

Research Paper

Dawsonite deposition and metal transport during natural carbon capture and storage in a geothermal system

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ABSTRACT

Dawsonite is an Al–Na carbonate that is documented in several geological environments. This mineral gained global attention due to its potential role in Carbon Capture and Storage (CCS) via long-term mineral trapping, but its genesis in nature is incompletely constrained. In this work, we present a case of dawsonite mineralization that provides constraints on its genesis. The study area is the Mt. Amiata geothermal system (Italy), which hosts intense CO₂ venting and an historical district of Hg–Sb mineral deposits. Here dawsonite is long known to form within the cap rocks of the geothermal system. We combine remote sensing data, field mapping, microthermometry and Raman spectrometry of fluid inclusions, mass transfer calculations, elemental imaging by Laser Ablation-Inductively Coupled Plasma-Time of Flight Mass Spectrometry, C–O isotopic compositions, and geochemical modeling to provide constraints into the process of dawsonite deposition. We show that at Mt. Amiata dawsonite deposition is extensive, fracture hosted, and is probably a product of *chemical vapor deposition*, i.e., mineral deposition from heterogeneous reactions involving a vapor phase. Dawsonite deposited from an effervescing H₂O–NaCl–CO₂ fluid at c. 100 °C, P_{CO2} ≥ 2 MPa, and a_{Na+}/a_{H+} > 10⁶ together with a group of transition metals (Ni, Co, Fe, Cr, Cu, Pb, Zn) and geothermal pathfinder elements (Hg, Sb, Ga, Tl, Ag), which occur as oxides or as trace elements in the host rock minerals. Dawsonite-bearing joints and veins are interpreted as escape structures of fracture-controlled, metal-bearing, low-T hydrothermal fluids in an area of intense CO₂ venting of this geothermal system.

1. Introduction

Although limited by risks and uncertainties (Gidden et al., 2025), carbon capture and storage (CCS) is still considered one of the milestones that will lower anthropogenic CO₂ emissions because of its long-term objective of storing carbon in geological formations (Snæbjörnsdóttir et al., 2020). However, the present deployment of CCS is small because it does not exceed 40–50 MtCO₂ yr^{−1}, i.e. a figure that is still insufficient to reach the estimated 2000 GtCO₂ of global storage aimed by the end of the century to achieve the goals of the United Nations Paris Agreement (Gidden et al., 2025). There is therefore a need to scale up, diversify, and improve CCS technologies to maximize its role in

the global mitigation initiatives.

Dawsonite (NaAlCO₃(OH)₂) is considered a good candidate for long-term CCS because of its presence in oil and gas fields (Cseresznyés et al., 2021; Király et al., 2018; Moore et al., 2005) and because of its predicted stability at CCS conditions (Marini, 2007; Xu et al., 2004). Compared to other carbonates, dawsonite is expected to be abundant in sedimentary basins dominated by sandstone and shale and experiencing high CO₂ fluxes (Xu et al., 2004; Xu et al., 2005). The formation of dawsonite was experimentally determined to occur in alkaline fluids at c. 50–180 °C, relatively high CO₂ partial pressure (P_{CO2} = 4–20 MPa) and high Na, but relatively low Ca-, Mg-, and Fe concentrations (Bénézech et al., 2007; Kaszuba et al., 2011; Takaya et al., 2019). Field-based studies showed

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that dawsonite forms within rocks at the expense of common aluminosilicates like albite (Csereznyés et al., 2021; Király et al., 2018) and K-feldspar (Comerio et al., 2014). These constraints explain why natural dawsonite is typically documented within sedimentary sequences rich in sandstone and shale, but it does not explain how exactly this mineral forms in nature. Questions that are still unanswered are why dawsonite is only a minor phase in CO₂ charged gas reservoirs and why it is considered difficult to synthesize in laboratory experiments mimicking CCS (Hellevang et al., 2010; Stoica and Pérez-Ramírez, 2010; Takaya et al., 2019; Zhang et al., 2004). Notwithstanding this lack of knowledge, in addition to oil and gas fields (Liu et al., 2022; Wilkinson et al., 2009) dawsonite was found in volcanic (Stevenson and Stevenson, 1965) and volcanoclastic rocks (Comerio et al., 2014), coal fields (Limantseva et al., 2008; Ming et al., 2017), and within fluid and melt inclusions of pegmatites (Hulsbosch et al., 2016; Sirbescu and Nabelek, 2003) and mineral deposits (Coveney and Kelly, 1971; Spooner and Bray, 1977). All these occurrences indicate that dawsonite is probably not rare in the geological record, but rather incompletely constrained from a genetic standpoint.

In this work, we present a field-based study that constrains dawsonite formation within a geothermal system, i.e., the hydrothermal

environment that harbors intense CO₂ venting (Hedenquist, 1991; Minissale et al., 1997) and epithermal (e.g., Au, Ag, Sb, Ga) ore deposits (Henley, 1985; White, 1981). The study area is Mt. Amiata, i.e. the second-largest geothermal resource of Italy (Bertani, 2016), a global carbon source (Fronzoni et al., 2009), and a historical district of hot-spring Hg—Sb mineral deposits (Garofalo et al., 2026). Dawsonite was long known in the Mt. Amiata mineral deposits (De Castro, 1914), but the factors controlling its occurrence were never explored to any extent. In this geothermal system, we combine remote sensing data, field mapping, and several analytical techniques to constrain the process of dawsonite deposition within the framework of geothermal fluid flow, which involved the venting of a CO₂-rich gas and the transport of a suite of geothermal pathfinder elements (e.g., Hg, Sb, Ga, Tl, Ag). Our results indicate that dawsonite crystallization was essentially a *deposition* process, i.e. a vapor-solid phase transition that involved a CO₂-rich, effervescing geothermal fluid flowing through a fracture network. This process sheds light on the mechanisms of dawsonite formation in natural environments.

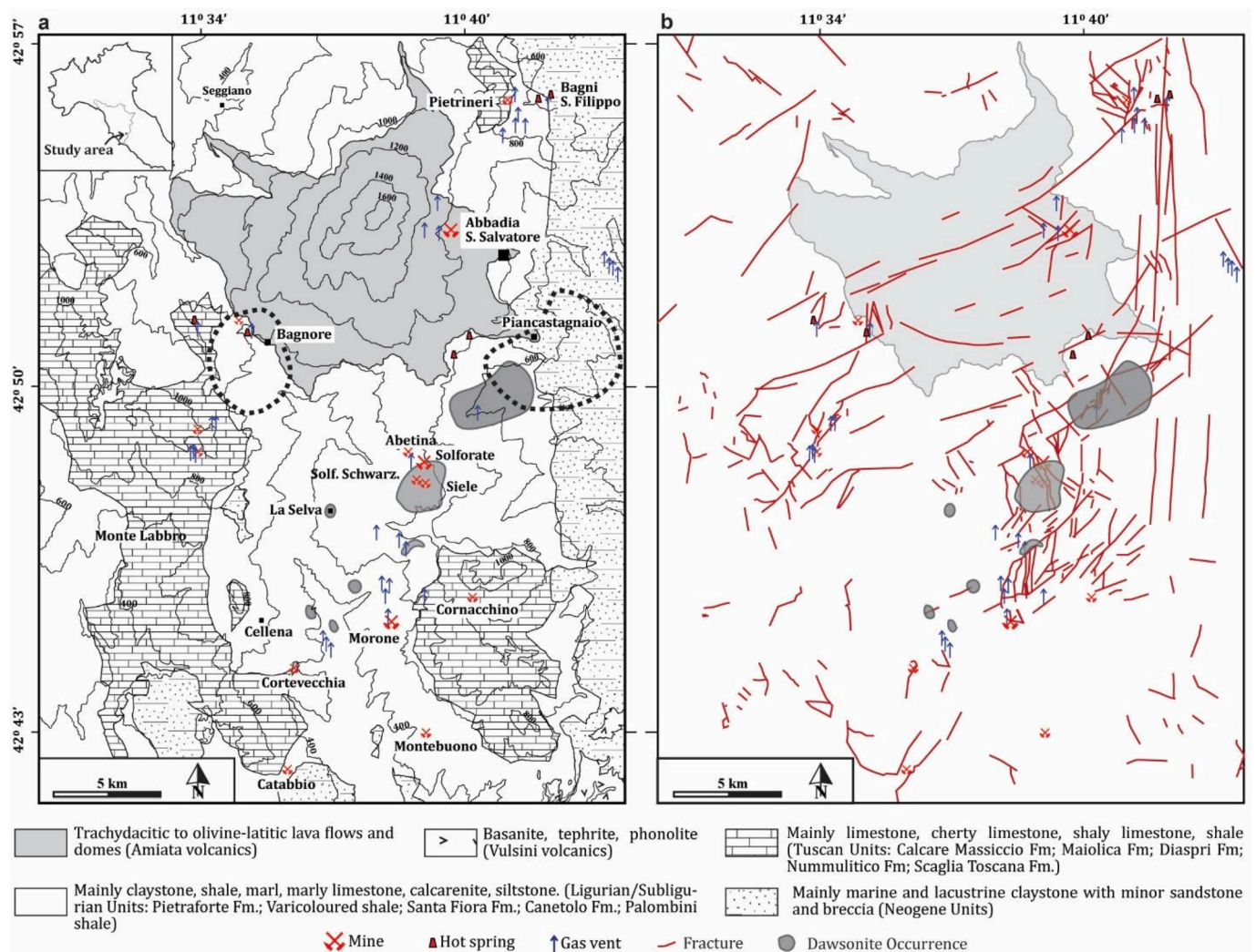


Fig. 1. Schematic geological map of the Mt. Amiata geothermal system and distribution of its dawsonite occurrences. (a) Mapped dawsonite occurrences overlaid on a simplified geological map (WGS 84 geodetic system, EPSG: 4326) of the Mt. Amiata geothermal system of S. Tuscany (modified after: Garofalo et al., 2026). The map shows the exploited cinnabar ($\pm$ stibnite) deposits, the hot springs, and the gas vents of the system. The thick dotted lines mark the geothermal well fields (from: Barelli et al., 2010). Notice that dawsonite is hosted only by rocks belonging to the Ligurian/Subligurian tectonic units. (b) Map of the dawsonite occurrences overlaid on the map of fracture population in the geothermal system.

