

Strontium isotopes in the Zechstein (Upper Permian) anhydrites of Poland: evidence of varied meteoric contributions to marine brines

Rodger E. DENISON and Tadeusz Marek PERYT



Denison R. E. and Peryt T. M. (2009) — Strontium isotopes in the Zechstein (Upper Permian) anhydrites of Poland: evidence of varied meteoric contributions to marine brines. Geol. Quart., **53** (2): 159–166. Warszawa.

Strontium isotope ratios have been determined on 74 anhydrite samples from seven borehole cores in the Polish Zechstein. Five of the borehole cores are located in the basin and isotope results from these samples show a nearly pure marine signal. Results from one borehole core, located near the Zechstein coastline that migrated through time, record a stronger, inconsistent influence of continental strontium to a marine base. Intermittent meteoric influence is recorded in anhydrites from other borehole cores close to the carbonate platform that was emergent during the anhydrite deposition. Consistency of isotope values indicates a marine signal and there is a narrow range in consistent values from ⁸⁷Sr/⁸⁶Sr near Asw –215 (0.70702) for the oldest anhydrites and near Asw –205 (0.70712) for the youngest anhydrites. Comparison with a seawater ⁸⁷Sr/⁸⁶Sr curve based on samples in West Texas and a Permian-Triassic boundary value from China shows that the Polish Zechstein in these seven boreholes is latest Permian in age and major deposition represents a short time interval (~2 million years). Strontium isotope ratios reported by other workers indicate some of the younger Zechstein elsewhere indicate even greater continental influence is in agreement with the interpreted sedimentological setting for those anhydrites.

Rodger E. Denison, Department of Geosciences, University of Texas at Dallas, Richardson, TX 75083 USA, e-mail: denison@utdallas.edu; Tadeusz Marek Peryt, Polish Geological Institute-National Research Institute, Rakowiecka 4, PL-00-975 Warszawa, Poland, e-mail: Tadeusz.Peryt@pgi.gov.pl (received: July 10, 2008; accepted: November 15, 2008).

Key words: Poland, Zechstein, Late Permian, anhydrite, strontium isotopes.

INTRODUCTION

Gypsum precipitating from a salina will record the ⁸⁷Sr/⁸⁶Sr of that brine. If the salina is derived from marine water, the isotope ratio can be used to determine or constrain the age of deposition (Denison *et al.*, 1998). But many brines are, in fact, mixtures of water derived from two or more sources (Hardie, 1984). Evaporite basins can be sourced by marine, continental or even hydrothermal waters. If there is a significant meteoric contribution to a marine based brine pool, the precipitated gypsum will record an ⁸⁷Sr/⁸⁶Sr on a mixing line anchored by the isotope ratio and concentration of seawater strontium and the mean meteoric contribution.

The strontium isotope ratio of 74 Upper Permian Zechstein anhydrite core samples have been determined from seven boreholes in Poland. These measurements were made to better understand the Zechstein salina and determine if the evaporites are derived from marine waters. Geographic and stratigraphic consistency of isotopic results indicates a retained marine signal (Denison *et al.*, 1998). If a retained marine signal can be de-

termined, the age of Zechstein deposition can be accurately defined with a seawater ⁸⁷Sr/⁸⁶Sr curve. We have chosen to use a Late Permian seawater curve defined from samples in West Texas and China. U/Pb ages from zircons in interbedded tuffs in the Chinese sections provide a numeric base for the seawater strontium curve.

GEOLOGICAL SETTING

The Upper Permian Zechstein sequence was deposited in a vast epicontinental basin extending from England in the west to Lithuania and Latvia in the east. The basin is composed of two parts: the Northern and Southern Permian basins and was established due to a catastrophic transgression from the Barents Sea which inundated Late Permian intra-continental topographic depression. During periodic cut-off of those basins from the Barents Sea, evaporates were precipitated in the arid conditions which prevailed during the Zechstein deposition. Four salt cyclothems have been distinguished by Richter-Bernburg (1955) throughout the basin (Table 1). Younger

 $$\rm T\ a\ b\ l\ e\ 1$$ Stratigraphic position of the studied Zechstein anhydrite units (in bold)

	Four		
Zechstein	Third cyclothem, Leine (PZ3)	Younger Halite and Younger Potash	Na3 + K3
		Main Anhydrite	A3
		Platy Dolomite	Ca3
		Grey Salt Clay	Т3
	Second cyclothem, Stassfurt (PZ2)	Older Halite and Older Potash	Na2 + K2
		Basal Anhydrite	A2
		Main Dolomite	Ca2
	First cyclothem, Werra (PZ1)	Upper Anhydrite	A1g
		Oldest Halite	Na1
		Lower Anhydrite	A1d
		Zechstein Limestone	Ca1
		Kupferschiefer	T1

cycles have been recognized in Germany but in Poland these are regarded as subdivisions of the fourth cycle (Wagner and Peryt, 1997). Each of the first three cyclothems is composed of a succession of essentially basinwide lithologies beginning with a thin claystone at the base followed by carbonate, anhydrite and halite (some with potash units). The top of the cyclothem is marked by regressive halite and anhydrite. The final cyclothem begins with claystone followed by anhydrite, then halite, which is commonly interbedded with claystones. The anhydrites of the first cyclothem are the Lower Werra

Anhydrite (A1d) and the Werra Upper Anhydrite (A1g) followed by the Basal Anhydrite (A2) of the second cyclothem and the Main Anhydrite (A3) of the third cyclothem. This is overlain by the Aller Anhydrite. The sequence stratigraphic synthesis of Wagner and Peryt (1997) interprets A1d, A2 and the upper part of A3 as lowstand systems tracts, A1g as transgressive systems tracts and the upper part of A1g and lower part of A3 as highstand systems tracts. The evaporites of the first cyclothem built an evaporite platform that controlled the deposition of overlying units, especially the Main Dolomite and Basal Anhydrite.

