

Rare-earth elements and stable isotopes in carbonate associated with fluorite-barite mineralizations in northwestern Sicily

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ABSTRACT. — Mesozoic limestones outcropping in northwestern Sicily contain fluorite and barite mineralizations of hydrothermal origin. These minerals are also associated with carbonate materials deriving from alteration of the host rock by mineralizing fluid and from CaCO_3 recrystallization.

The rare-earth distribution patterns show that mineralizing solutions supplied REE in addition to F^- ions which gave rise to fluorite formation. Limestone samples highly enriched in REE are the result of water-rock interactions due to which the carbonates exchanged Ca^{2+} versus REE^{3+} . The negative Ce anomalies decrease in patterns with increased REE probably because the hydrothermal fluids were not deficient in Ce^{3+} and therefore originated from a different source. Rhombohedral calcites crystallize from such fluids probably in paragenesis with fluorite. Scalenohedral calcites may represent a recrystallized limestone.

During the mineralization event the limestones are depleted in ^{18}O due to increased temperatures during water-rock interactions. In later stages of interaction two different processes can be suggested on the basis of changes in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. High changes in $\delta^{18}\text{O}$ correspond to samples (scalenohedral and rhombohedral calcites) which, as also shown by REE data, crystallized at relatively high temperatures, under conditions close to those which lead to the crystallization of fluorite. The changes in $\delta^{13}\text{C}$ indicate dissolution of carbonates by CO_2 -enriched fluids and recrystallization of calcite from such fluids.

Key words: rare-earth elements, oxygen and carbon isotopes, carbonates, hydrothermal fluids, fluorite.

RIASSUNTO. — Nella Sicilia nord-occidentale affiorano calcari mesozoici, di facies « Imerese », che

ospitano mineralizzazioni di fluorite e barite di genesi idrotermale. Questi minerali si ritrovano associati anche a materiali carbonatici che derivano da alterazione della roccia ospite ad opera dei fluidi mineralizzanti e da ricristallizzazione di CaCO_3 .

I modelli di distribuzione delle terre rare indicano che le soluzioni mineralizzanti trasportavano questi elementi, oltre agli ioni fluoro (F^-) che hanno dato origine alla formazione di fluorite. Campioni di calcari fortemente arricchiti in terre rare sono il risultato di interazioni fluido/roccia con scambi Ca^{2+} contro TR^{3+} . Anomalie negative di Ce risultano meno evidenti nei campioni con elevati tenori di terre rare; ciò potrebbe indicare che i fluidi idrotermali erano caratterizzati, al contrario del calcare ospite, da un modello di distribuzione di terre rare senza anomalie di Ce e, pertanto, indicativo di una diversa origine. Tra gli individui cristallini associati alla fluorite, le calciti romboedriche sembrano cristallizzare in paragenesi con la suddetta fase, mentre le calciti scalenoedriche potrebbero rappresentare un calcare ricristallizzato.

Per effetto dell'incremento della temperatura durante le prime fasi dell'interazione acqua/roccia i calcari vengono impoveriti in O^{18} . Variazioni più consistenti nella composizione isotopica dell'ossigeno corrispondono a campioni (calciti romboedriche e scalenoedriche) che, come mostrano anche i dati degli elementi delle terre rare, cristallizzano in condizioni non molto differenti da quelle di formazione della fluorite. Nelle fasi tardive, l'interazione acqua/roccia avviene sotto mutate condizioni di P_{CO_2} e si concretizza nella dissoluzione dei calcari per azione di fluidi arricchiti in CO_2 di probabile origine organica e ricristallizzazione da tali fluidi di una calcite con valori di $\delta^{13}\text{C}$ abbastanza negativi.

Parole chiave: terre rare, isotopi stabili, carbonati, fluidi idrotermali, fluorite.



Fig. 1. — Aerial view of the Rocca Grande area: faulted strata of Mesozoic calcareous rocks emerging from plastic terrains of the Tertiary.

