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Polymetamorphic Relations in Iron Ores from the Iron Quadrangle, Brazil: The Correlation of Oxygen Isotope Variations with Deformation History

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Abstract. This study deals with the oxygen isotope composition of hematite-rich ore bodies in the Iron Quadrangle, Brazil. The area studied can be divided into two different regions: a western (W) zone of greenschist facies assemblages and an eastern (E) zone of amphibolite facies with transitions into granulite facies assemblages.

The $\delta^{18}O$ values of 136 quartz-iron oxide pairs have been determined and "temperatures of formation" have been calculated. The $\delta^{18}O$ values of quartz vary between $+6$ and $20‰$ except one value near $+23‰$, whereas the iron oxides fall between -4 and $+10‰$, with nearly 80% of the iron oxide values between -0.5 and $4.0‰$. The regional distribution of the $\delta^{18}O$ values is as follows: in the W-region 85% of the quartz are $>12‰$, whereas in the E-region only 46% fall in this range. In contrast to quartz the iron oxides do not show any regional differences.

The variation of oxygen isotope fractionations between quartz and iron oxides is obviously related to the complex deformation history of the iron ores. Samples with a primary schistosity (S_1) only represent peak metamorphic conditions. In the E-region the (S_1) high temperatures $>700°$ C seem to correspond to orogenic events in the Archaen basement 2,700 m.y. ago. In the W-region S_1-temperatures between 460° and 560° C seem to represent peak metamorphic conditions of the Proterozoic Minas metamorphism 2,000 m.y. ago. Iron ores which have been overprinted by later deformation events are selectively reset to lower "isotopic" temperatures. The more closely spaced the schistosity planes the larger the extent of a temperature lowering.

The genetic processes associated with these hematite-rich ore bodies appear to be sedimentary-metamorphic rather than metasomatic processes. Furthermore, there is no evidence for secondary leaching by weathering solutions.

Introduction

Metamorphic banded iron ores of sedimentary origin are found on all continents in Precambrian shield areas. Virtually all commercial iron ores are derived from this type of deposit, and the economic importance of these terrains has generated much discussion (see for instance: Economic Geology 68, 1973 and UNESCO Symposion Kiev 1970, Earth Science 9, 1973).

Precipitation of banded quartz iron formations – known as itabirites in Brazil – appears to have been a dominant process in the Late Archean and the Early Proterozoic oceans. Among the problems associated with these formations is the genesis of hematite rich ores such as those found in the Iron Quadrangle, Minas Gerais, Brazil. While these ores comprise only a few per cent of the primary itabiritic quartz iron formations, they are the source of nearly all the iron ore mined today in Brazil. The extent of enrichment is shown by the differences between the mean iron content (38%) in the Minas Gerais banded iron formations and the iron contents ($>63\%$) in the hematite-rich ore deposits.

According to Dorr (1965) the high-grade metamorphic hematite-rich ores were enriched by synmetamorphic metasomatic replacement of quartz in the host itabirite by hematite derived from the iron formation itself. Dorr assumed that transport of iron to and quartz from the sites of replacement was carried out by high-temperature fluids. Dorr also proposes that the hard massive hematite ores were partially converted to soft ores by the leaching action of surface waters during Mesozoic and Tertiary time. If metasomatic solution of quartz and replacement by iron oxides took place, huge quantities of fluids were required to dissolve immense masses of quartz which would amount to more than 50% of the itabirite volume. There is no evidence for quartz-leaching in the country rocks. If metasomatism was operative there should be field evidence for the substantial amounts of dissolved quartz which would be transported and eventually redeposited. This was the starting point of our investigation.

As is well known, oxygen isotope studies are especially useful in geothermometry as well as in suggesting possible sources of water. Earlier studies of $^{18}O/^{16}O$ ratios in iron formations – primarily concerned with the effects of metamorphism – are those by James and Clayton (1962), Sharma et al. (1965), Perry and Bonnichsen (1966), Perry et al. (1973), Becker and Clayton (1976), Perry et al. (1978), and Perry and Ahmad (1981). In our study it is demonstrated that metamorphic rather than metasomatic processes explain the measured $\delta^{18}O$-values. It will be also shown that from the calculated "temperatures of formation" more than one metamorphic event can be deduced.

Geologic and Petrographic Background

Figure 1 shows a map of the area under study comprising about $\sim 11{,}000$ km^2 in which the iron ore deposits and sample locations are given.

The basement of the Quadrilátero Ferrifero is composed of migmatites, gneisses, amphibolites, soapstones and probably limited occurrences of banded iron ores which were strongly metamorphosed in the Archaen 2,7 billion years ago (Table 1). As is well known, this orogenic cycle about 2,7 billion years ago

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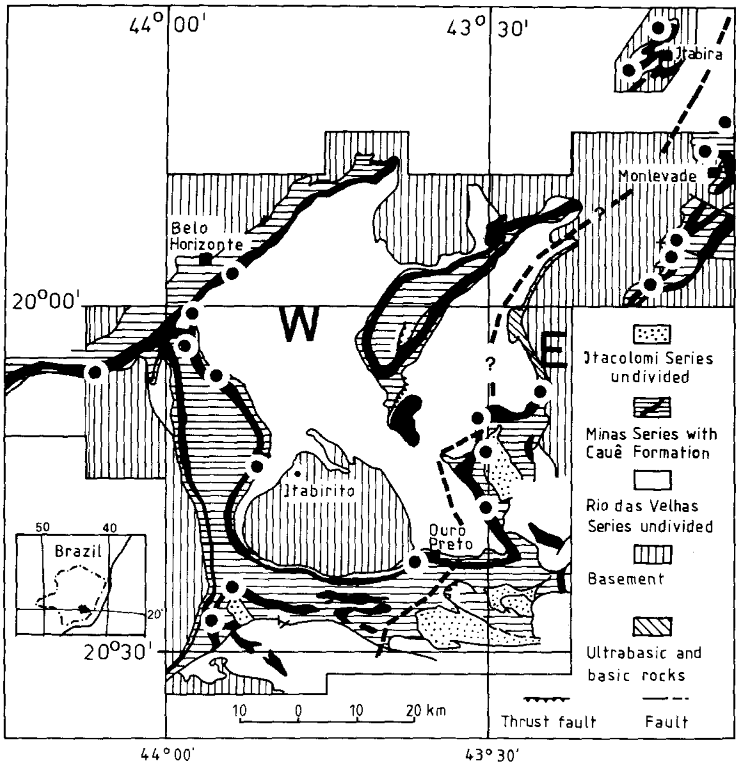

Fig. 1. Map of sampling points (Geology after Dorr et al. 1969); *dashed line* = "staurolite in" after Schorscher 1975, Roeser 1977, Glöckner 1981 and own observations near Ouro Prêto. W-area = greenschist facies; E-area = amphibolite and granulite facies

Table 1. Simplified stratigrafic column of the Quadrilátero Ferrifero (after Dorr 1969)

Age	Series	Lithology	Orogenic cycles and their ages
		Unconformity	Transamazonian cycle 2.0 – 1.8 b.y.
Early Proterozoic	Minas	Metavolcanics, metatuff. Phyllitic quartzite, chlorite phyllite and schist, graphitic phyllite, dolomitic phyllite, ferruginous phyllite. Dolomite, siliceous dolomite, dolomitic itabirites. Itabirite (banded iron ore) and hard hematite ore (± magnetite). Conglomerate, quartzite.	
	Rio das Velhas	Unconformity Conglomerate, quartzite, phyllite, graywacke, subgraywacke	
		Unconformity	Jequie Cycle 2.8 – 2.7 b.y.
Archean	Basement	Granitic rocks, migmatite, schists, gneisses, amphibolite, metavolcanics, soapstone, banded iron ore (?)	

forms a worldwide pattern (Moorbath 1976) and is documented for instance in the Guayana shield of northern South America (Hurley et al. 1976). Rb/Sr determinations of basement rocks in the Quadrilátero Ferrifero (Herz 1970; Cordani et al. 1980) and from other regions of Central Brazil (Hasui and Almeida 1980; Cordani et al. 1973, Cordani and Iyer 1979; Brito Neves et al. 1979; Sighinolfi et al. 1981) yield similar ages between 2,7 and 2,8 billion years. In Brazil these ages represent the Jequié Cycle.

