Chemical Geology 261 (2009) 286–302

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Fluid-induced disturbance of the monazite Th–Pb chronometer: In situ dating and element mapping in pegmatites from the Rhodope (Greece, Bulgaria)

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ARTICLE INFO

Article history:
Accepted 19 October 2008

Keywords:
Monazite
U–Th–Pb geochronology
LA-ICPMS
Oxygen isotopes
^{39}Ar–^{40}Ar
Rhodope

ABSTRACT

The monazite Th–Pb chronometer is widely used in a variety of geological contexts but may be affected by interaction with fluids. In the central part of the Rhodope Massif (Greece, Bulgaria), synfolial pegmatite veins were emplaced within two major synmetamorphic shear zones. In the Chepelare shear zone (CZS), which displays no evidence of post-metamorphic fluid flow, consistent monazite Th–Pb ages of ~36 Ma are interpreted as dating vein emplacement. Higher in the metamorphic pile, zircon and monazite give U–Th–Pb ages of ~42 Ma for vein emplacement. In the Nestos Shear Zone (NSZ) pegmatites show evidence of post-emplacement interaction with fluids during greenschist facies ductile deformation. Evidence for this includes the precipitation of calcite in microscale tension gashes within feldspar porphyroclasts, and the oxygen isotope disequilibrium between quartz and feldspar. Aqueous carbonic fluids deriving from carbonate lithologies in the footwall of the NSZ are identifiable in the pegmatites by the high $\delta^{18}O$ value of quartz (up to 21.8‰) and the presence of calcium in calcite veinlets. In these samples, some of the monazite grains show large intragrain scattering of Th–Pb age spanning up to ~12 Ma, with intergrain scattering reaching ~16 Ma (from ~39 to ~55 Ma). Within individual grains, age domains correlate with chemical heterogeneities, and some show a characteristic Ca-excess. These chemical and isotopic alterations are interpreted to be caused by interaction with fluids derived from carbonate lithologies. Complementary U–Pb data on zircons from the NSZ pegmatites yield mostly Mesozoic ages related to an older metamorphic cycle, and an age of ~48 Ma for one grain with typical magmatic zoning. The Th–Pb ages of 49.3 ± 1.6 to 54.9 ± 1.7 Ma probably relate to the emplacement of the pegmatites. The spread of younger Th–Pb ages (from 38.6 ± 1.1 to 46.2 ± 1.6 Ma) probably reflects the period of fluid circulation during progressive cooling to greenschist facies conditions, or variable perturbations of the monazite isotope system during fluid-assisted greenschist facies deformation. This is consistent with ^{39}Ar–^{40}Ar mica ages of ~32 to 34 Ma, interpreted as a tighter constraint for the timing of the greenschist facies metamorphism. This study illustrates the capacity of monazite to record distinct events in a single rock and highlights the need for identifying the potential involvement of fluids in order to interpret monazite ages.

1. Introduction

Monazite [(Ce, La, Nd, Th) PO_4] occurs as an accessory mineral in many metamorphic and magmatic rocks, and is thus extensively used for dating crustal processes. The development of in situ methods to analyze isotopes and chemistry has enabled us to examine the behaviour of the monazite Th–Pb and U–Pb chronometers in various environments (e.g. Poitrasson et al., 2000; Catlos et al., 2002; Goncalves et al., 2005; Pyle et al., 2005; Jercinovic and Williams, 2005; Rasmussen et al., 2006; Hinchey et al., 2007; McFarlane and McCulloch, 2007; Williams et al., 2007; Di Vincenzo et al., 2007). Other studies have pointed out that the diffusion rate of many elements, especially Pb, is very low in monazite (Smith and Giletti, 1997; Cherniak et al., 2004; Seydoux-Guillaume et al., 2002; Gardés et al., 2006). Thus, in principle, monazite should be particularly adapted to record various stages during a sequence of high-temperature geological events.

