successful attempts have been made to date glauconites by the potassium-argon method and to correlate the ages with the biochronologic time scale. For instance, N. I. POLEVAYA and coworkers (1961) apparently obtained good results with Precambrian glauconites from geologically stable regions.

For our project we selected two marker beds in the Upper Jurassic of northern Switzerland containing pure, authigenic, potassium-rich glauconite. The beds are biochronologically dated and were never deeply buried or tectonically deformed.

(2) Previous work

The principal studies of glauconite formation, the mineral structure, and of the influence of the embedding sediment during glauconitization on the final chemical and structural character of glauconite have been published since 1935, when E. W.

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GALLIHER presented evidence for glauconite forming out of biotite in Monterey Bay, California. J.-I. TAKAHASHI (1939) showed that glauconite can be formed out of a number of source materials and even replaces faecal pellets. E. D. MCKEE (1945, p. 56) described glauconite concentrated in isochronous marker beds. P. E. CLOUD (1955) gave a summary of the environmental conditions for glauconite formation. J. F. BURST (1958a and b) proposed a classification of glauconites based on the mineral structure. He noted a connection between the structure and chemical composition of authigenic glauconites and the embedding sediment, for which J. HOWER (1961) and BENTOR & KASTNER (1965) gave evidence in detail.

Many workers have attempted to establish criteria for identifying glauconites which will give reliable potassium-argon ages. All authors agree that heating will cause argon loss in glauconite more readily than in biotite. EVERNDEN et al. (1960, 1961) feel that this is the main cause of low apparent ages but their attempts to quantify this factor using diffusion experiments in the laboratory have been frustrated, apparently by the complex nature of the glauconite lattice and the extremely fine grain size. They recommended the use of as coarse glauconite pellets as possible. However, since glauconites are invariably aggregates of tabular, randomly oriented crystals 2–3 microns in diameter (see electron microscope photograph in GYGI 1969, pl. IV, fig. 14), the physical dimensions of the pellets are not the units of diffusion. HURLEY et al. (1960) have emphasized a gradual uptake of potassium associated with decreasing of the expandable layers in the glauconite structure as a cause of low apparent ages. However, sedimentologic evidence shows that glauconitization occurs during early diagenesis, and the major argument of HURLEY et al. that older glauconites generally have higher potassium contents has been disproved by the large compilation of data by OBRADOVICH (1965). The apparent success of POLEVAYA et al. (1961) in dating Precambrian glauconites must mean that tectonic stability and a thin overburden of younger sediments play an important role in the argon retentivity of glauconites (cf. HURLEY 1961, p. 295).

Thus, glauconites *may* give reliable age results if they

(1) are pure and have a well-ordered lattice, which is only the case with dark green, heavy glauconites rich in potassium and ferrous iron;
(2) have not been critically heated after formation
   - by the accumulation of younger sediments on top, or burial by overthrust nappes and consequent isostatic displacement into deeper, warmer levels,
   - by intrusive igneous bodies,
   - by regional metamorphism;
(3) are not tectonically deformed;
(4) are fresh.

(3) **Problem**

The Permian to Tertiary sedimentary column of northern Switzerland north of the folded Jura Mts. was scanned for marker beds containing authigenic glauconite and fossils sufficient to provide correlation with the biochronologic time scale. Only two beds, one in the Randen Mts. (Canton Schaffhausen) marking the base of the Ox-