2. The Mt. Amiata geothermal system

The geothermal system of Mt. Amiata is located in the northern Apennine thrust-and-fold belt (Fig. 1a). Its geological evolution and properties were constrained by comprehensive geological, geophysical, petrological, and drill hole exploration data, which are summarized in the Supplementary material. Here, we report on the regional and local key features that are relevant to the genesis of dawsonite.

The main geological trait of the area is defined by the presence of a thick stack of nappes made of sedimentary rocks, which deposited onto the oceanic (Ligurian/Subligurian Units) and continental crust (Tuscan Units) and form most of the caprocks of the geothermal system (Batini et al., 2003). The lithologies that make these nappes are mainly claystone, shale, marl, marly limestone, and siltstone. The reservoir rocks of the geothermal system are represented by the carbonates of the Tuscan nappe and by the largely unexposed Paleozoic basement rocks.

The Mt. Amiata volcano is made of lava flows and domes of trachyte-dacite to olivine-latitic compositions, which emplaced between 305 and 231 ka ago (Cadoux and Pinti, 2009; Conticelli et al., 2015). Indirect constraints on the dimensions and composition of the Mt. Amiata pluton (Gianelli et al., 1997; Gianelli et al., 1988) are based on petrological data on metasedimentary xenoliths hosted by the volcano lava flows (van Bergen and Barton, 1984; van Bergen et al., 1983) and on the uplift of late Pliocene and early Pleistocene sediments (Marinelli et al., 1993, and ref. therein). They indicate that the pluton emplaced in the Lower Pliocene and is probably located below the volcano at a depth of 5–6 km.

Two well fields that occupy an area of about 70 km², namely Piancastagnaio and Bagnore (Bertani, 2016), exploit two wet-steam high enthalpy geothermal systems (Fig. 1a). Relevant to this work is the alkaline pH of the geothermal fluid, which was determined between 6.78 and 8.31 at 300–350 °C (Minissale et al., 1997).

Mount Amiata hosted 14 historical Hg (±Sb) mineral deposits, which were active from 1864 to 1982, produced >117 kt of Hg, and formed the 3rd largest district of hot-spring deposits of global importance (Garofalo et al., 2026; Rimondi et al., 2015). These ore bodies consisted of cinnabar, marcasite, pyrite, and minor stibnite hosted by rocks belonging to both the Tuscan and Ligurian Units.

Finally, the entire Northern Apennine belt is characterized by upward migration of deeply sourced, overpressured CO₂ considered to be the product of subducted lithosphere (Frezzotti et al., 2009). Several localized and diffuse, CO₂-dominated, deeply sourced gas vents are found at Mt. Amiata (Chiodini et al., 2020a; Frondini et al., 2009; Frondini et al., 2008). The magnitude of this venting was estimated to be between 226 and 326 t/d in individual hot springs (Chiodini et al., 2020a), i.e. values that are c. 30 times higher than those estimated in other geothermal systems (Seward and Kerrick, 1996). The total annual CO₂ discharge was calculated to be 2.1 10⁹ mol, or 92,421 t (Frondini et al., 2009). This makes Mt. Amiata a globally significant carbon source.

3. Methods

We conducted this study by combining field mapping of dawsonite occurrences with remote sensing data and several analytical techniques. These include petrographic and X-ray powder diffraction analyses, fluid inclusion microthermometry, Raman spectrometry and relative spectral processing and Monte Carlo uncertainty quantification, determination of dawsonite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ by isotope ratio mass spectrometry, elemental imaging by LA-ICP-TOFMS, and geochemical modeling. Here we summarize the key information that is relevant for data discussion. Details on the applied analytical techniques and all datasets are reported in the Supplementary material.

3.1. Field mapping and sampling

Field mapping of dawsonite occurrences was conducted in the years 2023–2024 along roads, forest trails, quarry cuts, rivers, and creeks in

267 outcrop exposures of all lithologies of the geothermal system (Fig. 1a). This documentation was limited by the extensive forest cover of the geothermal system, which extends from an altitude of about 400 m (Catabbio mine, Fig. 1a) to about 1700 m (summit of Mt. Amiata volcano). Mapping consisted in the identification of the key features of dawsonite-bearing outcrops (Figs. 2, S1), which was carried out identifying altered and mineralized rocks in the field and using where possible quantitative estimates of mineral/vein abundance and cross-cutting relationships. This method is used in ore deposit studies for a genetic understanding (Garwin et al., 2022). During mapping, 14 samples of dawsonite and associated host rocks and joints/veins were collected (Table S1) to carry out the set of analyses detailed below.

3.2. Fracture population from remote sensing data

Considering the importance of fault zones for geothermal fluid and steam circulation in geothermal systems (Jolie et al., 2016), we constrained the large-scale fault population of the mapped area using remote sensing data (Fig. 1b). These data focused on the identification of linear features in satellite imagery, which were subsequently digitized and compared with existing geological maps using a Geographic Information System (GIS). These linear features, commonly observed in satellite images, typically correspond to polygenetic planar structures such as fractures, faults, and strike-parallel features of resistant strata. For simplicity, and following the terminology of O'Leary et al. (1976), we refer to these features as “linears” or “lineamentary” irrespective of their diverse origins.

For our analysis of fault population, we used the processed band combinations from raw Landsat TM imagery (WRS Path 192, Row 030, 2011) and SPOT imagery (SPOTCIBN43E011, 1986–1987), both obtained from the USGS EarthExplorer platform. The lineamentary features identified in the remote sensing data appear as straight valley segments or geomorphological alignments associated with brittle structures within the bedrock. The integration of remote sensing interpretation with previous studies on the area (Bonciani et al., 2005; Brogi et al., 2015; Calamai et al., 1970) enabled the construction of a map of fault population (Fig. 1b). Over 400 lineamentary features were identified, ranging from several hundred meters to a few kilometers in length. These features were correlated with a structural framework indicative of fault zones. Comparative analysis with geological maps supports the presence of displacement along multiple faults. The satellite-based interpretation aimed to verify whether the identified lineamentary features correspond to actual geological structures. A GIS software (ArcMap v.10.2, Esri®) was used to analyze the remote sensing data and the geological features for this region.

3.3. Fluid inclusion microthermometry

Microthermometry of fluid inclusions was conducted on samples of platy calcite crystals associated with dawsonite from two studied locations (i.e., *Fosso dei Renajoli* and *Campo Renajoli*; cf. Fig. 2 and Table S1). Thirteen of these crystals hosted a significant number of fluid inclusions; however, sample preparation showed that they were plagued by re-equilibration due to cutting and polishing, which is particularly severe in the soft calcite (Bodnar, 2003a). This limited our study to the groups of inclusions hosted in the portions of optically clear calcite with minimal intracrystalline deformation and cleavage.

