Geologie en Mijnbouw 67: 177–188 (1988)

Carbonate rocks from W. Bergslagen, Central Sweden: isotopic (C, O, H) evidence for marine deposition and alteration by hydrothermal processes

IUGS UNESCO IGCP 247

P.A. De Groot[1,2] & S.M.F. Sheppard[1]
[1] Centre de Recherches Pétrographiques et Géochimiques, B.P. 20, 54501 Vandoeuvre-lès-Nancy, France and [2] Geologisch Instituut, Universiteit van Amsterdam, Nieuwe Prinsengracht 130, 1018 VZ Amsterdam, The Netherlands

Received 22 September 1987; accepted in revised form 4 January 1988

Key words: Carbonate rock, stable isotopes, Proterozoic, Bergslagen, Sweden

Abstract

Carbon and oxygen isotope ratios for calcite and dolomite from stratabound carbonates, carbonate veins and clots in W-(Mo-) and Zn-Pb sulphide skarns, and for a calcite from a Mn-skarn from the Bergslagen region, central Sweden, are presented. Stratabound carbonate carbon isotopes ($\delta^{13}C \sim 0‰$) imply a marine milieu of deposition.

The $\delta^{18}O$ values of stratabound carbonates can be divided into two groups: one associated with stratiform iron-oxide deposits (RSC) and the other unrelated (NRSC). Stratabound dolomites of the NRSC are depleted in ^{18}O compared to the 'most Proterozoic dolomite' field. NRSC calcites have a range of $\delta^{18}O$ values (+12 to +19‰) similar to the lower half of the 'most Proterozoic calcites' field. Whether the RSC $\delta^{18}O$ values (+6 to +11‰) are primary values or values formed by exchange of the RSC with a hydrothermal fluid during the skarn alteration of associated stratiform iron-oxide deposits, is not clear. Calcites and dolomites, from skarn altered iron-oxide deposits, W-(Mo-)skarns, and a sulphide skarn, as late phase veins and clots, have distinguishable $\delta^{13}C$ and $\delta^{18}O$ values, placing the respective skarns into separate fields. They have, in general, low $\delta^{13}C$ (−2 to −8‰) and low $\delta^{18}O$ (+6 to +12‰) values, except for the calcite veins in the sulphide skarn. The ^{18}O-depletion of the carbonates most probably occurred during exchange with sea water at temperatures of 300 ± 50° C, or meteoric waters if the temperatures were lower. The types of $\delta^{18}O$ values and their range are comparable to well documented sea water hydrothermal systems of younger age from ocean floor ophiolites and many relatively low altitude meteoric–hydrothermal systems.

The low carbon and oxygen isotope values of the carbonate veins and clots in W-(Mo-)- and Fe-skarns are typical for such skarns. They indicate the influx of CO_2-bearing hydrothermal fluids where the CO_2 is either of magmatic origin or derived from sedimentary carbonate formations after major loss of CO_2 through decarbonation reactions.

Slate hosted calcite from a Ca-Mn-skarn, is isotopically similar to both the skarn associated carbonates and a concretionary carbonate. Diagenetic modifications of organic matter-bearing sediments, exchange of a sedimentary carbonate with hydrothermal fluids, or, more probable, a combination of these two events, were responsible for the isotopic composition of the calcite in this skarn.

Introduction

This paper presents some initial results of an ongoing stable isotope (C, O, H) study on carbonate minerals and fluid inclusions from the 1.8–1.9 Ga ensialic belt of Bergslagen, Central Sweden (Fig. 1). Different types of carbonate-bearing samples were chosen to determine whether the sediments were deposited in a marine or fresh water milieu, and what type of fluids circulated through this sedimentary crust and caused the formation of associated mineralizations.

Regional geology

The ensialic belt of Bergslagen (Oen et al. 1982; Vivallo & Rickard 1984; Oen 1987) consists of a supracrustal sequence (dated 1.9–1.8 Ga by U-Pb: Welin et al. 1980; Åberg et al. 1983) comprising a thick pile (>10 km) of felsic volcanics (historically named Hälleflinta and Leptites: Sundius 1923; Magnusson 1925, 1970), overlain by a sedimentary packet of black and grey slates (dated 1.86 Ga by Sm-Nd: Miller et al. 1986), which are at least 2 km thick. The felsic volcanics are intruded by granite domes and continental tholeiitic (Hellingwerf & Oen 1986) dykes and sills, while a few meta-basaltic flows (spilites) occur in the black slates, at the base of the slate pile. Although basalts form a relatively small volume compared to the felsic rocks, this is an excellent example of bimodal, coeval magmatism (Van der Velden et al. 1982; Vivallo & Rickard 1984).

Oen et al. (1982) and Oen (1987) related the development of the belt, the deposition of the supracrustals, and the plutonism and volcanism with a continental rift process, resulting finally in an aborted rift. They divided the Bergslagen Supracrustal Sequence into a Lower Leptite Group, a Middle Leptite Group, and an Upper Leptite-Hälleflinta and Slate Group.

The supracrustals in the belt are generally tilted into a (sub-)vertical position by granitic diapirism and by gravity tectonism as described by De Groot et al. (1988). The supracrustals are weakly metamorphosed (greenschist facies) in the central part of the belt. They grade into amphibolite facies on the east and west sides of the belt, touching the 1.64–1.78 Ga granitoids (Oen & Verschure 1985) which encircle the belt (Fig. 1).

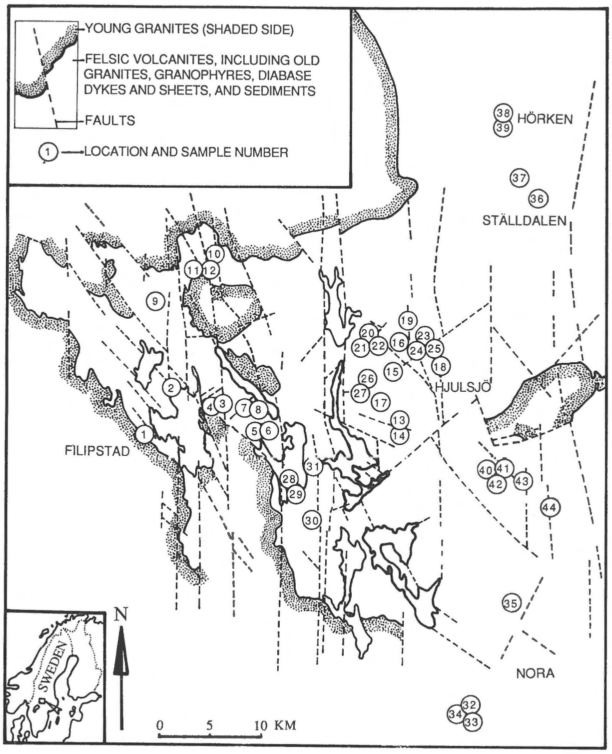

Fig. 1. Simplified map of W. Bergslagen after Oen et al. (1982) and Baker (1985a; p. 91, Fig. 1) showing sample locations and sample numbers (see Table 1).

