

Petrology and petrogenesis of carbonatitic rocks in syenites from central Anatolia, Turkey

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Abstract The late Cretaceous A-type Karaçayır pluton in Central Anatolia, Turkey, intrudes and entrains xenoliths of Palaeozoic limestone. Carbonatitic magmatic rocks within the syenite have been previously interpreted (Schuiling in *Nature*, 192:1280, 1961) to result from metasomatic alteration and syntectic melting of marble. Carbonatites and associated calcite-syenites exhibit mineralogical characteristics (Ab-rich plagioclase, Ba-rich K-feldspar, low-Mg# biotite) that are petrogenetically more evolved than the host syenitic suite. Geochemically, carbonate-rich magmatic rocks are greatly enriched in Sr, Ba, Th, and REE and have higher LREE/HREE ratios than either syenites or marbles. In terms of O–C–Sr–Pb isotope ratios, the carbonatite/calcite-syenite suite form a consistent and geochemically coherent group that is distinct from the marble country rock and xenolith population, but similar to some of the syenitic, and particularly the nepheline syenite components of the Karaçayır pluton. Other silicate magmatic rocks are geochemically, isotopically, and geochronologically different,

suggesting the pluton is composite. Overall, the mineralogical and geochemical characteristics of the carbonatites are incompatible with binary mixing of syenite and marble but are consistent with derivation of carbonatite from petrogenetically evolved foid syenite. Carbonate–silicate rock types have modal variations compatible with an origin by fractional crystallisation, rather than by liquid immiscibility.

Keywords Carbonatite · Syenite · Marble · Mineralogy · Geochemistry · O–C–Sr–Pb isotopes · Fractional crystallisation · Turkey

Introduction

In 1961 R.D. Schuiling published a short note on an occurrence of pegmatitic carbonatite in a syenite pluton at Karaçayır, a village 17 km north of Sivas, in east-central Anatolia, Turkey (Fig. 1). Schuiling's observation was that part of the marble country rock, protruding into the syenite, was converted into a pegmatitic carbonatite composed of calcite, biotite, apatite, and rare thorianite. The Karaçayır field relationships and associations, supported by Wyllie and Tuttle's (1960) experimental data, led Schuiling to interpret the carbonatite as the crystallisation product of marble permeated by fluids and 'liquified' by the syenite.

Although it is now acknowledged that carbonatites can occur in a range of geological environments and as a consequence of a variety of petrogenetic processes (see review by Mitchell 2005), the role of crustal limestones or marbles in carbonatite petrogenesis is considered to be of minor significance. Indeed, Mitchell (2005) effectively dismisses carbonatites whose origin involves limestone assimilation/interaction despite the fact that they would

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A

30°0'0"E 40°0'0"E

40°0'0"N

Eurasian Plate

Black Sea

NAFZ

Anatolian Plate

TURKEY

Sivas

EAFZ

DSFZ

Arabic Plate

Mediterranean Sea

African Plate

0 500 km

30°0'0"E 40°0'0"E

B

39° 56' 42" N

▲ Ağrağan T.

★ KAY-7

★ BAL-74

★ BAL-75

▲ Paşadımı T.

▲ ÇELTEK MOUNTAIN

★ KAY-8

★ KAY-6

★ KAY-5

★ BAL-76

▲ Keleşen T.

★ KAY-1

★ KAY-2

★ K-7-12, KAY-3-4, KAY-12

★ KAY-17

▲ Yellice T.

★ BAL-77

▲ Evliya T.

★ K-4

▲ Catalçam T.

★ BAL-78

★ BAL-79

▲ Eşiköy

▲ Sebüler T.

★ K-1

★ K-2, 3

▲ Evliya T.

▲ Eğrek T.

▲ Karaçayır

39° 54' 37" N

8° 25" E 37° 01' 55" E

0 1 km.

▲ N

Geological units:

- Alluvium
- Evliya-tepe Basalt
- Sandstone-marl-siltstone
- Fossiliferous limestone
- Karaçayır biotite-calcite pegmatite
- Karaçayır Syenite
- Limestone
- Volcano-sedimentary rocks
- Serpentinite
- Akdağmadeni Metamorphics

Structural features:

- Fault
- Strike and dip of bedding
- Schistosity
- Fold axial plane

Other features:

- Village
- Hill
- Sample location

Tekelidağ Complex

Tokuş Formation

Cenozoic-Tertiary

Late Cretaceous

The role of limestone assimilation has had a chequered history in igneous petrogenesis. It was originally championed by Daly (1910, 1933) and Shand (1930, 1947) to

explain the origin of alkaline igneous rocks then dismissed as petrologically implausible on the basis of experimental evidence by Watkinson and Wyllie (1964, 1969), Wyllie and Watkinson (1970), and Wyllie (1974). Despite this history, the field association of “carbonatite” with marble

and granite in places such as the Central Metasedimentary Belt (CMB) of the Grenville Province in the Haliburton-Bancroft area of Ontario (Chayes 1942) is well known. Recently, Lentz (1998, 1999) has resurrected the hypothesis of assimilation to explain the petrogenesis of fluorite-apatite-calcite vein dykes in the CMB of Quebec. After an exhaustive mineralogical and geochemical study, Lentz (1998) interpreted the CMB vein dykes as the carbonatitic products of volatile fluxing and partial melting of marble by fluids released from adjacent A-type granite pegmatites. Weakly alkaline granites are inferred to yield only minor carbonatite and associated dominantly calcic (silicate) fenite-like skarns, but the more strongly peralkaline parent silicate magmas are argued to result in major carbonatite systems with the development of sodic fenites. Lentz (1999) emphasised that carbonatites produced by volatile fluxing in crustal environments would inherit their elemental abundances and isotopic signatures from a binary mixing of components from the silicate magma and the country rock marble and that these would differ radically from the mantle-derived signatures that dominate most of the carbonatite clan. Similarly, Barnes et al. (2005) in the Hortavaer complex, Norway; Wenzel et al. (2002) in the Ioko-Dovyren intrusion of Eastern Siberia; Chadwick et al. (2007) in the Merapi Volcano, Java; and Pappalardo et al. (2004), Piochi et al. (2006), Marziano et al. (2007, 2008), Freda et al. (2008), and Gaeta et al. (2009) in the Roman Province, Italy, invoke limestone assimilation as an important process in igneous petrogenesis.

The Turkish occurrence, interpreted by Schuiling (1961) to result from involvement of crustal carbonate rocks in the origin of carbonatite magmas, has been ignored for almost 50 years. This paper presents a detailed mineralogical and geochemical analysis of the carbonatitic rocks of the Karaçayır pluton and re-evaluates Schuiling's hypothesis.

Regional geology

Central Anatolia has a complex geological history determined by the evolution of the northern branch of the Neo-Tethys Ocean. The ocean is divided into two seaways, the İzmir-Ankara-Erzincan Ocean between the Eurasian plate in the north and the Tauride-Anatolide platform in the south, and the Inner Tauride ocean located within the Tauride-Anatolide platform (Sengor and Yilmaz 1981; Bozkurt and Mittweide 2001; Boztuğ and Jonckheere 2007). Neo-Tethyan seaways began to close in the early Cenomanian-Turonian (95–90 Ma, Garfunkel 2004) with convergence producing a subophiolitic metamorphic sole by intra-oceanic thrusting in the İzmir-Ankara-Erzincan ocean (Dewey et al. 1973; Le Pichon et al. 1988; Parlak

and Delaloye 1999; Parlak et al. 2006). Later in the Cenomanian-Turonian, the oceanic island arc was accreted to the Tauride-Anatolide platform with obduction of ophiolitic rocks (Parlak and Delaloye 1999; Dilek et al. 1999; Floyd et al. 2000; Garfunkel 2004; Robinson and Ustaomer 2004; Boztuğ and Jonckheere 2007). A post-collisional extensional regime established in the Turonian-Campanian is inferred to result from slab break-off and/or lithospheric delamination/detachment. In the central Anatolian crystalline complex, this post-collisional event was associated with medium–high grade metamorphism and the emplacement of central Anatolian granitoids of diverse character (Boztuğ et al. 2007a, b, 2008, 2009). The Karaçayır syenite, which constitutes the main subject of this study, is one of the members of the central Anatolian granitoids, cropping out in the northern part of Sivas city in central Anatolia, Turkey.

Karaçayır pluton-field relationships

The Karaçayır syenite is a 4 km × 3.5 km pluton intruding Palaeozoic metasediments, predominantly white marbles, of the Akdagmadeni lithodeme (Yilmaz et al. 1997) on the northern boundary of the village of Karaçayır (Fig. 1). The pluton is non-conformably overlain by sediments of the Palaeocene-Eocene Tokus Formation (Inan and Inan 1999). Field relationships and the general petrology of the pluton have been described by Boztuğ (1998) and Boztuğ et al. (2009). As is evident from Fig. 1, the Karaçayır syenite contains many rafts/enclaves of country rock marble up to 400 m long and 200 m wide. These enclaves range from banded, fine grained, foliated, and in places isoclinally folded, diopside-tremolite-quartz calc-silicate rocks, to massive, coarse-grained, monomineralic calcite marbles. A similar range of mineralogy and grain size occurs in marbles in the country rock, distant from the syenite contact. Marble has been sampled both from enclaves in syenite (e.g. KAY1A, 1B, 6, 17B) and from in situ outcrops of the country rock (e.g. KAY7, 8, K4)(Fig. 1).

