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Thermal effects of massive CO_2 emissions associated with subduction volcanism

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Abstract

Large volumes of CO_2 are emitted during volcanic activity at convergent plate boundaries, not only from volcanic centres. Their C isotopic signature indicates that this CO_2 is mainly derived from the decarbonation of subducted limestones or carbonated metabasalts, not as often admitted from magma degassing. On the example of Milos (Aegean Sea) it is argued that these fluids originate from intermediate depth in the mantle and carry sufficient heat to account for the generation of subduction-related magmas, as well as for the geothermal manifestations at the surface. The heat that is required for the decarbonation reactions is drawn by conduction from a wide zone surrounding the subducting slab and then rapidly transported upward by convection of the mixed CO_2–H_2O fluids that originate from the sediments in the slab. The transport takes place in a focused way through 'chimneys' in the upper mantle, where magmas are generated by the introduced heat and water. In the crust, the hot fluids cause thermal-dome-type metamorphism. In volcanic areas, magmas are commonly held responsible for the major part of heat transfer from the mantle to the surface. Here it is argued that most of the heat transfer is by hot gases. ***To cite this article: R.D. Schuiling, C. R. Geoscience 336 (2004).***

Résumé

Effets thermiques du CO_2 associé au volcanisme de subduction. Des quantités importantes de CO_2 sont émises dans l'atmosphère aux lieux de convergence de plaques (volcanisme de subduction). Bien que la liaison avec le volcanisme soit évidente, une bonne partie de ces gaz n'est pas directement liée aux centres effusifs (volcans centraux). La plus grande partie provient d'émissions gazeuses (gaz, vents) situées dans des régions de flux thermique élevé, caractérisées par une intense activité géothermique et des aquifères chargés en CO_2. Il est généralement admis que ces gaz proviennent du dégazage magmatique, mais plusieurs arguments, notamment la signature isotopique du carbone et le volume irréaliste des chambres nécessaires, suggèrent une autre hypothèse. Pour l'essentiel, le CO_2 ne proviendrait pas du dégazage magmatique à faible profondeur, immédiatement avant l'éruption, mais plutôt de la décarbonatation de marbres ou de métabasaltes carbonatés dans les zones de subduction, à plusieurs centaines de kilomètres de profondeur au sein du manteau. Les fluides ainsi produits sont non seulement carboniques, mais aussi aqueux. Leur effet thermique est à l'origine du volcanisme de subduction, la chaleur nécessaire pour les réactions de décarbonatation étant transmise par conduction à partir d'une zone étendue du manteau autour de la plaque subductée. Sur l'exemple de Milos (mer Égée), on propose que seule une faible partie de ces fluides mantelliques

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soit transportée par les magmas. L'essentiel migre rapidement par convection vers le haut sous forme de fluides mixtes CO_2–H_2O, rendant finalement compte des manifestations géothermiques associées au volcanisme. Au sein du manteau supérieur, les fluides migrent le long de voies privilégiées, générant un magmatisme intermédiaire (andésitique). Ils s'enrichissent ainsi progressivement en CO_2 et, au sein de la croûte, entraînent un métamorphisme de type dôme thermique. Près de la surface, quand les conditions P–T correspondent à la courbe d'ébullition de l'eau, le transport de chaleur est repris par l'eau bouillante, formant des réservoirs géothermiques. ***Pour citer cet article : R.D. Schuiling, C. R. Geoscience 336 (2004).***

Keywords: CO_2 production; heat transfer; subduction volcanism; Milos; Aegean Sea; Greece

Mots-clés : décarbonatation ; transfert de chaleur ; volcanisme de subduction ; Milos ; mer Égée ; Grèce

1. Introduction

In many places on Earth, particularly in the Mediterranean and the Circum-Pacific rim voluminous emissions of CO_2 are observed. This CO_2 has been generated at some depth in the mantle, and must have passed through the upper mantle and the crust. There is ample evidence that these CO_2-rich fluids migrated mainly through cracks and foliation planes [18,25], and not by intergranular flow. The migration may be facilitated because these rocks were probably undergoing deformation at the same time. The fluids are emitted cold or lukewarm, but were generated at temperatures well above 1000 °C, so they must have given off their heat content to the rocks through which they passed. It will be shown that during the active life of such venting areas with a probable duration of several million years, this heat exchange leads to extremely high local heat flows, which may reach more than 30 times the normal heat flow. The consequences of such excessive transient thermal states on the upper mantle, the crust and near-surface geothermal manifestations will be addressed in this paper.