Introduction

Fluorite and barite mineralizations outcrop in several localities in the western Madonie (northwestern Sicily). These minerals are mostly found in limestones of Jurassic and Cretaceous age and seem to be more abundant in proximity with faults, some of which were shown by field observation to be paths for uplifting mineralizing fluids. Geochemical and petrographic researches carried out on mineral and host-rock suggested a hydrothermal origin of the mineralizations and showed compositional and textural variations induced by the hydrothermal fluids on the host-rock (BELLANCA et al., 1981, 1984). Other papers on the same subject deal with strontium isotopes (BARBIERI et al., submitted to Chemical Geology) and fluid inclusions (BELLANCA et al., submitted to 1985 Fluid Inclusions Meeting Reports).

In the present work we report rare-earth

element and stable isotope compositions of different carbonate materials involved in the mineralizing event. The results allow us to draw conclusions on the chemistry of the fluorite-bearing solutions and on fluid-rock interactions.

Materials

Field and macroscopic observations show that the limestones hosting the mineralizations appear megascopically altered only near the mineralized fractures. In addition to evident chromatic variations, the fluid action gives rise to a considerable increase of pores and cavities and, consequently, to a lower compactness of the rock. For the aims in this work, we call « mineralized » those limestones containing fluorite and/or barite and « altered mineralized » those portions, of the same rocks, which show megascopic variations induced by the mineralizing fluids. « Unmineralized » limestones are the same limestone sample which, collected following sampling routes away from the fault lines, do not contain fluorite and barite. Moreover, we define as « guide levels » some porous, yellowish, and prevalently calcitic materials which, though containing the mineralization phases, outcrop as distinct bodies from the limestone beds. These levels are considered to be redeposited materials since their study never revealed the presence of original structures and textures, even in mould form. Textural investigations of both guide levels and altered mineralized limestones showed the presence of calcite late-formed with respect to fluorite and barite (BELLANCA et al., 1982-83, 1984; BARBIERI et al., submitted to Chem. Geol.).

We also study some newly-formed carbonates (rhombohedral and scalenohedral crystals of calcite) which are frequently associated with fluorite and/or barite.

Geological setting

The samples analysed for this work come from three areas (Poggio Balate, UC863025; Rocca Grande, UB817998; Cozzo Famo, UC816023), showing analogous geological and structural contexts, where the fluorite-barite mineralizations seem to be more abundant.

The geological structures of the mineralized areas consist of monoclines which separated from the main structure as a result of disjunctive processes of post-Pliocenic tectonics (CATALANO and MONTANARI, 1979) and emerge from the plastic terrains of the Tertiary. These monoclines themselves are in various parts raised up with respect to each other by a series of faults also due to distensive tectonics. Fig. 1 illustrates some of these aspects in one of the studied areas.

In all the outcrops the mineralizations appear mainly as cavity filling and in the form of veins or encrustations on parts of faulted walls. Calcite, quartz, and rarely aragonite and Fe-oxides are found in association with fluorite and barite. These minerals mainly occur in brecciated limestones with ellipsactinie of Tithonian age and in limestones with remains of rudists of Cretaceous age. Both these limestones belong to the Mesozoic formations of « Imerese » facies (MONTANARI, 1966) and their environmental significance is reported in the papers of SCHMIDT DI FRIEDBERG et al. (1959), BROQUET (1971) and SCANDONE et al. (1972). Fig. 2 reports location of the mineralized areas and stratigraphic profile of the type-sequence.

Methods

The samples were prepared for the analysis of their isotopic composition by heating in vacuo at 400°C and reacting with 100 % H_3PO_4 , according to well-known procedures (McCREA, 1950). Isotopic analyses were performed by means of a Varian Mat 250 mass spectrometer and the results are reported in terms of δ per mil units. Reference standard is PDB-1 for both oxygen and carbon. The standard deviation of the entire analytical procedure is about $\pm 0.05\text{‰}$ (1σ) for both O and C.