The original carbonatite locality described by Schuiling (1961) is unknown, but it probably lies in the area of relatively well-exposed biotite-calcite pegmatite at GR 29.429°E, 22.342°N in Fig. 1. Here, there is an apparently gradational change from normal syenite to feldspathic rocks containing an increased content of calcite either as granular interstitial crystals or as coarse acute rhombs (phenocrysts?) set in a finer grained, feldspathic ground-mass (Fig. 2a). In the central sections of this zone, these calcite-rich syenites grade into coarse grained pegmatitic rocks comprising 10–15 cm crystals of calcite and biotite, with interstitial, finer-grained magnetite and brownish prisms of apatite. These rocks have been referred to as

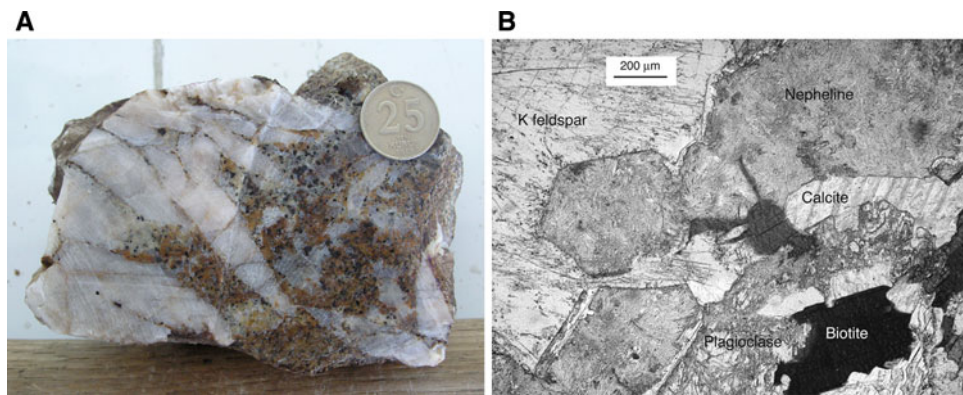


Fig. 2 **a** Sawn surface of one of the calcite-syenites (KAY3) occurring in the carbonatite zone. Coarse rhombic blades of calcite are enclosed within a syenitic groundmass composed of perthitic K-feldspar, albite, calcite, apatite, and magnetite. **b** Zeolite-muscovite

aggregates pseudomorphing inferred nepheline in syenite BAL76. Hexagonal pseudomorphs are enclosed in perthite as part of a plagioclase-calcite-biotite assemblage. Scale bar 200 μ m

carbonatites. Small amounts of K-feldspar and albite have been identified petrographically. Schuiling (1961) reports small idiomorphic thorianite crystals and coarser masses (2.5 cm) of allanite.

The zone containing biotite-calcite pegmatites is, in places, 15 m wide but thins to cm-wide biotite-rich segregations elsewhere along strike. The total strike length of the zone is approximately 140 m on a NNE trend, but outcrop is sporadic and the true length may be greater. Significantly, nowhere within or along this zone did we observe a locality where marble graded into carbonatite pegmatite, as reported by Schuiling (1961), although xenoliths of marble occur in the general vicinity (Fig. 1).

Similar biotite-calcite-rich rocks (KAY17A), here with a foliated texture, occur at an isolated locality (29.269°E, 21.945°N), where coarse-grained, equigranular, monomineralic calcite rocks (KAY17B) also occur scattered over the ground surface.

Petrography

The silicate-dominated and volumetrically dominant members of the Karaçayır pluton are broadly syenitic. Petrographically, there is a gradation between alkali syenites that are essentially devoid of carbonate (e.g. BAL74) to those containing accessory amounts (e.g. BAL78, 79), to varieties that contain up to 20% calcite as an intergranular phase in apparent textural equilibrium with the silicate minerals (e.g. BAL76, KAY9–12, Fig. 2b). Some rocks contain coarse (3–5 cm) euhedral blades of calcite in a syenitic groundmass (e.g. KAY3B, 3C) (Fig. 2a) and these rocks are referred to hereafter as calcite-syenites. They are intimately associated in the field with rocks that comprise predominantly pegmatitic calcite, with only accessory amounts of alkali feldspar, biotite and apatite (e.g. KAY3,

K7, K8, K9). These carbonate-dominated rocks are referred to below as carbonatites.

Syenites

Syenites are coarse-grained, hypidiomorphic granular rocks dominated by perthite and tabular plagioclase. Many varieties contain turbid plumose or radiating secondary aggregates of fibrous to acicular zeolite that pseudomorph distinctive hexagonal-shaped inclusions in feldspar interpreted to have been nepheline (Fig. 2b). These pseudomorphs are most abundant in BAL76 and 79, samples that are the most undersaturated syenites analysed (normative ne 19.67 and 14.61, respectively). Biotite with a green brown pleochroism is a ubiquitous phase, accompanied by apatite, interstitial calcite, and sporadic muscovite, titanite (niobian in KAY79, with $\text{Nb}_2\text{O}_5 \sim 3\text{wt.}\%$) and zircon. An epidote group mineral, ranging from a colourless pistacitic composition to a pale brown, pleochroic allanite occurs in several rocks both as a primary, orthomagmatic prismatic phase and as a reaction (?) rim between calcite and either nepheline pseudomorphs, hornblende (BAL79), K-feldspar or plagioclase, or between apatite and K-feldspar (BAL78). Magnetite, pyrite, haematite (KAY5), fluorite (BAL76), allanite (also occurring as a discrete prismatic phase in BAL76), and pyrochlore based on qualitative microprobe analysis (essential Nb, U, Ti, Ca) (KAY5 and KAY2) are accessory minerals. A monzonite and foid monzosyenite (BAL78, 79 respectively) contain hornblende, which in BAL78, rims and forms coaxial overgrowths on a pale green clinopyroxene.

Calcite-syenites

The dominant phase is perthitic K-feldspar, with coarse-grained calcite (Fig. 2a) and discrete albite grains, biotite,

magnetite, apatite, occasional muscovite both as coarse flakes and as finer grained aggregates with calcite apparently nepheline in K-feldspar (c.f. Fig. 2b). Zircon is a ubiquitous accessory, attaining the role of a minor phase in KAY10, and allanite occurs both interstitially and as a thin reaction (?) rim between calcite and either K-feldspar or biotite. KAY12 contains zeolitic aggregates, possibly pseudomorphous after nepheline.

Carbonatites

The carbonatites are dominated by coarse to pegmatitic, allotriomorphic granular calcite with interstitial prisms (up to 3 mm) of apatite, the latter in places forming radiating rosettes. Biotite flakes with brown or green–brown pleochroism are associated with, and enclosed in, magnetite. Perthitic K-feldspar, in some rocks forming 1–2 cm laths, has fine-grained albite granules along grain boundaries and as exsolved blebs. Polycrystalline aggregates of muscovite occur interstitially and have a similar texture and morphology to occurrences in syenite that are interpreted to be pseudomorphs of nepheline. Accessory minerals include rutile and titanite, the latter forming thin reaction rims along apatite–calcite grain boundaries. In most specimens, ubiquitous but accessory allanite forms fine granular aggregates or thin borders (reaction rims?) along grain boundaries, typically between calcite and K-feldspar. Monazite, zircon and thorium have been confirmed as accessories in three separate carbonatites. Schuiling (1961) also reported thorium and allanite in the Karaçayır carbonatites.

Analytical techniques

Mineral and rock analytical techniques for major and trace elements, oxygen, carbon, strontium and lead isotopes and U–Pb geochronology are described in supplementary material.

Mineralogy

Samples of Karaçayır syenites (KAY2, 5, BAL74, 76, 78, 79), calcite-syenites (KAY3C, 12) and carbonatites (KAY3, 17A, K8, K9,) as well as calcite in marble country rocks (KAY7B, 8) and xenoliths (KAY1A, 1B, 17B) were investigated mineralogically. Representative analyses are available in Tables A1 and A2 in supplementary material.