The deeper part of the Zechstein basin is in western west-central Poland, where four of the boreholes examined in this study were drilled (Gorzów Wielkopolski IG 1, Kamień Pomorski IG 1, Barnówko 11 and Zawisze 1 boreholes; Fig. 1). One borehole — Olsztyn IG 1 — is located in the peripheral part of the Zechstein basin (Fig. 1), and two others are in the palaeogeographic zone termed the Wolsztyn Ridge. On the central ridge, reefs of the Zechstein Limestone, the oldest Zechstein carbonate unit, were established on pre-Zechstein highs (Dyjaczynski et al., 2001). The relief created during Zechstein Limestone deposition ends with the deposition of the major Werra Lower Anhydrite (A1d), the less significant Werra Upper Anhydrite (A1g), and the locally occurring Oldest Halite (Na1) making the upper surface of the PZ1 (Werra) deposits roughly planar. Thus in local depressions, the stratigraphic profile of the PZ1 evaporites is complete. The Kościan 22 and Bonikowo 2 boreholes are in such depressions but close to the reef complexes.

The succession of lithologies of the anhydrite in the intervals studied here is shown in Figure 2. Four intervals of Zechstein anhydrite were studied and analyzed. The two lower intervals, the Werra Lower and Upper Anhydrites, are usually separated by the Oldest Halite. The facies and thickness of the Werra Lower Anhydrite vary greatly in the peripheral parts of

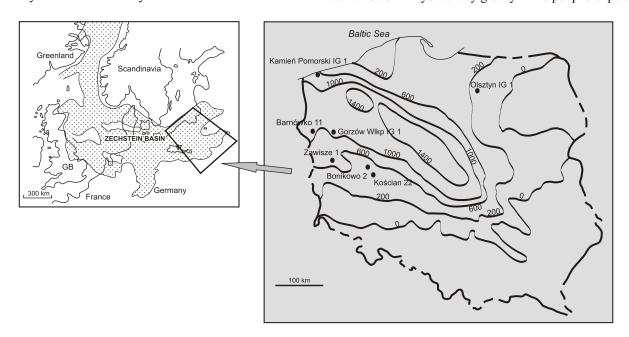


Fig. 1. The extent and thickness (in metres) of Zechstein deposition in Poland and the location of the seven borehole cores from which anhydrites were analyzed

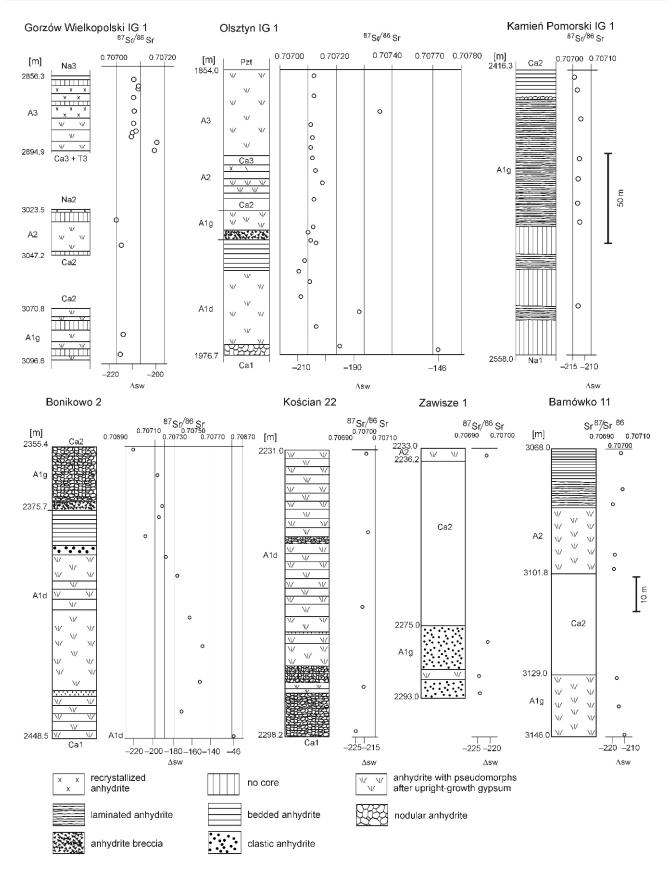


Fig. 2. Lithology of anhydrite cores and results of the strontium isotope measurements