On top of this basement a series of older sediments (Rio das Velhas) and of younger sediments (Minas) is deposited (Table 1). The rocks of these two series were metamorphosed into schists, quartzites, itabirites, rich iron ore bodies, amphibolites and marbles some 2.0–1.8 billion years ago. As shown by Hurley et al. (1967) in South America this orogenic cycle can be dated in Venezuela, in the Guayana States and in Brazil north of the Amazonas River and was named 'Transamazonian Cycle'. In the Quadrilátero Ferrifero the regional metamorphism of this orogenesis got the local name "Minas metamorphism" since the Minas sediments are the youngest deposits which were transformed by this metamorphic event (Table 1). All Precambrian rocks of the Iron Quadrangle underwent tectonic stress of locally different intensities, thus the itabirites and rich ores both exhibit all features of schistosity and brecciation. The complex tectonic style of the itabirites and their relation to the rich ore bodies are described by Harder and Chamberlin (1915), Dorr (1964, 1965), Dorr and Barbosa (1963), Eichler (1968), Hackspacher (1979) and Rosière (1981). A summary of the relationships between folding, shearing, fracturing and metamorphic recrystallization during the three main phases of deformation is reproduced in Fig. 3 after Guba (1981).

The main ore minerals are: hematite, magnetite, martite and limonite accompanied by quartz in variable quantities and sometimes iron amphiboles, iron-rich micas and chlorites. In carbonaceous, argillaceous and tuffaceous itabirites the mineral assemblages are more complex. Pure quartzites, formerly cherts, change layer by layer into thin-bedded itabirites and itabiritic ores. Hard massive and bedded hematite ores form numerous stratiform banks a hundred meters or more thick and of several kilometers strike length. But in other exposures the ore bodies occur as lenses discordantly cutting the adjoining beds and folds. With respect to the metamorphic grade Simmons (1968), Eichler (1968), Moore (1969), Schorscher (1975) and Lauenstein (1981) investigated the paragenesis of coexisting silicates in sedimentary iron ore bearing sequences of the Iron Quadrangle. In the country rocks of the western area typical mineral assemblages are:

a) albite + quartz + clinozoisite + chlorite + muscovite/phengite ± stilpnomelane ± biotite;

b) talc ± dolomite ± quartz;

c) chlorite + chloritoid + muscovite + quartz.

All these mineral assemblages indicate temperatures of greenschist facies.

With increasing metamorphic temperatures to the east albite is replaced by more calcic plagioclase and biotite + chlorite is replaced by green-blueish amphibole. Talc disappears and tremolite ± quartz + dolomite becomes stable (Lauenstein 1981).

In the eastern border zone Lauenstein observed the amphibolite facies assemblages: diopside + quartz + dolomite + Mg-riebeckite + biotite + magnetite/hematite. Also, kyanite + muscovite + quartz assemblages were described from this zone by several authors (Reeves 1966; Schorscher 1975, Lauenstein 1981 a.s.o.). Schorscher (1975) noted in high grade metamorphic rocks of the eastern border zone the assemblage: sillimanite + quartz + garnet + cordierite and interpreted the breakdown of amphibole and the formation of clinopyroxene in amphibolites as the beginning of a granulitization process.

In summary it seems that in the western part maximum temperatures corresponded to greenschist facies and in the eastern part to amphibolite facies with transitions into granulite facies. The border of the western zone is marked by the breakdown of chloritoid and the appearance of staurolite (Fig. 1). The subdivision into two areas is also reflected in the $\delta^{18}O$-values as will be shown later.

Sampling and Analysis

Most of the rocks in Central Brazil are overlain by a thick weathered cover, but due to large mining excavations and road cuts a lot of fresh samples are available. 375 samples of 3–5 kg weight were taken in the Iron Quadrangle (see Fig. 1) and supplemented by 5 samples from the Southern Serra do Espinhaco.

From the 380 samples 143 (see Table 2) were selected for mineral separation through jaw crushing, pulverizing in a disc mill, sieving, magnetic separation in series of different steps and fractionations, enrichment of specularite and talc on a vibrating table, heavy liquid separation, grinding in an agate mortar for separating the finest intergrowths, and in all cases stereomicroscopical selection of pure mineral concentrates by hand picking.

Minerals used in the oxygen isotope investigations were: quartz, hematite, magnetite, martite and a few concentrates of talc.

Initially, samples with small amounts of martite and magnetite were separated from the main constituent hematite and measured separately. Since the concentrates of martite, magnetite and hematite did not show any difference in $\delta^{18}O$ to that of the total iron oxide fraction, this complicated and time consuming procedure was considered unnecessary.

Oxygen was extracted from the minerals by reacting the samples with BrF_5 (Clayton and Mayeda 1963). The $\delta^{18}O$-values are defined in the usual way and given relative to SMOW. The analytical reproducibility is within $\pm 0.2‰$. Temperatures were calculated with a computer program (Hoernes 1980). We have used for the calculation the experimentally determined fractionation curves for quartz-water according to Matthews and Beckinsale (1979) and for magnetite-water according to Bertenrath et al. (1973). The latter curve has been applied also to the calculation of quartz-hematite and quartz-martite, temperatures. Furthermore for a comparative discussion (see p. 247) formation temperatures were also calculated using the curve compiled by Friedman and O'Neil (1977), which is based on the data given by Becker (1971).

Table 2. Raw-material classification of investigated itabirites and rich ores

Name	Fe%	Physical properties	n [a]
Quartz-itabirite	< 30	compact and hard or arenaceous or dusty weak	2
Itabirite (sensu stricto)	30–50	compact and hard or arenaceous or dusty weak, partially carbonaceous and silicate bearing	30
Rich itabirite	51–63	compact and hard or dusty weak	29
Hard hematite ore ± magnetite	> 66	Lumpy, hard, coarse grained, blueish-gray, magnetite ore sometimes very coarse grained	39
Soft hematite ores	> 66	fine flaky, platy, soft sliding, "blue dust"	39
Hydrothermal veins	variable	very coarse grained	4

[a] Number of samples

Results

All $\delta^{18}O$ data are given in the Appendix. Figure 2 summarizes the $\delta^{18}O$-values of 136 investigated quartz and 156 iron oxide samples. The difference in the number of samples is due to duplicated runs of the different iron oxide fractions of hematite, magnetite and martite which were separated from each other at the beginning of the investigation, but regarded unnecessary lateron. The lower histogram (a) in Fig. 2 shows the distribution curve for all quartz and iron oxide samples. The $\delta^{18}O$-values of quartz range between +6 and +20‰ except one heavy value near +23‰. The $\delta^{18}O$-variation range of the iron oxides is between −4 and +10‰; with nearly 80% of the values between −0.5 and +4‰. With respect to regional differences (histogram b and c) it is interesting that although the overall range of the δ-values is the same, on average the quartz of the low grade metamorphic W-area is isotopically heavier than in the high grade E-area. In the W-region 85% of the values are above +12‰, whereas in the E-region only 46% are in this range. In contrast to quartz the iron oxides do not show any regional differences, not only the range of the $\delta^{18}O$-values but also the distribution curves are very similar.