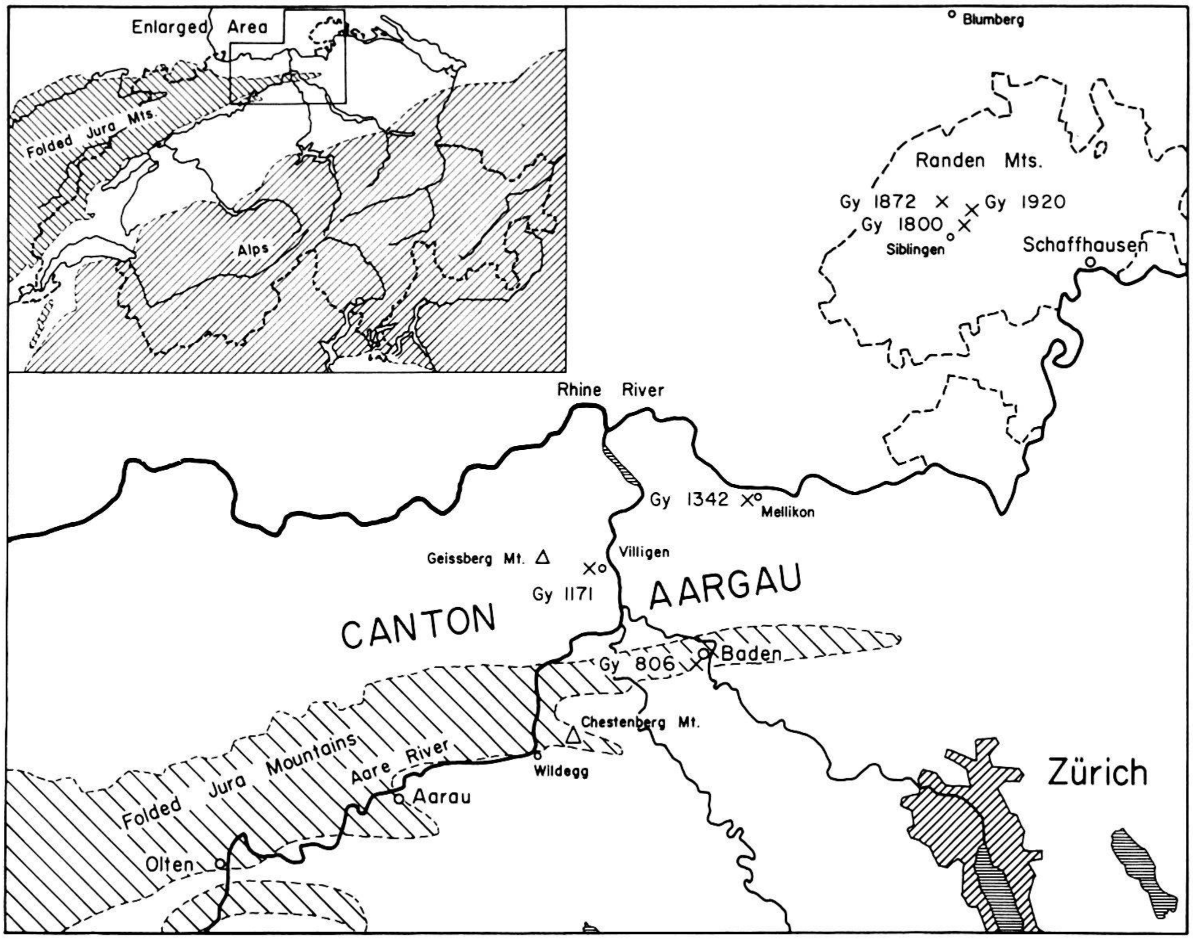

Fig. 1. Location of glauconite samples.

fordian stage and the other in Canton Aargau at the bottom of the Kimmeridgian, both Upper Jurassic, were found to be suitable (Fig. 1).

In Canton Aargau the Lower Oxfordian bed (Fig. 2) is a brown, marly limestone, 10 to 30 cm thick with chamosite and goethite ferruginous oolites and a shining hard-ground on top. In northern Switzerland it can be followed through the southern Jura Mts. to the Rhine River. From the Randen Mts. through the Swabian and Franconian Alb (southern West Germany) the horizon is a marly, dark grey clay with up to 30% glauconite and some quartz sand and mica, mainly biotite. The thickness varies between 10 cm in the Randen Mts. and 3 m east of Blumberg (Fig. 1). In the Aargau the bed is rich in ammonites but almost devoid of glauconite, whereas in the Randen Mts. there are few well-preserved ammonites and high percentages of glauconite. Two ammonites found in the Randen Mts., *Perisphinctes* (*Otosphinctes*) *paturattensis* (DE LOR.) and a *Cardioceras* s. str. sp., allow a time correlation with Canton Aargau, where the species are present together with *Lamberticeras lamberti* (QU.), *Goliathiceras* (*Goliathites*) (= *Herznachites*) *helveticus* JEANNET, and Cardioceratids of the cordatum zone (GYGI, 1966).