The rare-earth element (REE) distribution patterns were analysed by using the neutron activation technique. This method is described in detail by GORDON et al. (1968). The approximate precisions for the REE are: better than 2 % for La, Ce, Sm, Eu and between 2 % and 10 % for Tb, Yb, Lu.

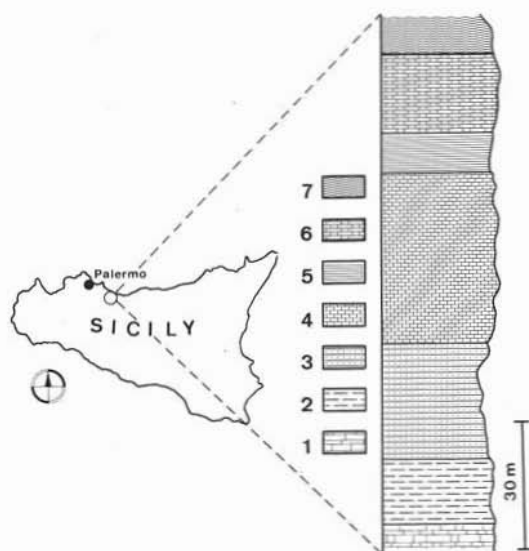


Fig. 2. — Location of the mineralized areas and stratigraphic profile of the type-sequence. Deposits of « Imerese » facies: 1) limestones with chert nodules (Upper Triassic); 2) dolostones and dolomitic breccias (Upper Triassic-Lower Jurassic); 3) bedded cherts with rhythmic interbeds of argillites (Lower Jurassic); 4) brecciated limestones with ellipsactinie (Upper Jurassic); 5) silicified limestones (Lower Cretaceous); 6) limestones with remains of rudists (Upper Cretaceous); 7) Numidian flysch (Oligocene-Miocene).

Results and discussion

Stable isotopes

Most of the isotopic values obtained from the studied samples are reported and discussed elsewhere (BELLANCA et al., 1982-83, 1984). In this paper a review of the main results is given along with a few new data.

The $\delta^{18}O$ and $\delta^{13}C$ values of the unmineralized limestones are similar to those of marine limestones not undergone extensive diagenesis and represent the isotopic composition of the host rock before reaction with the mineralizing fluids. A comparison between mineralized and unmineralized limestones shows only a $\delta^{18}O$ shift of the former samples towards more negative values. Consequently, one may suggest, in most cases, a moderate isotope exchange between $CaCO_3$ and hydrothermal fluids resulting, probably, from relatively short water/rock contact times and relatively low temperature

values. This slight isotopic alteration may also be attributed, according to SVERJENSKY (1981), to very low water to rock ratios. Some of the mineralized limestones show, however, a larger shift towards more negative $\delta^{18}\text{O}$ values probably due to heavier interactions of this material with the fluorite-bearing hydrothermal solutions.

Altered mineralized limestones and guide levels generally show similar isotopic com-

^{12}C from the underlying bedded cherts which contain organic matter arranged in small beds subparallel to stratification (CALDERONE et al., 1980). The $\delta^{18}\text{O}$ values of these materials are consistent with the hypothesis of ore-forming solutions essentially derived from meteoric waters (BELLANCA et al., 1984) and also indicate relatively moderate temperatures which agree with the presence of late-formed calcite, as shown on the basis