Microthermometric measurements of fluid inclusions were carried out at the Department of Biological, Geological and Environmental Sciences of the University of Bologna on 575 inclusions making 11 “fluid inclusion assemblages” (FIAs). These are petrographically discriminated, cogenetic groups of fluid inclusions located along trails or within clusters of the host mineral (Bodnar, 2003b), which are useful tools to discriminate generations of geofluids within geological samples, as well as their properties (Garofalo et al., 2014; Garofalo et al., 2023a; Garofalo et al., 2025). These FIAs have been divided into primary, secondary, and

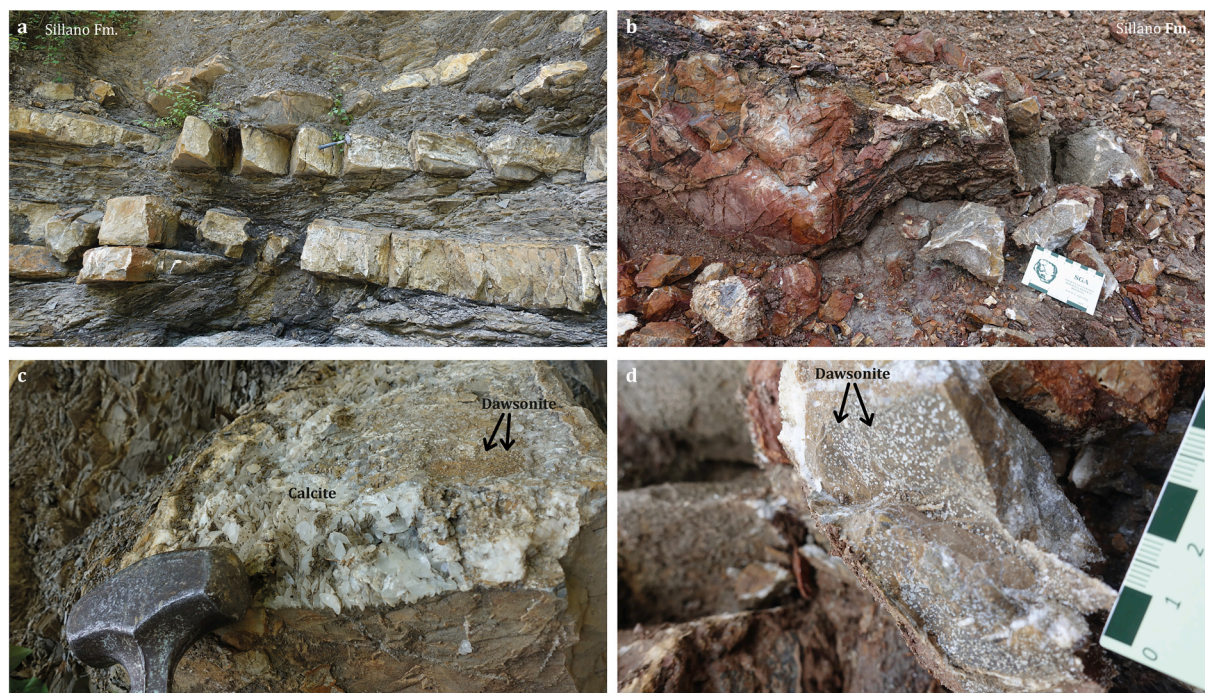


Fig. 2. Characteristic features of dawsonite outcrops at Mt. Amiata. (a) Dawsonite deposited within an alternation of claystone and sandstone (Renajoli location, adjacent to the Solforate mine). (b) Dawsonite occurrence within a sandstone (Cellena location). Notice the dense network of calcite veins and the intense reddening of this host lithology. (c) Close-up of panel (a) showing a vein filled with platy calcite and dawsonite crosscutting a reddish sandstone level. (d) Close-up of panel (b) showing the dawsonite coating of a joint plane. This joint is in turn crosscutting calcite veinlets.

pseudosecondary assemblages following [Roedder \(1984b\)](#).

The microthermometric properties of these FIAs were determined using a Linkam THMSG 600 heating/freezing stage coupled with an Olympus BX51 polarizing microscope. Stage calibration was carried out with synthetic fluid inclusions at -56.6 , 0.0 , and 374 °C, which correspond to the melting of CO_2 , ice melting, and final homogenization of H_2O inclusions, respectively. The instrumental accuracy was ± 0.1 °C.

For individual FIAs, all phase transitions were collected following the same standard procedure. Samples were first rapidly cooled to c. -180 °C and then slowly heated (5 °C/min) to determine the phase transitions potentially shown by the melting of a solid carbonic phase (T_{mCO_2}), eutectic phases (T_e), salt hydrates (T_{mHH}), ice (T_{mice}), and clathrates (T_{mclath}). In most of the studied FIAs, we determined only T_{mCO_2} , T_{mice} , and the temperatures of total homogenization (T_{htot}). The latter was determined by heating the samples from room temperature and recording the mode of homogenization of the inclusions (i.e., bubble or liquid disappearance). Low-T determinations were carried out in only 3 assemblages (FIAs 7, 9, and 11) to avoid potential risks of FI stretching during subsequent heating of the soft calcite. In these FIAs, only T_{mclath} and T_{mice} were measured. All phase transitions were determined recording the minimum and maximum values for each assemblage. Volume fractions of individual fluid inclusions were determined as the ratio $\phi = V_{\text{vap}}/V_{\text{tot}}$ ([Diamond, 2003](#)) estimated optically at room temperature. All the phase transitions were measured utilizing the cyclical measurements method described by [Goldstein and Reynolds \(1994\)](#). Bulk salinities of individual inclusions were computed using the algorithm of Steele-MacInnis for H_2O -NaCl- CO_2 fluids ([Steele-MacInnis, 2018](#)). Analytical precision could not be determined with duplicate or triplicate measurements of individual fluid inclusions because of the systematic stretching of calcite during heating, which showed as a slight modification of the initial ϕ of the inclusions after heating at c. 100 °C. Stretching limits the possibility to repeat measurements, consistent with the established tendency of soft minerals to re-equilibrate ([Bodnar, 2003a](#)).

The results of microthermometric measurements are summarized in

Table S4, which reports on the microthermometric properties of all FIAs, including the estimated range of P_{CO_2} calculated using the separation (Δ) between the two Raman bands of CO_2 (see below).

3.4. Raman spectrometry

The vapor phase of the calcite-hosted FIAs was studied by Raman spectrometry at the Department of Biological, Geological and Environmental Sciences, University of Bologna. All measurements were conducted before the microthermometric determinations. We used a WITec alpha300 R Raman microscope (Oxford Instruments, Ulm, Germany) equipped with a 785 nm excitation laser and a motorized stage. Spectra were acquired using a spectrometer grating set to 600 g/mm, an integration time of 60 s, and three accumulations per spectrum. A $50\times$ objective lens was deployed for all measurements. Laser power was adjusted between 10 and 27 mW depending on inclusion depth, with lower power for shallow inclusions and higher power for deeper ones.

Raman spectra were collected for 114 vapor rich inclusions belonging to FIAs 1–6, 8, and 10–11 (Table S5). Individual assemblages were characterized from a minimum of 5 measurements (FIA 1) to a maximum of 24 measurements (FIA 3). Only vapor-rich inclusions larger than c. 25 μm were analyzed because liquid-rich and smaller vapor-rich inclusions did not provide consistent Raman signals of sufficient intensity. Inclusions deeper than 45 μm were considered only if their spectra reached a minimum signal intensity of 500 counts.

Inclusion spectra showed only the presence of CO_2 and H_2O in the vapor phases, which occur at distinct spectral positions. We used the Raman spectra to estimate the CO_2 density in the inclusion fluid following the approach of [Kawakami et al. \(2003\)](#). Accordingly, the separation (Δ) between the two Raman bands of CO_2 generated by the Fermi diad peaks (i.e., $\nu_- \approx 1285$ cm^{-1} and $\nu_+ \approx 1388$ cm^{-1}) can be used as a densimeter of the CO_2 -rich fluid. Fig. S6 of the Supplementary material shows an example of how Δ was determined in the measurements. According to Kawakami et al., the relationship between CO_2 density (ρ , in gcm^{-3}) and Δ (cm^{-1}) is given by:

$$\rho = -0.03238697\Delta^3 + 10.08428\Delta^2 - 1046.189\Delta + 36163.67 \quad (1)$$

For each analysis with a significant CO₂ signal, the ambient laboratory temperature was recorded at the time of measurement, as the sample was not thermally isolated. Laboratory temperatures ranged between 19 and 23 °C. These values were subsequently used to calculate the CO₂ pressure inside the inclusions using the density-pressure relationship of Steele-MacInnis (2018). Notably, this pressure is a minimum estimation of fluid pressure (P_f) because it does not include the contributions of H₂O_{vap} and H₂O_{liq}.

Raman-derived CO₂ densities are highly sensitive to small variations of diad peak positions in the 1260–1420 cm⁻¹ region due to uncertainties derived from detector noise, baseline curvature, peak overlap, signal instability, fitting degeneracy, and other factors (Nasdala et al., 2004). These nonlinear error sources propagate into Δ , ρ , and ultimately into the calculated CO₂ pressure. To accurately assess the precision of our measurements, we quantified these uncertainties, especially those related to peak position and peak width (Gasda and Oglione, 2014), by implementing a Monte Carlo simulation framework. Details on this framework and on the calculated CO₂ densities are reported in the Supplementary material.

3.5. Isotopic compositions of C and O

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of dawsonite were determined for the samples collected in all mapped outcrops (Table S6). The dawsonite-rich coatings and the dawsonite crystals associated with vein calcite were removed from the bulk samples, crushed with an agate mortar, and hand-picked under a binocular microscope to obtain pure crystals and aggregates separated from the host rocks or from the associated oxides. This sequence of operations allowed obtaining 45–360 mg of dawsonite mass from only 10 samples, which were used for this type of analyses.

