Determination of Trace Metals in Hydrothermal Calcites by ICP-Methods*

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Abstract. Lanthanum, cerium, and europium in calcites from carbonate-sulfide banded ores were determined by standard addition using inductively coupled plasma mass spectrometry (ICP-MS). The concentration ranges in solution were for La 700-36 ng/g, Ce 2000–149 ng/g, and for Eu 140–2.4 ng/g. Only Ce was determined by both ICP methods, and the results agree within 3 to 4%. In a second step, a scan over the mass range of the rare earth elements (REE) was performed. The solutions were analyzed directly without applying preconcentration or separation procedures. ICP atomic emission spectrometry (AES) was used to determine Ca, Mn, and Fe. The matrix Ca is present in a concentration range from 1600 to 1300 μg/g and the major impurities Mn and Fe are 152–32 and 100–28 μg/g, respectively. The detection limits of ICP-MS for REE are found to be better by two orders of magnitude than for ICP-AES. A commercially available SCIEX Elan ICP-MS with additional software was used to make mathematical corrections for isobaric interferences and molecular ions.

Key words: banded ores, calcite, REE, ICP-MS, AES.

Rare earth elements (REE) in geological materials are determined routinely by inductively coupled plasma atomic emission spectrometry (ICP-AES) and instrumental neutron activation analysis (INAA). These two methods are widely established in geochemical research. INAA is particularly useful for REE determinations because of its high sensitivity. Routine INAA can only determine up to 7 or 8 REE in a calcite matrix. Some REE are determined with high precision at levels as low as 0.1 μg/g in solids with minimum sample preparation. The main problem with this technique is the time factor. Between starting with the radiation in a nuclear reactor and the finalizing measurement at least 6 weeks are necessary to determine isotopes with long half-lives accurately.

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As an alternative, the ICP-AES method has been widely adopted by the geo-chemical community. For detailed studies involving the REE group, however, preconcentration steps or matrix separation procedures with ion-exchange techniques have to be applied [1].

With the ICP-AES it is possible to determine all 14 REE (unlike INAA) from one solution at levels between ten and one times above the concentrations in chondrites if matrix separation is applied. The atomic and ionic emission spectra of the REE in ICP-AES are complex due to a large number of emission lines. An enhanced background occurs from the straylight in the presence of a large concentration of calcium in the solutions if no ion-exchange separation is included. Thus, an ICP in combination with a quadrupole mass spectrometer was used. The application of REE determination for geological purposes is documented for example in some research papers [2, 3]. In ICP-MS the background spectra are simpler and the detection limits are very close or even lower to those of the concentration levels in chondrites [4]. The spectra consist mainly of single charged ions and polyatomic ions formed from the solution (e.g. refractory elements like Ba, Ce, La, ... may form MeO^+). It is recommended to work in nitric acid, otherwise ions of the type $MeCl^+$ in the presence of HCl may occur.

Geochemical Background

Within the strongly folded sediments of the Upper Harz Mountains (FRG) many hydrothermal Pb-Zn vein mineralizations occur. Most important from an economic point of view are calcite(quartz)-sulfide banded ores (Fig. 1) which are still mined at the Bad Grund ore deposit.

The genesis of these banded ores is explained by a fluid-mixing model of a hot (300°C) metal-rich saline formation water with a colder (140°C) H_2S bearing solution [5–7].

Neutron activation analysis has shown that the calcites of the banded ores are rich in REE and iron. Only little is known about the chemical composition of the ore forming fluids. The aim of the analysis of these carbonates by ICP methods was to prove whether other metal ions (e.g. lead and zinc) were also transported in the calcium-rich fluid and whether different REE fractionations can be observed within single calcite layers. Thus, the determination of the REE is of extreme value as an