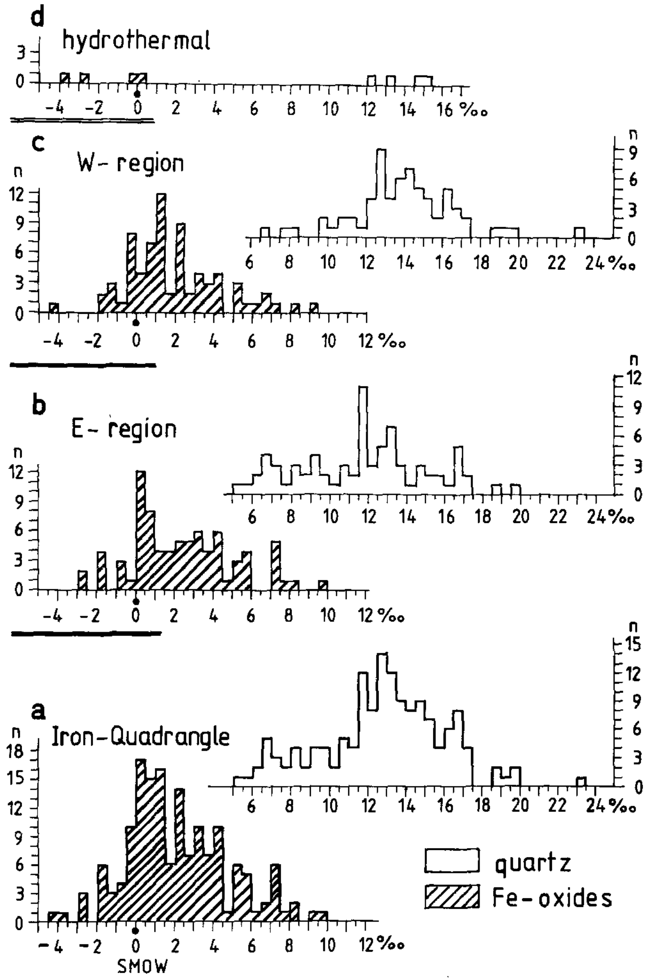

Fig. 2a–d. $\delta^{18}O$ values of iron oxides (dominantly hematite) and coexisting quartz relative SMOW from the Iron Quadrangle, Minas Gerais

The upper histogram (d) in Fig. 2 shows the $\delta^{18}O$-values of some hydrothermal quartz-specularite samples found in fissures. While the $\delta^{18}O$-values of the quartz samples coincide with the metamorphic samples, the iron oxides from big tabular specularites have relatively low $\delta^{18}O$-values.

The four hydrothermal quartz-hematite pairs show high Δ-values (δ_Q–δ_H) between 14.5–17.5‰ and therefore the calculated temperatures of formation are relative low (350–250° C, Appendix).

Talc was separated from 6 rock samples for oxygen analyses. The variation range and the Δ-fractionations between talc and hematite are tabulated in the Appendix. Since an experimentally determined or calculated fractionation curve for talc-water does not exist, "temperature of formation" for the talc-hematite pair cannot be derived. However, the data represent relative temperature differences. All 4 samples from the Cauê Mine show very constant Δ-values around 6.6‰ and indicate lower temperatures than the 2 other samples from the mines Morro Agudo (5.4‰) and Piçarrão (5.0‰). From our data it appears that the talc-iron oxide pair is a potential geothermometer.

To elucidate the $\delta^{18}O$-values, differences in the fractionation factors and in the temperatures of formation it is necessary to consider the complex deformation history of the iron ores in the Iron Quadrangle. Figure 3 presents a schematic drawing of the different deformation phenomena observed in the iron ores.

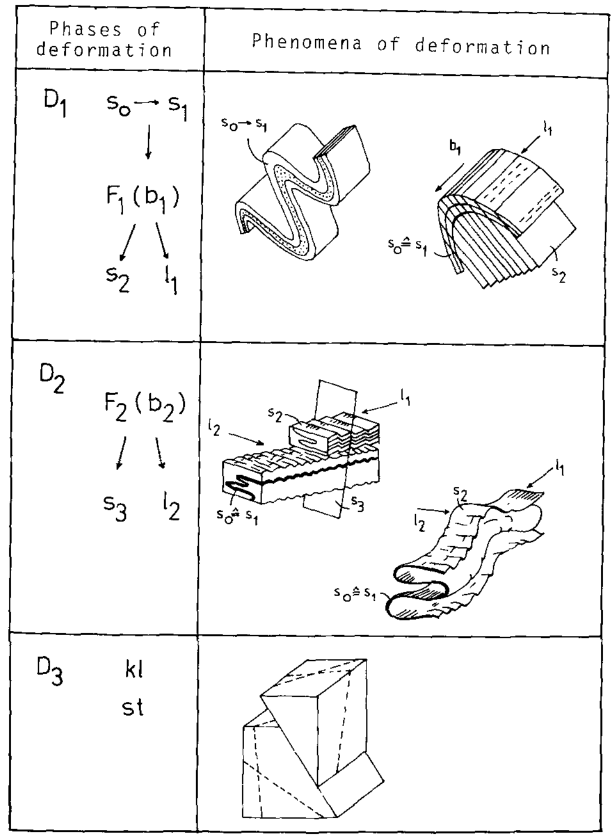

Fig. 3. Deformation and recrystallization history of the Iron Quadrangle rocks (after Guba 1981)

In some areas of the Iron Quadrangle three phases of rock deformation (Fig. 3) can be distinguished but normally the folding of only two (D_1 and D_2) was accompanied by strong recrystalliation of minerals even if detailed relationships were more complex. Samples showing S_1 only occur together with $S_1+S_2+S_3$ affected ones in the same outcrop. Sometimes distances of a few meters only are observed between compact and strongly schistosed samples. The oldest fabrics of the itabiritic ores in the W-region show equigranular anhedral grains of hematite, magnetite and quartz in microlayered itabirites and are probably of relictic diagenetic origin. In those parts of the rocks where the stress was weak, only the isometric magnetite crystals exhibit minor elongation (Fig. 4a, lower part). In those rocks where the stress was higher euhedral tabular hematite grew in direction of s_1-schistosity (Fig. 4a, upper part). Synmetamorphic folding is common (Fig. 4b and c).

Late kinematics produced another direct recrystallization and schistosity (s_2). The latter cuts the sedimentary itabiritic layering (s_0) as well as the older deformation fabrics (s_1) at various angles (Fig. 4a, b and c). S_2 is quite differently developed. Sometimes only a few newly formed tabular hematites indicate the direction of s_2 whereas in other samples all older fabrics were extinguished completely (Fig. 4a–c).