Monazite often displays distinct compositional and age domains together with complex chemical zoning patterns (Zhu and O'Nions,

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doi:10.1016/j.chemgeo.2008.10.025

1999a,b; Crowley and Ghent, 1999; Foster et al., 2000, 2002; Catlos et al., 2002; Kohn et al., 2005; Rasmussen et al., 2006; McFarlane and McCulloch, 2007; Hinchey et al., 2007). In some cases, these chemical patterns are associated with geologically meaningless ages (e.g., Seydoux-Guillaume et al., 2003). Fluid-assisted recrystallization constitutes an efficient way to reset the monazite chronometers under experimental conditions (Seydoux-Guillaume et al., 2002). In natural systems, Poitrasson et al. (1996, 2000) have described the behaviour of monazite during fluid–rock interaction processes that are classically observed within granitic rocks (chloritisation, greisenization, sericitization). They showed that Th–Pb and U–Pb systematics can be highly disturbed but may ultimately provide meaningful magmatic or fluid-alteration ages.

This study concerns monazite grains from synfolial pegmatite veins from the Rhodope Massif (northern Greece, Bulgaria). These rocks were emplaced within two high-grade shear zones several kilometers thick, classically described as Alpine synmetamorphic thrusts. Available geochronological data show that at least some of the rocks embedded in these shear zones experienced two major metamorphic cycles during Alpine orogenesis, with an apparent time gap of ~100 Ma in between. Careful investigation is thus needed to assess the exact meaning of new geochronological data. The two shear zones exhibit many characteristics in common, but differ strikingly in terms of footwall lithology; in one case it is carbonate-dominated, and in the other gneiss-dominated. Another difference is that deformation along the shear zone involving carbonates persisted during cooling down to greenschist facies conditions. Thrusting is commonly associated with dehydration–decarbonation of buried material, giving rise to large amounts of fluids that preferentially migrate into the hangingwall along high-permeability shear zones. Therefore, contrasting chemical signatures of fluids are expected between the two shear zones, probably with distinct chemical and isotopic evolution of their respective monazite grains. Moreover, because even low-temperature fluid circulation is capable of affecting monazite (Teufel and Heinrich, 1997; Hawkins and Bowring, 1997; Townsend et al., 2000), the influence of fluids on the monazite U–Th–Pb chronometer is expected to be more pronounced in the case of a shear zone that remained active during cooling to greenschist facies conditions.

This study presents electron microprobe analyses (in-situ analysis and element mapping) and back-scattered electron (BSE) imaging of monazite crystals separated from four pegmatite samples, together with in-situ Th–Pb dating by laser ablation-inductive coupled plasma mass spectrometry (LA-ICPMS). Oxygen isotope analyses performed on quartz and feldspar enable fluid–rock interactions within the pegmatites to be identified. ^{39}Ar–^{40}Ar dating of micas and U–Pb dates in zircon grains from the same samples provide additional and helpful constraints on the geological significance of the measured Th–Pb ages in monazite. In the light of these results, the alterations to the chemical and isotope systems of monazite during fluid-assisted greenschist facies deformation is discussed.

2. Geological setting

2.1. Tectono-metamorphic setting

The Rhodope Massif is a large crystalline complex lying in the northern part of the Aegean domain, straddling the border between Greece and Bulgaria (Fig. 1). It occupies a central position in the Alpine belt, between the southwest-verging Hellenides and the north-verging Balkanides. The massif mostly consists of high-grade metamorphic rocks and granitoids and represents the exhumed metamorphic core of the Alpine orogen. The precise timing of Alpine tectono-metamorphic events remains poorly known for much of the massif, available geochronological data suggesting a complex metamorphic evolution spanning Jurassic to late Cenozoic times (e.g., Krohe and Mposkos, 2002; Liati, 2005; Cherneva and Georgieva, 2005; Bonev et al., 2006).

