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Lithogeochemical patterns around Pb-Zn mineralizations in Dinantian carbonate rocks of (eastern) Belgium

R. Swennen and W. Viaene

Afdeling Fysico-chemische geologie, Katholieke Universiteit Leuven, Celestijnenlaan 200 C, B-3030 Heverlee, Belgium

Abstract. The lithogeochemical distribution patterns of Mg, Sr, Na, Zn, Pb, Fe, Mn, K, Corg (organic matter) and IR (insoluble residue) in the Dinantian limestones and dolomites from the eastern part of Belgium have been studied (Dinant and Verviers synclinorium). Comparison of geochemical data of non-mineralized strata revealed higher background values in the strata of the Verviers synclinorium where Pb-Zn mineralizations occur. In this area a relation may exist with the metallogenetic district (Herve-Vesdre-Theux district; proposed by Dejonghe 1985b). However, the higher background values also could relate to the more restricted sedimentation conditions in the Verviers synclinorium as opposed to the more open marine conditions in the Dinant synclinorium. The influence of mineralization on the geochemistry of limestones is limited and unpredictable. In dolomites, however, the effect can be important. In these rocks, the lithogeochemical distribution of Zn, Pb and Mn can be subdivided into three populations, i.e. a regional background, a local high background and a halo population. The higher trace element concentrations in the halo population is caused by the existence of disseminated sulfide minerals (sphalerite, galena and pyrite) and Zn-bearing goethite (mainly pseudomorphs after pyrite) and Mn-oxides. The sulfides relate to the ore emplacement. In the local high background only the Zn-bearing oxides occur. Their presence and thus the development of the local high background relates to weathering processes.

The most important Pb-Zn mineralizations in Belgium occur in the Dinantian carbonates of the Verviers synclinorium (Fig. 1) situated between Liège and Aachen (Germany). According to Dejonghe & Jans (1983), Dejonghe (1985b) and Scheps and Keyssner (1988), these mineralizations are classified as Mississippi-Valley type deposits. Mining was most active at the end of the nineteenth and the beginning of the twentieth century. Widespread mining in the past contaminated the environment significantly. Since the link between lithogeochemical patterns and mineralization is direct, lithogeochemistry has been tested for its usefulness in prospecting for Pb-Zn mineralizations in this area.

The aim of this paper is to document lithogeochemical distribution patterns within carbonates occurring in the mineralized Verviers synclinorium and the non-mineralized areas (the Dinant synclinorium and the barren western part of the Verviers synclinorium). Attention will be paid to the difference in distribution patterns especially of Zn, Pb, Mn and Fe in limestones and dolomites. The factors controlling the developments of anomalies will be investigated and attention will be paid to mineralogical phases which influence the lithogeochemical patterns around mineralizations.

Geological setting

The majority of the ore bodies in the Verviers synclinorium are hosted by Dinantian carbonates. The sedimentology and diagenesis of these strata have been reviewed by Swennen et al. (1982) and Swennen (1986). The Dinantian sequence in this area can be subdivided into four lithological units (from bottom to top: Fig. 1).

1. a crinoidal packstone to grainstone unit with a shale intercalation (30 m thick). The limestones mainly reflect subtidal sedimentation conditions;
2. a dolomite sequence (locally up to 300 m thick). These dolomites become less important towards the (unmineralized) Dinant synclinorium, i.e. towards the platform margin. Here limestones become intercalated. The overall trend is regressive. Dolomitization by reflux of hypersaline brines was proposed by Swennen and Viaene (1985);
3. a breccia unit, (particulate to cemented packbreccia up to 42 m thick). Brecciation resulted from the dissolution of intercalated evaporites (Swennen, Viaene and Cornelissen 1990);
4. a limestone sequence (more than 350 m thick). The limestones immediately above the breccia reflect peritidal

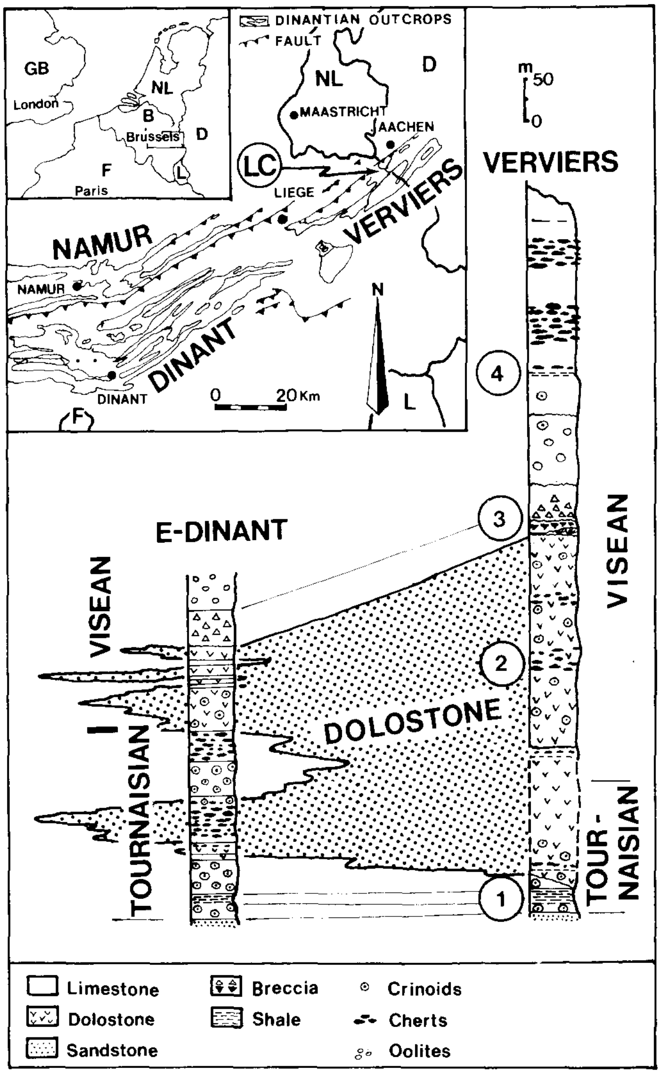

Fig. 1. Geological setting and lithostratigraphy of the Dinantian strata in the eastern part of Belgium. Numbers 1 to 4 respectively correspond to crinoidal limestones, dolomites, carbonate breccia and limestones LC = location of the "La Calamine" orebody

conditions. This is followed by oolitic and bioclastic limestone deposited within a shallow subtidal setting.

