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Natural Cd-contents of a Permo-Carboniferous-Mesozoic sequence in a drillhole in Weiach (N-Switzerland): A contribution to the geochemistry of Cd

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Abstract

Cd-contents in a 1800 m sedimentary sequence were determined. Cd correlates with Zn and higher contents seem to be incorporated in Zn-bearing sulfides. 70% of the samples contain less than 200 ppb Cd. The limiting total content of 800 ppb Cd in soils as a criterion for pollution will be applicable in most cases, but could be exceeded if the bedrock is enriched in natural Zn sulfides.

Keywords: Cd-content, sedimentary rocks, sulfide, Weiach drillhole, Switzerland.

Introduction

Together with Pb and Hg, cadmium is considered, from a medical point of view, to be one of the most hazardous common trace elements. Although there are quite a number of data on anthropogenically polluted soils and sediments (Förstner and Müller, 1974), very little is known about the natural Cd-content in rocks and soils (Bowen, 1979). The fully cored, continuous Permo-Carboniferous–Mesozoic, 1800 m long sequence in the Weiach drillhole of the NAGRA radioactive waste disposal research program offered the unique opportunity to investigate the natural Cd-concentrations. The availability of detailed geological, mineralogical and chemical data (Matter, Peters, Bläsi, Meyer, Ischi, 1987) permitted correlations of the Cd-concentrations with sedimentary environment, mineralogy and chemistry.

Analytical Method

The samples were ground in Tungsten carbide mills to a grain size below 5 microns.

In a first step, the samples (0.5 grammes) were treated according to the method described by Terashima (1984). After nitric and hydrofluoric acid decomposition of the sample, Cd and several other cations are extracted as iodide into methylisobutylketone (MIBK) from an aqueous solution of phosphoric acid. From the resulting MIBK extract, however, Cd was not determined directly by atomic absorption spectrometry (AAS) but was further extracted with 0.01 N HCl. Cd in the HCl extract was determined with dithizone, as described by Koch (1974, pages 581 and 582).

Reproducibility was ±10% and the detection limit 40 ppb. As no special Cd standard was available, 10 international rockstandards with specifications for Cd were analysed. The results are shown in table 1. Omitting the standards GA, GH and Sy-3, the published values and ours differ from 10 to 35 ppb for the range up to 500 ppb.

Results

The Cd-contents are presented in Fig. 1,

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Tab. 1 Comparison of Cd determinations on international rock standards with published values. Cd contents in ppb.

Standard	this study	published
NIM-L	919/944/1041/1006/862/851	910±12 /1005 / 630
SY-2	198/221/319/236	207
GA	156/147	77 /14 /85
GH	220/229	121 /83 /46
QLO-1	52/67	43
SY-3	393/481	194
SDC-1	89/59	40
JB-1	67/110	103±7 /94 /114
NIM-N	42/48	70 /82 /47
NIM-G	100	113±7 /116 /130

Elson et al., 1978

Govindaraju, and de la Roche, 1977

Heinrichs, 1979

Rosman and De Laeter, 1980

Terashima, 1984

Yamada et al., 1970 (AA, in: Terashima, 1983, in Japanese)

together with the schematic lithological profile, some mineralogical parameters and Zn-contents. Cd-contents vary from the detection limit (40 ppb) up to 3800 ppb, whereby most values are below 200 ppb.

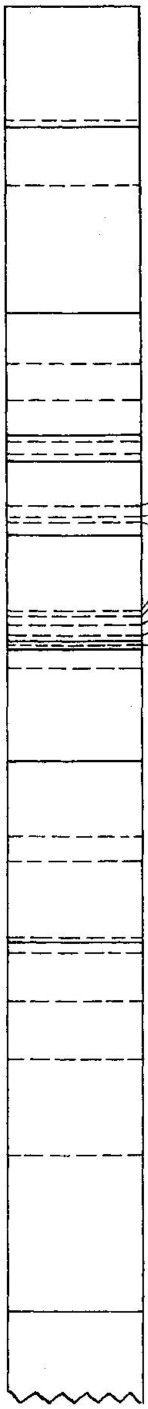
Within the stratigraphy there is no systematic trend of the Cd-contents. As reported previously by MATTER et al. (1987), a strong correlation between the amount of clay minerals and metallic trace elements was found. A similar trend was expected for Cd, but no such tendency could be detected, neither with other mineral phases such as quartz, carbonates or sulfates.

A significant correlation was observed between Zn and Cd, as was to be expected from earlier studies (IVANOV, 1964; BUTLER and THOMPSON, 1967). The correlation factor of R = 0.93 results from the higher Cd- and Zn-contents as well as for all results (Fig. 2).