□CaCO₃▨ ZnS

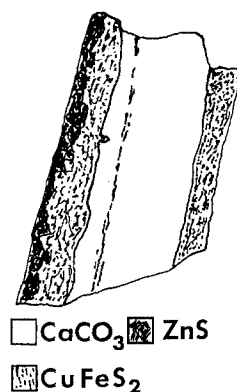▨CuFeS₂   Fig. 1. Calcite-chalcopyrite banded ore from the Bad Grund ore deposit

important tool for mineral-genetic studies of banded ores. The REE behave chemically similar and show only small but systematic changes of their ionic radii, the so-called lanthanide contraction. Only cerium and europium may exist in the quadrivalent and divalent stage, respectively, whereas the other REE are only trivalent. Due to the odd-even element abundance effects (the Oddo-Harkin's rule [8]) the concentrations of the REE are mostly reported relative to levels in chondritic meteorites [8]. The plots are smoothed by the chondrite normalization, and from the graphs geoscientists derive useful information about cerium and/or europium anomalies, and REE fractionation.

Experimental

A Perkin-Elmer SCIEX Elan 250 system (Thornhill, Canada) was used for this study. This instrument is described in detail elsewhere [9]. Analyses were done using a peristaltic pump (Gilson, Minipuls 2, France) and a home-made mass flow controller in order to minimize fluctuations in the nebulizer and auxiliary gas. In Table 1 details of the operation conditions are listed. Additional software, MS13 (3S Company, FRG) was installed in the originally delivered Matrox CCB-7 computer. Meanwhile a Compaq PC (USA) is added to the system for subsequent mathematical treatment of data off-line.

An ICP-AES model 3520 (Applied Research Laboratories, Switzerland) was used for the determination of the calcium content and cross-checks for lanthanum and cerium. Also magnesium, manganese, iron, zinc, and lead were determined by ICP-AES. Parameters of this method are given together with operating conditions in Table 2.

Table 1. Operating conditions of the SCIEX ICP-MS

R. F. power	1.2 kW
Reflected power	2–4 W
Plasma gas	14.0 l/min
Auxiliary gas	1.2 l/min
Nebulizer	Meinhard, C-type
Nebulizer gas	1.05 l/min
Nebulizer pressure	2.8 bar
Torch	Short, Fassel type
Spray chamber	Scott type
Sample uptake rate	0.95 ml/min

Table 2. Operating conditions of the 3520 ARL ICP-AES

R. F. power	1.2 kW
Reflected power	5 W
Plasma gas	12.0 l/min
Auxiliary gas	1.0 l/min
Nebulizer and spray chamber	GMK, cross flow
Nebulizer gas	0.8 l/min
Nebulizer pressure	2.1 bar
Torch	Fassel type
Sample uptake rate	2.0 ml/min

Sample Preparation

Small columns (approximately 4 to 5 cm length × 1 cm^2) of calcites between two sulfide bands have been cut out. The top and sides of these blocks were covered by UHU glue (endfest 300, 2-component epoxid compound from UHU Company, Bühl, FRG). The unglued surfaces of the prepared samples were fractionally dissolved (ca. 0.2 g) for 10 min in 50 ml 0.1 N suprapur HNO$_3$ (Merck, FRG). Double-distilled water was used for dilution to avoid contamination. After each fractional dissolution the weight loss was determined by weighing the dried sample block. The fractional dissolution experiments were continued until the calcite was totally dissolved. 25–50 fractions of solutions were obtained for ICP-AES and -MS analyses.

Calibration Strategies

All ICP-AES analyses have been done directly from the original solution without any further treatment. Only calcium was measured 100 times diluted due to its extreme concentration in the solution (0.8%). With respect to the concentration calibration, the matrix was simulated for the calcium and acid content. The AES was especially used to determine calcium, manganese, and iron because these are difficult elements for ICP-MS studies. Argon gives an isobaric interference on the main calcium isotope, and iron may be interfered by the molecular ions ArN^+, ArO^+, CaO^+ and /or $ArOH^+$. The monoisotopic manganese is in between the two iron isotopes $^{54}Fe^+$, $^{56}Fe^+$, and the molecular ions ArN^+, ArO^+ causing a higher background.