In the present study, Dinantian strata from the unmineralized eastern part of the Dinant synclinorium were also included. The Dinant and Verviers synclinoria both belonged to the same sedimentary basin. However, more restricted sedimentation conditions characterize the Verviers strata (Swennen 1986).

The mineralized Verviers synclinorium is intensly dissected by longitudinal (ENE-WSW: Variscan) and transverse faults (NNW-SSE: post-Variscan and related to the Rhine-Roermond graben tectonics; Fig. 4). Most of the ore deposits were located at the intersection between subvertical transverse faults and the lithological contact between carbonate rocks and sandstone/shale. Notice that no genetic relationship exists between the intra-Visean reflux dolomites and the mineralizations. The mineralization itself is believed to be Permo-Triassic in age (de Magnée 1967).

According to Dejonghe and Jans (1983) approximately 1100000 tons Zn and 130000 tons Pb were produced in this area. Mining was most important at and around the "La Calamine" deposit (Fig. 1). This mineralization, however, is exceptional. In contrast to other mineralizations, which are small and high-grade sulfide deposits, the "La Calamine" mineralization was oxidic in nature (mainly calamine-ore = mixture of smithsonite, willemite and hemimorphite). The mineralizations have been reviewed by Gussone (1967), Dejonghe and Jans (1983) and others, while metallogenetical concepts have been discussed by de Magnée (1967), Gussone (1967), Walther (1982), Cauet and Weis (1983), Dejonghe (1985a, b), Krahn et al. (1986), Scheps and Keyssner (1988) and others.

Methods

More than 1400 representative samples from about 25 major references sections have been collected by chip sampling. Additionally smaller dolomite outcrops have been sampled to increase sample density. After crushing and milling to a size lower than 100 µm, 2 g of the fine material were decomposed in 20 ml 12.5 N hydrochloric acid. After the reaction was completed, the dissolved sample was evaporated and the residue dissolved in 40 ml 2.5 N hydrochloric acid. After filtration the fluid was diluted to 100 ml. Mg, Sr, Na, Zn, Pb, Fe, Mn and K were analysed by atomic absorption spectrometry. Matrix interferences for Sr, Pb and K were corrected by comparing the samples with representative calcite and/or dolomite calibration curves (Van Orsmael 1982). Background-absorption interferences within residue-rich samples were corrected using the hydrogen lamp continuum (Govett and Whitehead 1973). The insoluble residue content (IR) was determined gravimetrically. Analytical precision was generally better than 10% at the 95% confidence level. The Mg and IR concentrations are given in percent while the other element concentrations are given in ppm. The Walkley and Black method (Allison 1965) was used to determine the content of organic matter (Corg). Unfortunately, sulfide phases (e.g. pyrite, . . .) are also affected by this method. Therefore, in sulfide-rich carbonates, anomalous results do not directly relate to the organic matter content [see also discussion in Barbier (1979)].

Statistical analyses were performed after log transformation of the data (log normality based on the Komogorov D test). Most of the samples group in a limestone population ($<1\%$ Mg) and in a dolomite population ($>10\%$ Mg). Partly dolomitized limestones (Mg% between 1 and 10%) were not considered in the statistical treatment (about 20% of the samples).

Lithogeochemical distribution patterns and interpretations

Based on the distribution patterns of the samples and data, different populations were recognized. The regional background population refers to the normal abundance of an element in the rocks studied. Threshold is defined as the upper limit of normal background fluctuations (Rose et al. 1979). Anomalies may occur in a broad area of higher than normal threshold values. The interval between a normal threshold and anomalous values is defined as local high-background interval.

Lithogeochemistry of carbonate strata in non-mineralized areas

Normal (regional) background

The normal (regional) background values of the limestones and dolomites were calculated on the basis of sections in non-mineralized areas of both the Dinant and Verviers synclinoria. The arithmetic mean values and the range of 80% of the samples around this mean value are given in Table 1. In dolomites a bimodal distribution for some variables was observed. In these cases, the mean values of both populations are given in Table 1. This bimodality often relates to the lower trace element contents in the coarse-grained dolomites occurring close to the dolomitization front (Swennen and Viaene 1985). Moore et al. (1988) explain the bimodal distribution pattern for Fe in the Smackover dolomites in a similar way.

The limestones of the Verviers synclinorium clearly have higher mean values and spreadings for Sr, Zn, Pb, Mn and K, while their Na, Corg and IR values are lower than for the limestones of the Dinant synclinorium. Fe contents are comparable in both regions (Table 1). The dolomites of the Verviers synclinorium behave in a rather similar way. However, here Fe and IR together with Sr, Zn, Pb, Mn and K are higher. For Corg and Na comparable values were recorded within both regions (Table 1).

In comparison with dolomites of each synclinorium, the limestones are characterized by higher Sr, Zn, Pb and K contents, while Na and Fe are clearly lower. The differences in trace element content between limestones and dolomites relate to several factors: sedimentation conditions, precursor composition of the carbonates, diagenetic influences, etc. . . . (see also Banner et al. 1988 and others). The discussion of these factors, however, is out of the scope of the present study.

From Table 1, threshold values in the limestones for Zn, Pb, Mn and Fe can be placed respectively at about 180 ppm, 32 ppm, 540 ppm and 2500 ppm; in dolomites threshold values are placed respectively at about 45 ppm, 6 ppm, 200 ppm and 3600 ppm. Only Zn, Pb, Mn and Fe are mentioned because, as will be discussed later, the patterns of these elements in particular are influenced around mineralizations.

Comparison of our results with literature data, however, can be misleading because of different analytical procedures and lack of information on sedimentology and diagenesis of the carbonate rocks. Therefore only results of the acid soluble fraction of carbonate rocks are compiled in Table 2.

The limestone data recorded in the Dinant and Verviers synclinorium have mostly a range of trace elements similar to the data reported in literature. Pb and Mn, however, are exceptionally low. In contrast, Zn values in the Verviers limestones are high. Only the data reported from the Visean limestones of the Aachen region (XRF and AAS-results by Scheps and Friedrich 1983) which in fact is the eastern continuation of the Verviers synclinorium are higher (Fig. 1). However, it is not clear whether the reported "Aachen-values" correspond to a background population or whether anomalous values were included in the statistical treatment of the data. The Dinant and Verviers dolomites possess relatively low Fe, Mn, Zn and Pb values when compared to literature data (Table 2). In summary, trace element concentrations are low or similar to reported literature data.