Associated with post metamorphic tectonic movements (described in detail by Rosière, 1980, p. 53–58), are fracture zones in which quartz and hematite were crashed strongly. Due to these low crashing temperatures recrystallization phenomena in the minerals are very slight. Kink folds and kink bands (s_3) are quite typical for those rocks (Fig. 4d). In the eastern part of the Iron Quadrangle premetamorphic fabrics were destroyed completely by intense high grade metamorphic recrystallization

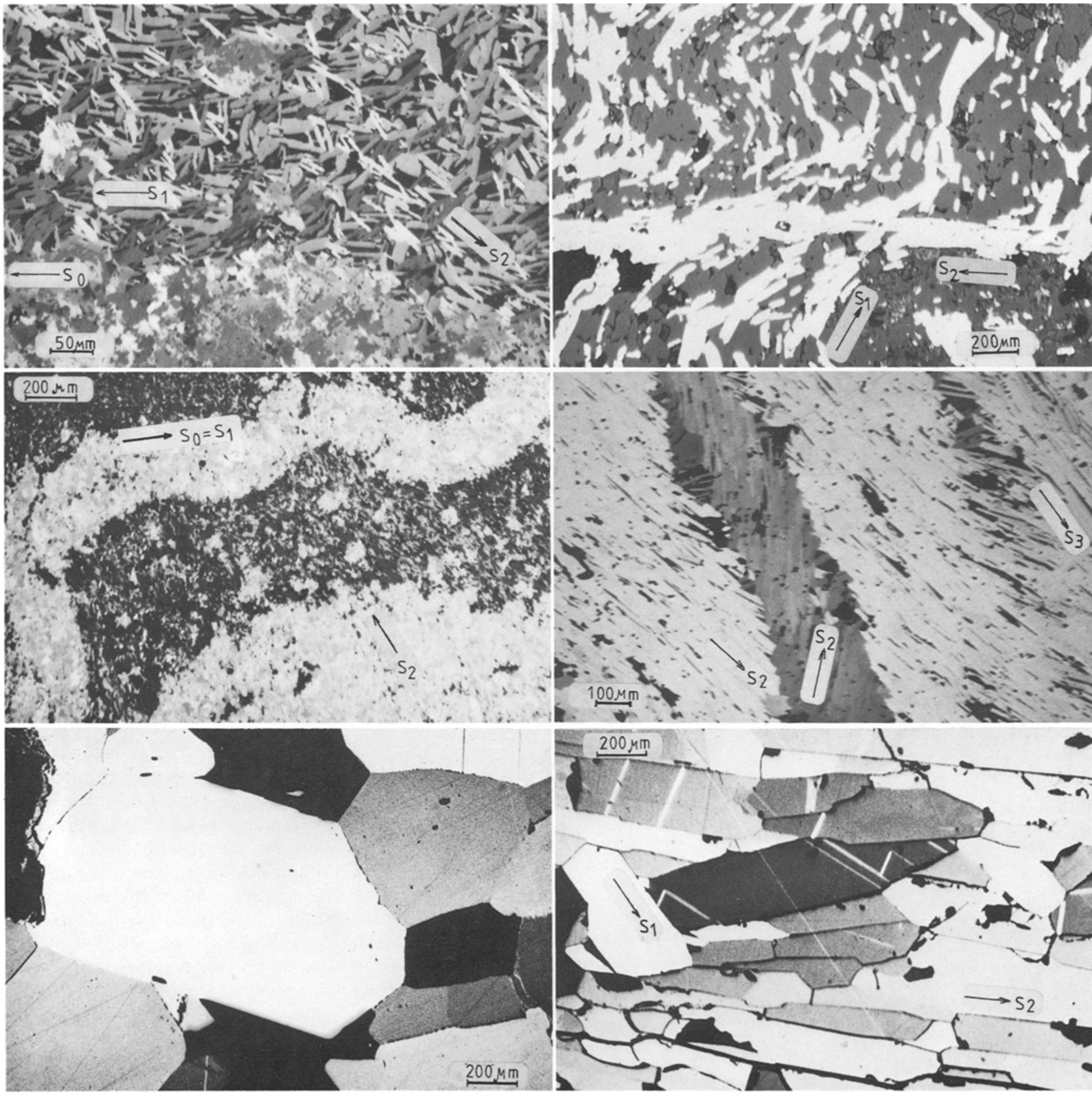

Fig. 4. Deformation phenomena in polished sections (a–f, from left to right). **a** Relictic (probably diagenetic) fabric of anhedral hematite, magnetite-martite and quartz (s_O) in the lower part. In the upper field euhedral tabular hematite reflects the schistosity s_1. Another generation of euhedral tabular hematite (s_2) cuts the older schistosity (s_1). Relics of martitised magnetite are preserved in the upper part of Fig. 4a. Sample no. 294, Mutuca Mine, W Belo Horizonte. **b** Quartz-rich itabirite layer with folded s_1-hematite strings cuts late-kinematic formed hematite (s_2) parallel to the b–c planes of the folds. Sample no. 248, Road cut, 5 km W Ouro Prêto. **c** Sedimentary iron ore and quartz layers (s_0) were folded (s_1) and recrystallized, but the schistosity s_1 was extinguished completely by the late kinematic schistosity s_2. Sample no. 298, Mutuca Mine, S Belo Horizonte. **d** Postmetamorphous "cold" deformation yields kink bands (s_3) which break through s_2. Sample no. 80, Germano Mine, N Mariana. **e** High grade coarse grained granoblastic texture (s_1) of the eastern zone. Sample no. 163, Piçarrão Mine, NW Nova Era. **f** Euhedral tabular hematite shows strong schistosity (s_2). s_1 (see Fig. 4e) is preserved only in a few relics. Sample no. 06, Espigão do Pico, SE Jõao Monlevade

which produced granoblastic coarse grained textures (Fig. 4e). These s_1-fabrics were more or less extinguished by recrystallization under stress and a schistosity (s_2) was formed (Fig. 4f).

Figure 5 shows the Δ-values of both regions subdivided after their predominant fabrics which were formed by different metamorphic and tectonic events. In the E-region s_1 represents coarse grained samples of high metamorphic grade and primary foliation (Fig. 4e). The secondary slaty fabrics (s_2) in the first deformation phase cutting (s_1) were produced by recrystallization under stress (Fig. 4f). In the W-region the three samples near $7^0/_{00}$ (Fig. 5c) represent probably relictic premetamorphic structures whereas most samples with Δ-values between 8 and $11.5^0/_{00}$ were recrystallized by metamorphic schistosity (s_1) parallel to layering of itabirite (Fig. 4a). Later the minerals were straight-