Because of analytical difficulties in the determination of sulfide-contents, a possible trend between Cd and sulfides is totally obscured. Even in the Lower Muschelkalk and the Buntsandstein, where stratabound sulfide mineralisations are frequent (HOFMANN, 1985).

Discussion

The high concentrations of Cd encountered in the sediments seem to be incorporated in Zn sulfides. As 18 out of 22 samples contain less than 200 ppb Cd, the upper limit of 800 ppb HNO_3 extractable Cd as foreseen in the Swiss legislation for soils is sensible as a guideline. However, considering the fact that 15 to 20% of the samples show higher concentrations, this limit should not be applied too rigorously.



Stratigraphy	Depth (m)	Depth of Sample (m)	Clay Content %	Quartz %	Carbonate %	Anhydrite %	S %	Zn ppm	Cd ppb
	0								
Molasse									
	186	178	87	10	3		0.2	113	n.d.
Malm		275	42	8	50		0.8	31	65
	478								
Dogger		551	40	7	53		0.1	91	81
		610	73	14	12		0.3	117	95
Lias	666	676	50	5	38		2.5	69	498
	704	697	49	2	48		0.6	27	113
Keuper		773	49	2	n.d.	70	16.4	n.d.	n.d.
		790	52	4	28	26	6.2	35	199
	820	799			1	90	21.2	n.d.	n.d.
		937			10	46	10.9	24	155
Muschelkalk		945	26	3	70	–	0.8	330	2450
		959	58	9	29	–	0.5	78	106
Buntsandstein	981	975	39	14	31	–	0.6	41	133
	991	988	40	35	13	1	0.2	298	2800
		1024			3	1	0.1	121	149
Oberrotliegendes									
	1170								
Unterrotliegendes		1287			21	–	0.2	157	681
		1323	90	8	–	–	0.1	61	89
	1450	1443		8	–	–	0.2	72	950
		1466	84	5	3		0.2	45	121
		1540	85	7	3		0.2	73	64
		1630	83	5	6	–	0.1	78	203
Carboniferous									
		1779	87	11	–	–	0.2	349	3900
	2020								
Crystalline Basement									

Fig. 1 Stratigraphic column with sample localities, mineralogy and Zn- and Cd-contents.