Table 1. Arithmetic mean values (after log transformation: $\bar{X}^2$) and range (80%) around the mean value within limestones and dolomites in non-mineralized areas

	Limestones			
	Dinant		Verviers	
	$\bar{X}$	Spreading (80%) of the data around $\bar{X}$	$\bar{X}$	Spreading (80%) of the data around $\bar{X}$
Mg	<1%	–	<1%	–
Na	145	75–201	66	32–138
Sr	315	240–510	380	188–1060
Zn	32	5–85	55	10–178
Pb	2.6	1.4–12.0	12.2	2–31
Mn	61	20–240	192	47–522
Fe	750	280–1820	770	250–2327
K	97	62–220	138	42–409
Corg	0.20	0.09–0.54	0.07	0.02–0.19
IR	4.8	2.1–8.5	3.4	1.0–5.8
	Dolomites			
	Dinant		Verviers	
	$\bar{X}$	Spreading (80%) of the data around $\bar{X}$	$\bar{X}$	Spreading (80%) of the data around $\bar{X}$
Mg	>10%	–	>10%	–
Na	88/208[a]	70–227	184	110–253
Sr	82	50–145	84/135[a]	62–200
Zn	8	2–25	26	10–43
Pb	1.7	1.4–4.2	3	2–5.6
Mn	78	35–166	139	67–190
Fe	696/1037[a]	338–1480	942/1642[a]	707–3548
K	34	22–150	42/150[a]	21–501
Corg	0.13	0.06–0.29	0.12	0.05–0.23
IR	2.4	1.0–7.0	4.5	1.9–6.8

[a] Variables with a bimodal distribution pattern

A regional variation, i.e. lower normal background values in the carbonates of the Dinant synclinorium than in the Verviers synclinorium (including the Aachen area; Scheps and Friedrich 1983), is apparent. The higher Zn, Pb, Mn and, to a certain extent, Fe contents in the Verviers carbonates may be interpreted as part of a geochemical province. However, a relationship between the geochemistry and the metallogenetic district is questionable. Differences in conditions of sedimentation with

Table 2. See text

	Reported values in limestones										Reported values in dolomites			
	1	2	3	4			5	6	7	8	10	11	12	13
				A	B	B								
Mg%	0.40–1.66	–	–	0.26	0.12	0.29	0.32–0.57	1.90	–	0.21	–	9.58	–	11.30
Sr	375–709	–	–	294	107	170	223–675	226	338	~382	–	38	–	98
Na	–	–	–	69	64	69	121–159	660	–	~1187	–	–	–	329
Fe	909–6433	250	–	2230	361	1190	–	8525	2345	~210	–	27 688	330	11 315
Mn	155–1161	17	–	255	173	791	52–294	449	–	~201	–	4 646	30	2 096
Zn	3–7	11	10–150	22	20	12	8–10	–	24	157	15–30	6.3	12.5	54
Pb	<1	<30	<5	–	26	–	–	–	–	74	2–5	0.2	<30	2
K	–	–	–	21	3	57	–	5394	285	664	–	–	–	28
IR%	3.2–10.0	1.9	–	1.9	0.6	4.0	–	8.33	7		–	11.90	3.5	1.1

1. Range of values reported by Barber (1974) (acetic-acid dissolution, Middle Jurassic Lincolnshire limestone and Carboniferous limestone).
2. Average values reported by Fruth and Scherreiks (1975) (heated HNO_3 (3N) dissolution; Norian limestone of the Alps).
3. Range of background interval reported by Kranz (1976) (HCl-dissolution, Middle Triassic Wettersteinkalk).
4. Background value reported by Wagner et al. (1980) (HCl conc.dissolution, Mississippian limestone of NW-Arkansas, A. Pitkin Fm., B. Boone Fm., C. St. Joe Fm.)
5. Range of mean values reported by Pascal (1979) (acetic acid and HCl dissolution, shallow marine Albian – Aptian limestones).
6. Mean values reported by Robinson (1979) (HCl (1M) dissolution, limestones values with IR < 10%; stratigraphic position not given).
7. Background values reported by Swennen et al. (1986) (analytical procedure see present paper; shallow marine limestones of Sikambr Fm. – NE. USSR).
8. Average values reported by Scheps and Friedrich (1983) (XRF and HF, HNO_3, HCl dissolution, Visean limestones of W-Germany).
10. Background values in the Dolomia Metallifera reported by Kranz (1974) (HCl-dissolution).
11. Data reported by Barber (1974) (acetic-acid, Middle Jurassic Lincolnshire dolomite and Carboniferous dolomites).
12. Average values reported by Fruth and Scherreiks (1975) (heated HNO_3 (3N) dissolution, Norian dolomites of the Alps).
13. Data reported by Muchez and Viaene (1990 in press) (analytic procedure see present paper; Fe-rich dolomites, Lower Carboniferous of the Halen borehole).

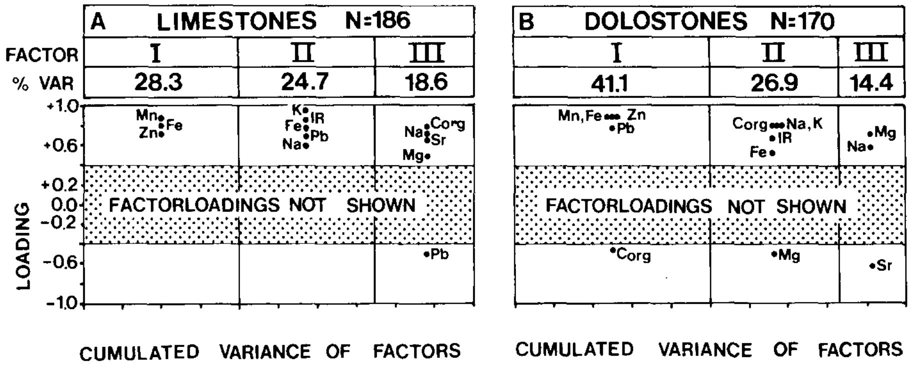

Fig. 2 A, B. Varimax factor results of trace elements in limestones and dolomites from non-mineralized areas

higher trace element contents in the more restricted Verviers environment could also account for the lithogeochemical contrast between both areas. Fruth and Scherreiks (1975) and Barbier (1979) also reported higher trace element contents (respectively Zn, Fe, Mn and Zn) in the near shore environment carbonates as opposed to the less-restricted subtidal environment carbonates. The higher trace element contents in the Verviers dolomites are also related to the fact that dolomitizing solutions were initially generated in the Verviers area (Swennen and Viaene 1985).