K-feldspar

Perthitic K-feldspar is the dominant phase in all Karaçayır syenites, comprising >50 volume per cent. It is a major

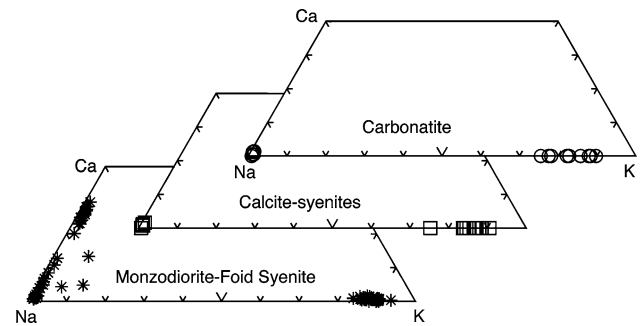


Fig. 3 Ca–Na–K ternary diagram illustrating the compositions of feldspars analysed from syenites, calcite-syenites, and carbonatites

phase in the calcite-syenites and a minor or accessory phase in some of the carbonatites. The total range of compositions is represented in an An–Ab–Or diagram (Fig. 3). K-feldspar typically has a restricted range of compositions within a single specimen, and overall, a very similar range of compositions across all lithologies (syenites $An_{0-2}Ab_{9-14}Or_{85-90}$, calcite-syenites $An_0Ab_{12-16}Or_{84-88}$, and carbonatites $An_0Ab_{10-25}Or_{75-91}$). K-feldspar in calcite-free syenite (BAL74, whole rock Ba 2,230 ppm) has a maximum concentration of 0.32 wt.% BaO, and in a syenite with accessory calcite (BAL79, whole rock Ba 6,620 ppm) the maximum BaO content reaches 2.22 wt.%. BaO contents in K-feldspar from both calcite-syenites (max. 3.31 wt.%) and carbonatites (max. 3.34 wt.%) are similar to, or more enriched than, their associated silicate-dominated lithologies.

Plagioclase

In syenites, plagioclase occurs as discrete grains, or as a perthitic intergrowth in K-feldspar. In some rocks, the plagioclases are homogeneous and approximate to an albite composition e.g. in syenites $An_1Ab_{98}Or_1$. In monzonite and syenite, the most calcic compositions ($An_{28-30}Ab_{69-71}Or_1$) show normal zoning, grading to more albitic compositions, $An_{4-6}Ab_{93-94}Or_1$, adjacent to K-feldspar, calcite, or epidote-allanite reaction rims. Calcite-syenites and carbonatites have uniform compositions of $An_{0-2}Ab_{98-99}Or_1$. Zoning profiles in the syenites and compositions in the calcite-syenites and carbonatites suggest progressive fractionation towards albitic compositions.

The total range of compositions determined by EDS analysis is represented in Fig. 3.

Biotite

Biotite occurs in all rocks as tabular grains with pronounced brown or green brown pleochroism. Compositions show a range in Mg# and TiO₂ from ~60, and 1.6–2.1% respectively in monzonite, to ~25, 2.4–2.7% in foid

syenite/monzodiorite, to ~ 16 , 3.1–3.4% in foid syenite. The more ferroan biotites are also enriched in MnO and depleted in SiO₂. Variation in these parameters is, in general, inferred (Woolley and Platt 1986, 1988) to result from igneous fractionation. Mg#s of the Karaçayır pluton biotites would suggest that monzonite is one of the more primitive magma compositions and foid syenite is one of the more evolved of the silicate-dominated magmas.

Corresponding Mg# and TiO₂ contents for biotites from the calcite-syenites are 19–29 and 3.1–4.5% respectively, and for carbonatites 29–47 and 2.2–3.4%. Biotites from the calcite-syenites and carbonatites are compositionally similar to those of the more evolved end of the syenitic spectrum, with the exception of carbonatite biotite (KAY17A), which has anomalous Mg# and TiO₂ contents of 83–84 and 0.3–0.4%, respectively. As is evident from Fig. 1, KAY17A comes from a different part of the Karaçayır pluton to the other samples, and its relationship there to the host silicate intrusion has not been explored.

Clinopyroxene

Pyroxene occurs in only one of the samples investigated, with compositions in monzonite (BAL78) ranging from Ca_{48–51}Mg_{37–38}Fe_{11–15}, with a considerable aegirine component Aeg_{6.2–9.7}Diop_{65–74}Hed_{20–25}. Clinopyroxene occurs as stubby prisms, partially overgrown, and replaced by hornblende.

Hornblende

As with coexisting biotites, the amphiboles in monzonite are enriched in Mg, Si, and depleted in Ti, Fe, and Mn compared with amphiboles from the more highly evolved monzo-syenite. There is also a small increase in Ca and depletion in K in the more magnesian amphibole. Compositions range from potassian subsilicic hastingsite with Mg# 0.27–0.32, TiO₂ 1.85–2.19% (KAY79) to potassian magnesian hastingsite to potassian ferroan pargasite with Mg# 0.53–0.57, TiO₂ 1.37–1.50% (BAL78; Tindle and Webb 1994).

Minor phases

Muscovite forms in four of the syenites (s.s.) it is typically ferroan (2.1–4 wt. % expressed as FeO) and barian (maximum 2.19 wt. % BaO).

Epidote group

Monzonite (BAL78), and foid monzodiorite (BAL 76) contain prismatic pistacite-rich (Ps₂₈) epidote and allanite

(La, Ce, Sm, Nd, U, and Th detected by EDS microprobe spectra), respectively, in apparent textural equilibrium with mafic silicates. They are interpreted as primary igneous phases (Zen and Hammarstrom 1984). Epidote zoned to allanite also occurs in foid monzo-syenite and monzo-diorite (BAL79 and BAL76), as thin, discontinuous reaction (?) rims between calcite and either hornblende, nepheline, or K-feldspar, and between nepheline and apatite. These reaction textures of epidote-allanite zoned grains probably represent late magmatic re-equilibration of primary orthomagmatic minerals with LREE-rich residual fluids, or conceivably to sub-solidus processes (c.f. Liferovich and Mitchell 2006; Fig. 7). Calcite-syenites (KAY3C and KAY12) and carbonatite (K8) also contain allanite as reaction rims between calcite and K-feldspar.

Zeolites

A prominent hexagonal pseudomorph that occurs in most syenitic parts of the pluton is composed of radiating and plumose aggregates of low index, low birefringent, zeolites (Fig. 2b). Ca:Na:K ratios, determined by microprobe analysis, suggest the presence of natrolite, thompsonite, and gonnardite (?) formed from primary nepheline.

Calcite

In the syenites, calcite forms coarse interstitial patches in apparent textural equilibrium with other silicate and phosphate minerals. Compositionally, the carbonate is predominantly calcic, with trace amounts of Sr detected by electron microprobe. Some of the calcites from calcite-syenites (KAY10, 12), marbles (KAY7, 8B), and carbonatites (KAY3) are lamellate, with the exsolution of dolomite. Trace element compositions of calcites are discussed in the geochemistry section.

Accessory phases

Zircon, titanite, haematite, fluorite, pyrochlore and pyrite are rare accessory minerals.

Apatite is a constant accessory phase, forming euhedral hexagonal prisms, in places in the form of radiating rosettes, poikilitically enclosed in other magmatic phases. Significant Sr has been detected in EDS spectra, a recognised characteristic of carbonatitic apatite (Hogarth 1989). Carbonatite K8 contains trace amounts of interstitial monazite, and carbonatite 17A has small amounts of thorianite (cf. Schuiling 1961).