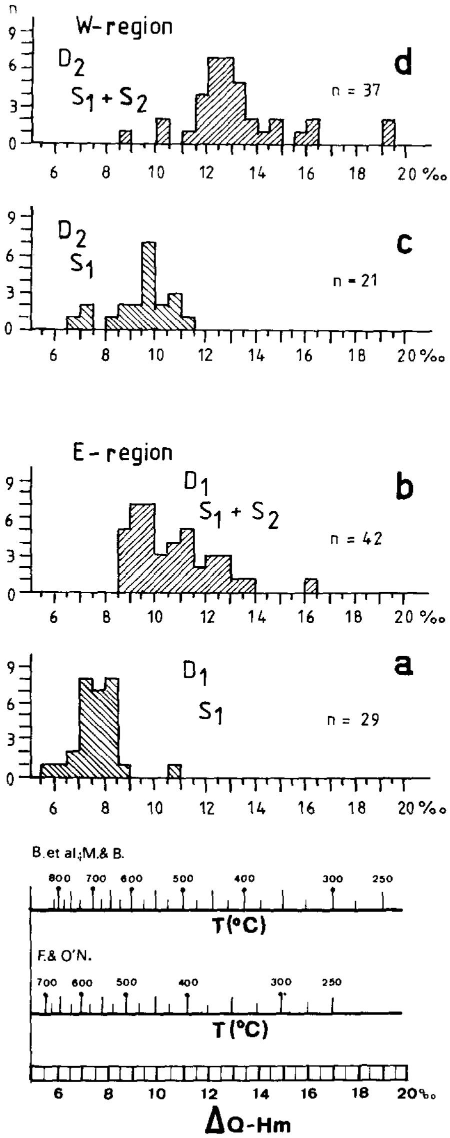

Fig. 5a–d. Δ-values qz-hem of the W- and E-region, Iron Quadrangle, subdivided after their predominant fabrics (*upper part* **a–d**) and two corresponding temperature scales (*lower part*). The upper scale (B. et al., M.B.) bases on data by Berthenrath et al. (1973) and by Matthews and Beckinsale (1979), the lower scale (F.+O'N.) bases on the curve given by Friedman and O'Neil (1977)

ened out to axial plane cleavages and strain slip cleavages by s_2. As Figure 5 demonstrates Δ-values diminish generally from s_2-samples in the west to s_1-samples in the east. The similiarity in the Δ-values of s_1 in W and of s_2 in E suggests metamorphic recrystallization of both regions under the same temperature conditions but in different tectonic phases. Another point is the partial overlapping of s_2-Δ-values and some s_1-Δ-values in both regions in the range between 10 and $14^0/_{00}$.

In the lower part of Fig. 5 two temperature scales, the lower according to the curve compiled by Friedman and O'Neil (1977), and the upper according to Matthews and Beckinsale (1979) for quartz-water and for magnetite-water after Bertenrath et al. (1973) are drawn. As seen, the upper scale indicates higher temperatures than the lower scale; more specifically the difference amounts to 140° C at the left side of the scale and reduces to 50° C at the right side. Besides these discrepancies, the most important point is that in the high grade metamorphic E-region as well as in the low grade W-area the s_2 affected ore samples always are associated with lower temperatures than the unaffected. Obviously, the closer the cleavage the more internal reaction surfaces favor isotopic exchange at lower temperatures. All s_1-samples of the E-region with coarse grained granoblastic textures are restricted to a high temperature field accompanied by a few s_1-samples from the southernmost part of the W-region. It is noteworthy that this high-temperature field is very different depending upon which scale is used in Fig. 5: upper scale: 815–635° C, lower scale: 675–500° C. The importance and meaning of this difference is discussed later.

Samples affected by s_2 in the E-region (Fig. 5b) partially overlap with samples affected by s_1 and s_2 in the W-region (Fig. 5c and d). Δ-values $> 14.5^0/_{00}$ and temperatures $< 375°$ C (Fig. 5, upper scale) resp. $< 310°$ C (Fig. 5, lower scale) represent samples of extreme schistosity (Fig. 4d) with secondary limonite on the cleavage planes and in addition specularite-quartz pairs from hydrothermal veins and fissures.

Discussion

a) Metamorphic Environment

There is a general agreement that the banded iron formations are of sedimentary origin and have been precipitated in sea water. Although the original isotopic composition of the SiO_2 and iron oxide phases are unknown, both mineral phases should be determined by the isotopic composition of the Proterozoic ocean. Assuming for the Precambrian ocean a $\delta^{18}O$-value of zero like today's ocean and the temperatures of precipitation were around 25° C, (we are fully aware that both assumptions are extremely controversial and may not be verified), we may estimate that the precipitating iron oxides should have $\delta^{18}O$-values around $-5^0/_{00}$ (see the calculated magnetite-water curve by Becker and Clayton 1976) and that the chert was around $+35^0/_{00}$. If such an assemblage is metamorphosed, fractionations between the two phases must decrease with increasing temperatures. If the amount of oxygen bound in both minerals is about the same and the water-rock ratio is sufficiently low the isotopic composition of both minerals should move towards each other. And this is observed in principle, but the $\delta^{18}O$-values of the quartz samples ($+6$ to $+17^0/_{00}$) are considerably more lowered than the $\delta^{18}O$-values of the iron oxides (-2 to $6^0/_{00}$) are raised. The reason for this relationship might be that the amount of oxygen in the iron oxides determines the isotopic composition of the quartz which reaches in some high-temperatures very unusual values of as low as $+6^0/_{00}$. In other words, during prograde metamorphism of the banded iron ore the fluid/rock ratio is progressively reduced by dehydration reactions and in the highest metamorphic grade the amount of fluid may be so small, that its isotopic composition may be buffered by that of the mineral assemblages especially that of the iron oxides, and that the fluid may act as a kind of catalyst to perform isotope exchange between minerals. Besides, to assume a closed system to water or low water/rock ratios there exists an alternative although geologically not very probable interpretation. From the measured $\delta^{18}O$-values of the quartz and of the iron oxide and the calculated temperatures, the isotopic composition of the fluid phase with which the mineral assemblage was in equilibrium may be calculated. Such a calculation exhibits that most waters have $\delta^{18}O$-values between $+5$ and $+15^0/_{00}$, the range being typical for metamorphic waters. However, the relatively dry mineral assemblages in the iron ores and in the country rocks contradict that large quantities of metamorphic waters have interacted with the rocks in an open system environment, but favor the closed system environment.

b) Metamorphic Temperatures

Concerning oxygen isotope thermometry in metamorphic rocks there is considerable discussion about whether the calculated temperatures may represent peak metamorphic conditions or whether they are influenced by some retrograde isotope exchange during cooling. Although both quartz and iron oxides seem to be fairly resistant to isotope exchange after formation, Deines (1977) and Dahl (1979) have convincingly demonstrated that reequilibration between quartz and iron oxides may occur after the peak of a metamorphic event. Graham (1981) argued that the availability of a fluid phase plays the decisive role in this respect. If the fluid is lost from the system at peak metamorphic conditions the calculated temperatures will reveal maximum temperatures. If on the other hand a fluid phase is available and able to catalyze isotope exchange, it will occur during cooling until isotope exchange ceases due to slow diffusion.

As demonstrated above oxygen isotope fractionations correspond to the various deformation and recrystallization phases and to the temperature record obtained from other field evidences. Relatively good agreement can be achieved when using the magnetite-water curve of Berthenrath et al. (1973) and the quartz-water curve of Matthews and Beckinsale (1979). Staurolite, for example, is a widespread mineral in the country rocks hosting the ore bodies in the E-region (see Fig. 6). The work of Hoschek (1967, 1969) indicates that the formation of staurolite needs minimum temperatures of some 550° C. The breakdown of hornblende and the formation of clinopyroxene takes place in the same temperature range. Schorscher (1975) observed sillimanite in the eastern border zone whose formation also needs relative high temperatures. From this point of view the s_1-temperature field between 635° and 810° C (Fig. 5, upper scale) shows better agreement with field observations than the lower scale in Fig. 5, which reaches down as low as 510° C.