Dispersion factors in non-mineralized carbonate strata

The correlation matrix and factor analysis of geochemical data of non-mineralized limestones suggest the following associations (Fig. 2a):

a) Mn, Fe and Zn correspond to weathering and co-precipitation processes. Goethite (oxidized pyrite crystals) and Mn-oxides have been detected within these limestones. Zn seems to be preferentially adsorbed/scavenged by the oxides (Robinson 1981). This is in contrast to the results by Vine and Tourtelot (1970) and Muchez and Viaene (1990) where Zn is mainly adsorbed by organic matter;

b) K, IR, Fe, Pb and Na relate to the non-carbonate fraction and adsorbed elements. The insoluble residue in these limestones is mainly composed by clays and some quartz. K, Na and Fe originate from partly dissolved clays (Parker et al. 1985) while the other metals are lixivated from the clays;

c) Corg, Na, Sr, Mg and $^{-}$Pb relate to the calcite phase and the organic matter present in limestones. This association is interpreted as a sedimentary-diagenetic association. Highest factor scores for this association occur in supratidal to intertidal limestones, which are often enriched in Corg. Despite the complex diagenetic history of these limestones this "sedimentary" effect is still preserved. The positive correlation between Mg, Sr and Corg may be explained by the inhibited lixivation of Mg and Sr during transformation of aragonite or high Mg calcite to low Mg calcite in limestones rich in organic material. Therefore a diagenetic shielding effect by higher Corg contents may have accentuated this association. Another explanation given by Wagner et al. (1979) for the association Mg, Sr, Na may be due to disorder in the calcite lattice and proxysites caused by Mg^{2+}-ions which facilitate substitution by cation impurities. Part of the Na also seems to relate directly to the calcite phase, be it lattice related or present within minute fluid inclusions.

In dolomites similar associations were found (Fig. 2b):

a) Mn Fe, Zn, Pb and $^{-}$Corg reflect a weathering and co-precipitation association. Zn and Pb both seem to be adsorbed/scavenged on Fe-Mn oxides;
b) Corg, K, Na, IR, Fe and $^{-}$Mg reflect the effect of the non-carbonate fraction on the geochemical distribution. An increase in IR and Corg content will cause a decrease in Mg content. This explains the negative correlation of Mg with all other constituents of this association;
c) Mg, Na and $^{-}$Sr relates to the dolomitization process. The loss of Sr during dolomitization explains the negative correlation. The addition of Na by dolomitizing brines probably relates to incorporation of liquid and solid inclusions in dolomite (Bein and Land 1983).

Similar dispersion factors in non-mineralized carbonates have been reported in literature (Barber 1974; Préat et al. 1983; Parker et al. 1985; and others). The important influence of the non-carbonate phase on the distribution of the trace elements in carbonate rocks is a well-documented phenomena (Barber 1974; Pascal 1979; Dejonghe 1987; and others). As long as selective dissolution techniques are not more adequate, interference of these non-carbonate components will be present (Barber 1974).

Lithogeochemistry of carbonate strata in mineralized areas

Lithogeochemical patterns in limestones. The lithogeochemical patterns in limestones are generally influenced by Pb-Zn mineralizations. The results from different geochemical profiles enabled us to make the following generalizations:

a) anomalous Pb, Zn, Fe and Mn patterns occur around mineralizations. However, the patterns are irregular and the elements do not necessarily display a covariant distribution;
b) the lateral extent of anomalous Pb, Zn, Fe and Mn concentrations is very limited (<4 m);
c) a clear halo rarely develops. Metal contents are not necessarily highest immediately next to the mineralization;
d) it is not possible to correlate the anomalous interval of trace elements with the importance of the vein or mineralization;
e) similar anomalies, however, caused by "shielding" and/or adsorption phenomena, may also occur in limestones enriched in clays and/or organic matter (Swennen and Viaene 1981).

Similar limited dispersion features for Zn and Pb have been reported by Kranz (1976) from the discordant Pb-Zn mineralizations from the eastern Alps (Wettersteinkalk) and by Lavery and Barnes (1971) from the Wisconsin Zn-Pb district (see also Barnes and Lavery 1977). The data reported by Ineson (1969, 1970) from the mineralized Dinantian limestones of the Pennine and Derbyshire ore fields are comparable.

The lithogeochemical pattern is caused by the irregular distribution of thin calcite veinlets. A more widespread influence on the geochemistry of these limestones probably was inhibited by the fact that these strata were intensively cemented before mineralizing fluids became available. Marine and meteoric cements occluding all pores have been recognized within these limestones. Mineralizing fluids only could pass along newly created fractures. Cathodoluminescence petrography clearly reveals a cross-cutting relationship of the thin veinlets with respect to the cement phases (Fig. 3). Webb (1959) also recorded erratic values in limestones around Pb-Zn deposits in the British Isles. He remarked that this was almost certainly due to the extent of pre-mineralization fracturing. Ineson (1969) also reported that there exists a strong relationship between the trace-element aureole around mineralizations and the width of the fractured limestone.