Table 1 U–Th–Pb isotope data for zircon from calcite-syenite, KAY 10

Grain-spot no.	Pb* (ppm)	U (ppm)	Atomic Th/U	Measured isotope ratios and 1 σ (%) internal errors				Measured and corrected ages and 1 σ absolute internal errors (Ma)				6/38–7/35 concordance(%)	Est'd % common 206Pb	Spot MSWD	Selected age and 1 σ absolute external error (Ma)
				$\frac{206\text{Pb}}{238\text{U}}$	$\pm$	$\frac{207\text{Pb}}{235\text{U}}$	$\pm$	$\frac{207\text{Pb}}{206\text{Pb}}$	$\pm$	$\frac{206\text{Pb}}{238\text{U}}$	$\pm$	$\frac{207\text{Pb}}{235\text{U}}$	$\pm$		
22	68.5	4700	3.30	0.00852	0.6	0.1722	1.6	0.1467	1.5	0.00275	0.8	161.3	2.4	3.49	
02	36.9	2618	1.80	0.00994	0.6	0.0662	2.1	0.0483	2.0	0.00319	1.1	111.5	1.4	2.86	
01	9.5	756	1.12	0.01016	0.8	0.0685	3.5	0.0489	3.4	0.00348	1.7	114.3	3.4	5.00	2.6
21	37.2	2772	1.46	0.01020	1.3	0.0868	3.7	0.0617	3.4	0.00323	3.0	65.1	1.3	3.59	2.6
03	46.4	3058	2.83	0.00928	0.6	0.1161	1.4	0.0908	1.2	0.00253	2.0	96.4	2.1	6.03	2.6
10	39.1	2635	1.95	0.01027	0.8	0.0765	2.4	0.0540	2.3	0.00309	1.5	84.5	3.0	4.92	1.0
13	11.5	1026	0.61	0.01045	0.8	0.0760	3.5	0.0528	3.4	0.00294	3.0	67.2	2.3	1.54	2.6
09	36.1	2476	1.82	0.01031	0.5	0.0699	1.7	0.0491	1.6	0.00315	1.0	98.1	2.2	7.74	2.6
20	38.4	2770	1.61	0.01026	1.1	0.0996	2.3	0.0704	2.1	0.00314	5.3	74.8	1.7	3.61	2.6
05	28.8	1883	1.97	0.01050	0.6	0.0723	1.7	0.0499	1.5	0.00325	1.0	68.6	1.1	3.70	2.6
23	18.9	1255	1.91	0.01049	0.7	0.0808	2.5	0.0559	2.4	0.00328	0.9	74.4	2.5	1.97	2.7
17	9.1	639	1.22	0.01119	0.9	0.0970	3.2	0.0629	3.1	0.00413	1.9	78.9	1.9	1.85	0.8
12	18.5	1300	1.43	0.01086	0.7	0.0742	2.1	0.0495	2.0	0.00349	1.1	70.9	1.1	3.54	2.7
18	19.7	1412	1.37	0.01091	0.8	0.1210	2.7	0.0804	2.6	0.00357	2.0	115.9	3.0	2.72	2.7
26	19.5	1286	1.89	0.01058	0.8	0.0729	4.0	0.0499	3.9	0.00319	1.1	105.8	1.7	9.32	0.9
04	7.2	508	1.23	0.01124	0.8	0.0950	3.2	0.0613	3.1	0.00398	1.5	71.4	2.8	1.72	0.8
07	24.3	1523	2.01	0.01085	0.5	0.0934	2.2	0.0624	2.2	0.00341	1.4	90.7	1.9	2.55	2.7
14	11.1	749	1.54	0.01110	1.0	0.0996	2.9	0.0650	2.7	0.00354	2.0	95.2	3.1	3.71	2.8
15	9.2	651	1.15	0.01139	0.9	0.0782	3.5	0.0498	3.4	0.00388	1.5	79.0	1.5	3.26	0.7
24	47.8	2871	2.32	0.01077	0.6	0.0809	1.9	0.0545	1.8	0.00319	0.8	105.3	2.7	3.0	2.8
28	41.7	2455	2.17	0.01123	1.2	0.0724	3.0	0.0468	2.7	0.00339	1.0	72.6	1.5	3.16	2.8
16	24.4	1758	1.39	0.01106	1.0	0.1093	2.7	0.0717	2.5	0.00281	4.4	96.4	2.6	1.91	2.8
27	39.8	1953	1.34	0.01412	1.2	0.1054	4.7	0.0542	4.5	0.00816	2.7	102.4	5.5	4.70	1.1
08	25.3	1694	1.75	0.01090	0.7	0.0983	3.4	0.0654	3.3	0.00278	4.3	94.0	2.9	2.21	2.9
19	27.6	1828	2.26	0.01024	1.0	0.1191	3.1	0.0844	3.0	0.00235	5.1	92.2	2.8	1.74	2.9
11	30.9	1550	2.16	0.01384	2.0	0.3714	5.0	0.1946	4.6	0.00585	5.3	71.0	2.0	3.59	1.1
29	60.1	3642	2.25	0.01116	1.1	0.1061	5.6	0.0690	5.5	0.00283	4.8	320.7	13.8	9.53	3.4
06	68.9	3286	3.93	0.01046	0.7	0.1015	2.4	0.0704	2.3	0.00305	2.2	76.5	2.6	2.62	3.0
25	90.4	4165	3.91	0.01084	0.9	0.1098	1.7	0.0734	1.4	0.00089	4.0	101.8	4.5	2.83	

Pooled age of selected data = 67.7 ± 1.1 Ma (2σ error), $n = 26$ of 29 grains, MSWD = 2.17Errors are 1 σ unless otherwise noted * = radiogenic component only

Age constraints

The emplacement age of a foid syenite (BAL 74) has been determined by ^{207}Pb – ^{206}Pb single crystal zircon evaporation methods at 99.0 ± 11.0 Ma (Boztuğ et al. 2007a), uplift to biotite retention temperatures (c. 300°C) occurred by 65 Ma (^{40}Ar – ^{39}Ar geochronology) and subsequent rapid exhumation (apatite fission-track dating) occurred between 58 and 61 Ma (Boztuğ et al. 2009).

Petrographic observations, outlined above, indicate that zircon is a constant accessory in many of the silicate-dominated and calcite-bearing facies of the syenite. In KAY10, a calcite-syenite, zircon is in apparent textural equilibrium with both the silicate phases (biotite and K-feldspar) and with calcite and was of sufficient abundance to be able to be separated by traditional techniques of heavy liquid and magnetic separation. Twenty-six out of a population of 29 grains (Table 1) analysed by ICP-MS techniques gave an average $^{206}\text{Pb}/^{238}\text{U}$ age of 67.7 ± 1.1 Ma, with an MSWD of 2.2 (Fig. 4). This age is compatible with the range in intrusive ages for A- and H-Type plutons in the Central Anatolian crystalline complex of 86 to 65 Ma summarised by Köksal et al. (2004).

The age differs significantly from the $^{207}\text{Pb}/^{206}\text{Pb}$ age of 99 ± 11 Ma for zircon documented by Boztuğ et al. (2009) but is within error of their biotite $^{40}\text{Ar}/^{39}\text{Ar}$ age of ~ 65 Ma, interpreted to represent uplift. One possible explanation for the discrepancy is that the Karaçayır pluton is composite, an interpretation suggested on the basis of Sr and Pb isotope ratios (see discussion). The syenite enriched in calcite, inferred to be related to the carbonatite (see discussion), would be the younger phase of the pluton and, as evidenced in KAY10, has entrained an inherited older grain (Grain 25, Table 1), possibly related to the earlier intrusion.

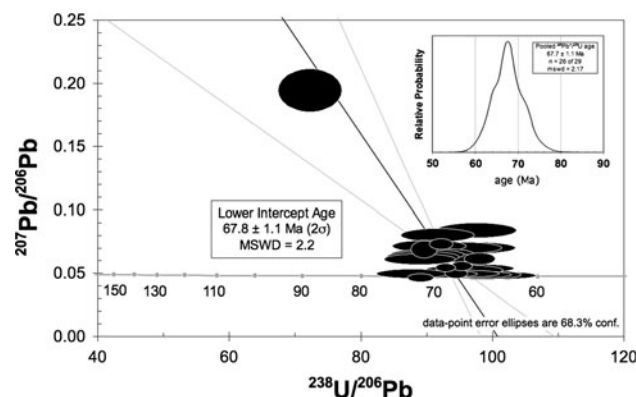


Fig. 4 $^{207}\text{Pb}/^{206}\text{Pb}$ – $^{238}\text{U}/^{206}\text{Pb}$ concordia diagram showing the ratios of 26 zircons from calcite-syenite KAY 10

Geochemistry

Major and trace elements

Syenites

Compositions of silicate plutonic rocks of the Karaçayır pluton (listed in Table 2) range in composition from foid monzodiorite (BAL76), through foid monzosyenite (BAL79) to syenite (BAL75, 77), monzonite (BAL78), and foid syenite (BAL74)(classification based on TAS diagram for plutonic igneous rocks of Middlemost 1994). On the basis of their elevated Cr, and low Ta, LREE, Sr, Ba, Cs, BAL78 and possibly BAL75 and 77 would qualify as relatively “parental” magma compositions, whereas BAL79, with elevated concentrations of Ba, Sr, LREE, Nb, Ta, and Cs, with low HREE, Hf and Zr would represent a more “evolved” composition, with A-type characteristics. Both BAL79 and BAL76 have high normative nepheline contents (16 and 22 wt per cent, respectively). BAL79 has anomalously high normative anorthite contents to be a residual magma composition, but the An content here reflects the calcite content of the rock, rather than reflecting the plagioclase composition.

Calcite-syenites and carbonatites

These rocks are either too heterogeneous in terms of texture, and/or too coarse grained for whole rock geochemistry to be representative of the chemical system from which they crystallised. Instead, since calcite is a mineral common to both rock types and in variable concentrations is also present in the syenites, its composition was determined by LA-ICP-MS analysis in order to assess the mutual relationships between the constituent rock types. REE and other trace element contents of calcite from marbles, syenites, calcite-syenites, and carbonatites are presented in Table 3.

Rare earth elements

On a chondrite-normalised plot (Fig. 5a), calcite in the carbonatite and calcite-syenite rocks shows pronounced LREE enrichment, with La_N up to ~ 4300 and La_N/Lu_N ratios as high as 51. HREE contents are high with Lu_N values typically 80–90. Eu anomalies are either absent, or negative but subdued.