If we use other isotopic fractionation curves such as the quartz-magnetite curve drawn by Friedman and O'Neil (1977) (basing on the data of Becker 1971) the calculated temperatures become considerably lower especially in the high temperature environment, and then the data must be interpreted in terms of retrograde effects. As we know from experimental petrology reaction rates below 400° C are very low. If the lower curve in Fig. 5 is correct the temperatures for one third of the samples will fall into the field of zeolite facies which is not consistent with the mineral assemblages of the adjoining phyllites and schists of greenschist facies. However, the upper scale of Fig. 5 shows only a few cataclastic s_3-affected samples in this low temperature range and in addition four hydrothermal mineral pairs. On the other hand three samples of the s_1-type in the W-region (Fig. 5c) indicate temperatures in the range 560–590° C but should correspond to temperatures below 550° C according to field evidence (Eichler 1968).

We thus propose that the Matthews and Beckinsale (1979) and Berthenrath et al. (1973) calibration curves should be used for quartz-iron oxide isotope thermometry. We are fully aware, however, that this is in contrast to some extent to the recently published (Downs et al. 1981) and directly determined isotopic fractionation values for quartz and magnetite at 600° and 800° C. The fractionation curves given by them, although lying between the Bertenrath et al. (1973) and Becker (1971) curve, fits more closely the data given by Becker (1971).

In many cases past discussions about the importance of retrograde effects might be due to the fact that other oxygen isotope calibration curves such as the magnetite-water curve of Becker and Clayton (1976) were used. Temperatures some 30° C below the upper temperature scale in Fig. 5 would give in the temperature range between 500° and 600° C the best agreement between the calculated isotopic temperatures and the field relationships (see Simmons 1968; Eichler 1968; Moore 1969; Schorscher 1975; Lauenstein 1981 and other authors) and would favor peak metamorphic conditions for those samples, which only show primary schistosity (s_1-foliation). In the eastern border zone very low Δ-values between 9 and 6‰ and correspondingly high temperatures from 600° to 800° C characterize this sample group (S_1) which are associated to sillimanite and cordierite-bearing garnet feldspar gneisses (Schorscher 1975). In metabasites he observed the breakdown of hornblende and the formation of clinopyroxene. Lauenstein (1981) found in metamorphic marls the evidence for the reaction of dolomite + quartz to diopside + CO_2. Thus, it appears obvious that these gneisses and metabasites recrystallized at temperatures > 600° C sharing the same geological history as the juxtaposed high grade metamorphic ores.

Stratigraphic relationships between high grade iron ores in the eastern border zone (Piçarrão, Andrade etc.) and adjacent gneisses, schists and amphibolites are still unknown but the iron ores and the country rocks should have experienced a similar metamorphic and tectonic history. Thus Schorscher (1975, p. 7) described the retrograde metamorphic transformation of migmatites into mylonites and greenschist facies rocks. Roeser (1977) found retrograde recrystallized gneisses in the Mariana Quadrangle. Relics of large microcline crystals yield Rb/Sr ages of some 2,7 billion years whereas the granoblastic recrystallized gneisses represent an isochron of 2.0 billion years (Cordani et al. 1980). Furthermore, Roeser and Müller (1977) studied two groups of amphibolites in the southeastern border zone. The first one shows dominant igneous relic textures whereas the second one is characterized by a pronounced alignment of minerals in s-planes. These observations may support our conception that high grade metamorphic iron ores as well as high grade silicate rocks of the eastern border zone were not completely overprinted by the recrystallization and tectonics of the Minas orogenesis. This is also documented by the staurolite-sillimanite assemblages in the E-region. Figure 6 shows the course of the staurolite isograd together with the highest temperatures of the rich ore bodies. East from Ouro Prêto the calculated temperature is 595° C (Fig. 6), west from Ouro Prêto it is 520° C, which agrees with petrological data given by Hoschek (1967, 1969) who showed that the formation of staurolite takes place at 540–565 ± 20° C. This relationship favors peak temperature for the W-region in the triangle Ouro Prêto-Itabirito-Congonhas do Campo. In addition, field observations by Simmons (1968), Schorscher (1975) and own microscopic studies of rocks between Mariana and Ouro Preto revealed the two following mineral reactions:

chloritoid + kyanite
$\rightarrow$ staurolite + quartz + H_2O;

chlorite + muscovite
$\rightarrow$ staurolite + biotite + quartz + H_2O.

The course of the staurolite isograd in the northern branch is unclear (see "Regional aspects").

c) Regional Aspects

As shown above high temperature ores (600°–800° C) are restricted to the eastern border zone of the Iron Quadrangle where great thrust faults and nappes were described by Barbosa (1960), Dorr (1965), Schorscher (1975), Reimer (1979) and Glöckner (1981). Schorscher (1975) studied the petrological relationships

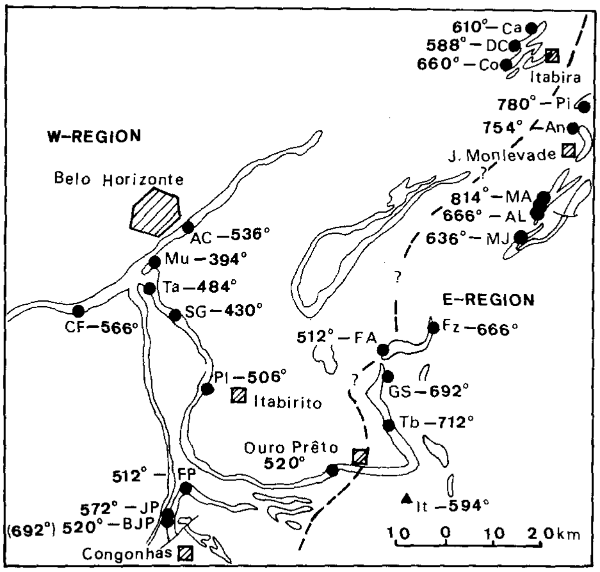

Fig. 6. Regional distribution of maximum temperatures calculated from the curves given by Matthews and Beckinsale (1979) and by Bertenrath et al. (1973). Due to field evidence the temperatures should be lower in the eastern region by 35° C and in the western region by 25° C (Full names of the mines, see Appendix)

of gneisses, amphibolites, schists and other metamorphic rocks in the area between the towns of Itabira and Nova Era. He concluded that the Minas metamorphism generally increased from west to east and changed from high-pressure Barrovian-type to low-pressure Abukuma type.

Our data offer a different interpretation of the petrological and geological setting in the eastern border zone. During the Minas orogenesis high-grade metamorphic rocks of Archean age were dislocated in the region east from the Iron Quadrangle and thrusted westwards above the sediment sequences of the Proterozoic Minas trough. The thrusted nappes include itabirites and rich ore bodies which were partially stressed by tectonic transport and recrystallized.

In many high grade metamorphic ore samples the old s_1-foliation is crossed by cleavages of s_2, which is accompanied by an increase of the Δ-values of s_2-samples from an average value of 7.5‰ to 8.5–14.0‰ depending on the extent of secondary recrystallization. The newly equilibrated samples give now mixed Δ-values. In case of complete recrystallization Δ-values reflect the temperatures of Minas metamorphism (Transamazonic cycle after Hurley et al. 1967). Besides the allochthonous ores of Pre-Minas age autochthonous Minas ores do also occur in the E-region. These itabirites and other sediment sequences of Minas age were only affected by the Minas metamorphism and therefore the bulk of the samples reflects in both regions the temperatures and Δ-values of this metamorphic event.