Discussions about a regional and local scale alteration in the W. Bergslagen area by e.g. Baker & De Groot (1983), Lagerblad & Gorbatschev (1985), and Baker (1985a, b), are mostly based on the chemistry and mineralogy of the altered and unaltered wall-rocks and their associated mineralizations. They indicate sources for fluids involved in the skarn-forming processes, but the arguments are not conclusive. Many of the W-(Mo-)skarns, from which carbonate isotopic analyses are reported in this paper (Table 1), are described by Hellingwerf & Baker (1985). A detailed description of the Gruvåsen area is given by Hellingwerf (1984). Carbonate, or carbonate bearing rocks are present throughout the entire supracrustal sequence, but are mostly concentrated in the Middle Leptite Group and in the lower part of the Upper Leptite-Hälleflinta and Slate Group of Oen et al. (1982). A

Table 1. Mineralogy and carbon, oxygen, isotope data for stratabound, and vein carbonates and hydrogen isotope values of fluid inclusions in vein calcite.

NO		SAMPLE		DESCRIPTION	COMPOSITION§ (in%)		CALCITE		DOLOMITE		
					ct	dol	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	δD
		Persberg area:									
1	s♦	GG1	Gåsgruvan	finegr. marble: cont. silic./>100m#	85		0.14	12.53			
2	s	HW Gt	Getön	adjac. mag +Pb,Zn,Ag sulf. min./>50m	67		-0.09	16.62			
		Gruvåsen area:									
3	s	HW B15-64	Gruvåsen	adjac. Cu,Zn,Fe sulf.min.+ chert b./700m	20	75	-0.22	15.80	0.10	15.60	
4	s	HW B15-184	Gruvåsen	adjac. Cu,Zn,Fe sulf.min.+ chert b./700m	28	65	-0.42	13.07	0.01	13.86	
5	s	77HW85	Limbergsåsen	finegr. marble: cont. silic./700m	22	45	0.40	18.45	1.01	19.62	
6	s	77HW86	Limbergsåsen	finegr. marble: cont. volc. fragm./700m	40	17	0.35	18.62			
7	s	77HW139	Bovik	finegr. marble: cont. mica/700m	32	63	-0.44	16.67	0.20	16.64	
8	s	77HW140	Bovik	finegr. marble: cont. silic./700m	15	60	-0.03	14.49	0.40	15.30	
		Långban area:									
9	s	LB1	Långban	adjac. Mn-skarn: pure dol	2	98			1.71	16.32	
10	s	Da78	Gåsborn	finegr. marble/<10m	*54		-0.15	14.42			
11	s	Da81	Gåsborn	finegr. marble/<10m	*96		0.10	15.16			
12	sf	DaA2	Gåsborn	finegr. marble/<10m	*95		-3.09	7.91			
		Hjulsjö area:									
13	vw	BJ Sk1	Skropen	ct clots in amph sch qz skarn	*100		-5.70	7.55			
14	s	BJ Sk2	Skropen	adjac. amph sch qz skarn/7-8m	98		0.30	14.89			
15	sf	BJ118L	Killingberget	adjac. Fe-ox. dep.+bt-sköll/7-8m	*67		0.35	8.33			
16	s	BJ152	Hjulsjö	finegr. marble/few m	*65		-2.82	6.51			
17	s	BJ366	Hjulsjö	marble-chert layer into sk. alt. grst./1m	*100		0.56	13.17			
18	s	BJ461C	Hjulsjö	finegr. marble: cont. gt+mag/2-3m	*44		-2.83	6.51			
19	sf	MM269B3	Bredsjö	finegr. marble	*94		0.33	8.32			
20	sf	Cab1B	Sirsjöberg	finegr. marble adjac. Fe-sk. horiz./120m	98		-2.87	17.59			
21	sf	Sir2	Sirsjöberg	finegr. marble adjac. Fe-sk. horiz./120m	95		0.01	6.83			
22	vf	Sir3	Sirsjöberg	skarnified Fe-oxide horiz./120m	35		-2.01	6.60			
23	vf	Öb2	Ösjöberg	vein-ct in Fe-skarn/>100m	*40		-2.24	7.77			
24	vf	Öb3	Ösjöberg	ct clots in Fe-skarn/>100m	*100		-3.47	6.86			
25	sf	Öb5	Ösjöberg	finegr. marble: cont silic./>100m	70		0.39	7.05			
26	s	St1	Stolpberget	marble adjac.Fe-skarn/±5-10m	98		0.49	16.65			
27	s	St2	Stolpberget	finegr. marble: cont. amph bt/±5-10m	*94		-1.91	7.60			
		Grythyttan area:									
28	s	HW BN1	Bjurskogsnäs	finegr. marble/>100m	60	28	-0.17	16.34			
29	s	HW BN2	Bjurskogsnäs	finegr. marble/>100m	65	18	0.89	16.28			
30	s	AR1	Djupviken	finely laminated dol-chert= strom./±10m	6	70			-0.19	13.04	
31	(v)	77Md302/18	Grythyttan	ct in exhal.-sed. Mn-skarn/<1-2m	17		-7.80	10.17			
		Erntorp area:									
32	s	HW NV576	Erntorp	breccia below Zn,Pb sulf.min./100m	18	45	-1.78	17.12	-1.25	17.67	
33	vs	ERN S1	Erntorp	vein-ct in Zn(Pb) sulf. cont. schist	*50		-0.79	20.15			
34	s	ERN M1	Erntorp	finegr. marble: cont. chert b./>100m	70	9	0.43	19.25			
		Striberg area:									
35	vw	HW HG2	Hultagruvor	ct clots in Fe-W -skarn	78		-4.87	6.15			-63
		Ställdalen-Hörken area:									
36	s	B9	Båtens	marble adjac. sch gt skarn/60m	27		-3.14	9.64			
37	vw	W71	Ställdalen	ct clots in amph gt sch skarn	*100		-8.09	6.48			-62
38	sf	Rr E19	Hörken	finegr. marble adjac. Fe-skarn	85		0.21	10.73			
39	sf	Rr E20	Hörken	finegr. marble adjac. Fe-skarn	85		-0.31	8.29			
		Grängen area:									
40	vw	Db1	Dunderbo	coarse dol clot in chl bt amph sch Fe-sk.		*100			-4.65	8.11	
41	vw	Db2	Dunderbo	dol clots in chl bt amph sch Fe-skarn	*4	75			-3.53	9.28	
42	s	Db-S	Dunderbo	marble: cont. silic.		55			-3.85	8.92	
43	vw	Ah	Annehill	interst. ct in px amph gt qz sch skarn	10		-3.63	8.27			
		Jämboås area:									
44	vw	Sp1	Sparrbergsgruvan	dol/ct clots in gt vesuv amph bt sch sk.	*17	70	-3.51	11.37	-3.51	10.17	

Delta (δ) values in per mil (‰). Abbreviations : adjac.= adjacent to; alt. = altered; amph = amphibole; bt = biotite; chert b. = chert bands; chl = chlorite; cont. = contains; ct = calcite; dep. = deposit; dol = dolomite; exhal. = exhalative; Fe-ox. = Fe-oxide; finegr. = fine grained; gt = garnet; grst. = greenstone; horiz. = horizon; interst. = interstitual; mag = magnetite; px = pyroxene; qz = quartz; sch = scheelite; sed. = sedimentary; silic. = silicate minerals; sk. = skarn; strom. = stromatilite; sulf.min. = sulfide minerals; vesuv = vesuvinite; volc. fragm. = volcanic (rhyolite) fragments.