All stable isotope measurements were conducted at the stable isotope laboratory of the *Istituto di Geoscienze e Georisorse* (IGG) of the *Consiglio Nazionale delle Ricerche* (CNR) of Pisa, Italy. Briefly, about 150 μg of each powdered dawsonite sample was placed in vacutainers, flushed with helium and reacted with 104% orthophosphoric acid at 70 °C for 1 h. The evolved CO₂ was analyzed using an automated GASBENCH sample preparation bench attached to a Thermo Finnigan Mat Delta Plus Isotope Ratio Mass Spectrometer (IRMS). The instrument was calibrated and quality control performed with the internal standards MS ($\delta^{13}\text{C} = +2.13$ ‰, $\delta^{18}\text{O} = -1.73$ ‰), MOM ($\delta^{13}\text{C} = +2.53$ ‰, $\delta^{18}\text{O} = -4.73$ ‰), and NEW12 ($\delta^{13}\text{C} = -3.86$ ‰, $\delta^{18}\text{O} = -9.61$ ‰) which are calibrated against the international reference materials NBS 19 ($\delta^{13}\text{C} = +1.95$ ‰, $\delta^{18}\text{O} = -2.2$ ‰) and NBS 18 ($\delta^{13}\text{C} = -5.01$ ‰, $\delta^{18}\text{O} = -23.00$ ‰). In each run, samples and standards were replicated 4–5 times. Our

estimated accuracy is better than 0.1 ‰ and the precision is 0.15 ‰ for both carbon and oxygen.

3.6. Elemental imaging by LA-ICP-TOFMS

Dawsonite and black oxide coating a joint crosscutting a quartz-carbonate sandstone (Fig. 3a) were analyzed using Laser Ablation-Inductively Coupled Plasma-Time of Flight Mass Spectrometry (LA-ICP-TOFMS). The setup included an Argon Fluoride (ArF) excimer laser (193 nm, GeoLas C, Lambda Physik, Germany) coupled with a TOF mass spectrometer (icpTOF2R, TOFWERK AG, Switzerland). Ablation was conducted in a helium atmosphere (99.999%, Linde Gas Schweiz AG, Switzerland) with argon (99.996%, Linde Gas Schweiz AG, Switzerland) used as carrier gas. A piezoelectrically driven xyz translational stage (1 nm resolution, SmarAct GmbH, Germany) enabled precise sample positioning. Laser, stage movement, and TOFMS acquisition were synchronized using a custom-built imaging control system (Neff et al., 2020).

The samples were ablated in hole-drilling mode, with 10 laser pulses fired at each position before advancing to the next. Laser fluence was set to 10 J/cm², with a repetition rate of 100 Hz and a spot diameter of 5 μm . Consecutive ablation spots were aligned edge-to-edge, resulting in a pixel size of 5 $\mu\text{m} \times 5 \mu\text{m}$. Two areas measuring 500 $\mu\text{m} \times 500 \mu\text{m}$ each were analyzed. NIST SRM 610, with reference values taken from the GeoReM database (Jochum et al., 2005), was used as an external standard and measured before, between, and after the sample runs to ensure quantification accuracy and to monitor instrumental drift. Average gas blank signal intensities were subtracted from all measurements.

Data were first processed with Tofware (TOFWERK AG, version 2.5.11) to sum spectra and define integration boundaries. Peak intensities from both samples and the reference material were then processed using a custom Python script tailored to this experiment. Elemental maps (Figs. 4 and S8) were quantified on a per-pixel basis using 100 wt% mass normalization (Liu et al., 2008), initially assuming all components to be oxides. To correct for this assumption, mineral phases were subsequently identified on the quantified images by applying a UMAP-driven dimensionality reduction of the elemental mass fractions followed by k-means clustering, a methodology that has been documented in detail by Umfahrer et al. (2026). Once calcite and dawsonite pixels were recognized, their mass fractions were corrected using 100 wt% normalization based on carbonate compositions rather than oxides.

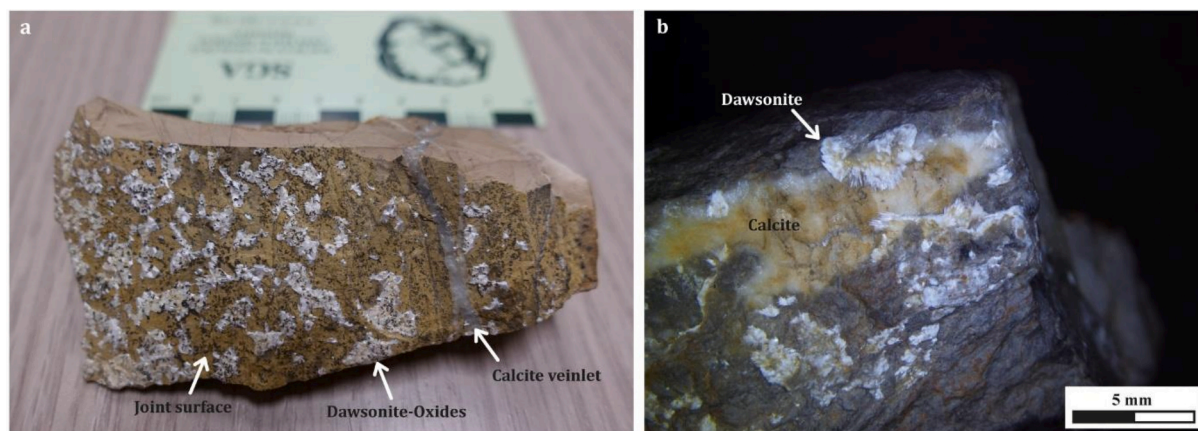


Fig. 3. Distinct types of dawsonite occurrences at Mt. Amiata. (a) Dawsonite and mixed oxides forming a coating on a joint crosscutting a sandstone of the Pietraforte Fm. (Cellena location). A calcite veinlet of this rock is crosscut by the dawsonite-bearing joint. (b) Calcite and dawsonite within a vein crosscutting a claystone of the Sillano Fm. (Renajoli location).

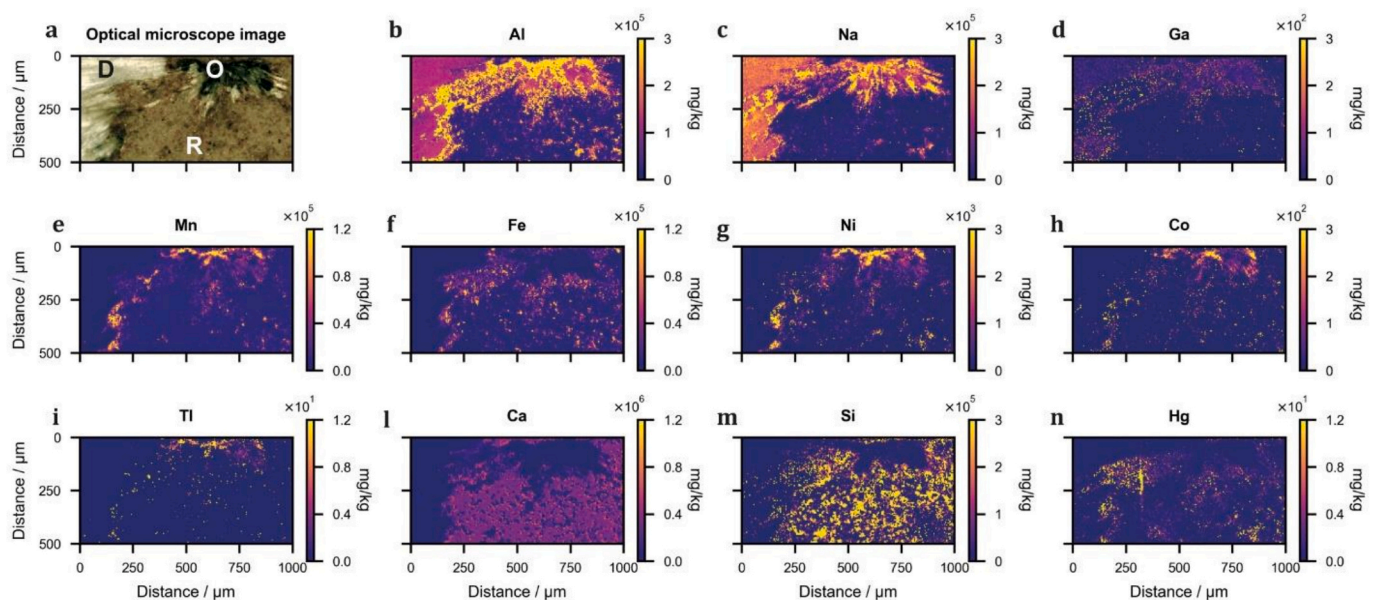


Fig. 4. Element distribution maps of dawsonite determined by LA-ICP-TOFMS. (a) Optical image showing textural relations and morphologies of dawsonite and Mn oxide (black phase) coating a joint plane (sample from Cellena locality, cf. Fig. 3a). (b–n) Element distribution maps of the same area of panel A showing the calculated mass fractions of major, minor, and trace components of dawsonite, oxides, and host rock in mg/kg (see also Fig. S8).