The Lower Kimmeridgian bed can be traced from Chestenberg Mt. northeast to the Rhine River (Fig. 1). It is a marly limestone about 1 m thick with abundant fossils, mainly ammonites, and up to 5% glauconite. Its upper part greatly increases in thick-

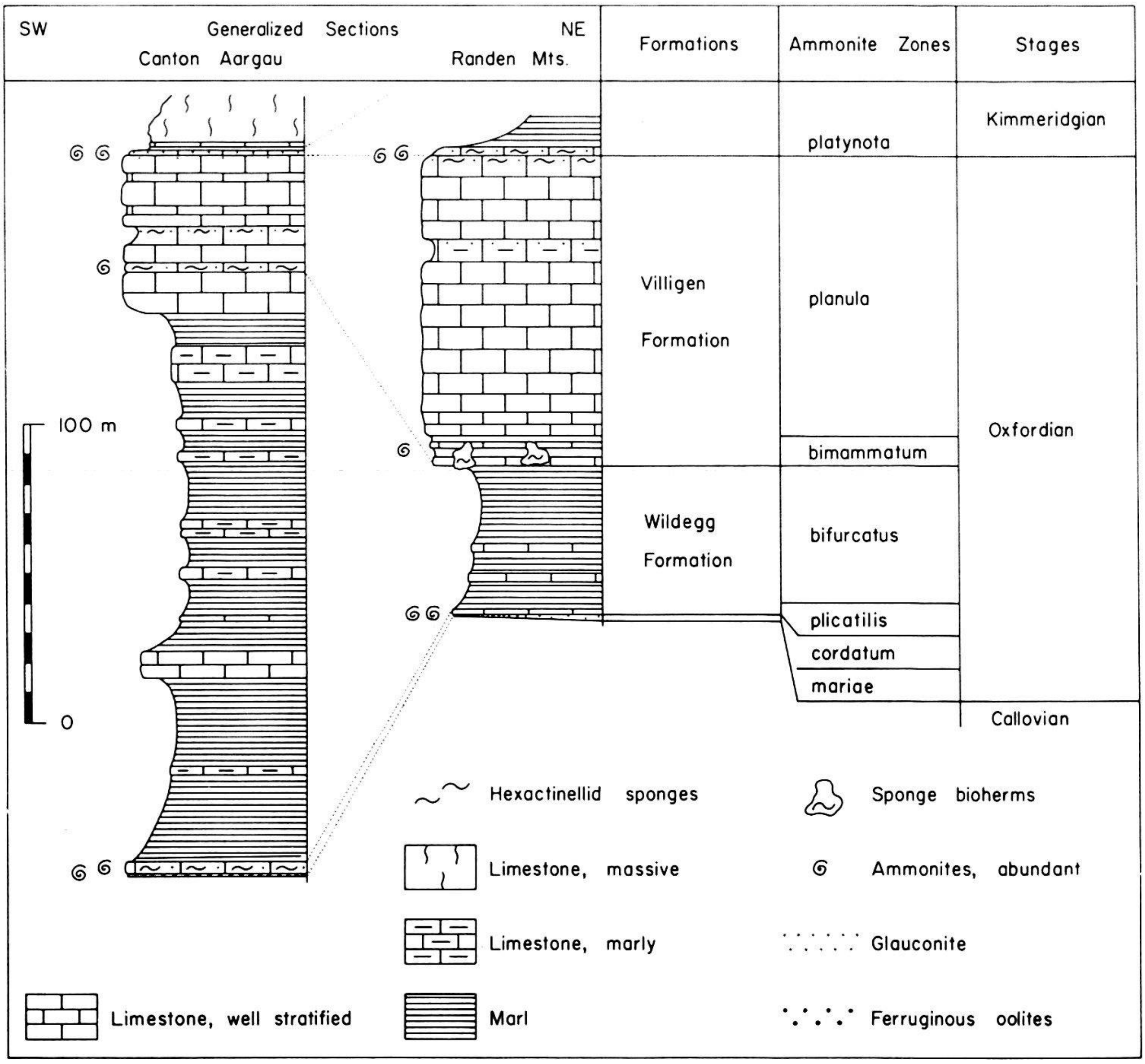

Fig. 2. Generalized sections of the Oxfordian in Canton Aargau and the Randen Mts. (Ct. Schaffhausen).

ness from Canton Aargau to the Randen Mts. There the corresponding sequence has a base of marly limestone about 1 m thick full of ammonites, but with very little glauconite, grading upward into a marl more than 20 m thick. Among the many ammonite species of this horizon found both in Canton Aargau and the Randen Mts., the small *Sutneria platynota* (REIN.) allows an unusually precise time correlation between the two regions.

Samples were taken at three different localities from the Lower Oxfordian (lamberti ?, mariae and cordatum zones) of the Randen Mts. and at three outcrops from the Lower Kimmeridgian (platynota-subzone) of Canton Aargau (Fig. 1). Their glauconite seems to be all authigenic (see below).

The Lower Oxfordian bed in the Randen Mts. was probably never buried deeper than 400 m. The Kimmeridgian bed in the Aargau once had an overburden of Upper Jurassic and possibly some Cretaceous estimated at less than 300 m. This was reduced during the Late Cretaceous and Early Tertiary to an average of 20 m. Then younger Tertiary and Quaternary sediments totalling less than 200 m were deposited. Thus the sampled Lower Kimmeridgian rocks were never buried more than 300 m.