♦ s = stratabound carbonate (NRSC); sf= stratabound carbonate associated with stratiform Fe-oxide deposits (RSC); vw = carbonate clots in W-(Mo)-skarn; vf = calcite clots or veins in skarn altered Fe-oxide deposits; vs = calcite veins in a (Zn-Pb) sulphide skarn; (v) = carbonate as granules, aggregates and veins in a Mn-skarn.

§ Proportion of carbonates in whole rock sample.

* Proportion of calcite in separates or partially separated minerals.

#Thickness of carbonate layer.

major division can be made between: (1) stratabound carbonates, and (2) carbonates formed as veins or clots during skarn[1] mineralization.

Within this division the following groups can be distinguished:

(1) a – Major and minor carbonate horizons which are not associated with mineralizations. The major horizons are formed by massive lenses of relatively pure, fine grained (grains ≤2 mm) carbonates more than 50 m thick; they are generally composed of calcite at lower stratigraphic levels and of calcite or calcite–dolomite mixtures at higher stratigraphic levels, and seldom show lamination or alternation with chert laminae or bands. The minor horizons of the same type of massive carbonate are 10 m or less thick; they are generally composed of calcite and, more often than the thick layers, show lamination and alternation with chert laminae or bands.

b – Major and minor carbonate horizons are associated with stratiform iron-oxide deposits; they further show the same characteristics as the carbonate horizons described under a.

(2) a – Clots of carbonate (calcite and dolomite) formed in W-(Mo-)skarns.

b – Calcite formed as veins or clots during skarn alteration of stratiform iron-oxide deposits.

c – Calcite veins associated with Zn-Pb-sulphide skarn mineralization

d – Small calcite bodies (several mm thick and up to 1 cm long) formed in layered Ca-Mn-skarns occurring in the slates of the Upper Leptite-Hälleflinta and Slate Group of Oen et al. (1982).

The stratabound carbonates, the calcites from the slates, and most of the skarn-related carbonates are recrystallized due to diagenesis and/or regional metamorphism. The stratabound carbonates are more or less intensely folded, which is best seen in the laminated carbonates. The carbonate grains often show undulatory extinction in thin section. Sample locations are given in Fig. 1, and sample descriptions are given in Table 1.

Analytical procedure

Rocks containing calcite, and mixtures of calcite and dolomite (Table 1) were crushed to a grain size below 63 μm for BJ118L, BJ152, BJ461C, MM269B3, Da78, Da81, and DaA2, and below 120 μm for the other samples. For samples HW HG2, BJ Sk1, W71, Öb2, Öb3, St2, Db1 and Db2 calcite was separated from the silicates in the rock and handled separately. The mineralogical composition of the carbonates was measured by standard X-ray techniques. The carbonates were reacted with >100% H_3PO_4 at 25° C using the method of McCrea (1950) and the CO_2-yields were measured manometrically. Calcites were reacted for at least 10 hours while dolomites were reacted for at least 5 days. Mixtures in which calcite was the major component were reacted for 3–4 hours to obtain the calcite-CO_2. Where dolomite was the major component, the samples were first reacted for 1–1$^1/_2$ hour to obtain the calcite-CO_2 (calcite content of total carbonate in rock at least 20%) and then for at least 5 days to obtain the dolomite-CO_2 (Epstein et al. 1964). The CO_2 from samples containing sulphides (Öb2, ERN S1, and Ah) were purified using Ag_3PO_4 (Smith & Croxford 1975). For 70% of the samples, duplicate extractions gave differences in $\delta^{13}C$ of less than ±0.2‰ and for $\delta^{18}O$ of less than ±0.12‰.

Calcite samples W71 and HW HG2 were crushed under vacuum to collect H_2O from fluid inclusions. The samples were weighed and evacuated in cleaned stainless-steel tubes, and then heated for 3 days at 100° C to remove all the absorbed water from the surface and pores of the minerals. After crushing, the H_2O from the fluid was purified using a combination of a liquid nitrogen and an acetone-

---

[1] Skarn in this paper is defined as a carbonate containing rock or layer, wall rock included, which is altered by hydrothermal processes into a calc – silicate rock. In Bergslagen skarns are not normally directly associated with an intrusive granitic body.

dry ice trap. The pure water was passed through an uranium furnace heated to 800° C and reduced to H_2 gas after the method described by Friedman (1953) and Godfrey (1962), and yields were measured manometrically. No duplicate extractions could be made because of the small amount of calcite available (<18 g). Isotopic ratios for carbon and oxygen were measured on CO_2 gas, and for hydrogen on H_2 gas with a VG – Micromass 602D double collector mass spectrometer. The values are reported here in the usual delta notation (δ) in per mil (‰) with $\delta^{13}C$ against PDB and $\delta^{18}O$ and δD against the SMOW standard. All carbonate values are corrected for ^{13}C and ^{17}O variations after Craig (1957).

Results

Carbon and oxygen isotope values of the analysed carbonates from Bergslagen are listed in Table 1 and are plotted as $\delta^{13}C$ against $\delta^{18}O$ values in Fig. 2. This figure includes calcite and dolomite reference fields for Early to Middle Proterozoic (1.6–2.5 Ga) marine carbonates based on the compilation of data given by Veizer & Hoefs (1976). For $\delta^{13}C$, the overwhelming majority of their data fall between +2 and −3‰ and these boundaries can be considered to be relatively well defined. In contrast the $\delta^{18}O$ boundaries are less well defined probably because the data base includes marine carbonates that have undergone varying degrees of diagenetic exchange. Most Proterozoic dolomites, however, display a very restricted range of $\delta^{18}O$ values (+25 to +21‰) in contrast to the wide range of values for calcite and lack of peak in the histogram (see Fig. 4 in Veizer & Hoefs 1976). Without entering into the problem of dolomitization and noting that, in general, calcite undergoes oxygen isotope exchange more readily than dolomite (Northrop & Clayton 1966), the more restricted field for Proterozoic dolomites is considered to more closely represent the field of 'unaltered' Proterozoic marine carbonates. Most of the stratabound carbonates, related (RSC; stars in Fig. 2) or not related (NRSC; circles in Fig. 2) to stratiform iron oxide deposits, have $\delta^{13}C$ values around zero, and all plot within the proposed range of Proterozoic marine carbonate values. The $\delta^{18}O$ values, however, show a large continuous range, with NRSC $\delta^{18}O$ values between +12 and +20‰ for both calcites and dolomites – a range lower than that of most Proterozoic dolomites and similar to the lower half of the 'most Proterozoic calcites' field (Fig. 2). The RSC $\delta^{18}O$ values of +6.5 to +11‰ are clearly depleted in ^{18}O compared with the former, NRSC group of carbonates. In the NRSC there does not appear to be a relationship between the $\delta^{18}O$ value of the calcite or dolomite and the nature or proportion of silicate minerals directly associated with the stratabound carbonates, or the nature of the immediately surrounding felsic volcanics.