Note the consistency of values, particularly in the basinal (Gorzów Wielkopolski IG 1 and Kamień Pomorski IG 1) boreholes indicating a strong marine dominance of the Zechstein salina at these locations; one sample with a $\Delta sw > -170$ from the Olsztyn IG 1 borehole not plotted; letter symbols are explained in Table 1

the basin where a complex system of local sulfate platforms are surrounded by halite filled basins (Peryt and Antonowicz, 1990; Peryt, 1994). The Werra Lower Anhydrite varies in thickness from less the 50 to more than 250 m. The upper section contains bedded anhydrite with some development of nodules at the top. Textural evidence, largely massive anhydrite containing pseudomorphs after upright-growth gypsum, indicates that the precursor gypsum was originally deposited in shallow subaqueous conditions (Peryt, 1994). The Werra Upper Anhydrite is usually a few tens of metres thick, but has a more sheet-like character. At its base, mudstones with anhydrite nodules are overlain by bedded and laminated anhydrite with abundant pseudomorphs after selenite crystals. In the peripheral part of the basin interbeds of nodular anhydrite are common and a few dolomite interbeds occur. The Werra Upper Anhydrite deposits near the margin of the basin originated in very shallow subaqueous and subaerial depositional environments, and those in the basin centre were formed under stable subaqueous conditions (Peryt et al., 1996a). The Basal Anhydrite is a few tens of metres thick above the Main Dolomite platform and a few metres thick in the basin centre. This anhydrite is composed of thin stromatolitic anhydrites (a few of tens of cm thick although these are sometimes lacking) passing into massive anhydrite with pseudomorphs of selenite crystals (a few mm to 20 cm high), formed in shallow subaqueous, salina environments, then into bedded and laminated anhydrite. Locally there are thin (cm to several tens of cm thick) intercalations of halite in the anhydrite (e.g., Peryt et al., 1996b). The Main Anhydrite shows a transgressive sequence. At the bottom nodular anhydrite is overlain by massive anhydrite, commonly with pseudomorphs after selenite crystals and (rarely) laminated anhydrite. Particular anhydrite units show a great lateral extent (Reimann and Richter, 1991).

SAMPLE PREPARATION AND ANALYSIS

The anhydrite samples were dissolved in ultra pure water, filtered and precipitated as CaCO₃ by adding a 1M NaCO₃ solution. The CaCO₃ was dissolved in HNO₃ and the strontium separated using a strontium specific resin. The isotope ratios were measured on a second order, double focusing mass spectrometer with a 60°, 13 inch (33.0 cm) radius of curvature magnetic sector and a 91°, 15.8 inch (40.1 cm) radius of curvature electric sector. Masses 85, 86, 87, and 88 were measured simultaneously in four separate faraday cups. The 8/Sr/86Sr values have been normalized to ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.1194$. The isotope ratio of the unknown samples were measured by comparison to a standard (Burke and Hetherington, 1984). The standard used in most of the measurements was NBS/987 for which a value of 0.710240 has been assumed. All samples are reported as the difference between modern seawater (Δ sw). We use the Δ sw difference notation followed by the ⁸⁷Sr/⁸⁶Sr.

 Δ sw = (87 Sr/ 86 Sr unknown – 87 Sr/ 86 Sr modern seawater) × 10⁵

More than 100 measurements of modern seawater and NBS/987 yield a weighted mean of $\pm 106.7 \pm 0.3$ for the NBS SrCO₃ standard. All published results have been normalized to these values.

POLISH ZECHSTEIN ISOTOPE RESULTS

The 74 analyzed anhydrite intervals from seven boreholes were chosen to cover the widest stratigraphic and geographic range available in the Polish Zechstein. The samples are representative of the individual cored stratigraphic units. The anhydrites contain minor water insoluble residue, determined petrographically to be dolomite where it could be identified. Only one samples had more than 1.0% water insoluble material (by weight) and most were <0.5%. Location of the samples and results of measurements are shown in Table 2 and are plotted in Figure 2.

Fifteen determinations were made on three separate anhydrite beds over a 238 m interval in the Gorzów Wielkopolski IG 1 borehole. The borehole drilled (Fig. 2) the Main Anhydrite (A3) underlain by a thin dolomite, through a thick halite into the Basal Anhydrite (A2), through another dolomite and into the Werra Upper Anhydrite (A1). Four determinations from the two lower intervals (A1 and A2) are indistinguishable with a mean of Δ sw -215 ± 1 (0.70702). There is no recognizable difference between results from the Werra Upper and Basal anhydrites. There is a pronounced isotope shift in the upper interval, assigned to the Main Anhydrite (A3). The upper nine determinations yield a mean of Δ sw of -209 ± 1 (0.70708), clearly higher than results from the underlying anhydrites.

Eight determinations were made over a 118 m interval in the Kamień Pomorski IG 1 borehole. The drilled interval is assigned to the Werra Upper Anhydrite (A1g). There is a small range in Δ sw values and all agree within error with the mean. The mean of the eight determinations is Δ sw -214 ± 1 (0.70703). This is within error of results from the Basal and Werra Upper Anhydrites in the Gorzów Wielkopolski borehole.

Twenty two anhydrites were analyzed over a 122 m interval in the Olsztyn IG 1 borehole drilled at a shelf location more than 300 km east of the basin boreholes (Gorzów Wielkopolski IG 1 and Kamień Pomorski IG 1). The interval is interpreted to extend from the lower part of the Werra (PZ1) through the Main Anhydrite (A3; Peryt, 1989). The determined Δ sw values (Table 2) range from -206 to -142 (0.70711 to 0.70775), a considerably greater scatter compared to the consistency of the more basinward sections (Fig. 2). The isotopic scatter is believed due to periods of meteoric influence. Nonetheless, examination of the results shows a consistent, established baseline. The mean of three lowest ratio anhydrites from the interval is Δ sw -211 ± 1 (0.70706). The baseline for the upper interval yields a mean of Δ sw -205 ± 1 (0.70712) on 13 analyses.