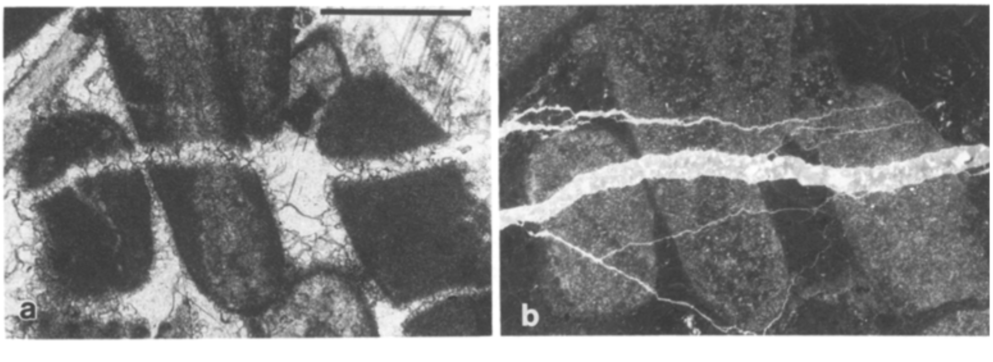

Fig. 3. Microphotograph (**a**) and cathodoluminescence (C.L.) microphotograph (**b**) of intraclastic packstone cemented by meteoric calcite cements characterized by a complex dull C.L. zoning. A cross-cutting relationship between cements and veins is expecially apparent under C.L. Scale: 100 µm (RS/B/39/20 and 21)

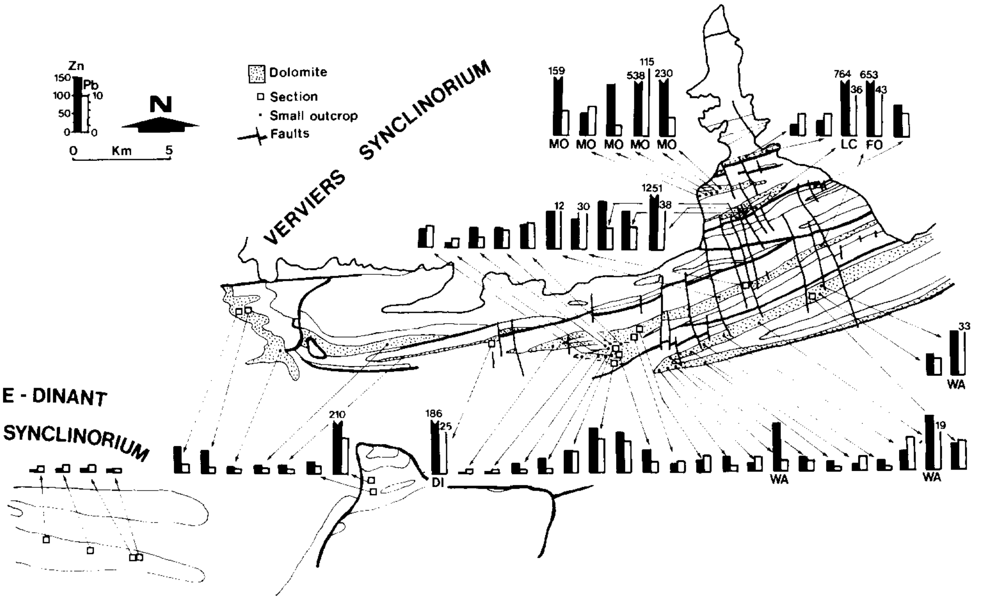

Fig. 4. Regional distribution patterns of mean values of Zn and Pb of dolomite outcrops of the Verviers synclinorium and the eastern part of the Dinant synclinorium (distance between both synclinoria is not to scale). LC = La Calamine, FO = Fossey, DI = Dison. Location of target areas: MO = Montzen syncline and WA = Walhorn syncline

Factor analysis of the affected limestones shows comparable results to limestones not affected by mineralization. The eigenvalue of the weathering/co-precipitation association (Zn, Pb, Mn, Fe) however, becomes more important. The factor scores for this association is highest within the anomalous samples. Due to the irregular distribution of Na- and Sr-poor calcite veinlets, the anomalous limestone intervals are commonly characterized by the decrease in Na and Sr modifying the sedimentary/diagenetic association.

The limited extent of influence around mineralizations together with occurrence of lithologically controlled anomalies of Zn, Pb, Mn and Fe suggests that lithogeochemistry of limestones can not be considered to be of significant use in prospecting vein-type deposits in the investigated area.

Lithogeochemical patterns in dolomites. In dolomites, the original lithogeochemical pattern of Zn, Pb, Mn and Fe around Pb-Zn mineralizations is modified. Only in a few cases epigenetic (re)dolomitization (Fe-rich saddle dolomite) has been observed.

The Zn, Pb, Mn and Fe distribution patterns around mineralizations display a covariant behaviour. These elements also form an association, extracted by the factor analysis, which henceforth is called the mineralization association. In the absence of epigenetic (re)dolomitization, Mg correlates negatively with this association, pointing towards the influence of Ca-bearing solutions. Where epigenetic dolomitization extensively occurs (four localities) no uniform pattern is observed. The influence on the distribution patterns of the other variables (Sr, Na, K, Corg and IR) is limited; they will not be further discussed.

The regional variation of Zn and Pb in the dolomites (arithmetic mean values from major reference sections and small outcrops) is shown in Fig. 4. A difference between the eastern part of the mineralized Verviers synclinorium and the barren Dinant synclinorium is obvious. The data in the latter area are below the normal (regional) threshold while in the first area important anomalous values are present. Highest concentrations occur in the vicinity of known mineralizations (La Calamine (LC), Fossey (FO) and Dison (DI); Fig. 4). A decrease in Zn and Pb concentration is observed at larger distances from an ore deposit. Furthermore, important anomalies are found in areas where no Pb-Zn mineralizations are documented (e.g. in the Montzen (MO) and Walhorn (WA) synclines). Similar trends occur for Mn while the influences on the pattern for Fe are less clear.

Clear halos within one section however, are difficult to recognize since most of the studied sections were sampled perpendicular to stratification (= parallel to the mineralized transverse faults). Therefore the mean values of all sampled sections and of small outcrops (some of which are displayed in Fig. 4) have been plotted in a histogram (Fig. 5). A trimodal pattern becomes apparent. The Zn, Pb and Mn distribution pattern is interpreted as follows:

a) population A represents the normal regional background. Its mean and threshold values correspond well with the values of Table 2;
b) population C groups anomalous values which mainly were recorded in sections occurring close to known ore deposits; this population represents a halo interval;
c) population B displays values higher than the normal (regional) threshold value. The values originate mainly from sections occurring at a certain distance from the mineralization. This population is considered to represent a local high background. The local threshold within these histograms occur for Zn, Pb and Mn respectively at 300 ppm, 16 ppm and 769 ppm.