3.7. Mass transfer calculations

Calculations of mass transfers were carried out with the multi-sample, immobile element method (Garofalo, 2004; MacLean and Kranidiotis, 1987). With this method, the mass fractions of rock components are measured in various aliquots of a rock mass (e.g., along a profile of an alteration zone) and plotted in pairs to determine their mobility during alteration (details in the Supplementary material). Element mobility is calculated with respect to a protolith. Mass transfers of individual components are calculated for each aliquot of rock mass. Petrographic documentation (Fig. S4) can be coupled with these calculations to couple mineral paragenesis with element mobility (Garofalo et al., 2023b).

Mass transfer calculations were carried out in a slab sample hosting a dawsonite-oxide joint (Fig. S2) collected from an outcrop of the locality named *Poggio del Gatto* (Table S1), south of Piancastagnaio. This sample is a typical sandstone caprock of Mt. Amiata (Sillano Fm.) hosting dawsonite-filled joints and showing intense reddening. It was cut into four aliquots located at progressive distance from the joint (Fig. S2b). Table S3 shows the mineralogical compositions of the four aliquots and Fig. S4 shows their microtextural features. The mass fractions of major, minor, and trace components of these aliquots were determined at the Activation Laboratories Ltd. (Ontario, Canada) using a combination of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Instrumental Neutron Activation Analyses (INAA), and titration for the determination of FeO. Details on the analytical techniques used and on the multi-sample, immobile element method are provided in the Supplementary material. Table S10 lists the chemical compositions of the four blocks and Table S11 the calculated mass transfers.

3.8. Geochemical modeling

Equilibrium calculations were carried out with the SUPCRTBL software package of Zimmer et al. (2016). This software calculates thermodynamic properties of reactions involving minerals, gases, and aqueous species at high temperatures (0–1000 °C) and pressures (100–500 MPa) and updates the structure of the SUPCRT92 package of Johnson et al. (1992). SUPCRTBL includes an internally consistent dataset of thermodynamic properties of dawsonite.

Equilibria were calculated at 100 and 150 °C and 2 MPa total pressure to simulate dawsonite deposition reactions from a vapor phase made of CO_{2g} and H_2O_v . The chemical reactions were calculated considering the $a_{\text{SiO}_2, \text{aq}}$ at equilibrium with quartz and at the conditions of chalcedony supersaturation. These distinct conditions were used to explore the effects of fluid compositions on dawsonite deposition. We considered chalcedony in our model because of its occurrence in the geothermal areas of the Northern Apennines (Morteani et al., 2011), although its presence at Mt. Amiata is uncommon (Zucchetti, 1964). A detailed account of fluid-mineral equilibria is given in Table S12.

4. Results

4.1. Large scale features

At the scale of the entire geothermal system, dawsonite outcrops within a restricted area that trends northeast-southwest and extends discontinuously for about 12 km from the town of Piancastagnaio to the village of Cellena (Fig. 1a). The surficial extensions of these outcrops vary from several km^2 to $<1 \text{ km}^2$ and their spatial distribution is strikingly coincident with the region of the geothermal system showing the densest fault population (Fig. 1b).

Individual dawsonite-bearing outcrops are characterized by a set of typical features. First, dawsonite is found mostly within joints and less commonly together with calcite within veins crosscutting sandstone, siltstone, marl, and claystone of the Ligurian formations. These lithologies invariably show a reddish tint that is evident at various scales of observation (Figs. 2 and S1–S2). Other typical features of host lithologies are the systematic hardening induced by intense silicification and the presence of a network of thin calcite veinlets together with the dawsonite-filled joints and veins (Figs. 2–3).

At the mesoscale, dawsonite is visible as a mm-thick coating of joints crosscutting the host rocks, where it forms rosettes or tufts of radial aggregates and acicular crystals (Figs. 3 and S3) often in association with dark (Mn-rich) oxides. Less commonly dawsonite is found within veins together with massive (Figs. 3b, S3b; S5) or platy calcite crystals (Fig. 2c). In all cases dawsonite forms tufts and rosettes at, or close to, textural equilibrium with calcite.

4.2. LA-ICP-TOFMS data

Element distribution maps of dawsonite aggregates coating the joint of a quartz-, carbonate-bearing sandstone (Fig. 4a) were calculated from LA-ICP-TOFMS data. Results show that dawsonite is a pure phase made of the major components Al (Fig. 4b) and Na (Fig. 4c) and trace amounts of Ga only (range: 50–150 $\mu\text{g/g}$; Fig. 4d). This feature contrasts with the composition of the other phases of the joint, which host many minor and trace components. In addition to Mn (Fig. 4e), the mass fractions of metals (Ni, Co, Fe, Tl, Zn, Sn, Ba, and Ag) within the oxide aggregates vary between 3 $\mu\text{g/g}$ and c. 1 wt% (Figs. 4 and S8). Similarly, the sandstone grains – which are highlighted by the spotty distribution of their major components Ca and Si – host variable mass fractions of Fe, K, Sr, Ba, and Cs (range: 30 $\mu\text{g/g}$ - 1.2 wt%). Significant is the determination within the sandstone grains of Hg (Fig. 4n) and Sb (Fig. S8l) in the 3–12 $\mu\text{g/g}$ range, which cannot be identified as pristine rock components. Together with Tl and Ag, these elements are long known to be typical hot-spring and geyser precipitates (Krupp and Seward, 1990; White et al., 1992).

4.3. Isotope compositions and fluid inclusion data

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic compositions of 10 dawsonite samples from several mapped sites (Table S5) show relatively narrow ranges of values ($\delta^{13}\text{C}$ from 5.02 to 5.67 ‰; $\delta^{18}\text{O}$ from –12.99 to –9.57), which form an array of negatively correlated values in a $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ plot (Fig. 5).

Fluid inclusion assemblages entrapped within platy calcite (Fig. 2c) allow determining the properties of the dawsonite-bearing fluid (Table S3). At room temperature, these assemblages host inclusions with variable phase proportions, i.e. FIs that are liquid- and vapor-rich within the same assemblage (Fig. 6). A combination of microthermometric determinations and Raman spectrometry shows the presence of a H_2O – NaCl – CO_2 model fluid in these assemblages, in which the liquid-rich inclusions have calculated bulk salinity of 2.2–2.4 wt% NaCl_{eq} and $X_{\text{CO}_2} \approx 0.05$. The vapor-rich inclusions are made of CO_2 and H_2O and their calculated P_{CO_2} ranges between about 2 and 8 MPa. The liquid- and vapor-rich inclusions of individual assemblages homogenize by bubble and liquid disappearance, respectively, and have T_{hot} ranging between c. 100 and 150 °C.

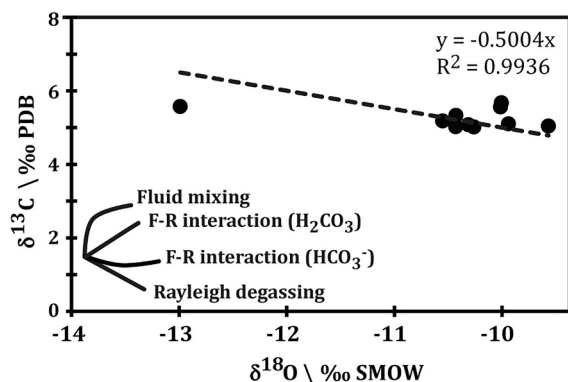


Fig. 5. Isotopic composition of Mt. Amiata dawsonite. The dotted line locates the correlation line between the data. The inset shows expected $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ covariations in carbonates resulting from distinct precipitation processes (Zheng, 1990; Zheng and Hoefs, 1993). The “F-R interaction” curves mark the trends expected in carbonates precipitating from fluids in which the dominant C species are H_2CO_3 or HCO_3^- .

5. Discussion

5.1. Large scale factors controlling dawsonite occurrences

A fundamental geological factor affecting dawsonite deposition at Mt. Amiata is shown by the correlation between dawsonite outcrops and faults (Fig. 1). The occurrence of dawsonite in the areas of dense fracture population and gas venting indicates that at Mt. Amiata faulting played a primary role in controlling local crustal permeability, geothermal fluid flow, and dawsonite deposition. This is consistent with studies showing CO_2 venting being most intense along faults of Mt. Amiata (Chiodini et al., 2020a; Frondini et al., 2009) and with the evidence in the Northern Apennines for a correlation between deep CO_2 degassing and location of seismogenic faults (Chiodini et al., 2020b). In other geothermal systems, gas vents were found to occur within volumes of fault networks showing an increased tendency to dilate and slip during fluid flow (Jolie et al., 2016). These features suggest that dawsonite occurrences at Mt. Amiata are the surface expressions of a fault network that was highly interconnected and conductive at the time of mineralization.

Another geological factor controlling dawsonite deposition is its occurrence within lithologies rich in micas, plagioclase, clay minerals, and K-feldspars (Table S2), i.e., sandstone, siltstone, marl, and claystone as emphasized by previous studies (Comerio et al., 2014; Cseresznyés et al., 2021). Our work confirms these previous findings; however, it also shows that a combination of structural and lithological factors must have controlled dawsonite deposition efficiently. Such combination is important because it explains why at Mt. Amiata dawsonite did not form in the relatively less fractured, but extensive, outcrops of Ligurian formations and provides useful indications on the mechanism of dawsonite precipitation from fluid-rock interaction.