The samples of the mine Piçarrão (no. 159–174, appendix) are with one exception (no.161) s_2-unaffected and have very low Δ-qu-hem values between 8.4 and 6.2‰ which is equivalent to high metamorphic temperatures in the range of 640°–780° C. Similar relationships show the samples of the mine Morro Agudo (no. 008–033, appendix). There is no doubt that these rich ore bodies belong to the Archean. ^{18}O temperatures of granulitic rocks from the Archean granulitic belt in eastern Minas Gerais (unpublished results by Herbert and Hoefs 1980) yield temperature values in the same range between 600° and 800° C.

In other mines of the eastern border zone such as Cauê Conceição, Dois Côrregos, Agua Limpa, Morro Jacutinga, Fazendão, Germano and Timpopeba the s_2-unaffected high grade ores range between 590° and 710° C (Fig. 6). They may represent thrusted units of Archean age.

Of great regional importance is an itabirite pebble (no. 005G, appendix), which was found in a conglomerate near Pico de Itacolomi by Glöckner (1981). Its formation temperature was calculated to be 594° C. Glöckner (1981) describes occurrences of staurolite and kyanite from Chapada and near Passagem de Mariana. One of the authors (Müller) found staurolite and kyanite in mica schists east of Ouro Prêto and furthermore Roeser (1977) described the paragenesis staurolite + garnet + biotite + quartz in mica schists east from Mariana. Thus the calculated temperature of 594° C is in good agreement with the petrological relationships. Glöckner (1981) points out that the eastern part of the complex Itacolomi nappe system in the area of Côrrego de Belchior consists very probably of Maquiné metasediments. These quartzites and garnet schists of Pre-Minas age were thrusted upon the Minas sequences.

In the soft ore region near Congonhas do Campo we sampled some big hard blocks which look like erratics (Mine Baixa de João Pereira, no. 205 and 210, appendix). Normally in this region the calculated temperatures belong to the field of greenschist facies between 400 and 520° C (no. 186–203, appendix), but the "erratic block temperatures" are 650° and 690° C and indicate an allochthonous position of high grade metamorphic rocks.

The majority of the samples from the W-region show also a subdivision due to the recrystallization phenomena, since s_2-affected ores are restricted to the greenschist facies, $< 520°$ C and Δ-values > 10‰ (see Fig. 5). Only a minority of the samples which seem to be s_2-unaffected show Δ-values < 10.5‰, like sample no. 213, 221, 225, Côrrego de Feijão and others. Another sample group with no clear-cut evidence of s_2 ranges between 10.5 and 11‰ and indicates formation temperatures between 525° and 500° C. Thus, a lot of samples yield peak formation temperatures in the upper greenschist facies.

All samples of the mines Cauê, Conceição and Dois Côrregos were attached on the diagrams to the W-region (Figs. 2, 5 and 6), since the staurolite isograd after Schorscher (1975) runs some kilometers east from these mines. The presentation of the oxygen data and metamorphic temperatures in the above mentioned graphs would be clearer, if the compact and s_2-unaffected samples of this mining district belonged to the sample group of the E-region.

Schorscher (1976) discussed discrepancies of some metamorphic reactions with respect to metamorphic P-T-relationships in that area. He observed that chloritoid disappears far to the west of Itabira whereas staurolite is evident only several kilometers east of Itabira. In the intermediate area chloritoid exists only in armored relics included in garnet. Torres et al. (1969), Geisel et al. (1972) and Schorscher (1975) described parauthochthonous and allochthonous nappes from the Itabira mining district, namely from the mines Cauê, Conceição and Dois Côrregos, where tectonic units of quite different stratigraphic positions were thrusted West and Northwest during the Minas orogenesis. Probably the high grade metamorphic ores of the Itabira area belonged originally to the E-region and were displaced by tectonic tansport into their present position. Additional investigations in the ore bodies and related country rocks are certainly needed to solve this problem.

Rosière (1981) made a very interesting observation near the contact of the Pico de Itabirito ore bodies with the Archean basement. He found an intense fracturing s_3 in the s_2-affected iron ores due to the tectonic uplift of the Archaic Complexo de Bação, which caused drag tectonics in the adjacent Minas metasediments. Those s_3-affected ore samples yield Δ-values about 13‰ and recrystallization temperatures as low as 310° C (no. 245 Pico de Itabirito), 326° C (no. 268 Aguas Claras, 250° C (no. 112 Fazenda Alegria), 310° C (no. 063 Andrade).

In conclusion, oxygen isotope data and calculated temperatures of metamorphic recrystallizations support earlier results published by Barbosa (1960), Torres et al. (1969), Geisel et al. (1972), Schorscher (1975) and Glöckner (1981) namely that in the eastern and southern border zone of the Iron Quadrangle nappes were thrusted upon the Minas series. Our results show that units of banded iron formation in the nappe systems are polymetamorphous. These units underwent an earlier high grade metamorphic event and later during the Minas metamorphism they became more or less reequilibrated. Some ore samples from the northeastern border zone show analogous "formation temperatures" between 600° and 800° C like granulite facies rocks (charnockites) from eastern Minas Gerais.

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Appendix. $\delta^{18}O$ values of quartz and iron oxide minerals and calculated temperatures of formation

Remarks to the temperature values: C.C. = These values were calculated with a computer program (Hoernes, 1980) using curves of Bertenrath et al. (1973) and of Matthews and Beckinsale (1979). F.O = These values were obtained from a curve given by Friedman and O'Neil (1977) which bases on data given by Becker (1971). Qu and Hem represent $\delta^{18}O$ values relative SMOW. S_2 = Besides a primary foliation a secondary schistosity is present (+) or absent (−), sometimes additional s_3-planes are developed (++); H = Hydrothermal filled fissures