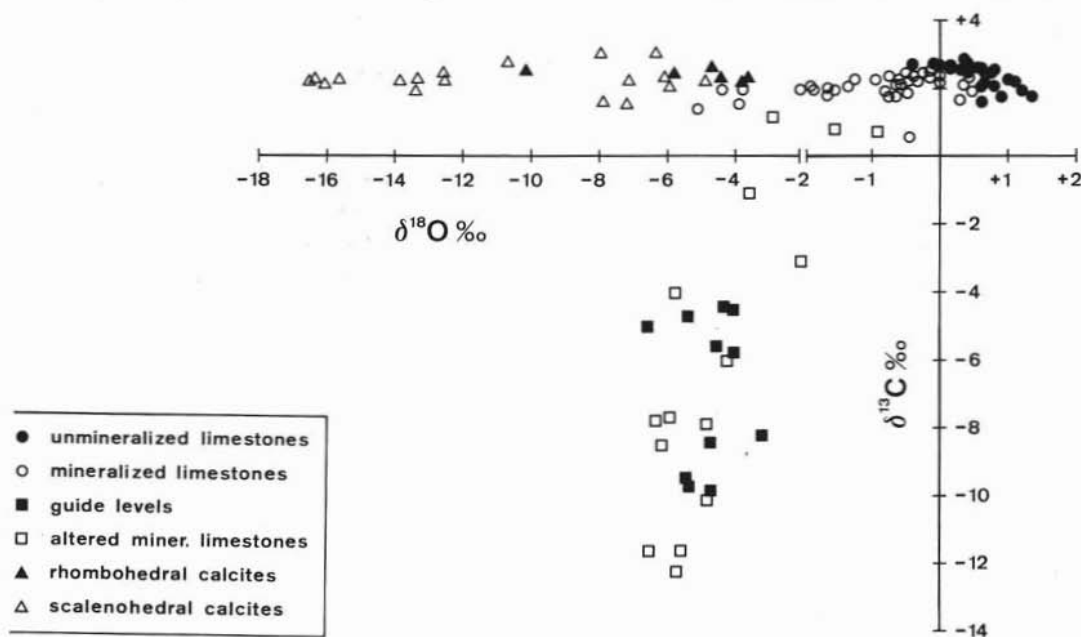


Fig. 3. — Oxygen- and carbon-isotopic compositions of the carbonate materials studied (reference standard PDB-1).

positions which, particularly for carbon, are considerably more negative than those of the above described lithotypes. The wide variability of $\delta^{13}\text{C}$ negative values (from about -1 to about -12 per mil) indicates different origins of the carbon in the system and can be explained e.g. by the dissolution of carbonates by CO_2 -enriched fluids and recrystallization of calcite from such fluids. The additional CO_2 may originate from deep sources or from decomposition of organic material. Since $\delta^{13}\text{C}$ of organic matter could be very light ($-8 \rightarrow -24$ ‰, HOEFS, 1980) even a small addition of organically derived CO_2 may decrease significantly the $\delta^{13}\text{C}$ of the recrystallized calcites. It is possible that the mineralizing fluids are enriched with

of textural evidences, with respect to fluorite and barite.

As to the rhombohedral and scalenohedral calcites, their $\delta^{13}\text{C}$ values are practically identical to those of the host-rock suggesting a formation of crystals at the expense of carbonate species deriving from dissolution of the limestones. The $\delta^{18}\text{O}$, on the contrary, shows a wide range of values reaching very negative terms (the overall range is from about -4 to about -17 per mil). This should reflect a wide variability of the temperatures of precipitation with higher temperatures for the scalenohedral calcites, generally characterized by more negative $\delta^{18}\text{O}$ values.

Rare earth elements

The REE distribution patterns of the unmineralized limestone samples are characterized by a conspicuous negative Ce anomaly and rather flat running patterns (fig. 4). Only the normalized La values exceed all the others. The samples from the mineralized limestone (BELLANCA et al., 1981, fig. 5), show patterns mostly identical with those of the unmineralized ones. Two patterns, however, show high normalized values, thereby indicating that the metal-liferous fluid was REE-enriched with respect to a fluid in equilibrium with the autochthonous limestone. The negative Ce anomaly decreases with increasing REE contents of the sample. This points to the fact that the altering fluid is characterized by a REE pattern without noticeable Ce anomaly. The REE patterns of the altered mineralized limestone samples (fig. 6) only exhibit minor Ce anomalies to none. The patterns are systematically declining from La through Eu. Unlike the wide spread of normalized REE values of the previous limestone groups the carbonates from the so-called guide levels (fig. 7) show a narrow band with a negative Ce anomaly in each pattern. All patterns are more systematically declining from La through Lu than those of the altered mineralized limestones. The scalenohedral and