Previous work did not document in detail the role of fault networks in controlling dawsonite formation in geological environments. The work carried out in oil and gas fields from many locations (e.g., Baker et al., 1995; Cseresznyés et al., 2021; Liu et al., 2022; Wilkinson et al., 2009) showed that dawsonite is essentially an authigenic sedimentary phase and this somehow guided research on dawsonite synthesis (e.g., Kaszuba et al., 2003; Kaszuba et al., 2005). However, authigenesis explains only in part how dawsonite forms in these fields. For instance, the samples used to study the Mihályi-Répcelak field of the Pannonian Basin were collected close to a large regional fault zone (the Rába tectonic line: Cseresznyés et al., 2021) that might have controlled flow and distribution of CO_2 within the sedimentary sequence. This structural control would explain how CO_2 of established magmatic origin was “injected” into this basin to form dawsonite. Similarly, the dawsonite of the Songliao Basin (China's largest oil and gas basin) fills the intergranular pore space of the sandstone making the local reservoir, but a recent study acknowledged the role of a network of open fractures to enable large volumes of mantle-derived CO_2 into this basin (Liu et al., 2022). We propose that fracture-controlled flow of CO_2 and consequent formation of dawsonite within sedimentary basins and other geological environments is more common than currently claimed. This is consistent with the first documentation of dawsonite in its type locality (Montreal, Canada: Harrington, 1874), in which dawsonite was reported together with calcite as a coating of a set of joints crosscutting a trachyte dyke, and with other occurrences in marine sedimentary sequences (Okuyama and Take, 2011; Smith and Milton, 1966), mineral deposits (Coveney and Kelly, 1971; Ferrini et al., 2003; Spooner, 1991), and coalfields (Ming et al., 2017).

5.2. Mass transfer constraints

Immobile element analysis (Fig. S7, Supplementary material) carried out in a typical wall rock hosting a dawsonite-filled joint (sample Poggio del Gatto, Fig. S2) shows that at Mt. Amiata the reddish hydrothermal alteration developed in a regime of mass gain. This implies that while

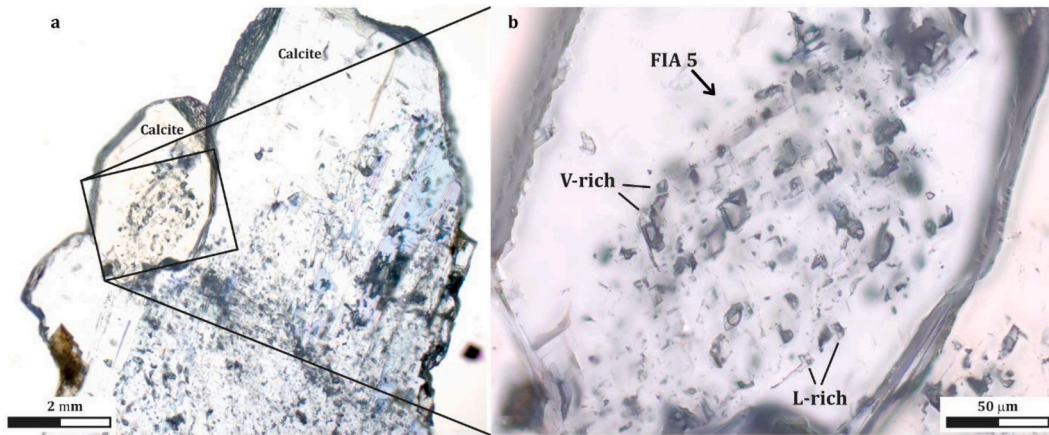


Fig. 6. Petrographic characteristics of the calcite-hosted fluid inclusions from *Fosso dei Renaioli*. (a) Small scale photomicrograph showing the cores of typical platy calcite cogenetic with dawsonite and hosting abundant fluid inclusions (cf. Fig. 2c). (b) Close-up of one of the primary fluid inclusion assemblages studied here (FIA 5) showing the simultaneous occurrence of liquid- and vapor-rich fluid inclusions within the same assemblage. Together with the microthermometric properties, this is evidence for heterogeneous entrapment of the vein fluid at the time of calcite growth.

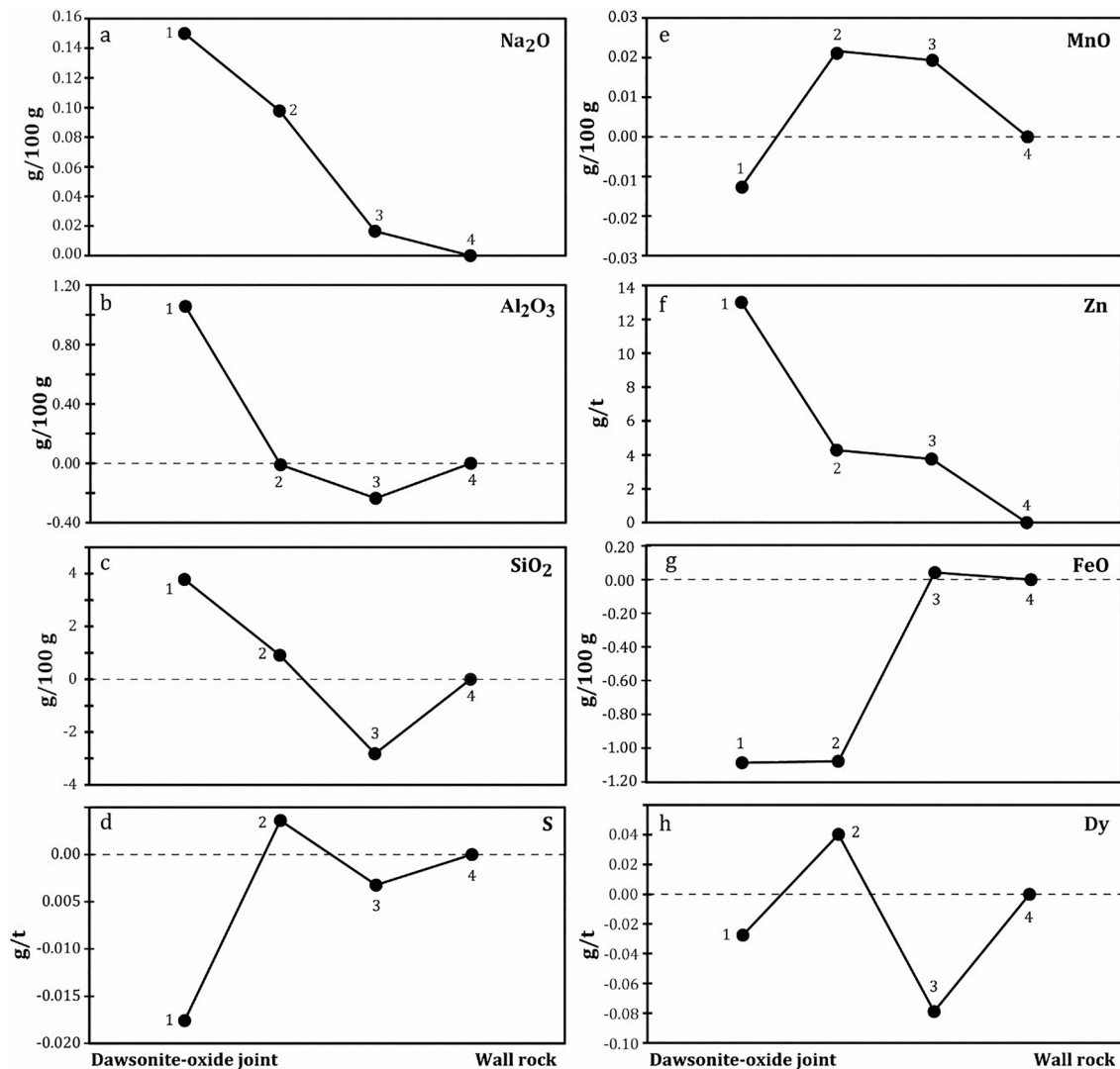


Fig. 7. Mass transfer profiles calculated for selected major, minor, and trace components of the wall rock of a dawsonite-filled joint (sample *Poggio del Gatto*). The abscissas of these plots are the relative positions of the 4 blocks with respect to the joint (cf. Fig. S2), while the ordinates are the calculated mass changes. Mass changes are calculated with respect to the considered protolith (block 4 of sample *Poggio del Gatto*). Positive values (a, b, c, f) denote mass gains of the wall rock close to the joint, whereas negative values (g, d) denote mass losses. Profiles showing small mass changes around the zero-mass-change line (e, h) denote limited mobility of the chemical component.

the dawsonite-bearing joints and veins were forming at Mt. Amiata, the wall rocks gained mass mainly as a result of diffusional transfers from the geothermal fluid (Garofalo, 2004; Garofalo et al., 2023b; MacLean and Kranidiotis, 1987; Mountain and Williams-Jones, 1996). Gains are documented for major (Al_2O_3 , Na_2O , SiO_2 , Fe_2O_3 , TiO_2) and trace rock components (Zn, Ba, Co, Cu), while mass loss is evident only for FeO and S.