A finely laminated carbonate-chert (AR1) is thought to be a stromatolite, partly silicified during a later alteration (Boekschoten et al. 1988). Carbon isotopic values are consistent with Proterozoic marine values and oxygen isotopic values are ^{18}O depleted in a similar way to the above described carbonates. One calcite (Cab 1B) connected with a stratiform iron-oxide deposit altered into skarn gives a relatively low $\delta^{13}C$ value of −2.87‰ which is comparable with $\delta^{13}C$ values of calcites formed in the skarn phase, but it has a normal $\delta^{18}O$ value for NRSC.

Calcite clots and veins (stars in solid circles in Fig. 2), formed during skarn alteration of the stratiform iron-oxide deposits, have lower $\delta^{13}C$ values ($-3.5<\delta^{13}C<-2$‰) than the RSC, and are similar in $\delta^{18}O$ values to most of the RSC calcites. Minor (≤10 m thick) carbonate horizons of NRSC (3 samples) and RSC (1 sample) show the same $\delta^{13}C$ and $\delta^{18}O$ values as calcites in these skarns. Carbonates in W-(Mo-)skarns (squares in Fig. 2) have both low $\delta^{13}C$ and $\delta^{18}O$ values compared with the marine Proterozoic field. Their $\delta^{18}O$ values are similar to the $\delta^{18}O$ values of the RSC-type carbonates. Such $\delta^{13}C$ and $\delta^{18}O$ values are comparable to vein-type carbonates in skarns from contact aureoles associated with granitic intrusions (see Valley 1986: p. 455, Fig. 6). They define a separate field from that defined for Fe-skarn calcite isotope values. The δD values for fluid inclusion H_2O from two of the W-(Mo-)skarn calcites are very similar at −60‰. These values are plotted in Fig. 3 against

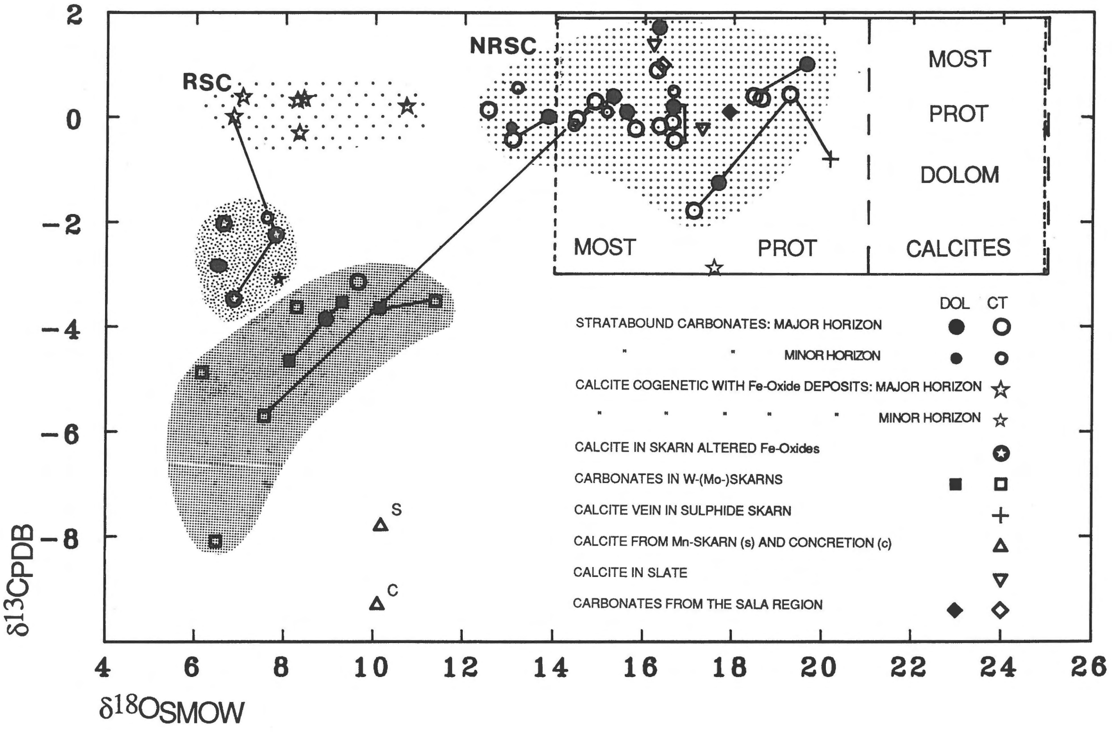

Fig. 2. Values of $\delta^{18}O_{SMOW}$ against $\delta^{13}C_{PDB}$ of calcites (open symbols) and dolomites (solid symbols) from stratabound carbonates (circles and stars), and carbonates in skarn altered Fe-oxide deposits (stars in solid circles), W-(Mo-)skarns (squares), and a sulphide skarn (cross). Also given are calcite from a Mn-skarn (triangle marked with s), calcite from the mass of a septarian concretion (Ehlin & Koark 1980) (triangle marked with c), and disseminated calcites from two slate samples containing the concretion (Ehlin & Koark 1980) (inverted triangles). Two carbonate samples from the Sala region (Schidlowski et al. 1975) (diamonds) are included for comparison. Connected samples are linked by tie-lines. *Square-pattern stippled* and *diamond-pattern stippled* areas define fields of stratabound carbonates (NRSC, see text) and stratabound carbonates related to stratiform iron-oxide deposits (RSC) respectively. The *irregular stippled* field defines carbonate veins and clots in skarn altered iron-oxide deposits, and the *densely stippled* field carbonate clots in W-(Mo-)skarns.