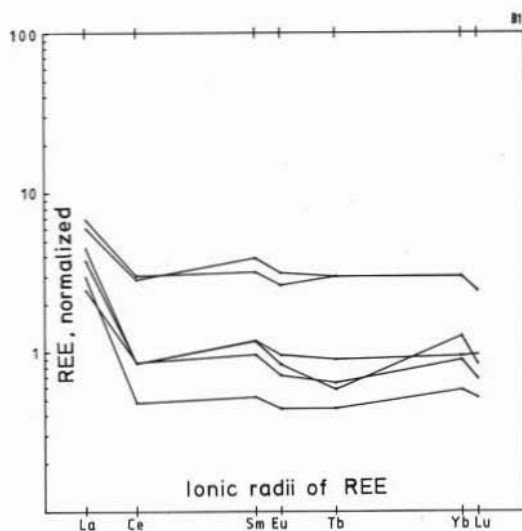


Fig. 5. — Distribution patterns of REE in mineralized limestones.

rhombohedral calcites (fig. 8) exhibit conspicuous negative Ce anomalies. The patterns of the scalenohedral calcites resemble those of the mineralized and unmineralized limestones. Those of the rhombohedral ones show similar trends to those of fluorites in paragenesis (BELLANCA et al., 1981).

The unmineralized limestone samples represent of course the least altered carbonates

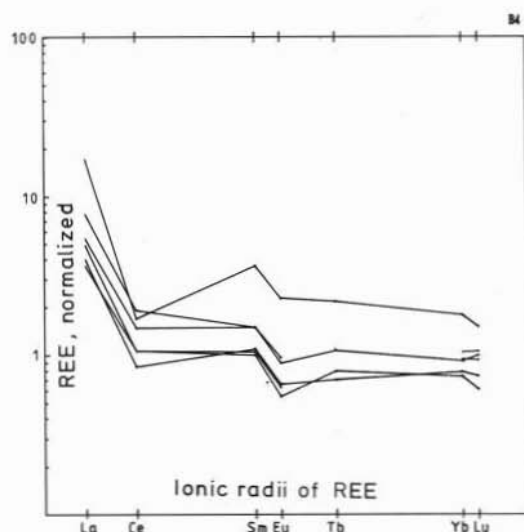


Fig. 4. — Distribution patterns of REE in unmineralized limestones.

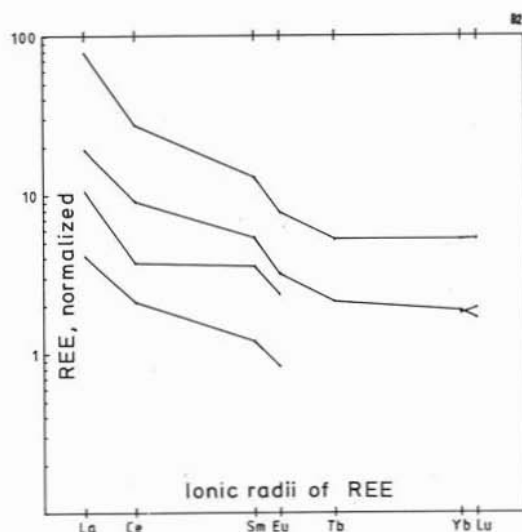


Fig. 6. — Distribution patterns of REE in altered mineralized limestones.