Calculated mass transfers plotted as a function of distance from the joint wall (Fig. 7) show gradually increasing mass gain trends of Na_2O (Fig. 7a), Al_2O_3 (Fig. 7b), and transition metals (e.g., Zn, Fig. 7f) at the joint wall. These gains reflect the degree to which these components were introduced into the wall rock by the geothermal fluid, presumably during the precipitation of dawsonite and oxides/hydroxides onto the joint surface. These mass transfer profiles represent a strong indication that the fracture-hosted geothermal fluid transported not only the CO_2 that was necessary for the deposition of dawsonite, but also all the constitutive metals of the solid phases. The proportions of Na_2O and Al_2O_3 gained by the wall rock are equal to 13% and 19% of the considered protolith, respectively, but those of the transition metals are much higher (>100% for Cu, Zn, and Ba). Notably, close to the joint wall Fe_2O_3 gain is coupled with FeO loss (Fig. 7g). This shows that the intense reddening of the wall rock is a product of Fe oxidation.

5.3. A model of dawsonite formation

In the samples studied, key constraints on the conditions of dawsonite deposition are provided by the physicochemical properties of the fluid inclusion assemblages hosted by the platy calcite (Fig. 2c). For these (Fig. 6), the combined evidence for opposite modes of homogenization of the liquid- and vapor-rich inclusions (by bubble- and liquid disappearance, respectively) within the same T range (Table S4) shows that calcite deposited from a *heterogeneous fluid*. This implies that a pristine, H_2O - NaCl - CO_2 homogeneous fluid separated into a CO_2 -rich vapor phase and a H_2O - NaCl liquid phase at about 100 °C, i.e. at the lowest T_{htot} value determined in the studied assemblages (cf. Bodnar et al., 1985). At these conditions, the pressure of the vapor and liquid end members were between 2 and 3 MPa, but mixtures of these end members – corresponding to the vapor-rich fluid inclusions with T_{htot} up to 150 °C – had P_{CO_2} as high as 8 MPa (Tables S4–S5). The pristine homogeneous fluid had physicochemical properties that were probably similar to those documented for the deep, high-T geothermal fluid (i.e., TDS: 3000–21,600 mg/kg, Minissale et al., 1997).

This fluid inclusion evidence shows that dawsonite formed due to effervescence, i.e., separation of a H_2O - CO_2 vapor from a H_2O - NaCl solution (Roedder, 1984a), which is established to be effective for the deposition of all carbonates in geothermal systems (Simmons and Christenson, 1994), especially the platy calcite (Fig. 2c). These conditions are indistinguishable from those of CCS for which they define a chemical environment in which CO_2 is sequestered into a mineral phase. The depth at which calcite and dawsonite formed can be estimated from the 2–3 MPa P_{CO_2} of the vapor-rich end member fluid. This is in the 80–110 m range under the assumption that this pressure records lithostatic conditions of formation of the dawsonite-calcite assemblage but is of the order of few m under the assumption of formation under the hydrodynamic conditions defined by effervescence. This very shallow depth is in fact the one at which a CO_2 -rich, low salinity, buoyant geothermal fluid effervesces at 100 °C (Henley, 1985), i.e. at a temperature that is equal to that of pure H_2O at ambient pressure. It should be considered that the real conditions of formation were probably intermediate between lithostatic and hydrostatic due to possible fluctuations of fluid pressure and stress conditions of the sedimentary pile at the time of geothermal fluid flow (Suppe, 2014). Thus, the depth interval within which dawsonite deposited within the fracture network is approximately 5–100 m.

Experimental data show that in H_2O - NaCl - CO_2 solutions the largest proportion of CO_{2g} formed by phase separation at equilibrium,

quantified by the λ Ostwald distribution coefficient (Ellis and Golding, 1963), is typically reached at 100–200 °C (Fig. 8a). This partitioning into the vapor phase indicates that geological fluids flowing down their geothermal gradient would typically increase their fraction of CO_{2g} . Hence, at Mt. Amiata the geothermal fluid flowing within fractures and joints experienced this increased partitioning, which triggered effervescence when the fluid pressure equated the lithostatic pressure (Roedder and Bodnar, 1980). Batches of this fluid having high P_{CO_2} (e.g., up to 8 MPa and hence supercritical) might have caused hydrofracturing when the fluid pressure equated or exceeded the critical tensile strength of the rock (Bons et al., 2022; Gudmundsson et al., 2002), forming the network of joints and veins documented in the dawsonite outcrops (Figs. 2, S1, S2). Hydrofracturing must have established pathways that enhanced local fluid advection and chemical diffusion of elements within the host rocks, causing the intense reddening systematically found in the outcrops.

Deposition from an effervescing geothermal fluid is consistent with the *negatively correlated* range of dawsonite ^{13}C - ^{18}O compositions (Fig. 5). Such correlation cannot result from typical carbonate-depositing processes (Zheng and Hoefs, 1993), i.e., mixing of fluids having distinct compositions and T, or interaction between host rock and fluid (see trends of Fig. 5). The covariation is best explained by C–O isotopic fractionation occurring during Rayleigh degassing (Zheng, 1990), i.e., consistent with phase separation in a hydrodynamic regime. The trend could result from moderate degassing (X_{CO_2} : 0.1–0.2) of an alkaline fluid (like that of Mt. Amiata), or from vigorous degassing of an acidic (H_2CO_3 -dominated) fluid.

A feature that is consistent with deposition from an effervescing fluid is the evidence for dawsonite being an almost pure phase (Fig. 4), which suggests peculiar mineral growth. Pure dawsonite might have formed via heterogeneous reactions involving the H_2O - CO_2 vapor and the minerals of the Ligurian formations (i.e., albite, kaolinite, mica; cf. Supplementary material). These reactions identify the process called *chemical vapor deposition*, which is defined as a reaction in which a solid is dissolved by a gas phase that acts also as a transport agent (Schmidt et al., 2013). These reactions, which take place typically under a temperature gradient, were acknowledged also in geological processes (King et al., 2018), especially at high temperatures (Henley and Seward, 2018). At Mt. Amiata, chemical vapor reactions took place during Knudsen diffusion, i.e. during free flow of molecular CO_2 under a pressure gradient. Due to the high P_{CO_2} , gas convection within joints/veins probably dominated. Deposition was facilitated by the large interfacial surface areas of joints and fractures, which assisted CO_{2g} chemisorption onto the minerals of the Ligurian formations (Henley and Seward, 2018). The H_2O_v and the liquid phase of the effervescing fluid mediated gas-solid reactions by enabling ion transport (Loring et al., 2019), especially that of Na and Al for dawsonite deposition. Some of the metals that make the oxide/hydroxide assemblage were probably transported by the effervescing liquid phase.

In line with established experimental data (Bénézech et al., 2007; Kaszuba et al., 2005), high P_{CO_2} was functional to dawsonite deposition because at 100–150 °C and 2 MPa total pressure these reactions are non-spontaneous (i.e., the standard free energies of reactions are all positive) and necessitate a P_{CO_2} increase to generate dawsonite. Fluid-mineral equilibria at 100–150 °C based on these reactions allow determining some key constraints. The first is that dawsonite is stable in silica-undersaturated fluids having a very high $a_{\text{Na}^+}/a_{\text{H}^+}$ (Fig. 8b), consistent with previous experimental data showing dawsonite stable in a wide pH range but in absence of silica minerals (Bénézech et al., 2007). An important aspect to consider for dawsonite supersaturation is however that the *activity ratios* $a_{\text{Na}^+}/a_{\text{H}^+}$ (also, the $a_{\text{Al}^{3+}}/(a_{\text{H}^+})^3$ not shown in Fig. 8) are more important than individual pH or metal concentration values. Thus, considering an $a_{\text{CO}_{2g}}$ of 2 MPa in the geothermal fluid, an $a_{\text{Na}^+}/a_{\text{H}^+} > 10^6$ would be required to deposit dawsonite in equilibrium with kaolinite from a silica saturated fluid at 100 °C (Fig. 8c, point A). This ratio could be reached in an alkaline fluid at relatively low Na