Two of the syenite calcites, BAL76 and KAY2, have unusual, relatively flat REE patterns (Fig. 5b), with LREE enriched 50–280 times relative to chondrite, although La and Ce show minor depletion relative to Pr and Nd, and there is a subdued negative Eu anomaly ($\text{Eu}^* 0.85$ – 0.87). HREE are enriched 108–122 times, a distinctive feature

Table 2 Major and trace element analyses of silicate plutonic rocks from the Karacayir pluton

Specimen rock type	BAL-74 foid syenite	BAL-75 syenite	BAL-76 foid monzo-diorite	BAL-77 syenite	BAL-78 monzonite	BAL-79 foid monzo-syenite
SiO ₂	59.06	65.66	43.82	60.64	58.30	51.13
TiO ₂	0.19	0.13	0.48	0.15	0.24	0.35
Al ₂ O ₃	21.01	17.76	19.93	18.71	20.01	18.75
Fe ₂ O ₃	0.31	0.25	0.98	0.33	0.36	0.53
FeO	1.56	1.26	4.89	1.66	1.78	2.63
MnO	0.03	0.05	0.22	0.06	0.05	0.09
MgO	0.16	0.21	1.08	0.85	1.48	0.60
CaO	1.62	0.79	8.73	4.68	7.01	6.26
Na ₂ O	3.72	6.25	4.29	4.80	5.65	3.42
K ₂ O	9.30	6.67	5.16	5.77	2.84	8.36
P ₂ O ₅	0.04	0.06	0.23	0.11	0.16	0.15
LOI	2.40	0.71	8.44	0.69	1.51	6.17
Total	99.40	99.80	98.25	98.45	99.39	98.44
Mo	3	4	nd	4	4	3
Cu	nd	21	nd	30	10	11
Pb	61	14	49	34	21	30
Zn	71	32	138	34	nd	47
Bi	1	2	1.6	1.3	1	1.9
Tl	1.6	1.6	2.1	0.9	0.3	1.3
Co	1	4	6	3	6	3
Cr	27	45	nd	28	31	nd
V	36	22	139	38	48	55
Ba	2,230	1,840	5,130	2,550	1,180	6,620
Cs	2	1.6	6.3	1	0.8	2.4
Ga	21	26	18	14	17	10
Hf	5	6.2	1.7	2.1	2.2	1.3
Nb	53	21	38	11	20	34
Rb	234	175	167	100	48	150
Sn	nd	nd	nd	nd	1	nd
Sr	1,080	513	3,620	2,080	1,880	3,570
Ta	4.4	1.1	1.5	0.9	1.3	3.5
Th	55.5	16.5	36	5.7	14.1	8.9
U	5.2	5.9	4.7	1.8	4.7	1.8
W	nd	nd	2	nd	nd	4
Zr	318	345	134	123	124	64
Y	15	12	42	7	10	13
La	51.1	19.9	68.2	18.9	27.9	76
Ce	86.2	45.4	132	41.3	58.6	144
Pr	9	5.33	15.1	5.27	6.89	16
Nd	28.1	18.2	55.3	19	24.3	54.2
Sm	4.2	3.1	10.5	3.2	3.9	7.3
Eu	1.15	0.71	3.18	0.97	1.22	1.79
Gd	3	2.4	9.3	2.2	2.8	4.7
Tb	0.4	0.3	1.3	0.3	0.3	0.5
Dy	1.9	1.7	6.3	1.2	1.6	2.3
Ho	0.4	0.3	1.2	0.2	0.3	0.4
Er	1.1	1.1	3.7	0.6	0.8	0.9
Tm	0.16	0.18	0.57	0.08	0.11	0.12
Yb	1.1	1.2	3.8	0.5	0.7	0.7
Lu	0.17	0.21	0.53	0.08	0.1	0.08

Table 3 LA-ICP-MS trace element analyses of calcites from syenites, calcite-syenites, carbonatites, and marble

	Sr	Y	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Syenite																	
KAY2	1,570	184	63.2	65.7	216	37.0	171	45.6	11.3	36.6	5.88	33.4	6.76	17.9	2.76	19.8	2.74
BAL76	4,470	202	18.8	12.2	49.8	9.13	58.8	24.7	7.78	30.2	5.32	33.1	7.04	20.1	2.97	21.9	3.10
BAL78	971	22.7	1.02	0.42	0.88	0.17	0.98	0.49	0.06	1.01	0.19	1.85	0.51	2.21	0.38	3.80	0.68
Marble																	
KAY1A	314	19.1	3.64	7.94	7.21	1.72	7.68	1.85	0.46	2.16	0.34	2.16	0.53	1.37	0.17	1.08	0.14
KAY1B	356	19.7	1.99	0.38	0.83	0.36	2.36	1.13	0.33	1.90	0.38	2.52	0.51	1.34	0.17	1.06	0.13
KAY7	411	15.4	23.4	46.3	82.6	8.51	25.6	4.17	0.69	2.50	0.36	2.13	0.42	1.28	0.19	1.34	0.18
KAY8B	176	4.43	7.16	9.53	10.1	1.28	4.43	0.80	0.15	0.64	0.11	0.58	0.13	0.33	0.05	0.22	0.04
KAY17B	190	1.90	19.0	19.7	25.4	1.82	4.93	0.49	0.10	0.29	0.03	0.22	0.04	0.13	0.02	0.12	0.02
Carbonatite/calcite-syenite																	
KAY3	14,460	157	73.2	616	1,159	117	423	62.4	13.9	41.0	5.46	29.4	5.33	14.5	2.14	14.6	2.03
KAY3C	13,270	171	57.6	1,018	1,785	161	553	75.3	16.4	47.3	6.28	31.4	5.93	16.0	2.20	15.2	2.12
KAY11	12,320	125	50.3	147	332	42.2	175	33.9	9.49	27.1	3.93	21.9	4.38	11.5	1.71	11.3	1.61
KAY12	8,408	180	30.0	428	911	105	416	68.7	14.4	43.8	5.95	32.0	6.04	15.7	2.24	16.1	2.16
KAY10	10,860	136	60.2	239	567	67.9	274	47.5	11.0	32.7	4.43	23.5	4.56	12.3	1.84	12.3	1.76
KAY17A	9,482	158	19.5	643	1,403	139	465	69.1	14.4	42.4	5.64	30.6	5.73	15.8	2.29	16.0	2.14
K8	9,570	163	25.8	170	532	68.1	292	58.7	13.3	40.3	5.58	29.8	5.69	15.7	2.19	15.6	2.26

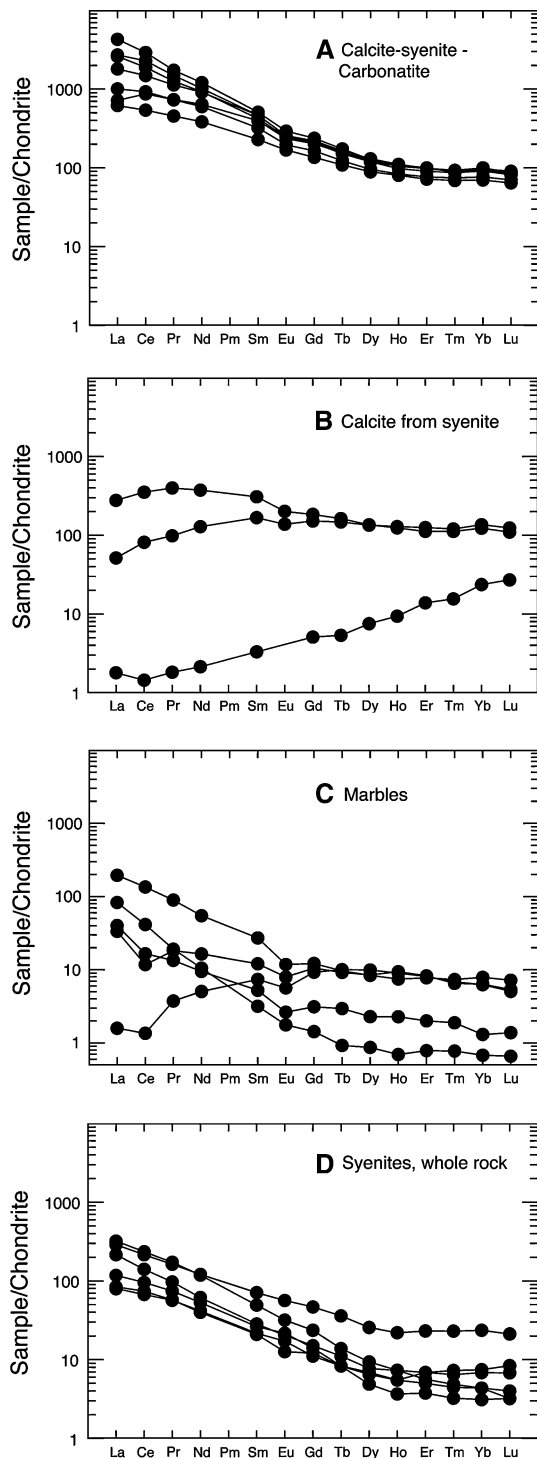


Fig. 5 Chondrite-normalised REE plots **a** Calcite from carbonatite and calcite-syenite, **b** Calcite from syenite, **c** Calcite from marbles, **d** syenite, whole rock analyses. Normalising factors are from McDonough and Sun (1995)

they share with the calcite-syenite/carbonatite suite. The third syenite calcite, BAL78, shows lesser enrichment relative to chondrite, with slight LREE depletion relative to

HREE (La_N/Lu_N 0.1) and much lower total enrichment relative to chondrite. The REE patterns for the calcite contrast with the REE profiles of whole rock syenites (data in Table 4) (Fig. 5d), which consistently show LREE enrichment with La_N up to 320 and La_N/Lu_N of up to 102, and with very subdued, either positive or negative Eu anomalies (Eu^* 0.80–1.13).