the vein calcite and the calculated $\delta^{18}O$ of water in equilibrium with the host calcite for 200° C, 250° C, 300° C, and 400° C. This temperature range was measured on fluid inclusions ($T_{\text{homogenisation}}$) in the calcite, although most of the values obtained were close to 250° C; for this reason the calculated water composition at 250° C is marked with a small box on Fig. 3. The temperatures are not very precise and the salinity of the fluids could not be determined because of the small size of the inclusions (<10 μm); halite-cubes were observed in some inclusions and imply the existance of a highly saline fluid (>15% equiv. NaCl) in some of them. All the inclusions have a regular rectangular shape. They are, however, probably secondary because they are situated in trails touching the crystal-boundaries. The calcites did not necessarily reequilibrate isotopically with such secondary fluids. Therefore, the calculated $\delta^{18}O$ H_2O value in equilibrium with calcite is probably not identical to that of the secondary inclusions measured for δD. For this reason, vertical arrows are given on Fig. 3 to emphasize that the δD value of the fluid associated with the *crystallization* of the calcite is not known. The single vein calcite (ERN S1) in a Zn-Pb sulphide skarn, formed in a fault zone, is totally different compared to the other skarn carbonates. The veins are only 2 to 3 mm thick and are associated with major sphalerite and galena (Hellingwerf pers. comm. 1987). Its mineral paragenesis and geological setting is different from the W-(Mo-) and Fe-skarn carbonates.

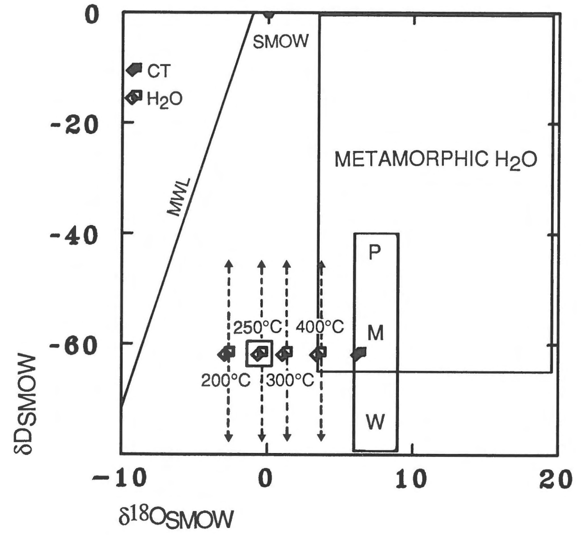

Fig. 3. Skarn calcite $\delta^{18}O_{SMOW}$ plotted against δD_{SMOW} from H_2O of secondary fluid inclusions in the skarn calcite (solid symbols). Calculated values of H_2O in equilibrium with calcite containing given δD values, at 200° C, 250° C, 300° C, and 400° C are plotted as open symbols. The vertical broken lines are drawn to stress the fact that the fluid of the secondary inclusions most probably did not equilibrate with the calcite (see text). The box around the 250° C value points to the most probable temperature of the (secondary) fluid phase. Fields for metamorphic H_2O and primary magmatic H_2O (PMW) (from Sheppard, 1986; p. 171; Fig. 4), the meteoric water line (MWL), and the standard mean ocean water (SMOW) point are shown for reference.

Slate (quartzitic siltstone) from the Grythyttan region contains Ca-Mn carbonates as disseminated granules, interstitial aggregates, and fracture filling veinlets (Oen et al. 1986). Calcite from such a slate sample (77Md302/18) from the Grythyttan region has $\delta^{13}C$ of −7.8‰ and $\delta^{18}O$ of +10.2‰. These values are very similar to those of the massive part of a septarian concretion in the Grythyttan slate quarry, 500 m north of our sample location ($\delta^{13}C$ of −9.3‰ and $\delta^{18}O$ of +10.1‰; Ehlin & Koark 1980). Two calcite-bearing slate samples surrounding the concretion, reported by Ehlin & Koark (1980), give $\delta^{13}C$ values of +1.4‰ and −0.2‰ and $\delta^{18}O$ values of +16.2‰ and +17.3‰ respectively, which are comparable with the isotopic values of the stratabound carbonates of Bergslagen.

Discussion

Stratabound carbonates

All of the $\delta^{13}C$ values of the stratabound carbonates (NRSC and RSC, Table 1, Fig. 2) fall within the proposed range of marine carbonate values for the early to middle Proterozoic period. It is probable, for the following reasons, that most of these carbonates have essentially retained their primary pre-diagenetic and pre-metamorphic $\delta^{13}C$ values. Most of the carbonates, whether dolomite or calcite, have the same $^{13}C/^{12}C$ ratio (~0 ± 0.5‰) on a regional scale, despite the wide range of $\delta^{18}O$ values. Many of the samples come from massive carbonate dominated units with no petrographic evidence for decarbonation. During diagenesis and low to middle grade metamorphism carbon isotope ratios are often not significantly modified (Keith & Weber 1964; Sheppard & Schwarcz 1970). These ratios are therefore characteristic of their marine origin. By analogy, then, the felsic volcanics in Bergslagen were deposited under sea water. Although this interpretation has been proposed previously (e.g. Oen et al. 1982; Van der Velden et al. 1982; Baker & De Groot 1983; Vivallo 1985) it was based on less definite evidence than the carbon isotope data. The $\delta^{18}O$ values of the NRSC calcites and dolomites are up to 8‰ depleted in ^{18}O compared to the 'most Proterozoic dolomites' field, which is considered to be the most probable field of marine Proterozoic carbonate $\delta^{13}C$ and $\delta^{18}O$ values. The majority of the calcite $\delta^{18}O$ values, however, are consistent with the range found for 'most Proterozoic calcites'. Calcites and dolomites from the Svecofennian of central Sweden commonly show $\delta^{18}O$ values of between +14 to +18‰. Such values are also reported for two carbonate samples from the Sala region, about 100 km east of Ställdalen, by Schidlowski et al. (1975) (diamonds in Fig. 2) and for some samples of the Bergslagen region by Billström et al. (1986). The results of Billström et al. (1986) are, however, not integrated with our results because no information was given on whether a carbonate sample was stratabound or skarn-related.

Thus *all* NRSC type calcites and dolomites from central Sweden are systematically ^{18}O-depleted relative to the 'most Proterozoic dolomite' field. This suggests that *all* of the $\delta^{18}O$ values of the carbonates either were modified during diagenetic, hydrothermal and/or metamorphic processes or have closely retained their primary sedimentary values. This latter interpretation implies that either the temperature of formation of these carbonates was about 15 to 60° C higher than that for 'most Proterozoic dolomites' assuming isotopically similar waters, or the associated waters were depleted in ^{18}O, if the temperatures were similar. Isotopic homogenisation on a scale greater than a few metres during regional metamorphism does not appear to have been an important process because nearby samples can have $\delta^{18}O$ differences of 1‰ or more. Thus the $\delta^{18}O$ variations of the calcites could in part be due to local scale exchange with the associated silicates during the regional metamorphism or be inherited from the pre-regional metamorphic alteration processes. The latter may be the dominant process because of the relatively restricted range of $\delta^{18}O$ values of the dolomites and some of the carbonate units are essentially pure (>95%) calcite or dolomite.