The Fe data also display a trimodal distribution which, however, has to be interpreted in a different way. The Fe-pattern is complicated by the bimodal nature of the regional background population (Table 2) and by the influence of mineralizations. Population A is a background population grouping data from the dolomitization front.

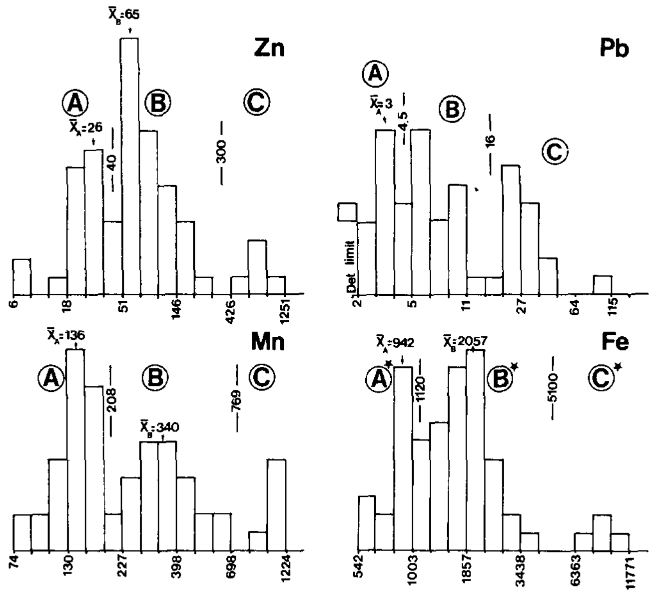

Fig. 5. Histogram of the arithmetic mean values of Zn, Pb, Mn and Fe of dolomite outcrops in the Verviers synclinorium (E-Belgium). □ = Mean value of one section or one small outcrop

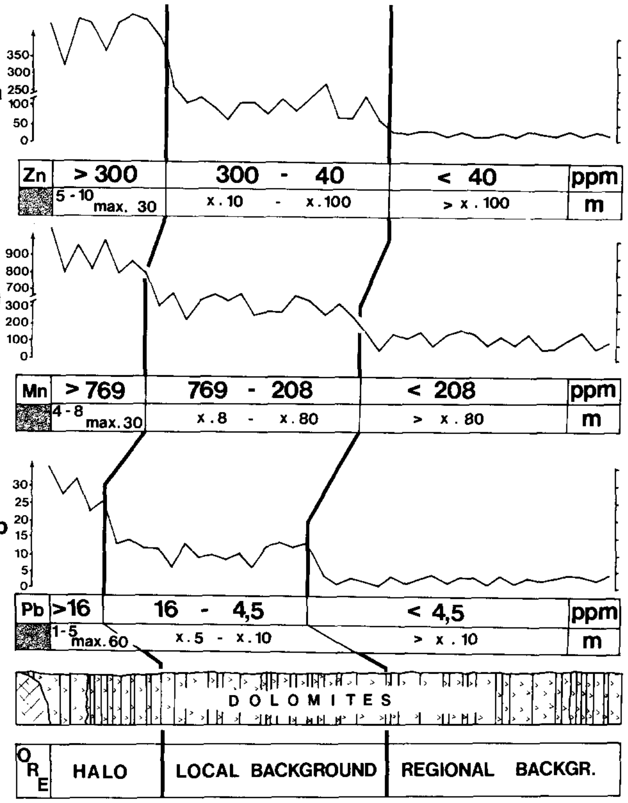

Fig. 6. Geochemical distribution model for Zn, Pb and Mn around Pb-Zn ore deposits

Population B reflects a mixture of influenced and non-influenced strata, and population C is derived from epigenetically (re)dolomitized strata. For Fe we thus may conclude that, as far as epigenetic (re)dolomitization did not occur, the iron introduced by Pb-Zn mineralizing solutions was insufficient to modify or overprint to any significant extent the original Fe content.

The geochemical distribution model. Knowing the position of a section with respect to proven mineralizations and taking into account the different populations for Zn, Pb and Mn, a model for the metal distribution patterns was worked out. Concentration ranges and the distances from ore deposits for these elements are given in Fig. 6. Because of the complexity of the Fe distribution, it is difficult to incorporate Fe into this model. This model is similar to the models reported in other literature (compare Rose et al. 1979; and others).

The metal values of dolomites associated with Pb-Zn mineralizations is most prominently influenced for Zn and Mn; for Pb the influence is limited (Fig. 6). This contrasts to a certain extent with the conclusions of Barbier (1979) who noticed that Zn and Pb are most prominently influenced by the presence of mineralizations while the use of Mn is uncertain. On the basis of Zn, Pb and Mn analyses it is possible to outline new target areas where the metal content falls within hte local high background and halo interval. Such areas have in fact been delineated. One of them was the Montzen syncline (MO in Fig. 4), where a follow-up study revealed interesting soil geochemical anomalies (research in progress).

The influence on the lithogeochemical patterns of Zn, Pb, Mn and Fe around mineralizations certainly relates to the more porous-permeable nature of the dolomites. Within most of the dolomites an intercrystalline porosity is present. Its importance, however, is limited; average estimated porosity never exceeds 5%. A moldic porosity may be present due to the selective leaching of crinoids. However, it is not clear at which stage these molds developed. The extension of the local high background and halo interval is limited when compared to reported literature values. This probably relates to the low porosity/permeability of these dolomites.

Enhancing the sample density could help to find new target areas. Unfortunately, in the investigated area dolomite outcrops are rather scarce. Therefore, sample density can only be enhanced by drilling shallow boreholes (1–5 m).

Mineralogical phases occurring in the anomalous dolomites. The question arises which mineralogical phases are responsible for the development of the halo and the local high background interval. Therefore a detailed mineralogical analysis involving semi-quantitative EDAX-microprobe analyses was carried out.

In the halo interval minute sulfide (sphalerite, galena and pyrite) and oxide phases (goethite, Mn-oxides) have been discovered. These phases are sometimes associated with calcite rhombohedrons. Within the local high background and normal background interval oxide phases predominate. As with sulfides, only small intracrystalline pyrite crystals have been observed here. The distribution of these opaque mineralogical phases is schematized in Fig. 7.

