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Enhanced CO_2-mineral sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into serpentinites at Malentrata (Tuscany, Italy)

C. Boschi [a,*], A. Dini [a], L. Dallai [a], G. Ruggieri [b], G. Gianelli [a]

[a] *CNR-Istituto di Geoscienze e Georisorse, Sede di Pisa, Via Moruzzi 1, 56124, Pisa, Italy*
[b] *CNR-Istituto di Geoscienze e Georisorse, U.O. di Firenze, Via La Pira 4, 50121, Florence, Italy*

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ABSTRACT

The magnesite deposits of Malentrata (Tuscany, Italy) were derived from serpentinite silicification–carbonation of the Ligurian ophiolite, and represent a natural analogue of in situ CO_2 mineral sequestration. Carbonation of magnesium silicate minerals (e.g. serpentine, olivine) at temperatures below 200 °C is an exothermal process, involving incorporation of carbon dioxide into stable carbonates (e.g. magnesite, dolomite). Serpentinites at Malentrata were transformed to a brownish friable rock characterized by the occurrence of opal, chromian montmorillonite, Fe-rich magnesite and minor iron sulfides and oxides. Widespread lenses of cohesive rocks occur within the altered serpentines, resulting from the complete silicification of the protolith. The pervasive alteration of serpentinite was accompanied by the formation of a network of magnesite and dolomite veinlets, and large magnesite–dolomite veins along major structures. Field observations, petrography and mineral chemistry define the following crystallization sequence in the major veins: i) early microgranular Fe-poor magnesite, ii) comb-textured Fe-rich magnesite and dolomite cementing the early brecciated magnesite vein infill, and iii) late quartz, chalcedony, and rare opal in the cavities. The mineral assemblage observed both in veins and in host rock is indicative of low-temperature hydrothermal alteration driven by Si- and CO_2-rich fluids under relatively low pH conditions. Pervasive and cyclic hydraulic fracturing maintained a high structural permeability during the whole hydrothermal event, creating conduits for the input and output fluids. The concomitant presence of CO_2 and silica in the fluid enhanced the congruent dissolution of serpentine and hampered immediate carbonate deposition. The Mg-bearing solutions were focused out of the reactor zone, and promoted massive carbonate veining along the main structural discontinuities. This two-steps reaction (dissolution of serpentinite followed by carbonate precipitation outside the reacting volume) seems to be very efficient and provide new insights on in situ and ex situ induced mineral carbonation and its industrial applications.

1. Introduction

Carbon dioxide mineral sequestration through carbonation of natural silicate minerals is a potential alternative in CO_2 geological storage and consists of an induced exothermic alteration of metal-rich non-carbonate minerals (i.e., Mg_2SiO_4 olivine, $Mg_3Si_2O_5(OH)_4$ serpentine, $CaSiO_3$ wollastonite) to geologically and thermodynamically stable mineral carbonates (i.e., $MgCO_3$ magnesite, $MgCa(CO_3)_2$ dolomite, $CaCO_3$ calcite, $FeCO_3$ siderite, $NaAl(CO_3)(OH)_2$ dawsonite). This technology attempts to mimic natural low-temperature alteration (carbonation) of widespread silicate rocks (i.e., peridotite, serpentinite, basalt) that trap safely CO_2 over geological times (Seifritz, 1990; Goff and Lackner, 1998; Lackner, 2003).

Since Seifritz (1990) proposed the idea of an induced industrial ex situ mineral sequestration (where CO_2 and solids reactants require transport to a surface sequestration site), many carbonation approaches were proposed and several gas–solid and aqueous–solid carbonation processes have been investigated in order to design more effective and economic reactions (Lackner et al., 1995; Butt et al., 1996; Lackner et al., 1997; Béarat et al., 2002; Park et al., 2003; Park and Fan, 2004; Schulze et al., 2004; Xu et al., 2004; Zevenhoven and Kavaliauskaite, 2004; Giammar et al., 2005; Maroto-Valer et al., 2005; O'Connor et al., 2005; Hänchen et al., 2006; Huijgen et al., 2006; Alexander et al., 2007; Marini, 2007; Teir et al., 2007; Hänchen et al., 2008; Daval et al., 2009–this issue; Dufaud et al., 2009–this issue). Most of the experimental studies on serpentine have shown that induced carbonation does not go to completion because precipitated carbonates or remaining silica-rich layers of the serpentine act as diffusion barrier, inhibiting the evolution of the process (Butt et al., 1996; Béarat et al., 2002; Park et al., 2003; Cipolli et al., 2004; Park and Fan, 2004; Schulze et al., 2004). In addition, slow rate of serpentine dissolution and decrease of porosity during the reaction lower the efficiency of the reactions (Hänchen et al., 2006; Maroto-Valer et al., 2005; O'Connor et al., 2005; Alexander et al., 2007; Teir et al., 2007).

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[*] Corresponding author. Tel.: +39 050 31 53 410; fax: +39 050 31 52 360.
E-mail address: c.boschi@igg.cnr.it (C. Boschi).