Eight anhydrite samples were analyzed over a 110 m interval in the Barnówko 11 borehole and four samples over a 60 m interval in the Zawisze 1 borehole. Both boreholes are drilled at the deep basin — PZ1 evaporite platform boundary, and the drilled intervals extend from the upper part of the Werra Upper

 $$T\ a\ b\ l\ e\ 2$$ Strontium isotope analyses of Zechstein anhydrites from Poland

Laboratory number	Unit	Depth [m]	⁸⁷ Sr/ ⁸⁶ Sr	$\Delta \mathrm{sw}$			
Olsztyn IG 1							
10823	A3	1854.7	0.707122 ±16	-205.1			
13081	A3	1863.3	0.707128 ± 11	-204.5			
10822	A3	1870.3	0.707366 ± 12	-180.7			
13080	A3	1876.1	0.707108 ± 19	-206.5			
13079	A3	1881.1	0.707119 ±12	-205.4			
13078	A3	1884.3	0.707104 ±16	-206.9			
13077	A3	1890.4	0.707117 ±15	-205.6			
10821	A2	1894.9	0.707130 ± 15	-204.3			
13076	A2	1900.5	0.707146 ± 17	-202.7			
10820	A2	1908.6	0.707119 ± 16	-205.4			
10819	A1g	1919.8	0.707116 ± 19	-205.7			
13075	Alg	1922.4	0.707105 ± 13	-206.8			
13074	A1g	1926.0	0.707114 ± 12	-205.9			
10818	A1d	1926.9	0.707134 ± 15	-203.9			
13073	A1d	1935.1	0.707078 ± 9	-209.5			
13072	A1d	1940.1	0.707070 ± 17	-210.3			
10817	A1d	1943.9	0.707115 ± 13	-205.8			
13071	A1d	1951.8	0.707077 ± 17	-209.6			
13070	A1d	1957.7	0.707273 ± 12	-190.0			
10816	A1d	1965.1	0.707134 ± 19	-203.9			
13069	A1d	1972.0	0.707219 ± 14	-195.1			
10815	A1d	1976.2	0.707710 ± 11	-146.3			
		Kamień P	omorski IG 1				
10814	A1g	2418.0	0.707019 ± 16	-215.4			
10813	A1g	2425.9	0.707030 ± 15	-214.3			
10812	A1g	2439.0	0.707043 ± 18	-213.0			
10811	A1g	2460.1	0.707039 ± 11	-213.4			
13082	A1g	2470.5	0.707033 ±9	-214.0			
10810	A1g	2482.3	0.707030 ± 8	-214.3			
13083	A1g	2492.0	0.707039 ± 10	-213.4			
10809	Alg	2535.8	0.707029 ± 19	-214.4			
			elkopolski IG 1				
13092	A3	2857.8	0.707079 ±16	-209.4			
13091	A3	2862.4	0.707094 ±13	-207.9			
10808	A3	2863.6	0.707097 ±18	-207.6			
13090	A3	2867.3	0.707081 ±14	-209.2			
13089	A3	2874.9	0.707085 ±19	-208.8			
13088	A3	2880.0	0.707081 ±12	-209.2			
13087	A3	2885.0	0.707086 ± 14	-208.7			
10807	A3	2885.3	0.707069 ±19	-210.4			
13086	A3	2888.0	0.707074 ± 19	-209.9			
13085	A3	2891.5	0.707175 ±15	-199.8			
13084	A3	2894.8	0.707163 ±16	-201.0			
10803	A2	3029.7	0.707007 ±16	-216.4			
10804	A2	3041.4	0.707025 ± 10	-214.7			
10805	A1g	3082.9	0.707027 ±19	-214.6			
10806	A1g	3095.5	0.707015 ±12	-215.8			

Laboratory number	Unit	Depth	⁸⁷ Sr/ ⁸⁶ Sr	Δsw				
	Barnówko 11							
14310	A2	3069.0	0.707032 ±11	-214.1				
14309	A2	3079.6	0.707051 ±16	-212.2				
14308	A2	3083.2	0.706980 ± 13	-219.3				
14307	A2	3097.0	0.706992 ± 12	-218.1				
14306	A2	3101.0	0.706988 ± 19	-218.5				
14305	A1g	3129.1	0.707002 ±15	-217.1				
14304	A1g	3139.0	0.707018 ± 16	-215.5				
14303	A1g	3144.8	0.707073 ±16	-210.0				
Bonikowo 2								
14322	A1g	2357.0	0.706974 ± 17	-219.9				
14321	A1g	2365.0	0.707228 ± 14	-194.5				
14320	A1g	2374.3	0.707273 ±11	-190.0				
14319	A1d	2378.2	0.707243 ±14	-193.0				
14318	A1d	2384.1	0.707107 ±13	-206.6				
114317	A1d	2391.4	0.707309 ± 14	-186.4				
14316	A1d	2397.7	0.707439 ± 14	-173.4				
14315	A1d	2411.0	0.707561 ±10	-161.2				
14314	A1d	2419.3	0.707703 ±17	-147.0				
14313	A1d	2430.6	0.707687 ± 14	-148.6				
t14312	A1d	2439.8	0.707494 ±16	-167.9				
14311	A1d	2448.3	0.708715 ±11	-45.8				
Kościan 22								
14327	A1d	2232.0	0.70703 8±6	-213.5				
14326	A1d	2249.1	0.707044 ±14	-212.9				
14325	A1d	2266.2	0.706999 ±16	-217.4				
14324	A1d	2284.2	0.707000 ± 10	-217.3				
14323	A1d	2294.8	0.706924 ± 14	-224.9				
Zawisze 1								
14331	A2	2234.9	0.706980 ± 13	-219.3				
14330	A1g	2279.8	0.706997 ±15	-217.6				
14329	Alg	2288.0	0.706930 ±11	-224.3				
14328	Alg	2292.0	0.706939±14	-223.4				