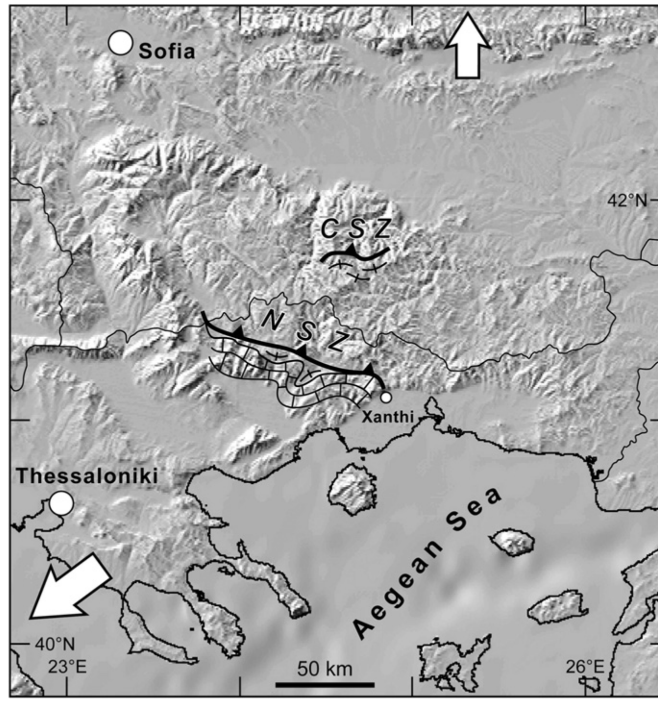

Fig. 1. Topographic map of the northern Aegean domain centered on the Rhodope Massif, with the locations of the two main shear zones (CSZ, Chepelare Shear Zone; NSZ, Nestos Shear Zone). The footwall of the CSZ consists of orthogneisses while that of the NSZ is dominated by carbonates. The arrows indicate the vergence of Alpine thrusting in the Balkanides, to the north, and the Hellenides, to the southwest.

This study focuses on two major synmetamorphic shear zones located in the central part of the Rhodope Massif (Fig. 1). The Nestos Shear Zone (NSZ) is exposed in Greece and was first described in the 1980s (Papanikolaou and Panagopoulos, 1981; Ivanov, 1981; Zachos and Dimadis, 1983). The Chepelare Shear Zone (CSZ) is exposed in Bulgaria and was first reported by Burg et al. (1990). Both shear zones dip northward and consist of a >1 km-thick pile of mylonites displaying top-to-southwest shear sense criteria (e.g., Kilias and Mountrakis, 1990; Dimov et al., 1996; Barr et al., 1999). According to these authors as well as others (e.g., Dinter, 1998; Krohe and Mposkos, 2002), the two shear zones represent synmetamorphic thrusts. For Ricou et al. (1998), they represent main structures which accommodated Alpine convergence in the innermost part of the Hellenides.

The hangingwall unit of both shear zones is composed mainly of migmatites developed at the expense of orthogneisses and minor paragneisses in the two localities. In contrast, the footwall unit differs in each case. The footwall of the NSZ exposes a thick pile of marbles. In the area of Xanthi, where the samples of this study come from, marbles are at least 1.5 km thick and form the immediate footwall of the main tectonic contact associated with the NSZ (Fig. 1). The footwall of the CSZ exposes a pile of mesocratic to felsic orthogneisses at least 3 km thick. These orthogneisses are overlain by a <1 km-thick layered package of mylonitic gneisses, marbles, micaschists and amphibolites, known as the 'Chepelare Formation'. According to Gerdjikov et al. (2003), the Chepelare Formation constitutes the hangingwall immediately above the main tectonic contact associated with the CSZ.

Both the NSZ and the CSZ represent high-grade shear zones, however deformation along the NSZ persisted at lower temperature conditions. Our observations of the NSZ in the area north of Xanthi indicate that top-to-SW shearing at lower levels of the hangingwall unit occurred first at higher amphibolite facies conditions, with concurrent anatexis, and persisted during cooling down to greenschist facies conditions, at which stage deformation became more localized