The ICP-MS has been operated in the following two modes:

(1) Scanning for atomic mass units (amu) ranging from 130–180 amu in the high resolution mode with 10 points over the peak. At this mode the quadrupole mass spectrometer can resolve 0.05 amu, i.e. 20 points per mass unit. Only 10 points are used to avoid overlapping of peaks. The interpretation of the data is performed with the MS13 software package and takes about 3 min depending on the number of molecular ions to be controlled. Isobaric corrections are made by software to increase the number of useful isotopes per element. This program is parameter-controlled and can be preset by the operator. After the complete evaluation of the scan data the PAT program (PAT: graphical pattern recognition, here: chondrite normalization from 3S Company, FRG) is started giving directly a visual control of the REE data on the screen.

(2) Standard addition: The sample solution was 10-fold diluted. For the elements lanthanum, cerium, and both europium isotopes the standard addition procedures were performed. The additions

Table 3. Standard addition for sample solution 2/30 from Bad Grund 0.241 g in 50 ml 0.4 N HNO$_3$. Dilution factor 10

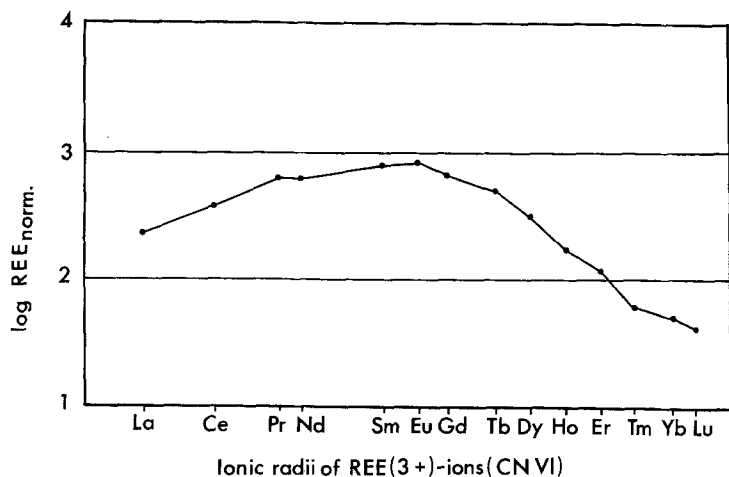| Element	Isotope	Solution ng/g	Solid μg/g
La	139	35.7 ± 1.0	74.1 ± 2.1
Ce	140	148.6 ± 3.8	308.3 ± 7.9
Eu	151	20.4 ± 1.4	42.3 ± 2.9
Eu	153	20.0 ± 1.2	41.4 ± 2.5

Fig. 2. REE distribution pattern in calcite sample 2/30 from Bad Grund (see Table 3)

ranged from 10 to 500 ng/g. ^{153}Eu was measured to ascertain that there was no molecular interference from barium oxide (^{137}Ba + ^{16}O = ^{153}[BaO]).

Four readings with 10 points over each peak were recorded with standard deviations as given in Table 3. The standard addition results for lanthanum were used to convert the intensities of all REE scans into absolute contents in the calcite samples and chondrite normalized plots were made. An example for the sample 2/30 from Bad Grund is shown in Fig. 2.

Results

If there is any significantly lower Ca content than the theoretical 40% (derived from pure $CaCO_3$), this is a hint for possible small quartz inclusions which were observed in thin sections of calcite bands. Another interpretation may be paragenesis of calcite and other carbonates (e.g., Mg, Fe, Mn). Therefore the calcium of all samples was determined and an example is given in Table 4. A comparison for La and Ce values obtained by different ICP methods shows very similar results (Table 5).

Table 4. Elemental contents of dissolved calcite bands. Impurity values in μg/g for the solid phase. Sample Bu 5 may have a certain amount of silicate material (e.g. unsoluble quartz). ICP-AES analyses were performed after matrix simulation for the high calcium content

Experiment no.	Ca (%)	Mg	Pb
Bu 1	39.8	520	94
Bu 5	32.2	393	26
Bu 10	37.7	470	46
Bu 15	40.2	395	64

Table 5. Results for some selected samples determined by ICP-AES and MS. All values in μg/g in solution. For ICP-MS analyses samples were 10 times diluted. Samples originate from Burgstädter Vein