Anhydrite (A1g) through the Main Dolomite to the lower part of the Basal Anhydrite (A2). The determined Δsw values (Table 2) for A1g and A2 in the Barnówko 11 borehole are similar: -214 and -216 (0.70703 and 0.70701), respectively. Limited results from the Zawisze 1 borehole are lower, -222 (0.70695) for A1g and -219 (0.70698) for A2. The significance of these low values is not known.

Twelve determinations were made on two anhydrite units — Werra Lower Anhydrite (A1d) (9 samples) and Werra Upper Anhydrite (A1g) (3 samples) — over a 93.3 m interval in the Bonikowo 2 borehole. Five anhydrites were analyzed over a 67.3 m interval in the Kościan 22 borehole that is assigned to the Werra Lower Anhydrite (A1d). Those two boreholes occur

within the broad PZ1 evaporite platform and are located within the Wolsztyn Ridge, outside the reef zone although not far away from it. In the Bonikowo 2 borehole there is a considerable scatter of Δ sw values in both anhydrite units (Δ sw -147 to -220 in the Werra Lower Anhydrite and Δ sw -46 to -149 in the Werra Upper Anhydrite). There is a moderate range in Δ sw values in the Kościan 22 borehole over 63 m; the mean of the five determinations is Δ sw -217 ±5 (0.70700).

INTERPRETATION

The results from the Bonikowo 2 borehole show much greater scatter to higher ratios. Two anhydrite intervals from the Gorzów Wielkopolski IG 1, four from the Olsztyn borehole yield higher values. These higher values are considered to record of the mixing of marine and meteoric water containing radiogenic strontium. Meaningful mixing models cannot be determined because the strontium isotope ratio and concentration cannot be determined for the meteoric component. The highest ratios determined in our study imply that locally the meteoric input may be many times the volume of gypsum-saturated seawater (see Bryant *et al.*, 1995; Denison *et al.*, 1998).

The small range of Δsw values in the Kamień Pomorski IG 1 borehole indicates that the water body from which these anhydrites were precipitated was well mixed with open marine waters. There is no recognizable difference in age within the 118 m section.

The Olsztyn IG 1 borehole was drilled at a location near the shifting Zechstein coastline. Not surprisingly the strontium isotopes record the intermittent and sometimes strong influence of strontium carried in continental water in five of the analyzed anhydrites. The consistency of the results from the upper sequence is remarkable given the shelf site where stronger meteoric influence would be expected. This upper section contains by only one continentally influenced anhydrite. Even at this shelf locality the Zechstein salina is overwhelmingly marine. The strontium isotope results from the lower interval are identical to those from Main Anhydrite in the Gorzów Wielkopolski borehole.

The strontium isotope results from the Werra Upper Anhydrite and Basal Anhydrite in the Barnówko 11 borehole (–214 and –216, respectively) are similar to those in the Gorzów Wielkopolski IG 1 (–215 and –215, respectively). In contrast, the limited results from the Zawisze 1 are slightly lower from the same stratigraphic horizon. The reason is not understood but could be due to recycling of the evaporites.

Similarly, although Bonikowo 2 and Kościan 22 boreholes have similar palaeogeographic position, they differ substantially in their strontium isotope record. The reason may be a greater depth during the Werra Lower Anhydrite deposition in the Kościan 22 location and thus negligible meteoric water contribution compared to the Bonikowo 2 location. This explanation is supported by the considerably greater thickness of the Werra Lower Anhydrite in the Kościan 22 borehole (116.5 m *versus* 76.5 m in the Bonikowo 2 borehole) as well as common occurrence of clastic, redeposited anhydrite in the Bonikowo 2 borehole. This shelf site may not have been close to a meteoric point source.

Consistency is the hallmark of a retained marine signal and Zechstein strontium isotope results are remarkably consistency

for anhydrite from the two central basin core sites and reasonably consistent from the shelf site. The scatter of isotope ratios is to higher values, a common result of mixing the high ratio strontium from continental waters. There may be a meteoric component in other samples as well that cannot be recognized because of what Bryant et al. (1995) called the measurable effect. But because Late Permian seawater ratio is lower than any other time during the Palaeozoic, the system is sensitive to radiogenic influence from meteoric sources. The lowest ratio determined from the cored Zechstein anhydrites is near Δ sw -210(0.70707) and the highest consistent ratio is Δ sw -200(0.70717). There is a small but regular decrease in the Δ sw with depth in the Gorzów Wielkopolski IG 1 and Olsztyn IG 1 borehole cores. Three anhydrites from two boreholes (Kościan and Zawisze) yield anomalously low ratios (<-220) which, if taken at face value, would imply a wider range in depositional age or perhaps recycling of older evaporites.