2. CO_2 venting

CO_2 venting is common in the circum-Pacific orogenic belt and the Mediterranean part of the Tethys belt [22]. Other CO_2-emissions outside these belts are mostly linked to mafic (i.e. along mid-ocean ridges), alkaline or carbonatitic volcanic activity [11–13,16]. Gases may be emitted from central volcanoes, like Etna, or from gas vents in areas of high heat flow, regionally associated with volcanic activity or with geothermal fields, or they may be released from CO_2-rich aquifers in such areas [22]. As gas venting is observed in all stages of volcanic evolution, it is assumed that gas venting is of similar duration as the associated volcanic activity. Gas vents are extremely efficient pathways for transporting large amounts of deeply derived CO_2 from gas reservoirs to the surface [22]. Not uncommonly, the CO_2 is accompanied by a few% of CH_4 and minor amounts of H_2S. In this paper, we will show that the classical hypothesis that the gases are transported in dissolved form by magmas and released during solidification is untenable. There is equally little proof that geothermal fields or phreatic explosions are caused by underlying magma chambers. The arguments are threefold. In the first place, the quantities of the gases are several orders of magnitude larger than can ever be dissolved in the available magmas. Secondly, the isotopic signature of the CO_2 shows clearly that the gases derive from decarbonation of marine carbonates. Finally, there is no unequivocal relation, neither in time nor in place, between gas vents and magma centres, nor have magma chambers with molten magma been found under these locations.

We will mainly discuss the role of these CO_2 streams as heat carriers. Gas vents are not only extremely efficient pathways for the rapid transport of large amounts of CO_2, but of their heat content as well. It will be shown that the heat carried by deep-seated CO_2 in selected areas can easily exceed the normal heat flow by a factor of 30 or more. This has important consequences for the generation of subduction-related magmas, for deep-seated metamorphic processes and the origin of geothermal fields close to the Earth's surface. As an example, we have selected the CO_2 emissions around Milos, Greece (Fig. 1), because they have been well quantified and analysed [3,4], and several of their associated phenomena, like high heat