The marble calcites show the most variation (Fig. 5c), with La_N/Lu_N ranging from 0.3 to 26.7, and significant negative Eu anomalies. KAY7 exhibits modest LREE enrichment (La_N up to 195, but with MREE and HREE relatively flat) but KAY1B, a diopside-tremolite marble, has a La-Nd segment depleted relative to Sm-Lu and La_N of only 1.6. KAY1A was collected at the same locality as KAY1B but shows, in contrast, a slight La enrichment (La_N 33.5) in a pattern where the Sm-Lu segment is relatively flat, enriched relative to chondrite by a factor of ~ 10 .

Other trace elements

Significant differences exist in the abundance of other trace elements in calcites from the three groups of rocks. Sr, Ba, and Y contents of calcite from carbonatites, and calcite-syenites at Karaçayır are higher than other rock types but show greatest similarity to the syenites, rather than the marbles, where calcite has low concentrations of Sr, Ba, and Y. For examples, Sr contents average 11,196 ppm in calcite-syenites/carbonatites, 2,337 ppm in syenites but only 289 ppm in marbles. An identical pattern exists for Ba and Y, as indicated in the analyses listed in Table 3.

Oxygen and carbon isotopes

Oxygen and carbon isotope ratios for calcite, expressed in terms of $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$, are listed in Table 4 and graphically represented on a $\delta^{13}\text{C}_{\text{VPDB}}$ versus $\delta^{18}\text{O}_{\text{VSMOW}}$ plot in Fig. 6.

Analyses form three distinct groups. Marbles have +ve $\delta^{13}\text{C}_{\text{VPDB}}$ of 1.54 to 2.70‰ and elevated $\delta^{18}\text{O}_{\text{VSMOW}}$ of 18.91 to 26.30‰. Compared to stable isotope ratios of other carbonate rocks worldwide, the Karaçayır marbles have the typical signature of crustal rocks with +ve $\delta^{13}\text{C}_{\text{VPDB}}$ and high $\delta^{18}\text{O}_{\text{VSMOW}}$.

At the other end of the spectrum, calcite-syenites and carbonatites form a tight, elongate cluster at $\delta^{18}\text{O}_{\text{VSMOW}}$ 10.4 to 11.5‰ with a range of $\delta^{13}\text{C}_{\text{VPDB}}$ between -2.10 and -3.51 ‰. Like most carbonatites worldwide, $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ ratios for Karaçayır samples plot outside the Primary Igneous Carbonatite box (Taylor et al. 1967) inferred to represent mantle values. They show a positive $\delta^{13}\text{C}_{\text{VPDB}}-\delta^{18}\text{O}_{\text{VSMOW}}$ trend, similar to that of other carbonatite suites (Hubberten et al. 1988; Deines 1989; Reid and Cooper 1992) and attributed to variation during

Table 4 C, O, Sr, and Pb isotope ratios of Karacayir calcites

Rock type	Sample	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{se}$	206Pb/204Pb	$\pm 2\text{se}$	207Pb/204Pb	$\pm 2\text{se}$	208Pb/204Pb	$\pm 2\text{se}$
Syenite	KAY2	-2.11	16.49	0.707511	0.000075	19.41067	0.00095	15.74291	0.00090	39.32439	0.00253
Syenite	BAL76	-0.94	11.31	0.706660	0.000130	18.96992	0.00076	15.71238	0.00072	39.11323	0.00213
Syenite	BAL78	-1.36	13.59	0.706563	0.000041	19.29484	0.00111	15.72991	0.00077	39.89892	0.00327
Calcite-syenite	KAY3	-2.88	10.58	0.707860	0.000041	18.97284	0.00086	15.72148	0.00084	39.09890	0.00257
Calcite-syenite	KAY3C	-3.29	10.40	0.707464	0.000091	18.96390	0.00079	15.71946	0.00071	39.10545	0.00193
Calcite-syenite	KAY11	-2.86	10.85	0.707380	0.000520	18.97261	0.00135	15.72070	0.00086	39.11421	0.00416
Calcite-syenite	KAY12	-2.31	10.99	0.707320	0.000160	18.99059	0.00082	15.72208	0.00072	39.11755	0.00206
Calcite-syenite	KAY10	-3.51	10.42	0.707429	0.000175	18.96812	0.00073	15.71937	0.00073	39.10064	0.00212
Biotite carbonatite	KAY17A	-2.10	11.28	0.707436	0.000470	18.97039	0.00097	15.72048	0.00087	39.10161	0.00246
Biotite carbonatite	K-8	-2.57	11.50	0.707552	0.000125	18.99681	0.00096	15.72598	0.00088	39.11803	0.00255
Marble country rock	KAY7	2.09	18.91	0.708024	0.000092	18.96277	0.00083	15.70850	0.00079	39.05054	0.00230
Marble country rock	KAY8B	2.70	24.14	0.708099	0.000086	18.83920	0.00087	15.70048	0.00085	38.93184	0.00244
Marble xenolith	KAY17B	2.34	18.95	0.707970	0.000380	18.81698	0.00095	15.70257	0.00085	38.93787	0.00237
Marble xenolith	KAY1A	1.54	23.17	0.707962	0.000199	18.81194	0.00088	15.67922	0.00083	38.85526	0.00230
Diopside marble xenolith	KA1B	2.08	26.30	0.708091	0.000075	18.77358	0.00086	15.68799	0.00082	38.90361	0.00236

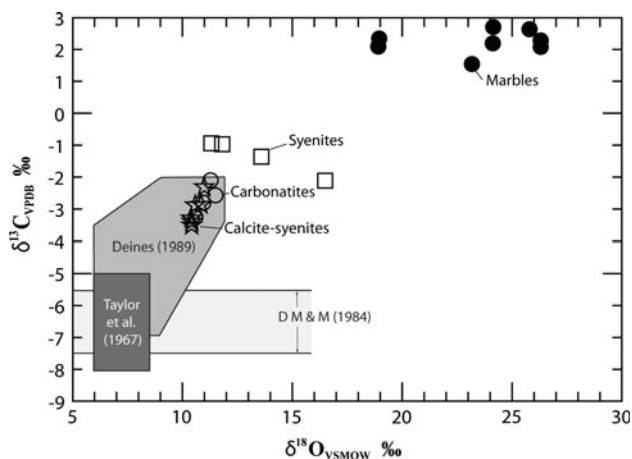


Fig. 6 $\delta^{13}\text{C}_{\text{VPDB}}$ vs. $\delta^{18}\text{O}_{\text{VSMOW}}$ plot of calcites of marbles, syenites, calcite-syenites, and carbonatites from the Karacayir area, compared with the most common carbon and oxygen isotope variations observed in carbonatite minerals (Deines 1989, Fig. 13.39), the “primary igneous carbonatite” box defined from Laacher See (Taylor et al. 1967, Fig. 6) and the $\delta^{13}\text{C}_{\text{VPDB}}$ range of ocean ridge basalt glasses (Des Marais and Moore 1984)

moderate to high temperature igneous Rayleigh fractionation (Deines 1989).

Syenites, containing between 0 and 10% calcite, have calcite stable isotope ratios that are intermediate between marbles and calcite-syenites/carbonatites, but they lie considerably closer to the carbonatite group. There is some dispersion of these ratios to high $\delta^{18}\text{O}$ values, possibly a function of minor meteoric or hydrothermal alteration.

Strontium isotopes

Strontium isotopes of a mineral phase should faithfully reflect the composition of the fluid and therefore the source of the fluid responsible for the precipitation of the mineral.

Strontium isotope ratios for Karacayir samples were determined on the same calcite fragments analysed for trace elements. Analyses from Karacayir marbles, syenitic rocks, and calcite-syenites/carbonatites are listed in Table 4. Since calcite contains no detectable Rb in LA-ICP-MS analyses, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ reflects the ratio at the time of crystallisation, providing there has been no subsequent alteration. The calcite-syenites and carbonatites have a range in $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70732 to 0.70786, with an average of 0.70749, a value that is very similar to that of the foid syenite, 0.70751. In contrast, the monzonite and monzodiorite have ratios (~ 0.7066) that differ significantly from the other rocks. On the basis of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the contrasting U/Pb ages, it is possible that the Karacayir pluton is composite and comprises more than one intrusive phase.

Marbles, collected from both xenoliths within the pluton and from in situ country rock, show a very restricted range of $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.70796 to 0.70809 (average 0.70806) that is similar to that documented for other Lower Palaeozoic marbles (Veizer 1989). The Karacayir marble ratios, even those from xenoliths within the syenite, lie exclusively outside the range of both the silicate plutonic rocks and the carbonatitic lithologies.