Three clusters of values (Δ sw -215, -210, -205 [0.70702, 0.70707 and 0.7012]) are interpreted as recording the Δ sw of contemporaneous seawater. The differences are small and it is only when results from stratigraphically adjacent samples in all the boreholes are evaluated does the significance becomes apparent. The difference in results from individual stratigraphically adjacent anhydrites is just outside error but the difference between the highest and lowest cluster is clear. In the two boreholes that show a trend in isotope results, the youngest samples have the highest Δ sw values, indicating these intervals are younger than the Permian minimum shown in Figure 3. We are unable to recognize any petrographic difference or stratigraphic association between anhydrite samples yielding high ratios and those recording a marine strontium signal.

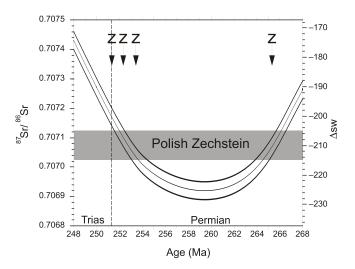


Fig. 3. The estimated path of the strontium isotope seawater ratio during the later Permian and earliest Triassic and the range of marine values for anhydrite core examined here (from Table 2)

The age of the Polish Zechstein is latest Permian because the youngest anhydrites have the highest isotope ratios. The arrows marked with a Z are the numeric ages on ash beds reported by Bowring *et al.* (1998). The path of seawater strontium is from latest Permian samples from the same localities in China used by Bowring *et al.* (1998). The path of the seawater isotope ratio older than 254 Ma is based on results from samples West Texas and New Mexico (Denison *et al.*, 1994; Kirkland *et al.*, 2000)

DISCUSSION

Strontium isotope ratios have been determined on Late Permian–Early Triassic samples by a number of workers (e.g., Popp *et al.*, 1986; Brookins, 1988; Kramm and Wedepohl, 1991; Gruszczyński *et al.*, 1992; Denison *et al.*, 1994; Martin and Mcdougall, 1995; Kampschulte *et al.*, 1998; Kirkland *et al.*, 2000; Korte *et al.*, 2003, 2006). These results outline an ⁸⁷Sr/⁸⁶Sr low in the latest Permian and a sharp rise in the Early Triassic, the general shape shown by Burke *et al.* (1982). There is, however, considerable scatter in published values leading uncertainty as to the true path of seawater strontium isotopes during the Permian.

Recent work has resolved some of this uncertainty. There is now general acceptance of Permian-Triassic boundary definition in the Meishan area in China based on conodont biostratigraphy (Mei et al., 1998). Zircons from tuff beds in the earliest Triassic-latest Permian in South China have been used by Bowring et al. (1998) establish a boundary age of 251.4 ±0.3 Ma. Other ages were determined both above and below the contact. A zircon age of 252.3 ± 0.3 was determined from a bed \sim 10 m below the top and another of 253.4 \pm 0.2 Ma 27 m below the top. Limestones used by Denison et al. (1994) to define the path of seawater strontium are from the same quarries that contain these crucial tuff beds. For this study, 18 additional samples were analyzed and the original limestones were reanalyzed from the Meishan section. The analyses confirm, within error, the results originally reported. Becker et al. (2002) report a U-Pb age of 251.3 ±2.8 Ma on calcite layers within gypsum of the Castile Formation (Ochoan) in West Texas, well within error of the results shown in Figure 3. Values from the Rustler Formation in West Texas (Denison et al., 1998) overlap those determined from the oldest analyzed limestones from Meishan and there is a near continuous definition through the Ochoan into the latest Guadalupian (Kirkland et al., 2000). Bowring et al. (1998) report a zircon age of 265.3 \pm 0.2 Ma for a tuff near the middle of the Guadalupian in West Texas. This numeric age anchors the older part of the curve and strontium isotope results from West Texas limestones trace the seawater path shown in Figure 3. Korte et al. (2003, 2006) do not give a preferred Permian-Triassic boundary value but results from their European localities are very close to those from China.