The RSC calcites are directly associated with iron-oxide deposits. If the RSC were deposited on a sea floor then the isotope values should be comparable with the NRSC values or the 'most Proterozoic dolomite' field. The far lower $\delta^{18}O$ values of RSC calcites (+7 to +11‰) compared to the NRSC, implies that either these calcites exchanged with more ^{18}O-depleted fluids at approximately the same temperature of formation as the NRSC or, if the $^{18}O/^{16}O$ ratios of the fluids were relatively comparable, the temperatures of formation of the RSC calcites must have been $\geqslant 30°$ C higher than those of NRSC, or 100° to 250° C higher than 'most Proterozoic dolomites'. Alternatively the range of $\delta^{18}O$ values reflects both variations in temperature and fluid composition. Waters in equilibrium with the most ^{18}O-depleted calcites ($\sim +6‰$) have $\delta^{18}O \sim 0 \pm 2‰$ for $T \sim 300 \pm 50°$ C, a value similar to that proposed for Proterozoic sea water (e.g. Muehlenbachs 1986; Sheppard 1986). Lower temperatures require more ^{18}O-depleted waters; such waters could be of meteoric origin. These fluids could be similar to those involved in forming the clot and vein carbonates in the skarn alteration of the stratiform iron oxide deposits.

The C- and O-isotope compositions of RSC calcites are different for either one or both isotopic ratios in carbonates from BIF-type deposits (Becker & Clayton 1972). Also the carbonates associated with BIF-type deposits are usually Fe-Mg rich (siderite, ankerite, dolomite) and not calcitic like the RSC.

This sea water or meteoric hydrothermal alteration process operated on a regional scale and could also have been responsible for the large scale alteration of the associated volcanics. Such systems often produce alteration assemblages or minerals with quite variable $\delta^{18}O$ values because of variations in water/rock ratio, permeability, etc., as well as temperature. In fact the types of $\delta^{18}O$ values of the carbonates (NRSC and RSC) and their range are comparable to those observed in well documented sea water hydrothermal systems of younger age – ocean floor, ophiolites (e.g. Muehlenbachs 1986 and references therein) and many meteoric hydrothermal systems where $\sim -60 < \delta D < 0‰$ (e.g. Clayton et al. 1968). This interpretation implies that the isotopic composition of the different rock units were often not significantly modified by subsequent processes and therefore the later regional metamorphic event was not associated with large scale fluid transport processes.

Carrbonates from W-(Mo-)skarns

This group of samples has low $\delta^{13}C$ values (between −3 and −8‰) and low $\delta^{18}O$ values (between +6 and +11‰). Although these carbonates are associated with skarn mineralizations they cannot have formed during in situ decarbonation because they occur as clots, a late mineralized phase in the skarns. A hydrothermal fluid must therefore have been involved. The nature and source of this fluid has not yet been clearly documented because the regional metamorphism may have modified the fluid inclusion evidence. All the fluid inclusions which have been observed are secondary and are therefore probably post-skarn formation. Also, no hydrous minerals are found in these clots.

In skarns the CO_2/H_2O ratio is usually quite small ($X_{CO_2} < 0.1$; e.g. Taylor & O'Neil 1977) and therefore the oxygen isotope composition of the calcite or dolomite is controlled by the $\delta^{18}O$ value of the aqueous fluid and the temperature of precipitation. As discussed above, the H_2O part of the fluid phase could be either of sea water or meteoric origin. The ^{13}C-depleted carbonates with $\delta^{13}C \sim -3$ to -8‰ imply that the $\delta^{13}C$ value of the CO_2 in the fluid was about -2 to -7‰ at temperatures above 200° C (Bottinga 1968). The more ^{13}C-depleted values of this range could be of magmatic origin, could come from decarbonation reactions or could come from the hydrolysis of organic carbon.

Magmatic carbon with $\delta^{13}C \sim -5 \pm 3$‰ has often been proposed as the dominant source of vein carbonate carbon in skarn deposits (e.g. Taylor & O'Neil 1977; Einaudi et al. 1981). Identical ^{13}C-depleted values could also be generated during decarbonation of carbonates initially with sedimentary type $\delta^{13}C$ values. For example, using a Rayleigh type fractionation model, 60% to essentially 100% decarbonation would be necessary to produce the wide range of $\delta^{13}C$ values. This process requires that decarbonation occurred in one place and was followed by precipitation of vein carbonate in another place from the residual CO_2 in the hydrothermal fluid. It also implies that the volumetric importance of the carbonates decreases rapidly with decreasing $\delta^{13}C$ values. Similarly, the observed $\delta^{13}C$ values could be reflecting the hydrolysis of organic carbon, which is strongly ^{13}C-depleted. The necessary organic matter would have to be associated with either the stratabound carbonates, which are found within the volcanic sequence, or the overlying shales. Although the present data cannot distinguish among these three possibilities, they all require the transfer of a CO_2-bearing fluid to form the carbonate clots.

Two of the stratabound (NRSC) samples have isotopic values in the same range as the W-(Mo-) skarn carbonates. A possible explanation is that because of their short distance from a skarn they were altered by the same fluid as that forming the skarn.

Calcite in skarn altered iron oxide deposits

Most of the stratiform iron-oxide deposits in W. Bergslagen are altered into a skarn during later hydrothermal events. Mobilization of elements and mineral phases occurred during the skarn forming processes, as well as late formation of calcite veins or clots in the skarn. The $\delta^{13}C$ (-2 to -4‰) and $\delta^{18}O$ ($+6$ to $+8$‰) ranges are small (perhaps because only three samples were analysed). They define a distinct field (irregular stippled area in Fig. 2) from the W-(Mo-)skarn carbonate field (densely stippled area in Fig. 2). Keeping in mind the smaller range of isotopic values and the less negative $\delta^{13}C$ values for the former, similar explanations as for the W-(Mo-) skarn carbonates can be given.

Minor (<10 m thick) calcite horizons of the NRSC (3 samples) and RSC (1 sample) have similar isotope values as the 'Fe-skarns' discussed here. These NRSC horizons are situated close to 'Fe-skarn' or are expected to be close. They are, because of their limited thickness, altered isotopically (and eventually chemically) by the same fluids as involved with the skarn. Sample St2 of the NRSC contains clots of silicate minerals (amphibole, mica). It is situated in the border zone of an Fe-skarn at Stolpberget, which is unambiguously not stratiform. This skarn most likely formed along or in a (meta-) diabase dyke, striking N340E – a general strike direction for major joint systems and diabase dykes in this part of Bergslagen – and cuts the Stolpberget stratabound minor carbonate horizon with a distinctly different isotopic signature. Alteration processes and the isotopic compositions of this fluid associated with this skarn seem to be similar to those for the skarn alteration of the stratiform iron-oxide deposits.