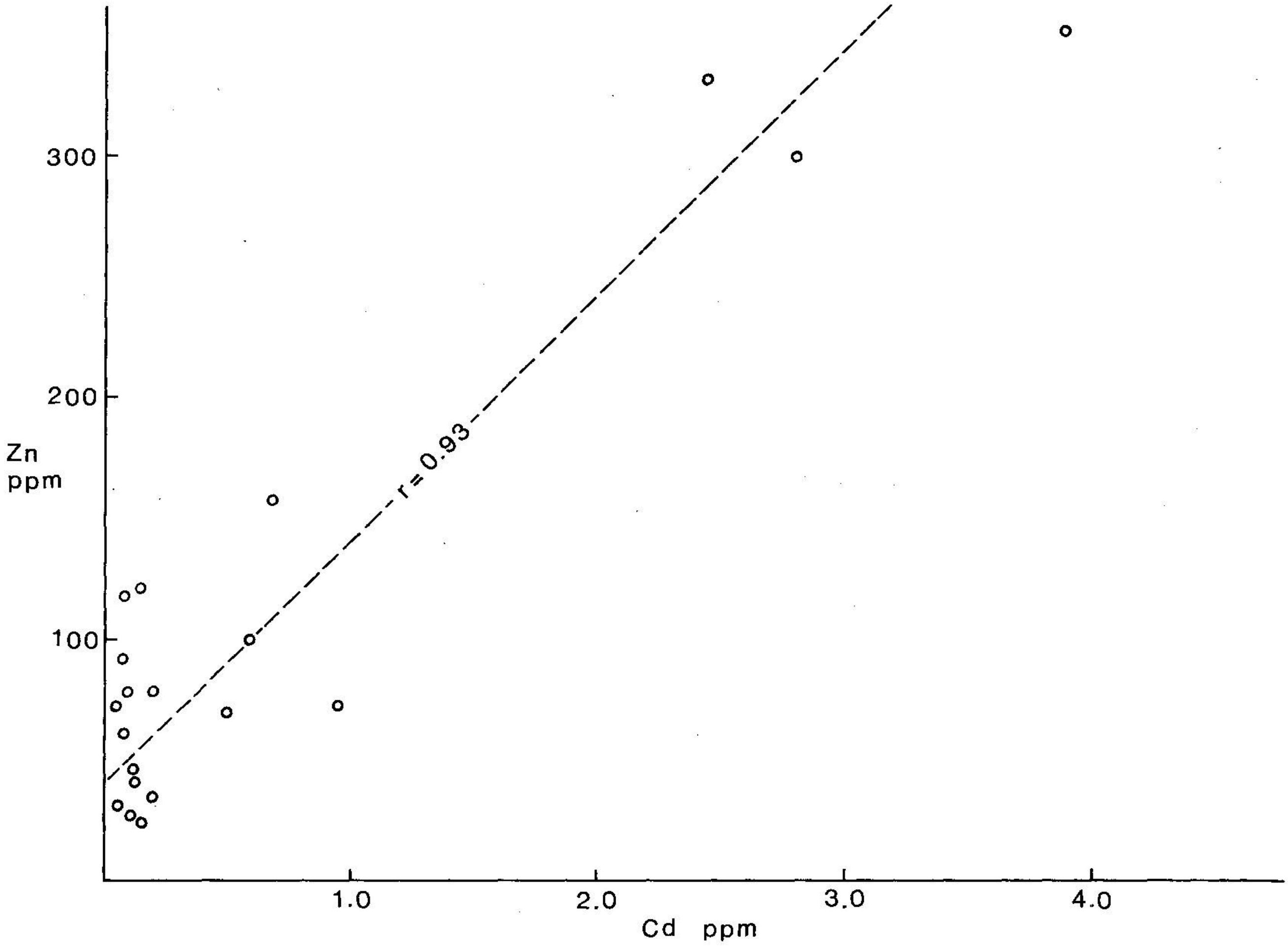


Fig. 2 Zn-Cd correlation diagram.

Especially if the subsoil contains small amounts of Zn-bearing sulfides, this limit is exceeded without any additional anthropogenic contribution.

For all practical purposes, samples containing less than 100 ppb Zn hardly need to be analyzed for Cd.

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References

BOWEN, H.J.M. (1979): Environmental chemistry of the elements. Academic Press, London.

BUTLER, J.R. and THOMPSON, A.J. (1967): Cadmium and Zinc in some alkali acidic rocks. Geochim. Cosmochim. Acta 3, 97.

ELSON, C.M., DOSTAL, J., HYNES, D.L. and DE ALBUQUERQUE, C.A.R. (1978): Ag, Cd and Pb-contents of some rock reference samples. Geostandard Newsl. 2/2, p. 121.

FÖRSTNER, U. und MÜLLER, G. (1974): Schwermetalle in Flüssen und Seen als Ausdruck der Umweltverschmutzung. Springer-Verlag Berlin. 225 p.

GOVINDARAJU, K. and DE LA ROCHE, H. (1977): Rapport (1966-1976) sur les éléments en traces dans trois roches standards géochimiques du CRPG: Basalte BR et Granites, GA et GH. Geostandards Newsl. 1, 67-100.

HEINRICHS, H. (1979): Determination of bismuth, cadmium, and thallium in 33 international standard reference rocks by fractional distillation combined with flameless atomic absorption spectrometry. Fresenius Z. Anal. Chem. 294, 345-351.

HOFMANN, B. (1985): Mineralisationen von Pb, Zn, Cu und As in der Trias des südöstlichen Schwarzwaldes. Das Kristallin an der Oberen Wutach als Beispiel eines möglichen Liefergebietes von Sedimentmaterial und erzbildenden Elementen. Lizentiatsarbeit Univ. Bern, 188 p.

IVANOV, V.V. (1964): Distribution of Cadmium in ore deposits. Geochemistry (Engl. translation) 8, 757.

KOCH, O.G. und KOCH-DEDIC, G.A. (1974): Hand-

buch der Spuren-Analyse. 2. Aufl., Springer-Verlag.
MATTER, A., PETERS, TJ., BLÄSI, H.R., MEYER, J. und ISCHI, H. (1987): Sondierbohrung Weiach - Geologie. NAGRA Techn. Bericht NTB (88-01). NAGRA Baden.
ROSMAN, K.J.R. and DE LAETER, J.R. (1974): Mass spectrometric isotope dilution analyses of cadmium in standard rocks. Chem. Geol. 13, 49-74.
ROSMAN, K.J.R. and DE LAETER, J.R. (1980): Mass spectrometric isotope dilution determination of cadmium in geochemical reference samples. Geostandards Newsl. 4, 1-3.
TERASHIMA, S. (1983): Determination of trace amounts of cadmium and lead in geological samples by solvent extraction and atomic absorption spectrometry. Bull. geol. Surv. Japan 34, 553-559.
TERASHIMA, S. (1984): Determination of Cadmium and Lead in Seventy-seven Geological Reference Samples by Atomic Absorption Spectrometry. Geostandards Newsl. 8/1, 13-16.

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