Several studies have examined Upper Permian strontium isotopes in Germany (Zechstein) and Austria. These samples sites are geographically separated from those examined here and the evaporites were deposited in sub-basins separated from the Polish anhydrites. Kramm and Wedepohl (1991) reported nine Zechstein strontium isotope values from five localities in north-west Germany. Their results ranged from Δsw -231 to -131 (0.70686 to 0.70786) and showed the same general trend of higher values with decreasing age. There is also a large range in Asw values determined on the Austrian Haselgebirge evaporites by Spötl and Pak (1996). But the lowest values are <∆sw −200 (0.70717), indicating an apparent marine Permian signal for some of the samples. Kampschulte et al. (1998) report both sulfur and strontium isotope values from five German Zechstein evaporite cycles. Their 59 sulfur values are very consistent but 29 strontium isotope determinations show a considerable scatter. They speculated that the high ratios might be the result of in situ 87Rb decay or, alternatively, mixing of marine and meteoric water. Our experience favors the meteoric mixing explanation. They interpret the lowest ratio as closest to the true seawater value. Their lowest value from the Werra cycle is Δ sw -208 (0.70709); for the Stassfurt Δ sw -198 (0.70719); for the Leine Δ sw –217 (0.70700); for the Aller Δ sw –161 (0.70856) and for the Ohre, Δ sw -109 (0.70808). The high values from the Aller and Ohre cycles indicate a large meteoric contribution at the locations sampled. The plots of Kampschulte et al. (1998) data indicate an extended period of sedimentation. Because their lowest points are from the Leine, nearer the middle of the Zechstein, they plot their Zechstein results extending on both sides of the Late Permian minimum. The result of this interpretation is an implied depositional interval of five to eight million years for the Zechstein (their fig. 4). The results from Poland suggest a much shorter interval of deposition for deposition for the sequence we examined, approximately 2 million years from Figure 3. Certainly the deposition of evaporites can occur with amazing rapidity, e.g., the 640 m of anhydrites and higher salts of the Castile Formation took only an estimated 175,000 years (Anderson, 1982). The highest consistent ratios determined from Poland are within error of boundary value determined from China, indicating an end of the Permian age of deposition for this sequence.

It should be noted that biostratigraphic studies led Kozur (1989, 1994) to the conclusion that the Zechstein was of Changxingian age. Our results confirm this age assignment for the Zechstein, argued on different grounds.

CONCLUSIONS

Strontium isotopes are a potentially powerful tool in making worldwide correlations (see discussion of MacArthur, 1994). The requisite base for these correlations is the accurate definition of the seawater strontium isotope variation with time. The isotopic and palaeontologic boundary work in China together with results from the well-studied West Texas stratigraphic sections provides this base. The exact correlation of the European Stages to those in North America remains to be determined.

The assignment of the Zechstein to the latest Permian by Menning (1995) is in agreement with our results from Poland. His discussion makes it clear that, in the sense of Central Europeans, the Zechstein belongs in the Permian. The range in strontium ratios reported by Kampschulte *et al.* (1998) is large, suggesting a substantial component of continental water at their sample sites in the younger Zechstein salinas. This is certainly possible given the geologic setting. The small range in strontium isotope peaks for the Polish Zechstein during a period of rapid seawater change indicates a short interval of sedimentation, about two million years.

Strontium isotopes are a potentially powerful tool in determining the age of ocean derived gypsum/anhydrite beds. The results from six Polish Zechstein boreholes show the great consistency, characteristic of a marine origin, and the case of one borehole (Bonikowo 2) showing the great variability, records a clear meteoric contribution to the ocean based hypersaline water body.

In addition, some of the anhydrite beds in other boreholes, at different brief periods, particularly at the marginal location, record an intermittent meteoric contribution to the ocean based hypersaline water body. Regional studies using strontium isotopes can be used to gain important insights into the hydrologic setting and shifting influences affecting evaporite deposition.

Acknowledgements. The study was supported by the Polish State Committee on Scientific Research (Grant No. P04D 024 28). We thank A. Becker and P. B. Wignall for helpful remarks.

REFERENCES

- ANDERSON R. Y. (1982) Long geoclimatic record from the Permian. J. Geophys. Res., **87**: 7285–7294.
- BECKER M. L., RASBURY E. T., MEYERS W. J. and HANSON G. N. (2002) — U-Pb calcite age if the Late Permian Castile Formation, Delaware Basin: a constraint on the age of the Permian-Triassic boundary (?). Earth Planet. Sc. Lett., 203: 681–689.
- BOWRING S. A., ERWIN D. H., JIN Y. G., MARTIN M. W., DAVIDEK K. and WANG W. (1998) U/Pb zircon geochronology and tempo of end-Permian mass extinction. Nature, **280**: 1039–1045.
- BROOKINS D. G. (1988) Seawater ⁸⁷Sr/⁸⁶Sr from the Late Permian Delaware Basin evaporites (New Mexico, U.S.A.). Chem. Geol., **69**: 209–214.
- BRYANT J. D., JONES D. S. and MUELLER P. A. (1995) Influence of freshwater flux on ⁸⁷Sr/⁸⁶Sr chronostratigraphy in marginal marine environments and dating of vertebrate and invertebrate faunas. J. Palaeont., 69: 1–6.
- BURKE W. H., DENISON R. E., HETHERINGTON E. A., KOEPNICK R. B., NELSON H. F. and OTTO J. B. (1982) Variation of ⁸⁷Sr/⁸⁶Sr throughout Phanerozoic time. Geology, **10**: 516–519.
- BURKE W. H. and HETHERINGTON E. A. (1984) Normalized ⁸⁷Sr/⁸⁶Sr by multiple collection and comparison to a standard. Chem. Geol. (Isot. Geosci. Sect.), 2: 265–268.
- DENISON R. E., KOEPNICK R. B., BURKE W. H., HETHERINGTON E. A. and FLETCHER A. (1994) Construction of the Mississippian, Pennsylvanian, and Permian seawater ⁸⁷Sr/⁸⁷Sr curve. Chem. Geol., **112**: 145–167.
- DENISON R. E., KIRKLAND D. W. and EVANS R. (1998) Using strontium isotopes to determine the age and origin of anhydrite and gypsum beds. J. Geol., 106: 1–17.
- DYJACZYNSKI K., GÓRSKI M., MAMCZUR S. and PERYT T. M. (2001) Reefs in the basinal facies of the Zechstein Limestone (Upper Permian) of Western Poland: a new gas play. J. Petrol. Geol., 24 (3): 265–285.
- GRUSZCZYŃSKI M., HOFFMAN A., MALKOWSKI K. and VEIZER J. (1992) — Seawater strontium isotopic perturbation at the Permian-Triassic boundary, West Spitsbergen, and its implications for the interpretation of strontium isotope data. Geology, 20 (9): 779–782.
- HARDIE L. A. (1984) Evaporites: marine or non-marine? Am. J. Sc., **284**: 193–240.
- KAMPSCHULTE A., BUHL D. and STRAUSS H. (1998) Sulfur and strontium isotope compositions of Zechstein evaporites from northern Germany. Geol. Rundsch., 87: 192–199.
- KIRKLAND D. W., DENISON R. E. and DEAN W. E. (2000) Parent brine of the Castile evaporites (Upper Permian), Texas and New Mexico. J. Sed. Res., 70: 749–761
- KORTE C., JASPER T., KOZUR H. W. and VEIZER J. (2006) ⁸⁷Sr/⁸⁶Sr record of Permian seawater. Palaeogeogr. Palaeoclimatol. Palaeoecol., 224: 89–107.
- KORTE C., KOZUR H. W., BRUCKSCHEN P. and VEIZER J. (2003) Strontium isotope evolution of Late Permian and Triassic seawater. Geochim. Cosmochim. Acta, 67: 47–62.
- KOZUR H. (1989) The Permian-Triassic boundary in marine and continental sediments. Zbl. Geol. Paläont. Teil I, 1988 (11/12): 1245–1277.