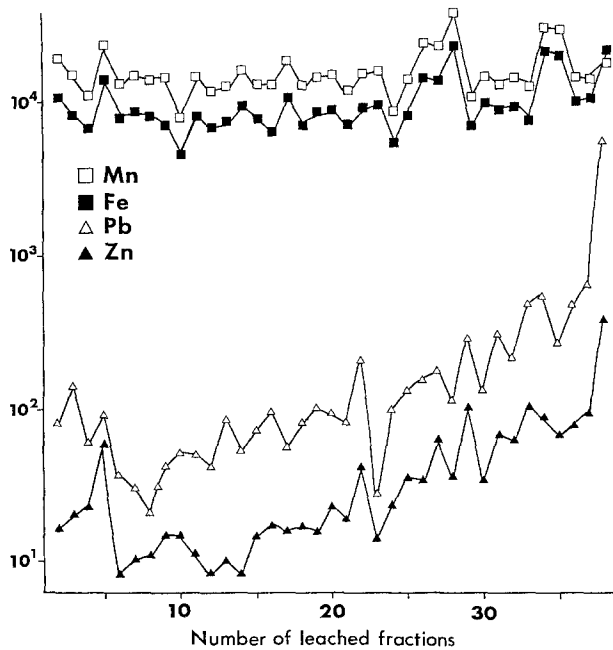|	La		Ce	
Sample	AES	MS	AES	MS
Bu 1	1.62	1.67	2.64	2.60
Bu 5	1.49	1.56	2.33	2.34
Bu 10	1.89	1.94	2.91	2.81
Bu 15	1.78	1.72	2.72	2.68
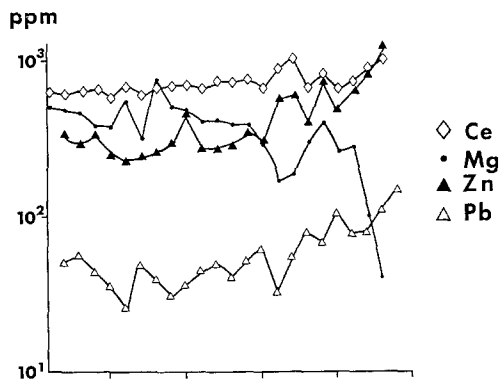
Fig. 3

Fig. 4

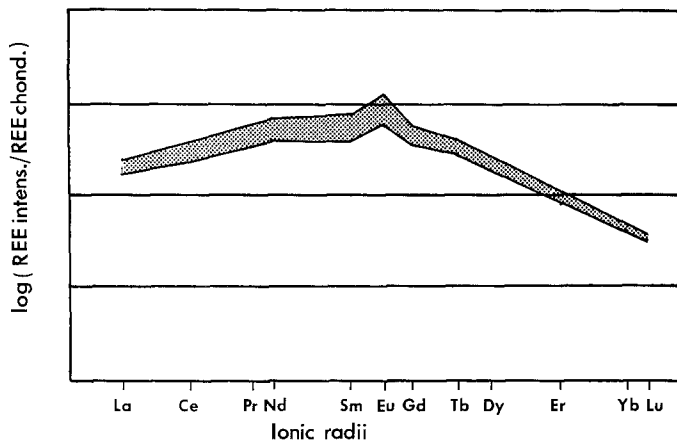**Figs. 3 and 4.** Element concentrations in calcites versus number of dissolution experiments (by ICP-AES)

Fig. 5. REE distribution pattern from calcites of the Bad Grund deposit. 27 samples by ICP-MS