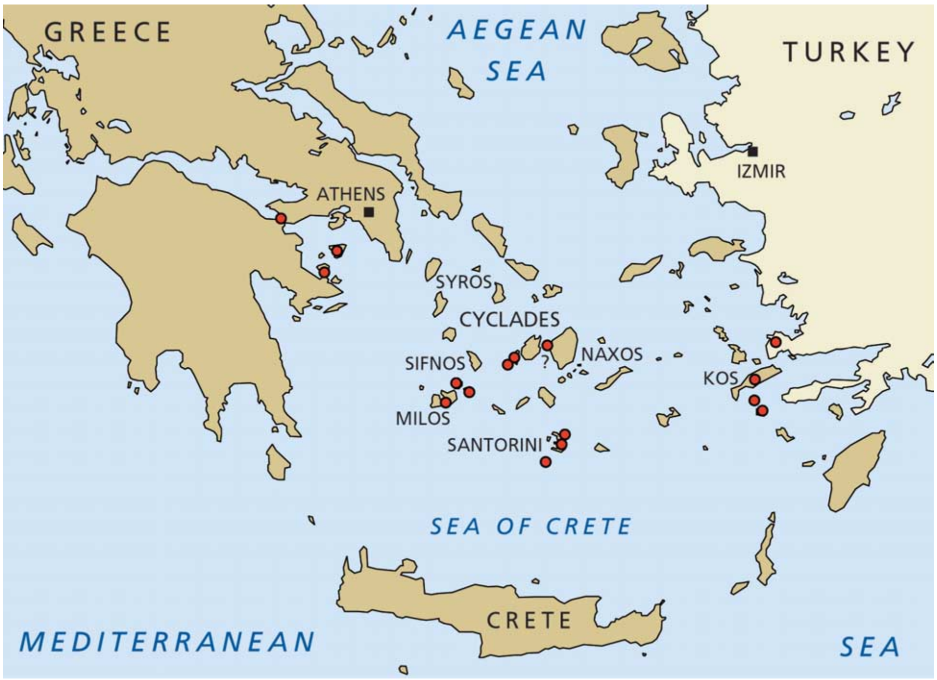

Fig. 1. Location of Milos and Naxos in the Aegean; dots indicate the location of volcanic manifestations in the volcanic arc.

Fig. 1. Localisation de Milos et de Naxos dans la mer Égée ; l'emplacement des éruptions volcaniques est indiqué par des points.

flow, intensive hydrothermal alterations, geothermal fields and phreatic explosions can be clearly observed on land.

3. Milos

The island of Milos, with a surface area of 105 km^2, forms part of the South Aegean volcanic arc. Volcanism started more than 3 million years ago [5]. Although erosion has removed already part of the erupted rocks, it can be concluded from the fact that the basement is encountered at rather shallow depth (0 to a few hundred metres, with a maximum depth around 700 m), and the highest volcanic edifice is only 750 meter high, that the cumulative amount of erupted material is probably less than one hundred km^3. The Milos Bay may have formed as the result of a caldeira collapse. No evidence for a magma chamber underneath Milos has been found, however, and it is stated explicitly that "no deep zone of low resistivities was observed which could be attributed to a deep geothermal reservoir *or to a large chamber of molten magma* (italics mine)" [26].

The volcanic rocks at Milos range from rare basaltic andesites to dacites and rhyolites [6,7]. The youngest eruptions are approximately 80 000 years old, but phreatic eruptions have continued till historic times, and active fumaroles and hot grounds are common. Near Paleochori, in the southeastern part of the island, many active vents in the shallow sea emit CO_2 over an area of 35 km^2 [3,4]. The emissions amount to 2.2×10^6 tons of CO_2 annually, equivalent to a cumulative amount of 7×10^{12} tons if the gas emissions had continued for the same time as the associated volcanism. This makes it one of the larger, but not the largest venting area in the Mediterranean.

Milos, and particularly its eastern part, where the CO_2 vents are concentrated, is characterized by extreme geothermal gradients of 8 to 10 °C per 10 m, about 30 times higher than the world average [7]. The $\delta^{13}C$ of the gases is between -1.0 and $+1.1‰$ [2], typical of marine carbonates [10]. This rules out that they have originated by magma degassing, as shown also by the following calculation. Intermediate and acid magmas like found on Milos can dissolve 0.5% CO_2 [8]. The dissolution of 7×10^{12} tons of CO_2

would require 14×10^{14} tons of magma, equivalent to 5×10^{14} m^3, or 5×10^5 km^3. A magma chamber with a cross section of 35 km^2 (the area over which gas emissions are observed) should then have a vertical extension of 14 000 km!

In order to explain the geothermal manifestations, the existence of small (they should be small to escape geophysical observation) magma chambers is often invoked. Not only is this an ad hoc hypothesis, but the obvious heat source that does cause the geothermal manifestations and the phreatic explosions is provided by the hot gases that are associated with the geothermal phenomena and that are responsible for a heat flow that is approximately 30 times larger than normal.