- KOZUR H. (1994) The correlation of the Zechstein with marine standard. Jb. Geol. B.-A., 137: 85–103.
- KRAMM U. and WEDEPOHL K. H. (1991) The isotopic composition of strontium and sulfur in seawater of late Permian (Zechstein) age. Chem. Geol., 90: 253–262.
- MARTIN E. E. and MacDOUGALL J. D. (1995) Sr and Nd isotopes at the Permian/Triassic boundary: a record of climate change. Chem. Geol., 125: 73–99.
- McARTHUR J. M. (1994) Recent trends in strontium isotope stratigraphy. Terra Nova, 6: 331–358.
- MEI S., ZHANG K. and WARDLAW B. R. (1998) A refined succession of the Changhsingian and Griesbachian neogondolellid conodont from the Meishan section, candidate of the global stratotype section and point of Permian-Triassic boundary. Palaeogeogr., Palaeoclimatol., Palaeoccol., 143: 213–226.
- MENNING M. (1995) A numerical time scale for the Permian and Triassic period: an integrated time analysis. In: The Permian of Northern Pangea (eds. P. A. Scholle, T. M. Peryt and D. S. Ulmer-Scholle), 1: 77–97. Springer, Berlin.
- PERYT T. M. (1989) Zechstein deposition in the Polish part of the Peri-Baltic Gulf. Bull. Pol. Acad. Sc., Earth Sc., 37 (1–2): 103–119.
- PERYT T. M. (1994) The anatomy of a sulfate platform and adjacent basin system in the Łeba sub-basin of the Lower Werra Anhydrite (Zechstein, Upper Permian), northern Poland. Sedimentology, **41** (1): 83–113.
- PERYT T. M. and ANTONOWICZ L. (1990) Facje i paleogeografia cechsztyńskiego anhydrytu dolnego (A1d) w Polsce. Prz. Geol., 38 (4): 173–180.
- PERYT T. M., KASPRZYK A. and ANTONOWICZ L. (1996a) Upper Werra Anhydrite (Zechstein, Upper Permian) in Poland. Bull. Pol. Acad. Sc., Earth Sc., 44 (3): 121–130.
- PERYT T. M., KASPRZYK A. and CZAPOWSKI G. (1996b) Basal Anhydrite and Screening Anhydrite (Zechstein, Upper Permian) in Poland. Bull. Pol. Acad. Sc., Earth Sc., 44 (3): 131–140.
- POPP B. N., PODESEK F. A., BRANNON J. C., ANDERSON T. F. and PIER J. (1986) ⁸⁷Sr/⁸⁶Sr ratio in Permo-Carboniferous sea water from the analysis of well-preserved brachiopod shells. Geochim. Cosmochim. Acta, **50**: 1321–1328.
- REIMANN M. and RICHTER M. (1991) Lithological sequence of the Main Anhydrite (Zechstein 3) in the Piła IG1 borehole (Poland) in comparison with the normal sequence in the Hannover area (NW Germany). Prz. Geol., 39 (4): 203–206.
- RICHTER-BERNBURG G. (1955) Über salinare Sedimentation. Z. Dt. Geol. Ges., **105**: 593–645.
- SPÖTL C. and PAK E. (1996) A strontium and sulfur isotopic study of the Permo-Triassic evaporites in the Northern Calcareous Alps. Chem. Geol., 131: 219–234.
- WAGNER R. and PERYT T. M. (1997) Possibility of sequence stratigraphic subdivision of the Zechstein in the Polish Basin. Geol. Quart., **41** (4): 457–474.