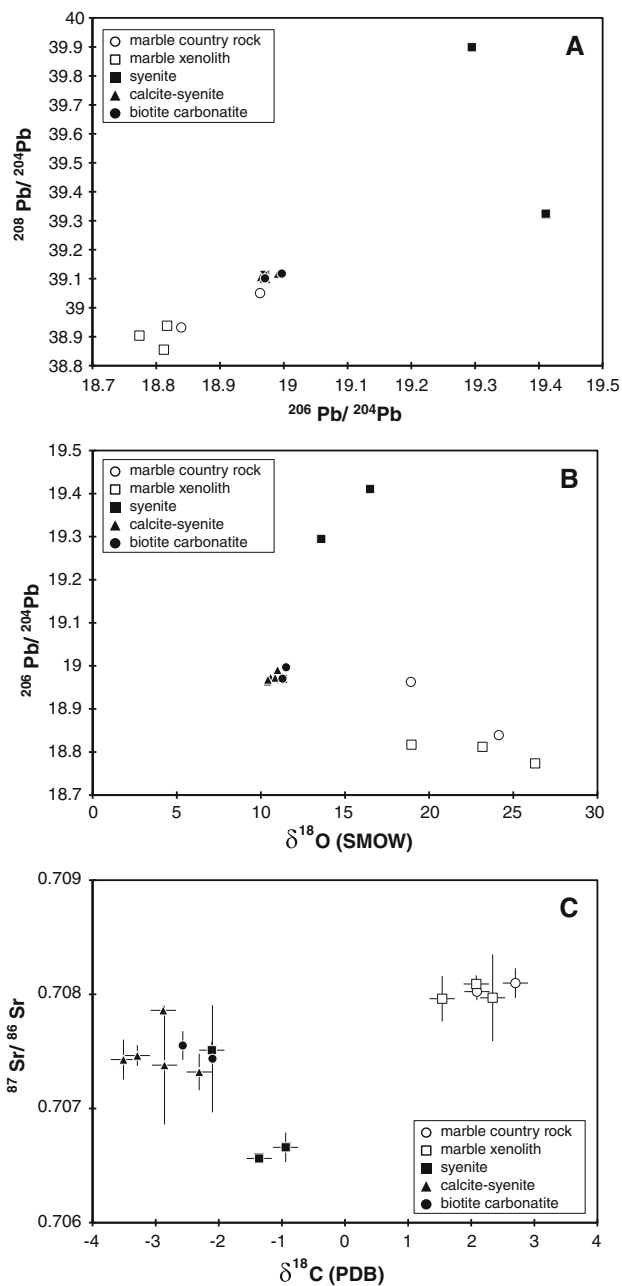


Fig. 7 **a** $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. **b** $^{206}\text{Pb}/^{204}\text{Pb}$ versus $\delta^{18}\text{O}$, and **c** $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\delta^{13}\text{C}$ for calcites from marble, calcite-syenite, syenite, and carbonatite

Lead isotopes

Lead isotope ratios of calcites are tabulated in Table 4. The calcite-syenites and carbonatites show restricted and overlapping ranges for $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.9639, $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.7260 to 15.7194, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 39.1180 to 39.0989. The foid monzodiorite, BAL76, has Pb isotope ratios that also lie in this range. Corresponding Pb isotope ratios for syenitic rocks KAY 2 and BAL 78 are, however, consistently higher (e.g. $^{206}\text{Pb}/^{204}\text{Pb}$ 19.9699 and

19.2948) and those for marbles (KAY 1, 7, 8, 17B) are consistently lower (e.g. $^{206}\text{Pb}/^{204}\text{Pb}$ 18.9628 to 18.7736). Plots such as $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $\delta^{18}\text{O}$ (Fig. 7a, b) emphasise the tri-partite subdivision of isotopic populations in the Karaçayır pluton, with (1) the calcite-syenites and carbonatites forming a tight grouping, sharing some characteristics with feldspathoidal syenites, (2) the other magmatic silicate components, and (3) the marbles.

Discussion

Schüiling (1961) interpreted the Karaçayır carbonatitic rocks as having formed from marble by “(partial) liquefaction” and “obvious permeation with magmatic fluids” as a consequence of intrusion by syenite magma. Schüiling recognised that Th, REE, P, (Fe, Mg)O, SiO_2 , and H_2O had been metasomatically introduced during the proposed melting event. He was at pains to point out that he did not consider all carbonatites formed by this process, merely that in this occurrence it was physically possible.

Although previous work has cast doubt on the viability of limestone assimilation, recent work has suggested that under certain geological circumstances, evidence for limestone–magma interaction is compelling. The various field and geochemical characteristics of the Karaçayır carbonatites are reviewed in the light of Schüiling’s hypothesis and recent studies.

Stable isotopes evidence

Change in O and C isotope signatures of marbles through fluid infiltration from adjacent igneous intrusions has been documented (e.g. Blattner and Cooper 1974; Lapin et al. 1987), with metasomatically altered rocks in contact aureoles having isotope ratios that are intermediate between the country rock marble and intrusive end members.

Assimilation of marble by gabbro and diorite in the Hortavaer complex, Norway, is described by Barnes et al. (2005). The extensive silicate and carbonate assimilation they advocate occurred in an extensional environment, where the CO_2 generated was able to escape from the system, with the CaO taken up in the crystallisation of Ca-bearing minerals, principally clinopyroxene and amphibole. Variation in $\delta^{13}\text{C}_{\text{VPDB}}$ from +3.75 to +5.0‰ for marbles to −1.2‰ for calcite in monzonite is attributed to Rayleigh fractionation of CO_2 during assimilation of as much as 70 volume per cent of marble by mafic magmas.

Modelling of isotope exchange in simple closed systems in which the $\text{H}_2\text{O}/\text{CO}_2$ ratios, fluid/rock ratios, starting isotope ratios, and temperature were varied showed that decreases in the order of a few per mille $\delta^{13}\text{C}_{\text{VPDB}}$ (the

magnitude of the difference between Karaçayır marbles and syenites/carbonatites) could be achieved by high temperature ($\sim 500^\circ\text{C}$) interaction of calcite with fluid under extremely high (approaching infinite) fluid/rock ratios (Santos and Clayton 1995). Although there are local zones of sericitisation within the Karaçayır pluton, which could be attributed to fluid pathways, there is not the pervasive alteration, veining, or other evidence for the vast release of CO_2 that would be expected in a fluid-dominated system capable of achieving the observed variation in $\delta^{13}\text{C}_{\text{VPDB}}$ ratios.

The $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values of the Karaçayır carbonatites are the most primitive and mantle-like in terms of both ^{13}C and ^{18}O of any of the samples from the local intrusive and country rock suites and are incompatible with the closed system binary mixing of marble and host syenite that would be expected from Schuiling's (1961) hypothesis. Variation of O and C isotope ratios as a function of CO_2 degassing and associated precipitation of calcite at low temperature from bicarbonate-bearing hydrothermal solutions (Zheng 1990) is considered inappropriate at Karaçayır. The association of perthitic alkali feldspars with the calcite-bearing rocks indicate moderate to high temperatures ($>550^\circ\text{C}$), and a similar degassing origin in carbonatitic rocks has been shown to result in negative rather than positive O–C co-variation (Cordeiro et al. 2010).

Sr isotope evidence

The Sr isotope ratios of carbonatites worldwide are typically similar to those of oceanic basalts (e.g. Faure and Powell 1972; Nelson et al. 1988; Bell and Tilton 2001) with initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as low as 0.7030. Together with other geochemical, including isotopic, and experimental evidence, carbonatites are interpreted as having been derived from the mantle either by direct partial melting or by separation from a carbonated silicate parent magma by either fractional crystallisation or liquid immiscibility. However, the Amba Dongar carbonatite, India (Deans and Powell 1968; Simonetti et al. 1995), has initial ratios between 0.70549 and 0.70626, and sövites and alvikites from Mt Vulture, Italy, have ratios slightly greater than 0.7060 (Rosatelli et al. 2000; D'Orazio et al. 2007). Both Italian and Indian carbonatites are associated with mantle-derived nephelinites so their high Sr isotope ratios are interpreted to result from an enriched mantle source. In Italy, this enrichment is interpreted to reflect mantle carbonation associated with subduction of the Adriatic lithosphere. Similar isotopically enriched carbonatites, although rare, are reported from Phalaborwa (Eriksson 1989), Walloway, Australia and Jacupiranga, Brazil (Nelson et al. 1988), southwest Transbaikalia (Doroshkevich et al. 2008),

and eastern Tibet (Hou et al. 2006). Transbaikalia and Tibet carbonatites, with initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70583–0.70599 ($n = 3$) and 0.70602–0.70792 ($n = 22$) respectively, are associated with silicate magmas (alkaline basic rocks, and potassic felsic rocks with calc-alkaline lamprophyres, respectively) that have equally elevated initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Both carbonatites and silicate magmas have other geochemical characteristics that indicate derivation from the mantle and are interpreted to have originated from an enriched source region (Transbaikalia) or to have undergone subsequent contamination by crustal materials (Tibet).