Sphalerite and galena mainly consist of small (0.05–0.1 mm) crystals. They occur only in intercrystalline pores close to the mineralization. Pyrite or pyrite relicts are also present. The intercrystalline pyrite crystals often have an idiomorphic outline. Besides these pyrite crys-

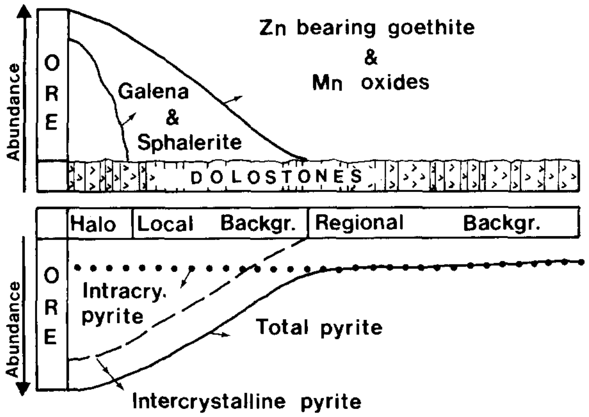

Fig. 7. Distribution of mineralogical phases occuring in dolomites adjacent to the Pb-Zn mineralization

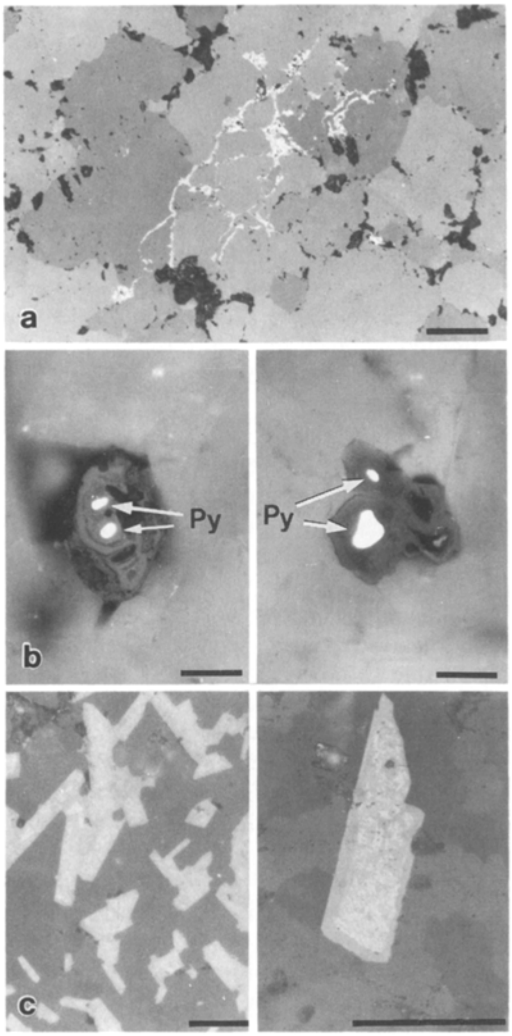

Fig. 8. **a** Zn-bearing Mn-oxides irregularly distributed as intercrystalline infillings. Scale: 50 μm (RS/B/39/7); **b** Zn-bearing goethite pseudomorphs after pyrite. Pyrite (Py) still occurs in the centre. Scale: 22 μm (RS/8/39/0 and 1); **c** Zn-bearing lath-shaped goethite crystals occurring in epigenetically (re)dolomitized strata. Scale: 50 μm

tals, intracrystalline pyrite inclusions within dolomite occur. Idiomorphic pyrite crystals have a wider aureole than the sphalerite and galena. The intracrystalline pyrite phases, however, occur in all studied samples. These sulfides do not necessarily display a covariant distribution.

It is believed that the pore-filling Zn and Pb sulfides and idiomorphic pyrites have been precipitated from circulating mineralizing solutions. Their idiomorphic crystal morphology and their decreasing content away from the mineralization argues in favour of this interpretation. The intracrystalline pyrite phases or relicts are believed to be diagenetic in origin. This interpretation is based on their intracrystalline nature and the fact that these phases (or their oxidation products) display a uniform distribution and occur in areas where no mineralizations are known.

The oxide phases are dominated by Mn-oxides and goethite. Mn-oxides consist of individual crystals (maximum 0.05 mm) and of irregularly distributed intercrystalline infillings (Fig. 8 A). Further identification of these Mn-oxides was not possible. Goethite also may occur as irregularly distributed intercrystalline infillings. However, the majority of the Fe-oxides are pseudomorphous after pyrite. This is attested by their cubic outline as well as by the presence of relict pyrite spots in these oxides (Fig. 8 B). Intracrystalline goethite also occurs; it is interpreted as an oxidization product of the intracrystalline pyrite spots described above. Lath-shaped goethite crystals (Fig. 8 C) are less common. They were only observed in association with epigenetic saddle dolomites.

Microprobe (EDAX) analyses of the Fe-oxide phases (Fe-oxide rim around pyrite, inter- and intracrystalline and idiomorphic goethite) showed that these Fe-oxides bear percentage levels of base metals (Fig. 9). Zn contents up to 11% have been recorded. Their distribution is bimodal with mean values of 2.9% and 9.2% respectively. The Pb content is limited (0.1–1.3%). Ca (1% to 3% with values up to 9%) and Si (2% to 5% with values up to 9%) are omnipresent. Traces of Al, Na, and Mn were sometimes detected. Also within the Mn-oxides up to 3.4% Zn and traces of Pb have been detected.

The general association between Al, Si and Na reflects their occurrence as contaminants (mainly clay minerals) while Ca is related to the surrounding lithology. In the oxide phases Zn, Pb and Mn however, probably originated from metal-enriched circulating groundwaters. During recycling, galena and sphalerite are leached by meteoric ground waters and metals were transported. Subsequently they were adsorbed and incorporated under oxidizing conditions onto goethite and Mn-oxides (comparable to the supergene recycling model of Haynes and Mostaghel 1982).