Calcite veins in a sulphide skarn

A small vein containing calcite and Zn-Pb-sulphides in a fault zone near Erntorp (Ern S1) is isotopically close to the NRSC values. Two stratabound carbonate samples, one (HW NV576), a fragment in a breccia from below the major zone of stratiform Zn-Pb-sulphide mineralisation, and the other (ERN M1) from a massive marble bed containing chert horizons up to several dm thick (Hellingwerf et al. 1988, see Table 1 and Fig. 2), have NRSC type values. The genesis of this mineralization is not yet fully understood.

Calcites from slate

The carbon and oxygen isotope compositions of calcite from the Ca-Mn-skarn vein carbonates (SVC) in the Grythyttan slate are similar to both the values of calcite and dolomite from the skarns and a calcite from a concretion in the slates (Fig. 2). The latter has been interpreted by Ehlin & Koark (1980) to be precipitated during the diagenesis of organic matter-bearing sediments.

Oen et al. (1986) have presented evidence for microbial fossils in a Ca-Mn skarn and suggested that the sediment was composed of laminae of mats of organic material interlayered with cherts. During the diagenesis of such a sediment ^{13}C-depleted carbonates could have been precipitated. The δ^{13}C values of the SVC could thus have been inherited from the diagenetically modified sediment.

Alternatively the isotopic compositions of the SVC were produced during the reaction of hydrothermal fluids on the sediment and their origin could be similar to that of the skarn associated carbonates. This interpretation implies that preexisting sedimentary carbonates were isotopically modified by the hydrothermal fluids, as part of the carbonate is not in veins but is disseminated in the slate. The observed isotopic compositions may well be reflecting a combination of the sedimentary and diagenetic processes and a hydrothermal event.

Conclusions

Different groups of carbonates can be distinguished in the W. Bergslagen region. The stratabound carbonates were deposited in a marine environment as based on their carbon isotopic compositions. They can be divided into two groups with different δ^{18}O values. One group (RSC; +6 – +11‰) is associated with iron-oxides whilst the other (NRSC; +12 – +20‰) is not. This difference could be an useful tool in exploration to trace the proximity of stratiform iron-oxide deposits (eventually altered into skarn). The moderate (NRSC) to low (RSC) δ^{18}O values of these carbonates probably record a sea water or meteoric hydrothermal process with the RSC carbonates forming at a higher temperature (possibly 30 to 200° C) than the NRSC carbonates, assuming similar fluids.

Carbon dioxide of magmatic and/or decarbonation origin was introduced during deposition of calcite and dolomite veins and clots in the skarns. Different types of skarns show different ranges for both δ^{13}C and δ^{18}O values, and thus define different fields without any overlap. Discrimination between such skarn types can therefore be made based on the isotopic composition of carbonates.

Further studies to obtain more detailed information about the insufficiently understood hydrothermal processes and oxygen isotopic depletion in the vein, clot, and RSC carbonates and skarns are in progress.

Acknowledgments

We thank I.S. Oen and an anonymous reviewer for their useful suggestions on this paper. We are grateful to the Geological Museum of the University of Amsterdam and to J.H. Baker and R.H. Hellingwerf for donating some of the samples used in this study. A.A. de Maesschalck is thanked for supplying sample 77Md302/18.

A special word of thanks is given to J.H. Baker and R.H. Hellingwerf for their stimulating discussions and useful information about the geological setting of most of the sample sites. We also like to mention P. Coget for his assistance in the laboratory and J. Gorau for photographing the figures.

One of the authors (P de G) was supported during this study by a grant from the French CIES organisation.

References

Åberg, G., Levi, B. & Fredriksson, G. 1983. Zircon ages of metavolcanic and synorogenic granitic rocks from the Svärdsjö and Yxsjöberg areas, South Central Sweden – Geol. För. Förh. 106: 199–203

Baker, J.H. 1985a. The petrology and geochemistry of 1.8–

1.9 Ga granitic magmatism and related sub-seafloor hydrothermal alteration and ore-forming processes, W. Bergslagen, Sweden – PhD thesis. GUA Papers of Geology, Ser. 1, 21, Amsterdam: 204 pp

Baker, J.H. 1985b. Rare earth and other trace element mobility accompanying albitization in a Proterozoic granite, W. Bergslagen, Sweden – Min. Mag. 49: 107–115

Baker, J.H. & De Groot, P.A. 1983. Proterozoic seawater – felsic volcanics interaction W. Bergslagen, Sweden. Evidence for high REE mobility and implications for 1.8 Ga seawater compositions – Contrib. Mineral. Petrol. 82: 119–130

Becker, R.H. & Clayton, R.N. 1972. Carbon isotopic evidence for the origin of a banded iron-formation in Western Australia – Geochim. Cosmochim. Acta, 36: 577–595

Billström, K., Åberg, G., & Nord, A.G. 1986. Stable isotope data of Bergslagen carbonates and their potential use for sulphide ore prospecting – Geol. För. Förh. 107: 169–173

Boekschoten, G.J., Van der Raad, A.C. & Van Kenter, J. 1988. Note on a mid-Proterozoic stromatolite limestone, south of Grythyttan, Bergslagen, Sweden. In: Baker, J.H. & Hellingwerf, R.H. (eds): The Bergslagen ore province, Central Sweden – Structure, stratigraphy and ore-forming processes I.G.C.P. project 247 – Geol. Mijnbouw 67: 467–469 (this issue)

Bottinga, Y. 1968. Calculation of fractionation factors for carbon and oxygen exchange in the system calcite-carbon dioxide-water – J. Phys. Chem. 72: 800–808

Clayton, R.N., Muffler, L.J.P., & White, D.E. 1968. Oxygen isotope study of calcite and silicates of the River Ranch No. 1 Well, Salton Sea geothermal field, California – Am. J. Sci. 266: 968–979

Craig, H. 1957. Isotopic standards for carbon and oxygen and the correction factors for mass spectrometric analysis of carbon dioxide – Geochim. Cosmochim. Acta, 12: 133–149

De Groot, P.A., Baker, J.H., & Oen I.S. 1988. Evidence for gravity subsidence and granite diapirism in the 1.8–1.9 Ga Proterozoic successions of W. Bergslagen, Sweden – Geol. Mijnbouw, 67: 19–29

Ehlin, P.-O. & Koark, H.J. 1980. Svecofennian paradiagenetic concretions – N. Jb. Geol. Paläont. Mh. 3: 145–154

Einaudi, M.T., Meinert, L.D. & Newberry, R.J. 1981. Skarn deposits – In: B.J. Skinner (ed.): Econ. Geol. 75th Anniversary Volume: 317–391