In contrast, dolomitic and rarer calcitic carbonatite-like dykes, intruding granulites of the eastern Himalayas, have $^{87}\text{Sr}/^{86}\text{Sr}$ ranging from 0.709 to 0.712 (Liu et al. 2006) and are interpreted to have been produced by anatectic melting of sedimentary carbonates at crustal levels.

Clearly, the absolute value of the initial Sr isotope ratio cannot be used to distinguish between marble and magmatic carbonate or carbonatite (Gittins et al. 1969), but the comparison of carbonatite ratios with those of associated cogenetic silicate-rich magmas has considerable petrogenetic potential.

The carbonatitic vein dykes of Ontario have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7038 to 0.7049 (Powell 1965; Lentz 1998), similar to associated granitic pegmatites (0.7040 to 0.7052, Lentz 1998), but generally lower than marbles and skarns (0.7048 to 0.7060, Powell 1965; Gittins et al. 1969; Lentz 1998). Using this and other mineralogical and geochemical evidence, Lentz (1999) argued that the vein dykes result from volatile fluxing and syntectic melting of Grenville marble by granitic magmas.

For Karaçayır, initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonatites and calcite-syenites are lower than for the marbles, but similar to a foid syenite. Ratios for syenite are higher than for typical primitive mantle melts and may reflect regional mantle enrichment of Central Anatolia, as suggested by Ilbeyli et al. (2004).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Karaçayır samples, like the stable isotope results, fall into two distinct populations, with the carbonatites and calcite-syenites overlapping those of the syenitic rocks but with no overlap with the marbles. On the basis of stable and Sr isotopes, the Karaçayır carbonatites cannot result simply from the binary mixing of country rock marble and syenitic end members (Fig. 7c).

Lead isotopes

Significant variation in the Pb (and Sr) isotope ratios amongst the syenitic population (Fig. 7) indicates a complicated plutonic history, consistent either with different magma batches derived by melting of heterogeneous sources (possibly at different times as suggested by U-Pb

dating) or that some components have undergone contamination. However, as indicated in previous sections, the contaminant cannot be the immediate country rock marbles.

In contrast to the variable nature of isotopic data from the silicate magmas, there is a tight grouping of the carbonate-rich rock ratios. If the carbonate had been derived by melting of marble by syenite, as advocated by Schuiling (1961), then the wide range in modal proportions of calcite in the calcite-syenites and carbonatites (resulting from melting and admixture of different amounts of marble) should result in highly variable Pb isotope ratios. However, the tight clustering of Pb isotope ratios for the carbonate-rich rocks and one of the syenites and their substantial difference to the marbles (Fig. 7) is considered highly significant. This coherence is only compatible with closed system, magmatic differentiation, with the carbonate fraction derived by either fractional crystallisation or liquid immiscibility from a syenitic parent.

Trace element concentrations

The geochemistry of carbonatites has been extensively reviewed (e.g. Nelson et al. 1988; Woolley and Kempe 1989) with the general conclusion that they contain typically high concentrations of Sr, Ba, Th, and REE (particularly LREE) and, in many complexes, Nb. As indicated above, Sr, Ba, Y, and REE contents of calcite from carbonatites, and calcite-syenites at Karaçayır are higher than other rock types, with similar high concentrations in the syenites, but low concentrations in marble. A binary mixture of marble and syenite is incapable of producing the observed trace element concentrations in carbonatite.

Chondrite-normalised REE patterns of calcites from carbonatites/calcite-syenites are all concordant and show extreme LREE enrichment and flat and substantial HREE segments, characteristics that are matched by the syenites. In particular, the coherence of the HREE_N segments of the profiles suggests derivation from the same source with subsequent fractionation generating the LREE enrichment in carbonate-rich residua. In contrast, the profiles of marble calcites are heterogeneous with varied LREE-enriched, LREE-depleted and flat patterns.

Origin of the karaçayır carbonatites

Trace element geochemical and radiogenic and stable isotopic analyses suggest that the petrogenesis of Karaçayır carbonatites does not, in contrast to Schuiling's hypothesis, involve interaction of syenite with crustal materials at the exposed level of intrusion. There is, however, a consistent geochemical and mineralogical affinity of carbonatitic

rocks with the Karaçayır syenites. This affinity can be summarised briefly as:

1. Apart from the calcite present in calcite-zeolite pseudomorphs after nepheline in various syenites, all other carbonate occurrences appear to be in textural equilibrium with the silicate phases and are inferred to have a primary magmatic origin.
2. Compositions of silicate phases in carbonatites and calcite-syenites are similar and in general are more evolved than in Karaçayır monzonitic and syenitic rocks. The BaO contents for K-feldspar and the albite contents of plagioclase generally increase in the sequence syenites < calcite-syenites ≤ carbonatites. These mineralogical variations and the incoming of REE-bearing phases allanite and monazite are compatible with carbonatites having been produced from, and to have been in equilibrium with, an extensively evolved, calcite-bearing, foid-syenite magma.
3. Trace element concentrations (Sr, Ba, REE) in calcite show the enrichment carbonatites ≥ calcite-syenites > syenites >> marbles.
4. The oxygen, carbon, strontium, and lead isotope signatures of calcite in the calcite-syenites and carbonatites are coherent and similar to (although in the case of O heavier than, and for C isotopically lighter than) accessory calcite in syenite. Isotopically, they are totally dissimilar to calcites in marble that occurs as roof pendants or as in situ country rock. If, as implied by Schuiling's (1961) hypothesis, the carbonatites are formed by the interaction and liquefaction of marble adjacent to syenite, then the carbonatite calcite compositions should have O, C, Sr, and Pb compositions intermediate between the two end members, produced by binary mixing (c.f. Barbieri et al. 1975). Assimilation of limestone by silicate magma (e.g. Barnes et al. 2005; Chadwick et al. 2007) is generally reflected in the CaO-rich nature of the plutonic suite, with Ca accommodated by crystallisation of clinopyroxene, Ca-amphibole or anorthite-rich plagioclase. In contrast, in the Karaçayır pluton, small modal amounts of clinopyroxene and hornblende occur only in the most primitive monzonite component, and the plagioclases show uninterrupted fractionation to extremely albite-rich compositions.

Any of these individual chemical characteristics, and certainly the collective evidence listed above, precludes an origin of calcite in calcite-syenite or carbonatite from nearby marble enclaves or, more distally, from in situ marble at the syenite-country rock contact. The analytical data do, however, suggest affinities of the carbonatite with the syenite, a very similar relationship to that described by Worley et al. (1995) for carbonatitic rocks

associated with nepheline syenites in southern Victoria Land, Antarctica.

Based on experimental evidence and on published petrogenetic accounts, two main hypotheses might explain syenite-carbonatite evolution:

- (a) separation of the carbonatite as an immiscible fraction from a syenite parent magma (e.g. Beccaluva et al. 1992; Halama et al. 2005), or
- (b) progressive fractional crystallisation of a carbonate-rich silicate magma to yield a carbonatitic residuum (Bell and Rukhlov 2004; Downes et al. 2005).

Field evidence is somewhat ambiguous due to less than perfect exposure. However, the wide variety of rock types collected from the carbonatite-rich zone, with an abundance of mixed carbonate-silicate rock types (e.g. Fig. 2a), coupled with the absence of sharp boundaries between rock types, would suggest that relationships between the silicate-dominated and carbonate-dominated lithologies are gradational.

Geochemical analytical data, specifically REE, and other trace elements (e.g. Sr, Ba) are compatible with the carbonatites representing a more advanced stage of fractionation than the syenites. This evolutionary process is supported and reinforced by the mineral analyses of silicate minerals that generally show more evolved characteristics (lower Mg# of mafic minerals, higher Ab contents of plagioclase, greater BaO contents of K-feldspar) in carbonatites than in syenites. One feature common to many of the syenites, some of the calcite-syenites, and one of the carbonatites is that the final crystallisation phases include monazite and allanite, the latter forming a corona or reaction rim along grain boundaries. This is interpreted to result from in situ fractionation.

Although marble syntexis by evolved silicate magmas may be appropriate for the origin of apatite-calcite $\pm$ fluorite vein dykes in the CMB of the Grenville Province (Lentz 1998), it would appear to be unlikely to explain the carbonatitic rocks of the Karaçayır pluton.

Conclusions

The Karaçayır syenite pluton, Central Anatolia, Turkey, is inferred, on the basis of radiometric ages and Sr–Pb isotope ratios, to be a composite intrusion. It encloses a number of xenoliths of country rock marble. Coarsely crystalline, calcite-rich rocks, rich in Ba, Sr, REE, and Th and spatially associated with calcite-syenites, have been previously interpreted by Schuiling (1961) to be of magmatic, carbonatitic affinity, formed by metasomatic alteration and melting of limestone by the syenite host. However, in terms

of mineralogy, trace element geochemistry, and Pb–Sr–O–C isotope compositions, calcite-syenites and carbonatites show compositional ranges that are compatible with progressive fractionation of parental carbonate-bearing syenite, without involving melting or assimilation of marble.

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