Incorporation of base metal cations to and/or adsorption onto Mn- and Fe-oxides, implying derivation from sulfides during weathering, have been reported in the literature. Many of the recent publications deal with the scavenging capacity of several metals in Mn- and Fe-oxide coatings in stream sediments, soils and sea-water (Chao and Theobald 1976; Murray and Brewer 1977; Carpenter et al. 1978; Robinson 1981; Buckley 1989; and others). Other data are available from gossan studies

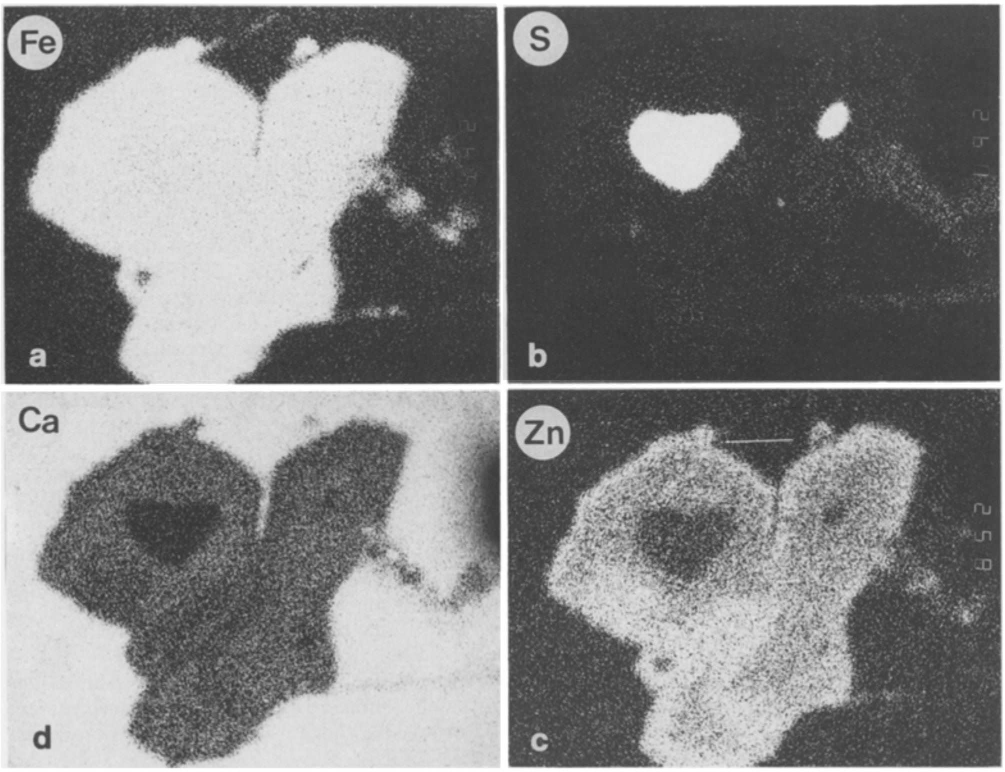

Fig. 9a–d. Distribution of Fe, S, Zn and Ca in goethite pseudomorphs after pyrite (see Fig. 8b) occurring within dolomites Scale: 10 μm

(Thornber and Wildman 1984; and others). Scott (1986) reported high Zn-Pb contents from Fe-oxides (Pb: 0.07–0.84% and Zn: <0.20–2.94%) in gossans formed from dolomitic shale-hosted sulfides. This author showed that Mn-oxides may even accommodate more than 20% Pb in coronadite and 10% Zn in chalcophanite as reported from the Mount Isa Field. Experiments confirm the high sorption capacity for base metals by Fe-Mn oxides (Benjamin and Leckie 1981; Gerth and Brümmer 1983).

The Mn-oxides studied in the dolomites possess much lower base metal contents than reported by Scott (1986). The low Zn population in goethite (mean: 2.9%) could be explained by incorporation on and/or adsorption of Zn onto goethite. The high Zn population (mean: 9.2%) possibly relates to minute secondary Zn-minerals (hemimorphite, smithsonite, chalcophanite or recrystallized Zn-Fe-pyrsaurite type minerals (Thornber and Wildman 1984) or hetaerdite (Buckley 1989) inclusions within goethite. However, such phases have not been identified.

It is possible that a certain amount of Zn, Pb, Mn and/or Fe in the halo and in the local high background is adsorbed or incorporated in clay minerals (Graf and Kerr 1950). However, to what extent these constituents contribute to the development of the halo and local high background interval it is difficult to infer. In the dolomites this influence seems to be limited since no significant correlation occurred between clay constituents and Zn, Pb, Fe or Mn. Finally, it is interesting to notice that the presence of 1% goethite with a Zn-content of 3% alone would account for the Zn-threshold value of 300 ppm of the local high background.

Conclusions

The lithogeochemical patterns in the Dinantian limestones and dolomites in the Verviers synclinorium can be related to mineralizations. In limestones the influence is limited and irregular and anomalies may be misleading. This relates to the poor permeability/porosity of these limestones. In dolomites the influence is much more important and can be explained by their porous/permeable nature. Therefore the lithogeochemistry of dolomites may be an important prospecting tool.

The general lithogeochemical distribution patterns of Zn, Pb and Mn in dolomites can be subdivided into three populations:

a) a normal (regional) background. Dolomite strata of this group are not influenced by mineralization;
b) a local high background. An influence of the mineralization on the dolomite lithogeochemistry is apparent. This local high background is caused by the presence of Zn-bearing goethite (mostly pseudomorphous after pyrite) and Mn-oxides. It seems likely that supergene processes were involved in the formation of these Mn- and Fe-oxides enriched in Zn, Pb, ... These oxides possess an important scavenging capacity. A supergene recycling model, as proposed by Haynes and Mostaghel (1982) could be invoked. Development of a local high background in these dolomites thus relates to weathering processes. Notice that goethite occurring in the normal regional background contains no detectable Zn;
c) a halo, developing in dolomite strata in the vicinity of the mineralizations. This halo is caused by pore-filling

sphalerite, galena, pyrite and Zn-bearing goethite and Mn-oxides. The sulfides relate to the ore emplacement.

False anomalies may occur within organic-rich dolomites since these strata often possess a high intracrystalline pyrite content. Higher Zn- and Pb-values in these strata thus rather relate to the higher content of pyrite/goethite rather than to the existence of mineralizations. Therefore, lithogeochemical data of dolomites rich in clay and organic material have to be interpreted with care.

This regional lithogeochemical reconnaissance survey revealed not only anomalies around known mineralizations but also in areas where mineralizations have not yet been reported. This suggests that a more detailed regional lithogeochemical research on dolomites may be a helpful tool in delineating new target areas for follow-up studies.

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