Milos is overlying a subduction zone that originates in the Hellenic Trench south of Crete. Originally the subduction started farther north, and part of the mainly Mesozoic rocks that were dragged down to a depth of 60 to 90 km have been exhumed again and can be studied, e.g., at Syros and Sifnos [17,23]. They comprise high-pressure rocks, like eclogites, jadeite rocks, glaucophane schists, and abundant marbles, with aragonite pseudomorphs. The subducted slab bends steeply and can be followed in an almost vertical position to more than 1500-km depth by seismic tomography (Fig. 2) [1,28]. It is likely that the subducted material has a composition similar to the metamorphic material on Syros. This means that large amounts of carbonate rocks have been dragged down to great depth. Although temperatures in the slab lag behind those of the surrounding mantle, both temperatures rise as the slab descends further. As a result of this temperature rise, the carbonates will start to dissociate by reaction with the surrounding silicate rocks, while clay-rich rocks in the sedimentary pile will undergo dehydration. The subvertical position of the sediments permits the generation of large amounts of fluids over a limited area.

4. Origin and nature of the fluids released during subduction

Dehydration and decarbonation reactions are endothermic reactions. Whatever the precise carbonate-silicate reactions involved, the enthalpy of the overall reactions is dominated by the enthalpies of the reactions $CaCO_3$ (or $CaCO_3 \cdot MgCO_3$) $\rightarrow CaO + CO_2$ and hydrous silicates $\rightarrow$ anhydrous silicates $+ H_2O$, and is fairly independent of the precise silicates that are formed. If we translate the amount of CO_2 emitted over an area of 35 km^2 into the required enthalpy to produce it, this turns out to be vastly more than can be provided by normal mantle heat flow over the same area. It seems likely that this energy is tapped from a large volume of surrounding, hotter mantle, and transported by conduction to the subducted slab. Inspection of Fig. 2 shows that the subducted slab (or more properly the low-temperature zone) widens indeed to over 400 km, pointing to an effective cooling mechanism, like provided by the dehydration and decarbonation of sediments dragged down into the subducting slab.

5. Compositional changes and thermal effects of fluid transfer

5.1. *Effects of mixed CO_2/H_2O fluids on the upper mantle*

Once the fluids reach the upper mantle, water is preferentially retained by reactions like:

$$2\,CaMg(SiO_3)_2 + 5\,MgSiO_3 + H_2O \rightarrow Ca_2Mg_5Si_8O_{22}(OH)_2 + Mg_2SiO_4$$

(in this reaction, tremolite proxies for hornblende).

Another general reaction would be:

$$\text{Dry peridotite} + H_2O \rightarrow \text{basaltic andesite (melt)} + \text{olivine rich residue}$$

Both types of reactions cause the remaining fluid to become richer in CO_2. The change from a dry mantle to a water-rich mantle, coupled with the rise in temperature by the introduction of hot gases induces the formation of intermediate magmas (basaltic andesites) and their suite of more acid differentiation products. In this way, the preferential conduits of hot fluids become the birthplace of magmas. A conservative estimate shows that the heat brought in by the gases in Milos can easily generate 150 km^3 of volcanic rock, which is more than the estimated volume of erupted rocks on Milos. The process outlined here explains the regional association of volcanic activity and gas emissions. It also explains why volcanoes are more or less evenly spaced along a volcanic arc, and not continuous. Their location is determined by preferential gas conduits that always form