In Figs. 3 and 4 the metal contents in calcites are shown as a function of fractional dissolution. Lead and zinc contents in calcites rise from contact of the older to the younger sulfide band. Manganese, iron, and cerium are homogeneously distributed in two thirds of the fractional solutions. The contents of these metals rise towards the end of calcite crystallization (Figs. 3 and 4). For 34 solutions in Fig. 4 manganese and iron show a compact distribution in a calcite from Bad Grund. The manganese/iron ratio is about two, which is extremely unusual for calcites. Merely the last solution shows a higher iron content than manganese. The chondrite normalized REE pattern of a calcite from the economically most important mining district Bad Grund are always the same (Fig. 5). The magnesium content in calcite shows a different trend, when approaching the younger sulfide band (Fig. 3). From solution experiment 16 to 19 the calcite sample was partially silicified. Due to this fact it can be observed (Fig. 3) that the cerium content in the calcite rises to a factor of 1.4. All patterns show small positive europium anomalies. The REE distribution in a calcite sample from the Burgstädter Vein in Clausthal-Zellerfeld (about 15 km away from Bad Grund) is quite different. The fractional dissolution experiments indicate no significant europium anomalies in the chondrite normalized REE patterns (Fig. 6 a). Approaching the younger sulfide band a small negative europium anomaly was noticed (Fig. 6 b). Cerium anomalies could not be detected in all samples.

Conclusions

With respect to the geochemical fluid-mixing model, the ICP analyses of calcites prove that crystallization happened from a calcium-rich solution which was also the main carrier of REE and other metals, e.g. zinc, iron, manganese, and magnesium. The calcite-forming solution must be derived from a magnesium-rich environment.

The increase of cerium in silicified parts of the calcite can be explained by the dissolution of very small lanthanide minerals like Y-synchisite (Y, Ce, La,...) $Ca(CO_3)_2F$, which have been observed on the surfaces of calcite aggregates from the Western Harz Mountains [10]. In consideration of the distribution coefficient for Zn^{2+} in a $CaCO_3$-saturated solution the total zinc concentration was about 120 $\mu g/g$ [7, 11]. This is high enough to form ore deposits [12]. Increasing of Zn and decreasing of Mg in calcite at the latest stage of crystallization reflects the different behaviour of the distribution coefficients with decreasing temperature of the mineral forming fluid. Calcite crystallization happened without participitation
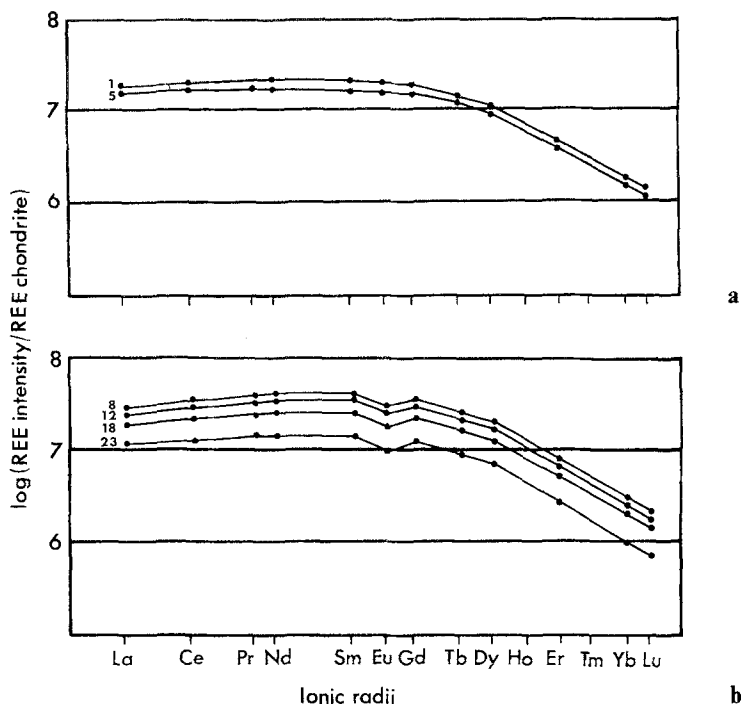
Fig. 6 a. REE distribution pattern in the early crystallization stage of calcite band (dissolution experiments 1 and 5) from Clausthal-Zellerfeld. **b.** REE distribution pattern of later stages of crystallization from the calcite band from Clausthal-Zellerfeld (dissolution experiments 8, 12, 18, and 23)

of ocean waters because no negative cerium anomalies in the REE pattern of the calcites were found. The necessary H_2S for sulfide formation is assumed to be mixed to the metal-rich solution. High H_2S supply caused a decrease of temperature and a change of the redox potential during calcite crystallization which is indicated by negative europium anomalies in the final stage of crystallization.

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