In both areas tectonic activity during the Tertiary produced only insignificant faulting and jointing of the strata.

We have attempted to compare the glauconite ages both within the individual beds and between the two. Comparison of Oxfordian and Kimmeridgian ages is handicapped by the fact that all Lower Oxfordian samples are from the Randen Mts. and the Lower Kimmeridgian ones from Canton Aargau. However, this is believed to be unimportant because the time correlation between these regions can be made with an estimated error not greater than 3 million years for the Lower Oxfordian bed, which contains in the Randen Mts. two, possibly three condensed ammonite zones, and less than 1 m.y. for the Lower Kimmeridgian bed representing one subzone. The average time for an Upper Jurassic ammonite zone can be estimated at about 1 m.y.

(4) Methods

The Lower Oxfordian clay was dried after sampling and immersed in acetone followed by water. The samples were then sieved into fractions between 88 and 420 microns. Many glauconite pellets had an oxidized brown surface crust which is probably a product of diagenesis rather than weathering (GYGI, 1969). The oxidation also penetrated deep grooves found on many of the larger grains. Ultrasonic grinding rapidly removed the brown crust on the outer pellet surface, but the grooves with oxidized material could not be eliminated without losing most of the glauconite. By grinding away about 50% of the glauconite sample the oxidized impurities were reduced to 1% or less. Calcite, quartz and most mica could be separated magnetically and the rest of biotite and goethite in bromoform adjusted with acetone.

