

## Werk

**Jahr:** 1979

**Kollektion:** fid.geo

**Signatur:** 8 Z NAT 2148:46

**Digitalisiert:** Niedersächsische Staats- und Universitätsbibliothek Göttingen

**Werk Id:** PPN1015067948\_0046

**PURL:** [http://resolver.sub.uni-goettingen.de/purl?PPN1015067948\\_0046](http://resolver.sub.uni-goettingen.de/purl?PPN1015067948_0046)

**LOG Id:** LOG\_0025

**LOG Titel:** Rinneite-dating of episodic events on potash salt deposits

**LOG Typ:** article

## Übergeordnetes Werk

**Werk Id:** PPN1015067948

**PURL:** <http://resolver.sub.uni-goettingen.de/purl?PPN1015067948>

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*Short Communication*

**Rinneite-Dating of Episodic Events  
in Potash Salt Deposits**

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**Introduction**

When reviewing the state of isotope chronometry on salt rocks (Lippolt, 1977) we directed our attention to the salt mineral rinneite ( $\text{NaK}_3\text{FeCl}_6$ ) which occurs as metasomatic secondary product in salt deposits. Rinneite is formed as well in the early phases of metamorphism (Kokorsch, 1960; Siemeister, 1969) as during late tectonic disturbances of the salt beds (Hartwig, 1922). Siemeister (1969) distinguished six types of rinneite paragenesis in bed Ronnenberg of the Salzdetfurth mine, Southern Hannover. Though the chemical formula and analyses by Kühn (1972) prove that rinneite contains plenty of potassium and rubidium, this mineral has not been used for isotopic dating so far. When clean, rinneite appears transparent, otherwise pink, yellow or violet. At open air the surface turns brown by oxidation. Rinneite is soluble in water, but as long as it is protected by the salty environment, it was shown to be stable above 26.4°C. Rinneite was discovered in 1908 in the Wolkramhausen mine south of the Harz mountain and investigated by Boeke (1908; 1909). In this mine it occurred in large, meter-sized lenses within carnallites. Later on it was found in all the mining districts around the Harz mountain and in the Hannover plain, occasionally as layer but as well as single crystals or very fine-grained in kieserite – sylvinehalite rocks. Rinneite also occurs fairly commonly in the English potash fields (Stewart, 1956).

**The Samples**

In order to get some experience with rinneite as dating mineral we asked Dr. R. Kühn (Hannover) for some of the samples which he had used for his review of Rb abundances in salt minerals (Kühn, 1972). Four samples were selected for Rb-Sr analyses, two of them representing vein fillings and the two others secondary components in rocks of the salt beds:

1. Pure rinneite from a fissure vein in the Grey Salt Clay, 1,050 m floor of field Siegfried in the salt mine Giesen.

2. Rinneite, carnallite and clay from a patchy filling of a vein in the Grey Salt Clay T3, 1,050 m floor, field Rössing-Barnten, mine Giesen.

3. Pure rinneite clusters in seam Staßfurt of the mine Hildesia/Diekhöhlen (corresponding with sample 1 of Table 5 in Kühn, 1972)

4. Pure rinneite from rinneite patches above the upper part of the carnallite seam below sylvine bed Ronnenberg (corresponding with sample 2 of Table 5 in Kühn, 1972), Salzdetfurth mine.

The salt mine Siegfried-Giesen belongs to the Sarstedt-Lehrte diapir (mining district Central Hannover), Hildesia and Salzdetfurth are situated in the Hildesheim-Wald salt structure (district Southern Hannover). Both districts are about 20 to 40 km SE of the city of Hannover. The geologic and petrologic settings of these salt mines have been described by Middendorf and Kühn (1966) and by Kokorsch (1960) and Siemeister (1969) respectively. Jaritz (1973) compiled the observations concerning the ages of diapir formation in this area.