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The study of natural analogues (for example, low-temperature carbonated ultramafic rocks and associated magnesite deposits), can complement laboratory and demonstration studies and provide opportunity to constrain the boundary conditions and the mechanisms for CO_2-bearing phases to form. This paper presents a peculiar example of natural analogue of CO_2 mineralogical sequestration, a serpentinite-

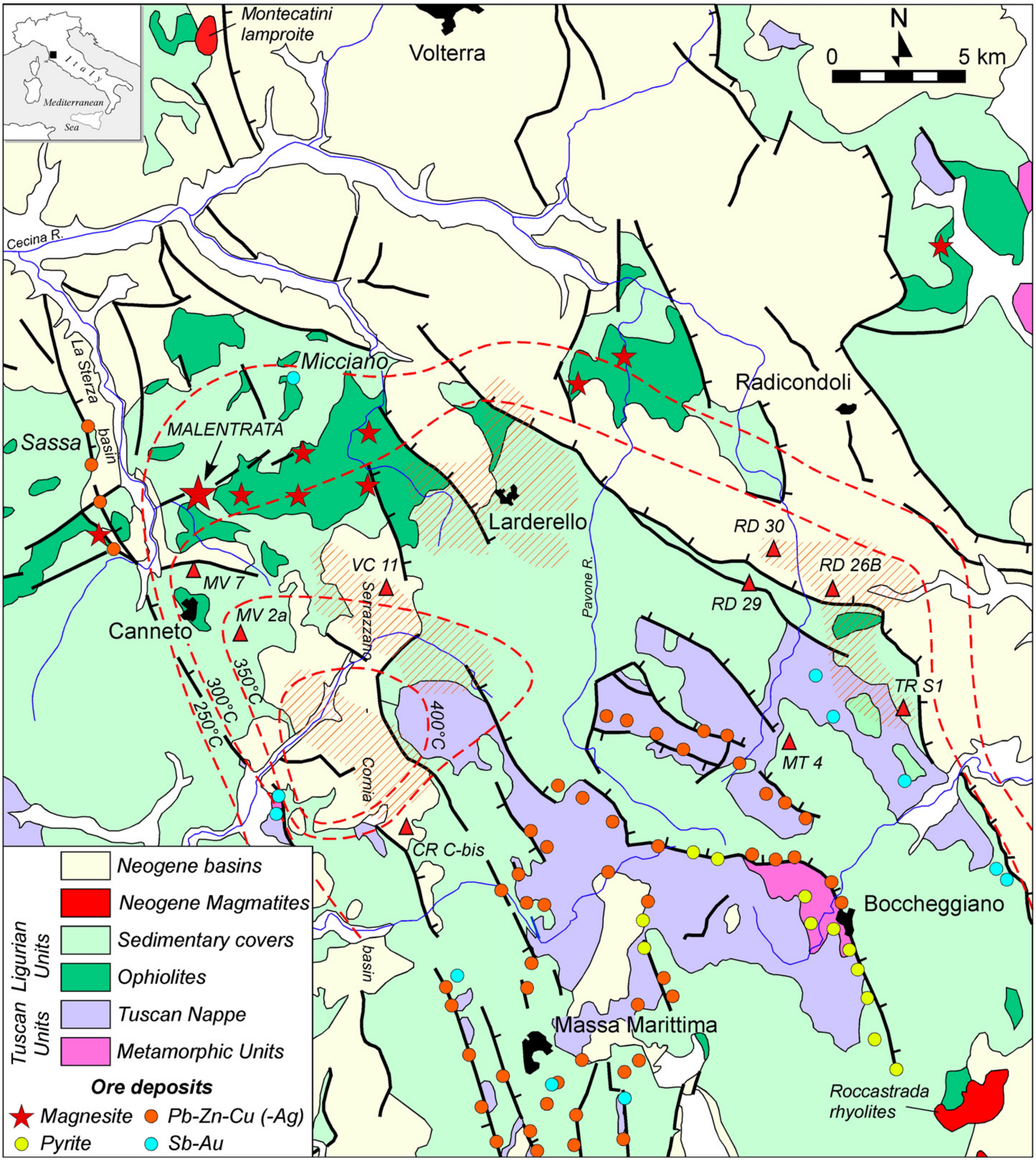

Fig. 1. Geological map of southern Tuscany (Italy) showing the distribution of magnesite, and other ore deposits with respect to the Larderello–Travale geothermal field. Numerous ore deposits (Pb–Zn–Cu(–Ag), pyrite, and Sb–Au), controlled by the extensional structures trending NW–SE, crop out in the southern part of the region and have been exploited since Etruscan time. The occurrence of magmatic rocks at the surface and at depth (red triangles highlight geothermal wells that intersected Pliocene–Quaternary granites at depth of about 2500–5000 m) is also reported. Red dashed contour lines display the temperature distribution at depth of 3000 m below sea level. Super heated steam production reservoirs are indicated by dashed orange areas. Black areas indicate main towns. Modified after Barelli et al. (2000), Carmignani et al. (2004), Cuteri and Mascaro (1995). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)