	Sample number	Qu (‰)	Hem (‰)	ΔQ-H (‰)	C.C. (°C)	F.O. (°C)	S_2
W-region							
Côrrego	213	12.3	2.2	10.1	545	445	−
de Feijão	219	12.8	−0.6	13.4	404	335	+
	221	15.1	5.4	9.7	566	460	−
	222	14.7	1.3	13.4	404	335	+
	idem	14.1	1.3	12.8	426	350	+
	225	14.4	4.0	10.4	530	430	−
	226	14.1	1.3	12.8	426	350	+
Águas Claras	267	15.6	5.3	10.3	536	435	−
	268	16.9	0.9	16.0	326	280	++
	idem	17.1	1.4	15.7	338	290	++
	270	18.6	7.0	11.6	474	390	−
	271	16.8	4.5	12.3	446	370	+
	284	16.4	4.2	12.2	450	370	+
	W46a	16.2	1.4	14.8	358	300	?
Mutuca	298	14.0	0.3	13.7	394	330	+
Tamanduá	302	13.8	2.4	11.4	484	400	−
Serra da Gama	306	14.0	1.3	12.7	430	355	+
Pico de Itabirito	228	10.5	−4.3	14.8	358	300	++
	239	16.3	3.7	12.6	434	355	+
	240	15.0	2.1	12.9	422	350	+
	243	17.0	6.1	10.9	506	410	−
	245	14.8	−1.7	16.5	310	265	++
	247	16.5	5.2	11.3	488	400	−
Fábrica	186	14.9	2.6	12.3	446	370	+
Patriótica	187	14.9	3.1	11.8	466	380	+
	idem	15.9	1.0	14.1	380	320	+
	189	14.0	3.2	10.8	512	420	−
João Pereira	191	7.8	−1.8	9.6	572	465	−
	194	12.9	2.3	10.6	520	425	−
Baixa de	195	13.0	−0.4	13.4	404	335	+
João Pereira	198	12.8	2.2	10.6	520	425	−
	202	12.3	1.3	11.0	502	400	−
	203	14.3	2.4	11.9	462	380	+
	205	11.5	3.2	8.3	648	525	−
	210	10.0	2.4	7.6	692	560	−
Road cut west	248	15.1	4.2	10.9	506	410	−
from Ouro Prêto	249	16.3	5.7	10.6	520	425	−
Fazenda Alegría	092	13.3	−0.4	13.7	394	330	+
(Attachment	094	14.5	2.7	11.8	466	380	+
to the W- or to	096	12.9	1.5	11.4	484	400	+
the E-region	099	13.5	0.6	12.9	422	350	+
is still not clear	104	13.1	1.6	11.5	480	390	+
by field	105	13.0	2.2	10.8	512	420	−
relationship	106	13.9	1.0	12.9	422	350	+
but isotopically	110	12.9	0.8	12.1	454	375	+
the ores belong	110a	12.2	−0.3	12.5	438	355	+
to the W.)	111	13.8	1.4	12.4	442	360	+
	112	23.3	4.1	19.2	250	?	++
	113	12.2	−0.2	12.4	442	360	+
	007L	15.1	0.0	15.1	350	295	H
	008L	14.8	0.1	14.7	360	300	H
Cauê	135	9.6	0.7	8.9	610	495	−
Conceição	147	19.4	9.1	10.3	536	435	−
	150	19.8	0.7	19.1	252	?	++
	153	10.8	−1.1	11.9	462	380	+
	154	6.8	−1.3	8.1	660	535	−
	155	13.0	−0.3	13.3	408	340	+
	179	14.2	2.3	11.9	462	380	+
Dois Côrregos	181	13.3	4.0	9.3	588	475	−
E-region							
Pico do Itacolomi	005G	12.0	1.8	9.2	594	480	+
Timbopeba	001L	17.4	7.1	10.3	536	435	+
	006L	12.3	0.2	12.1	454	375	+
	024L	15.1	3.5	11.6	474	390	+
	031L	15.4	4.2	11.2	492	400	+
	032L	13.8	3.3	10.5	526	430	+
	045L	16.4	7.2	9.2	594	480	+
	046L	15.8	4.3	11.5	480	390	+
	052L	16.9	7.9	9.0	606	490	+
	053L	17.0	9.7	7.3	712	580	−
	054L	16.6	8.1	8.5	636	510	−
	057L	15.0	7.1	7.9	672	540	−
	058L	15.8	6.0	9.8	562	450	+
	059L	17.1	7.3	9.8	562	450	+
	idem	16.9	7.3	9.6	572	465	+
	064L	14.8	5.3	9.5	578	470	+
Germano-	011L	13.4	0.5	12.9	422	350	+
Samarco	012L	18.9	5.9	13.0	418	345	+

	Sample number	Qu (‰)	Hem (‰)	ΔQ-H (‰)	C.C. (°C)	F.O. (°C)	S_2
	017L	16.6	4.3	12.3	446	370	+
	077	12.0	2.4	9.6	572	465	+
	078	13.3	3.8	9.5	578	470	+
	079	8.6	0.1	8.5	636	510	−
	080	13.6	6.0	7.6	692	560	−
	081	14.3	3.2	11.1	498	400	+
	idem	13.8	2.9	10.9	506	410	+
	082	13.1	−0.9	14.0	384	320	++
	085	12.7	1.4	11.3	488	400	+
	086	10.9	0.2	10.7	516	420	+
	088	11.6	0.6	11.0	502	400	+
	089	12.8	0.4	12.4	442	360	+
	090	11.6	1.7	9.9	556	450	+
	idem	12.0	2.3	9.7	566	460	+
Fazendão	035L	13.3	5.3	8.0	666	540	−
	038L	12.8	2.4	10.4	530	430	+
	039L	10.9	0.9	10.0	550	450	+
	180	13.2	3.8	9.4	584	470	−
Morro	048	9.3	0.7	8.6	636	510	−
Jacutinga	0.54	14.9	5.6	9.3	588	475	+
	x44	12.2	−2.9	15.1	350	295	H
	044	13.2	−3.9	17.1	296	250	H
Agua Limpa	037	9.5	0.4	9.1	600	485	+
	idem	9.5	0.3	9.2	594	480	+
	039	12.0	4.0	8.0	666	540	−
Rio Piracicaba	006	11.6	0.4	11.2	492	400	+
Morro Agudo	008	6.3	−2.7	9.0	606	490	+
	010	9.3	1.1	8.2	654	530	−
	011	7.8	0.7	7.1	726	590	−
	0.13	7.5	0.6	6.9	740	600	−
	015	6.9	0.8	6.1	798	660	−
	018	6.3	0.4	5.9	814	675	−
	020	8.9	0.8	8.1	660	535	−
	022	11.9	4.2	7.7	686	550	−
	027	7.4	−1.6	9.0	606	490	+
	033	8.4	1.0	7.4	706	570	−
	idem	8.2	1.0	7.2	720	585	−
Espigão do Pico	007	11.8	2.8	9.0	606	490	+
Andrade	059	11.7	3.8	7.9	672	540	−
	063	19.6	3.1	16.5	310	265	++
	066b	11.2	−1.8	13.0	418	345	+
	066c	9.8	3.1	6.7	754	615	−
	069	10.4	1.4	9.0	606	490	+
Piçarrão	159	6.7	−1.7	8.4	642	520	−
	160	7.2	0.1	7.1	726	590	−
	161	6.9	−2.7	9.6	572	465	+
	163	8.1	1.6	6.5	764	630	−
	idem	8.1	1.9	6.2	780	650	−
	164	13.0	4.9	8.1	660	535	−
	165	12.6	5.5	7.1	726	590	−
	166	11.9	4.5	7.4	706	570	−
	167	12.5	4.2	8.3	648	525	−
	169	9.8	2.6	7.2	720	585	−
	174	13.5	5.7	7.8	680	550	−
	175	10.8	2.3	8.5	636	510	−
Gouveia	358c	8.2	0.2	8.0	666	540	−
Diamantina	870b	11.2	0.2	11.0	502	400	+
	987	10.6	−1.2	11.8	466	380	+
	1217	14.2	1.3	12.9	422	350	+

	Sample number	Talc (‰)	Hem (‰)	ΔT-H (‰)
Talc hematite	122	13.4	6.7	6.7
Cauê	128	6.3	−0.4	6.7
	129	6.4	−0.1	6.5
	130	6.9	0.3	6.6
Morro Agudo	032	4.6	−0.8	5.4
Piçarrão	159a	3.2	−1.8	5.0
Mica-hematite		Mica	Hem	
Conceição	145	13.4	3.2	10.2

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