### The Rb-Sr Analyses

The results of our analyses are presented in Table 1. Six Rb-Sr and K analyses have been performed. Rb and Sr were measured by mass spectrometry, potassium by flame photometry. Calibrations were achieved by comparison with international chemical standard samples. The potassium concentrations measured are typical for rinneite. Our Rb-results on rinneite III and IV agree well with the values given by Kühn (1972). Sr had not been measured so far. In three cases its concentration was about 1 ppm, in one case we found

**Table 1.** Analytical results on rinneite samples

Sample	Salt mine	Concentrations			$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Model ages <sup>b</sup> [Ma]
		K (%)	Rb (ppm) <sup>a</sup>	Sr (ppm) <sup>a</sup>			
I. Rinneite	Siegfried/ Giesen	28.2	257	0.79	943	1.125	31.0 ± 0.8
II. Rinneite	Siegfried/ Giesen	29.3	218	6.54	96.7	0.735	19.8 ± 0.6
II. Carnallite (+ Rinneite)	Siegfried/ Giesen	20.4	207	3.95	152	0.726	8.5 ± 0.3
II. Clay	Siegfried/ Giesen	0.65	12	626	0.054	0.7077	—
III. Rinneite	Hildesia	30.6	131	1.18	322	1.091	83.4 ± 1.8
IV. Rinneite	Salzdetfurth	28.7	128	0.57	645	1.373	72.2 ± 1.8

<sup>a</sup> Analytical errors ≤ 1%

<sup>b</sup> Using  $\lambda = 1.42 \cdot 10^{-11} \text{a}^{-1}$  [Steiger and Jäger (1977)] and 0.7077 as initial ratio

6.5 ppm. This results in fairly high Rb/Sr ratios of about 30 to 300. For the time being only model ages can be calculated as only for rinneite II an approximative initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio could be determined (clay from sample II). We consider this value to be tentative because nothing is known about homogenization of Sr isotopes between salt minerals and clay during salt rock metamorphism. This lack of information however is insignificant as the Rb/Sr ratios and the present  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are fairly high. The analytical accuracy is given in the table. It seems to be better than necessary in order to come to geologically meaningful conclusions taking in account that the present level of knowledge on the feasibility of salt rock dating is still very low.

### Discussion of the Rb-Sr Ages

The model ages of the four rinneites are Cretaceous and Middle Tertiary. The four dates differ significantly from each other. As rinneite normally is thought to be a replacement mineral we have not expected them to yield Permian ages. Assuming appropriate retentivity we expected their ages to be equal to or lower than the time of the last regional metamorphism of these deposits. After Kokorsch (1960) and Siemeister (1969) this may have happened in Jurassic or Lower Cretaceous times. The isotopic ages of products of this metamorphism which have been determined so far rather date this metamorphism at the boundary Lower to Upper Cretaceous (K-Arges, langbeinite ages by Osterle and Lippolt (1976) and Trümmer-carnallite age by Büchler et al., 1979). Rather high ages which correspond to Upper Cretaceous times (83 and 72 m.y.) were found for the rinneites of the Hildesheim-Wald salt ridge. These ages obviously confirm the view of Kokorsch (1960) and Siemeister (1969) that the rinneite of this paragenesis was formed during the early stages of the late mesozoic metamorphism. Relatively low Rb-Sr ages were found for the rinneites from vein fillings close to the Grey Salt Clay in the Sarstedt salt structure. They correspond to Upper Oligocene (31 m.y.) and Lower Miocene times (20 m.y.). The geological situation from which the rinneites I and II were taken is very different from that of rinneite III and IV. Already Hartwig (1922) and later Kühn (1966) made it clear that the rinneite associated with vein fillings in the neighbourhood of the Grey Salt Clay was formed as late replacements following tectonic disturbances after the rise of the diapirs. We therefore conclude that also in this case the rinneite ages point to a geological event in the history of the salt dome.

For the time being we can only speculate if the age difference between the members of the Cretaceous and the Tertiary rinneite pairs could have a geological meaning. As Osterle and Lippolt (1976) observed that langbeinite ages of different salt seams within one mine show systematic age differences, it might be possible that the rinneite ages III and IV indicate that the time of metamorphism for the potash seams Staßfurt and Ronnenberg was not the same. The differing ages of rinneites I and II could mean that they date tectonic activities in central Germany just before and after the main volcanic phase in many volcanic centers of the Rhenish shield (~25–23 m.y.).

There can be no doubt that the feasibility of rinneite dating and the speculations mentioned above have to be checked by further analyses. In order to do this we have already taken more samples from the two salt structures Hildesheimer-Wald and Sarstedt-Lehrte.

The carnallite associated with the rinneite II yielded a much younger Rb-Sr age (8.5 m.y.). At present we do not know whether this means that the carnallite was formed later than the rinneite or that it lost radiogenic  $^{87}\text{Sr}$  after its deposition.

*Acknowledgement.* We thank Professor Kühn (now Wilhelmsfeld/Odenwald) for providing the samples and advice and H. Funke for technical assistance.

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Received May 22, 1979; Revised Version July 17, 1979; Accepted August 10, 1979