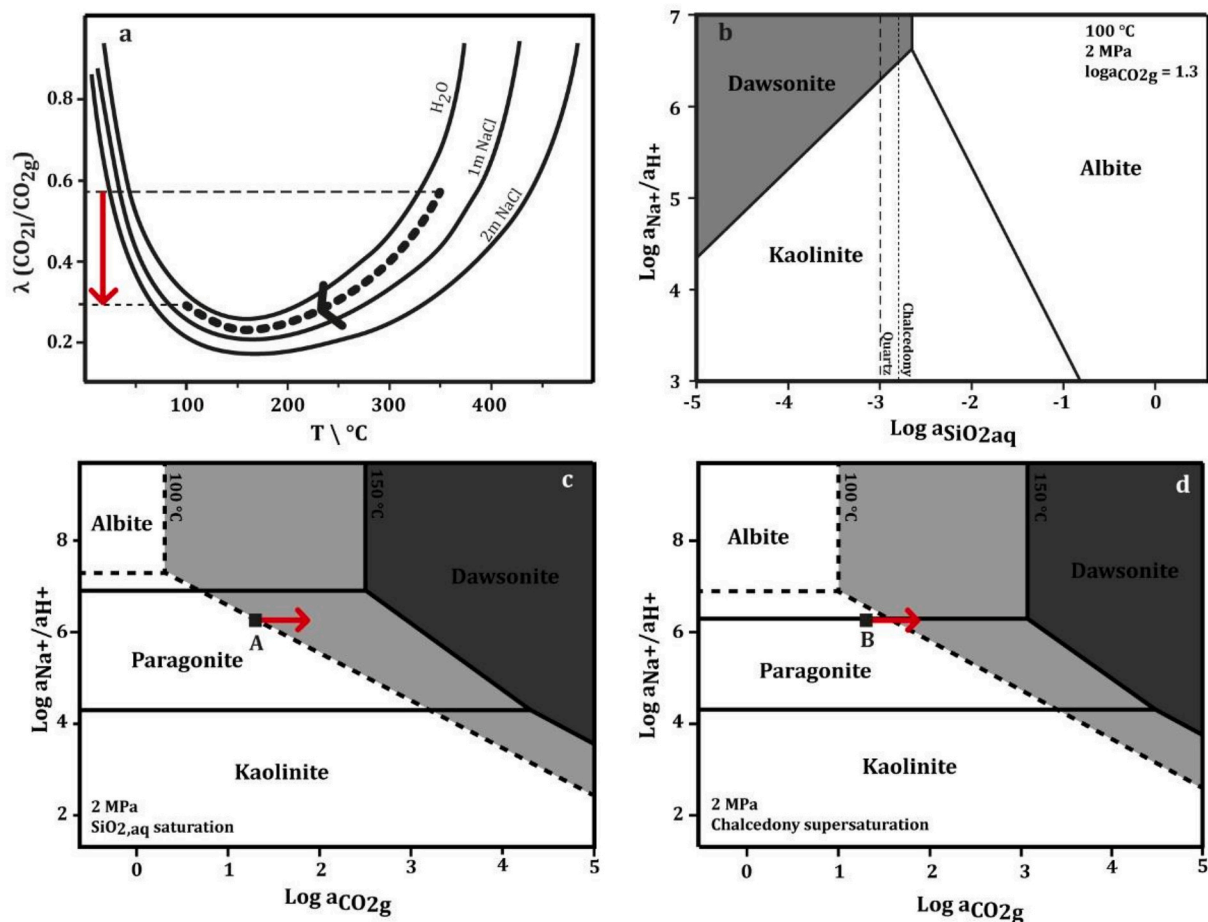


Fig. 8. Fluid-mineral equilibria constraining dawsonite formation at Mt. Amiata. (a) Experimental Ostwald distribution coefficients λ of model H_2O -NaCl- CO_2 solutions at variable T (from: Ellis and Golding, 1963). The curves indicate that, irrespective of bulk salinity, hydrothermal fluids having this composition and flowing at equilibrium along a geothermal gradient would experience significant partitioning of CO_2 into the vapor phase. The thick dotted line highlights the ideal λ variations from 350 to 100 °C of a 2 wt% NaCl hydrothermal fluid of Mt. Amiata (from: Minissale et al., 1997). This variation corresponds to a doubling of CO_2 in the fluid (red arrow). (b) Dawsonite stability calculated from heterogeneous reactions at 100 °C and 2 MPa total pressure as a function of a_{Na+aq} , a_{SiO_2aq} , a_{H_2Og} , and pH. The two vertical lines denote the supersaturation conditions of quartz and chalcedony. (c) Dawsonite stability calculated at 100–150 °C in a vapor-rich fluid as a function of activity of a_{Na+aq} , a_{CO_2g} , and pH at quartz saturation conditions. Notice that the scale of the x axis is different from that of the y axis to highlight the effect of a_{CO_2g} on the equilibria. This has an effect on the slopes of the univariant lines. Paragonite is plotted only in the 150 °C diagram because at lower T this mineral is metastable. This implies that at 100 °C the albite-kaolinite is the stable equilibrium. Point A: minimum a_{Na+}/a_{H+} necessary to deposit dawsonite from a fluid having P_{CO_2} of 2 MPa at equilibrium with kaolinite at 100 °C. Red arrow: effect of CO_2 overpressure up to 8 MPa on dawsonite stability. (d) Dawsonite stability calculated at the same conditions as in (c) but at chalcedony supersaturation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration but could be reached also by a relatively acidic fluid with a higher a_{Na+} provided $a_{Na+}/a_{H+} \geq 10^6$. Notably, a fluid with identical T , a_{CO_2g} , and a_{Na+}/a_{H+} but in contact with silica-rich rocks – as is the case of the Mt. Amiata fluid – would be in equilibrium with kaolinite alone (Fig. 8d, point B) and would not deposit dawsonite. In this case, higher a_{CO_2g} and/or a_{Na+}/a_{H+} would be needed for deposition (indicated by arrow). At 100 °C and fixed fluid composition, an increase of a_{CO_2g} (Fig. 8c, arrow) favors dawsonite deposition. Within a fault network, this P_{CO_2g} increase would open and propagate rock discontinuities, possibly at supercritical conditions (at $P_{CO_2g} > 7.4$ MPa), increasing hydrothermal alteration and mass transfer between fluid and rock (Garofalo et al., 2023b), which in turn might modify the fluid a_{Na+}/a_{H+} (or its bulk composition in general). At a fixed fluid composition and a_{CO_2g} , fluid-mineral equilibria predict that irrespective of the silica content of the rocks even a small T increase would decrease significantly dawsonite stability. This is shown by a comparison between the dawsonite stability fields at 100 and 150 °C, which shows significant contraction at higher T (Fig. 8c,d). This implies that very high a_{CO_2g} – of the order of tens of MPa – would be necessary to deposit dawsonite at T

higher than c. 150 °C from natural fluids. These are probably the conditions at which dawsonite forms in pegmatites (Hulsbosch et al., 2016; Sirbescu and Nabelek, 2003) and mineral deposits (Coveney and Kelly, 1971; Spooner and Bray, 1977) in high- T geological environments.

5.4. Metal transport and dawsonite deposition

Our data show that in the carbonate-dominated, hot spring environment of Mt. Amiata a group of transition metals (Ni, Co, Fe, Zn, Cu, Cr, Pb) deposited within the dawsonite-bearing joints as oxides or trace elements of detrital minerals at mass fractions ranging between 3 $\mu\text{g/g}$ and c. 1 wt%. The occurrence of these metals together with Hg, Sb, Ga, Tl, and Ag – i.e., the typical metals and semi-metals of geothermal systems (Barnes, 2015; Krupp and Seward, 1990) – demonstrate that dawsonite deposition and metal transport and precipitation should be considered an integral part of geothermal fluid flow. These features are similar to those of the “escape structures” of skarn deposits, i.e. the planar/wavy veinlets that extend beyond skarn ore bodies and that contain typical skarn metals (Meinert et al., 2005; Meinert et al., 1997).

Together with hydrothermal alteration and isotopic haloes, these escape structures are considered distal features of skarn deposits that can be critically important in mineral exploration. Similar to the skarn escape structures, the dawsonite-oxide joints and veins might be interpreted as an indicator of low-T, fracture-controlled metal-transport from heterogeneous geothermal fluids. These joints and veins might be useful to identify zones of intense CO₂ venting found over the top of geothermal systems, at boiling zones or at their margins as documented in other geothermal systems (Belkin et al., 1985; Hedenquist, 1990).

6. Conclusions

At Mt. Amiata, the evidence for dawsonite deposition together with a suite of metals within joints and veins from an effervescing, CO₂-rich vapor at c. 100 °C and high P_{CO2} shows that chemical vapor deposition is a process that might sequester dawsonite and metals at high CO₂/H₂O mass ratios. This process leaves mappable and measurable features that can be used to identify and characterize the steam-heated zones of geothermal systems.

Chemical vapor deposition, which was not considered in previous studies of CCS, represents an additional mode of dawsonite occurrence in geological environments characterized by intense CO₂ venting and could be more common than previously anticipated.

CRedit authorship contribution statement

Paolo S. Garofalo: Writing – original draft, Supervision, Project administration, Methodology, Investigation, Data curation, Conceptualization. **Farshid Kiani:** Writing – original draft, Software, Investigation, Formal analysis, Data curation. **Barbara Umfahrer:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Francesco Dellisanti:** Writing – original draft, Formal analysis. **Simone Beccari:** Investigation, Formal analysis. **Ivan Callegari:** Writing – original draft, Methodology, Formal analysis. **Daniele Rap-puoli:** Writing – original draft, Investigation, Funding acquisition. **Detlef Günther:** Writing – original draft, Project administration, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2026.123695>.

Data availability

Data will be made available on request.

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