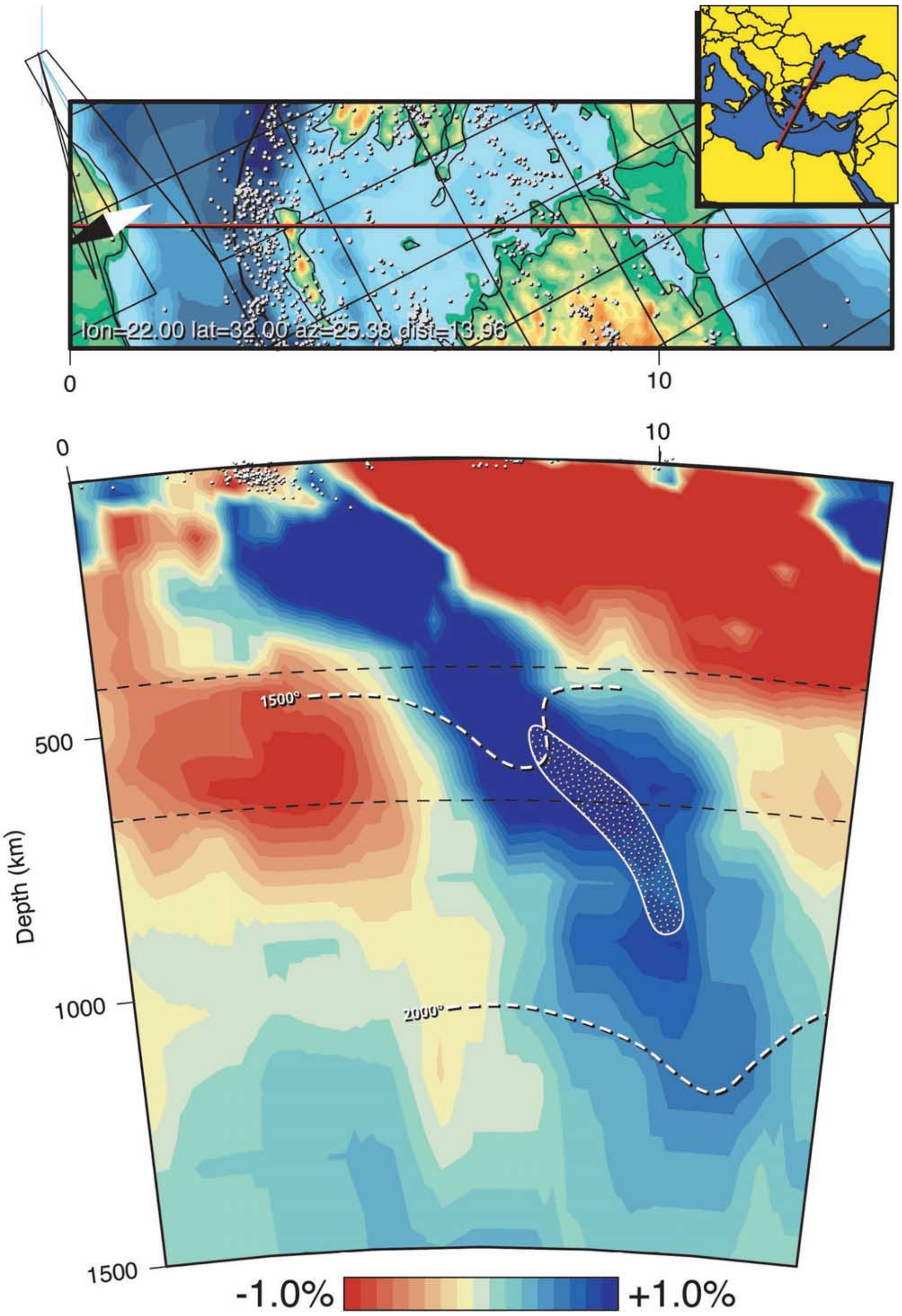

Fig. 2. Tomographic section of the steeply dipping subducted slab under the Aegean. The position of the 1500 and 2000 °C isotherms is indicated, as well as the zone where thermal decarbonation of subducted limestones would take place.

Fig. 2. Section tomographique de la plaque subductée sous la mer Égée. La position des isothermes de 1500 et de 2000 °C est indiquée, ainsi que la zone où la décarbonatation des calcaires subductés peut se produire.

when fluids move through a porous medium. Such preferential passageways draw most of the fluid flow, while sections in-between will be stagnant.