The Lower Kimmeridgian samples Gy 806 and Gy 1342 were carved out of clayey veins within the nodular limestone and were processed like the Oxfordian ones. The limestone sample Gy 1171 was run through a crusher and a mill. Sample Gy 806 contains unaltered biotite and all intermediate stages to pure glauconite, indicating that the glauconite is authigenic and formed from biotite. However, a satisfactory separation was impossible. In the other samples part of the glauconite can similarly be shown to be derived from biotite. In the Lower Kimmeridgian bed a part of the glauconite occurs in the interior of skeletal grains or algal nodules, replacing calcite. Thus, it is authigenic. Since both the Oxfordian and the Kimmeridgian marker beds contain some detrital quartz, a portion of their glauconites may as well be of detrital origin. Transported glauconites are well rounded and have a dull surface without grooves (GYGI, 1969). No such grains were noted in an examination of the samples prior to ultrasonic treatment.

The glauconites were examined in thin section and under the electron microprobe for inclusions and were found to be pure. The X-ray diffraction diagrams showed monomineralic, disordered glauconite (after BURST). The lattice of the Kimmeridgian glauconites is slightly better ordered than that of the Oxfordian ones (Fig. 3). This correlates with the potassium values found by isotope dilution; the Oxfordian glauconites are all below 6% potassium whereas the Kimmeridgian ones are well above this value (Table 1). This observation supports the results of HOWER (1961) and BENTOR & KASTNER (1965) that the potassium content of glauconite is related to the amount of clay in the embedding sediment during glauconitization, and is another indication that these glauconites are authigenic.

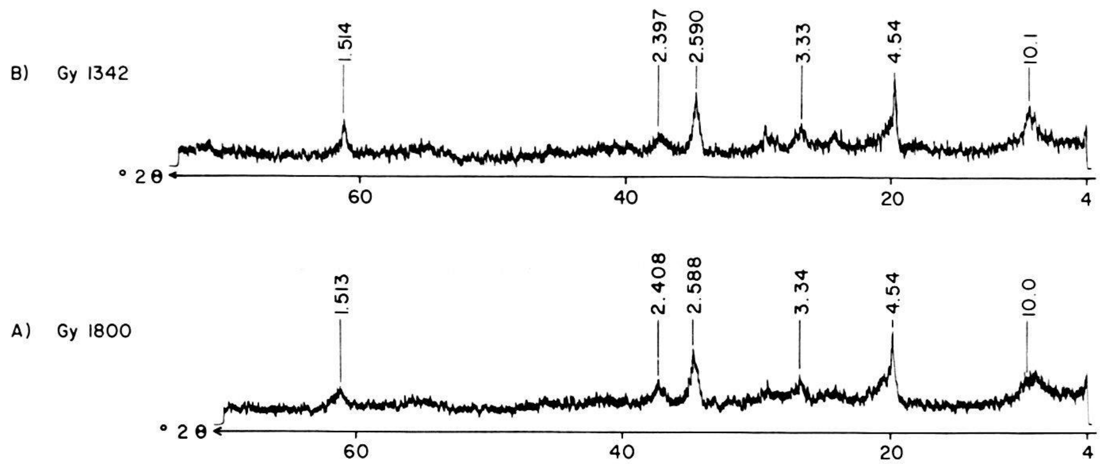

Fig. 3. X-ray diffractograms of a Lower Oxfordian (A) and a Lower Kimmeridgian sample (B). Source: Cu. Localities of samples see Figure 1.

Potassium was determined by the isotope dilution method using K^{41} as the diluent (spike). The isotope ratios were measured on an Atlas CH 4 solid-source mass spectrometer using a double filament technique. Mass discrimination was frequently monitored by measuring the isotopic ratio of unspiked samples and shelf solutions and was found to be constant within $\pm 0.6\%$. Analyses of interlaboratory standards and 119 duplicate determinations indicate an accuracy better than 1% and a standard deviation of $\pm 0.56\%$ (MCDOWELL, in prep.).

Argon was extracted from the minerals at about 1800 °C with a resistance furnace and measured by the isotope dilution technique with an Ar^{38} spike. Isotope ratios were obtained on a Reynolds-type mass spectrometer operated statically. The detailed apparatus and operating techniques are described by SIGNER & MCDOWELL (in prep.). Analyses of interlaboratory standard minerals indicate an accuracy of 1%, while 167 replicate measurements indicate a standard deviation of $\pm 1.00\%$ for a single measurement.