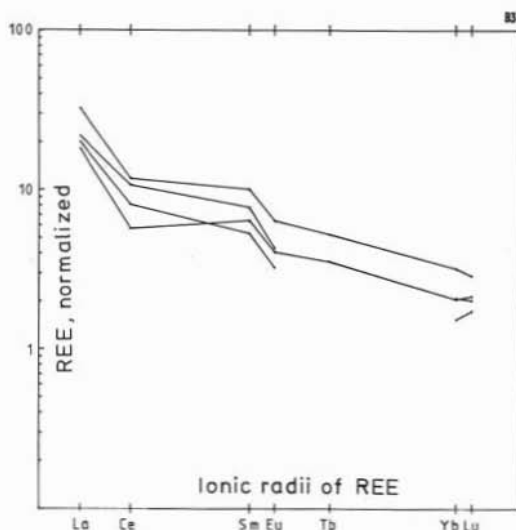


Fig. 7. — Distribution patterns of REE in guide levels.

within the suite analyzed. The concentrations of REE in all the other samples are equal to or higher than those of the diagenetic marine carbonates (PAREKH et al., 1977). The mineralizing fluid supplied REE in addition to F^- ions which gave rise to fluorite formation. As was shown earlier (BELLANCA et al., 1981) this fluorite crystallized from a fluid which interacted with limestone at varying degree. The calcite crystallizing from such fluid, probably in paragenesis with the fluorite, may be represented by the rhombohedral calcites. The scalenohedral calcites may represent a recrystallized limestone. The limestone samples highly enriched in REE are the result of a water-rock interaction due to which the carbonates exchanged Ca^{2+} versus REE^{3+} . For that reason the Ce anomalies decrease in patterns with increased REE probably because the hydrothermal fluid was not deficient in Ce^{3+} and thereby indicating that the fluid originated from a different source. Equilibrium distribution of the REE between crystallizing fluorite and calcite may be obtained locally, but not throughout the samples analyzed.

Conclusions

The fractionation of REE, oxygen, and carbon isotopes indicates that the alteration

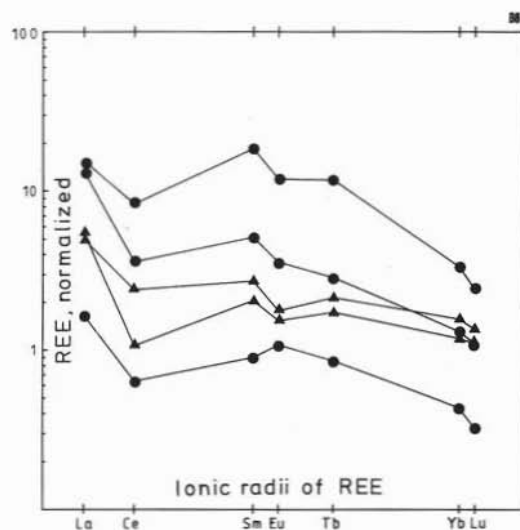


Fig. 8. — Distribution patterns of REE in rhombohedral (●) and scalenohedral (▲) calcites.

of carbonate host rocks by mineralizing fluids occurred under varying conditions. The $\delta^{18}O$ - $\delta^{13}C$ values follow essentially two trends. Starting with the composition of the unmineralized limestones there is one trend in which only $\delta^{18}O$ is changing widely towards negative values. The other one shows moderate changes in $\delta^{18}O$ and considerably larger ones in $\delta^{13}C$ both the variables shifting towards negative values. These two different trends are not always reflected in conspicuous differences in the REE distribution patterns. During mineralization of the limestone $\delta^{18}O$ is decreased due to increased temperatures during water-rock interactions. Changes in REE contents as well as $\delta^{18}O$ are not very significant. The REE-enriched patterns, however, show that the mineralizing solutions supplied REE in addition to F^- ions which gave rise to fluorite formations. In later stages of interaction two different influences can be read from the changes of $\delta^{18}O$ and $\delta^{13}C$ values. The high changes in $\delta^{18}O$ as observed in the scalenohedral and rhombohedral calcites seem to represent samples which, as also suggested by REE data, are probably close to equilibrium with the fluorite fluids at increased temperatures. The samples from the guide levels and the altered mineralized limestones exhibit a trend very different from those of mineralized limestone samples. The obser-

ved changes in $\delta^{13}\text{C}$ indicate water-rock interaction, under conditions of changed P_{CO_2} . The dissolution of carbonates by CO_2 -enriched fluids and recrystallization of calcite from such fluids may explain this trend.

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