5.2. Thermal effects in the crust

The crust is thin in the Aegean, and the temperature at the base of the crust is high [15]. The CO_2-rich fluids enter the base of the crust at temperatures around 1300 K, and finally bubble out at the surface at 300 K. The enthalpy difference between 1 g of CO_2 at 1300 and 300 K is about 1.13 kJ [21], so 2.2 million tons of CO_2 bring about 2.5×10^{12} kJ each year to an area of 35 km^2, completely overshadowing the normal heat flow, which is only 0.7×10^{11} kJ yr^{-1} for the same area. The fluids release their heat content as they move along channels (foliation planes or cracks) in the crust. Quartz is deposited along these channels on cooling, along with some other synmetamorphic minerals [20]. Appropriate pelitic rock compositions are transformed into anatectic gneisses. Systems of metamorphic rocks through that hot fluids have travelled will show up as gneiss domes mantled by metamorphic rocks of rapidly decreasing metamorphic grade at greater distance from the dome. Primary fluid inclusions betray the composition of the fluids that have passed through the system. In the case of the gneiss dome of Naxos, an island not far from Milos (Fig. 1), the molar fractions of CO_2 in the primary fluid inclusions are consistently between 0.5 and 0.8 [14]. The amount of fluid of probable mantle origin that has passed through the Naxos system has been calculated as 7.5×10^{12} tons [24], comparable to the situation in Milos. The heat carried by these fluids is enough to raise the temperature of this system by several hundred degrees, which explains the formation of the thermal dome and the melting of its core.

In the fairly young terrains of the Aegean, the erosion has not yet reached into the lower crust, so no granulites are exposed which are seen to accompany thermal domes in more deeply eroded sections of the crust. An indication that granulite facies conditions were approached on Naxos is the discovery of sapphirine in the core of the gneiss dome [9].

Present model implies thus that granulites at Naxos extend below the dome, and that these are related to CO_2-influx originating in the mantle. The idea of CO_2-streaming in granulite metamorphism, a most debated issue in present-day metamorphic petrology, is strongly opposed by tenants of 'fluid-absent metamorphism', mainly on the argument that CO_2 intergranular migration is impossible on account of the wetting angle [27]. Fluid inclusion studies indicate, however, that fluid migration occurs less at grain boundaries than along a discrete network of open microcracks (secondary inclusions), and that by this mechanism large volume of fluids can pass through the lower crust and upper mantle along channelised pathways. Best examples are found in southern Madagascar, where CO_2 flow in major shear zones, deeply rooted in the mantle, was able to achieve isotopic homogenisation at regional scale [19], and in the well-known 'incipient charnockites' of southern India [18].

5.3. Thermal effects at shallow depth

When the hot fluids come close to the Earth's surface at a depth of 1–2 km, they will reach the boiling line of water. Most of the heat transport is now taken over by boiling water. Geothermal reservoirs will form, if there are impermeable caprocks, or if overlying rocks become impermeable by substances precipitating from the hot solutions. This is the situation on Milos, where boiling reservoirs at temperatures around 320 °C have been discovered by drilling to a depth of 1100 m [7], and where many volcanic rocks have become impermeable by extensive silicification, kaolinitisation and bentonite formation. Hot grounds and emanating steam are common on Milos. If local conditions make it impossible for the steam to escape, pressures may build up to the breaking point of the overlying formations, resulting in phreatic explosions. Many circular explosion features with diameters up to 1000 m pockmark the landscape of Milos [7].

6. Conclusions

- Large volumes of mixed CO_2/H_2O fluids can be generated in subducting slabs. The heat required for their production is drawn by conduction from a large volume of surrounding mantle.
- These fluids migrate rapidly upward. When they reach the upper mantle, the fluids will precipitate hydrous silicates, leaving the remaining fluid richer in CO_2.

- The change from a dry to a wet mantle, and the rise in temperature caused by the hot fluids generate intermediate-type water-rich magmas.
- In the crust, the heat provided by the migrating fluids can cause temperature rises of several hundred degrees, leading to the formation of domes of anatectic gneisses.
- At shallow depth, the heat transport is taken over by boiling water, leading to the formation of permanently boiling geothermal reservoirs or intermittent phreatic explosions.

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