The analytical data are given in Table 1. The errors represent 2σ limits calculated from pooled replicate Ar and K data.

(5) Interpretation

J. L. KULP (1961a) placed the beginning of the Callovian at 150 m.y. According to time scale estimates of KULP (1961b), POLEVAYA et al. (1961) and M. K. HOWARTH (1964), the Jurassic/Cretaceous boundary occurs at 135 m.y. Using these figures our Oxfordian ages (145–146 m.y.) fall about as expected. If the average time of an ammonite zone is 1 m.y., the interval between the Oxfordian and Kimmeridgian horizons would be about 5 m.y. The measured ages indicate about double the span.

Table 1. Potassium-argon ages of Upper Jurassic glauconites from northern Switzerland.

Sample	Locality/horizon	% $CaCO_3$	% K	rad. Ar^{40} / total Ar^{40}	rad. Ar^{40} $\times 10^{-5}$ scc/g	Age (m.y.)
Gy 1171	Villiger Geissberg	86.7	6.39	0.935	3.61	137 ± 3
	Lower Kimmeridgian			0.955	3.62	
	62/121*)					
Gy 1342	Mellikon	73.4	6.29	0.937	3.54	134 ± 3
	Lower Kimmeridgian		6.44	0.962	3.51	
	70/124*)		6.40			
Gy 1800	Schlossranden	21.4	5.81	0.948	3.47	145 ± 3
	Lower Oxfordian		5.80			
	80/5*)					
Gy 1872	Lang Randen	18.7	5.95	0.946	3.59	146 ± 3
	Lower Oxfordian		5.99			
	81/3*)					
Gy 1920	Churz Tal	24.3	5.75	0.890	3.46	145 ± 3
	Lower Oxfordian			0.954	3.43	
	82/5*)					

$\lambda\beta = 4.72 \times 10^{-10}$ year^{-1}, $\lambda e = 0.585 \times 10^{-10}$ year^{-1}, $K^{40}/K = 1.19 \times 10^{-4}$ atoms per atom.
*) Detailed stratigraphic data of the samples are given in Gygi (1969).

As mentioned above, some of the Oxfordian glauconites are oxidized superficially and along grooves extending well beneath the surface of the pellets. There is evidence that this oxidation occurred shortly after glauconitization and consequently had no significant influence on the measured ages. Since the pellets were formed in an impermeable sediment they were probably not exposed to later diagenetic processes other than compaction of the embedding clay. In contrast the Kimmeridgian horizon was at both sampled localities within about 10 m of the surface for several million years during the Late Cretaceous and Early Tertiary. The bed is a marly limestone. In some places on the south slope of Chestenberg Mt. the Jurassic limestones directly below the Tertiary are thoroughly weathered many meters down from the old surface. Fossil caliche (calcareous crusts, probably of Early Oligocene age, see Hofmann & Gygi, 1961) on top of the limestones indicates that intense leaching of calcium carbonate has taken place. However, the Kimmeridgian glauconites show no signs of oxidation or any other alteration and have a somewhat better ordered lattice than the Oxfordian ones. We have found no evidence in thin section, X-ray, electron microscope or microprobe observations for any late- or post-diagenetic alteration of the Kimmeridgian glauconites. Thus the unexpectedly large time interval between our Oxfordian and Kimmeridgian ages cannot be interpreted.

Borsi et al. (1966) found a 150 m.y. age of an Upper Jurassic (post Kimmeridgian) intrusive from the Hellenides. This indicates that our glauconites may have lost about 10% of their radiogenic argon content since formation. At this time we cannot evaluate our results relative to the contradictory time scale data. An attempt will be made to check the Kimmeridgian ages by dating hornblende of possible volcanic origin, which was observed in thin section and during the separation of sample Gy 806.

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