Epstein, S., Graf, D.L., & Degens, E.T. 1964. Oxygen isotope studies on the origin of dolomites – In: H. Craig, S.L. Miller, & G.T. Wasserburg (eds): Isotopic and Cosmic Chemistry, dedicated to H.C. Urey 70th birthday North Holland, Amsterdam: 169–180

Friedman, I. 1953. Deuterium content of natural waters and other substances – Geochim. Cosmochim. Acta, 4: 89–103

Godfrey, J.D. 1962. The deuterium content of hydrous minerals from the East-central Sierra Nevada and Yosemite National Park – Geochim. Cosmochim. Acta, 26: 1215–1245

Hellingwerf, R.H. 1984. Paragenetic zoning and genesis of Cu-Zn-Fe-Pb-As sulfide skarn ores in a Proterozoic rift basin, Gruvåsen, Western Bergslagen, Sweden – Econ. Geol. 79: 696–715

Hellingwerf, R.H. & Baker, J.H. 1985. Wall-rock alteration and tungsten and molybdenum mineralisations associated with older granites in Western Bergslagen, Sweden – Econ. Geol. 80: 479–487

Hellingwerf, R.H., Lilljeqvist, R. & Ljung, S. 1988. Stratiform Zn-Pb-Fe-Mn mineralization in the Älvlången-Vikern area, Bergslagen, Sweden. In: Baker, J.H. & Hellingwerf, R.H. (eds.): The Bergslagen ore province, Central Sweden – Structure, stratigraphy and ore-forming processes. I.G.C.P. project 247 – Geol. Mijnbouw, 67: 313–332 (this issue).

Hellingwerf, R.H. & Oen, I.S. 1986. Some geochemical aspects of altered and less altered metabasic rocks in the Saxå area, Bergslagen, Sweden – N. Jb. Miner. Mh. 2: 65–81

Hudson, J.D. 1978. Concretions, isotopes, and the diagenetic history of the Oxford Clay (Jurassic) of central England – Sedimentology, 25: 339–370

Keith, M.L. & Weber, J.N. 1964. Carbon and oxygen isotopic composition of selected limestones and fossils – Geochim. Cosmochim. Acta, 28: 1787–1816

Lagerblad, B. & Gorbatschev, R. 1985. Hydrothermal alteration as a control of regional geochemistry and ore formation in the central Baltic Shield – Geol. Rundsch. 74: 33–49

Magnusson, N.H. 1925. Persbergs malmtrakt – Beskrivningär över mineralfyndigherter, 3, Kungl. Kommerskollegium: 231 pp

Magnusson, N.H. 1970. The origin of the iron ores in central Sweden and the history of their alterations – Sver. Geol. Unders., Serie C, 643: 364 pp

McCrea, J.M. 1950. The isotopic chemistry of carbonates and a paleotemperature scale – J. Chem. Phys. 18: 849–857

Miller, R.G., O'Nions, R.K., Hamilton, P.J. & Welin, E. 1986. Crustal residence ages of clastic sediments, orogeny and continental evolution – Chem. Geol. 57: 87–99

Muehlenbachs, K. 1986. Alteration of the oceanic crust and the ^{18}O history of seawater – In: J.W. Valley, H.P. Taylor Jr. & J.R. O'Neil (eds.): Stable isotopes in high temperature geological processes – Reviews in Mineralogy, 16: 425–444

Northrop, D.A., & Clayton, R.N. 1966. Oxygen isotope fractionation in system containing dolomite – J. Geol. 74: 174–196

Oen, I.S. 1987. Rift-related igneous activity and metallogenesis in S.W. Bergslagen, Sweden – Precambr. Res. 35: 367–382

Oen, I.S., De Maesschalck, A.A., & Lustenhouwer, W.J. 1986. Mid-Proterozoic exhalative-sedimentary Mn skarns containing possible microbial fossils, Grythyttan, Bergslagen, Sweden – Econ. Geol. 81: 1533–1543

Oen, I.S., Helmers, H., Verschure, R., & Wiklander, U. 1982. Ore deposition in a Proterozoic incipient rift zone environment: a tentative model for the Filipstad – Grythyttan – Hjulsjö region, Bergslagen, Sweden – Geol. Rundsch. 71: 182–194

Oen, I.S. & Verschure, R.H. 1985. Isotopic age determinations in Bergslagen, Sweden: VII The Fellingsbro-type granite east of Kopparberg – Geol. Mijnbouw, 64: 385–388

Schidlowski, M., Eichmann, R., & Junge, Ch.E. 1975. Precambrian sedimentary carbonates: carbon and oxygen isotope geochemistry and applications for the terrestrial oxygen budget – Precambr. Res. 2: 1–69

Sheppard, S.M.F. 1986. Characterization and isotopic variations in natural waters – In: J.W. Valley, H.P. Taylor Jr. & J.R. O'Neil (eds.): Stable isotopes in high temperature geological processes – Reviews in Mineralogy, 16: 165–183

Sheppard, S.M.F. & Schwarcz, H.P. 1970. Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite – Contrib. Mineral. Petrol. 26: 161–198

Smith, J.W. & Croxford, R.J.W. 1975. An isotopic investigation of the environment of deposition of the McArthur mineralisation – Miner. Deposita, 10: 269–276

Sundius, N. 1923. Grythyttefältets geologi – Sver. Geol. Unders., Serie C321: 354 pp

Taylor, B.E. & O'Neil, J.R. 1977. Stable isotope studies of metasomatic Ca-Fe-Al-Si skarns and associated metamorphic and igneous rocks, Osgood Mts., Nevada – Contrib. Mineral. Petrol. 63: 1–49

Valley, J.W. 1986. Stable isotope geochemistry of metamorphic rocks – In: J.W. Valley, H.P. Taylor J.R., & J.R. O'Neil (eds): Stable isotopes in high temperature geological processes – Reviews in Mineralogy, 16: 445–489

Van der Velden, W., Baker, J., De Maesschalck, S., & Van Meerten, Th. 1982. Bimodal early Proterozoic volcanism in the Grythytte field and associated volcano-plutonic complexes, Bergslagen, Central Sweden – Geol. Rundsch. 71: 171–181

Veizer, J. & Hoefs, J. 1976. The nature of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ secular trends in sedimentary carbonate rocks – Geochim. Cosmochim. Acta, 40: 1387–1395

Vivallo, W. 1985. Subseafloor hydrothermal alteration during the Early Proterozoic at Garpenberg, Central Sweden – Miner. Deposita, 20: 33–42

Vivallo, W. & Rickard, D. 1984. Early Proterozoic ensialic spreading – subsidence. Evidence from the Garpenberg enclave, Central Sweden – Precambr. Res. 26: 203–221

Welin, E., Wiklander, U. & Kähr, A.M. 1980. Radiometric dating of a quartz-porphyritic potassium rhyolite at Hällefors, South Central Sweden – Geol. För. Förh. 102: 269–272